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Equilibrium and Non-Equilibrium Heating in Plasma-Based Deposition of Thin Films and Coatings

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Abstract

The involvement of plasmas in deposition processes opens the possibility for non-equilibrium processes including atomic scale heating by ions and electrons. This can be very beneficial from several points of view, including, but not limited to, a reduction of the requirements for conventional substrate heating, the possibility to deposit films on temperature-sensitive substrates, the formation of metastable or otherwise unattainable phases, and the combination of deposition and etching effects. Non-equilibrium heating implies transient (sub-picosecond to picoseconds) and highly localized (nanometer-squared) events associated with the arrival of energetic particles from the plasma. These particles carry kinetic and potential energies to the substrate or film surface. While conventional heating drives the system always toward equilibrium, non-equilibrium heating events involve competing effects of defect generation (affected by momentum transfer) and annealing (by localized heating). Non-equilibrium heating is complex and enables the formation of metastable, non-equilibrium phases. The most often used approach to control the kinetic energy of ions is tuning the difference between plasma and surface potentials, i.e., using suitable substrate or plasma bias. When the kinetic ion energy exceeds the displacement energy, film growth can occur under the surface (very shallow ion implantation or “subplantation”), which is utilized, for example, in the deposition of diamond-like carbon and of metastable cubic phases of ternary nitrides. Besides kinetic energy, potential energy is brought to the growing film, especially if the arriving ion flux contains multiply charged ions, which is common in cathodic arc deposition. The extremely fast and localized heating events accumulate and thereby lead to an increase of the global film surface temperature. The relation of equilibrium and non-equilibrium heating is captured by generalized temperature and energy axes in structure zone diagrams. This review focuses on non-equilibrium heating processes by ions and electrons.

1. Introduction

It is well-known that the substrate temperature is a key parameter affecting the growth and microstructure of thin films and coatings. Temperature results from the balance of various heating and cooling processes as described by the energy conservation equation that takes into account all forms of energy supply and loss including heat conduction, thermal radiation, particle loss, etc.. In this review, we will not assess the complete balance but focus on various processes leading to heating, especially the extremely fast events associated with the arrival of ions and electrons from plasma.

Heating energy can be supplied to the substrate in a gradual way that involves the entire substrate, which shall be called *equilibrium heating*. For example, a substrate heater such as shown in Fig. 1 is used for equilibrium heating.



Fig. 1. Conventional substrate heater used to establish a desired substrate temperature, which in the context of this review we call the equilibrium temperature (image courtesy of the Kurt J. Lesker Company).

In addition to the equilibrium substrate temperature, heating can occur in a transient, extremely fast, highly localized way, which can be called *non-equilibrium heating*. Non-equilibrium heating is closely related to *energetic deposition* where the film-forming particles provide significant energy affecting film nucleation and growth processes. In energetic deposition, many of the film-forming species have hyperthermal kinetic energies (such as 10 eV and greater). Energetic deposition is characterized by numerous surface and subsurface processes that are activated or enabled by the kinetic and potential energies of the particles arriving at the surface. However, it should be stressed already at this point that not all of the energies provided by arriving particles lead to localized heating because some energy is consumed by the defects that are generated and by secondary processes such as secondary electron emission.

In this review, we start by looking at conventional film nucleation and growth modes and processes, highlighting the role of temperature. We then proceed to the case where at least some of the arriving particles have high kinetic energy, where “high” is to be understood in relation to material-characteristic energies such as the displacement energy, the minimum kinetic energy that an atom in a solid needs to receive to be permanently displaced from its normal lattice site. The displacement energy is chosen because higher kinetic energies allow arriving ions to penetrate the substrate or growing film. The description of energetic deposition requires taking into account not only the contribution of kinetic energy but the potential energy of each of the arriving particles. Non-equilibrium heating has a profound

effect on the microstructure and film properties that follow because the surface atoms of the growing films are repeatedly subject to short-lived temperature spikes that provide the energy for surface and sub-surface mobility as well as defect generation and annealing.

2. The three conventional nucleation and growth modes

Let us start by looking at nucleation and film growth for conventional (low energy) physical vapor deposition. Depending on whether the bonds between adatoms of the same kind are stronger than between adatom and substrate atoms, one generally distinguishes three basic growth modes [1, 2]:

- (i) a three-dimensional or island growth mode, also known as the *Volmer-Weber mode*,
- (ii) a two-dimensional or layer-by-layer growth, also known as the *Frank-van der Merve mode*, and
- (iii) a mixed mode that starts with two-dimensional growth that switches into island mode after one or more monolayers; this mode is also known as the *Stranski-Krastanov mode*.

