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# A structure zone diagram including plasma-based deposition and ion etching

André Anders [*]

*Lawrence Berkeley National Laboratory, University of California, 1 Cyclotron Road, Berkeley, California 94720, United States*

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ABSTRACT

An extended structure zone diagram is proposed that includes energetic deposition, characterized by a large flux of ions typical for deposition by filtered cathodic arcs and high power impulse magnetron sputtering. The axes are comprised of a generalized homologous temperature, the normalized kinetic energy flux, and the net film thickness, which can be negative due to ion etching. It is stressed that the number of primary physical parameters affecting growth by far exceeds the number of available axes in such a diagram and therefore it can only provide an approximate and simplified illustration of the growth condition–structure relationships.

## 1. Introduction

A structure zone diagram (SZD) is a convenient way of illustrating common features of relatively thick (>100 nm) polycrystalline films by reducing the many deposition parameters to as few as possible and illustrating their effect on the film structure. They are often ambitiously called structure zone models, though they are not really models but overly simplistic representations of expected film microstructure trends versus deposition parameters. As will be stressed throughout this contribution, the proposed new representation does not change this rather critical assessment but it addresses the need for an extended and improved SZD while clearly stating its fundamental limitations.

The concept of an SZD evolved over the years as deposition technology expanded from evaporation to sputtering and ion beam assisted deposition. In recent years, plasma-based deposition technologies are increasingly applied, such as high power impulse magnetron sputtering (HIPIMS), and therefore once again the need appeared to modify existing SZDs by including plasma-related deposition parameters. In this contribution, existing SZDs are briefly surveyed before an extended SZD is proposed. It covers the use of high energy ions as they are obtained, for example, by biasing the substrate to high negative potential, and consequently ion etching is considered, too.

## 2. A brief (and necessarily incomplete) review of structure zone diagrams

The idea for an SZD was introduced by Movchan and Demchishin [1] in 1969 for very thick films made by evaporation. In this case, the only reduced parameter was the homologous temperature, $T_h$, defined as the film growth temperature normalized by the melting temperature of the deposited film material (both in Kelvin),

$$T_h = T / T_m. \tag{1}$$

The film temperature is usually not known and one often uses the substrate temperature; a point that warrants closer examination and that will lead to a more general temperature concept developed in the next section. Based on the analysis of many samples Movchan and Demchishin concluded that three zones can be distinguished. In zone 1, at $T_h < 0.3$, the adatom mobility is low leading to continued nucleation of grains. This results in a fine-grained structure of textured and fibrous grains, pointing in the direction of the arriving vapor flux and ending with domed tops [2]. There is a high density of lattice imperfections and pores at grain boundaries. At the higher temperatures of zone 2, $0.3 < T_h < 0.5$, surface diffusion sets in, leading to uniform columnar grains. The grain size increases with $T_h$ and may extend all the way throughout the film thickness. The surface ends of the grains lead to a faceted surface. At even higher temperature, $T_h > 0.5$, bulk diffusion and recrystallization leads to dense films with large grains.

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* Tel.: +1 510 486 6745.
*E-mail address:* aanders@lbl.gov.

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Barna and Adamik [3] set the boundaries slightly differently and introduced a transition zone T between zones 1 and 2. In this transition zone, for $0.2 < T_h < 0.4$, surface diffusion is "remarkable" but grain boundary diffusion is strongly limited leading to competitive grain growth and resulting in V-shaped grains with a grain structure that is not homogenous through the film thickness. They stressed that a more realistic SZD should include process-induced segregation of co-deposited impurities or additive species. This qualification is an example that the simplistic representation of an SZD does not include all parameters, and that an SZD may not be directly applicable to a material a researcher is interested in. It is also emphasized that SZDs are designed to illustrate the microstructure of relatively thick films, i.e., those that are grown much beyond their nucleation phase.

With the advent of the broad use of magnetron sputtering, the SZD needed to accommodate a new parameter: the process pressure. Thornton [4] published an SZD showing the film structure being governed by two important parameters: the homologous temperature and the pressure. This SZD has become a classic and is reproduced in many text books on physical vapor deposition [2,5–7].

