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Review Article: Tracing the recorded history of thin-film sputter deposition: From the 1800s to 2017

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Thin films, ubiquitous in today's world, have a documented history of more than 5000 years. However, thin-film growth by sputter deposition, which required the development of vacuum pumps and electrical power in the 1600s and the 1700s, is a much more recent phenomenon. First reported in the early 1800s, sputter deposition already dominated the optical-coating market by 1880. Preferential sputtering of alloys, sputtering of liquids, multitarget sputtering, and optical spectroscopy for process characterization were all described in the 1800s. Measurements of threshold energies and yields were carried out in the late 1800s, and yields in reasonable agreement with modern data were reported in the 1930s. Roll-to-roll sputter coating on flexible substrates was introduced in the mid-1930s, and the initial demonstration of sustained self-sputtering (i.e., sputtering without gas) was performed in 1970. The term magnetron dates to 1921, and the results of the first magnetron sputtering experiments were published in the late 1930s. The earliest descriptions of a parallel-plate magnetron were provided in a patent filed in 1962, rotatable magnetrons appeared in the early 1980s, and tunable "unbalanced" magnetron sputtering was developed in 1992. Two additional forms of magnetron sputtering evolved during the 1990s, both with the goal of efficiently ionizing sputter-ejected metal atoms: ionized-magnetron sputtering and high-power impulse magnetron sputtering, with the latter now being available in several variants. Radio frequency (rf) glow discharges were reported in 1891, with the initial results from rf deposition and etching experiments published in the 1930s. Modern capacitively-coupled rf sputtering systems were developed and modeled in the early 1960s, and a patent was filed in 1975 that led to pulseddc and mid-frequency-ac sputtering. The purposeful synthesis of metal-oxide films goes back to at least 1907, leading to early metal-oxide and nitride sputtering experiments in 1933, although the term "reactive sputtering" was not used in the literature until 1953. The effect of target oxidation on secondary-electron yields and sputtering rates was reported in 1940. The first kinetic models of reactive sputtering appeared in the 1960s; high-rate reactive sputtering, based on partial-pressure control, was developed in the early 1980s. While abundant experimental and theoretical evidence already existed in the late 1800s to the early 1900s demonstrating that sputtering is due to momentum transfer via ion-bombardment-induced near-surface collision cascades, the concept of sputtering resulting from local "impact evaporation" continued in the literature into the 1960s. Modern sputtering theory is based upon a linear-transport model published in 1969. No less than eight Nobel Laureates in Physics and Chemistry played major roles in the evolution of modern sputter deposition. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1116/1.4998940]

OUTLINE

| I. | INTRODUCTION | 2 |) |
|----|--------------|---|---|
| 1. | | - | • |

- II. HISTORY OF THIN-FILM DEPOSITION FROM THE VAPOR PHASE
- III. TECHNOLOGICAL ADVANCES IN THE 1600S AND THE 1700S NECESSARY FOR

| THE DEVELOPMENT OF SPUTTER | |
|---|----|
| DEPOSITION | 5 |
| A. Evolution of early vacuum technology | 5 |
| B. Pulsed to dc power | 7 |
| IV. HISTORY OF THIN-FILM SPUTTER | |
| DEPOSITION | 9 |
| A. Glow-discharge sputtering | 9 |
| B. Mechanism of sputtering | 14 |
| C. Early sputter-yield measurements | 16 |

4

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| D. Ion-bombardment-induced secondary- | |
|--|----|
| electron emission | 16 |
| E. Use of thermionically- and mercury-pool- | |
| supported glow discharges for measuring | |
| sputtering yields. | 18 |
| 1. Use of ion guns to measure sputtering | |
| yields | 20 |
| F. Closed-field magnetrons | 21 |
| 1. Cylindrical-post and inverted hollow- | |
| cathode magnetrons | 21 |
| 2. Planar magnetrons | 23 |
| 3. S-gun magnetron | 26 |
| 4. Rotatable magnetrons | 26 |
| 5. Magnetically-unbalanced magnetrons | 27 |
| G. Threshold energies for sputtering | 27 |
| H. More on mechanisms of sputtering: Theory. | 28 |
| I. rf sputter deposition | 30 |
| J. Reactive sputter deposition | 34 |
| 1. Bias-sputtering for composition control. | 37 |
| 2. Seminal events in the development of | |
| reactive sputtering | 37 |
| 3. High-rate reactive sputtering | 37 |
| 4. Pulsed-dc and midfrequency ac reactive | |
| sputtering | 39 |
| 5. Modeling reactive sputtering | 41 |
| 6. Metal/metalloid reactive sputtering | 43 |
| K. Roll-to-roll web coating | 44 |
| L. Even more on mechanisms of sputtering: | |
| Sputter-yield amplification | 44 |
| M. Sustained self-sputtering | 46 |
| RECENT DEVELOPMENTS AND | |
| CONCLUSIONS | 47 |
| A. Ionized-metal magnetron sputter deposition. | 48 |
| B. High-power impulse magnetron sputter | |
| deposition | 49 |
| C. MPP magnetron sputtering | 50 |
| D. Conclusions | 51 |
| | |

I. INTRODUCTION

V.

The use of thin films to enhance the physical and chemical properties of materials is ubiquitous in today's world. Examples are shown in Fig. 1: copper metallization layers for electronic communication among billions of transistors in a silicon integrated-circuit; coated architectural glass in office buildings for which the thin films are designed to enhance energy efficiency and comfort by, depending on the time of year and latitude, reflecting ultraviolet and infrared sunlight, while transmitting visible light, to minimize air conditioning usage, or reflecting infrared radiation from within offices to minimize heating; and coated cutting tools developed to reduce friction and wear during use and, hence, increase tool lifetimes. Other common examples include magnetic thin films for electronic data storage; transparent conductive oxide and absorber layers in solar cells; thin film resistors and dielectrics; catalytic layers for toxic-gas sensing; superconducting thin films for high-frequency devices, data storage, and magnetic circuitry; corrosion-, friction-, and wear-protective layers on automotive and airplane engine parts (spark-plug electrodes, pistons, cylinders, turbine blades, etc.); and multiple layers on eyeglasses to correct vision, minimize ultraviolet light transmission, and provide scratch resistance.

The adjective "thin" in the term "thin films" is ambiguous and poorly defined. It is used to describe, depending on the application, "coating" layers ranging in thickness from less than a single atomic layer (a partial monolayer) to films that are a significant fraction of a millimeter thick. The earliest *documented* purposefully made inorganic thin films were gold layers produced chemo-mechanically, for decorative (and later, optical) applications, by the Egyptians during the middle bronze age, more than 5000 years ago.^{1,2} Gold films, with thicknesses <3000 Å (~1465 atoms), have been found in ancient tombs, including the Pyramid of Djoser (actual name, Netjerykhet, second King of the Third Dynasty, Old Kingdom; ruled from ~2667 to 2648 BC)³ in Saqqara,^{1,3–5} southwest of Cairo, Egypt. The films were often gilded on copper and bronze statues, jewelry, and religious artifacts using mercury-based, compositionally graded, interfacial adhesion layers as discussed in Ref. 1.

The gold used to produce early thin films was mined by the Egyptians in the Eastern Desert, between the Nile River and the Red Sea. Ancient mining sites in Wadi Hammamat, along the trade route from Thebes (modern-day Luxor) to the Red Sea port of Al-Quseir, are accurately located on a papyrus map drawn by a scribe of Ramses IV during a quarrying expedition in approximately 1160 BC (Refs. 7 and 8) and now on display in the Museo Egizio, Turin, Italy.

Gold ore was purified by melting it in a mixture of "alum" [the mineral alunite: KAl₃(SO₄)(OH)₆], salt (NaCl), and chalcopyrites (e.g., CuFeS₂). The process produces sulfuric and hydrochloric acids (H₂SO₄ and HCl) which dissolve base metal impurities.^{9,10} The purified gold still had several to a few tens of atomic percent of silver, copper, or both, depending upon where it was mined, thus giving rise to variations in color. Flattening of purified bulk gold was initiated by beating with a rounded stone and mechanical rolling, followed by many stages of thinning and sectioning of composite structures consisting of Au leaf sandwiched between layers of animal skins, parchment, and vellum.⁶ Figure 2 shows an image of a fresco from a tomb (~ 2500 BC) in Saggara, illustrating melting and purification of Au during which the temperature is adjusted by craftsmen using blowpipes (reeds) with clay tips.

Today, gold leaf can be beaten to \sim 500 Å thick (partially transparent to visible light) by highly skilled craftsmen.⁵ In fact, the production of gold leaf, primarily for decorative purposes, remained a viable industry for craftsmen until the development, in the mid-1930s, of roll-to-roll sputter and evaporative coating technologies (see Sec. IV K).

Highly skilled ancient Egyptian craftsmen mastered the art of gold sheathing—the direct application of thin gold layers onto wooden and plaster objects (mostly for noble families) to provide the impression that the object is solid gold—at least as early as 2600 BC.^{11,12} Striking examples were found in the tomb of Queen Hetepheres (wife, and half-sister, of Pharaoh Sneferu, Fourth Dynasty, Old



FIG. 1. (Color online) (Left panel) Copper interconnect metallization in a transistor, courtesy of IBM, 1997. The bus bar (metallic frame) in the lower part is $\sim 20 \,\mu$ m wide, about 1/5 the size of a human hair (average diameter, $\sim 100 \,\mu$ m). A colorized scanning electron micrograph view after removal of insulating layers by chemical etching is shown. Figure courtesy of International Business Machines Corporation, International Business Machines Corporation; http://www-03.ibm.com/ibm/history/ibm100/us/en/icons/copperchip/. (Middle panel) Coated architectural glass in office buildings. Figure courtesy of Hy-Power Coatings Ltd. (Nano) Brampton, ON, Canada. (Right panel) TiN, TiAlN, and TiB₂ (left to right) coated tools. Figure courtesy of KYOCERA SGS Precision Tools, Inc., Munroe Falls, OH.

Kingdom, $\sim 2613-2589$ BC). Other spectacular specimens of early thin-film technology were found in the tomb of Pharaoh Tutankhamun ("King Tut," 18th Dynasty, ruled $\sim 1332-1323$ BC). Gold sheets were beaten into position over carved wooden structures to provide embossed hieroglyphic texts and decorations as shown in Fig. 3.

An autocatalytic solution-growth technique involving oxidation/reduction reactions was developed by the Moche Indians utilizing minerals available in the local area, the northern highlands of Peru, beginning ~100 BC to deposit gold (as well as silver) films on copper and bronze artifacts.¹³ The technique is still in use today, although carried out in a more efficient manner, and referred to as electroless plating.¹⁴ Moche artisans first dissolved gold in a hot aqueous solution of equal parts potassium aluminum sulfate [KAl(SO₄)₂], potassium nitrate (KNO₃), and salt (NaCl), a process that took several days. The resulting mixture was then buffered with sodium bicarbonate (NaHCO₃) to form a weakly alkaline solution ($pH \sim 9$), which was allowed to



FIG. 2. (Color online) Fresco from a tomb (\sim 2500 BC) in Saqqara, Egypt, which depicts the gold melting and purification process, as well as the initial thinning of purified bulk gold with a rounded stone. The reed blowpipes, tipped with baked clay, were used to both increase and control the temperature of the charcoal fire in the ceramic pot. Reproduced with permission from Darque-Ceretti *et al.*, Rev. Mater. **16**, 540 (2011). Copyright 2011 by Creative Commons Attribution License 4.0.

boil for several minutes before immersing the copper artifact to be plated. The overall reaction is

$$2AuCl_3 + 3Cu \rightarrow 2Au + 3CuCl_2$$
.

Metallographic studies of Moche artifacts, coated with gold films whose thicknesses ranged from $\sim 2000 \text{ Å}$ to $1 \mu \text{m}$, exhibit evidence of post-deposition heat treatment (annealing) to obtain a film/substrate interdiffusion zone, presumably for



FIG. 3. (Color online) Photograph of Egyptian gold embossing, thin layers of gold cover a wooden structure with raised carved text and decorations, found in the tomb of Pharaoh Tutankhamun (ruled \sim 1332–1323 BC). Reproduced with permission from James, Gold Bull. **5**, 38 (1972). Copyright 1972 by Peter Clayton. Open Access, licensed under Creative Commons Attribution License 4.0.



FIG. 4. (Color online) Electroless gold-plated copper mask discovered near Lorna Negra (northern Peru, close to the Ecuadorian border). Ref. 13. Image Open Access, courtesy of the Metropolitan Museum of Art under Creative Commons Zero (CC0).

better adhesion. An excellent example of craftsmanship is depicted in Fig. 4.

II. HISTORY OF THIN-FILM DEPOSITION FROM THE VAPOR PHASE

The first thin films grown from the vapor phase, as discussed in Ref. 1, were likely metal layers deposited accidently on the ceramic pots and rocks surrounding hot charcoal fires used to reduce metal ores, a process which can be traced back more than 7000 years.¹⁵ Based upon both archeological evidence and metallurgical analyses, copper smelting (extraction from ore) and metal working originated independently in the Balkans (Serbia and Bulgaria) by ~5500 BC and in Anatolia by at least 5000 BC.^{16–19} The Roman philosopher Pliny the Elder (23–79 AD) discussed this process in his 37-book Naturalis Historia, the first encyclopedia, published in ~79 AD.²⁰

The earliest reported purposeful growth of metal films from the vapor phase was in 1649 when Johann Schroeder, a German pharmacist, described a method for reducing arsenic oxide $[As_2O_3]$ with charcoal^{21,22} through the overall endothermic reaction

$$2As_2O_3 + 3C \rightarrow 4As + 3CO_2.$$

This is an example of a film-growth methodology which today is termed chemical vapor deposition.^{1,23} As discussed in a 1966 review article by Rolsten,²⁴ carbon reduction of oxides was an important method for obtaining relatively pure metals, in order to investigate their fundamental physical properties, during the 1700s and the early 1800s.

The physical-vapor deposition (PVD) techniques of sputtering and evaporation were developed in the middle to late 1800s following the evolution of vacuum and electricalpower technologies beginning in the mid-1600s.¹ The first publication focused on sputter deposition of thin films was in 1852,²⁵ as discussed in Sec. IV A, while the first documented evaporation experiments were carried out in the early 1870s by Josef Stefan (1835–1893),^{26–28} an Austrian physicist best known for his research in thermal conductivity of gases and blackbody radiation of solids,²⁹ and the early 1880s by Heinrich Hertz (1857–1897),^{30,31} a German physicist well known for his work on electromagnetics³² and contact mechanics.³³ Reliable early measurements of the vapor pressures of solids (sublimation) and liquids (evaporation) were made by Martin Knudsen (1871–1949, Danish physicist) using what is now termed a Knudsen cell,^{34,35} an isothermal enclosure with a very small orifice.

Historical footnote: The term "PVD" appears to have been coined by John M. Blocher, from Battelle Columbus (OH) Laboratory, while chairing a session on Vapor Deposition at the 1960 Electrochemical Society meeting in Houston, TX. Blocher sought to distinguish deposition techniques by employing chemical reactions (he was also the first to use the term "chemical vapor deposition") from processes such as sputtering and evaporation.³⁶ The expression physical vapor deposition first appeared in print in a book entitled *Vapor Deposition*, edited by Powell *et al.*, published in 1966.³⁷

Sputter deposition, in its simplest configuration (Fig. 5), is carried out in an evacuated chamber which is backfilled with a low pressure of a rare gas such as argon. Argon is often the rare gas of choice for sputtering, primarily due to two reasons: (1) argon comprises approximately 1% of the earth's atmosphere and, hence, is relatively inexpensive and (2) the mass of argon (39.95 amu) is a reasonable match, resulting in significant collisional momentum transfer, to a wide range of metals in the middle of the periodic table (see discussion in Sec. IV H). A dc voltage is then applied between a metal target (the source of the film atoms) such as Cu and an electrically conducting substrate upon which the film is deposited. The voltage breaks down the gas to form a



FIG. 5. (Color online) Schematic illustration of the essential features of a basic dc-diode sputtering system. Argon gas flows through a controlled leak valve into an evacuated deposition chamber; some Ar atoms are ionized by a dc potential applied between the copper target and an electrically conducting substrate on a metal substrate table. Ar^+ ions are accelerated toward the target in order to sputter-eject copper atoms, which are deposited on the substrate, as well as the chamber walls, to form a Cu film.

glow discharge consisting of Ar^+ (with a much smaller fraction of Ar^{2+}) ions and electrons. The positively charged ions are accelerated to bombard the target and, via momentum transfer, sputter-eject target atoms, some of which are deposited on the substrate. A reactive gas can also be added in order to form compound films (see Sec. IV J). Important commercial examples are the reactive sputtering of titanium and titanium-aluminum alloys in Ar/N_2 mixtures to deposit hard ceramic TiN and TiAIN coatings^{38–40} on cutting tools, drill bits [see Fig. 1 (right panel)], gear hobs, and dies.

Historical footnote: While sputtering was in use for the deposition of thin films by the mid-1800s, the etymology of the word sputtering remains unclear. The term "spluttering," an intensified form of the English word sputtering, meaning "to spit with explosive sounds" (a cognate for the Dutch word "sputteren"),⁴¹ may have been used as early as the late 1800s.⁴² In a 1970 book chapter, Gottfried (Fred) Wehner (German-born American physicist, 1910–1996) and Gerald Anderson⁴³ noted that a search of the literature revealed that Joseph John (J. J.) Thomson (English physicist, 1856-1940; Nobel Prize in Physics, 1906) still used the term spluttering in 1913: "A well-known instance of this is the spluttering of the cathode in a vacuum tube;..."⁴⁴ The quote implies that the term was in use even earlier. Don Mattox pointed out^{45} that the third edition (1955) of the Shorter Oxford Dictionary⁴⁶ lists, in addition to sputter (verb, 1598) and sputter (noun, 1673), the English term splutter meaning "to spit out a spray of particles in noisy bursts."

Kenneth Kingdon and Irving Langmuir (American surface chemist, 1932 Nobel Laureate in Chemistry for his research in surface science), from the General Electric Research Laboratory, dropped the "l" in favor of the word sputtering in their 1923 *Physical Review* paper on "The removal of thorium from the surface of a thoriated-tungsten (light bulb) filament by positive ion bombardment."⁴⁷ Nevertheless, in the same year, in an article on the sputtering of tungsten published in the *Philosophical Magazine* by the "Research Staff of the General Electric Company and communicated by the Laboratory Director," the term "cathode disintegration" was used in place of sputtering.⁴⁸ With time, however, the term sputtering prevailed and is now universal.

III. TECHNOLOGICAL ADVANCES IN THE 1600s AND THE 1700s NECESSARY FOR THE DEVELOPMENT OF SPUTTER DEPOSITION

The rapid development of sputter deposition in the middle to late 1800s required the evolution of vacuum technology, beginning in the 1600s, and the invention of dc power supplies (batteries) in the late 1700s and the early 1800s. For a more detailed discussion of early vacuum technology and power supplies, see Ref. 1.

A. Evolution of early vacuum technology

Progress in vacuum technology (the word vacuum is derived from the Latin vacuus, meaning empty space) was essential for providing cleaner deposition environments necessary for the advancement of thin-film science. In 1652, Otto von Guericke (1602-1686) of Magdeburg, Germany, a scientist, inventor, and politician, developed a mechanical piston pump that achieved a vacuum of 2 Torr (~0.003 atm).^{49,50} (For comparison, a typical household vacuum cleaner produces enough suction to reduce standard atmospheric pressure, 760 Torr, to \sim 610 Torr).⁵¹ von Guericke's third-generation vacuum system, a model of which is shown in Fig. 6^{52} consisted of a bell jar separated from the piston pump by a cylinder with a stopcock. The pump was equipped with two valves near the entrance to the nozzle at the bottom of the bell jar; the first valve was located between the nozzle and the cylinder and the second valve between the cylinder and the atmosphere. During the piston down-stroke, valve one is closed to stop air from entering the nozzle and the bell jar, while valve two is forced to open by the air displaced from the cylinder. During the piston return stroke, valve two is closed and valve one is forced to open by the pressure of the remaining air in the bell jar and the nozzle. The percentage of pressure decrease per complete piston stroke diminishes continuously as the bell-jar pressure is reduced toward the base pressure.

Much better vacuum was required in order for scientists in the 1800s to obtain longer gas-phase mean-free paths, higher deposition rates, and increased purity in films grown from the vapor-phase. This was solved by a German chemist,



Fig. 6. Model of an early mechanical piston pump developed by Otto von Guericke in \sim 1652. Reproduced with permission from Hablanian, J. Vac. Sci. Technol., A **2**, 118 (1984). Copyright 1984 by American Vacuum Society.



FIG. 7. (Color online) Drawings of (a) a prototype and (b) an initial version of Sprengel's mercury transfer pump. Reproduced with permission from Sprengel, J. Chem. Soc. **18**, 9 (1865). Copyright 1865 by Royal Society of Chemistry. (c) A later version of the pump, presently housed in the Dr. Guislain Museum, Ghent, Belgium. Photograph courtesy of Luca Borghi for Himetop, The History of Medicine Topographical Database.

Herman Sprengel (1834–1906), who developed a practical mercury momentum-transfer pump in 1865.⁵³ The pump is related to a trombe in which water falls from an upper reservoir, while trapping air, into a pipe and deposits the air in a lower reservoir at higher pressure (a type of air compressor),^{54,55} which had been known for "some hundreds of years."56 The base pressure claimed by Sprengel in his initial publication was $\sim 6 \times 10^{-4}$ Torr and limited by leaks in vulcanized rubber joints connecting the glass tubes (the rubber connectors were cemented to the glass tubes, and the joints were bound with copper wire). While lower pressures were achieved with later versions of the pump,⁵⁷ pressures of 10^{-3} -10⁻⁴ Torr were sufficient to provide ballistic environments (i.e., gas-atom mean-free paths of the order of, or larger than, system dimensions) for investigating gas discharges and sputter deposition in the small evacuated chambers of that era.

An initial prototype of the Sprengel mercury pump is shown in Fig. 7(a).⁵³ Droplets of mercury (a heavy metal which is liquid at room temperature), falling through a smalldiameter (2.50–2.75 mm) glass tube, trap and compress air by momentum transfer. The tube, labeled CD in Fig. 7(a), was \sim 76 cm long and extended from funnel A to enter glass bulb B through a vulcanized-rubber stopper. The bulb has a spout several mm above the lower end of tube CD.

In operation, mercury was added to funnel A and the stopcock at C opened, allowing mercury droplets to fall, trap air, and reduce the pressure in chamber R. Air and mercury were exhausted through the spout of bulb B. The mercury collected in basin H was poured back into funnel A for continuous pumping. The second version of the Sprengel pump, described in the same paper,⁵³ is shown in Fig. 7(b). It was approximately 1.8 m tall, and Sprengel reported using 4.5–6.8 kg of mercury during operation. The pump contained a mercury pressure gauge (similar to the one described below) attached to the evacuated chamber and a mechanical-piston backing pump S. Later versions incorporated continuous mercury recycling. With the combination of the mechanical and mercury pumps, a 0.5 l chamber could be evacuated in ~ 20 min. The importance of Sprengel's work was recognized by the Royal Society of London which elected him as a Fellow in 1878. A later version of the pump, presently housed in the Dr. Guislain Museum, Ghent, Belgium, is shown in Fig. 7(c).

Improvements in vacuum technology required better gauging in order to measure the increasingly lower pressures produced. In 1874, Herbert McLeod (1841–1923), a British chemist, developed what today is termed the McLeod mercury gauge,^{58,59} which operates based upon Boyle's law. Boyle (1627–1691), another British chemist, showed in 1662 that for a closed system at constant temperature, the product of pressure P and volume V remains constant.⁶⁰ In operation, the gauge compresses a known volume V₁ of gas at the unknown system pressure P₁ to a much smaller known volume V₂ in a mercury manometer with which the pressure P₂ is measured.^{61,62} Thus, by Boyle's law, the system pressure P₁ is given by the expression P₂V₂/V₁. Liquid mercury wets glass and thus forms the required glass/metal seals in the gauge.

Historical footnote: Egyptian frescos clearly illustrate that siphon pumps were used to decant liquids, including wine,⁶³ from large earthen storage jars, by \sim 1500 BC (Ref. 64) (and probably much earlier). Hero of Alexandria (\sim 10–70 AD), a Greek mathematician and engineer, wrote extensively about siphon pumps in his famous essay *Pneumatica*,⁶⁵ in which he borrowed

heavily from earlier treatises by Philo of Byzantium (~280–220 BC), a Greek engineer who spent most of his life in Alexandria,⁶⁶ and, especially, Ctesibius of Alexandria (285–222 BC),^{67,68} a Greek inventor and mathematician who is considered the father of pneumatics. Marcus Vitruvius Pollio (~75–15 BC), commonly known as Vitruvius, a Roman architect and engineer, reported in his 10-volume *De Architectura*⁶⁹ on Greek and Roman architecture, technology, and natural sciences that Ctesibius wrote a book in which he described the invention of, among many other things, an air pump, with valves, connected to a keyboard and rows of pipes (a water organ, in which water is the actuator)⁷⁰ and a force pump for water (the up-stroke of a piston draws water, through a valve, into the cylinder;

on the down-stroke, the water is discharged through a

valve into an outlet pipe).⁷¹ Unfortunately, the original writings of Ctesibius were lost. The first mercury "pump" is attributed to Evangelista Torricelli (1608-1647), an Italian physicist and mathematician who, in 1644,72 invented the barometer to measure atmospheric pressure.⁷³ (The modern pressure unit Torr is in honor of Torricelli.) His initial experiments were carried out with an \sim 100-cm-long glass tube, open at one end, filled with liquid mercury, and tightly closed with a fingertip. The tube was then inverted and partially immersed in a mercury reservoir, and the fingertip was removed from the tube opening. Some of the mercury flowed out of the tube leaving space at the top such that the height of the liquid column corresponded to the ambient atmospheric pressure. The empty volume at the top of the barometer was "Torricelli's void;" he had produced vacuum!

The earliest actuated mercury pump was developed by Swedenborg (1688–1772), Swedish scientist/theologian, as described in his 1722 book Miscellanea.⁷⁴ The pump consists of a metal funnel attached to a plate which holds a glass bell jar to be evacuated. The lower end of the funnel is attached to a leather tube with a metal lever. The funnel and leather tube are filled with mercury, and the lever is used to compress the mercury and force air out of the bell jar through a set of inward and outward opening valves. Basically, the solid piston of von Guericke's mechanical pump was replaced by a mercury column. Over the next 155 years, a large variety of mercury pumps were reported, as reviewed in detail in a wonderful paper, with more than 130 references, by Thompson in 1877.³⁰ In addition to the important Sprengel momentum-transfer pump described above, a type of mercury-based vacuumsiphon pump, with a three-way stopcock, was developed by Heinrich Geissler (1814–1879), a German glassblower, in 1855, which could achieve a vacuum of ~ 100 mTorr.⁷⁵ The first public mention of the pump was in a pamphlet published in 1858 by Mayer⁷⁶ (also see Refs. 56 and 77).

B. Pulsed to dc power

In addition to vacuum, electrical power was necessary for initiating early experiments in thin-film sputter deposition.

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von Guericke also played an important role in this field through his development in 1663 of a crude friction-based electrostatic generator which transformed mechanical work into electrical energy.^{78,79} The generator was based on the triboelectric effect (although the term did not exist at the time), in which a material becomes electrically charged ("static electricity") through friction.

