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Review

Overview of thin film deposition techniques

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Abstract: Surface properties of the material can affect the efficiency and behavior of the material when in service. Modifying and tuning these surface properties to meet the specific demand for better performance is feasible and has been vastly employed in a different aspect of life. This can be achieved by coating the surface via deposition of the thin film. This study provides a review of the existing literature of different deposition techniques used for surface modification and coating. The two major areas of interest discussed are physical and chemical vapor deposition techniques, and the area of applications of surface coating was briefly highlighted in this report.

Keywords: chemical vapor deposition; physical vapor deposition; surface coating; thin film

1. Introduction

The selection process for the majority of the materials may be founded on the texture, aesthetic and color, but functional engineered materials cannot only depend on the physical appearance and bulk properties but also on the surface characteristics composition especially in the area of applications where surface contact behaviour is of paramount priority. In addition, a thorough scrutiny of the external factors should also be considered when making use of these components. Functional engineered components must be able to satisfactorily perform desired purposes efficiently and successfully, under numerous situations in hostile environments without deteriorating or yielding into disastrous calamity when in service [1]. The performance of the material is greatly reliant on the properties of the material surface. Alteration of the surfaces can be manifested using different techniques of surface engineering of materials. The surfaces of metallic materials are made up of a matrix of individual discrete grains with variation in sizes and bond strength. Surface engineered materials have augmented and improved performance, added functionality, reduced cost, improved material usage efficiency and provided performance which would not be possible with bulk materials [2].

Surface engineering is a division of science that focuses on techniques for attaining desired surface finishing and near-surface region properties for engineering components to make them suitable in a desirable way for various applications in service [1,3,4]. Surface engineering techniques are now being applied effectively in vast areas of engineering industries. The industries include but are not limited to industries that deal with improvising wear resistant and corrosion behavior like aerospace, biomedical, power, military, machine tools, etc. Surface engineering has also found application in design companies for coating surfaces. They are also being used to modify surface properties like magnetic, chemical, electrical, electronic, physical and mechanical properties of advanced functional materials to meet services which are difficult to achieve with the bulk material only. With the versatile nature of the process, virtually all natures of materials (metals, ceramics, polymers, and composites) can be deposited onto similar or dissimilar materials depending on the desired properties and can be modified to meet specific demands. It is also probable for advanced materials to be coated with a film (e.g., met glass, polymers, superlattices, photocatalysts), graded deposits, metamaterials and multicomponent deposits [2,5–7].

Surface engineering encompasses an overlay process, surface modification techniques, and surface coating techniques. In an overlay process sometimes referred to as hard facing, a protective material with superior physical and chemical properties is deposited on the surface of the substrate and the underlying material (substrate) is covered and not noticeable on the surface resulting into a thick and solid film [8]. This process involves applying one or more metals with specific characters to a base metal to improve desirable properties or to restore the original dimension of the component. Unlike general welding, in which two pieces of material are joined together, weld overlay applies a corrosive-resistant or hard-facing layer onto the parent material to increase its lifespan. Laser cladding, laser additive manufacturing, and weld overlays are methods used for overlaying process [9–11]. The surface modification technique alters the chemistry of the properties of the surface while maintaining the bulk properties of the substrate materials. Examples are heat treatment, implantation, carburizing, nitriding, etc. [8,12,13]. The surface coating technique requires the deposition of thin film layers on the surface, thereby altering the properties of the surface. Examples of surface coating techniques are vapor phase processes deposition (physical and chemical vapor deposition), solution state processes and fusion process. This process can be achieved via the deposition of a thin film process, plasma enhancement, ion bombardment, self-assembly, nanomachining, chemical treatment to mention a few [14–19]. The term thin film is usually applied to surface deposition layers which are 2-dimensional and have the thickness range below 1 micron (10^{-6} meters) and thicker layers above the range of 1 micron are referred to as coating or sometimes called thick film. The resulting thin film can range from single crystal to amorphous, fully dense to less than fully dense, pure to impure and thin to thick. Thin films offer enormous potential due to the following [5,20,21]:

- Conservation of scarce materials,
- Production of nanostructured coatings and nanocomposites,
- Ecological considerations—a reduction of effluent output and power consumption,
- Improved functionality of existing products,
- Solution to previously unsolved engineering problems and,
- Creation of entirely new and revolutionary products.

The area of review interest is on the thin film deposition; therefore, this review has been carefully selected to focus more on the surface coating techniques used for deposition and grow of the thin film below the thickness of ten micrometers.

2. Deposition techniques

Thin films have distinct advantages over bulk materials because most of the deposition techniques used for formation of thin films are non-equilibrium in nature, thereby, the formation of the thin film is not inhibited by the metallurgical phase diagram [6,22–24]. A deposition technique is considered as the integral key for the creation of thin film new materials to meet the ever-increasing demand from industries for versatile and multi-dynamics materials. The deposition techniques determine virtually all the properties of the thin film and can also be used to modify the existing properties. Proper consideration needs to be given to the deposition techniques depending on the area of application because not all the deposition techniques result into the identical properties such as microstructure, surface morphology, tribological, electrical, biocompatibility, optical, corrosion and hardness [7,25]. A single material can be used for different application and tailored to the properties to meet the optimum requirements by using different deposition techniques. Combination of different techniques can also be used to form a hybrid deposition process with each contributing to the outcome of the thin film. Most deposition techniques follow these three major sequences:

1. Synthesis of the deposition species,
2. Conveyance from source to substrate,
3. Deposition and adhesion of the source onto the substrate and subsequent film growth.

There are several types of deposition techniques, but since the focal point of this review is on thin films deposition for forming layers below one micron, priority will be given to the two major deposition techniques used for thin films. The prominent subsets of deposition techniques are physical vapour deposition (PVD) and chemical vapour deposition (CVD). The distinguishing feature between PVD and CVD is in the vapour. In PVD, the vapour is made up of atoms and molecules that simply condense on the substrate, and for CVD, the vapour undergoes a chemical reaction on the substrate which resulted into a thin film [26–30]. Figure 1 depicts the types of thin film deposition which are purely in the gaseous state, solution state, and molten or semi-molten state.