It is understood that the sputtering pressure is a convenient proxy for the kinetic effects of particle impingement on film growth [8]. At low pressure, sputtered particles are likely to experience no collisions before arriving at the substrate, and their energy distribution is approximately described by a Thompson distribution [9,10], which has a maximum at $E_{SB}/2$ and a tail $\sim E^{-2}$, with $E_{SB}$ being the surface binding energy. Sputtered atoms have typically several eV of kinetic energy, which is very significant for the promotion of adatom rearrangement on the surface. At high pressure, the sputtered atoms suffer collisions with the process gas before arriving at the growth surface, and their distribution function is shifted to much lower energies [10]. In light of this, Thornton has already introduced a parameter for kinetic effects on film growth, and one may read the "classic" SZD having one axis describing thermal effects and the other kinetic effects.

As ion beam assistance was added to some deposition processes, Messier [11] proposed a modified SZD, with zones 1, *T*, 2, and 3, where the pressure axis is replaced by an ion energy axis, and "T" refers to a transition zone that is unique when ion assistance is present. However, the use of the ion energy does not take into account that very different ion-to-atom arrival ratios may be involved, the ion mass may not match the mass of film atoms, and that the ions may have a broad or time-varying energy distribution function, as typical for pulsed bias situations.

To address the concern of various ion-to-atom ratios, an intuitive suggestion was to use the average energy per deposited atom as defined by

$$\langle E_d \rangle = E_i J_i / J_M, \tag{2}$$

where $E_i$ is the average energy of ions, and $J_i/J_M$ is the ratio of the energetic ion flux to the flux of condensing atoms; the latter are assumed to arrive with thermal energies. Although both $E_i$ and $J_i/J_M$ can be correlated with film microstructure, the product $\langle E_d \rangle$ was shown *not* to be a universal parameter [12]. Films grown at low ion energy and high flux have a different structure and different properties from films deposited with high ion energy but low ion flux. Therefore, $\langle E_d \rangle$ is not a suitable parameter for an SZD.

Limiting the considerations to the special case of anodic arc deposition of copper, where the growing film is subject to a significant flux of low energy ions, Mausbach [13] proposed using the energy flux, as defined by Eq. (2), as a characteristic parameter that determines how much the system is formed away from equilibrium and therefore subject to change. He stated that for $T_h < 0.3$, a metastable film structure exists if the mean kinetic ion energy exceeded about 1 eV. Consequently, his version of an SZD consists of two main zones, a zone "M" for $T_h < 0.3$, describing metastable films, and a continuous zone "K" at higher temperature that includes the Thornton zones 2 and 3 but with a very gradual transition.

Focusing on film growth conditions dominated by very large ion fluxes, also known as 'energetic deposition' or 'energetic condensation' from the plasma phase [7,14–16], such as filtered cathodic arc deposition [7,17,18], HIPIMS [19–22], or sustained self-sputtering [23–26], and other forms of ionized physical vapor deposition [27,28], researchers have called for a more comprehensive SZD that includes the effects of ions on film growth. In response, an extended SZD is presented here that generalizes the illustration by Thornton; it is also made clear that any such presentation can only serve for rough orientation and that each combination of substrate, film material, and deposition conditions represents a unique system that is not adequately described by an SZD.

## 3. An extended structure zone diagram that explicitly includes plasma and ion effects on film growth

HIPIMS is a deposition technology that currently enjoys much interest, with first industrial applications emerging. Associated with its development, attempts are made to include the new deposition parameters such as peak current or plasma pulse duty cycle. For example, Alami and coworkers [29] found a good correlation between the HIPIMS target current and the tantalum film microstructure and they suggested that this might be used in a future SZD. However, the (peak) target current depends on the specifics of the magnetron (geometry, magnetic field), target material and surface conditions (which in turn affect the secondary electron yield), and pulse duration [30]. One has to acknowledge that the target current is a proxy for the fluxes of particles and energy to the substrate but does not describe the processes on the growing film itself.