Historical footnote: The concept of static electricity was known by the ancient Greeks (e.g., rubbing amber on wool) and first recorded by Thales of Miletus (624–546 BC),⁸⁰ a pre-Socratic Greek philosopher, mathematician, and one of the Seven Sages of Greece.^{81–83}

In 1745, the Dutch scientist Pieter van Musschenbroek (1692-1761) of Leiden University [mathematics, philosophy, medicine, and astrology (the latter is closer to theology than science!)] and Ewald Georg von Kleist (1700-1748), a German lawyer, cleric (Bishop of Pomerania, Prussia), and physicist, are credited with independently inventing what today is known as the Leiden jar (Leyden jar),^{84,85} an early form of the modern capacitor, to provide pulsed power. Both Kleist and van Musschenbroek studied at Leiden University, and it is likely that Kleist developed his interest in electricity from lecture demonstrations in the Physics Department. However, it appears that van Musschenbroek obtained the idea for his research from Andreas Cunaeus (1712-1788), a lawyer who often visited van Musschenbroek's laboratory and had learned Kleist's experiments.⁸⁶ Cunaeus carried out the initial experiments that led to the Leyden jar while attempting to reproduce even earlier results by Andreas Gordon (1712-1751), a Professor at Erfurt, Germany, and Georg Mattias Bose (1710-1761) at the University of Wittenberg, Germany.⁸⁷ The device accumulates static electricity between electrodes on the inside and outside of a glass jar. The first mention in the literature of the Leyden jar experiments was by Trembley in February, 1745 (there is some controversy regarding the exact publication date).⁸⁸

In order to store charge in Leyden jars, the glass cylinder of an electrostatic generator was rotated, via a hand crank, against a leather (or wool) strip pressing on the glass. The friction resulted in positive charge accumulating on the leather and negative charge (electrons) on the glass. The electrons were collected by an insulated (perhaps combshaped) metal electrode. When sufficient charge accumulated, a spark jumped from the generator collector to the central collector electrode of a nearby Leyden jar, where the charge was stored. Originally, the capacitance of the device was measured in units of the number of "jars" of a given size or by the total area covered with metal. A typical 0.5-1 Leyden jar had a maximum capacitance of approximately 1 nF.⁸⁹

The earliest devices were hand-held glass jars partly filled with water (the inner conductor) in contact with a nail inserted through a cork stopper in the top of the jar. Both Kleist and van Musschenbroek reported receiving significant shocks when they touched both the nail and the outside of the jar! Eventually, van Musschenbroek realized that adding a conductor (other than his own body) such as a metal foil to the outside of the jar was far more practical.

Benjamin Franklin (American scientist and inventor, 1706–1790) was the first to understand that charge is stored in the glass dielectric, not the electrodes. He realized that the water merely served as an electrode and was not essential. To prove it, he produced flat capacitors consisting of a sheet of glass between metal-foil electrodes.⁹⁰ Franklin discussed his findings in a letter dated 1749.⁹¹ The Leyden jar was also used by Franklin in his famous kite experiment in a thunderstorm to "capture lightning in a bottle."⁹² (Note, however, that it is disputed whether the experiment was actually performed.)⁹³

Daniel Gralath (1708–1767), physicist (founder of the Danzig Research Society) and Mayor of Danzig, Poland, repeated the Leyden jar experiments and was the first to combine several jars, connected in parallel (see Ref. 1), to increase the total stored charge.⁹⁴ The term "battery" was reputedly coined by Benjamin Franklin,^{95,96} who likened the group of jars to a battery of cannon.

Historical footnote: Georg Bose, one of the first to work on charge-storage devices, was a scientific stuntman who became famous for public demonstrations. He was known, for example, to produce flames by lighting alcohol floating on the surface of water via a spark generated by his friction machine. However, his most famous stunt was the "Electric Kiss."97 An attractive young woman in the audience was invited to stand on a block of an insulating material (Bose was, by all accounts, a charming and persuasive fellow), and she was given a moderate static charge from an electrostatic generator. Gentlemen in the audience would then be invited to kiss her, but, as they tried to approach her lips, a strong spark would discourage the attempt, while greatly amusing both the young woman and the rest of the audience.

Gentlemen's Magazine reported the following in 1745.⁹⁸ "Could one believe that a lady's finger, that her whalebone petticoat, should send forth flashes of true lightening, and that such charming lips could set on fire a house? The ladies were sensible of this new privilege of kindling fires without any poetical figure, or hyperbole, and resorted from all parts to the public lectures of natural philosophy, which by that means became brilliant assemblies."

The invention of the electrochemical battery to provide low-voltage dc power is generally attributed to Count Alessandro Volta (1745–1827),¹ Professor of Natural Philosophy at the University of Pavia, Italy, based upon his work in the 1790s resulting in a classic paper published first in French⁹⁹ and then in English¹⁰⁰ in 1800.

Volta's interest in electrochemistry led him to discover that voltage can be obtained from stacks consisting of several pairs of different metal disks, each pair separated by an electrolyte (initially pieces of cloth saturated in brine), connected in series to form a "voltaic pile."¹⁰¹ The first metals used were copper and zinc, but Volta found, based upon electrometer measurements, that silver and zinc produce a larger electromotive force, a term Volta introduced in 1796.¹⁰² Figures 8(a) and 8(b) show an illustration and a photograph, respectively, of an early voltaic pile. Such devices could only provide a few volts; obtaining larger potentials required a series (i.e., a battery) of many large voltaic piles. An example of a small double voltaic pile is shown in Fig. 8(c).¹⁰⁰

Historical footnote: Volta not only introduced the term electromotive series, but was the first to use the term "semiconductor" in describing "materials of semiconducting nature" in a 1782 paper published in the *Philosophical Transactions of the Royal Society*¹⁰³ and presented at a Royal Society of London meeting on March 14 of that year.

A practical problem with voltaic piles, especially with larger ones used to obtain higher voltages, is that the weight of the disks squeezes the electrolyte out of the cloths. In 1801, William Cruickshank (1745–1810), a surgeon and Professor of Chemistry at the Royal Military Academy, Woolwich (southeast London), solved this problem and designed the first electric battery for mass production.¹⁰⁴ In the initial version, Cruickshank arranged 60 pairs of equal-sized zinc and silver sheets cemented together with rosin



FIG. 8. (Color online) (a) Schematic illustration of a voltaic pile. (b) Photograph, attributed to GuidoB and licensed under the Creative Commons Attribution-Share Alike 3.0 Unported, of a single voltaic pile. The battery is on display at the Tempio Voltiano Museum, Como, Italy. (c) Sketch of a double voltaic pile consisting of two sets of eight pairs of silver and zinc plates. Reproduced with permission from Volta, Philos. Mag. 7, 289 (1800). Copyright 1800 by Taylor and Francis Publishing.

and beeswax in a long resin-insulated rectangular wooden box such that all zinc sheets faced one direction and all silver sheets the other. Grooves in the box held the metal plates in position, and the sealed box was filled with an electrolyte of brine or dilute ammonium chloride (NH_4Cl), which has higher conductivity.

IV. HISTORY OF THIN-FILM SPUTTER DEPOSITION

A. Glow-discharge sputtering

From the mid- to late-1800s, several papers were published on the use of optical emission to investigate the transition between a continuous glow discharge and an arc, the electrical structure and configuration of dc glow discharges, and the nature of metal atoms sputter ejected from the cathode (target). Michael Faraday (1791-1867), an English scientist, reported on the electrical and optical characterization of glow discharges in 1838.¹⁰⁵ His glass discharge tube contained brass electrodes and was operated in air, nitrogen, oxygen, hydrogen, and other gases at a pressure of 4.4 inches of mercury (~112 Torr). While Faraday must certainly have deposited films during these experiments, this was not the objective. His later work on the optical properties of vacuum-arc-deposited thin metal films was discussed in his fifth Bakerian Lecture¹⁰⁶ in 1857 and published in the same vear.¹⁰⁷

Historical footnote: The Bakerian Medal and Lecture of the Royal Society of London was established by a gift from Henry Baker (1698–1774) in 1775. It is awarded annually to a person (one per year) working in the fields of "natural history or experimental philosophy" (i.e., the physical sciences). Baker was described by Turner, Senior Assistant Curator of the Museum of Science in Oxford:¹⁰⁸ "Henry Baker was a typical polymath in the eighteenth-century manner. Although he did not contribute to scientific research in any significant way, he did make valuable contributions to the dissemination of scientific knowledge, particularly in the field of microscopy, an enthusiastic participator in the scientific and literary life of London."

Historical footnote: Michael Faraday, known primarily for his research in electromagnetics and electrochemistry, is considered by science historians to be one of the most influential scientists and the best experimentalist, in history,^{109,110} even though he had no formal education past grade school. Faraday, during the years between 1829 and 1857, was invited to present five Bakerian Lectures to the Royal Society.

Heinrich Geissler, in 1857, used his mercury pump (see the *Historical Footnote* in Sec. III A) to evacuate small glass enclosures and develop the "Geissler tube" to study the optical and electrical properties of glow discharges in rare gasses, air, mercury, etc.⁷⁵ He reported observing a wide variety of discharge colors due to optical emission resulting from the decay of excited gas atoms. This gave rise to the production, beginning in the 1880s, of the first gas-discharge lamps which were sold primarily as novelty and artistic items.¹¹¹ Julius Plücker,¹¹² also at the University of Bonn, and his ex-graduate student Johan Wilhelm Hittorf¹¹³ used Geissler tubes to study gaseous electronic effects resulting from ion bombardment of metal targets (see Sec. IV D).

In 1852, William Robert Grove (1811-1896), a Welsh lawyer (later, judge) and physicist, published the earliest recorded description of sputter deposition and ion etching experiments.²⁵ A sketch of his equipment is shown in Fig. 9. Vacuum was achieved with a mechanical piston pump, similar to that developed by von Guericke as described in Sec. III A, with power supplied by Grove's version of a troughstyle dc voltaic pile (following Cruickshank, Sec. III B)¹⁰⁴ combined with an "induction coil" step-up transformer supplied by Heinrich Ruhmkorff (1803-1877),¹¹⁴ a famous German instrument maker living at the time in Paris. The electrodes consisted of a copper plate, with a polished electroplated silver surface, and a rod, which passed through a leather stopper in the top of the glass vacuum chamber, with a steel needle attached to its end. The gas used to sustain the discharge was stored in a bladder.

Historical footnote: Based upon a passing comment in Grove's later papers, the small vessel attached to the rod electrode shown in Fig. 9 contained "potassa fusa" [the ancient name for potassium hydroxide (KOH), a caustic deliquescent desiccant which can capture large quantities of water]. This was an early adsorption (i.e., getter) pump.

The experiments were carried out at rather high pressures, ranging from ~ 100 to 500 mTorr, with the steel needle target quite close to the silver-plated substrate (generally a separation of 0.25 cm, "but this may be considerably varied").



FIG. 9. System used by William Grove to investigate target "disintegration" (sputtering) in a gas discharge. Reproduced with permission from Grove, Philos. Trans. R. Soc. **142**, 87 (1852). Copyright 1852 by Taylor and Francis Publishers. See text for details.

When using a mixture of hydrogen and air with the silver plate positive and the steel needle serving as the (negative) cathode, Grove observed thin-film deposition on the silver substrate. The layer was primarily iron oxide, i.e., reactive sputtering (although the term did not come into existence until more than a century later, Sec. IV J). The color of the oxide film "presented in succession yellow, orange, and blue tints" with increasing thickness (longer deposition time). Grove reported optical interference effects (as he noted later in the paper), which for a given substrate/film combination can be calibrated to provide film thickness versus color as is commonly done today for SiO₂ and Si₃N₄ dielectric layers on Si(001) wafers used in microelectronic device fabrication.

When Grove switched polarity such that the silver plate became the cathode (negative), he reported that the iron oxide film was removed by ion etching. Continuing the experiment, a polished region "occasioned by molecular disintegration" remained. Thus, Grove had not only removed the original oxide film, but also sputter-etched into the silver substrate layer. The word "sputter" did not yet exist (as discussed in Sec. II), and Grove described the process throughout the paper as "molecular disintegration."

Grove repeated the above experiment by sputtering the steel target in an "air vacuum" (a term Grove attributed to Faraday) to produce a more fully oxidized film on the silverplated copper substrate and then switched gases and electrode polarity to "sputter clean" the silver plate in a nitrogen discharge. In actuality, there must have been a thin silveroxide layer remaining due to the competition between the rates of silver oxidation from the discharge, arising from the relatively poor vacuum, and sputter etching. However, this layer, a few tens of Å in thickness,¹¹⁵ would have been too thin for Grove to observe. Several more experiments in which he substituted different metals for the target needle and changed discharge gases were also reported. The results were similar, but he described observing differences depending upon the atomic masses of the target material and the gas, the ionization potential of the gas, and the oxidation tendency of the metals.

Interestingly, Grove realized that oxygen can form negative ions which are accelerated by the applied target voltage toward the substrate (anode). The significance of the fact that oxygen has a high electron-attachment probability¹¹⁶ was not fully appreciated until almost 130 years later. Researchers investigating the growth of piezoelectric and transparent conducting oxides (TCOs) in the early 1980s^{117–119} and hightemperature oxide superconductors in the late 1980s,¹²⁰ all of which are typically deposited today by reactive magnetron sputtering (see Secs. IV F and IV J), were confronted with the deleterious effects of O⁻ and O⁻₂ irradiation.

Negative ions, accelerated by the same potential used to produce sputtering by positive ions incident at the target, bombard the growing film with energies which can produce residual defects, change the preferred orientation of polycrystalline layers, degrade film properties, and decrease deposition rates by resputtering.^{115,117–121} Irradiation of the growing film by fast neutral O and O₂ species can also occur, as attached electrons are stripped from the corresponding

ions in the plasma.^{118,120,122} Early solutions involved increasing the discharge pressure in order to decrease particle mean-free paths and hence lower the average energies of ions and fast atoms via collisions,¹²¹ while later solutions focused on off-axis deposition and facing-target sputtering (Sec. IV F 1).^{119,123–127}

A few years after Grove's seminal paper, John Gassiot (1797-1877), a highly successful English businessman and gentleman scientist, presented his Bakerian Lecture (March 4, 1858) "On the stratifications and dark bands in electrical discharges as observed in Torricellian vacuums," which was published in the Proceedings of the Royal Society of London¹²⁸ (also see Ref. 129). Most of the lecture was concerned with his observations of alternating bright and dark bands formed in rarefied-air discharges contained in glass tubes partially filled with clean boiled mercury and evacuated with a mechanical pump [as air is extracted, the mercury level sinks in the tube and a "Torricelli vacuum" is formed (see the *Historical footnote*, Sec. III A)].^{1,72,73} During these experiments, Gassiot noted that the luminous discharge regions move under the influence of a magnetic field. However, he conceded in the conclusion of Ref. 128 that "I refrain for the present from any observations as to the action of the magnet on the discharge."

Gassiot also reported that for discharges formed between two platinum wire electrodes hermetically sealed about 4 inches (~ 10 cm) apart in a discharge tube: "a black deposit takes place on the sides of the tube nearest the negative terminal. This deposit is platinum (analyzed by Michael Faraday)¹²⁹ in a state of minute division emanating from the wire, which becomes black and rough as if corroded. The minute particles of platinum are deposited in a lateral direction from the negative wire, and consequently in a different manner from what is described as occurring in the voltaic arc."¹²⁸ "The platinum coating is deposited on the portion of the tube surrounding the negative wire, but none at or near the positive."¹²⁹ Gassiot described sputter deposition from the platinum target. He noted that "...when this deposit is examined by transmitted light, it is translucent, presenting to the eye an extremely thin bluish-black film; but by reflected light, either on the outside or inside (i.e., viewed either from the glass or the film side), it has the appearance of highly polished silver, reflecting the light as from the finest mirror."129

Historical footnote: Gassiot, in addition to being a successful businessman, was a very enthusiastic amateur scientist interested in electricity. He maintained a well-equipped laboratory and library in his home where young James Maxwell (1831–1879), a Scottish mathematical physicist who developed electromagnetic theory and presented a unified model of electricity, magnetism, and light,¹³⁰ did much of his own scientific work during the 1860s. Gassiot was a founder of the London Electrical Society in 1837 and the Chemical Society in 1845 and was elected as a Fellow of the Royal Society in 1841. He was also a close associate of Grove.

Practical applications of sputter-deposited single and multilayer metal films as mirrors and optical coatings on telescope lenses and eyepieces were discussed in papers published in 1877 by Arthur Wright (American physicist, 1836–1915, Yale University).^{131,132} The first of the two articles reported the growth of adherent noble-metal films sputter-deposited from wire targets onto glass microscope slides.¹³¹ Unfortunately, the films had large lateral thickness variations since the target was the tip of a wire whose length was encased in a glass tube. However, an ingenious solution was presented in Wright's next paper.¹³² He designed a deposition system, evacuated with a Sprengel mercury pump (see Sec. III A), in which the substrate was mounted on a pendulum to provide motion in two orthogonal directions with respect to the target such that films of uniform thickness could be "painted" onto the substrate (Fig. 10). In Wright's words: "The perfect control of the process obtained by the use of the movable electrode will even make it possible to apply the method of local correction for the improvement of a defective figure, or to parabolize a spherical mirror by depositing the metal in a layer increasing in thickness toward the center."

Historical footnote: Wright was a member of the first Ph.D. graduating class in the United States. The 1861 class consisted of three scholars at Yale University. Wright's doctoral dissertation was on satellite mechanics.^{133,134} As an undergraduate and graduate



FIG. 10. Illustration [reproduced with permission from Mattox, Vac. Technol. Coat. **2**, 34 (2001). Copyright 2001 by Vacuum Technology and Coating (Ref. 135)] of Wright's sputter deposition system, based upon his description in Ref. 132.

student, he studied mathematics, mineralogy, botany, and modern languages, in addition to physics. He also studied law and was admitted to the bar. Following teaching positions and postdoctoral research programs at Heidelberg and Berlin, Wright became Professor of Molecular Physics and Chemistry at Yale University in 1872 and later Professor of Experimental Physics. His sputter-deposited thin films were used extensively in the first studies of polarized light emitted from the solar corona (plasma surrounding the sun, most easily observed during a solar eclipse). Wright became a member of the U.S. National Academy of Sciences and a Fellow of the UK Royal Astronomical Society.

Wright characterized the sputtering process spectroscopically using optical emission from gas, and ejected target atoms, which were excited in the discharge (following earlier work by Faraday).¹⁰⁵ As-deposited platinum films, some with thicknesses <350 Å (estimated using a combination of weight change, to within 10 μ g, for thicker films, deposition rate calibrations, and optical interference rings for thinner layers), were analyzed using optical transmission as a function of wavelength. Mirror-like sputter-deposited films were found to be more adherent than solution-grown layers and less sensitive to local delamination caused by water penetration to the film/glass interface. By the late 1800s, sputter-deposition was routinely used in manufacturing commercial mirrors.

Wright described his films as "...surfaces of exquisite perfection and the most brilliant polish. They can only be compared to the surface of clean liquid mercury, far surpassing in luster anything that can be obtained by the ordinary methods of polishing." Wright tuned the reflectivity of his mirrors based upon interference effects to obtain brilliant "white light" by depositing multilayer films with predetermined layer thicknesses.

In the late 1860s, William Crookes (1832–1919), a British chemist, developed what are now referred to as Crookes discharge tubes [Fig. 11(a)]¹³⁶ based on the earlier Geissler tubes.¹¹¹ Crookes also took advantage of the Sprengel mercury pump to obtain better vacuum, and hence longer meanfree paths, in his tubes which he used to promote research on gas-discharge electronics. Crookes tubes were instrumental in the discoveries of x-rays¹³⁷ (Wilhelm Röntgen, 1896, Nobel Prize in Physics, 1901), electrons¹³⁸ (J. J. Thomson, 1897, Nobel Prize in Physics, 1906), and thermionic emission^{139,140} (Owen Richardson, 1901, Nobel Prize in Physics, 1928), which enabled vacuum-tube electronics.^{141,142}

Crookes published a very significant paper on sputter deposition of thin films in 1891.¹⁴³ During a long series of experiments, he employed a Sprengel-type mercury pump⁵³ to evacuate his discharge tube to pressures of the order of 7×10^{-4} Torr. He then used the residual air to sputter Ag, Al, Au, Cd, Cu, Fe, Ir, Mg, Ni, Pb, Pd, Pt, and Sn targets as well as AlAu and CuZn (brass) alloys and measure the erosion rates via target weight loss.

Although the experimental details (sputtering pressure, voltage, and ion current densities) were not well specified, Crookes, in order to obtain comparable results, designed a



FIG. 11. (Color online) Reproduction of a Crookes tube, containing a Maltese cross between the cathode and the far end of the glass envelope, used to investigate the electronic characteristics of, and the optical emission from, glow discharges. (Left panel) No power applied to the tube. (Middle panel) Power applied to the cathode gives rise to green fluorescence emanating from the glass behind the Maltese cross which casts a shadow by blocking "cathode rays (radiant matter)" from the target. (Right panel) A magnet was used to rotate the shadow image. Photographs are attributed to Zátonyi Sándor. Licensed under a Creative Commons Attribution-Share Alike 3.0 Unported license. The labels were added by the present author.

multitarget sputtering system with indexed motorized external electrical contacts as illustrated in Fig. 12.143 Every experiment was carried out using four wire targets, 0.8 mm in diameter and 20 mm in length, in which one of the four was always a gold reference electrode. Power was alternately applied to each target in succession, using a revolving commutator, for the same length of time (typically 6 s) over periods of several hours. By this means, variations in current and sputtering pressure were accounted for in order to obtain a set of metal sputtering rates, all referenced to that of gold. Aluminum and magnesium targets were reported to be "practically nonvolatile." Today, we know that this was due to the formation of strongly-bonded oxynitride (primarily oxide) dielectric layers at the target surfaces due to the use of air (approximately 78% nitrogen and 21% oxygen by volume) as the sputtering gas.



FIG. 12. Four-target sputtering system used by Crookes to measure the sputtering rates of different metals. The targets were 0.8-mm-diameter metal wires. Reproduced with permission from Crookes, Proc. R. Soc. London **50**, 88 (1891). Copyright 1891 by Royal Society.

The "rich purple color" of the aluminum-gold alloy target turned to the "dull white color of aluminum" as gold was preferentially sputter removed. This was the first mention in the literature of preferential sputtering from alloy targets. While this occurs for all alloys, the target surface composition during sputtering in rare gases rapidly (depending on the ion energy, current density, and relative ion and targetatom masses) reaches a steady-state value as the surface coverage of the low-sputtering-rate component increases to compensate for the difference in elemental removal rates as shown experimentally by Tarng and Wehner¹⁴⁴ and theoretically by Eltoukhy and Greene.¹⁴⁵ In Crookes' aluminumgold alloy experiments, oxidation further decreased the aluminum sputtering rate.

Since the targets in Crookes' experiments were uncooled, low-melting-point metals such as tin, cadmium, and lead quickly melted. For these materials, he devised a holder to sputter liquid metals. It is likely that a significant part of their measured weight loss, especially for the high-vaporpressure element cadmium, was due to evaporation, in addition to sputtering.

In his April 4, 1879 Bakerian Lecture,¹⁴⁶ Crookes, like Faraday¹⁰⁵ and Gassiot^{128,129} before him, discussed the use of optical spectroscopy to characterize plasmas, in many discharge-tube configurations, at working pressures from "0.08 mm Hg (80 mTorr) down to a low of 0.00001 mm Hg (0.01 mTorr)."¹⁴⁷ He often specified the sputtering pressure not in pressure units but as the thickness of the cathode dark space, which came to be known as the Crookes dark space, adjacent to the very bright glowing region in front of the target. He noted that during long sputtering runs, it was necessary to periodically bleed some air into the discharge tube "to reduce the vacuum." After examining metal films deposited on the inside of the discharge tube and finding them to be porous with rough surfaces, he concluded that sputtering gas (residual air in these experiments) was "occluded" in the growing films. While some gas was likely trapped in the growing films, most was captured (adsorbed) via reactions with the fresh metal layers, deposited on surfaces throughout the system, which acted as a getter pump.

Francis Aston (1877–1945, English chemist and physicist, Nobel Prize in Physics, 1922, for discovery of isotopes in nonradioactive elements) also made important contributions to the modern understanding of glow discharges. After three years working as a chemist in a brewery, Aston joined Birmingham University with a scholarship in 1803 to study glow discharges. In 1907, he discovered a very narrow region in gas discharges, now called the Aston dark space,¹⁴⁸ immediately adjacent to the target and preceding the bright cathode-glow region. The area is "dark" (less luminous) since the *average* energy of electrons emitted from the target due to ion bombardment (see discussion in Sec. IV D) is less than that required for the excitation of gas atoms. However, the electrons are rapidly accelerated by the applied electric field to produce the cathode glow.

Aston carried out his own glass blowing to fabricate gasdischarge tubes with movable aluminum electrodes in order to measure the distance from the target to the end of the "Crookes dark space" and, hence, provide an estimate of the width of the "cathode fall" over which ions are accelerated to the target. He showed, for a wide range of gases, that the cathode fall distance d is given by

$$d = \frac{A}{P} + \frac{B}{J_T^{0.5}},$$
 (1)

in which P is the gas pressure, J_T is the target current density, and A and B are functions of the gas and target material.^{149–151} This empirical relationship is now referred to as the Aston equation. Aston was appointed lecturer at the University of Birmingham in 1909 but moved to the Cavendish Laboratory in Cambridge in 1910, on the invitation of Thomson, to continue working on gaseous electronics.

In 1902, Thomas Edison (1847–1931), an American inventor and businessman, patented a very early forerunner to copper contact technology in modern microelectronic device fabrication.^{152,153} Edison's U.S. patent 713,863 ("Process of coating phonograph records") describes the use of dc sputtering for the deposition of metal films on wax phonograph masters as "seed" (and adhesion) layers for electroplated overlayers.¹⁵⁴ This follows an earlier 1892 Edison patent in which the seed layers were deposited by vacuum-arc deposition.¹⁵⁵ Edison claimed in the 1902 patent that the arc process was too slow and that sputter-deposited films had much more uniform thickness distributions.

Historical footnote: Thomas Edison, a prolific inventor who was issued 1,093 U.S. patents (phonograph, motion picture camera, sound recording, etc.) and many patents in other countries, is often credited with the invention of the light bulb. While Edison was issued a U.S. patent for an "Electric lamp" in 1880,¹⁵⁶ he did not "invent" the light bulb. Rather, he took advantage of the availability of better vacuum due to the development of the mercury momentum-transfer pump⁵³ by Sprengel in 1865 (see discussion in Sec. III A) to develop a much longer-lived bulb which was commercially viable. In fact, a year before Edison was born, Grove, who published the earliest recorded description of sputter deposition and ion etching,²⁵ as discussed above, used a

platinum-filament electric light to illuminate the lecture theater¹⁵⁷ during his first Bakerian Lecture before the Royal Society on November 19, 1846, as he described the use of his improved voltaic dc battery to dissociate water:^{158,159} "On Certain Phenomena of Voltaic Ignition and the Decomposition of Water into its Constituent Gases by Heat." The history of the light bulb is rich and interesting, stretches back to at least 1802, and involves many previous researchers as chronicled in Ref. 160.

Grove's and Crookes' research on sputtering attracted the attention of scientists worldwide. A review paper, entitled "Cathode Sputtering, a Commercial Application," published in 1932 by Fruth,¹⁶¹ of Western Electric Company (Chicago), lists 113 references published in the field between the time of Grove's 1852 pioneering article²⁵ and 1930. Fruth described commercial equipment (Fig. 13, left panel) and procedures for sputter-depositing gold electrodes, from six gold cathodes, onto multiple radio-broadcasting microphone diaphragms. A photograph of the deposition chamber, which contains a rotating McLeod gauge⁵⁸ and a "bleeder" valve in order to maintain constant pressure, with diaphragms ready to be coated, is shown in the right panel of Fig. 13. Fruth described the system operation as follows.

"In order to maintain a constant residual gas pressure, the pump is operated continuously and air is allowed to leak in slowly through the bleeder valve which is located near the pump. This practice was found necessary in order to overcome variations in pressure due to the early evolution of gases and the later cleanup usually accompanying electrical discharges *in vacuo*. A pressure of 0.100 mm (100 mTorr) is readily maintained by this method. After a new charge has been placed in the bell jar, the bleeder valve is temporarily cut off by closing a stopcock so that the required vacuum can be more quickly obtained. By this means, sputtering can be started in about 4 min after the bell jar has been placed in position."

Fruth demonstrated that dc sputter-deposited gold films, $<1 \,\mu$ m thick, offer substantial lifetime advantages over previous electroplated films which developed "blisters," peeling, and pinholes after three months of continuous use, while the sputter-deposited films exhibited no sign of wear or degradation.

An early ion-beam source was developed by Louis Maxwell in 1931.¹⁶² A hydrogen discharge at pressures of 3.5-120 mTorr, with a liquid-air cold trap to remove water vapor and minimize mercury contamination due to backstreaming from the pump, was established in a small brass vacuum vessel. The ion current was controlled by thermionic electron emission from a hot, low-work-function filament. Large magnetic fields, $\sim 12-17 \times 10^3$ G, parallel to the positive ion beam were used to minimize ion losses to the wall and provide 0.1-3 mA through a 1-mm-diameter circular extraction electrode to a collector electrode in a small 3.3×10^{-3} attached chamber maintained at to 1.5×10^{-4} Torr.