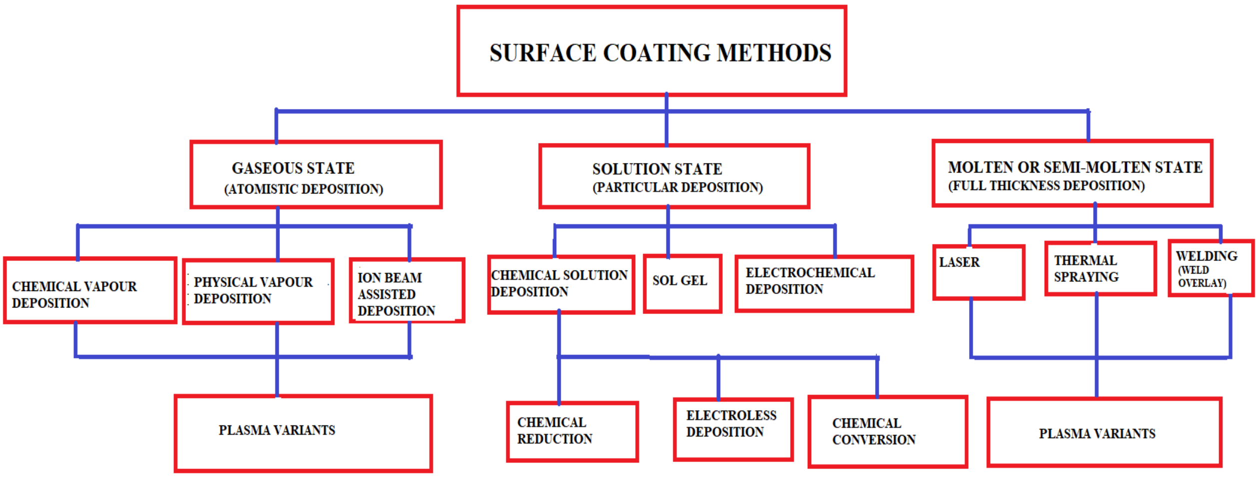


Figure 1. Variants of thin film deposition techniques.

3. Physical vapour deposition (PVD) process

Physical vapour deposition (PVD) is a generic term used to quantify thin film deposition processes that require condensation of the vaporized solid material on top of the surface of the solid material under a partial vacuum condition [31,32]. PVD is an atomistic deposition process in which there is a physical discharge of atoms or molecules and condensation and nucleation of these atoms onto a substrate through a vacuum or low pressure gaseous or plasma environment. Plasma or ions are usually the constituents of the vapour phase. Sometimes, the reactive gas can be introduced to the vapour during the deposition process and this is called reactive deposition. The atoms or molecules are conveyed in the form of a vapour via a vacuum or low pressure gaseous or plasma environment to the surface of the substrate for condensation to take place. Commonly, PVD processes are used to deposit thin films with thickness in the range of a few nanometres to a thousandth of nanometres. They can also be applied for multilayer deposition coating, graded composition deposits, very thick deposits, free-standing structure and in hybrid form with other deposition techniques [7,33].

Every PVD process can be attributed to three basic step which they all obeyed [1,7,21,34].

- Creation of vapor-phase species. This requires conversion of materials to be deposited from a solid state to a vapour phase by evaporation, sputtering or ion bombardment.
- Movement or transportation from source to the substrate. The ejected atoms or molecules from the target will be transported through molecular flow conditions and thermal scattering processes. Also, if the partial pressure of the metal vapour or gas species in the vapour state is high enough for some of these species to be ionized, there will be a large number of collisions in the vapour phase during movement to the substrate.
- Film growth on the surface. The transported atom or molecule will start to nucleate around the substrate and grow by a number of processes. The incipient growth of the film determines the types of interface formation between the substrate and the atom or molecule. The composition and microstructure of the thin film can be altered by bombardment of the growing film by ions from the vapour phase, resulting in sputtering, re-condensation, and nucleation of the film atoms and enhanced surface movement of the atoms around the surface of the film.

The major variants of PVD are listed in Figure 2 below, but the three basic processes of PVD are vacuum or thermal evaporation, ion plating and sputtering.

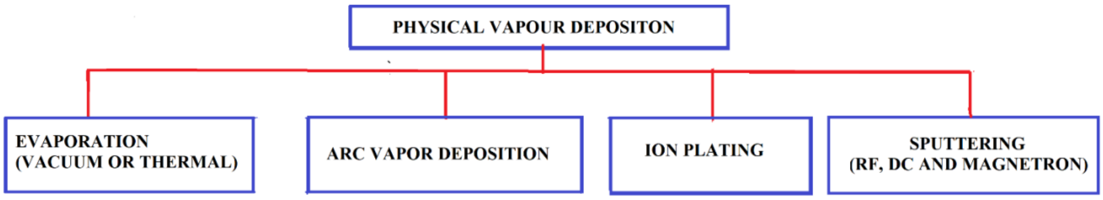


Figure 2. Variants of Physical Vapour Deposition.

During the evaporation process, thermal effect causes ejection of atoms from the source, whereas, for ion plating process, the growing film is exposed to concurrent ion bombardment. During sputtering, the atoms are ejected from the surface of the solid target by the impact of gaseous ions and then deposited on the surface of the substrate [35,36].

3.1. Thermal (or vacuum) evaporation

Thermal (or vacuum) evaporation is an old deposition process used for the formation and growth of the thin film on the surface of solid materials. The process is still beneficial in a contemporary environment and extensively applicable in the laboratory and industries for deposition of the thin film. The basic sequential steps for thermal or vacuum evaporation are given below:

- The vapour is created from subjecting the target material to very high temperature by subliming or boiling,
- The ejected vapour from the target material is transported to the substrate through a vacuum,
- Condensation of the vapour takes place to form a solid thin film on the surface of the substrate, and further repeatability of the deposition cycles result in thin film growth and nucleation.

During the thermal evaporation process, the target material vaporized from the thermal process sources gets to the substrate material with minimal interference. The process is often carried out at a high vacuum pressure (HV), and the trajectory of the movement of the target material to the substrate is a straight path trajectory termed line of sight [13]. Vapour flux is created by heating the surface of source material to a sufficiently elevated temperature in a vacuum. The flux can then condense to the surface of the substrate material to form a thin film. The vacuum environment creates a safe zone to reduce gaseous contaminants in the deposition process to an acceptable and minimal level and allows the evaporated atoms to undergo essentially collisionless transport from the source onto the substrate. The gas pressure range is usually between 0.0013 Pa to 1.3×10^{-9} Pa depending on the degree of the contamination in the deposition system, with the mean free path (MFP, the average distance between collisions occurring between species) no smaller than 5 mm. The thermal vaporization rate might be very high compared to other PVD processes [13,27]. Tungsten wire coils are commonly used as the source of the thermal heat or by using high energy electron beam for heating the target material to an elevated temperature.