In order to develop an SZD that is as universal as feasible, it should have axes that are directly related to the film growth processes, as opposed to primary parameters. One should accept that the many primary parameters such as target current, voltage, pressure, substrate distance from target, pulse length (if pulsed), etc., will affect growth processes but are impractical to display in a multi-dimensional SZD. Therefore, an SZD is only a qualitative illustration of the physical reality of film properties resulting from growth processes. The best one can hope to achieve is getting an approximate orientation on some typical features that are often observed. It is proposed to extend and modify the Thornton SZD by maintaining the number of process axes but generalizing their meaning.

The changes proposed are as follows:

(I) Replace the linear $T_h$ axis with a generalized temperature, $T^*$, which includes the homologous temperature plus a temperature shift caused by the *potential* energy of particles arriving on the surface.
(II) Replace the linear pressure axis with a logarithmic axis for a normalized energy, $E^*$, describing displacement and heating effects caused by the *kinetic* energy of bombarding particles.
(III) Replace the until now unlabeled *z*-axis with a net film thickness, $t^*$, which will allow us to maintain the familiar qualitative illustration of film structure while indicating thickness reduction by densification and sputtering; it also allows us to include "negative thickness", i.e. ion etching.

A possible presentation of such extended SZD is shown in Fig. 1, where some of the illustrating features of the Thornton diagram are included and new emphasis is put on the effects of potential and kinetic energy of particles arriving on the surface.

The *potential* energy includes the heat of sublimation, or cohesive energy, $E_c$, as well as the ionization energy, $E_i$, reduced by the work function of the electron needed for neutralization; hence $E_{pot} = E_c + (E_i - \phi)$. Of course, the ionization term does not apply to atoms but is very significant for multiply charged ions. $E_c$ and $E_i$ are between 1 and 9 eV/atom, and 4 and 10 eV/ion, respectively, for the case of elementary metal films and singly charged ions; $\phi$ is about 4 eV for many materials. A generalized homologous temperature may be defined as

$$T^* = T_h + T_{pot}, \tag{3}$$

where $T_h$ is given by Eq. (1), and $T_{pot} = E_{pot}/(kN_{moved})$ is the characteristic temperature of a heated region affecting the rearrangement of $N_{moved}$ atoms ($k$ is the Boltzmann constant). Ions arriving at the substrate but not remaining with the growing film can contribute potential energy, too. Upon neutralization on the surface they leave behind the ionization energy reduced by the electron work function.

The *kinetic* energy of arriving positive ions is comprised of an initial component from the plasma, $E_0$, plus a change due to acceleration in the sheath, $E_{kin} = E_0 + QeV_{sheath}$, where $Q$ is the ion charge state number, $e$ is the elementary charge, and $V_{sheath}$ is the voltage drop between plasma and substrate surface. Although we mostly think of positive ions, the general discussion also applies to energetic neutrals [31], and negative ions [32], observed in sputtering.

Interestingly, by choosing a logarithmic scale, the kinetic energy also represents the momentum through the relation $\log(mv^2/2) \propto 2\log(mv)$. Momentum is associated with atomic displacement cascades if the kinetic energy exceeds the bulk displacement energy, which is in the 12–40 eV range [33].

Non-penetrating ions (or atoms) may have enough energy to promote surface diffusion of atoms. There is an interesting energy window where the particle's kinetic energy is between the surface displacement energy and bulk displacement energy: epitaxial growth is promoted because no defects are created in the film bulk [34].

For penetrating particles one can distinguish a very short (~100 fs) ballistic phase, when displacement cascades occur, which is followed by a thermal spike phase (~1 ps) during which the mobility of atoms in the spike volume is very high. The thermal spike can be considered as a transient liquid. As soon as atoms have found their place, i.e. the liquid “freezes”, large amplitude thermal vibrations still facilitate diffusion, especially the migration of interstitials inside grains and adatoms on the surface. The driving force is the gradient of the chemical potential [35], leading to minimization of the volume free energy and surface free energy density, respectively, with contributions of interface and elastic strain energies [15], and often resulting in a film where grains have a preferred orientation.