The first recorded description of a dc glow discharge ionbeam sputtering system was given by Seeliger and



FIG. 13. (Left panel) Commercial sputter-deposition unit, with six gold targets, for depositing metal electrodes on microphone diaphragms. (Right panel) A closer view of the deposition chamber, showing the diaphragms. Reproduced with permission from Fruth, Physics **2**, 280 (1932). Copyright 1932 by American Institue of Physics; labels were added by the present author.

Sommermeyer in 1935.¹⁶³ They drilled a 2-mm-diameter hole in the cathode of their discharge tube to "collimate" an Ar^+ ion beam (the beam was actually divergent) to strike solid silver or liquid gallium targets at energies of 5-10 keV and observed that sputtered-atom emission can be approximated by a cosine distribution.

In 1960, Wehner and Rosenberg,¹⁶⁴ using a mercurypool-supported glow discharge (see Sec. IVE) to sputter polycrystalline metal targets with normally incident 100 to 1000 eV Hg⁺ ions, showed that sputtered-atom angular ejection distributions ranged from under-cosine at lower energies toward cosine at higher energies and noted that the crystalline orientation (texture) of the target was important. Much later (1986), Matsuda et al.¹⁶⁵ reported, based on normally incident Ar⁺ ion-beam experiments, that the angular distribution of sputtered iron atoms varied from cosine at 600 eV to slightly over-cosine at 1000 eV and increasingly overcosine at 2 and 3 keV. With a simple cosine emission distribution, often used as a first approximation in sputter deposition (see Sec. IVF2), the sputtered flux ejected from a given point on the target surface along any angle φ is just the flux at normal incidence multiplied by the cosine of φ .¹⁶⁶

B. Mechanism of sputtering

Crookes, in his classic 1891 paper on metal sputtering rates,¹⁴³ compared the sputtering process with evaporation and described differences in the two processes as arising from coupling electrical versus thermal energy to the source material. That is, sputtering in his terminology was "electrical evaporation." Charles Townes (1915–2015, Physics Nobel Laureate in 1964, sharing the prize for the invention of the maser) published a theory in 1944 based on ion-irradiation-induced local evaporation in which the sputtering yield (the average number of atoms ejected per incident ion, a measure of the process

efficiency) depended on the ion-energy but not on the ratio of the ion-to-target atom masses.¹⁶⁷ Even though contradictory evidence had been accumulating since the late 1890s, the concept that sputter ejection of target atoms occurs by local "hot spot" evaporation persisted well into the 1900s. In fact, a review article published as late as 1962 (Ref. 168) followed Adolph Güntherschulze (1878–1967, German physicist, Technical University of Dresden) in attempting to popularize the term "impact evaporation."¹⁶⁹

A half century after Grove's initial sputter-deposition and ion-etching experiments,²⁵ Eugen Goldstein (German physicist,1850–1930) in 1902 provided additional (although, by this time, unnecessary) evidence that sputtering is initiated by positive-ion bombardment. In his experiments, he used a perforated negatively-biased target and demonstrated sputter etching of a gold film on the wall of the discharge tube behind the target.¹⁷⁰ Goldstein called the positively charged beams "canal rays." In 1908, Johannes Stark (1874-1951, Physics Nobel Laureate in 1919 for the discovery of electricfield-induced splitting of atomic spectral lines) argued strongly in favor of sputter-ejection occurring by ion-impact-initiated collision cascades.^{171,172} There was abundant evidence to support these claims, including the relative insensitivity of sputtering rates to the thermal conductivity of the target and to target temperature.^{173,174} Stark and Wendt,¹⁷⁵ in 1912, reported experimental evidence for sputter-rate variations with grain orientation in polycrystalline targets.

In 1931, Mayer¹⁷⁶ and later Sporn¹⁷⁷ (1939) provided early indications that the ejection energies of sputtered atoms are of the order of several electron-volts, much higher than typical evaporated-atom energies of a few tenths of an electron-volt. The authors investigated optical emission due to the decay of atoms sputter-ejected from thin, low-workfunction, alkaline-earth-oxide and alkaline-metal layers on metal targets and excited in the discharge. Ejection velocities

05C204-15

were estimated from measurements of the thickness of the luminous discharge region together with known excited-state lifetimes. Güntherschulze¹⁷⁸ contributed supporting data in 1942 showing that sputtered atoms have much longer mean-free paths (and hence higher kinetic energies) than would be expected for thermal atoms.

Fetz added further evidence in favor of sputtering via collision cascades in 1942 when he showed that sputtering yields (determined by dividing the measured target weight loss by the ion current to ground) increase with increasingly oblique angles of ion incidence due to more effective momentum transfer in the near-surface region of the target.¹⁷⁹ In 1954, Fred Wehner, often referred to as the father of modern sputtering, found that atoms tend to be sputter ejected in a specular direction when subjected to oblique low-energy (<1 keV) ion bombardment.¹⁸⁰

None of the above results are compatible with target "disintegration" by an evaporation process. Wehner¹⁸¹ added yet another point in favor of momentum-transfer sputtering in 1955, while confirming the previous observations of Stark and Wendt.¹⁷⁵ He showed that during low-energy (150 eV Hg⁺) sputtering from single-crystal targets under conditions (see Sec. IV D) for which ion energies are monoenergetic and incident orthogonal to the target surface, sputtered atoms are ejected along close-packed crystalline directions.¹⁸¹ Examples are shown in Fig. 14 for sputtering of single-crystal (111)-, (110)-, and (001)-oriented face-centered-cubic (fcc) silver targets; the "spots" correspond to preferential sputtering along close-packed directions in all three cases. These results captured the imagination of scientists working in the sputtering field; several papers confirmed Wehner's "spot pattern" observations for fcc metals^{182,183} and showed similar effects for body-centered^{184,185} and hexagonal¹⁸⁶ metals as well as diamond-^{182,183} and zinc-blende-structure¹⁸⁷ semiconductors. The latter authors noted that preferred ejection directions are not observed for sublimation from single crystals.¹⁸⁷

Historical footnote: the spot patterns first published by Wehner rapidly led to sputtering theories based upon long-range collision sequences along close-packed directions ("focusons"); one of the earliest was by Silsbee.¹⁸⁸ The focuson sputtering concept was highly popular and lasted for many years even though it was shown early, by both computer modeling¹⁸⁹ and analytical calculations based upon experimental results,¹⁹⁰ that

the spot patterns can be explained simply by nearsurface collision effects. This is especially the case for low-energy sputtering, where penetration depths are only several atomic layers, but it is also true even for high-energy sputtering for which experimental results show that the average focuson range is only a few atomic distances (see discussion in Ref. 190).

The existence of spot patterns as a function of target orientation indicates that the original lattice structure is at least partially intact during the violent sputtering events, further evidence against fully developed cascade focusons for which the lattice would lose orientational information. Overall, it is clear that the probability of sputtering an atom from the surface layer (i.e., providing sufficient energy to overcome the surface binding energy) will be higher due to a central collision initiated by a close lower-lying neighbor atom. The width (broadening) of sputtered-atom spots is determined by a variety of factors including thermal vibrations and deviations from the ideal surface structure due to previous ion impacts.

Stuart and Wehner^{191,192} also provided additional definitive evidence that the earlier indications by Mayer¹⁷⁶ and Sporn¹⁷⁷ were correct: atoms sputtered by low-energy ions are ejected with average energies that are of the order of ten times larger than that for evaporation at the same rate. Wehner and colleagues used time-of-flight optical spectroscopy in low-pressure Hg-pool-supported discharges (see Sec. IVE) for which the sputtered-atom mean-free path was larger than the distance from the target to the measurement sampling region. In these experiments, the target was sputtered during sequential $1-\mu s$ pulses and the sputtered atoms were excited by electrons in the discharge. As each group of sputtered atoms moves away from the target, it becomes spatially dispersed due to the distribution in ejection velocities. The dispersion is detected as a time distribution of characteristic photons emitted by the sputter-ejected atoms as they pass through the observation volume, defined by a narrow slit, at a known distance from the target. The measured time distribution is then converted into an ejection velocity and/or an energy distribution. Time-of-flight results were verified by determining the Doppler shift for light emitted by sputtered atoms in the direction of travel.¹⁹²

Figure 15 shows a plot of the average energies E_{at} of atoms ejected orthogonal to 22 different polycrystalline metal targets due to bombardment by 1.2 keV Kr⁺ ions.¹⁹²



FIG. 14. Typical deposited spot patterns obtained from low-energy sputtering of (111)-, (110)-, and (001)-oriented fcc single-crystal silver targets. Courtesy of Fred Wehner and permission from American Institue of Physics. See also Ref. 181.



FIG. 15. (Color online) Average energies E_{at} of atoms sputter ejected orthogonal to the surface of elemental polycrystalline targets bombarded with normally incident 1200 eV Kr⁺ ions. Z is the atomic number (the number of protons per atom). $Z_{Kr} = 36$. Reproduced with permission from Stuart *et al.*, J. Appl. Phys. **40**, 803 (1969). Copyright 1969 by American Institute of Physics.

The data conclusively establish that sputtering is not a local evaporation process. Average ejection energies for elements in the middle of the periodic table are $\sim 10 \text{ eV}$, with considerably higher E_{at} values for heavy elements such as Ta, Pt, W, Re, and U which have atomic masses between 180.95 and 238.03 amu. The heavy-target-atom effect is directly related to the relatively shallow penetration depths of the much lighter Kr⁺ (83.80 amu) ions. That is, kinetic energy is deposited closer to the surface of heavy-atom targets. However, there is clearly more to the story; as discussed in Sec. IV H, even though the mass of Au (196.97 amu) is higher than that of the other heavy atoms, except for U, shown in Fig. 15, Au exhibits a lower average ejection energy.

C. Early sputter-yield measurements

Kingdon and Langmuir⁴⁷ published, in 1923, argon, cesium, helium, hydrogen, neon, and mercury sputtering yields (average number of sputtered atoms per incident ion) for thoriatedtungsten wire targets (light-bulb filaments) as a function of target voltage V_T between -50 and ~ -400 V in a glass dc-diode system. Although the sputtering conditions were poorly defined, the authors discussed the process in terms of momentum transfer. In 1926, Eric Blechschmidt¹⁹³ carried out exhaustive studies of the sputtering yields of 19 metals by hydrogen, 13 metals by neon, and 15 metals by argon ion bombardment. Unfortunately, Blechschmidt's results suffered from severe target contamination due to poor vacuum.

In addition to contamination, another issue in early sputter-yield measurements is the unknown contribution to the total measured current of the ion (as well as the fast-neutral-atom and photon) bombardment induced secondary-electron flux (see the *Historical footnote* below) from the target. The secondary-electron yield from clean metals is typically ~0.1 for Ar⁺ ion energies less than ~1 keV.^{194,195} Thus, the *direct* effect on reported low-energy metal sputtering yields is not large. However, the *indirect* effects turn out to be very important indeed. A secondary-electron yield of 0.1 requires that each ejected electron must, on average, produce 10 new ions to maintain the discharge. This, in turn,

requires operating at relatively high pressures in dc-diode systems, often near, or above, 100 mTorr, depending on the target-to-substrate distance, in order to provide sufficient collisions since the extremely small size of electrons results in them having correspondingly small scattering crosssections and, hence, long mean-free paths.

Historical footnote: the evolution of the understanding of ion-bombardment-induced secondary-electron emission from a metal target is fascinating, involves many of the giants in the early days of gaseous electronics, and, due to its importance in the sputtering process, is briefly recounted in Sec. IV D.

Sputtering at high pressures introduces, in turn, yet another uncertainty in the accurate determination of sputter yields. The mean-free path of sputter-ejected target atoms, which have much higher collision cross-sections than electrons, is very short at these pressures. In 1926, Artur von Hippel¹⁹⁶ estimated that in typical sputtering systems at the time, the short mean-free paths result in up to 90% of the sputtered atoms being reflected back to the target at an Ar pressure of 100 mTorr. This not only dramatically reduces film deposition rates, it means that sputter yields based upon target weight-loss measurements are greatly underestimated.

An additional issue in determining reliable sputter yields S as a function of ion energy Ei at such high pressures is the inherent assumption that $E_i = eV_T$. However, at high pressures, the ion mean-free path is much less than the distance over which the applied voltage V_T "falls" to the target (the cathode fall or "target sheath" distance). Thus, ions make many collisions while transiting the ion sheath, and hence, their average energy upon striking the target is much less than eV_T. This further reduces the sputtering yield (and the resultant film deposition rate). von Hippel¹⁹⁶ used a retarding field to measure the energy-dependent ion-current distribution arriving at a probe positioned a short distance behind a small hole in a metal cathode immersed in a 100 mTorr, 15 mA, $V_T = -1000 \text{ V}$, argon discharge. He reported that the average ion energy E_i was $\sim 250 \text{ eV}$, with an energy spread ranging across the full cathode-fall potential. Most of the ions arrived at the cathode with kinetic energies near zero. That the average value of E_i is much less than eV_T was confirmed years later by Davis and Vanderslice¹⁹⁷ who showed that the primary energy-loss mechanism for ions in highpressure dc glow discharges is due to quantum-mechanical charge-exchange processes which have higher cross-sections than hard-sphere collisions.¹⁹⁸ It should be noted that the decrease in the sputtering yield as a function of V_T, compared to expected values if E_i was equal to eV_T, is partially mitigated due to sputtering by fast neutral atoms (i.e., accelerated ions which undergo charge-exchange reactions near the target), a process not accounted for in the measured ion currents.

D. Ion-bombardment-induced secondary-electron emission

In 1858, during his investigation of electrical conduction through glow discharges,¹¹⁰ Julius Plücker (1801–1868), a

German Professor of Mathematics (and later Physics) at the University of Bonn, observed a green fluorescent region in the glass discharge tube across the metal cathode [Fig. 11(b)].¹⁹⁹ He also found that the position of the luminescence could be deflected by a magnetic field [Fig. 11(c)]. Johan Hittorf (1824-1914), who studied under Plücker, reported similar results in 1869,¹¹³ leading him to infer that the glowing spot at the end of the glass discharge tube was due to what he termed "glow rays" which emanate from the cathode and proceeded in straight lines to cause the luminescence. In 1878, Goldstein demonstrated that the particles (he referred to them as "cathode rays") did, in fact, originate at the cathode²⁰⁰ and had a charge opposite to that of the "canal rays" (positive-ions) he observed during sputtering of a perforated target (Sec. IV B).¹⁷⁰ Crookes¹⁴³ (Sec. IV A) used the term "radiant matter" and established that the rays were not due to fast sputtered atoms.²⁰¹ He proposed (incorrectly) that radiant matter was due to negatively-charged ions ejected with high velocity from the cathode.²⁰²

The German-born British physicist Arthur Schuster (1851-1934), a friend and competitor of Thomson, 203,204 expanded upon Crookes' experiments by placing metal plates parallel to the cathode rays and applying a potential between the plates. He observed that the rays were deflected toward the positive plate, thus proving (again!) that they are negatively charged.^{204,205} This was confirmed, using a different approach, by Jean Baptiste Perrin (1870–1942), a French physical chemist, and discussed at a lecture before the Paris Academy of Sciences on December 30, 1895 (English translation, Ref. 206). In his experiments, he allowed a beam of cathode rays to enter a metal cylinder through a small hole and showed that the cylinder became negatively charged to a value which was determined using an electrometer. No negative charge was measured if the beam was deflected away from the cylinder hole by a magnetic field. Perrin, more famous for his studies of Brownian motion, received the 1926 Nobel Laureate in Physics "for his work on the discontinuous structure of matter, and especially for his discovery of sedimentation equilibrium (the atomic nature of matter)."

Schuster, in his 1884 Bakerian Lecture,²⁰⁵ made an important contribution to cathode-ray research by noting that "a particle of charge e and mass m, moving at speed v at right angles to a magnetic field \overline{B} , would be deflected such that it moves in a circle of radius r = mv/Be, so that (the cathoderay charge-to-mass ratio) e/m = v/Br." Unfortunately, the pressure in Schuster's cathode tube was too high, 300 mTorr, for accurate measurements of v.

In his second Bakerian Lecture,²⁰⁷ 1889, Schuster combined the above equation with conservation of energy $1/2mv^2 = eV_T$, in which V_T is the cathode-fall voltage, to yield the expression $e/m = 2V_TB^2r^2$. He used this equation to provide an upper limit to e/m since it assumes that no energy is lost by collisions between cathode-ray particles and gas atoms (i.e., the use of low discharge pressures, which was not the case). He also provided a lower limit by assuming that the lowest cathode-ray particle speed v would be the root-mean-square speed of gas atoms at room temperature and the discharge-tube pressure. Again, however, he had experimental issues: "I have met with very considerable difficulties in the attempt to carry out the measurements in a satisfactory manner, and have only hitherto succeeded in fixing somewhat wide limits (which differed by a factor of ~1000) between which the molecular charges must lie."²⁰⁷ Moreover, Schuster's results were found to vary strongly with the gas composition²⁰³ due to the dependence of the cathode-ray collision frequency, in high-pressure discharges, on the size of the gas atoms.

Walter Kaufman (1871–1947), a German physicist, used the approach suggested by Schuster in his second Bakerian lecture,²⁰⁷ to determine e/m in better vacuum.²⁰⁸ The result, published in November, 1897, was much closer to today's accepted value than that of Thomson.¹³⁸ In addition, Kaufmann's e/m value, in contrast to that of Schuster, was independent of the discharge gas. He later showed, in his best-known work, that the electron mass is velocity dependent (i.e., relativistic).²⁰⁹ In January of 1897, Emil Weichert (1861–1928) published results in which he obtained an e/m value for cathode-ray particles that was 2000–4000 times larger than that of hydrogen ions.²¹⁰

Historical footnote: 1897 was a watershed year for cathode-ray research with seminal papers by Schuster, Kaufmann, Weichert, and Thomson, with the latter leading to the 1906 Nobel prize in Physics.

Thomson, generally acknowledged as the "discoverer" of the electron (which he called a "corpuscle"), first presented his cathode-ray results during a lecture at the Royal Institution in London on April 30, 1897.¹³⁸ Employing energy conservation to obtain e/m, he equated the kinetic energy of the cathode-ray particles to the heat generated by their collisions with the interior surface of a cylinder. Six months later, he reported more fully on the details of these experiments, together with the results of a second experimental approach based on the deflection of cathode-ray particles in electric and magnetic fields.²¹¹ When they were subjected to the electric field \overline{E} alone, $e/m = v^2 \theta / EL$, in which θ is the deflection angle and L the distance traveled by the particles at speed v in the field. The particles were next subjected to only a magnetic field \overline{B} , which deflected them through an angle φ , yielding $e/m = v\varphi/BL$. The two equations were then solved for the two unknowns: v and the ratio e/m.

Thomson then adjusted \overline{B} such that $\theta = \varphi$, resulting in v = E/B and $e/m = E\theta/B2L$, from which he obtained, based upon seven independent measurements, an average e/m value of 0.77×10^{11} C/kg, more than a factor of two lower value, 1.759×10^{11} C/kg. today's accepted than Nevertheless, Thompson realized that his result was still nearly $1000 \times$ larger than e/m for a hydrogen ion. Further, he reasoned that the absolute value of the corpuscle charge was the same as that of a hydrogen ion (although of opposite sign). Hence, the corpuscle must have a mass approximately 1000 times smaller. Thus, in his Royal Institution Lecture, Thomson announced the discovery of particles that are small compared to atomic dimensions. "We have in the cathode

05C204-18

rays matter in a new state... in which all matter—that is, matter derived from different sources such as hydrogen, oxygen, etc.—is of one and the same kind; this matter being the substance from which all the chemical elements are built up."^{138,211,212}

While the term electron was well known at the time (see the *Historical footnote* below), Thomson nevertheless continued to use the term corpuscles "...until about 1910, during a period when electron theory flourished and was considered the most important topic of physical theory."²¹² It is also interesting to note that: "In Thomson's Nobel-Prize citation there is no explicit mention of his discovery of the electron, but Thomson's (Nobel) lecture²¹³ was devoted almost exclusively to that topic."²⁰³ The citation states: "in recognition of the great merits of his theoretical and experimental investigations on the conduction of electricity by gases."

Historical footnote: The first use of the word "electron" to describe cathode-ray corpuscles appears to have been in 1894 by George J. Stoney (an Anglo-Irish physicist, 1826–1911), not to be confused with George G. Stoney (1863–1942) who is well known for the Stoney equation²¹⁴ which is still used today to evaluate thin-film stress). G. J. Stoney wrote, in an article entitled "*Of the* 'electron,' or atom of electricity,"... that an estimate was made of the actual amount of this most remarkable fundamental unit of electricity, for which I have since ventured to suggest the name electron.²¹⁵ Earlier, Stoney had used the term "electrolion" in describing experiments in which he estimated the charge of the "elementary particle of electricity."²¹⁶

The next breakthrough in understanding ion-induced emission of "corpuscles" or cathode-rays (i.e., secondaryelectrons) came much later. In 1954, Homer Hagstrum (1915–1994), an American surface physicist at Bell Laboratories, published a paper on the theory of ion-bombardment-induced secondary-electron emission, based primarily on Auger neutralization and, to a lesser extent, Auger deexcitation processes.²¹⁷ Hagstrum described Auger neutralization as "a process in which the interaction of two conduction electrons causes one electron to neutralize the (incident) ion and the other to be excited into the continuum above the filled band. The observed (secondary-electron yield) γ is determined by the probability that the excited electrons escape from the metal." Hagstrum's theoretical predictions proved to be a good fit to his experimental results for 10-1000 eV raregas irradiation of polycrystalline tungsten in an ultrahigh vacuum system with a base pressure of $\leq 10^{-10}$ Torr.²¹⁸ Secondary-electron ejection due to ion bombardment in this ion energy range, the upper half of which is commonly employed in modern glow-discharge sputter deposition, is today called "potential" electron emission. At ion bombardment energies $E_i \gtrsim 1000 \,\text{eV}$, (the "kinetic" electron emission range), γ increases with ion energy.^{219,220}

With $E_i < 1000 \text{ eV}$, γ is not a strong function of ion energy and is found experimentally to be approximately 0.11 for 500 eV Ar⁺ irradiation of tungsten and 0.25, 0.06, and 0.02 for Ne⁺, Kr⁺, and Xe⁺ irradiation. Similar results were presented by Hagstrum for rare-gas bombardment of molybdenum (see Fig. 16).²²¹ Variations in γ with the choice of rare gas primarily arise from differences in first-ionization energies which range from 21.56 eV for Ne to 15.75 for Ar, 14.00 for Kr, to 12.13 eV for Xe. The observed decrease in the secondary-electron yield for Ne⁺ with $E_i \leq 200 \text{ eV}$ (Fig. 16) results from the decreasing probability of Auger de-excitation processes involving short-lived excited states (thus the requirement for higher ion velocities) of the incident ion.^{217,222}

E. Use of thermionically- and mercury-pool-supported glow discharges for measuring sputtering yields

Several of the issues described in Sec. IV C which limited the accuracy of early sputter-yield $S(E_i)$ measurements were solved by Güntherschulze and Meyer in 1930 using their newly developed triode glow-discharge sputtering system.²²³ Large electron currents were obtained by thermionic emission from a separate filament electrode in order to overcome the low secondary-electron yield of the target. This provided a sufficiently dense plasma to allow sustained discharge operation at pressures between 1 and 10 mTorr. Thus, the mean-free path of ions and sputtered atoms was of the order of the discharge-tube dimensions (ballistic transport) with minimal scattering and back-diffusion to the target. Güntherschulze and Meyer immersed planar 5-cm-diameter Ag and Cu sputtering targets, during separate experiments, in dense plasmas as a third independent electrode. The ion current density at the target was approximately 1 mA/cm² and the ion-sheath thickness at $V_T = -1000$ V was ~ 5 mm such that the energy of ions (Ar⁺ or Ne⁺) incident at the target was $\sim eV_T$ with a nearly monoenergetic distribution. The



Fig. 16. (Color online) Total secondary-electron yield γ vs incident ion kinetic energy E_i for singly charged rare-gas ions incident at a clean molybdenum target in ultrahigh vacuum. Reproduced with permission from Hagstrum, Phys. Rev. **104**, 672 (1956). Copyright 1956 by American Physical Society.



FIG. 17. (Upper curve) Copper sputter yield S (atoms/ion), corrected for the secondary-electron yield γ , vs the negative cathode potential V_T in an argon discharge at a pressure of 10 mTorr. The lower curve is uncorrected for the secondary-electron emission yield γ . Reproduced with permission from Güntherschulze and Meyer, Z. Phys. **62**, 607 (1930). Copyright 1930 by Springer.

sputtering gas continually flowed and was spectroscopically monitored for purity.

Güntherschulze and Meyer sputter etched the target before initiating yield measurements and carried out separate experiments to determine the secondary-electron currents in order to obtain the actual ion current at the target. Figure 17 shows S(E_i) for Cu sputtered in Ar with and without accounting for the secondary-electron yield γ .²²³ The results are in reasonable agreement with modern sputtering yield data.²²⁴ The Cu target was uncooled and reported to reach a temperature of ~530 °C during long sputtering runs. In a later publication,²²⁵ the same authors measured the sputtering rates of 16 different metals by Hg⁺ ions at a gas pressure of 5

mTorr, controlled by adjusting the temperature of an oil bath in which the glow-discharge tube, containing a liquidmercury pool, was partially submerged.

In 1956, Wehner²²⁶ improved the design of an earlier (1940) version of a mercury-pool-supported glow-discharge tube developed by Fetz.²²⁷ An illustration of Wehner's initial mercury-pumped (see Sec. III A) glass sputtering system is shown in Fig. 18.²²⁶ While the base pressure was not specified, from comments in later papers, it was $\sim 10^{-6}$ Torr.^{228,229} The target in this system is immersed as a large Langmuir probe^{226,230} in a low-pressure, high-density plasma created by a vacuum-arc discharge between the liquid-pool cathode and an anode. The Hg pool is in the bottom of the tube, and the vacuum-arc is ignited by a SiC rod inserted into the liquid pool.²²⁸ The cathode spot is anchored to a molybdenum strip that is partially submersed. An auxiliary (secondary) anode is required to maintain the cathode spot firmly anchored. The mercury pool is heated by an external water bath to 17 °C to provide a Hg gas pressure of ~ 1 mTorr.

The system consisted of two parts; a stainless-steel ring, sealed with rubber O-rings, joins the upper tube, containing the primary anode and the target, to the lower rounded section. The plasma density was increased by inserting a finemesh grid in the ring to separate the upper anode space from the lower liquid-pool cathode space. Fetz²²⁷ had previously shown that an electrical double layer is formed in, and near, the grid holes and that electrons reaching this layer from the cathode side are accelerated toward the anode space. These energetic "beam" electrons (controlled by the potential applied to the grid) are more efficient in ionization and



Fig. 18. Mercury-pool discharge tube for high-current, low-pressure sputtering of the target (in the upper part of the tube) with low-energy Hg^+ ions. Reproduced with permission from Wehner, Phys. Rev. **102**, 690 (1956). Copyright 1956 by American Physical Society.

greatly increase the plasma density in the anode space. An additional enhancement in plasma density was achieved by placing the anode outside the direct path of the beam electrons and adding a repeller electrode with a negative potential to reflect beam electrons back into the intense region of the plasma. (Note that the glass walls of the tube became negatively charged and performed the same function.) Both the repeller and the grid were typically set to ~ -50 V relative to the anode.

The electrical conductivity of the resulting highlyionized plasma was sufficiently high that the plasma and anode potentials were nearly identical and the applied target potential V_T determined the kinetic energy, eV_T , of the bombarding ions. The ion-current density at the target was approximately 10 mA/cm² and could be increased to 100 mA/cm² by the addition of a magnetic field near the target.²²⁹ Therefore, sputtering rates were large enough to minimize the effect of contamination on sputter-yield measurements. The targets in these experiments were metal rods which were heated to temperatures >300 °C, via a connection to an externally temperature-controlled sealed Kovar²³¹ tube, to prevent Hg accumulation prior to initiating sputtering experiments.^{226,228} Heating was not necessary *during* sputtering since the targets reached much higher temperatures due to the large ion currents. For low melting-point targets, the Kovar tube was used to cool the target during sputtering.²²⁶ At an operating pressure of 1 mTorr with a target voltage of $V_T = -200 V$, the thickness of the cathode fall region in the discharge was less than 1 mm. Thus, the mean-free path of ions incident at the target was much larger than the width of the ion sheath, and sputtered-atom mean-free paths at 1 mTorr were larger than the distance from the target to the substrate.^{226,228}

Figure 19 shows Wehner's results for the Hg⁺ sputtering yield $S/(1 + \gamma)$, uncorrected for the secondary electron yield



FIG. 19. Low-energy mercury-ion sputtering yield $S/(1 + \gamma)$, uncorrected for the secondary-electron yield γ , of polycrystalline platinum vs incident Hg⁺ ion energy E_i. The upper curve corresponds to a Pt target temperature of 650 °C and the lower to 300 °C. The experiments were carried out using the mercury-pool discharge tube shown in Fig. 18. Reproduced with permission from Wehner, Phys. Rev. **102**, 690 (1956). Copyright 1956 by American Physical Society.