In the two-dimensional growth mode, the arriving particles have a strong affinity for the substrate atoms: they bond to the substrate rather than to each other. When the opposite is true, adatoms build three-dimensional islands that grow in all directions, including the direction normal to the surface. Growing islands eventually coalesce and form a contiguous and later continuous film. In the mixed mode, the relations of bond strengths between like-atoms and dislike-atoms are more subtle. The bonding environment is initially such that layer growth is preferred. This changes once the substrate atoms are covered and hidden by one or several monolayers of the arriving material, and islands start to form. To explain this, one needs to carefully consider the energy of the whole system, which includes contributions of strain energy caused by lattice mismatch and the surface free energy. This has been the subject of many texts [1-7].

The substrate temperature is a key parameter (but not the only one) that influences nucleation and growth modes. At low temperatures, adatom surface diffusion is limited, which promotes adatoms to preferentially bond with each other forming islands. In contrast, at high temperatures, adatom mobility is high, promoting adatoms to cover the substrate completely. Accordingly, the mixed mode is more likely to be found at intermediate temperatures. In addition to driving a specific growth mode, temperature has several other important functions during thin-film deposition, namely

- Promoting crystalline growth: Higher temperatures increase adatom mobility, allowing atoms to find lower-energy sites, thereby promoting a crystalline structure of films. In contrast, low temperatures often result in amorphous films.
- Influencing surface roughness: The ability of adatoms to diffuse and settle into stable sites generally reduces surface roughness unless one operates in a region of faceted growth of crystalline columns.
- Determining grain size: For higher temperatures, the diffusion length of adatoms is increased, promoting larger grain sizes.
- Impurity reduction: Higher temperatures provide the energy needed to drive off impurities of high vapor pressure, which can improve the purity and all resulting properties of the film.

Some of these features will be revisited when we discuss Structure Zone Diagrams.

3. Energetic deposition, the subplantation growth mode, and thermal spikes

Film deposition from the plasma phase can be categorized as *energetic deposition* if many of the arriving ions have hypersonic velocity or high kinetic energy. If many of the film-forming ions exceed the

displacement energy, E_d , they will penetrate the substrate surface and reach the subsurface region [8]. Film growth can therefore occur *under* the surface rather than *on* the surface, in contrast to the conventional growth modes mentioned before. When the arriving particles come to rest under the surface, we speak of shallow ion implantation or *subplantation* [9-11], a kinetically driven, non-equilibrium process. The subplantation growth mode has been associated with dense, and often hard films that exhibit very high compressive stress. Subplantation is critical for, but not limited to, the growth of diamond-like carbon films [9, 10]. Due to film-substrate intermixing and formation of chemical bonds between substrate and film atoms, films deposited by subplantation are typically well-adherent unless the intrinsic stress is excessive, in which case the compressive forces cause film delamination. More recently, subplantation growth has been used to obtain desired material compositions and metastable phases, for example in the V-Al-N system, not obtainable by equilibrium processes [12, 13].

If the kinetic energy of arriving ions is high (in this context we mean typically hundreds or thousands of electron volts), many displacements of substrate and/or film atoms occur. The ion-induced collision cascade can be seen as a liquid that exists only for picoseconds or even less, described as *thermal spikes* as early as in the 1950s [14, 15]. The liquid or liquid-like phase exists because the vibrational amplitude could be in excess of atom distance in the surrounding lattice [15]. As the liquid volume quenches, the material freezes into an amorphous phase or, depending on the material, a crystalline phase with defects. While the liquid phase exists usually for less than 1 ps, the thermal effects such as diffusion in the vicinity of the spike volume may be important for as long as 100 ps [16]. The speed of cooling determines the residual stress and many other film properties as further discussed in Section 8. Thermal spikes are associated with breaking and reforming many bonds. Defects are generated and most, but not all, are annealed.

Thermal spikes were identified to greatly enhance sputtering when the material is already at a temperature close to the melting temperature [17]. In the 1960s to 1990s, hundreds of papers contributed to the development of a deeper understanding of thermal spikes as outlined in important papers [16, 18-20]. In the following, just a few important aspects will be mentioned.