Energetic particle bombardment promotes competing processes of defect generation and annihilation. While kinetic energy causes displacement and defects followed by re-nucleation [2], the release of potential energy and the post-ballistic thermal spike cause atomic scale heating and annihilation of defects. Therefore, the ratio of potential energy to kinetic energy per incident particle as well as the absolute value of the kinetic energy will shift the balance and affect the formation of preferred orientation and intrinsic stress [36]. A maximum of intrinsic stress exists for kinetic energies of about 100 eV; the actual value depends on the material and other factors. The existence of such maximum can be explained by insertion of atoms under the surface yet still very little annealing [36].

At higher temperature, either via higher homologous temperature or as the result of a temperature increase due to the process itself, the grains are enlarged because the increase of adatom mobility dominates over the increased ion-bombardment-induced defects and re-nucleation rates [2].

As the kinetic ion energy is increased, e.g. by biasing, the sputtering yield is increased and the net deposition rate is reduced. Film growth ceases as the average yield approaches unity, which is for most elements between 400 eV and 1400 eV, and the surface is etched as the energy is increased even further. Metal ion etching is technologically used, for example, in the pre-deposition step in arc bond sputtering with unfiltered arcs [37], filtered arcs [38], and more recently with HIPIMS [39].

Returning to the presentation of Fig. 1, and keeping the previous discussion in mind, the meaning of the generalized temperature $T^*$ and kinetic energy $E^*$ can be a bit more precisely defined by considering the energy flux associated with arriving particles. Unfortunately, time is not available as an explicit parameter and therefore we resort to averaging — one of the fundamental limitations of the SZD presentation. The energy flux should be weighted by the fraction of the species $\alpha$ arriving and normalized by a characteristic energy of the material, $E_c$, such as the cohesive energy (one may consider selecting other energies related to bond strength but they generally scale with the cohesive energy and therefore the selection is not critical). Furthermore, in order to make $E^*$ a measure for displacements, the

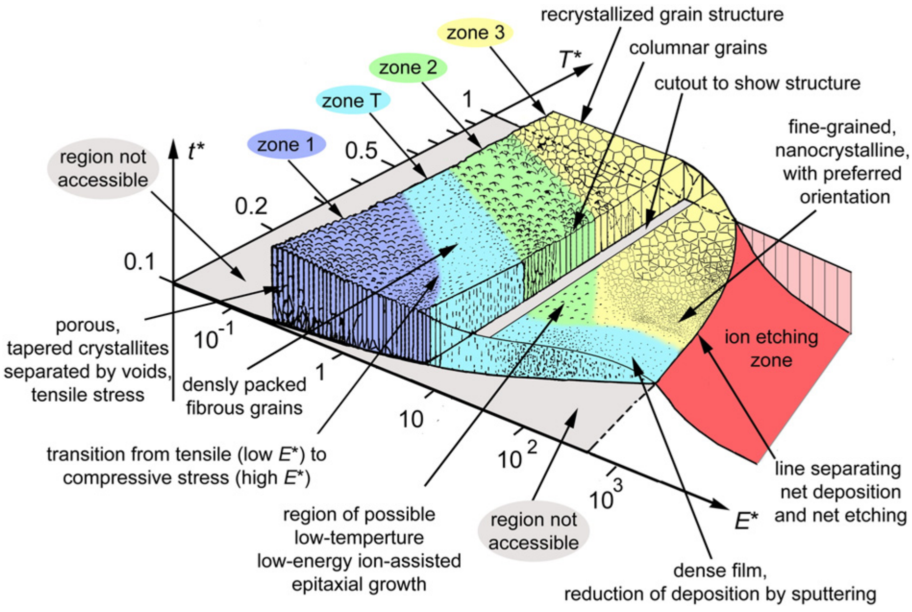

**Fig. 1.** Structure zone diagram applicable to energetic deposition; the generalized temperature $T^*$ is given by Eq. (4), the normalized energy flux $E^*$ by Eq. (5), and $t^*$ represents the net thickness. The boundaries between zones are gradual and for illustration only. The numbers on the axes are for orientation only — the actual values depend on the material and many other conditions and therefore the reader should avoid reading specific values or predictions.