 γ , of polycrystalline platinum versus ion energy E_i.²²⁶ These, together with Refs. 223 and 225, are among the earliest reliable low energy yield measurements and were carried and states

able low-energy yield measurements and were carried out at target temperatures set to both 300 and 650 °C to show that Hg contamination of the target is negligible since the two data sets were within experimental uncertainty. Over the ion-energy range investigated, 100 to 410 eV, $S/(1 + \gamma)$ increases essentially linearly with E_i .

The mercury-pool-supported discharge was also used by Wehner to measure low-energy rare-gas sputtering yields in an effort to determine "threshold" energies for different gas/ metal combinations as discussed in Sec. IV G.

In order to measure rare-gas sputtering yields over an energy range more typical of that used in film deposition, Laegreid and Wehner,²³² as discussed in a previous paper,²³³ returned to the heated thermionic-cathode-supported triode discharge tube pioneered by Güntherschulze and Meyer.²²³ The upper part of the demountable tube, permanently connected to the vacuum pumping system, contains the thermionic cathode, while the target and the anode are in the lower section, with the two parts sealed by a copper gasket. The system base pressure, 10^{-7} Torr, was measured using an ionization gauge. After baking the system for 14 h at 340 °C, the oxide cathode²³⁴ temperature was slowly increased, "never allowing the pressure to exceed 7×10^{-5} mm Hg $(7 \times 10^{-5} \text{ Torr})$." After filing the liquid-nitrogen trap, the background pressure with the cathode at temperature, but prior to introduction of the noble gas, did not exceed 8×10^{-7} Torr.

The targets were uncooled, but the authors reported that "The influence of the target temperature (on measured sputtering yields) seems to be negligible (tested by varying ion current densities from 1 to 10 mA/cm^2)." During sputtering, target temperatures ranged from 300 to $500 \,^{\circ}$ C. Sputtering yields S(E_i), uncorrected for secondary-electron emission, were determined by combined target-current and weight-loss measurements. Example results are plotted in Fig. 20 for 15 different polycrystalline elements (of 28 studied) sputtered in argon with ion energies from 50 to $600 \, \text{eV}^{.235}$ The elements shown in Fig. 20 represent a significant fraction of the periodic table including p-block (Al), noble (Ag), base (Pb), ferromagnetic (Co and Ni), transition (Ti, V, Cu, and Y), lanthanide-series (Er), and actinide-series (U) metals, semiconductors (Si and Ge), and carbon.

1. Use of ion guns to measure sputtering yields

It is interesting to note that while ion guns were available, and improving in quality,^{236,237} during the prolific era of the 1950s and the early 1960s when supported glow discharges were being used to probe, and make enormous progress in understanding, the physics of sputtering over the energy range of interest for thin-film growth, they had little effect on the field. Although early ion guns were of poor vacuum design with highly divergent beams,¹⁶³ these issues were resolved over time.^{236–238} However, the current densities provided by ion guns based upon dc-diode glow discharges remained low, and since the primary approach to determining absolute



FIG. 20. (Color online) Argon-ion sputtering yields $S/(1 + \gamma)$, uncorrected for the secondary electron yields γ , of 15 polycrystalline elements plotted vs incident Ar^+ ion energy E_i . Reproduced with permission from Thornton and Greene, "Sputter deposition processes," in *Deposition Technologies for Films and Coatings*, edited by R. Bunshah (Noyes, Park Ridge, NJ, 1994). Copyright 1994 by Noyes Publications.

sputtering yields required measuring target weight loss, ion guns were not very practical for this purpose. The accuracy for measuring extremely small amounts of material loss due to low-energy ion bombardment was poor.

Conversely, at high ion energies, typically in the range of 10 to 100 keV, where sputtering yields are large, high-purity ion beams obtained from accelerators, which provide high current densities, were used in the early 1960s to measure $S(E_i)$.^{239,240} Almén and Bruce reported, for example, a sputtering yield of 48 atoms/ion for 45 keV Hg⁺ bombardment of polycrystalline silver.²⁴⁰ Figure 21 shows interesting results for a silver target sputtered by normally incident, extremely light, hydrogen and deuterium ion beams with energies in the low kilo-electron-volt range. The ions were obtained from an isotope separator and focused with an einzel lens.²⁴¹ The poor momentum transfer and large penetration depths due to the low mass of H⁺ (1.01 amu) and D⁺



FIG. 21. Light-ion (hydrogen H^+ and deuterium D^+) sputtering yields for silver, corrected for secondary-electron emission, plotted vs incident ion energy E_i . Reproduced with permission from Grønlund and Moore, Chem. Phys. **32**, 1540 (1960). Copyright 1960 by American Institute of Physics.

(2.01 amu) ions, compared to that of the Ag target (107.87 amu), result in S(E_i) maxima at energies of a few kilo-electron-volt. For silver sputtered with Ar^+ (39.95 amu), the S(E_i) maximum occurs at ~40 keV.²⁴²

F. Closed-field magnetrons

1. Cylindrical-post and inverted hollow-cathode magnetrons

An early investigation into the use of magnetic fields for supporting dc glow discharges was reported by Albert Hull in May 20, 1921, during a lecture delivered at the annual meeting of the American Institute of Electrical Engineers in New York City (published in September).²⁴³ Hull described a new vacuum-tube device, the magnetron, a member of the kenotron family of rectifiers and switches, which functions as an electronic valve controlled by a magnetic field. "If a constant voltage is impressed between cathode and anode, the current that flows through the tube is not affected by a magnetic field weaker than a certain critical value, but falls to zero if the field is increased beyond this value."

Historical footnote: Reference 243 contains the first use of the term "magnetron" in the literature. Today (2017), in the thin-film community, magnetron refers to the most common type of glow-discharge sputter-deposition device, available in a wide range of configurations, which provides high deposition rates due to having a closed, crossed electric and magnetic field ($\bar{E} \times \bar{B}$) tunnel at the target as explained in the text below (see Fig. 26).

Hull discussed two types of magnetron switches, whose geometries are illustrated schematically in Fig. 22, both having coaxial cylindrical symmetry.²⁴³ In the first one, Fig. 22(a) (referred to as the cylindrical-post configuration), the cathode is a thermionic filament surrounded by a cylindrical anode, while the second one [Fig. 22(b)], an inverted hollow-cathode magnetron, consists of a rod-shaped anode surrounded by a helical thermionic filament. With both types of magnetrons, the radial electric field is orthogonal to an axial magnetic field, parallel to the cathode surface, provided by a solenoid coil. In a previous publication (May of the same year), Hull²⁴⁴ presented analytical models describing the motion of thermionically-emitted electrons in the two magnetron geometries (although he did not use the term magnetron in the earlier paper). He also described results for the case of a parallel-plate diode with a magnetic field parallel to the electric field.

In the mid-1930s, Frans Penning (1894–1953) reported the first use of the cylindrical magnetron geometry, in which Hull's filament cathode²⁴³ was replaced by a rod, for sputter deposition.^{245–247} There is no indication that Penning was aware of Hull's previous results. In 1936, Penning filed a U.S. patent (issued in February, 1939)²⁴⁵ describing a cylindrical-post magnetron (the word magnetron was not mentioned) as a competing approach to the supported glow discharge (Sec. IV E) for developing high ion currents at reduced gas pressures. Penning employed an axially



FIG. 22. (Color online) Illustrations of the essential features of (a) a cylindrical magnetron in which the cathode is surrounded by a coaxial anode and (b) an inverted hollow-cathode magnetron consisting of a central anode surrounded by a coaxial cathode, first described in Ref. 243. (c) A tubular, water-cooled cathode with end plates as described in Ref. 247. For all three cases, there is a uniform axial magnetic field [see panel (c)] between the cathode and anode; the electric field is radial.

symmetric magnetic field, provided by a Helmholtz coil, between a rod-shaped target and a concentric anode tube [Fig. 22(a)] in order to enhance the ion current by increasing the electron residence time in the discharge. More importantly, he produced (perhaps unknowingly) the conditions for magnetron sputtering, a closed electric- and magneticfield trap which increases the plasma density at the target (cathode).

Secondary electrons emitted from the target respond to the $\overline{E} \times \overline{B}$ Lorenz force by initiating a cycloidal rotation around the cylindrical cathode. Those electrons which, during the first orbit, lose even a small amount of energy by making collisions or interacting with plasma oscillations 235,248 cannot return to the target against the radial $\bar{\mathrm{E}}$ field. Instead, they continue their cycloidal motion in the closed-field trap. (Thus, varying the pressure in a magnetron discharge changes the fraction of secondary electrons returning to the target which, in turn, alters the plasma ionization rate and, hence, the target sputtering rate.) In order for the gyrating electrons to travel radially toward the anode, crossing axial B-field lines, they must make collisions, thereby increasing the ionization probability near the target. However, as the electrons move away from the strong \overline{E} field in the cathode-fall region, their $\overline{E} \times \overline{B}$ drift velocity decreases, they trace a more helical path, and their motion becomes primarily along B-field lines, allowing them to escape from the intense region of the plasma. This gives rise, for the configuration shown in Fig. 22(a), to significant end losses, an issue which was solved a few years later by Penning and Moubis,²⁴⁷ who placed end caps on the post cathode [Fig. 22(c)] to form a more complete plasma trap.

Penning realized that the magnetic field strength in the plasma should not be so large as to affect the ions in the discharge, only the electrons.²⁴⁵ With the crossed electric and

J. Vac. Sci. Technol. A, Vol. 35, No. 5, Sep/Oct 2017

magnetic fields, "...the electrons are prevented from reaching the anode directly along the electric lines of force so that they traverse a materially longer path than in the absence of a magnetic field." That is, "...the electrons describe, however, more or less helical paths around the magnetic lines of force..." With a metal target operated at 1000 V in Ar, a magnetic field of 300 G "brought about a 300-fold amplification of the current." Penning noted that: "This leads to strong disintegration of the target and the cathode particles disintegrated readily pass though the gas at a reduced pressure." The patent thus describes many of the key operational features of modern magnetron sputtering. It also proposes the use of the dc magnetron for what today is termed a sputterion vacuum adsorption pump²⁴⁹ in which sputter-deposited metal atoms "getter" (adsorb) reactive gases to reduce the background pressure in a vacuum system.

Penning's 1939 patent goes on to describe a parallel-plate geometry in which two planar targets (cathodes) face each other inside a cylindrical anode which is surrounded by a Helmholtz coil. In this case, the magnetic field is primarily parallel to the electric field, thus giving rise to magnetically enhanced, but not magnetron, sputtering (i.e., no closed-field trap at the target). However, Penning presaged, by almost 60 years, invention of the "facing-target" sputtering configuration which today is used to minimize bombardment of growing films by negative oxygen ions during reactive sputter-deposition of oxide films onto substrates arranged radially about the axis connecting the targets.

about the axis connecting the targets.²⁵⁰ Penning and Moubis,²⁴⁷ in 1940, described a system, with a base pressure of $\sim 1 \times 10^{-5}$ Torr, consisting of a 10-cmdiameter glass discharge tube with a tubular water-cooled cathode (2 cm in diameter by 25 cm long) which had an opposing set of end plates for plasma confinement [thus, the shape of a wooden spool for storing thread or wire, Fig.



FIG. 23. Current/voltage (I vs V) characteristics, during sputtering of a copper target in a 14 mTorr flowing Ar gas discharge, plotted as a function of the magnetic field strength in units of gauss. The target geometry was a water-cooled cylindrical tube with end plates as in Fig. 22(c). Reproduced with permission from Penning and Moubis, Proc. K. Ned. Akad. Wet. **43**, 41 (1940). Copyright 1940 by KNAW.

22(c)], and a coaxial anode. The magnetic field was parallel to the cathode cylinder. They showed that with this arrangement, the plasma is strongly confined near the target surface yielding increased ionization and resulting in a narrow, ~ 1 mm thick, essentially collisionless target sheath. Sputterdeposition rates were estimated by measuring the increased weight of small mica substrates. Several mica disks were successively exposed, using a magnetic transfer rod, without opening the tube.

The current/voltage characteristics during sputtering of a copper target in a 14 mTorr flowing Ar gas discharge are plotted in Fig. 23 as a function of the magnetic field strength \bar{B} .²⁴⁷ Penning and Moubis reported that with $V_T = -500$ V, a discharge current of 3 A, $\bar{B} = 350$ G, and a target-to-substrate distance of ~4.5 cm, the film deposition rate was ~0.3 μ m/min, a very high rate for the time. In discussing their experimental results for aluminum targets, they noted that when the target is oxidized, a lower discharge voltage is obtained for the same discharge current, which they attributed (correctly) to a higher secondary-electron yield for aluminum oxide than for aluminum.^{251,252} There are even earlier indications in the literature of the same effect during the sputtering of oxidized magnesium.²⁵³

W. Gill and Eric Kay, in 1965, described the construction of an inverted (hollow-cathode) magnetron sputter deposition system²⁵⁴ as well as its operational characteristics as a function of magnetic-field strength. Approximately a decade later, Alan Penfield and John Thornton at Telic Corporation developed large commercial cylindrical-post (>1 m in length) and inverted magnetron sputtering systems with closed-field $\bar{E} \times \bar{B}$ traps for thin-film deposition at the industrial scale.^{248,255,256} An early application for cylindrical-post magnetron sputtering was the deposition of chromium layers on glass photomask plates used for metallization lithography during silicon device fabrication.²⁵⁷

2. Planar magnetrons

In the parallel-plate dc-diode geometry (Fig. 24), the use of a transverse magnetic field, orthogonal to the axial electric field,



Fig. 24. (Color online) Parallel-plate diode sputtering geometry with the circular target, substrate, and anode.

increases the ionization efficiency (magnetically enhanced sputtering, as noted above). Unfortunately, it does not form a closed-field trap and simply sweeps the glow discharge to one side.²⁴⁸ In 1939, Rokhlin²⁵⁸ suggested the use of a quadrupole magnetic field that is radially symmetric, but with large transverse components, in a parallel-plate configuration. Kay,²⁵⁹ in 1963, investigated the use of such a system for thin-film deposition. He reported an increase in the ion current density at an aluminum target by more than an order of magnitude, which resulted in a corresponding enhancement in the film deposition rate. Mullaly, in 1969, also reported high deposition rates using a magnetron supported with a quadrupole magnetic field.²⁶⁰ In his case, the target was hemispherical. The crossed fields, in both Kay's and Mullaly's experiments, formed highsputtering-rate rings at the target surface, yielding circular racetrack-shaped erosion profiles. The hemispherical target geometry of Mullaly resulted in a more uniform radial deposition rate at the substrate.

The earliest report of a parallel-plate sputtering geometry with a closed $\overline{E} \times \overline{B}$ field formed by a pair of permanent magnets having opposing poles was by Wolfgang Knauer of Hughes Research, Malibu, CA, in a patent filed on September 10, 1962, and issued on November 9, 1965.²⁶¹ Most of the patent discusses a closed-field configuration with a cylindrical magnetron (a "Penning cell") for use as a sputter-ion vacuum pump, "which results in the removal of reactive gas due to adsorption by freshly deposited reactive sputter material as well as by ion burial." However, Knauer also described a circular ring-shaped planar magnetron with an annular closed-field region of high sputtering rate at the target surface [Fig. 25(a)]. The magnets in Knauer's design were placed behind the targets as in modern magnetron sputtering systems.

In 1969, Wasa and Hyakawa described both a Penningtype cylindrical magnetron and a dc-diode parallel-plate closed-field magnetron [Fig. 25(b)].²⁶² In the latter device, the electrodes were circular disks facing each other in a sputter-down configuration. The solenoidal magnet was placed behind the substrate platen. However, no details were provided regarding operation of the planar magnetron, and all reported discharge characterization and film properties were obtained using the cylindrical magnetron.

The modern planar magnetron is often attributed to the patent of John Chapin, assigned to Airco, filed on January 31, 1974, issued on August 28, 1979,²⁶³ and discussed by



FIG. 25. (Color online) (a) Set of dc-diode parallel-plate magnetrons. The annular ring-shaped targets (blue, 18) are facing annular anodes (gray, 12). Permanent magnets (orange, 22) are mounted behind the targets. Adapted with permission from Knauer, "Ionic vacuum pump," U.S. patent 3,216,652 (9) November 1965). (b) A parallel-plate diode magnetron sputtering system with a circular target ("disk cathode," blue) and substrate platen ("disk anode," gray) supporting disk-shaped substrates ("substrate," green). A solenoid magnet ("solenoid coil," orange) is placed behind the substrate table. Reproduced with permission from Wasa and Hayakawa, Rev. Sci. Instrum. **40**, 693 (1969). Copyright 1969 by AIP Publishing.

Chapin in a 1974 industrial-magazine article.²⁶⁴ The device described in the patent was a water-cooled rectangular magnetron with a closed field, resulting in a continuous rectangular erosion profile into the target surface. However, Chapin pointed out: "Because of the planar cathode, the erosion region may be made in any desired configuration, depending upon the shape of the substrate ... " The rectangular configuration was designed for commercial production in which substrates to be coated are continuously passed over the target (in a sputter-up configuration). "Thus, a plate having a width less than the length of the long parallel segments... will be provided with a highly uniform coating across its entire width. Accordingly, the apparatus of the invention not only achieves a high deposition rate, but may be utilized in high-production operations such as in connection with moving strip material."

Figure 26 shows an illustration of Chapin's planar magnetron which he describes as follows:²⁶⁴ "...the magnetic field in the region just above the cathode surface or sputtering surface 12 forms a closed loop, indicated by 65 (the red shaded region defined by dashed lines) in Figs. 26(a) and 26(b). In this way, the electrons are confined in a sort of endless magnetic bottle adjacent the cathode and apart from the anode, further enhancing the rate of sputtering from the erosion region 15. In addition to trapping electrons, the magnetic bottle thus formed narrows the cathode dark space so that the space-charge-limited ion current is large. Because the cathode-anode circuit is entirely insulated from ground except through the ionized gas, there is little charge transfer to the substrate upon which the material is being deposited except for the small amount initially required to balance the cathode and anode at their natural potential, and except for a small amount due to the substrate contacting regions of the plasma at slightly different potentials."

The first review article on modern planar magnetrons was published by Robert Waits in 1978.²⁶⁵ Figure 27, from Ref. 265, provides Illustrations of both circular and rectangular planar magnetron geometries, showing magnet placement and representative magnetic-field lines. The discharge electrons experience a complex trajectory with a general drift velocity, due to the closed $\overline{E} \times \overline{B}$ field, guiding them through the azimuthal ("racetrack") magnetic tunnel.

An obvious disadvantage of the parallel-plate closed-field magnetron in the configurations shown in Fig. 27 is that the racetrack erosion profile consumes only a small fraction of target material giving rise to poor target utilization, originally $\sim 25\%$, which was increased to $\sim 33\%$ by spreading out the magnetic field and opening up the racetrack. Since the permanent magnets of the parallel-plate magnetron are typically outside the vacuum system, further improvements in target utilization were obtained by rotating the magnet assembly, initially in a circular path and then in ever more complex hypotrochoidal paths allowing up to $\sim 60\%$ of large rectangular targets to be sputtered.²⁶⁶

Another potential issue with magnetron sputter deposition is lateral film-thickness uniformity. This is relatively easy to achieve in the case of smaller substrates continuously translating under one or more larger rectangular targets for which deviations in the film thickness of $\leq \pm 1\%-2\%$ have been reported for reactive magnetron sputtering onto 2.5-m-wide architectural glass plates.²⁶⁷ Achieving this degree of thickness uniformity is more challenging for "single-wafer processing" on static substrates using circular targets as employed, for example, by the semiconductor industry during silicon-based device fabrication^{152,268} and the optical storage industry for production of compact disks and digital video disks.^{269,270} The measured and simulated filmthickness t results, published by Swan in 1988,²⁷¹ as a



FIG. 26. (Color online) (a) Top view and (b) side view of a dc-diode parallelplate magnetron in a sputter-up configuration. The red shaded region 15, defined by dashed lines 65, is the closed $\overline{E} \times \overline{B}$ field "tunnel" defining the high-sputtering-rate target erosion area. The annular magnet (orange, 13) is placed behind the rectangular target (blue, 11). The substrates (six small discs, green, in upper panel) are mounted on a substrate platen (gray), which is translated over the target in the direction indicated by the black arrows (69). Reproduced with permission from Chapin, "Sputtering process and apparatus," U.S. patent 4,166,018 (28 August 1979). Color was added by the present author.

function of substrate radius r for copper deposition from a 10-cm-diameter circular target sputtered in Ar at 3.75 mTorr (target/substrate separation not reported) are shown in the left panel of Fig. 28. t(r) decreases from the maximum thickness, under the center of the target, to 59% at r = 5 cm, corresponding to the edge of the target.

Figure 28 also shows that Swan's calculated results, based upon an analytic geometric model developed much earlier, 272,273 provide good agreement with the measurements. The model assumes that the racetrack on a pristine flat circular magnetron target is composed of a set of narrow rings in which every point on each ring emits with a cosine distribution (see Sec. IV A) and that the sputtered atoms undergo no gas-phase scattering between the target and the substrate (ballistic transport). Film thickness distributions t(r) are calculated for each ring and summed. All terms, other than the mass of the film material and the film density, are purely geometric. For



FIG. 27. (Color online) (Upper) Illustrations of circular and rectangular planar-magnetron geometries showing magnet placement and magnetic field lines. Reproduced with permission from Waits, "Planar magnetron sputtering," in *Thin Film Processes*, edited by Vossen and Kern (Academic, New York, 1978). Copyright 1978 by Elsevier. (Lower) Photographs of circular (courtesy of Gencoa Ltd.) and rectangular (courtesy of Oerlikon Balzers) magnetrons during operation in gas discharges are shown.

operation at higher pressures or larger target/substrate separations, gas-phase scattering must be accounted for, typically with Monte Carlo (MC) simulations.^{274,275} Even though the target/substrate separation was not provided in Ref. 271, the good agreement between measured and model results indicates that deposition was essentially ballistic. After the extended target use, measured erosion profiles, for which the highest sputtering rate is in the middle of the profile, must be used as weighting factors in the model.

The right panel in Fig. 28 displays the calculated t(r) results obtained from the analytic model used by Swan compared with t(r) curves acquired from an MC code, with the acronym simulation of metal transport (SIMTRA), developed by Diederik Depla and W. Leroy at the University of Ghent.²⁷⁶ In this case, copper was sputtered from a 5-cm-diam target onto a parallel substrate 10 cm from the target. The MC code was run for 3 mTorr Ar pressure and assuming purely ballistic deposition; both curves are in good agreement with the analytic model. Note that t(r) at the substrate position corresponding to the target edge is 91% of the maximum, compared to 59% in the 1988 results. This is, in large part, due to significant improvements in magnetron manufacturing and magnetic-field design during the period between 1988 and 2012.

For the semiconductor-device-fabrication industry, where high thickness uniformity is required, the solution was again, as discussed above for rectangular magnetrons, complex rotation of the magnet assembly. In this case, the magnet motion typically follows "heart-shaped" pathways which, in turn, are rotated circularly^{277,278} behind targets approximately 50% larger than the size of the wafer being coated. This allows target utilization up to ~75% with filmthickness uniformity >98%.²⁷⁹ There are many other rotating magnet designs for different applications, and examples are described in Refs. 280 and 281.



FIG. 28. (Color online) (Left panel) Calculated and measured thicknesses t of a copper film, dc-magnetron sputtered from a 10-cm-diameter circular target in argon at a pressure of 3.75 mTorr, as a function of substrate radius r. Reproduced with permission from Swann, Vacuum **38**, 794 (1988). Copyright 1988 by Elsevier. (Right panel) Calculated thicknesses t of a copper film, sputtered from a 5-cm-diameter circular target unto a parallel substrate at a distance of 10 cm, as a function of substrate radius r. The calculations were carried out using the analytical model in Ref. **271** and the SIMTRA Monte Carlo code for both an Ar sputtering pressure of 3 mTorr and ballistic transport though the gas phase. Reproduced with permission from Depla and Leroy, Thin Solid Films **520**, 6337 (2012). Copyright 2012 by Elsevier.

3. S-gun magnetron

The "S-gun" magnetron, patented in 1977 (filed in 1975) by Peter Clarke (1931–2002)²⁸² and illustrated in Fig. 29, was an early competitor of the planar magnetron. The device is designed such that the target, anode, water cooling, and power feedthroughs are all mounted on a single flange. The target is annular with a triangular (or truncated triangular) cross-section, the anode is a circular plate, and the permanent magnet is toroidal in shape to encircle the two electrodes. The device geometry is such that a strong $\mathbf{E} \times \mathbf{B}$ closedfield trap is formed at the target, as in the case of the planar magnetron, yielding high sputtering rates. Since both the target and the anode are in the dense region of the plasma (and hence both require water cooling), electron and ion bombardment of the substrate, typically placed across from the S-gun, is minimized. This can be an advantage for deposition on thermally sensitive substrates such as polymers and low melting-point metals.

A primary disadvantage of S-guns stems from a combination of the complex crossing of the electric- and magneticfield lines coupled with the shape of the target; together, these factors result in a complicated sputter-erosion profile,



FIG. 29. (Color online) Cross-sectional view of the essential features of a typical s-gun magnetron. Reproduced with permission from Clarke, "Sputtering apparatus and method," U.S. patent 4,060,470 (29 November 1977). Color was added by the present author.

leading, in turn, to a continuously changing film thickness distribution at the substrate, which varies more rapidly than that of planar magnetrons (Sec. IV F 2). Thus, full planetary substrate motion, utilizing all three axes of rotation, is required to obtain film-thickness uniformity. As a consequence, s-guns today are primarily used in small-volume specialty applications. Nevertheless, s-gun targets are still commercially available. The earliest review article covering operation of s-guns was by Dave Fraser, Bell Laboratories, in 1978.²⁸³

4. Rotatable magnetrons

Rotatable tubular magnetrons, available in lengths >4 m, are increasingly popular for industrial applications, especially for high-deposition-rate coating of larger substrates such as architectural glass, for which standard "jumbo" panes in large office buildings are presently $6 \times 3.2 \text{ m}^2$ (Ref. 284). The permanent magnet array in a rotatable magnetron is similar to that used in planar rectangular targets, with a corresponding rectangular racetrack, as shown schematically in Fig. 30. The earliest rotatable magnetron was described in



FIG. 30. (Color online) The dashed lines (orange) adjacent to the inside and outside of the racetrack erosion zone on the rectangular target correspond to the transition zone, which is at highest risk for arcing (Ref. 292). The remaining area (green) of the rectangular target, outside and inside the transition zone, is fully "poisoned." In the case of the rotatable target, the transition zone is only along the short ("turn-around") lengths of the racetrack, with the fullypoisoned regions at the ends of the cylinder. Most of the cylinder area (yellow), while adsorbing reactive gas when rotated outside of the racetrack, is sputter etched each time it once again rotates through the racetrack. Figure courtesy of Wilmert de Bosscher, Soleras Advanced Coatings.



Fig. 31. (Color online) Schematic side-view illustrations of (left panel) a standard circular magnetron during operation and (right panel) a tunable magnetically-unbalanced magnetron. J_i/J_{Me} is the ion/metal flux ratio incident at the substrate and growing film. A few representative magnetic field lines are shown. Reproduced with permission from Petrov *et al.*, J. Vac. Sci. Technol., A **10**, 3283 (1992). Copyright 1992 by American Institute of Physics.

a series of patents in the early 1980s by McKelvey.^{285–287} The original concept was to provide greater target utilization. After a local erosion profile was etched nearly through the target, the magnetron was rotated to sputter a fresh area.