For the sake of discussion and order-of-magnitude estimates, one could use the classical heat transfer equations and assume that an incoming ion, for example of 100 eV kinetic energy, produces a point-like heat source on the surface. In this case, an analytical solution for the time-dependent temperature distribution into the half-sphere of the solid can be written as [18]

$$T(r, t) = T_0 + \frac{E_{heat}}{8C_v (\pi K_d t)^{3/2}} \exp\left(-\frac{r^2}{4K_d t}\right) \quad (1)$$

where

$$K_d = A + BT^m, \quad (2)$$

is the temperature-dependent thermal diffusivity, A , B and the exponent m are constants, and the other symbols are as follows: E_{heat} is the heating energy delivered by the ion, T_0 is the substrate temperature before ion impact, E_i is the energy provided by the arrival of the ion, C_v is the volume specific heat, r is the radius (distance) from the location of ion impact (the source point of energy), and t is time. Such analytical approach gives results like shown in Fig. 2.

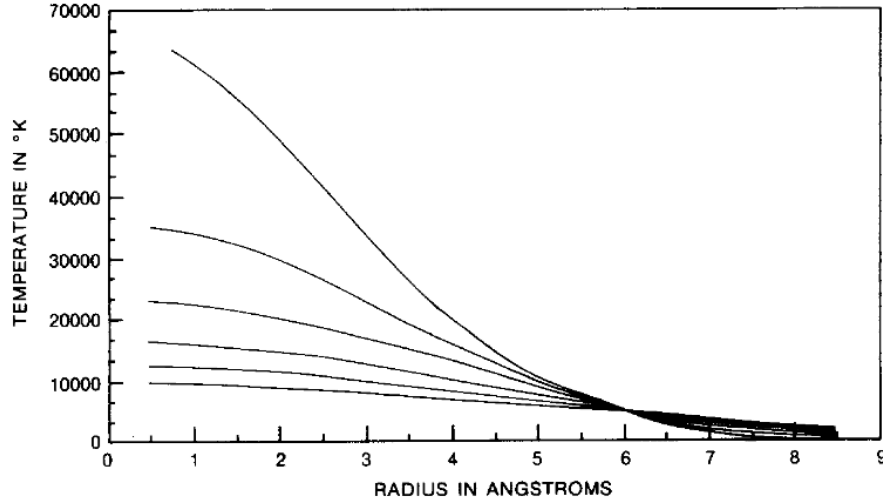


Fig. 2. Analytically calculated temperature distribution resulting from the impact of a 100 eV particles onto NaCl assuming a substrate temperature of 0 K but utilizing constant thermal properties appropriate to 300 K. The top curve is at 10^{-14} s and each lower curve is for a time increment of 0.5×10^{-14} s (from [18], reprinted with permission by Elsevier)

Such calculations provide estimates for the order of magnitude of the shortness of the process (~ 1 ps) and the strong limitation of the impacted area ($\sim 1 \text{ nm}^2$) or volume ($\sim 1 \text{ nm}^3$), however, as the authors themselves point out [18], precisely the smallness of the magnitude points to limitations of the applicability of any analytical approach and the validity of continuum terminology. Computational methods such as molecular dynamics are more appropriate. The analytical result is still interesting because it shows (i) the formal “temperatures” that are reached far exceed any melting and boiling temperatures and (ii), the shortness of the process indicates that equilibrium, as defined by the establishment of equilibrium distribution functions, is likely not established. In other words, the heating provided by thermal spike events should be classified as “non-equilibrium”. Experiments and simulations of mixing of heavy metal atoms indicated that motion occurs predominantly in the spikes’ liquid-like zones, while electron-phonon coupling plays a minor role [20]. Due to energy and momentum conservation laws in collisions, arriving ions of equal or greater mass can create large collision cascades, whereas light ions can be reflected. Often, Monte Carlo codes such as the popular TRIM [21], SRIM [22], T-DYN [23] and SDTrimSP [24] codes are used to determine average penetration depth, lateral size of the cascade, sputtering yields and other parameters of interest. Their dynamic versions (where the composition of the target is dynamically updated) can be used to simulate deposition processes. Additional tools, like the Monte Carlo transportation code SIMTRA [25] and pySIMTRA [26] serve to understand particle transport from the target to the substrate.

We may use the above-mentioned analytical estimate of short times and small impact area to address other questions, namely: Do thermal spikes overlap as they occur or are they individual events? What flux would it take to make them overlap? The ion flux Γ_i (ions per area and time) arriving at the surface is related to a measured ion current density j_i by the relation

$$\Gamma_i = \frac{j_i}{\bar{Q}e} = \frac{n_i (k_B T_e / m_i)^{1/2}}{\bar{Q}e} \quad (3)$$