Evaporation process has been reported to be performed using different configurations. These are Molecular beam epitaxy, reactive evaporation and activate reactive evaporation. Molecular beam epitaxy (MBE) was discovered by J.R Arthur and Alfred Y. Cho at Bell telephone laboratories around 1960. MBE is used for growing epitaxy through the active interaction of distinct or numerous atomic or molecular beams on the surface of a heated crystalline substrate material. The evaporation occurs at an ultra-high vacuum for deposition of the controlled composition of uniform thickness of the thin film from specific deposition rate. This process has been applied in the manufacturing of semiconductor devices like cellular phone, transistor conductors and Wi-Fi [37–40]. Reactive Evaporation involves the evaporation of atoms of metal from a target material in a chamber with the presence of reactive gas at a partial pressure. During the evaporation process, the atoms react with the gas chemically to form a compound thin film on the surface of the substrate. Reactive evaporation can form stoichiometric oxides, alloys [41,42]. Another variant of evaporation technique is Activated Reactive Evaporation (ARE). ARE takes place by evaporation of atom from the surface of the target material in the presence of plasma and react this with the reactive gas within the chamber to form compounds with faster deposition rate and improved adhesion property. The plasma improves the rate of reaction between the target and the substrate, ionization of both coatings of metals and gas atom in the vapour phase and higher conversion of the neutral atoms into ions or energetic neutrals thus enhancing reaction probabilities and rates to deposit refractory compounds. If ARE process substrate is held at a negative bias voltage, it becomes biased activated reactive evaporation [43–45].

3.2. Sputtering

Sputtering is a vital and prominent procedure among the PVD processes. It’s a non-thermal vaporization process whereby individual atom escapes from the target surface due to atomic collision cascades by suitable high energy ion bombardment. Unlike evaporation, the source is no longer created by thermal but by ion impact on the target. Also, the target to substrate distance is shorter and, in many cases, it has outperformed other PVD processes with more functionality and performance like improved adhesion and thicker film. During the sputtering process, atoms are removed from the surface of the target material by transfer of sustainable momentum from an atomic-sized energetic bombarding particle usually gaseous ion accelerated from a plasma. Sputtering deposition can be achieved in a vacuum at low pressure plasma of <0.67 Pa where the sputtered particles is in line of sight and can also be done at higher plasma pressure of 0.67 to 4 Pa, where energetic particles sputtered or reflected from the sputtering target are thermalized by gas phase collision before they reach the substrate surface. Sputtering is also being used as an etchant for cleaning the surface of solid materials and for pattern delineation because of its potential to eject atoms from an electrode surface [27,46,47].

The sputtering deposition has become a generic name for a variety of sputtering processes. These processes are named based on their source and the orientation of the process. Variants of sputtering are diode sputtering (cathode or radio frequency), reactive sputtering, bias sputtering, magnetron sputtering and ion-beam sputtering [25,48].

Sputtering deposition technique employs various sources for power, and the working pressure varies depending on the power configuration. DC sputtering is made up of a pair of planar electrodes (referred to as the cold cathode and anode). The target material to be deposited is placed on the cathode, and the substrate is positioned at the anode. The working gas inside the deposition chamber is usually argon gas due to the larger mass compared to neon and helium because higher mass correlates to more energetic collision with the target material and lower cost when compared to xenon and krypton. DC voltage is supplied between the cathode (target material) and anode (substrate) to sustain the glow discharge. The gaseous ions resulted from the sustained glow discharges are accelerated towards the target material, and sputtering takes place resulting in deposition of a thin film on the surface of the substrate material. In the DC sputtering system, the target is composed of conducting material usually metal since the glow discharge (current flow) is maintained between the metallic electrodes [49–51].

Radio Frequency (RF) Sputtering is another variant of sputtering which involves alternating the electrical potential of the current in the vacuum environment at radio frequencies to avoid charge building up on certain types of sputtering target materials. In RF sputtering, the cathode (the target) which is to become the thin film coating and an anode is connected in series with a blocking capacitor in between. The capacitor is part of an impedance-matching network that provides the power transfer from the RF source to the plasma discharge. The cathode is bombarded by high voltage in a vacuum chamber leading to high energy ions sputtering off atoms as a thin film covering the substrate to be coated at a fixed frequency of 13.56 MHz. The essence of the capacitor is to develop DC self-bias and increase the optimization of power transfer for the target material to the plasma generated. RF sputtering offers numerous advantages like possibility of deposition on insulating materials, ability to sustain plasma at low pressure of 0.13 to 2 Pa, diffusion of RF plasma throughout the entire chamber, reduction of the creation of race track erosion on the surface of the target and ability to clean up the target materials after each cycle from building up charge to reduce arcing effect [52–54].

During sputtering process, secondary electrons are usually emitted from the target surface as a result of ion bombardment and magnetron sputtering makes use of the magnetic field to restrict the movement of the secondary electron to the vicinity of the target material. The configuration and strength of the magnetic field array determine the rate of the ionization efficiency current delivers to the target material resulting in higher deposition rate at the substrate. The increased ionization efficiency noticed during magnetron sputtering allows running of the sputtering process at a lower pressure of 100 Pa and lower voltage of −500 V compare to 10 Pa and −2 kV to 3 kV for the conventional sputtering process. The two major configurations for magnetron sputtering are conventional (balanced) and unbalanced magnetron sputtering. In balanced configuration, the plasma is confined to the target region while for unbalanced configuration, not all the magnetic field lines are closed but some are directed towards the substrate while some follow the closed field path. Further reading on this can be found in [55]. Conductive materials can be deposited using a direct current (DC) power supply and insulators can be deposited by using a radio frequency (RF) power supply. Magnetic arrays in magnetron sputtering configuration can be varied in situ without tempering with the electromagnet [31,56–60].