The first *continuously* rotating magnetron was the subject of a patent issued to the Von Ardenne Laboratory, Dresden, Germany, in 1982.²⁸⁸ The device was described a year later by Robinson at a conference in the US (Ref. 289) and discussed in the open literature in 1986 by Wright and Beardow of BVT Ltd., UK.²⁹⁰ As summarized in an excellent review article²⁹¹ by De Gryse, who was directly involved in the development of the modern rotatable magnetron, and colleagues from Ghent University, the continuously rotating magnetron has many advantages, in addition to increased target utilization, over the flat rectangular magnetron. These include:

- (1) a larger material inventory compared to a planar magnetron of the same length;
- (2) better target cooling efficiency which allows the use of higher powers in order to provide higher deposition rates (water flows through the rotating tube; thus, most of the tube is being cooled, while narrow regions rotate though the intense plasma zones); and
- (3) reduced arcing during reactive sputtering (Sec. IV J) since the length of the transition zone (the region at the highest risk of arcing)²⁹² between the high-sputtering-rate area and the poisoned-target area is greatly reduced, due to target rotation, as illustrated schematically in Fig. 30.

The Ghent group developed the first laboratory-scale rotatable magnetron and used it to carry-out fundamental investigations of target poisoning and hysteresis effects as a function of rotation rate.²⁹³

5. Magnetically-unbalanced magnetrons

Chapin correctly pointed out in his 1978 patent²⁶³ that the substrate in a magnetron sputtering system is typically not located near the intense region of the plasma, which is trapped very close to the target by the crossed-field Lorentz force. While this configuration yields high sputtering rates, the disadvantage is that it is difficult to provide low-energy, high-flux ion irradiation to the growing film surface in order

to control the film composition, preferred orientation, density, surface roughness, and physical properties^{294–297} or to allow the growth of metastable phases via near-surface ionmixing.^{298–301} An initial step toward resolving this issue was provided a decade later by Brian Window and Nick Savides, from CSIRO in Sydney, Australia, who "unbalanced" the magnetron magnetic circuit. In a standard circular magnetron (for example), the permanent magnets are designed such that the magnetic field of the central pole is stronger than that of the outer annular magnet (see the left panel of Fig. 31). Windows and Savides replaced the permanent magnets with a pair in which the outer annular magnet was stronger than the central pole, thus opening a leak in the plasma trapped at the target and allowing low-energy ion bombardment of the substrate.³⁰²

A more useful approach leading to modern *tunable* unbalanced magnetrons was developed in 1992 by a University of Illinois group who added a pair of external Helmholtz coils with iron pole pieces to controllably unbalance the magnetic circuit through the addition of an adjustable axial magnetic field in the region between the target and the substrate (Fig. 31).²⁹⁶ The external field ("external" to that of the magnetron permanent magnets) provides the ability to controllably shape the discharge near the substrate to provide independent control of the energy and flux of ions incident at the growing film, while having a negligible effect on the target sputtering rate. This approach to film synthesis is now employed in a wide variety of commercial applications with magnetron designs ranging from circular to rectangular to rotating cylindrical tubes.

G. Threshold energies for sputtering

"Threshold" energies for sputtering have been discussed in the literature since the late 1800s. Wehner and Anderson⁴³ noted that until 1912, a value of 495 eV was thought to be valid for all gas/metal combinations.³⁰³ Based upon the results presented in Sec. IV E, including Figs. 17, 19, and 20, this is far too large. Later reports (1928) described sputter damage of thoriated-tungsten filaments in gas rectifier tubes when ion bombardment energies exceed 20–30 eV.³⁰⁴ In the limit, the threshold is the minimum incident ion energy, for a given ion/target combination, that provides sufficient energy transfer during a near-surface collision cascade to allow a target atom to overcome its surface binding energy and be sputter ejected.

From the discussion in Sec. IV E, it is clear that measuring the threshold energy for a given ion/target pair is exceptionally challenging. Sputtering rates near threshold are far too low for standard direct weight-loss measurements, which do not extend much below sputter yields of ~ 0.1 atoms/ion. More sensitive techniques are required. Interest in threshold energies in the middle 20th century derived not just from their importance in understanding the physics of sputtering and testing theories, but also for practical reasons. The sputtering threshold is related to radiation-damage thresholds in devices ranging from vacuum-tube electronics to sensitive detectors on orbiting satellites.

In a 1962 paper, Stuart and Wehner²²⁹ summarized sputtering threshold measurements starting from the work by Kingdon and Langmuir⁴⁷ and Hull and Winter,³⁰⁵ both in 1923, who used the change in thermionic emission from thoriated-tungsten wires, as thorium was sputter removed, to determine relative yields versus ion energy, to experiments based upon the resistance change of sputtered metal wire targets (1935),³⁰⁶ measurements of the surface ionization energy of low work-function alkali metals under ion bombardment (1954),³⁰⁷ radioactive-tracer methods (1956),³⁰⁸ and the use of an *in situ* microbalance (1957).³⁰⁹ The results yielded thresholds Eth for different ion/target combinations ranging from $E_{th} = 45-55 \text{ eV}$ for Ne⁺, Ar⁺, and Hg⁺ irradiation of Th-W wires⁴⁷ to $\sim 8 \text{ eV}$ at a sputtering yield of $\sim 10^{-4}$ for Hg⁺ and Ar⁺ bombardment of Ni.³⁰⁸ However, Stuart and Wehner²²⁹ provided arguments as to why each of these results had significant uncertainties: low ion current densities compared to background-impurity chemisorption rates, thin wire targets leading to oblique ion incidence, plasma-tube design resulting in bombardment by doubly charged ions, etc.

In 1954, Wehner and Medicus,³¹⁰ using a glow-discharge tube supported via thermionic emission from a tungsten filament (Sec. IV E), reported yet another method for measuring relative $S(E_i)$ values at very low ion energies E_i , in this case for Xe⁺ irradiation of platinum with E_i between 30 and 200 eV. A Langmuir probe was inserted in the discharge, and the authors took advantage of the fact that small changes in the probe work function can be accurately determined by displacements of the probe current/voltage characteristic along the voltage axis. The shift was calibrated versus the relative amount of platinum sputter deposited onto the probe. McKeown^{311,312} in 1961 used the frequency change of a Aucoated piezoelectric quartz oscillator to obtain thresholds of 20–30 eV for Ne⁺, Ar⁺, and Xe⁺ ion bombardment with sputtering yields of ~10⁻³ atoms/ion.

Stuart and Wehner^{229,313} recorded threshold sputtering energies of ~15 to 35 eV for several metals, plus germanium, bombarded by rare-gas and mercury ions. In these experiments, they employed a mercury-pool-supported discharge similar to that shown in Fig. 18, but with a planar target arrangement and a ring magnet to focus the discharge to the center of the target, thereby avoiding edge effects. The system, which had a liquid-nitrogen cold trap in the upper (target/anode) section to freeze the mercury out of the primary discharge and allow sputtering with a noble gas, provides ion current densities at the target of up to 100 mA/cm^2 with a background gas pressure of $< 10^{-6}$ Torr. Mass spectroscopy measurements showed that double-charged ions contributed less than 1% of the ion current.

Relative sputtering yields $S(E_i)$ at low bombardment energies were determined using optical-emission spectroscopy calibrated, at higher ion energies, with absolute weightloss measurements.^{229,313} The spectroscopic yield measurement geometry is shown in Fig. 32. Optical emission data were obtained close to the target in order to average the spectral line intensity over all ejection directions and thus minimize errors due to the variation in sputtered-atom ejection angles.

Example S(E_i) results, with E_i between ~ 20 and 300 eV, are presented in Fig. 33.³¹³ From the yield curves in Fig. 33(a), as well as additional results in Ref. 229, the agreement between relative and absolute yield measurements at lower ion energies is better for rare-gas than for Hg⁺ ion sputtering, perhaps due to mercury contamination in the latter case. Figure 33(b) shows yield data for five metals, from relatively light Ti (47.87 amu) to very heavy Th (232.04 amu) targets, sputtered in Ar (39.95 amu). Based upon the results for 23 metals, ranging in atomic mass from Be (9.01 amu) to U (238.04 amu), sputtered with four different rare gases (Ne⁺, Ar^+ , Kr^+ , and Xe^+), Stuart and Wehner concluded that metal sputtering thresholds, 15 to 35 eV, can be crudely approximated as being four times the target heat of vaporization.²²⁹ This was consistent with reports for radiationdamage induced lattice-atom displacement thresholds in solids.³¹⁴

H. More on mechanisms of sputtering: Theory

Results from the earliest glow-discharge sputtering experiments, beginning in the mid-1800s, overwhelmingly support the momentum-transfer collision-cascade model of sputtering (see discussion in Sec. IV B). This is clearly reflected in review articles published in the 1960s^{315–317} as well as in theoretical developments.^{318–322} During cascade sputtering, the sputtering yield is expected, as noted by Wehner and coworkers,^{43,228} to be proportional to an energy-transfer factor $4m_im_T/(m_i + m_T)^2$, in which m_i is the mass of the incident ion and m_T is the target-atom mass. This simple function has a maximum when $m_i = m_T$. The



FIG. 32. Schematic illustration of the experimental arrangement for the use of optical-emission spectroscopy to determine relative sputtering yields at low ion energies. Reproduced with permission from Stuart and Wehner, J. Appl. Phys. **33**, 2345 (1962). Copyright 1962 American Institute of Physics.



FIG. 33. (a) Sputter-yield measurements, determined by optical-spectroscopy calibrated with absolute weight-loss measurements (X), plotted as a function of ion energy for argon and mercury ions bombarding a chromium target. Reproduced with permission from Stuart and Wehner, Phys. Rev. Lett. **4**, 409 (1960). Copyright 1960 by American Physical Society. (b) Low-energy sputter yields for argon ion irradiation of five metals. Reproduced with permission from Stuart and Wehner, J. Appl. Phys. **33**, 2345 (1962). Copyright by 1962 American Institute of Physics. Data in both plots are uncorrected for secondary-electron emission.

sputtering yield should also vary inversely with the targetatom surface binding energy, often approximated for elemental targets as the heat of vaporization U_{vap} .³²³ Finally, for incident ion energies used in glow-discharge sputter deposition, typically a few hundreds to < 1000 eV, S for a given metal is approximately proportional to E_i^{224} (also see Fig. 20).

Modern sputtering theory is based upon a linear-transport model published in 1969 by Peter Sigmund from Aarhus University, Denmark.^{324,325} He assumed that sputter ejection of target atoms by recoiled energetic ions or target atoms results from atomic collision cascades in an infinite medium. Edward Lamar and Karl Compton,³²⁶ in 1934, appear to be the first to suggest that sputtering can occur via momentum transfer as an ion penetrates the target and is reflected from a lower layer to collide with a surface atom. However, they neglected the important role of energetic displaced target atoms in collisional cascade processes.

Sigmund described collision cascades using a generalized Boltzmann transport equation with, for ion energies used in sputter deposition, a Born-Mayer type collision cross-section. He found that while lattice-atom scattering events take place over a thickness which is a sizable fraction of the ion range, depending on the ion mass and energy, target-atom mass, and ion/target geometry, the majority of sputtered particles originate from a very thin (~5 Å) surface layer. For the simplest (although still quite complex) case of an amorphous target with a flat planar surface and normal ion incidence with $E_i < 1 \text{ keV}$, the sputtering yield is given by

$$S(E_i) = \frac{3}{4\pi^2} \alpha \frac{4m_i m_t}{(m_i + m_t)^2} \frac{E_i}{U_{vap}},$$
(2)

consistent with the experimental observations discussed above. The term α depends only on the ion and target-atom masses:

$$\alpha = 0.1 + 0.155 \left(\frac{m_l}{m_i}\right). \tag{3}$$

The fact that the above formulas provide a reasonable fit to sputter-yield data from polycrystalline and single-crystal targets in the few hundred electron-volt to 1 keV range is another indication that long-distance focusons (see Sec. **IV B**) do not play a significant role in determining sputtering rates. Related formulas developed by Sigmund, using a Thomas-Fermi collision cross-section, provide even better fits to high-energy, several kilo-electron-volt to megaelectron-volt, sputtering results.

Returning to Wehner's data in Fig. 15 (Sec. IV B) showing the average energies Eat of atoms which are sputter ejected, due to bombardment by Kr⁺ ions, orthogonal to the surface of a large number of elemental polycrystalline targets, the relative Eat results for the heavy elements Ta through U can now be understood based upon Eqs. (2) and (3). A "light" ion hitting a very heavy target does not penetrate deeply and has a high probability of being scattered sideways. Thus, more energy is deposited near the surface than would be the case for a collision of the same ion with a light-atom target; therefore, the product of the sputter yield S and the average ejection energy E_{at} will be high. However, as shown in Eq. (2), S \propto 1/U_{vap}. Comparing the E_{at} results for Pt (195.08 amu) and Au (196.97 amu), whose masses are essentially the same with respect to the 83.80 amu mass of Kr⁺ (thus momentum transfer differences can, to first order, be ignored), S_{Au} is predicted to be larger than S_{Pt} , as observed experimentally, since $U_{vap,Pt} = 5.8 \text{ eV}$ while $U_{vap,Au}$ is only 3.7 eV.³¹⁵ As a consequence, the average Au atom ejection energy is much lower than that of Pt, in agreement with the results in Fig. 15.

In the early 1980s, German physicists Bohdansky et al.³²⁷ developed an empirical formula for the sputtering yield in the near-threshold regime. Yamamura et al., from Nagoya University, Japan, proposed three different versions of a correction term to Sigmund's yield formula^{324,325} to account for threshold-energy effects.^{328–330} A fourth correction term was proposed by Bodansky.³³¹ In 1991, Ivan Petrov, Orlinov, and Grudeva,332 of the Bulgarian Academy of Sciences concluded, based on comparisons of published experimental results with the predictions of Bohdansky et al.,³²⁷ Yamamura et al.,³²⁸ and Matsunami et al.,³²⁹ that for raregas sputtering (i.e., using Ne⁺, Ar⁺, Kr⁺, or Xe⁺) under conditions relevant to film deposition, the best fit is obtained with the latter two formulas using, in the case of heavy ions impinging on targets composed of lighter-mass atoms, for which $m_T/m_i < 0.3$, an additional small correction in the threshold-energy value.

Petrov *et al.*³³³ also showed that the energy efficiency of sputtering,

$$\eta = S(E_i)U_{vap}/E_i,\tag{4}$$

has a maximum η_{max} at an ion energy $\text{E}_{i} \simeq 7\text{E}_{\text{th}}$, in which E_{th} is the threshold energy (see Sec. IV G) For sputtering with argon (39.95 amu), η_{max} is between ~0.4% and 4% for elemental targets from boron (atomic number $Z_{\text{T}} = 5$) to uranium ($Z_{\text{T}} = 92$), with periodic oscillations within each row of the periodic table as shown in Fig. 34. While the oscillations have been attributed to systematic changes in U_{vap} across the rows,³³⁴ Petrov *et al.* pointed out that this explanation is not sufficient; U_{vap} cancels out in Eq. (4) since from Eq. (2), $S(\text{E}_i) \propto 1/U_{\text{vap}}$.

The use of neon (20.18 amu) as the sputtering gas for the same elements yields higher sputtering efficiency with an increase by up to ~20%, compared to argon, for elements with $Z_T \leq 20$; while krypton (83.80 amu) and xenon (131.30) are more efficient for targets with $Z_T \gtrsim 40$ and $Z_T \gtrsim 50$,



FIG. 34. Maximum energy efficiency η_{max} for argon-ion sputtering of elemental targets, plotted as a function of atomic number Z_T . Figure courtesy of Ivan Petrov, University of Illinois.

respectively, by up to $\sim 65\%$. Argon is more efficient for sputtering elements in the middle of the periodic table.

Beginning in 1980, Jochen Biersack (Hahn-Meitner-Institut, Berlin Germany), Jim Ziegler (IBM Research, Yorktown Heights, NY), and colleagues developed transport of ions in matter (TRIM), a Monte Carlo computer code,^{335–338} which now forms the core of a larger program, stopping and range of ions in matter (SRIM), designed to simulate the complex interactions associated with fast-ion bombardment of solids. SRIM is available as freeware on the worldwide web.³³⁹ The programs are continuously upgraded with major changes occurring every few years. The SRIM and TRIM codes are based upon the binarycollision approximation,³⁴⁰ with a randomly-selected impact parameter for each ion incident at the target. The required input parameters are the ion type, ion energy, and the target material (which is assumed to be amorphous). Outputs from the code include the average ion penetration depth (projected range), and standard deviation (straggle), into the target; the target sputtering yield; sputtered-atom energy and angular distributions; and the backscattering probability and backscattered energy distribution of incident ions. SRIM/TRIM is a very useful tool for estimating the magnitude of effects due to the change in the ion mass, ion energy, and/or the target material. TRIM can also be used to evaluate the role of ion and target choice on fast backscattered neutral-species bombardment of the growing film and to model the transport of sputter-ejected atoms through the gas phase.³⁴¹

MARLOWE, another code based on the binary collision approximation, was developed by Mark Robinson (Oak Ridge National Laboratory, TN)^{340,342,343} to treat ionbombardment of crystalline targets. Wolfhard Möller and Wolfgang Eckstein (Max-Planck-Institut für Plasmaphysik, Garching, Germany) created TRIDYN,^{344,345} a dynamic version of static TRIM, which accounts for changes in the target composition, including implantation of incident ions, during sputtering of multicomponent systems.³⁴⁶

Peter Sigmund, the father of modern sputtering theory,^{324,325} published a wonderful invited review article in 2012 that recounts, from a theorist's perspective, the recent (from ~1955) evolution in the understanding of ion-bombardment-induced sputtering processes.³⁴⁷ The paper has the charming title: "Recollections of fifty years with sputtering."

I. rf sputter deposition

It was clear to those involved in the earliest studies of dcglow-discharge sputtering that the technique cannot be used with insulating targets. The accumulation of positive charge at the target, which cannot be conducted away, will decrease, and eventually eliminate, the ion sheath (cathode fall), thus extinguishing the discharge if the process has not already been terminated due to arcing. An ac discharge is required in order that electron bombardment during the positive part of each cycle neutralizes the accumulated positive-ion charge from the previous negative half cycle. However, this, by itself, is still not sufficient to produce significant sputtering from a dielectric target.

Several researchers during the period from the mid-1950s to the mid-1960s recognized that the discharge frequency is a crucial parameter for optimizing dielectric sputtering. At low frequencies, discharges can be established, but there is no net dc potential at the target (i.e., there is no ion sheath) since the ion flux reaching the target during the negative half cycle is sufficient to neutralize the negative charge from the positive half cycle. However, electron mobilities, due to their low mass, are very much higher than ion mobilities; thus, as the discharge frequency is increased, at some point, there will not be enough time for the majority of ions to reach the target in a single half cycle. That is, the ions become inertially confined (their transit time across the ion sheath is much less than the ac period). At this point, the target surface accumulates negative charge and the net dc potential repels "excess" electrons to maintain a zero net dc current over each cycle. As the positive-ion sheath potential, which accelerates ions to the target, increases with increasing frequencies, sputtering begins to occur. The lowest frequency at which an ion sheath can form was estimated by Butler and Kino³⁴⁸ in 1962 to be $\sim 10 \text{ kHz}$, but simple estimates made by Wehner and colleagues³⁴⁹ in 1962 show that frequencies in the MHz range are more useful for sputtering since the net dc cathode-fall potential V_T increases with frequency. Both estimates are in the radio-frequency (rf) range which extends from approximately 3 kHz to 1 GHz.³⁵⁰

Historical footnote: Today, rf power supplies used in sputter deposition systems are typically operated at 13.56 MHz to avoid the additional expense of electromagnetic shielding. 13.56 MHz, and the harmonics 27.12 and 40.68 MHz (together with other frequencies, such as 2.45 GHz for microwave ovens) were set aside by international agreement at the telecommunication conference in Atlantic City, NJ, in 1947,³⁵¹ as industrial, scientific, and medical (ISM), bands not to be used for telecommunications.

The earliest report on rf gas discharges was by J. J. Thomson in 1891.^{1,352} He employed a Sprengel-type mercury pump (Sec. III A) and applied power inductively from a Leyden jar battery (Sec. III B) at frequencies in the MHz range ("...currents change their directions millions of times in a second..."). In his experiments, Thomson noted that it was important to have flowing gas: "It is essential to success that the gas in the bulbs or tubes should be quite dry and at a suitable pressure; there is a pressure at which the brilliancy of the discharge is a maximum, and as endeavoring to get to this pressure the exhaustion may be carried too far, it is convenient to use a form of mercury pump which will allow of the easy admission of a little gas."³⁵² His experiments were carried out in air, carbonic acid (H₂CO₃), hydrogen, oxygen, coal gas, and acetylene (C_2H_2) . In the same paper, Thomson also described the effect of the addition of a magnetic field, oriented both along and perpendicular to the discharge axis, on the distribution of discharge luminosity as observed by the naked eye and via spectroscopic analyses.

In 1933, Banerji and Ganguli performed experiments with 4 MHz inductive rf plasmas to deposit mercury films on the glass walls of a discharge tube.³⁵³ They realized that mercury atoms, evaporated from a heated source, were ionized in the discharge [an early example of ion plating,³⁵⁴ a term introduced by Don Mattox, Sandia National Laboratories, Albuquerque, NM, in 1964 (Ref. 355)]. In the same year, Robertson and Clapp reported the use of an inductive rf discharge for removing (ion-etching) metal layers deposited on Pyrex, soda glass, and quartz discharge tubes.³⁵⁶ "On applying a high-frequency field by means of external wire electrodes so that a luminous discharge was obtained [in air at a pressure of a few millimetres (a few Torr)], in a few minutes the deposit was removed in the neighborhood of the electrodes. By shifting the position of the electrodes, the whole tube was cleaned in a short time... A high-frequency potential (frequency not specified) applied to the electrodes caused no removal unless a gas or vapor was present to carry an actual discharge. Most of the work was done with air as ionized gas, but a few observations with hydrogen, nitrogen, and oxygen showed that with hydrogen and oxygen the action was extremely rapid, with nitrogen very much less so."

A sketch of Robertson and Clapp's apparatus is shown in Fig. 35. The electrode positions are indicated by the letters E, and the cross-hatched region corresponds to the luminous area of the discharge. Hay, in 1938, reported similar results using frequencies of 3, 60, and 300 MHz in air, nitrogen, oxygen, and hydrogen discharges operated at pressures ranging from 70 mTorr to 3.5 Torr.³⁵⁷

In a 1955 review article on dc sputtering, Wehner³⁵⁸ described the concept of rf sputtering: "The positive charge on the insulator surface (due to ion bombardment) can be removed or the negative potential part time increased when a high-frequency potential is applied to a metal base underneath the insulator." Jackson and Kane, in 1959,³⁵⁹ reported that the application of an rf field in a low-pressure environment (in their case, two collinear antennas, driven at 7.75 MHz, on a rocket passing through the ionosphere) results in a sheath accelerating positive ions to an insulator. This was demonstrated in 1961 by Butler using an inductively powered ring-electrode around a glass discharge tube; the results are described in a 1961 Stanford University Report.³⁶⁰ Two years later, Butler and Kino published both experimental and theoretical results in the open literature.³⁴⁸



FIG. 35. Sketch of an inductively-powered rf discharge tube in which the plasma was used to remove (ion etch) metal layers previously deposited on the inside of the Pyrex tube. The electrode positions are indicated by the letter E; the cross-hatched region corresponds to the luminous area of the discharge. Reproduced with permission from Robertson and Clapp, Nature **132**, 479 (1933). Copyright 1933 by Nature Publishing Group.

Anderson, Mayer, and Wehner,³⁴⁹ in 1962, are credited with designing the first modern capacitively-coupled rf discharge for depositing dielectric thin films. "We describe a simple method for large-area sputtering of insulators which promises to be useful in many applications. The trick is to use a high-frequency potential at the target whereby the positive charge which accumulates on the target is periodically neutralized with plasma electrons during a portion of each cycle."

The electrode configuration in the discharge tube used by Anderson et al.³⁴⁹ is shown in Fig. 36 and described as follows. "The dielectric target is immersed in the plasma of a low-pressure gas discharge. Immediately behind the dielectric target is a conducting plate to which a high-frequency potential [typically in the Mc (MHz) range] is applied with respect to the plasma. The potential of the dielectric surface, measured with respect to the plasma potential as a function of time, would be roughly as pictured in Fig. 37(a)." What the authors realized in sketching the figure was that the entire input waveform has to float down in potential such that the highly mobile electrons are captured only during a very small fraction of each cycle, while the rest of the cycle time is used to attract the slower ions. That is, the ions respond to the time-averaged electric field, while the much lighter electrons respond to the instantaneous field. Thus, although not mentioned explicitly in the article, the ions are accelerated on average by approximately half the peak-topeak rf potential.

In Fig. 37(a), the positive portions of each cycle were drawn with *clipped* sine waves following Ref. 360. Butler and Kino³⁴⁸ showed experimentally that this is correct and explained it theoretically as being due to nonlinear charge transport as the electrons expelled from the ion sheath during the negative part of each cycle respond extremely rapidly, while the ions respond very slowly, to the target voltage becoming positive.

Anderson *et al.*³⁴⁹ went on to further explain the system operation. "The (target) potential will bias negatively an amount V since the electron mobility is much higher than



FIG. 36. Electrode configuration in the rf discharge tube used in Ref. 349 to sputter insulating targets. Reproduced with permission from Anderson *et al.*, J. Appl. Phys. **33**, 2991 (1962). Copyright 1962 by American Institute of Physics.



FIG. 37. Schematic illustration of the time variation in the (a) potential V at the target and (b) the cathode sheath thickness d during operation of a capacitively-coupled rf discharge. Reproduced with permission from Anderson *et al.*, J. Appl. Phys. **33**, 2991 (1962). Copyright 1962 by American Institute of Physics.

the ion mobility and no net current can flow through the dielectric. When the potential of the dielectric is negative with respect to the plasma potential, the electric field will produce an ion sheath by forcing the plasma electrons away from the surface. The ion sheath will extend into the plasma a distance d as a function of time, as schematically illustrated in Fig. [37(b)]... In general, it will require several cycles before an ion has traversed the distance d_{max} [defined in Fig. 37(b)], and the ion will finally strike the target with an energy less than the maximum potential difference." Anderson *et al.*³⁴⁹ primarily employed rf sputtering to clean the inside of their mercury-pool-supported discharge tubes used for investigating the physics of sputtering.

The potential differences between the plasma and both electrodes in a symmetric parallel-plate rf sputter-deposition system can be approximated by assuming that the plasma is a (leaky) capacitively-coupled voltage divider, i.e., as two capacitors in series for which the applied voltage is distributed as¹⁹⁴

$$\frac{V_T}{V_s} = \left(\frac{A_s}{A_T}\right)^4.$$
(5)

 V_T and V_s are the target and substrate average dc voltages and A_T and A_s are the corresponding electrode areas. An rf plasma is far from an ideal circuit element, and thus, the power-law exponent in Eq. (5) is generally closer to 1.5 to 2. In order to provide most of the applied voltage to the target, the metal substrate table is typically connected electrically to the entire vacuum system (including all grounded fixtures) such that $A_s \gg A_T$. Nevertheless, the substrate in an rf discharge will always experience ion bombardment (bias sputtering) with peak-to-peak voltages ranging from $\sim 20-25$ V up to much more than 100 V depending on system design, gas pressure, etc. A schematic illustration of the ideal voltage distribution is shown in Fig. 38.

Pieter Davidse and Leon Maissel at IBM East Fishkill, New York, filed a U.S. patent in 1961 for the design of a capacitively-coupled rf diode sputtering system to deposit





FIG. 38. (Color online) Schematic illustration of the target and substrate potentials in an rf sputtering system.

dielectric thin films.³⁶¹ Figure 39 shows a sketch of the target apparatus³⁶² described in the patent. The back of the dielectric target "can be metallized and bonded to the electrode" to which the rf power is supplied. In order to decrease sputtering from other parts of the system, which would result in film contamination and decrease the total power applied to the target, a ground shield is placed behind the target at a spacing less than the cathode-fall distance. Davidse later recommended a spacing of ~5 mm.³⁶³ The patent states that a matching network is required in order to tune "the load" (the discharge) to match the rf power supply. Modern rf power supplies are designed to connect to a purely resistive load; thus, the discharge capacitive and inductive reactances must be compensated by the matching network.