mass ratio of arriving ions and atoms on the surface, $m_i/m_s$, should be taken into account because momentum transfer in displacing collisions scales with that ratio. This leads to the following expression:

$$E^* = \sum_\alpha \frac{E_{\mathrm{kin},\alpha}}{E_c}\frac{m_\alpha}{m_s}J_\alpha \bigg/ \sum_\alpha J_\alpha. \tag{4}$$

As the film grows in an "energetic deposition" process, the energetic particles have the same mass as the film atoms, hence $m_\alpha = m_s$ and Eq. (4) simplifies somewhat. In analogy, Eq. (3) can be generalized to

$$T^* = T_h + \frac{1}{k}\sum_\alpha \frac{E_{\mathrm{pot},\alpha}J_\alpha}{N_{\mathrm{moved},\alpha}} \bigg/ \sum_\alpha J_\alpha. \tag{5}$$

Expressions (4) and (5) do not take into account time variations as they are typical for pulsed processes. In those cases, like with HIPIMS, one would take the parameters and average over the pulse duration.

It is clear that all energy forms brought by particles to the surface will ultimately contribute to broad, non-local heating of the film and thereby shift the working point of process conditions to higher homologous temperature. In other words, it is impossible to do a film growth process at very low $T^*$ when $E^*$ is high, hence a "not accessible region" exists in the SZD. Another "non-accessible region" exists for very low $E^*$ because ions from the plasma cannot be arbitrarily slowed when approaching the surface.

## 4. Some final remarks

Many aspects of this discussion remain to be considered, such as the differences between pure elemental films and compound films, phase separation and nanostructured films, the existence of amorphous films at low temperature, etc. The aim of this contribution was to extend the concept of an SZD to energetic deposition where the flux of ions is large. Many refinements and other presentations are conceivable. In any case, the representation of the film microstructure evolution by an SZD is doomed to be qualitative, due to the necessary simplifications of the actual processes. Even with the suggested generalizations, which admittedly are less directly related to the simple parameters like temperature and pressure, which could be read off instruments during deposition, the extended SZD remains just a vehicle toward grasping the many different processes occurring in actual film growth.

The motivation to present yet another SZD at all is two-fold. First, the simplicity of the approach to a big-picture process-microstructure order, which can be overwhelmingly complex, can help to grasp the overarching tendencies and provide general ideas for process modifications. Second, the proposed extension stresses the generalization of energy axes and objects to the use of primary plasma-related deposition parameters, which necessarily would make the SZD less general.