Reactive Sputter Deposition is used for creating the compound thin film. During sputtering, a reactive gas such as nitrogen or oxygen is introduced to the deposition chamber and gas react with the target material to form a compound thin film on the surface of the substrate. This process is referred to as reactive sputtering. An increase in reactive gas causes the topmost layer of the target material to transform from single phase to compound phase, which often results in changes in the properties such as the conductivity, e.g., conductive surfaces become non-conductive, and vice versa. The inert gas usually used for this process is Argon and its possible to combine the inert gas with ionized non-inert gas (reactive gas) or introduced the ionized non-inert gas (reactive gas) alone in the chamber. The percentage of reactive gas added to the chamber is controllable to produce a specific stoichiometric ratio of the compound. Argon is in most cases the main gas and the amount of a reactive gas introduced into a process chamber is controlled to either achieve a certain amount of doping or produce a fully reacted compound. The resulting deposited thin film is different from the target [61,62].

Of recent, another variant of magnetron sputtering was invented called Pulsed Magnetron Sputtering PMS regarded as an emerging technology. The technique provides a solution to the challenging problems with other magnetron techniques like low deposition rate experience with RF magnetron sputtering and target poisoning and arc event associated with reactive magnetron sputtering. PMS concept is based on short or intermittent pulsing the medium frequency range between 10–200 kHz of the magnetron discharge for tens of microseconds at a low duty circle. The two modes for operating PMS are unipolar PMs where the voltage of the target material is pulsed between the ground and standard operating voltage and bipolar pulsed sputtering where the voltage of the target material is being reversed and turns to positive during the pulse-off duration. The pulsing process leads to the creation of super-dense plasma with exquisite properties which result in the creation of more uniform thin film and the possibility of achieving a smooth surface coating with complex and irregular shaped substrate materials [63–66]. Due to the limitation of the sputtering process, a new method of sputtering deposition is now being used called duplex sputtering where two or more deposition techniques are used to produce a functionally graded material with broad areas of application and improved properties [55].

3.3. Ion plating

Mattox [27] was the first to report Ion plating technique in 1960. It uses continuous or intermittent bombardment in an inert gas discharge system for the deposition of a film by atomic sized energetic particles to amend and regulate the properties of the depositing film. The plasma is created in a hollow cathode discharge source. The substrate material is subjected to bombardment by a high energy flux ions adequate to cause substantial sputtering on the surface of the substrate before and during thin film growth [67–69]. The deposition material may be vaporized by other physical vapor deposition techniques like evaporation, sputtering, arc erosion or by decomposition of a chemical vapour precursor but the evaporated atoms pass through the gaseous glow discharge on their way to the substrate which causes some of the vaporized atoms to be ionized [70,71]. The ions bombardment during film growth helps to create denser films with the densities closer to that of the bulk material and thus make it suitable for depositing a hard-thin film on compound materials. The gas pressure for ion plating process is between the ranges of 1 to 0.1 Pa. This pressure is enough to sustain glow discharge as well as scatter the vapour particles in all direction through numerous collisions to improve the overall coating of the substrate during film growth. A reactive gas can be added to form a compound surface coating, and the process is known as reactive ion plating.

3.4. Arc vapour deposition

Arc vapour deposition is a deposition process that uses electric arc at high current and low voltage to vaporize a cathodic electrode (cathodic arc) or anodic electrode (anodic arc) and deposit the vaporized material on a substrate. The substrate is usually biased so as to fast-track the film ions to the surface and also, the vaporized material are highly ionized. Flux is generated by creating an arc that travels across the surface of the target [25]. The arc strikes lead to ejection of atoms from the target materials and condense on the substrate as a thin film coating. A substantial proportion of the metal atoms become ionized and makes it distinguished from vacuum or thermal evaporation. This substantial proportion of ionized atom makes it reliable for the formation of a thick coating and can be used for hard decorative surface-coating operations.

4. Chemical vapour deposition (CVD) process

CVD is a generic term for deposition of the thin film via series chemical reaction. The process of material synthesis occurs when the constituent of the target in the vapour phase reacts via a chemical process near the surface or onto the surface of the substrate, leading to the growth of the thin film. Note that the mechanisms behind CVD differ drastically from the PVD process. In PVD, thin film formation is caused by condensation of atoms or molecules on the surface of the substrate due to evaporation, ion bombardment, or sputtering [18,72–74]. On the other hand, CVD is a thermodynamically complex process involving chemical reactions under specific conditions such as temperature, pressure, reaction rates, and momentum, mass, and energy transport. Several process factors and chemical reaction between the reactant and substrate are responsible for the quality of films produced during CVD and the quality of the film can be controlled and modified by using the appropriate combination of process parameter like flow rates, pressure, temperature, concentration of chemical species, reactor geometry, etc. [75,76]. The main characteristics unique features of chemical vapour deposition are its resourcefulness for producing both simple and complex compounds with relative ease at generally low temperature, excellent throwing power and production of a coating of uniform thickness. CVD coating growth rate is high with ease of growth epitaxial film and offers good reproducibly of coating with same or almost similar mechanical, optical, chemical and physical properties. In addition, CVD has the ability to deposit materials which are problematic to evaporate with low porosity property on a substrate of complicated shapes which are difficult to produce by other deposition techniques [18,48]. During CVD, the chemical composition of the reaction and physical structure can be tailored by monitoring and regulating the chemical reaction and deposition process parameters such as temperature, input concentration, pressure, gas flow rates, and reactor geometry [25,48]. CVD essential principles comprise of an interdisciplinary range of gas phase reaction chemistry, thermodynamics, kinetic and transport mechanisms, film nucleation phenomena, and reactor engineering. It should be noted that not all types of chemical reactions are desired in all kinds of CVD processes. There are various types of chemical reaction possible during CVD. The CVD reaction types possible are pyrolysis, reduction, oxidation, compound formation, disproportionation, and reversible transfer. The chemical reaction taking place depends on the reactant (precursor) gas and the by-products. In addition, the reaction has to be thermodynamically predicted, i.e., there is a need for availability of adequate energy for the reaction to take place and the Gibbs free energy (total available energy) has to decrease in order to allow the temperature and pressure of the reaction to be altered [5,14,18,77]. This process involves the reaction of one or more volatile precursor transported via the vapour phase to produce a non-volatile solid that deposits atomistically on a suitably placed substrate within the confinement of a reaction chamber [13,78]. The fundamental sequential steps that occur in every CVD process are stated below [79]:

- Convection or diffusion movement of reactant in a gas phase to the reaction chamber,
- Chemical and gas phase reactions leading to the formation of reactive species and by-products,
- Transport of the reactants through the boundary layer to the substrate surface,
- Chemical and physical adsorption of the reactants on the substrate surface,
- Heterogenous surface reactions leading to the formation of a solid film,
- Desorption of the volatile by-product to the main gas stream by diffusion through the boundary layer,
- Removal of gaseous by-products out of the reactor via convection and diffusion process.