In the initial design, Davidse and Maissel placed a set of toroidal permanent magnets above the anode to provide a



FIG. 39. (Color online) Target electrode design for rf sputtering of dielectrics. Reproduced with permission from Davidse and Maissel, J. Appl. Phys. 37, 574 (1966). Copyright 1966 by American Institute of Physics. Color (the dielectric target is blue) was added by the present author.

curved magnetic field extending between the cathode and the anode (substrate holder) in order to increase ionization as discussed in Sec. IV F. The patent claims that the magnetic field also stabilizes the discharge and makes it easier to match the power supply to the discharge. For 5-in.-diameter (12.7 cm) quartz and Pyrex targets rf-sputtered at 13.56 MHz, 3000 V peak-to-peak, in Ar at 5 mTorr with $\bar{B} = 110$ G, deposition rates of 10.2 and 3.3 µm/h were reported for an ~2.5 cm separation between the target and Si wafer substrates.

Davidse and Maissel, in a 1966 paper, noted that their rf-sputter-deposited oxide films had a "slight oxygen deficiency" as deduced from their optical properties.³⁶² However, when they mixed oxygen with the Ar sputtering gas in an attempt to obtain stoichiometric oxides, they observed a large decrease in the deposition rate, thereby anticipating issues in modern reactive sputtering (see Sec. IV J). During separate experiments in which a Pyrex target was rf sputtered in pure Ar and in a 10 mol. % O₂/Ar mixture, the deposition rate loss in the mixed gas was greater than 50%. The films sputtered in Ar, although oxygen deficient, exhibited relatively uniform film thicknesses over a radial distance approximately equal to that of the target radius and were reported to contain low pinhole densities.

In 1966,³⁶³ Davidse pointed out that a metal target can also be sputtered in an rf system by simply adding a capacitor between the power supply and the cathode; data were shown for rf sputtering of aluminum as a function of target power. He also noted that for deposition onto insulating substrates, applying rf power to the substrate allows the use of positive ion bombardment of the growing film (bias sputtering) to tune film properties such as density, surface roughness, and preferred orientation.^{38–40,115,224,296,297} However, no data were provided.

Soon after commercialization of the modern planar magnetron in the mid-1970s (Sec. IV F), rf power supplies were used to deposit dielectric films by "rf magnetron" sputtering.364,365 However, deposition rates were lower since magnetron sputtering, which relies on a closed electromagnetic trap at the target, is fundamentally a dc concept.³⁶⁶ The rf field alternately opens and closes the trap, allowing electrons to escape when the trap is open and forcing electrons to cross magnetic field lines, an added impedance which decreases the available power at the target, as the trap is reformed. For a given applied magnetron target power, the film deposition rate decreases with both increasing frequency³⁶⁷ and increasing magnetic field.³⁶⁸ The fact that rf magnetrons do not function as a magnetron is clear from examining the average target current/voltage (I_T/V_T) characteristics, in which $I_T \propto V_T^n$. The exponent n for an rf magnetron is closer to that of rf (and dc) diode sputtering, 1-2,³⁶⁹ than that of dc magnetron sputtering, ≥ 10 .^{224,248} Because of this, plus the added expense of an rf (versus dc) power supply and matching network, rf magnetron sputter deposition of dielectrics has largely been replaced by reactive sputtering from metal targets using much lower frequencies, typically 50-300 kHz, and pulsed-dc or midfrequency ac power supplies (Sec. IV J 4).

J. Reactive sputter deposition

The majority of early experiments on sputter deposition of metallic thin films actually involved the growth of metal-oxide layers (reactive deposition), with other contaminants including nitrogen and carbon, due to poor vacuum, and most researchers realized this. Karl Bädeker (1877-1914, German physicist at the University of Jena) published an early (1907) paper on the purposeful synthesis of several metal-oxide thin films.³⁷⁰ Of particular interest was CdO, the first TCO, produced by sputter-depositing cadmium layers on glass, followed by thermal oxidation. TCOs are important today for use as electrical contact layers on many optoelectronic devices, including solar cells.³⁷¹ CdO is an n-type semiconductor due to oxygen vacancies in the lattice, and Bädeker obtained resistivities as low as $1.2 \times 10^{-3} \ \Omega$ cm, which is only about 1 order of magnitude higher than the resistivity of the best indium tin oxide TCO layers available today.

Clarence Overbeck (Northwestern University),³⁷² in 1933, was the first to publish an article devoted specifically to the investigation of reactive sputter deposition, although the term was not used until two decades later (see the *Historical footnote* below). He sputtered tin from a liquid target, held in a Pyrex cup, using dry air, oxygen, nitrogen, and hydrogen discharges with dc potentials ranging from 1.8 to $2.6 \,\text{kV}$. In initial experiments, carried out at a fixed (non-flowing) pressure of dry air, he observed a pressure decrease that he realized was due to gas incorporation in the film. Subsequent experiments were carried out at constant gas flow. Films deposited in flowing air and oxygen were oxides, with similar appearance, exhibiting interference rings which changed systematically with the film thickness. Overbeck assumed that the films were stannic oxide, SnO₂.

Historical footnote: The first use of the term "reactive sputtering" was by Gabor Veszi, from Megatron Ltd. (London), on January 5, 1953, during a lecture at a British Institution of Radio Engineers conference in London. The corresponding paper was published in April, 1953,³⁷³ approximately a century after the earliest recorded sputter-deposition experiments²⁵ and 20 years after Overbeek's pioneering reactive-sputtering experiments.³⁷² Veszi used reactive sputtering to deposit cadmium-oxide TCO electrodes on selenium photocells, but provided few details. He did note that the CdO layers deposited on glass exhibited "transparencies up to 85% and surface resistances of 100 ohms per square or less." Film thicknesses were not given, so sheet resistance cannot be converted to resistivity for comparison to Bädeker's 1907 results. Later, in April and October of the same year, two articles published by Leslie Holland and George Siddall of Edwards High Vacuum Ltd., Sussex, UK, used the term in the titles of their papers on the design of a reactive-sputtering system³⁷⁴ and the properties of reactively sputtered metal-oxide films.³⁷⁵

Layers deposited by sputtering tin in nitrogen discharges were opaque with a brown color. Based upon wet-chemical analyses, the films were understoichiometric SnN_x . However, they were apparently underdense since Overbeck reported that "exposing the film to air caused it to gradually lose its opacity and take on the transparent nature of films produced in air." Films grown in hydrogen, which required "higher pressures," were metallic Sn with highly reflecting metallic-mirror surfaces.

Overbeck was also the first, by several decades, to report problems with arcing during reactive sputter deposition of oxides. While he did not use modern terminology, his description of the process, as in the following quotation, was correct. "Frequently the discharge became unstable, giving rise to a sudden high current density which pitted the cathode surface and produced a granular metallic deposit on the plate. A microscopic examination revealed that these metallic particles were of ...a rough spherical shape... it appeared that they had been flattened on striking the deposit plate, which indicated considerable velocity of impact and heating. The metallic nature of the deposit might be explained by the fact that the particle, rapidly deposited, was of large size and therefore its combination with gas molecules would not be favored."

It is now well understood that arcs can occur during dc reactive sputtering of electrically-conducting targets due to the formation of local insulating regions (often oxides) on the target surface.³⁷⁶ The system rapidly switches from a high-voltage, low-current glow discharge to a low-voltage, high-current arc. All power is then applied to the local arc region at the target, which typically ranges from ~ 0.01 to $100 \,\mu\text{m}$ in diameter, resulting in the current density increasing by many orders of magnitude, giving rise to local heating leading to thermionic emission and a microexplosion. Thermal runaway causes local melting and boiling of solid targets, over time scales of order ns, causing the ejection of macroscopic liquid droplets, with very high velocities, which can land on the growing film surface,³⁷⁷ as Overbeck reported in 1933.³⁷² Scanning electron micrographs showing the effect of an arc on a target surface (leaving, in this case, an ~ 12 -µm-diameter pit) and collateral effects of arcing on film growth are shown in Fig. 40. There are, today, a variety of solutions available for solving, or at least minimizing, the arcing problem; they all involve fast arc detection circuitry, dumping excess power into a massive bus bar, and periodically (typically 50-350 kHz or 13.56 MHz) switching the target voltage via pulsed-dc, midfrequency ac, or rf power supplies to neutralize accumulated positive charge, by attracting electrons, as discussed in Refs. 115 and 378.

The mercury-pumped deposition system used by Overbeck,³⁷² Fig. 41, is itself of interest since it contained, in 1933, many of the features, although in a slightly different guise, found in modern ultrahigh vacuum systems: vacuum gauging (a McLeod gauge, see Sec. III A), multiple chambers, liquid-air traps, gas scrubbers, facilities for multiple substrates, a magnetically coupled rod to transport substrates in and out of the deposition chamber, and the capability to controllably vary the target-to-substrate distance via a second magnetically coupled rod. Note that opening the system to retrieve the deposited films required breaking the end of



FIG. 40. Left figure is a scanning electron micrograph of an ~ 12 -µm-diameter pit formed at a metal target surface due to arcing (image courtesy of Dr. Andre Anders, Lawrence Berkeley National Laboratory). The right figure shows embedded metal droplets in an underdense Al₂O_x film deposited by reactive sputter deposition from an Al target in a mixed Ar/O₂ atmosphere. Reproduced with permission from O'Brien and Kelly, Surf. Coat. Technol. **142**, 621 (2001). Copyright 2001 by Elsevier (Ref. 379).

the side tube (the reason, of course, for multiple depositions per system pump down), and reforming it by glassblowing. A description of the apparatus, in Overbeck's words, follows.

"A steady potential, variable from 1800 to 2600 V, was applied between the aluminum anode D and the tin cathode, F (2 cm in diameter and 2 cm long [tall]). The cathode was placed in a Pyrex cup with its surface flush with the top of the cup. The deposit formed on a Pyrex plate E (3 cm wide and 45 cm long). The distance between cathode and plate was adjustable and held by an electromagnet acting on a glass-enclosed piece of soft iron M. The deposit plate could be drawn back and forth in the side tubes by a second electromagnet. This permitted making from six to ten deposits before blowing out the end of the side tube to remove the deposit plate. The sputtering chamber was separated from the remainder of the system by liquid air traps C and G. A McLeod gauge was attached above C. A 12 liter bottle B was placed in the system to stabilize the gas pressure. This added volume reduced the pressure variation caused by the vigorous "cleanup" action that was especially large at the beginning of a run. A high-vacuum pump (with a mechanical backing pump) was attached beyond the mercury cut-off (a



FIG. 41. Pyrex vacuum system used by Overbeck [Reproduced with permission from Overbeck, J. Opt. Soc. Am. **23**, 109 (1933). Copyright 1933 by Optical Society of America.] to investigate sputter-deposition of Sn in dry air, O_2 , N_2 , and H_2 environments. See text for a detailed description.

liquid-air trap to prevent mercury and mechanical-pump oil vapor from back-diffusing into the deposition chamber). The lower right-hand corner of the figure shows the gas purifying chambers. Water vapor, carbon dioxide, and oxygen were removed from the incoming gas by phosphorus pentoxide in J, sodium hydroxide in L, and hot copper gauze at K. The gas was finally collected for use in flask I, from which it could be admitted into the sputtering system by either of two methods: (1) A capillary opening at H permitted a constant flow of fresh gas through the system. With the pump in operation, proper adjustment of the pressure in I gave any desired pressure in the system. (2) Known quantities of gas could be admitted periodically by means of the stopcocks at H."

While Veszi, in 1953, was the first to use the term reactive sputtering in discussing his results on the deposition of CdO (see *Historical footnote* above),³⁷³ he was not the first to report the reactive sputter deposition of transparent conducting oxides. Preston, in 1950, described experiments in which he used dc sputtering of a Cd target in flowing Ar to deposit a layer on a "metal" substrate.³⁸⁰ (The system base pressure, the sputtering pressure, and the film thickness were not reported.) Electron diffraction analysis showed that the film was cadmium oxide, presumably due to gettering of oxygen and water vapor in the chamber, present as residual impurities due to desorption from the walls and fixtures (which had not been outgassed) upon establishing the discharge. Preston noted that "Sputtering in air (instead of argon) was found to give films having a far lower conductivity." Preston, like Vesci, was interested in CdO as a transparent contact layer on selenium photocells.

More definitive experiments on the conductivity and structure of CdO layers deposited on glass substrates were described in a 1952 paper by Hellwig.³⁸¹ He showed that the conductivity of CdO_x layers decreased (due to fewer O vacancies, i.e., larger x) with increasing oxygen partial pressure in the mixed Ar/O₂ sputtering gas and that post-annealing as-deposited CdO_x films at reduced pressures increased the conductivity (due to loss of oxygen). Holland and Siddall³⁷⁵ later reported that the post-annealing step for obtaining low-resistivity CdO_x can be avoided by simply not cooling the glass substrate and allowing the deposition temperature to increase. The application, in this case, was for

transparent heating elements to prevent the formation of mist and ice on aircraft windows.

As described in the book *Sputter Deposition* by Bill Westwood,³⁸² an early industrial application of reactive sputtering in the 1950s derived from research on the deposition of TaN_x films, by dc sputtering from a Ta target in mixed Ar/N₂ discharges, for use as trimming resistors in hybrid circuits.³⁸³ Controlling the N₂ flow rate also resulted in the formation of TaN_x films with the appropriate temperature coefficient of resistivity (TCR) for use in tuned circuits in touch-tone telephones which first appeared in the early 1960s. Figure 42 is a plot of film resistivity ρ and TCR versus N₂ flow rate.

Similar curves for TaN_x film resistivity ρ vs N₂ partial pressure P_{N2} were published in the mid-1960s (see, for example, Refs. 384 and 385). When combined with electron diffraction, the general trends in Refs. 384 and 385 showed that ρ initially increases slowly with increasing P_{N2}, resulting in N-doped Ta films (Ta:N), then a rapid increase is observed corresponding to the formation of two-phase layers consisting of Ta:N with an increasing fraction of Ta₂N, followed by a saturation region in which single-phase Ta₂N is formed. At still higher P_{N2} values, two-phase Ta₂N + TaN layers and, eventually, TaN films are obtained. The absolute values of ρ vs P_{N2}, as well as the exact curve shapes, depend on system geometry and operating conditions (base pressure, outgassing conditions, target voltage and current, target-tosubstrate distance, substrate type and temperature, etc.).

The complexity in the above experimental results is highlighted by the phase map in Fig. 43 for the growth of TaN_x on SiO₂ and MgO(001) substrates by reactive dc planar-magnetron sputtering in an ultrahigh vacuum system, with a base pressure of 5×10^{-10} Torr, as a function of the deposition temperature T_s and the mole fraction f_{N_2} of N₂ in high-purity Ar/N₂ gas mixtures at a total pressure of 20 mTorr.³⁸⁶ The growth phase map contains nine different phases of which body-centered cubic α -Ta, hexagonal



FIG. 42. (Color online) Variation, as a function of the N_2 flow rate, of the resistivity and the temperature coefficient of resistivity (TCR) of TaN_x films grown by dc sputtering Ta in mixed Ar/N₂ atmospheres. Reproduced with permission from Westwood, *Sputter Deposition* (AVS, New York, 2003). Copyright 2003 by American Vacuum Society.



 $f_{N_2}^{0.2}$

FIG. 43. (Color online) Growth phase map showing the phase composition

of TaN_x layers grown on SiO₂ and MgO(001) substrates by reactive magne-

tron sputter deposition in mixed N₂/Ar atmospheres as a function of film growth temperature T_s and N₂ fraction f_{N_2} . Reproduced with permission

from Shin et al., Thin Solid Films 402, 172 (2002). Copyright 2002 by

 γ -Ta₂N, and hexagonal ε -TaN are thermodynamically stable,

realized, based on target color changes and decreases in film

deposition rates, that reactive gas was poisoning the target

surface by both simple adsorption and by reactive-gas ioni-

zation in the discharge followed by acceleration to the target.

However, it was unclear at the time where the primary reac-

From the early days of reactive sputtering, investigators

0.3

1.0

Γ_s (°C)

0

the rest are metastable.

Elsevier.

0

0.1

tive-gas/metal-atom reaction controlling film composition occurred. Holland and Siddall,³⁷⁴ in 1953, wrote the following. "When sputtering from a metal cathode in an oxygen atmosphere, there are three possible mechanisms by which a metal oxide film can be formed, all three of which may occur simultaneously: (1) The initial formation of an oxide layer on the cathode surface by bombardment with oxygen molecules or ions, which is removed in molecular form during subsequent bombardment. (2) Oxygen absorption by sputtered metal atoms during transit to the receiver due to collisions between gas molecules and metal atoms. (3) Absorption of oxygen molecules impinging on the deposited film during its condensation."

Esther Krikorian and Richard Sneed (General Dynamics, Pomona, CA),³⁸⁵ in 1966, first deduced the correct answer based upon experiments in which they established a direct connection between film impurity concentration and the combination of the background partial pressure of reactive gas P_r with the film growth rate R. In their tantalum dc sputter-deposition experiments in argon discharges, carried out in a vacuum system with a base pressure of 1×10^{-7} Torr, they measured (1) film resistivities ρ as a proxy for incorporated impurity concentrations and (2) the deposition rate R on glass substrates at $T_s = 450$ °C as a function of the sputtering pressure P. The reactive-gas partial pressure P_r, which they implicitly assumed was proportional to P, is directly related, through gas kinetics,³⁸⁷ to the rate per unit area N_i at which background impurity reactive-gas molecules strike the film-growth surface and react with a sticking probability s_i. From previous results of Maissel and Schaible,³⁸⁸ the impurity concentration C_i in an as-deposited film can be expressed as a function of R and N_i through the relationship

$$C_i = s_i N_i / (s_i N_i + R).$$
(6)

In their experimental analysis, Krikorian and Sneed made the reasonable assumption, based upon their resistivity results, that the impurity concentration is in the few percent range. Thus, s_iN_i in Eq. (6) is much less than R, yielding $C_i \simeq s_i N_i/R$, from which they concluded that the film resistivity should increase approximately linearly with P/R. The results, shown in Fig. 44, are in agreement with this simple model. From this, and the fact that they observed that the reactive sputter deposition rate of TaO_x in mixed O₂/Ar atmospheres increases with T_s, due to a corresponding increase in $s_i(T_s)$, Krikorian and Sneed correctly concluded that while reactions occur at both the target and the substrate, the *primary* reaction controlling film composition during reactive-sputter deposition occurs dynamically at the film-growth surface.



FIG. 44. Resistivity of Ta films deposited by dc sputtering as a function of the ratio of the sputtering pressure P to the film growth rate R. Reproduced with permission from Krikorian and Sneed, J. Appl. Phys. **37**, 3674 (1966). Copyright 1966 American Institute of Physics.

1. Bias-sputtering for composition control

Maissel and Schaible³⁸⁸ showed that the application of a small negative substrate bias (bias sputtering) during dc-sputtering of Ta in argon can be used to tune film impurity concentrations (again, as determined by resistivity measurements). At low substrate bias, the primary effect was to preferentially sputter remove impurities from the growing film (thereby decreasing the resistivity), while at higher biases, this effect was counteracted by trapping (i.e., near-surface ion implantation) of accelerated ionized impurity species (the resistivity increases again).

Much later, Barnett, Bajor, and Greene³⁸⁹ used the same approach to grow the first sputter-deposited high-resistivity single-crystal GaAs films on GaAs(001) substrates in a vacuum system with a base pressure of 1×10^{-7} Torr. Residual oxygen and carbon contamination was minimized through the use of a liquid-nitrogen-cooled shroud surrounding the 20 mTorr argon rf discharge during deposition. Excess arsenic was provided to the growing film, deposited at 600 °C, by a separate sublimation source (reactive deposition utilizing As₄ molecules) to account for arsenic loss by desorption. Figure 45(a) shows the unintentionally-incorporated oxygen concentration, as determined by secondary-ion mass spectrometry, in as-deposited GaAs layers. The oxygen concentration decreases, resulting in higher electron mobilities up to a maximum of $\sim 4000 \text{ cm}^2/\text{V}\text{ s}$ at a peak-to-peak rf substrate bias of -150 V. Higher bias voltages give rise to increased oxygen concentrations, via trapping, with an associated decrease in the electron mobility.

Bias sputtering was also used to control the concentration of sulfur (an n-type dopant) in GaAs/GaAs(001) films.³⁹⁰ In these experiments, the films were grown at 30 mTorr Ar and 570 °C with hydrogen sulfide (H₂S) partial pressures P_{H_2S} between 1×10^{-7} and 1×10^{-5} Torr. Systematic variations in P_{H_2S} and the substrate bias resulted in controlled S concentrations ranging from 7×10^{18} to 1.2×10^{21} cm⁻³ (0.00016 to 0.027 at. %). Figure 45(b) shows results with $P_{H_2S} = 1 \times 10^{-5}$ Torr.

2. Seminal events in the development of reactive sputtering

Three seminal events occurred between the mid-1970s and the early-1990s which resulted in reactive sputtering becoming a major thin-film synthesis technique for both research and industrial applications: the development of *high-rate* reactive sputtering, the availability of pulsed-dc and midfrequency power supplies, and the evolution of atomic-scale models for understanding and controlling the complex processes inherent in reactive sputtering.

3. High-rate reactive sputtering

From the 1930s to the early 1980s, reactive sputtering was a relatively slow, and hence uneconomic,³⁷⁸ process compared to competing techniques such as reactive evaporation and chemical vapor deposition. While magnetron sputtering of metal targets provides high deposition rates, as soon as the metal target is covered with reactive gas



FIG. 45. (a) Electron mobilities and relative oxygen concentrations in unintentionally-doped single-crystal GaAs films as a function of the peak-to-peak rf applied substrate bias V_a during film growth. The argon sputtering pressure, peak-to-peak target voltage, and film-growth temperature were 20 mTorr, 1000 V, and 600 °C. Reproduced with permission from Barnett *et al.*, Appl. Phys. Lett. **37**, 734 (1980). Copyright 1980 by American Institute of Physics. (b) Sulfur concentrations and incorporation rates in as-deposited single-crystal GaAs films as a function of the applied substrate bias V_a during film growth. The argon sputtering pressure, peak-to-peak target voltage, film-growth temperature, and hydrogen sulfide [H₂S] partial pressure P_{H₂S} were 30 mTorr, 1000 V, 570 °C, and 1×10^{-5} Torr. Reproduced with permission from Greene *et al.*, J. Cryst. Growth **56**, 389 (1982). Copyright 1982 by Elsevier. In both sets of experiments, solid arsenic was sublimed at 263 °C to provide excess arsenic incident at the growth surface in the form of As₄.

(poisoned), the sputtering rate in many metal/reactive-gas systems decreases dramatically³⁹¹ due primarily to the much higher binding energies of, for example, metal-oxygen than metal-metal bonds, as well as changes in ion-bombardment momentum-transfer probabilities since oxygen has a lower mass than most metals and is also much lower than that of argon [see Eqs. (2) and (3) in Sec. IV H].

Target poisoning during reactive sputtering often occurs as an avalanche effect since the combination of oxygen adsorption (to continue the oxide example) on, and the nearsurface implantation of oxygen positive ions in, a strongly reacting metal target decreases the sputtering rate (from point A to point B in the upper panel of Fig. 46).³⁹² Thus, there are fewer metal atoms deposited per unit time on the substrate and chamber walls to adsorb oxygen; this causes the oxygen partial pressure to increase (the corresponding transition from A to B in the lower panel of Fig. 46³⁹³ leading to higher target coverages, and even lower deposition rates, until the entire target is rapidly oxidized. The slow sputtering rate of the oxidized target has the consequence that the system cannot be immediately returned to its cleantarget condition and the delay time results in characteristic hysteresis loops as shown in Fig. 46. Films obtained with the oxygen flow rate between zero and point A are metallic and doped with reactive gas ("metal mode"); films obtained with flow rates higher than that corresponding to point B are stoichiometric compounds ("compound mode"). Since TiO₂ is a dielectric, the experimental results in Fig. 46 were obtained using ac sputtering; rf (Sec. IV I) for the upper panel results

J. Vac. Sci. Technol. A, Vol. 35, No. 5, Sep/Oct 2017

and pulsed-dc magnetron sputtering (see Sec. IV J 4) in the lower panel.

There are, however, material systems, including In/N₂, which have very weak metal/reactive-gas bonds,³⁹⁴ and there are sets of (sometimes extreme) processing conditions such as very high pumping speeds,^{395,396} for which hysteresis effects can be minimized and even eliminated (see also Ref. 397). Nevertheless, in many (if not most) material systems and deposition conditions relevant to thin-film applications, loss of deposition rate and hysteresis loops are key issues.

For many years, researchers developed ever more complex feedback loops in attempts to obtain near-metal deposition rates, while accepting the tradeoff in depositing understoichiometric films (i.e., remaining just past point A of the hysteresis loop in the upper panel, Fig. 46). These experiments generally failed since the feedback element was a gas-flow meter whose actuator is a mechanical valve (flow-control mode) and therefore far too slow to halt the avalanche poisoning process.³⁷⁸ In 1983, Bill Sproul and J. Tomashek,³⁹⁸ working at Borg Warner in Chicago, filed a patent that contained the solution which, as is often the case, was surprisingly simple. Instead of using a flow meter as the control element, they used the reactive-gas partial pressure, measured by either a mass or an optical spectrometer. During reactive sputtering in partial-pressure control mode, the system can be operated at any point along the path of target poisoning without initiating the avalanche effect (provided the system response time is sufficiently fast).



FIG. 46. (Color online) (Upper panel) Plot of the titanium metal deposition rate R_{Ti} , in arbitrary units, vs the oxygen flow rate f_{O_2} during reactive rf sputter deposition, using flow control, of TiO_x from a Ti target in mixed Ar/ O₂ atmospheres maintained at an Ar partial pressure of 10 mTorr. Reproduced with permission from Barankova *et al.*, Thin Solid Films **260**, 181 (1995). Copyright 1995 by Elsevier. (Lower panel) Oxygen partial pressure P_{O_2} vs oxygen flow rate f_{O_2} during reactive pulsed-dc magnetron sputter deposition (see Sec. IV J 4), using flow-control, of TiO_x from a Ti target in mixed Ar/O₂ atmospheres maintained at an Ar partial pressure of 3.1 mTorr. Reproduced with permission from Sproul, Surf. Coat. Technol. **33**, 73 (1987). Copyright 1987 by Elsevier.

Sproul published initial papers demonstrating the partialpressure control process, with associated high reactivedeposition rates, in 1987³⁹³ while at Borg Warner and in 1989³⁹⁹ after he had joined Northwestern University. An example, the growth of TiO_x films by magnetron sputtering from a Ti target in mixed Ar/O₂ atmospheres is shown in Fig. 47^{399} for comparison to the lower panel in Fig. 46. The dashed gray lines correspond to results obtained when operating in flow-control mode. In contrast, operation is possible along the solid black lines AB and BD while in partialpressure mode. The highest deposition rates along AB are obtained by operating as close as possible to point A, but films with compositions closer to stoichiometric are obtained by moving away from A toward B.400 Reference 378 is an excellent review article describing the experimental aspects of high-rate reactive sputtering.

4. Pulsed-dc and midfrequency ac reactive sputtering

High-rate reactive sputtering of electrically conducting compounds and alloys such as most transition-metal nitrides, carbides, and some oxides was a reality by the late 1980s.



FIG. 47. (Color online) Oxygen partial pressure P_{O_2} vs oxygen flow rate f_{O_2} during reactive dc magnetron sputter deposition, using partial-pressure control, of TiO_x from a Ti target in mixed Ar/O₂ atmospheres. The dashed gray lines correspond to results obtained when operating in the flow-control mode. Reproduced with permission from Sproul *et al.*, Surf. Coat. Technol. **39/40**, 499 (1989). Copyright 1989 by Elsevier.

Progress in high-rate reactive sputtering of dielectric films occurred in parallel, but required additional steps. rf magnetron sputtering is always an available option for sputter depositing dielectrics, but, as discussed in Sec. IV I, it is slow and generally uneconomic.