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## References

[1] B.A. Movchan, A.V. Demchishin, Fiz. Met. Metalloved. (USSR), (Phys. Met. Metallogr.), vol. 28, 1969, p. 653.
[2] L. Hultman, J.E. Sundgren, in: R.F. Bunshah (Ed.), Handbook of Hard Coatings, Noyes, Park Ridge, NY, 2001, p. 108.
[3] P.B. Barna, M. Adamik, Thin Solid Films 317 (1998) 27.
[4] J.A. Thornton, J. Vac. Sci. Technol. 11 (1974) 666.
[5] J.E. Greene, in: R.F. Bunshah (Ed.), Handbook of Deposition Technologies for Films and Coatings, Noyes, Westwood, NJ, 1994, p. 681.
[6] D.M. Mattox, Handbook of Physical Vapor Deposition (PVD) Processing, Noyes Publications, Park Ridge, N.J., 1998.
[7] A. Anders, Cathodic Arcs: From Fractal Spots to Energetic Condensation, Springer, New York, 2008.
[8] J. Musil, Vacuum 50 (1998) 363.
[9] M.W. Thompson, Phila. Mag. 18 (1968) 377.
[10] T. Ono, T. Kenmotsu, T. Muranoto, in: D. Depla, S. Mahieu (Eds.), Reactive Sputter Deposition, Springer, Berlin, 2008, p. 1.
[11] R. Messier, A.P. Giri, R.A. Roy, J. Vac. Sci. Technol. A 2 (1984) 500.
[12] I. Petrov, F. Adibi, J.E. Greene, L. Hultman, J.E. Sundgren, Appl. Phys. Lett. 63 (1993) 36.
[13] M. Mausbach, Surf. Coat. Technol. 74–75 (1995) 264.
[14] J.S. Colligon, J. Vac. Sci. Technol. A 13 (1995) 1649.
[15] D.R. McKenzie, M.M.M. Bilek, Thin Solid Films 382 (2001) 280.
[16] O.R. Monteiro, Annu. Rev. Mater. Sci. 31 (2001) 111.
[17] I.I. Aksenov, V.G. Padalka, V.T. Tolok, V.M. Khoroshikh, Sov. J. Plasma Phys. 6 (1980) 504.
[18] P.J. Martin, A. Bendavid, H. Takikawa, J. Vac. Sci. Technol. A 17 (1999) 2351.
[19] V. Kouznetsov, K. Macak, J.M. Schneider, U. Helmersson, I. Petrov, Surf. Coat. Technol. 122 (1999) 290.
[20] J. Alami, P.O.A. Persson, D. Music, J.T. Gudmundsson, J. Bohlmark, U. Helmersson, J. Vac. Sci. Technol. A 23 (2005) 278.
[21] A. Ehiasarian, in: R. Wei (Ed.), Plasma Surface Engineering Research and its Practical Applications, Research Signpost, Kerala, India, 2008, p. 35.
[22] R. Chistyakov, B. Abraham, W.D. Sproul, 49th Ann. Tech. Conf. Proc, Society of Vacuum Coaters, Washington, D.C, 2006, p. 88.
[23] R.C. Krutenat, W.R. Gesick, J. Vac. Sci. Technol. 7 (1970) S40.
[24] W.M. Posadowski, Z. Radzimski, J. Vac. Sci. Technol. A 11 (1993) 2980.
[25] A. Wiatrowski, W.M. Posadowski, Z.J. Radzimski, J. Vac. Sci. Technol. A 26 (2008) 1277.
[26] J. Andersson, A. Anders, Phys. Rev. Lett. 102 (2009) 045003.
[27] J.A. Hopwood (Ed.), Ionized Physical Vapor Deposition, Academic Press, San Diego, CA, 2000.
[28] U. Helmersson, M. Lattemann, J. Bohlmark, A.P. Ehiasarian, J.T. Gudmundsson, Thin Solid Films 513 (2006) 1.
[29] J. Alami, P. Eklund, J.M. Andersson, M. Lattemann, E. Wallin, J. Bohlmark, P. Persson, U. Helmersson, Thin Solid Films 515 (2007) 3434.
[30] A. Anders, J. Andersson, A. Ehiasarian, J. Appl. Phys. 102 (2007) 113303.
[31] S.M. Rossnagel, J. Vac. Sci. Technol. A 9 (1989) 261.
[32] S. Mráz, J.M. Schneider, J. Appl. Phys. 100 (2006) 023503.
[33] W. Eckstein, Computer Simulation of Ion-Solid Interactions, Springer-Verlag, Berlin, 1991.
[34] D.K. Brice, J.Y. Tsao, S.T. Picraux, Nucl. Instrum. Methods Phys. Res. B 44 (1989) 68.
[35] G. Carter, Phys. Rev. B 62 (2000) 8376.
[36] M.M.M. Bilek, D.R. McKenzie, Surf. Coat. Technol. 200 (2006) 4345.
[37] W.-D. Münz, D. Schulze, F.J.M. Hauzer, Surf. Coat. Technol. 50 (1992) 169.
[38] A.P. Ehiasarian, A. Anders, I. Petrov, J. Vac. Sci. Technol. A 25 (2007) 543.
[39] A.P. Ehiasarian, J.G. Wen, I. Petrov, J. Appl. Phys. 101 (2007) 054301.