CVD process usually characterized by volatile reaction of by-products and unused precursor species. Many CVD reactions by-products are very hazardous volatile by-products such as H_2, Cl_2, HCl, HF or water vapour. Proper safety precaution is needed when using CVD. Venting, scrubbing of by-products and unreacted compounds are essential in CVD processes. CVD can be grouped based on energy used to drive the chemical reaction. Sources of energy can either be a photon, laser or temperature (thermal). Figure 3 illustrates the variants of the CVD process.

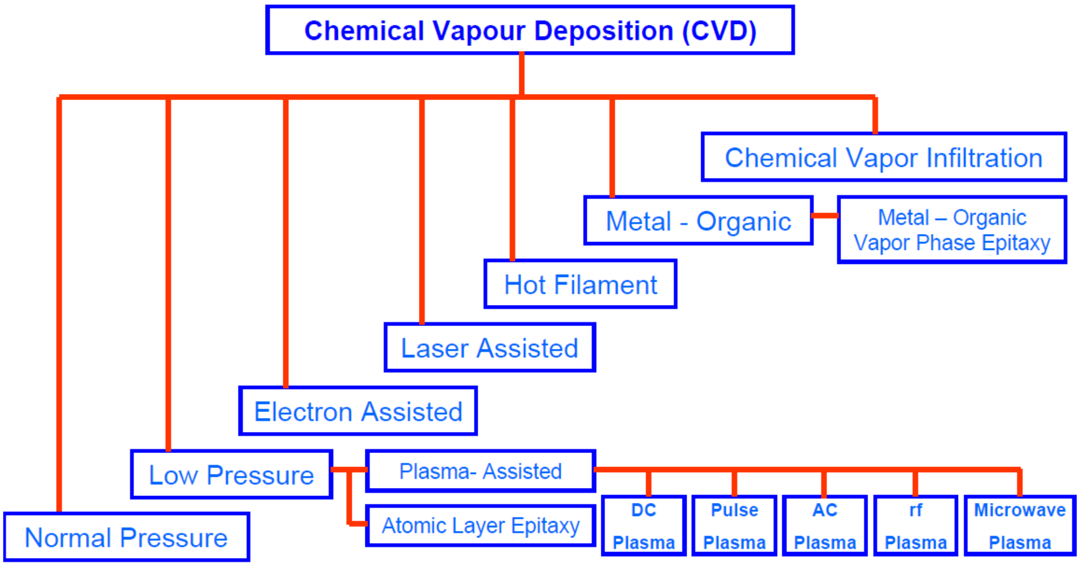


Figure 3. Variants of Chemical Vapour Deposition.

CVD encompasses a wide range of reactor and process types. The application determines the choice of process/reactor based on the requirements for substrate material and coating materials, surface morphology, film thickness and uniformity, availability of precursors, and cost.

4.1. Thermal CVD

Thermal CVD is a CVD process for depositing a thin film on various materials. This process uses heating lamps or other methods to heat the substrate rapidly and activate the energy needed for the reaction to take place. The growing film surface is exposed to thermal energy from either the condensing atoms or substrate heater to create the thin film. This thermal surface energy is responsible for mobilizing the atoms which lead to the creation of thin film with uniform thickness and good surface coverage and finishing. Since the thermal surface energy is dependent on the working temperature, an increase in temperature also resulted in a better thin film distribution on the surface of the substrate. The surface chemistry and surface atom mobility are aided by the substrate temperature alone [80,81].

4.2. Laser CVD (LCVD)

LCVD is also a variant of CVD process. It involves exposing a focused laser beam to locally heat the substrate of one or more volatile precursors which react on the surface to produce thin film deposition. The laser which occurs because thermal energy produces a coherent, monochromatic high-energy beam of photons can be used effectively to drive CVD reactor for deposition of the thin film [82–84].

4.3. Photon CVD

Photon CVD is another type of CVD. The chemical reaction is driven by the photon usually ultraviolet (UV) radiation which has the necessary energy to break the chemical bonds among the reactant molecules for deposition of the thin film [85,86].

4.4. Plasma-enhanced CVD (PECVD)

PECVD is a variant of CVD that is used to deposit a thin film from gaseous state to a solid state on the substrate. The chemical reaction takes place after the creation of a plasma in the reactor chamber and subsequently leads to deposition of a thin film on the surface of the substrate. PECVD uses an electrical source of energy to generate plasma and sustain the reaction process rather than thermal energy for the majority of the CVD processes. The electrical energy is used to initiate homogeneous reactions for the creation of chemically active ions and radicals that can partake in heterogeneous reactions, which, in turn, lead to layer formation on the substrate. The main benefit of PECVD over thermal CVD processes is the possibility of deposition to take place at a very low temperature close to the ambient temperature and permits materials sensitive to temperature change to be worked on [87–89]. The use of plasma to activate the gas phase chemistry opens up several new reaction paths for deposition at a significantly lower temperature [90].

4.5. Pulsed CVD

Pulsed CVD also was known as atomic layer deposition (ALD) or atomic layer epitaxy (ALE). Its origins can be traced back to two different places. ALD was first developed as a promising coating technology on inorganic materials by Aleskovskii during the 1960s in Russia and was referred to as molecular layering [91]. It became a major innovation when Suntola in the 1970s developed the atomic layer epitaxy technique to deposit ZnS for electroluminescent displays [92]. ALD is based on self-limiting reactions between two gaseous precursors and allows the deposition of thin films in a layer-by-layer fashion. The ability to deposit conformal films on high aspect ratio structures, with high uniformity over large areas, at (relatively) low temperatures and moderate pressure, as well as exquisite thickness control are well beyond the reach of other thin film technologies such as physical vapor deposition and chemical vapor deposition and has made ALD a technique of choice for the preparation of ultrathin films [91,93]. It uses only surface chemical reactions to build up ultrathin films with the ability to achieve a very precise control of thin film thickness down to atomic level [94,95]. ALD allows a wide range of deposition and also viewed as an alternative method for exploring more surface growth mechanisms to form new hybrid nanostructures. It has been extensively used for the nanofabrication processes for microelectronic applications. ALD became commercially important in the early 2000s when the semiconductor industry started to adopt ALD for manufacturing high-performance complementary metal–oxide–semiconductor (CMOS) transistors. Both Intel and IBM have utilized ALD to fabricate high-k dielectric layers in CMOS since 2007. Recently, Intel stated that the use of ALD was a key factor for the successful development of the high-k metal gate transistors that allowed further downscaling of the size of integrated circuit chips [96]. Nowadays, ALD has already percolated into the multitudinous application domain such as magnetic recording heads, optics, demanding protective coatings, and micro-electromechanical systems. Some more detailed information on ALD application has been summarized by Octavio [91], Hong [93] and Bo Yan [97].