In 1975, Robert Cormia, together with Terry Trumbly and Sigurd Andresen,⁴⁰¹ filed a U.S. patent application with the unassuming title "Method for Coating a Substrate" (issued in September, 1977) that would lead to solutions for high-rate deposition of dielectric films. The patent describes a single flat-plate magnetron target with an ac power source operated at frequencies up to ~ 60 kHz, far below the standard 13.56 MHz rf frequency, for the reactive sputtering of oxides and nitrides and states the following. "It is not necessary that the applied waveform be sinusoidal or have a symmetrical waveform." The goal was to minimize or eliminate arcing (see Sec. IV J), which as they pointed out, decreases the deposition rate, degrades film quality, and can harm the power supply. Thus, the key was to allow target polarity reversal for sufficiently long periods that the accumulated positive charge due to ion bombardment of the target is neutralized by electrons. The patent correctly describes many issues that were not understood in detail until many years later:

- the ac frequency must be high enough to neutralize the accumulated positive charge at the target before the breakdown potential of the insulting layer is exceeded,
- (2) the target area at most risk for arcing is immediately adjacent to the high-erosion rate (racetrack) region,
- (3) the thicker the insulating layer on the target, the higher the required frequency for a material with a given dielectric constant,

- (4) for the same insulting-layer thickness, materials with higher dielectric constants allow the use of lower frequencies,
- (5) if the charge is not fully neutralized, step-by-step accumulation occurring over many periods can also lead to arcing (i.e., charge build-up is cumulative).

In 1986, Fazle Quazi filed a patent, assigned to BOE Limited (San Francisco, CA), for reactive sputtering from a single magnetron target using two power supplies to provide discrete alternating positive and negative pulses, again with the goal of periodically neutralizing accumulated positive charge on poisoned regions of the target in order to prevent arcing.⁴⁰² This allowed independent control of the frequency f as well as the duty cycle $\eta = \tau_{on}/(\tau_{on} + \tau_{off})$, in which τ_{on} is the time during a given cycle that the target is powered negatively to enable sputtering and τ_{off} is the time that the target is powered positively in order to attract electrons for neutralizing accumulated positive charge. The frequency f of the applied power is related to the duty cycle η via the relationships

$$f = \frac{1}{\tau_{on} + \tau_{off}} = \frac{\eta}{\tau_{on}} = \frac{1 - \eta}{\tau_{off}}.$$
(7)

Note that τ_{on} is always much larger than τ_{off} due to the large difference in ion and electron mobilities.

In 1993, Siegfried Schiller and colleagues,⁴⁰³ from the Fraunhofer Laboratory in Dresden, Germany, described single-target pulsed-dc sputtering [Fig. 48(a)] in which a switching unit is placed in the circuit between the dc power supply and the magnetron target to provide square-wave pulses for which, in principle, the values of f, τ_{on} , and τ_{off} can all be controlled independently (in fact, it took some



FIG. 48. Schematic illustration of a pulsed dc sputtering system with (a) a single target and (b) two targets. Reproduced with permission from Schiller *et al.*, Surf. Coat. Technol. **61**, 331 (1993). Copyright 1993 by Elsevier.

time before such a system was available commercially). The square-wave pulses are highly distorted in the plasma due to the complex discharge reactance. Schiller *et al.* recommended an optimal operational frequency range of 10–100 kHz.

One issue affecting all single-target pulsed reactive sputtering approaches is that even at a target frequency that minimizes arcing (arc suppression circuitry will always be required during reactive sputtering of insulators to eliminate "random" arcs), as the anode becomes covered with an insulating layer, process parameters begin to drift and the discharge is eventually extinguished when the electron current can no longer reach ground (the "disappearing anode" problem)³⁷⁸ However, a practical solution, proposed earlier the same year by Frach et al.⁴⁰⁴ (also from Fraunhofer, Dresden), is to use an anode with a large surface area and place it in a region of the vacuum system which is hidden from the intense plasma immediately in front of the target. Providing a flow of argon over the anode is also desirable. While reactive gas will still reach the anode, the reaction probability of molecular species is much less than that of atomic species formed in the discharge. The goal is to maintain a stable ground (open regions on the anode) throughout the lifetime of the target, then replace the anode when the chamber is opened to replace the target.

In 1988, prior to Schiller's publication, Este and Westwood³⁶⁷ had described a different approach to minimizing arc formation during high-rate reactive sputtering of dielectrics: the use of two targets with an ac mid-frequency power supply wired such that when one target was negative with respect to the plasma, the other target was positive and acted as the anode for the system. During the following half cycle, the voltages are reversed and the target that had been the cathode becomes the anode which, if process conditions are chosen correctly, is now sputter cleaned. Thus, there is always a functioning anode and even though the chamber is being coated with an insulating layer, the disappearing anode issue is solved. In Este and Westwood's experiments, the two targets were opposite each other. The earliest report of two-target mid-frequency reactive sputtering with side-byside targets, as is typically practiced today, was by Scherer et al. in 1992.⁴⁰⁵ A schematic illustration of the pulsed-dc version of the two-target mid-frequency ac approach is shown in Fig. 48(b).

A comparison between pulsed-dc and mid-frequency ac dual-target sputtering is presented in Fig. 49.⁴⁰⁶ The term "voltage scrub" in the figure refers to attracting electrons for neutralizing the accumulated positive-ion charge at the target. Note that in the mid-frequency case, the sine wave is automatically half-wave rectified at the plasma potential; thus, more of the power per pulse is utilized for sputtering.

Mid-frequency ac reactive sputtering, with typical frequencies in the range 50–300 kHz (moving toward the higher end today), is commonly used in manufacturing for coating large-area products such as architectural and automotive glass and for roll-to-roll web coating of flexible materials such as polymeric sheets (Sec. IV K). In these applications,



FIG. 49. (Color online) Schematic comparison of two-target pulsed-dc vs midfrequency ac waveforms during reactive sputtering. Reproduced with permission from Carter *et al.*, Vac. Technol. Coat. 7, 60 (2006). Copyright 2006 by Vacuum Technology and Coating.

rotatable targets have, in many companies, replaced planar rectangular targets, for the reasons discussed in Sec. IV F4.

A disadvantage of the dual-target approach compared to single-target sputtering is that the racetrack current must be returned to its quasi-steady-state value each half cycle. This results in transients leading to voltage and current overshoots giving rise to substantial fluxes of hot electrons and ions bombarding the growing film. Therefore, substrate temperatures are considerably higher, which can pose problems for thermally sensitive substrates,⁴⁰⁷ during dual-target sputtering. Moreover, the transients are more severe for midfrequency-ac than for pulsed-dc dual targets^{408,409} since the plasma must be reestablished each half cycle (not required for pulsed-dc dual magnetrons unless τ_{off} is set too high) resulting in larger energy dissipation per cycle.³⁷⁸ Thus, there is less substrate heating during pulsed-dc, compared to mid-frequency ac, dual-magnetron sputtering and the film deposition rate is higher per unit power. Another advantage of dual-target pulsed-dc is the ability to independently control pulse widths and power to each target, which allows the controlled deposition of alloys⁴¹⁰ or films with compositional gradients. The primary advantage of mid-frequency ac is that it is easier, hence less expensive, to scale power supplies to higher power for continuous, high-rate, very-largearea deposition³⁷⁸ such as for jumbo $(6 \times 3.2 \text{ m}^2)$ architectural glass.²⁸⁴

5. Modeling reactive sputtering

Another important recent accomplishment in sputter deposition is the evolutionary development of very useful models, with are increasingly more accurate, of the highly complex reactive-sputtering process. All such models are basically expressions of atom conservation. A mixture of rare and reactive gases, or simply pure reactive gas, enters the sputtering chamber and all reactive-gas species are captured at one of three places: the substrate (in most modern models, the "substrate" includes the substrate platen, chamber walls, and fixtures) which acts as an internal getter pump, the target (the poisoning process), or the external vacuum pump. While the models contain simplifying assumptions in order to obtain closed-form solutions, their value is in allowing the researcher to pose "what if" questions before initiating experiments, thus greatly decreasing the number of iterations prior to achieving desired results. Example questions include: what happens if the reactive-gas partial pressure is changed, the total pressure, the target voltage, the target-to-substrate distance, the metal/gas binding energy, the external pumping speed, etc.

Between 1968 and 1975, several reactive sputtering models were proposed to account for changes in target sputtering rates R_T, and hence film deposition rates, with the partial pressure P_r of reactive gases. In metal-oxygen systems, E. Hollands and David Campbell⁴¹¹ from Plessey Ltd., UK, and later Johannes Heller,⁴¹² IBM West Germany, qualitatively modeled the effects of changing the relative target oxidation rates and sputtering rates leading to either abrupt or gradual decreases in R_T with increasing oxygen partial pressure P_{O2}. Tetsuya Abe and Toshiro Yamashina,⁴¹³ Hokkaido University, Japan, proposed a kinetic model and used it to fit experimental data for the reactive sputtering of Mo and Ti in O_2 and N_2 . However, the model neglected the dependencies of R_T on differences in target elemental sputtering yields, secondaryelectron yields, and discharge currents, all of which vary with changes in Pr. A modification of Abe and Yamashina's model, which included reactive-gas gettering by deposited metal atoms, was presented by Fujitoshi Shinoki and Akio Itoh⁴¹⁴ from the Electrotechnical Lab., Tokyo, Japan.

In 1980, a University of Illinois group^{394} developed a reactive-sputtering model which included terms for reactivegas sticking probabilities, sputtering rates of adsorbed reactive gases, secondary-electron yields, and ion fluxes incident at the target, all as a function of P_r. Calculated R_T(P_r) results provided very good fits to experimental sputtering rates obtained with both a strongly-bonded metal/gas system, In/ O₂, exhibiting an avalanche effect in deposition-rate reduction under flow control, and a weakly bonded system, In/N₂, which did not undergo an uncontrolled decrease in deposition rate. Model fits allowed a determination, vs P_r, of the steady-state target oxide and nitride surface coverages, as well as nitrogen and oxygen sticking probabilities, on the indium target.

The left panel in Fig. 50 is a schematic illustration of the University of Illinois reactive-sputtering model.³⁹⁴ The partial pressure of reactive gas P_r mixed with Ar can be shown from gas kinetics to result in a flux J_r of reactive gas incident at the target,⁴¹⁵



FIG. 50. (Color online) (Left panel) Schematic illustration of a reactivesputtering model, reproduced with permission from Natarajan *et al.*, Thin Solid Films **69**, 201, 217, 229 (1980). Copyright 1980 by Elsevier, for calculating the normalized target sputtering rate [the sum of the fluxes F from the reacted compound fraction θ_c of the target and the metal fraction $(1-\theta_c)$] as a function of the reactive-gas partial pressure in mixed reactive-gas/argon discharges. See text for definitions of terms. (Right panel) Schematic illustration of the reactive-sputtering model from Ref. 420 for calculating the target sputtering rate and the film composition as a function of reactive-gas partial pressure in mixed reactive-gas/argon discharges. See text for definitions of terms. Note that in both models, it was assumed, for convenience, that the compound phase is sputtered as molecules. This limitation was removed in later versions as discussed in the text.

$$J_r [molec/cm^2 s] = 3.513 \times 10^{22} (m_r T_g)^{-1/2} P_r [Torr], \quad (8)$$

in which m_r is the mass of the reactive-gas species and T_g is the gas temperature. The reactive-gas chemisorbs at the target with probability $s_r(P_r)$, resulting in the surface having fractional compound and metal coverages θ_c and $\theta_m = (1 - \theta_c)$, respectively. Concurrent with the adsorption of reactive gas, the target is sputtered at a rate R_T (particles/ s), the sum of the ejected compound and metal fluxes $F_c = J_i$ $(S_c\theta_c) A_T$ and $F_m = J_i \{S_m(1 - \theta_c)\} A_T$. The terms S_c and S_m are the compound and metal sputtering yields and A_T is the target area. J_i is the ion current density at the target, which is a function of P_r and related to the measured target current density J_T through the secondary electron yield $\gamma(P_r)$:

$$\mathbf{J}_{\mathbf{i}} = (1 - \gamma)\mathbf{J}_{\mathbf{T}}.\tag{9}$$

Thus,

$$\begin{split} R_{T}[\text{particles}/\text{s}] &= (F_{c} + F_{m})A_{T} \\ &= J_{i}\{S_{c}\theta_{c} + S_{m}(1-\theta_{c})\}A_{T}. \end{split} \tag{10}$$

At steady state, the compound-formation rate at the target surface equals the compound sputtering rate, and

$$\mathbf{J}_{\mathbf{r}}\mathbf{s}_{\mathbf{r}}(1-\theta_{\mathbf{c}})\mathbf{b} = \mathbf{J}_{\mathbf{i}}\mathbf{S}_{\mathbf{c}}\theta_{\mathbf{c}},\tag{11}$$

in which b is the number of compound molecules formed per reactive-gas molecule chemisorbed at the target.

The target secondary-electron yield γ in Eq. (9) is related to θ_c through P_r. γ_{In} in pure Ar was estimated to be 0.15, based on previous results, and remained approximately constant as a function of P_{N_2} due to low nitrogen coverages resulting from the extremely small In/N binding energy. γ for the surface oxide was determined to be 0.39. The reactive-gas capture probability $s_r(P_r)$ in Eq. (11) was expressed as a Langmuir isotherm^{416,417} for which the sticking probability is zero on the compound phase and

$$s_r(P_r) = P_r/(P_r + P_*),$$
 (12)

on the metal region of the target surface. P* is the Langmuir critical pressure.

 $R_T(P_r)$ is obtained by iteratively solving the above equations, as described in Ref. 394, beginning with an estimated value for P*, measured values for the target sputtering rate S_T with $P_r = 0$ (pure Ar) and $P_{Ar} = 0$ (pure reactive gas), and interpolating to determine S_c and S_m values. The solution yields new values of P* and $S_T(P_r)$; the procedure is continued iteratively until convergence is obtained with experimental $R_T(P_r)$ results. The primary outputs of this procedure are $\theta_c(P_r)$ and $s_r(P_r)$.

In 1982, Steenbeck *et al.*⁴¹⁸ extended Shinoki and Itoh's model⁴¹⁴ to include the hysteresis effect by adding a term for reactive-gas gettering at the substrate as a function of deposited metal-atom coverage. Two years later, John Affinito and Robert Parsons,⁴¹⁹ from the University of British Columbia, incorporated another mechanism for target poisoning, in addition to chemisorption: reactive-ion implantation (or trapping) in the near-surface region of the target during sputter erosion. They, like the Illinois group, chose material systems for which chemisorption is either strong (Al/O₂) or relatively weak (Al/N₂) and concluded, based upon both experiments and kinetic modeling, that the drop in R_T with increasing P_r was primarily controlled by chemisorption in the former case and trapping in the latter.

Sören Berg and colleagues at Uppsala University made a very important step forward in 1987 (Ref. 420) when they extended the model of the Illinois group to include, in addition to the target sputtering rate, both the film growth rate (i.e., metal deposition and reactive-gas gettering at the substrate) and the external pumping speed as a function of the reactive-gas partial pressure. This allowed them to reproduce and analyze a variety of experimental results for flowcontrolled reactive sputtering. Berg's initial model, which treats target poisoning as being controlled purely by reactive-gas adsorption, is easy to use and quite powerful.

The essential features of the original Berg reactive sputtering model⁴²⁰ are illustrated schematically in the right panel of Fig. 50. Equations (8)–(11) above were also incorporated; however, additional equations were required since the goal here was not only to calculate R_T vs P_r , but also to determine the film composition as a function of P_r . Thus, it was necessary to calculate the steady-state compound and metal surface coverages on the target, $\theta_{c,T}$ and $\theta_{m,T}$ (T = target), as well as on the growing film, $\theta_{c,s}$ and $\theta_{m,s}$ (s = substrate, which includes the actual substrate plus all exposed area in the vacuum system that receives deposited material). Note that $\theta_{m,i} = (1 - \theta_{c,i})$ with i = T or s. The fluxes F_c and F_m emanating from the target are bifurcated in order to keep track of the change in $\theta_{c,s}$ and $\theta_{m,s}$ at the substrate. The rate of sputtered-metal flux covering the compound phase at the "film" surface is $F_m \theta_{c,s} A_T$. The corresponding term for sputtering from the target compound phase and covering the substrate metal phase is $F_c(1 - \theta_{c,s}) A_T$.

In addition to Eq. (10) describing the steady-state condition at the target, a steady-state equation is also required for the growing film:

$$J_{r}s_{r}(1 - \theta_{c,s})A_{s}b + F_{c}(1 - \theta_{c,s})A_{T} = F_{m}\theta_{c,s}A_{T}/d, \quad (13)$$

in which b is defined below Eq. (11) and d is the number of metal atoms per compound molecule. The two terms on the left side of Eq. (13) are the reactive-gas gettering rate at the exposed metal region of the growing film and the rate at which compound covers exposed metal. The term on the right side is the rate at which metal is sputtered onto (i.e., covers) the exposed compound phase at the substrate.

Finally, the following equation assures overall atom conservation during the reactive sputter deposition process:

$$\begin{aligned} Q_{r} &= Q_{r,T} + Q_{r,s} + Q_{r,p} \\ &= J_{r}s_{r}(1 - \theta_{c,T})A_{T} + J_{r}s_{r}(1 - \theta_{c,s})A_{s} + uP_{r}\xi. \end{aligned} \tag{14}$$

That is, the input reactive gas flow rate Q_r (molec/s) is equal to the sum of the target and substrate gettering rates, $Q_{r,T}$ and $Q_{r,s}$, plus the reactive-gas pumping speed $Q_{r,p}$ in which u is a factor accounting for units and ξ is the pump speed. Equations (8)–(11), (13), and (14) are solved iteratively, as described in Ref. 420, to obtain plots of, for example, R_T , P_r , $\theta_{c,T}$, and $\theta_{c,s}$ vs Q_r for different J_T values.

The initial Berg model was expanded in 1998 (Ref. 421) to cover more complex experimental results including reactive cosputtering from a metallic-alloy target or two separate elemental targets,⁴²² reactive sputtering of a metal in two different reactive gases,⁴²³ and reactive sputtering of systems such as transition-metal nitrides for which multiple phases can coexist on the target surface and in the growing film (e.g., Cr, Cr₂N, and CrN for sputtering Cr in Ar/N₂ mixtures).⁴²⁴ A review of these, and additional model results, was published by Berg and Nyberg in 2005 (Ref. 425) as a parallel to Sproul's experimental review³⁷⁶ in the same journal.

In the early 2000s, Diederik Depla ad Roger De Gryse from Ghent University, Belgium, demonstrated in a series of papers on the reactive sputtering of Al in O_2 ,⁴²⁶ Ag in N_2 ,⁴²⁷ and Si in N_2 ,^{428–430} that their rather detailed experimental results could not be completely explained by assuming that target poisoning occurred only by chemisorption at the target surface. It was necessary, as proposed earlier by Affinito and Parsons,⁴¹⁹ to include target poisoning via implantation (trapping) of accelerated reactive-gas ions. A striking example of such effects is the fact that silver sputtered in mixed Ar/N₂ discharges reveals strong reactive-sputtering phenomena, including changes in γ ,⁴²⁷ even though there is no stable silver nitride. In (2004), Depla and De Gryse proposed a simple reactive-sputtering model which accounted for reactive-gas trapping.⁴²⁸

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Two years later, Tomas Kubart *et al.*⁴³¹ at Uppsala included a third target-poisoning mechanism, recoil implantation of surface chemisorbed reactive-gas species by incident ions, and presented a model which included chemisorption, recoil implantation, and direct trapping. This resolved an issue in the original Berg model associated with compound accumulation of up to several monolayers on the target, shown both experimentally^{428,432} and theoretically,⁴³³ which could not be explained by chemisorption alone since in many metal/gas systems, the process is self-limited to a single monolayer.

The Ghent group,⁴³⁴ in 2007, published a dynamic model similar to that of Kubart et al. while also accounting for the chemical reaction kinetics of target atoms with recoiledsurface and directly implanted reactive species. The model provided an explanation for a variety of experimentally observed effects which arise due to the binding energies of adsorbed surface reactive-gas species being quite different than those of species trapped below the surface. Depla and Stijn Mahieu edited a book on reactive sputter deposition, published in 2008,⁴³⁵ and the Ghent group further refined their model in 2012.436 Two years later, Koen Strijckmans and Depla presented a time-dependent and spatially resolved reactive-magnetron sputtering model⁴³⁷ which included all previously discussed processes, plus the possibility of redeposition back onto the target,⁴³⁸ a reaction pathway which can lead to arc formation.439 The same year, Berg and colleagues⁴⁴⁰ from Uppsala further updated their model to remove an initial simplifying assumption that material sputtered from poisoned regions of the target is ejected as compound molecules. This was done in order to include preferential sputtering^{441,442} and allow recoiled knock-in reactive-gas atoms which do not react with target metal atoms to be released to the vacuum during sputter erosion.

Reactive sputtering models, driven primarily by the Uppsala and Ghent University groups, are continuing to become more realistic, complete, and quantitative for analyzing complex results as well as for predicting parametric effects prior to carrying out experiments.

6. Metal/metalloid reactive sputtering

The models discussed in Sec. IV J 5 were developed to describe and analyze reactive sputtering of metal targets in "simple" reactive gas atmospheres such as O_2 and N_2 , that is, metal/gas systems. However, there has also been research as well as industrial interest in the reactive sputter deposition of metal/metalloid systems including silicides, borides, carbides, arsenides, etc. Thus, a parallel, but far smaller, effort has been devoted toward understanding and modeling the dynamics of sputtering metal targets in metalloid-containing gasses. Early experimental and modeling examples include the deposition of polycrystalline TiSi₂ silicide electrical contacts in 1982 by sputtering a Ti target in mixed argon/silane (Ar/SiH₄) atmospheres,⁴⁴³ single-crystal III–V GaAs layers (1983) from a GaAs target in mixed argon/arsenic (Ar/As₄),⁴⁴⁴ and polycrystalline TiC (1984) and TiB₂ (1989)

hard-coatings from Ti targets in argon/methane $(Ar/CH_4)^{445}$ and argon/diboride (Ar/B_2H_6) mixtures.⁴⁴⁶

A University of Illinois group⁴⁴⁴ demonstrated experimentally and theoretically that reactive sputtering kinetics of GaAs in Ar/As_4 behave in a manner similar to metal/gas systems, even though arsenic is a metalloid, since excess arsenic does not react with the GaAs compound phase, only with free gallium atoms. Thus, the GaAs film growth rate at excess arsenic partial pressure is completely controlled by the Ga deposition rate.

Berg and colleagues from Uppsala University found that the dynamics of the reactive sputtering of Ti in Ar/SiH₄ and Ar/B₂H₆ are very different from those of GaAs film growth since the metalloid anion species (Si or B) have a non-zero sticking probability on the compound phase as well as themselves.^{443,446} Thus, thick metalloid layers can accumulate on the target, giving rise to films which are nearly pure metalloid (highly overstoichiometric) in composition. In addition, H and H₂ formed in the discharge can have a strong effect on the sputtering process.⁴⁴⁶ For example, hydrogen ions carry current in the discharge, but do not contribute significantly to target sputtering [see Sec. IV H and Eqs. (2) and (3)]. In addition, the presence of hydrogen can lead to back reactions (Si and B hydride desorption) at both the target and growing-film surfaces. Thus, while reactive sputtering of most metal/metalloid material systems does not lead to hysteresis loops, great care is still required in controlling the reactive-gas partial pressure.

The experimental pathway leading to high-rate sputter deposition of, for example, TiSi₂ in Ar/SiH₄ is completely different from that described for metal/gas systems in Sec. IV J 5. The Uppsala group⁴⁴³ showed that accumulation of excess Si on the target is reduced and higher deposition rates are achieved, by increasing the target power. However, continuing to raise the target power will eventually lead to understoichiometric films (excess Ti) instead of overstoichiometry (excess Si). Thus, there is a critical reactive-gas partial pressure for each target power, making process control difficult. They demonstrated that a better approach for enhancing film deposition rates, while maintaining stoichiometry, is to apply a negative substrate bias V_a at high target power in order to crack, in this example, SiH₄ gas-phase molecules near the substrate and augment the Si deposition rate via processes similar to those operative in plasmaenhanced chemical vapor deposition.⁴⁴⁷ For a given high target power, stoichiometric films can be obtained over a range in V_a values.⁴⁴³ Thus, there is no longer a single critical operating point, and achieving process control is much easier.

K. Roll-to-roll web coating

The 1930s witnessed the advent of roll-to-roll web coating in which flexible substrate materials such as textiles, polymers, paper, and thin-metal foil sheets are unwound from a spool and continuously passed, via a winding system which maintains constant pressure (and often provides substrate cooling), over the vapor source. The coated material is then rewound onto a take-up spool. The evolution of this technology is described in a series of papers published from 1997 through 2005.^{448–451} The earliest roll-to-roll coaters employed sputter deposition, but there was a shift to evaporation beginning in the late 1930s in order to obtain higher deposition rates and then back to sputtering in the 1980s following the commercial availability of the rectangular planar magnetron (Sec. IV F).

The first industrial web-coating application was in 1934; systems were installed in London (UK) and in Fürth (Bavaria, Germany) to sputter-deposit gold on glassine (smooth glossy paper, with oriented fibers, which is highly impervious to moisture) to create foil for hot stamping in specialty-printing processes for the production of shiny decorative designs on textiles, wood, hard plastics, leather, and other materials. In initial operations, 400 m² of glassine, on a 1-m-wide roll, was coated in 23 h.⁴⁴⁸ This was equal to a week's production of gold leaf by 30 highly-skilled gold-beating craftsmen. In addition, the roll-to-roll product had a much more uniform thickness distribution.

An early industrial web coater (mid-1930s), designed by Bosch (Germany), for the patterned sputter metallization of paper to produce capacitors is illustrated in Fig. 51.⁴⁴⁸ By the time production was initiated, the system incorporated thermal evaporation rather than sputter deposition. In 1941, a dc-diode sputter web coater at the Hy-Sil Company in Boston produced silver layers on cellophane for decorative applications.⁴⁵⁰

Immediately following the commercial availability of the modern planar magnetron, the first magnetron sputterdeposited roll-to-roll commercial product, in the late 1970s, was indium tin oxide (ITO) layers on polyethylene terephthalate (PET) web⁴⁵² for use as a transparent-conducting electrode in x-ray imaging.^{449–451} A *large-scale* magnetron sputter roll coater was delivered to Southwall Technologies (Palo Alto, California) in 1980 for the production ITO/ metal/ITO trilayers on PET web for infrared-reflecting heatmirror applications.^{449,450} The ITO layers were deposited by reactive dc magnetron sputtering and the metal layers by rare-gas magnetron sputtering. The deposition system, produced by Leybold, contained five separate coating chambers with 1.828-m-long rectangular-shaped planar targets. A schematic illustration of a modern sputter roll-to-roll coating system is shown in Fig. 52.451 In many applications, particularly for large-area, high-rate (high target power) coatings, the rectangular planar magnetrons in Fig. 52 have been replaced by rotating tubular magnetrons (Sec. IV F 4).⁴⁵¹

L. Even more on mechanisms of sputtering: Sputter-yield amplification

Beginning in the early 1990s, Sören Berg and colleagues at Uppsala University, Sweden, showed experimentally, combined with static and dynamic TRIM simulations (see Sec. IV H), that the sputtering yield of a light-atom target such as carbon (12.01 amu) or silicon (28.09 amu) due to the impact of relatively low-mass ions (e.g., Ar^+ , 39.95 amu) can be significantly increased via the presence of a small



Fig. 51. Illustration of a separately pumped, four-chamber evaporative roll-to-roll web-coating system developed by Bosch (Germany) in the mid-1930s to deposit zinc electrodes on paper capacitors. Reproduced with permission from Dietrich *et al.*, "Vacuum web coating—An old technology with a high potential for the future," in *Proceedings of the Society of Vacuum Coaters* (1997), p. 354. Copyright 1997 by the Society of Vacuum Coaters.

concentration of heavy atoms (e.g., platinum at 195.08 amu) on the surface or in the near-surface region, during sputter etching.^{453–456} Initial experiments consisted of measuring the sputtering rates R_T of carbon and silicon targets due to ion bombardment by a 6 mA, 1 keV Ar⁺ ion beam in a vacuum system with base and operating pressures of 2×10^{-7} and 5×10^{-4} Torr. The experiments were then repeated while depositing Pt on the targets at 20 Å/min. The latter resulted in a dramatic increase in R_T , from 15 to 45 Å/min for carbon and from 45 to 92 Å/min for silicon targets. Clearly, as demonstrated in Ref. 456, the results depend strongly on the heavy-metal/ion flux ratio as well as the ion energy.

The explanation for this surprising effect, which also applies to the sputter removal of light-atom ultrathin films



FIG. 52. Cross-sectional view of a roll-to-roll sputter web-coating system containing five rectangular planar magnetrons, each in a separately pumped chamber. The flexible substrate is fed from the spool in the upper left, via rollers and tensioners, onto the coating drum and then sequentially through the deposition chambers. The final product is wound onto the output spool in the upper right. Reproduced with permission from Ludwig *et al.*, Proc. IEEE **93**, 1483 (2005). Copyright 2005 by IEEE.

on heavy substrates,^{455,456} is primarily related to the higher nuclear stopping power of the heavy element.⁴⁵⁶ The amplification effect is most pronounced when $m_T < m_i < m_h$, in which m_T is the atomic mass of the target atoms, m_i is the ion mass, and m_h is the mass of the heavy atoms. The introduction of the heavy atoms decreases the average incidention and target-recoil penetration depths, thus resulting in denser cascades. In addition, a fraction of the ions are reflected back toward the target surface. The increased energy deposited at the surface gives rise to the enhanced sputtering rate. Moreover, the high mass of the deposited species (or the underlying layer in the ultra-thin-film experiment) compared to that of the ions results in a disproportionately smaller sputtering yield for the heavy atoms. Furthermore, if the addition of heavy atoms increases the near-surface atomic density, the sputter-yield amplification effect is further enhanced since the hard-sphere collisional energy loss is directly proportional to the atomic density.

A practical example of yield amplification is selective deposition onto patterned substrates.^{455,456} Figure 53 illustrates experimental results described in Ref. 456 for the sputter deposition of aluminum (26.98 amu) onto a silicon wafer covered with 6000 Å of silicon dioxide, followed by a 3000-Å-thick tungsten (183.84 amu) layer, in which trenches of



FIG. 53. (Color online) Illustration of yield amplification effects in the ionassisted selective deposition of aluminum on silicon, but not on the adjacent tungsten layers. During aluminum deposition, the substrate and growing film were bombarded with 300 eV Ar⁺ ions. Note that the tungsten layers were ion etched as described in Ref. 456.

different widths (~1 to 2 μ m) were photolithographically opened to expose bare silicon (see Fig. 53, upper panel). During Al sputter deposition, the growing aluminum film was bombarded with 300 eV Ar⁺ ions. With the proper choice of the Al/Ar⁺ ratio, Al is selectively deposited on bare silicon to fill the trench, while there is no net aluminum deposition on the tungsten surface, which itself is partially sputter etched (Fig. 53, lower panel).

A recent application of sputter-yield amplification is to provide real-time control of AlN incorporation in singlecrystal Hf_{1-x}Al_xN films, grown on MgO(001) substrates at 450 °C, using high-flux, low-energy (10-40 eV) argon ion bombardment of the growing alloy film during magneticallyunbalanced reactive-magnetron sputter deposition (Secs. IV F 5 and IV J 3) from a single $Hf_{0.7}Al_{0.3}$ alloy target in an ultrahigh vacuum system.457 Incoming argon ions, and fast recoils in the growing film, have a high probability of being reflected, with significant energy, from heavy near-surface hafnium atoms (178.49 amu) to resputter (sputter remove) light deposited aluminum and nitrogen atoms (14.01 amu). Nitrogen surface vacancies, however, are immediately refilled due to the high nitrogen partial pressure compared to the metal fluxes. The normalized AlN concentration in the film decreases dramatically, by a factor of >200, with increasing Ar⁺ ion energy as shown in Fig. 54.457 AlN concentrations in Hf_{1-x}Al_xN films can be selectively controlled from those of the target concentrations, 30 mol. % (x = 0.3), to nearly 0% (x ~ 0, essentially pure HfN).

In order to obtain high-crystalline-quality alloy films, the Ar^+ ion energy incident at the growing film is maintained \leq 40 eV to minimize residual ion-irradiation-induced damage and avoid the onset of aluminum forward scattering, which increases the AlN concentration slightly (see Fig. 54). Single-crystal alternating-layer HfN/Hf_{0.7}Al_{0.3}N superlattices were also grown by periodically switching the Ar⁺ ion energy back and forth between 40 and 10 eV. Similar results were obtained for polycrystalline Hf_{1-x-v}Al_xSi_vN ($0 \leq x \leq 0.14$,



FIG. 54. (Color online) AlN concentration in single-crystal $Hf_{1-x}Al_xN$ films grown by magnetically unbalanced magnetron sputtering from a single $Hf_{0.7}Al_{0.3}$ target as a function of the ion energy E_i incident at the growing film. The ion/metal ratio was eight. Reproduced with permission from Howe *et al.*, Acta Mater. **59**, 421 (2011). Copyright 2011 by Elsevier.

 $0 \le y \le 0.12)$ single-layer and multilayer films grown on Si(001) substrates at 250 $^\circ C.^{458}$

M. Sustained self-sputtering

The experimental results of Fred Wehner^{43,228} and the theoretical work of Peter Sigmund^{324,325} demonstrated that the sputtering yield S during low-energy sputtering is proportional to an energy-transfer factor $4m_im_T/(m_i + m_T)^2$ [Sec. IV H and Eq. (2)], in which m_i is the mass of the incident ion and m_T is the target-atom mass. The realization that this function has a maximum when $m_i = m_T$ provided the initial motivation to increase the sputtering rates of metal targets by using metal ions of the same species (self-sputtering) with no rare-gas (or Hg⁺) ions. A secondary motivation, recognized later, was the elimination of rare-gas incorporation by implantation (trapping) in growing films.⁴⁵⁹ The incorporated rare gas degrades physical properties (e.g., decreases the conductivity of copper layers)⁴⁶⁰ and gives rise to high stresses and even film delamination.^{461,462}

The first report of self-sputtering in a glow discharge appears to be by Krutenat and Gesick (Pratt and Whitney Aircraft Company, Middletown, CT) who in 1970 sputtered liquid binary lead/tin, iron/vanadium, and iron/nickel alloy targets using thermionically-supported dc discharges in vacuum systems with base pressures of 2×10^{-6} to 5×10^{-7} Torr.⁴⁶³ In these experiments, an argon discharge was established, the power increased until the target melted, and the argon gas flow turned off to initiate sustained self-sputtering (SSS). A target power of 100 W/cm^2 provided film deposition rates of up to $4 \,\mu$ m/min (remarkably high for the time) due to a combination of self-sputtering and evaporation. Film compositions were found to be much closer to those expected from alloy sputtering than from coevaporation.

Hosokawa et al. (Nippon Electric, Tokyo, Japan), who coined the term "SSS" in 1980,464 and Kukla et al. (Leybold AG, Hanau, Germany)⁴⁶⁵ in 1990, used modified magnetron geometries and magnetic-field configurations with solid targets to obtain SSS. The earliest report of SSS using a planar magnetron was by Witold Posadowski, from the Technical University of Wroclaw, Poland, in 1991.⁴⁶⁶ Clearly, the absolute minimum requirement for a sustained metal-ion discharge is that the self-sputtering yield S_{self} must be at least unity. The reality, however, is that S_{self} has to be greater than one due to the less-than-unity probability that a sputtered atom is ionized in the discharge combined with ion losses to the vacuum chamber walls and the substrates.^{459,464} Moreover, in order to obtain significant film deposition rates, S_{self} must be even greater since a large fraction of the metal ions return to the target.

Although metal self-sputtering yield data at high irradiation energies were available from the ion-accelerator community since the early 1960s (see, for example, the 45 keV data in Ref. 240), the earliest S_{self} results in the lower-energy range corresponding to those used for magnetron sputter deposition were reported in 1969 by Hayward and Wolter from Boeing Company, Seattle, WA.⁴⁶⁷ Unity selfsputtering yields were obtained with silver, gold, and copper targets using ion-beam energies of ~115, 150, and 190 eV, respectively. Much higher and strongly oxygen-partial-pressure dependent ion energies were required for chromium (~460 eV) and aluminum (>700 eV, extrapolated).

Based upon the ion-beam self-sputtering data of Hayward and Wolter (and probably the relative prices of the three metal targets which exhibited facile self-sputtering!!), Posadowski chose a 10-cm diameter circular copper target for his early experiments.⁴⁶⁶ In a vacuum system with a base pressure of 5×10^{-5} Torr and a target-to-substrate separation of 5 cm, he established a discharge at an argon pressure PAr of 0.5 mTorr. While increasing the target power, Posadowski found that he could decrease PAr until at a threshold power density P* of 70 W/cm² (target current density of \sim 100 mA/ cm²), the argon flow could be turned off, and a stable sustained self-sputtering discharge was formed. He reported a copper deposition rate of $6 \,\mu m/min$ with a target power density of 80 W/cm^2 . Threshold power densities are a complex function of target size and shape (current densities, and hence power densities, are typically determined by dividing the current by the total target area, but as shown in Figs. 26 and 27, the current distribution over a planar magnetron target surface varies dramatically with the positions and strengths of the permanent magnets), target thickness (which affects the magnetic-field density distribution between the target and the substrate), the vacuum system size and design (which affects plasma density), etc.

In 1993 and 1995, Posadowski also demonstrated SSS for silver⁴⁵⁹ and Ta.⁴⁶⁸ Stanislav Kadlec and Jan Musil (Institute of Physics, Prague, Czech Republic) added lead and cadmium to the list in 1996 and reported $P^* = 57 \text{ W/cm}^2$ for self-sputtering of copper.⁴⁶⁹ In 2004, Cu_{1-x}Ni_x alloy films were deposited by SSS from two 5-cm-diameter metal targets mounted side-by-side and separated by 20 cm.⁴⁷⁰ For these experiments, P* was 370 W/cm² for copper and 490 W/cm² for nickel. Clearly, SSS requires metal targets with high self-sputtering yields (i.e., low surface binding energies Uvap [see Eq. (2) in Sec. IVH], but, as noted by Posadowski, good thermal conductance (low target thickness again!) is also important in SSS since the applied power densities are quite high. Thus, as he pointed out: "The temperature of the target surface can be very high in such systems, reaching even the melting point. Locally melted target material was observed in our work when the cooling efficiency was reduced because of low water pressure in the installation."459 In Posadowski's experiments, he used thin targets with direct water cooling (no target backing plate). It is likely that sublimation, together with self-sputtering, made a significant contribution to the SSS results for the highvapor pressure elements lead and cadmium.⁴⁶⁹

In 2008, Posadowski and colleagues⁴⁷¹ reported that in cases for which arcing limits SSS (due to large ion-current densities combined with, for example, background gas-phase contamination arising from high system base pressures, as is often the case in industrial processing), continuous SSS, without arcing, can be achieved using pulsed-dc sputtering (Sec. IV J 4). The authors demonstrated Cu SSS in a vacuum

system with a 2.5×10^{-5} Torr base pressure, using a starting Ar pressure of ~1 mTorr and a target power of 11 kW, at frequencies f of 60–90 kHz with duty cycles η (the fraction of each cycle in which the target is powered negatively) of 80%–90%. During the negative portion of each cycle, the on-time τ_{on} , during which the target is being sputtered, the ability to reach a critical plasma density for self-sustained sputtering depends on the target material and the applied voltage. In the positive parts of each cycle, the off-time τ_{off} , the target draws electrons to neutralize charge build-up and the plasma density decays at a rate which depends on the metal-ion lifetime.

Thus, the coordinated choice of f and η [Sec. IV J 4 and Eq. (7)] is essential in pulsed-dc SSS in order that the degree of plasma-density decay during τ_{off} does not prohibit SSS being achieved during the subsequent τ_{on} time. That is, as the voltage is switched to negative for the sputtering phase, the metal-ion current must still be large enough that sustained self-sputtering can be achieved. With a 50-cm-diameter Cu target operated at 60 kHz, Posadowski and colleagues⁴⁷¹ reported that the target voltage during τ_{on} decreased from ~530 to 480 V, while the target current increased from 8 to ~20 A. The target current starting value, 8 A, was due to charge carriers which did not recombine during τ_{off} .

Self-sputtering of copper without the use of gas at all (not even for plasma initiation) was demonstrated by Joakim Andersson and André Anders at the Lawrence Berkeley Laboratory (Berkeley, CA) in 2008.^{472,473} They used pulsed magnetron discharges (see Sec. VB) in which each pulse was triggered by short ($\sim 20 \,\mu$ s), $\sim 200 \,\text{A}$, vacuum arcs. The magnetron target voltage was applied simultaneously with the arc in a vacuum system having a base pressure of 7.5×10^{-7} Torr. The use of low pulse repetition rates, 1–5 per second, allowed relatively long, $\sim 3-9 \,\text{ms}$, self-sustained sputtering pulses at target voltages above 550 V.

Today, interest in SSS for dc magnetron sputter deposition has dwindled due to the complexity of SSS and the high deposition rates, combined with uniform film thicknesses, achievable with simple rotatable magnetrons (see Sec. IVF4). In addition, large metal-ion fluxes can be obtained using ionized-metal (Sec. VA) and high-power impulse magnetron sputter deposition (Sec. VB).

V. RECENT DEVELOPMENTS AND CONCLUSIONS

In a little more than 160 years, sputter deposition has metamorphosed from a scientific curiosity to a platform for investigating solid-state physics via atomic-scale billiards combined with quantum mechanics (e.g., ion-bombardmentinduced secondary electron emission) to a tool for massproducing industrial thin-film products. Typing "sputter deposition" in a Google search brings up approximately a million hits and Google Scholar lists more than 200 000 journal articles on the subject. In addition, several books, including Refs. 382, 474, and 475, are focused on the use of sputter deposition in manufacturing. Of the wide range of presently available vapor-phase thin-film deposition techniques, sputtering is the fastest growing and continues to find new applications. Much of this popularity stems from advantages including:

- the fact that sputtering is a physical-deposition technique (controlled by momentum transfer), and hence, it is relatively insensitive to deposition temperature, as opposed to chemical-vapor deposition, and can be applied to thermally sensitive substrates;
- (2) it is relatively easy to controllably deposit alloys with sputtering compared to evaporation (sputter yields are similar for all metals, while evaporation rates at a given temperature vary over many orders of magnitude); and
- (3) the use of low-energy ion (as well as fast-neutral atom) bombardment of the film growth surface to provide control of the film nanostructure and composition, while minimizing surface roughness, is inherent in approaches such as unbalanced magnetron sputtering (Sec. IV F).^{38,296,297}

These advantages explain, for example, why multilayer giant-magnetoresistance devices are fabricated using sputtering.⁴⁷⁶

The combination of readily available ultra-high-vacuum systems, magnetically-unbalanced magnetrons, and partialpressure-controlled reactive sputtering allows the growth of extremely high-quality single-crystal thin films for investigating fundamental material properties. Examples include:

- (1) electron/phonon coupling and superconductivity in group-IV transition-metal and rare-earth nitrides;⁴⁷⁷
- (2) demonstrating that the tetragonal-to-cubic phase transition in vanadium nitride (VN), first reported almost 30 years ago, but poorly understood, is due to strongly anharmonic phonon vibrations at temperatures above 250 K;⁴⁷⁸
- (3) solving a controversy in the literature to clearly establish the mechanism of vacancy-induced hardening in understoichiometric transition-metal compounds such as TiN_x (with x < 1.0)⁴⁷⁹ while providing the first complete set of elastic constants as a function of x;⁴⁸⁰ and
- (4) demonstrating that ceramic alloys such as $V_{0.5}Mo_{0.5}N_x$ and $V_{1-x}W_xN$ not only display increased hardness with decreasing x but also exhibit enhanced ductility (due to electronic-structure effects), that is, the alloys exhibit excellent toughness (the combination of hardness and ductility).^{481–483}

A. Ionized-metal magnetron sputter deposition

Today, magnetron sputtering remains a dynamic field; it not only continues to find new applications, but it also reincarnates itself in novel and useful manifestations. Two new forms of magnetron sputtering were created during the 1990s, both with the goal of efficiently ionizing sputterejected metal atoms. The first, ionized-magnetron sputter deposition, was developed in the early 1990s by researchers in the semiconductor industry in response to the fact that aspect ratios (depth-to-width) of interconnect vias and trenches, whose sides and bottom surface had to be coated with a uniformly distributed thin layer, increased rapidly. The lack of directionality in sputtered-atom fluxes emitted from the target with an approximately cosine distribution (see Sec. IV A) meant that at some size scale (which depends on the deposition conditions), the vias become clogged, giving rise to "bird's-beak" defects as illustrated in Fig. 55, with very poor coating uniformity.

An elegant solution, developed by Steve Rossnagel and Jeff Hopwood of IBM in 1993, was to ionize the sputtered metal flux and use an electric field to provide metal-atom directionality.^{484,485} The ionization was accomplished by adding a two-turn water-cooled coil to inductively couple rf power to the plasma between the target and the substrate during operation of a standard parallel-plate dc magnetron (Fig. 56, left panel). Since the ionization energies of the sputtering gases used in these experiments, 15.76 and 21.46 eV for Ar and Ne, were much larger than those of the metal atoms, 5.99 and 7.73 eV for Al and Cu, the sputtered metal atoms had a much higher ionization probability than the rare-gas atoms.

Energy and mass analyses were used to determine, as a function of Ar and Ne sputtering pressure, the ionized fraction of sputtered Al atoms incident at the substrate position. Initial results are plotted in the middle panel of Fig. 56.⁴⁸⁵ At high pressures, for which sputtered metal atoms have a longer residence time in the rf plasma region due to shorter mean-free paths and higher collision frequencies, ionization



FIG. 55. (Color online) Illustration of the formation of a bird's-beak defect while attempting to deposit a liner (or fill) coating in a via or trench due to the lack of directionality in the sputtered-atom flux. Figure courtesy of Steve Rossnagel, IBM.



FIG. 56. (Color online) (Left panel) Schematic illustration of a dc magnetron with an inductively coupled rf coil between the target and the substrate in order to post-ionize sputtered metal atoms. (Middle panel) Fraction of sputtered Al atoms ionized in Ar and Ne plasmas as a function of the sputtering pressure for constant magnetron power and 250 W rf induction. Reproduced with permission from Rossnagel and Hopwood, J. Vac. Sci. Technol., B **12**, 449 (1994). Copyright 1994 by American Vacuum Society. (Right panel) Metal liner coating deposited by ionized-metal sputtering. Figure courtesy of Steve Rossnagel, IBM.

fractions of 80%–90% can be achieved with deposition rates that are approximately equal to or somewhat larger than, depending on operating conditions, that without the rf coil. A liner coating deposited by ionized-metal sputtering is shown in the right panel of Fig. 55. Note that the high operating pressures employed in these experiments also contributed to the uniformity of sidewall coverage due to scattering resulting from short mean-free paths.

Rossnagel, collaborating with a group from the University of Illinois,⁴⁸⁶ also demonstrated that Al films deposited by ionized-magnetron sputtering have larger grain sizes and a higher degree of 111 preferred orientation, by more than an order of magnitude, with a much smaller azimuthal distribution, than with dc magnetron sputtering under otherwise identical deposition conditions. The films also exhibit low stress. Stronger 111 preferred orientation with minimal mosaic spread decreases the probability of electromigration failure in Al- and Cu-based metal interconnects.⁴⁸⁷

B. High-power impulse magnetron sputter deposition

Beginning in the mid- to late-1990s,^{488–490} another variation of magnetron sputtering, which later became known as high-power impulse magnetron sputtering (with several acronyms: HiPIMS, HIPIMS, and HPPMS),491,492 was developed. In HiPIMS, very-high-power pulses are applied to the target (power densities of several kW/cm^2 and peak voltages up to $\sim 1 \,\text{kV}$ or more) to produce ultradense plasmas with electron concentrations two to 4 orders of magnitude higher than obtained with standard dc magnetrons. Since the heat load deposited at the target surface during sputtering must still be carried away (typically by water cooling the back side of the target holder), the time-averaged power density is restricted to be essentially the same as in dc magnetrons; therefore, power in HiPIMS systems is applied in short pulses (\sim 50–200 µs) with low duty cycles (<10%) and frequencies (10 Hz-10 kHz).493

JVST A - Vacuum, Surfaces, and Films

The study of high-power pulsed plasmas, but without magnetic confinement, began at least as early as the late 1960s. As briefly outlined in an article on the history of HiPIMS power supplies,⁴⁹⁴ Malkin, of the Moscow Engineering and Physics Institute (a highly regarded technical University renamed the National Research Nuclear University in 2009), published experimental results covering the period from 1968 through 1972.⁴⁹⁵ The purpose of the research was not sputter deposition, but the development of intense light sources, including lasers, and the use of highpower plasmas for material processing by spark-erosion and welding. Malkin described power supplies based on both inductor/capacitor (LC) circuits and switched capacitor banks. He concluded that the latter type, the basis of modern HiPIMS power supplies, offers advantages due to versatility and sharper pulse shapes. In addition to the lack of magnetic confinement, another major difference in the early Russian work, compared to present HiPIMS discharges, was the use of a short rf pulse to initiate the plasma and preionize the gas prior to the application of a current pulse. In 1982, Tyuryukanov et al., 496 at the same Moscow institute, introduced magnetic confinement to form a magnetron-type race track (see Sec. IV F 2 and Fig. 27) on a 5-cm-diameter circular target. The group investigated the properties of pulsed plasmas, with pulse lengths up to 1 ms, but did not use the source for film deposition.

Film-deposition studies using high-power pulsed plasmas were published by Mozgrin *et al.*,⁴⁸⁸ also from the Moscow Engineering and Physics Institute, in 1995. They employed a pulsed LC supply to apply 200 kW, at a repetition rate of 10 Hz with pulse lengths up to 1.5 ms, to 12-cm-diameter planar magnetron targets (copper, titanium, molybdenum, and steel). However, the gas was still ionized prior to each plasma pulse, in this case by means of a continuous dc plasma. In 1999, the same group described pulsed sputter deposition of metal targets, this time including aluminum, in Ar as well as in reactive N₂ and mixed Ar/N₂ discharges.⁴⁸⁹

The first discussion of "modern" HiPIMS technology, which does not require preionization before initiating pulses,

appears to be that of Vladamir Kouznetsov *et al.*,⁴⁹⁰ with collaborators from Linköping University, Sweden, and the University of Illinois. They used a combination of plasma-probe and film-deposition-rate measurements to demonstrate that HiPIMS plasmas have much higher sputtered-metal-atom ionization probabilities than dc magnetrons.

The very high peak target powers applied during HiPIMS yield correspondingly high instantaneous sputtering rates such that sputtered-atom pulses rarefy the sputtering gas in front of the target due to the large momentum and thermal transfer. While rarefaction had been reported two decades earlier with dc magnetrons,⁴⁹⁷⁻⁴⁹⁹ the effect is much stronger in HiPIMS because of the higher powers. That is, during typical HiPIMS pulses, sputtering transitions from being initially dominated by rare-gas ions at the beginning of each pulse to sputtering dominated by metal ions later in the pulse^{500,501} An important advantage of the latter mode of operation is the extremely high degree of sputtered-metalatom ionization, with reports up to $70\%-90\%^{490,502}$ (compared to $\sim 1\%$ in dc magnetron sputtering).⁵⁰³ This, in turn, means that the use of low-energy ion bombardment of the growing film in order to control the film microstructure and composition, while minimizing surface roughness, can be achieved without a major disadvantage often inherent in dc magnetron sputter deposition: trapping of rare-gas ions in the growing film, where they reside in interstitial sites and lead to compressive stress.^{461,462}

Synchronizing the substrate bias to the metal-ion portion of the HiPIMS pulse results in irradiation of the growing film primarily by metal ions which are incorporated in lattice sites, thus resulting in a significant decrease in film stress.⁵⁰¹ A disadvantage of HiPIMS for commercial applications is that the return of metal ions to the target, among other effects, decreases the film deposition rate.^{504–506} However, the recent introduction of hybrid HiPIMS/dc-magnetron sputtering has been shown to provide, in addition to low stress, high deposition rates and fully dense films at low substrate temperatures (no externally applied heating).^{507–512} The film deposition rate is primarily controlled by continuous dc magnetron sputtering (in which small fractions of a monolayer are deposited between HiPIMS pulses) with no applied substrate bias V_a; metal-ion bombardment leading to densification of the growing film occurs only during the synchronized-bias metal-ion part of each HiPIMS pulse.

Reactive deposition is another mode of HiPIMS operation, R-HiPIMS, which is presently receiving significant attention of both the research and the application communities. It has been shown that, depending on operating conditions, transparent dielectric metal-oxide layers can be deposited in flowcontrol (i.e., without the requirement of spectroscopic partialpressure monitoring) with reduced hysteresis effects. This, in turn, yields higher deposition rates than with flow-control reactive dc magnetron sputtering at the same average power (even though corresponding pure-metal deposition rates are lower in HiPIMS). Two of the earliest groups to report this were Kostas Sarakinos *et al.* (Aachen University, Germany) and Erik Wallin and Ulf Helmersson (Linköping University, Sweden) whose work focused on the growth of ZrO_2^{513} and $Al_2O_3^{514}$ thin films, respectively. Over the past several years, similar results have been reported for a variety of oxides including TiO_2 ,⁵¹⁵ Al₂O₃ and CeO₂,⁵¹⁶ Nb₂O₅,⁵¹⁷ ZrO₂ and Ta₂O₅,⁵¹⁸ and HfO₂.⁵¹⁹

It was clear from early reports^{515,516} that gas rarefaction during reactive HiPiMS is important for establishing a more stable process by resulting in a lower time-averaged oxygen coverage on the target and, hence, a higher target sputtering rate. In a very recent (2017) review article,⁵²⁰ Koen Strijckmans et al. (Ghent University, Belgium) demonstrated, based upon their previously published reactive sputtering models^{436,437} (Sec. IV J 4), that while the overall R-HiPIMS sputter deposition process for aluminum in mixed Ar/O_2 discharges is highly complex with many variables being strongly interactive, the primary effect of gas rarefaction leading to decreased hysteresis is the enhanced density of metal ions during the metal-ion dominated part of each sputtering pulse.⁵²¹ As target sputtering becomes controlled by metal-ion (rather than gas-ion) bombardment, metal atoms are trapped via shallow implantation in the nearsurface region of the target. With continued sputtering, the target surface becomes increasingly metal rich with a correspondingly lower compound fraction, leading to reduced hysteresis and higher deposition rates.⁵²⁰

There are many other interdependent effects which also affect the dynamics of reactive-HiPIMS [as well as the "simpler" (but definitely not simple) case of reactive dc magnetron sputtering] and which, collectively, ensure that there will not be a single set of optimized deposition conditions for all systems. Two (of many) examples include: changes in the instantaneous oxygen coverage at the target change, in turn, the secondary-electron yield, and (if operating at, for example, constant target current) therefore alter the target voltage V_T which is approximately linearly related to the sputtering yield [Sec. IV H and Eq. (2)]; the choice of target material (and reactive gas) clearly affects the metal/reactive-gas bond energy, and hence the sputtering rate, from compound regions of the target. There are also more subtle effects: as the target erosion profile deepens with usage, the bottom of the racetrack intercepts more magnetic field lines and (again assuming constantcurrent operation) also results in a change in V_T.⁵²² In addition, target and deposition-chamber sizes, target-to-substrate separation, system configuration, and the pumping speed affect plasma density, magnetic-field distribution, and local reactivegas pressure for a given flow rate, thus altering reactivesputtering dynamics.

From the above brief discussion, it is not surprising that the "optimum" operating conditions reported for R-HiPIMS by different groups are quite dissimilar. The important point, however, is that most researchers agree that, compared to reactive dc magnetron sputtering, reactive sputtering in the HiPIMS mode generally leads to more stable operation under flowcontrol, with decreased hysteresis and higher deposition rates.

C. MPP magnetron sputtering

Another variant of HiPIMS, based upon a patent filed by Roman Chistyakov, (Zond Inc., Mansfield, MA) in 2002 and issued in 2006,⁵²³ is modulated-pulse-power (MPP) magnetron sputtering. In MPP, the pulse widths are much longer, ~500–3000 μ s, than in HiPIMS, but within each pulse, the on and off times can be independently varied from several to a few tens of microseconds to yield a higher duty cycle ($\leq 25\%$). Modulating the target voltage with a series of micropulses during each macropulse also provides more flexibility in tuning the peak current.^{524,525} The concept of MPP is to provide additional control over the process, maintain the high metal ionization probability, and obtain higher deposition rates than with HiPIMS.^{524–526} While the early results are intriguing, more data are required for a fair comparison of MPP and HiPIMS.

D. Conclusions

It seems perfectly safe to predict that sputter-deposition of thin films will remain a vibrant and active field of human endeavor incorporating fundamental scientific research, process development, deposition-system design, and newproduct manufacturing for periods far into the future.

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05C204-55 J. E. Greene: Tracing the recorded history of thin-film sputter deposition

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05C204-58 J. E. Greene: Tracing the recorded history of thin-film sputter deposition

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