Other notable mention deposition techniques that use CVD reaction principle of operation are metal organic vapour phase epitaxy, metal organic CVD, pyrolysis, reduction, oxidation, compound formation, disproportionation, and reversible transfer. Some CVD processes can also be carried out in atmospheric pressure known as Atmospheric pressure CVD or APCVD. APCVD are commonly used to form SnO_2 on hot glass using $SnCl_4$ or monobutyltn trichloride and dopants to make the coating on the surface [34,98].

5. Thin film

The thin film can be labeled as thin materials layers ranging from a fraction of nanometers to one micron (10^{-6} meters) in thickness. The paramount distinction between thin film and thick coating depositions is the thickness of the layers deposited. Thin film deposition involves deposition of individual atoms or molecules on the surface while thick coating deals with deposition of particles. It is being used to modify the physical and chemical properties and surface morphology of materials without altering the properties of the bulk material. A thin film can be personalized as one homogeneous composition, single layer, crystalline phase composition and microstructure, or have an inhomogeneous multilayer or composite structure depending on the envisaged properties and area of applications. The structure of the multilayer can be periodic, have a set pattern or be entirely random. Almost all thin films deposition techniques have four or five basic chronological steps. The steps are unique to the overall properties of the thin film and are listed below [13,68]:

- The source of the pure material to be deposited is selected. This source of material will act as a target during the deposition process,
- The target is transported through a medium to the prepared substrate. This medium can either be a fluid or vacuum, depending on the materials and the deposition technique used,
- The target is deposited onto the substrate, forming a thin film on the substrate surface,
- The thin film may be subjected to an annealing or other heat treatment processes, depending on whether or not this is necessary to achieve the desired film properties,
- The film properties are analyzed. If necessary, the analysis results can be incorporated to modify the deposition process.

5.1. Thin film growth and nucleation

Most often, the properties of the thin film are affected by the underlying properties of the substrate and can vary drastically depending on the thickness of the film and the deposition techniques employed for deposition. There are three major steps required in thin film growth and nucleation. The first step involves the creation of the deposition species, i.e., the substrate and the target material, follow by the transportation from the target to the substrate using any deposition technique and the final stage involves the growth of the target on the substrate to form the thin film. The atoms from the target impinge on the substrate, where they can either reflect immediately from the substrate, evaporating back into the gas phase after a certain residence time, or condense on the substrate surface. This process is affected by numerous factors, including activation energy, the binding energy between the target and substrate, the adhesion coefficient, etc. The ration between the condensing atoms to the impinging atoms is called sticking coefficient. During this process, the atoms lose energy and might not immediately react with the substrate. They will have some mobility over the surface before condensation and these mobile atoms are referred to as adatom which is a portmanteau for absorbed atoms. The energy lost during condensation of the atom on the surface can either be by chemical reaction with the substrate atoms, the collision of the diffusing surface atoms, finding a preferential nucleation site or collision of the absorbed surface species. If the surface mobility is low and the atom to atom interaction is strong, each atom can serve as nucleation site for growth but when the adatom–surface interaction is feeble, the surface mobility of the condensing adatom will be high and results in condensation at preferential nucleation sites where there is stronger bonding either due to an increase in the coordination number or a change in elemental or electronic chemistry. The condensing atoms react and bond with the atoms on the surface to form atom to atom chemical bonds. The chemical bond formed may be of any of these following bonding types: electrostatic attraction (van der Waals forces) due to the polarization of atoms, metallic (homopolar) bonding where the atoms share orbital electron or electrostatic (coulombic heteropolar) where the ions are formed due to electron loss or gain. The atom is said to have undergone chemisorption if the resulting bonding from the reaction between the condensed atom and the surface atom is very strong. This adatom transformed to nuclei by a conglomeration of numerous adatoms and resulted in the continuous thin film. Due to the nature of the deposition, the resulting nuclei formed at the initial stage are often thermodynamically unstable and might desorb with time depending on the deposition parameters used. After a while, the clustered nuclei reach a critical safe size and become thermodynamically stable and the nucleation challenge is said to have been overcome. This process involving the transition from thermodynamically unstable condition to a thermodynamically stable condition where a stable, critical-sized nucleus formed is termed the nucleation stage [67–69]. As the deposition process continues, the stable critical nuclei grow in number as well as in size until a saturated nucleation density is attained. The nucleation density and the average nucleus quantity depends on number of deposition parameters such as the temperature of the substrate, working pressure, adhesion properties, binding energy between the target and the substrate, energy of the impinging species, the activation energies of adsorption, desorption, thermal diffusion, the rate of impingement, topography, and chemical nature of the substrate.

A nucleus can grow in two modes named parallel and perpendicular depending on the configuration of the substrate and target, and the two scenarios can be experienced in a single deposition. Parallel growth occurs on the substrate by surface diffusion of the adsorbed atoms while perpendicular growth is because of direct impingement of the incident species. However, the rate of parallel growth sometimes called lateral growth at this stage is much higher than the perpendicular growth and the grown nuclei are called islands. In the coalescence stage, small islands start coalescing with each other on the surface of the substrate to reduce the substrate surface area and replace it with a thin film coating. This resulted in the formation of a bigger island and the process is called agglomeration. Increasing the surface mobility of the adatoms enhance the agglomeration process and growth density of the nucleation site, i.e., by increasing the temperature at the surface of the substrate. In some reactions, the formation of new nuclei may also take on areas newly exposed because of coalescence. Bigger islands grow together, leaving channels and holes of the uncovered substrate between the islands and leading to discontinuous film formation on the surface of the substrate creating a porous defect on the surface. Further growth of the larger islands causes continuous agglomeration and filling of the created channels and holes [23,67,68,99,100].

Nucleation mechanism of thin film growth has been classified into three major types depending on the interaction between the deposited atoms of the target and the surface of the substrate developed by Lewis and Anderson in their studies of evaporated films [101–104]. These are:

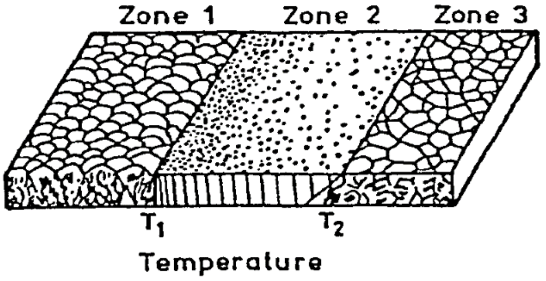
- Van der Merwe or island growth mechanism. This growth can be noticed when the adherence between the atom to atom is greater than the bonding between the substrate and the adatoms. Group of stable adatoms accumulate and coalesce on the surface and grow in three dimensions to form an island,
- Volmer Weber or layer mechanism. This occurs when the adhesion between the atom and the surface is greater. The film grows layer by layer on the surface of the substrate and can be used for dense coating,

- Stranski-Krastanov (S-K) mechanism. The SK mechanism combines both island and growth mechanisms. The adatoms begin to accumulate and form islands after an initial layer has grown.

5.2. Structure zone model (SZM) of thin film

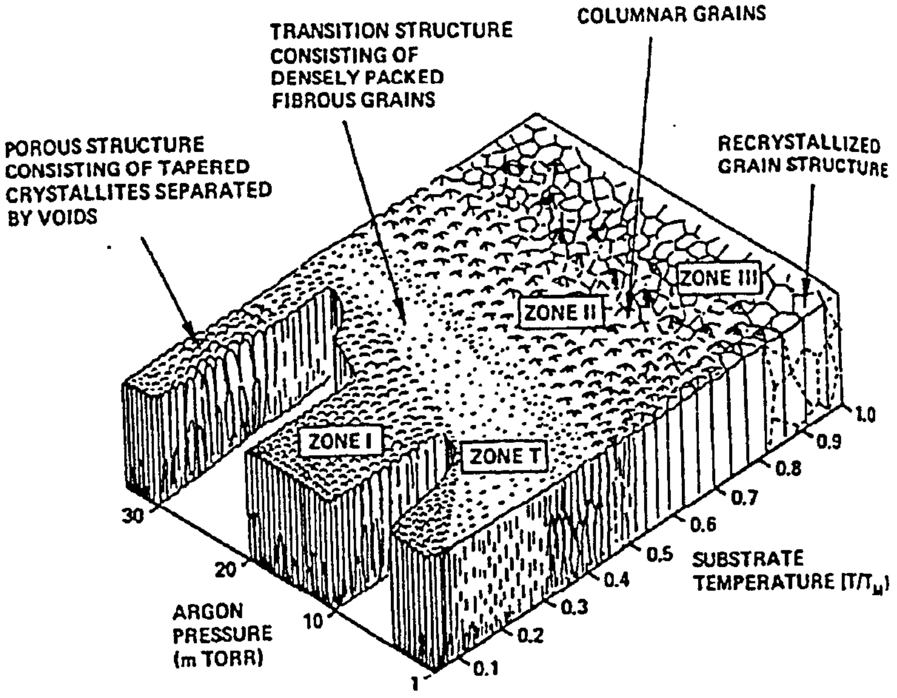
After film growth and nucleation, the surface morphology and microstructure can be described using structure zone model (SZM). The SZM of the film is related to the mobility of the adatom during growth. Chemical reaction, ionic bombarding, and thermal effect are the sources of atomic energy during film growth. The primary parameter determinants for SZM models are the temperature of the substrate, working pressure of the deposition technique, power supply to the target, the bias voltage applied to the substrate, gas flow and the thermal characteristic of the target. The first SZM was proposed by Movchan and Demchishin in 1969 [105]. Movchan and Demchishin SZ model only consist of three distinct zones named Zone 1, Zone 2 and Zone 3 shown in Figure 3. These zones were established based on the relationship existing between the film structure and the ratio of the temperature of the substrate T to the melting point of the target material T_m. Three distinct zones were noticed as the ration T/T_m known as homologous temperature increases. Zone 1 takes place when the ratio is below 0.3, at which the adatom energies are not high enough to overcome the shadowing effects from substrate irregularities, causing insufficient surface diffusion. The dominant growth mode is the island mechanism. The grains formed in zone 1 are small and elongated with the columnar structure of porous morphology and weakly bonded together. The low rate of diffusion, low mobility of the adatom by the substrate surface and atomic shadow effect which are produced by varying the velocity in the growth columns and the angle of the incident at which the atoms from the target reach the surface of the substrate are responsible for the columnar structure in this zone. In zone 2, the ratio of the T/T_m ranges from 0.3 to 0.5. The surface appears to be more uniform with a smooth and immaculate appearance as the substrate temperature increases homogenously. Diffusion of the adatoms dominates in zone 2 and denser columnar crystalline structure is formed with a higher degree of binding among the columns and the boarders between the columns, with the boarder grain beginning to grow. The size of the grains can be increased in zone 2, and the grains can be extended in equiaxed form from the substrate interface to film structure [100]. Zone 3 represents the region above the ratio of 0.5 for T/T_m. Volumetric diffusion processes like annealing and recrystallization have a great influence on the morphology of film growth at this region. Due to bulk diffusion occurrence at this zone into the grains, it leads to the formation of equiaxed grain and re-crystallization and produces growth of the grain. Zone 3 determines the final structure of the film and produces a greater crystalline structure.

This model was later modified and extended by Thornton to four distinct zones in 1977 [106,107]. Thornton added an additional zone to the above-listed zones that account for the effect of gas pressure during deposition shown in Figure 4. Thornton observed that the final working gas pressure can adversely change the orient the action of the microstructure by affecting the kinetic energy of the ions that arrive at the substrate and the mean free path of the particles. This subsequently results in either increase or decrease of the ion bombardment on the surface of the substrate and determines the rate of mobility of the adsorbed atoms on the surface of the substrate. A transition zone (Zone T) was introduced between zone 1 and zone 2. Zone T is formed by grains defined by limits of the low porosity. This zone is characterized by a structure with dense poorly defined fibrous grains [51,100,108,109].



	Zone 1	Zone 2	Zone 3
Metals	$<0\cdot3\ T_m$	$0\cdot3-0\cdot45\ T_m$	$>0\cdot45\ T_m$
Oxides	$<0\cdot26\ T_m$	$0\cdot26-0\cdot45\ T_m$	$>0\cdot45\ T_m$

(A)



(B)

Figure 4. (A) Movchan and Demchishin Structure Zone Model SZM, (B) Thornton Structure Zone Model SZM [26].

6. Simulation techniques used for thin film

Computer simulation is the discipline of designing a model of an actual or theoretical physical system, executing the model on a digital computer, and analyzing the execution output. In engineering, computer simulations are widely used in the realm of thermal transport, fluid flow, and stress analysis. Computer simulation acts as a bridge between the microscopic length and time scales (theory) and the macroscopic world of the laboratory (experiment). Simulations are often used to understand the properties of assemblies of molecules regarding their structural behavior and the microscopic interactions between them. This serves as a complement to conventional experiments, enabling us to learn about processes and behaviors that are difficult to analyze with experimental techniques. It enables us to solve complex theoretical models beyond certain approximations, provide a hint to experimentalists for further investigations and optimize process development time [110]. The typical simulation techniques used for studying the evolution of thin film are continuum method, density functional theory (DFT) model, Molecular Dynamics (MD) method and Monte Carlo (MC) method [76,111–115]. However, Molecular Dynamics (MD) and the Monte Carlo (MC) method are the two distinctive modeling techniques at the atomistic scale. MD simulations are often used to estimate time-dependent (transport) properties at the atomistic level, for example, thermal conductivity, viscosity, and diffusivity coefficients while MC method is applied to estimate equilibrium properties, for example, potential energy calculations, absorption studies, phase equilibria studies. Although these simulations help improve the understanding of thin film deposition concepts, they also come with key limitations such as expensive computational costs, high operating times, challenges in analyzing the microscopic physics accurately and challenges in analyzing the bond formation and breakage events on the atomic scale [116–119]. These limitations were resolved with the development of hybrid and multiscale methods. These methods combine the features of different simulation techniques for optimization and control schemes. This helps to improve the quality of the thin films, reduces the deposition cost and efficiently simulates the surface growth of thin film deposition processes [120–122]. Multiscale processes take into consideration both linear and nonlinear relationships between the process parameters and optimize them to produce accurate feedback [123]. Even with the development and advances in the multiscale modeling, the process still faces impending challenges and limitation. The simulation of a multiscale model is not trivial due to the numerical complexities that arise when coupling modeling methods with different characteristics. Also, the computational demands required to simulate phenomena at the fine length and time scales imposes additional limitations. Therefore, most of the current applications in multiscale modeling only couples phenomena that occur at two different length and time scales, that is, it only couples two different modeling methods. To circumvent this limitation, Kinetic Monte Carlo (KMC) model can be used in synergy with multiscale modeling to form hybrid model and curb the challenges. Kinetic Monte Carlo (KMC) method is often suitable to explain phenomena at different length and time scales. Due to its versatility, this stochastic method has been the preferred choice to model the events that are taking place at the atomistic, molecular or nanoscopic level. Thus, a multiscale modeling formulation often couples a KMC model with a continuum model, which predicts the behavior of the physical system at the microscopic/macroscopic level [124]. Consequently, simulation process improvement studies for thin film growth are most readily performed using multiscale modeling techniques that capture the relevant molecular and bulk phenomena on the scales in which they occur [125,126]. In recent years, improvements in our understanding of the physics and chemistry of films, surfaces, and interfaces have aided the fabrication and development of deposition techniques. However, this has also provided a platform for developing predictive models for thin-film growth which give the ability to control the film structure and properties [127–129]. The multiscale simulation also gives the ability to predict the effect of uncertainty which allows for robust control of small-scale systems [130,131]. Model predictive control (MPC) provides an effective framework employing the system model to predict the control actions which optimize a performance index in the presence of constraints resulting in improving deposition process while minimizing cost and time [132–134]. Model predictive control is also capable of accurately predicting the output feedback like statistical moments of surface roughness, growth rate, etching rate, surface morphology, dynamic behavior, film porosity and film thickness [132,133,135–139].

7. Application of thin film

Over time, the applications of thin films have grown exponentially and have become an integral part of both industrial and research processes. Deposition of the thin film can make a material to be versatile and be used for different applications, by improving the surface properties like wear, fatigue, corrosion, hardness, and other surface related phenomena. Applications of thin films may be grouped under the following generic areas:

- **Electronic component and display.** The production of electronic components such as semiconductors, single and multilayer metal conductor film and microelectronic integrated circuits have undoubtedly found enormous and vast applications for thin films deposition. Compound conductor films for semiconductor, dielectric and insulating material, and metal refractory silicide conductors have also benefited immensely from thin film deposition. The fabrication of electronic displays requires conductive and transparent films, luminescent or fluorescent film as well as dielectric and insulating layers [25,48].
- **Solid surface coating and biomedical.** The tribology resistance and corrosion performance of components can be improved by coating the surface of the component with thin film coatings of carbides, silicides, nitrides, and borides respectively. These coatings are being used in tools production, an area with sliding friction like bearing and machine parts. In recent time, more attention and interest has been given to films of diamond-like carbon because of this capability to dissipate heat, hardness, electrical insulation, and respectable resistance to high-temperature and high-energy radiation. It is also used for biomedical application to enhance proper osteointegration and adhesion properties.
- **Optical coating and optical data storage devices.** Thin film coating is essential for optical coating. It is used to filter interference on solar panels and acts as antireflection purpose. Thin films with appropriate refractive index gradients are being used on optical fibers to improve refraction and absorption coefficient performance. High reflective coatings that can withstand the extremely high radiation intensities without being degraded and failed when in use are needed for laser optics and are being achieved by deposition of thin films metal reflective coating with excellent properties. Infrared reflecting coatings are applied to filament lamps to increase the luminous flux intensity. Commercial demand for thin film coating is also on the rise in the optical data storage devices like computer memory and storage disk. They serve as a protective coating on the surface to and act as a shield against temperature rise. Thin film has also been used extensively in coating window glass and mirror to prevent heat from passing through [5,69].

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Conflict of interest

The authors declare no conflict of interest.

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