where $\bar{Q}$ is the average ion charge state number and $e = 1.602 \times 10^{-19}$ As is the elementary charge; for most process plasmas, we have $\bar{Q} = 1$, but laser ablation or cathodic arc plasma contain multiply charged ions leading to $\bar{Q} \approx 2$ or even higher values [27]); n_i is the ion density in the plasma, and the square root term is the ion velocity at the sheath edge, here written as the Bohm velocity with T_e the electron temperature, m_i the ion mass, and k_B the Boltzmann constant. In the case of supersonic ion flow, like for cathodic plasmas, the actual ion flow velocity should be used (typically 10^4 m/s [27]). The ion flux can then be put in relation to a characteristic impact area of a thermal spike $A_{spike} \sim 1 \text{ nm}^2$ and a thermal spike time $t_{spike} \sim 10 \text{ ps}$, where the quench and cooling time was included, thus the ratio

$$N_{overlap} = \Gamma_i / (A_{spike}^{-1} t_{spike}^{-1}) \quad (4)$$

gives the number of spikes overlapping within the characteristic spatial and temporal dimensions. For an order of magnitude estimate, let us consider the example of a high ion flux typical for growing a film with a cathodic arc process, assuming $j_i = 10^4 \text{ A/m}^2$ and $\bar{Q} = 2$, giving $N_{overlap} \approx 3 \times 10^{-7}$. We see that thermal spikes by arriving ions are isolated, individual events by a wide margin and that the choice of example parameters was not critical to come to this conclusion. This does not mean, however, that the effect of such spike events can be neglected. Quite contrary: they have an important effect on atom mobility and defect structure in the vicinity of ion impact, and they enhance the average surface temperature through their cumulative action, which can be described as *process heating*, further discussed in sections 4 and 5. The topic subplantation and thermal spikes will also be revisited in Section 8 when we discuss the relationship to stress generation and relief.

4. Structure zone diagrams

The properties of coatings and thin films are determined by their chemical composition and microstructure. The effect of key process parameters on coating microstructure can be generically visualized by a *structure zone diagram*, an approach originally introduced under the term *structure zone model* in the late 1960s by Movchan and Demchishin [28]. Considering thick coatings made by deposition of evaporated source material, their original structure zone diagram had only the substrate temperature as a process variable (Fig. 3).

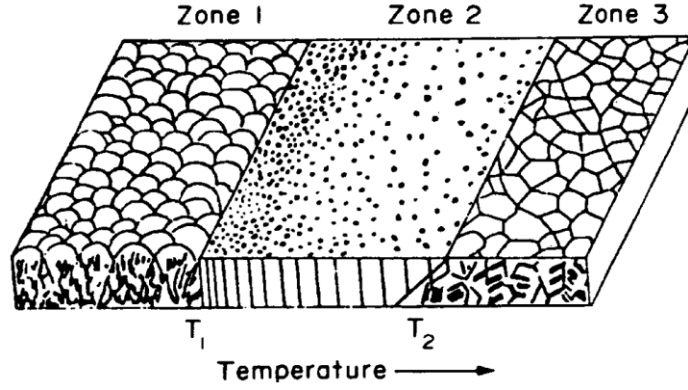


Fig. 3. Structure zone diagram for thick films and coatings deposited by evaporated materials. The coating microstructure depends on the deposition temperature; three main structural regions can be distinguished (figure courtesy of B.A. Movchan and A.V. Demchishin).

The substrate and film temperature T (in K) was normalized to the melting temperature of the coating material T_m (in K) to define a dimensionless *homologous temperature*:

$$T_{\text{hom}} = T/T_m. \quad (5)$$

Based on the analysis of many samples, Movchan and Demchishin [28] concluded that three zones can be distinguished:

Zone 1: $T_{\text{hom}} < 0.3$ for metals and $T_{\text{hom}} < 0.26$ for oxides, featuring tapered columns with domed tops due to low adatom mobility, continued nucleation of grains (metals) or fine-grained/amorphous for compound materials, the columns point in the direction of the arriving vapor flux [29]; there is a high density of lattice imperfections and pores at grain boundaries.

Zone 2: $0.3 < T_{\text{hom}} < 0.45$ for metals and $0.26 < T_{\text{hom}} < 0.45$ for oxides; surface diffusion sets in; columnar grains are rather uniform with increasing grain size as T_h increases, they may extend all the way throughout the film thickness and lead to a faceted surface morphology.

Zone 3: $T_{\text{hom}} > 0.45$ for metals and oxides, bulk diffusion and recrystallization leads to dense films with large, equiaxed grains with a polyhedral structure.

Movchan and Demchishin backed up this classification by studying the microstructure of nickel, titanium, tungsten, aluminum oxides, and zirconium dioxide coatings, indicating the rather universal nature of their observations. However, the boundary values separating the zones vary slightly in the literature [30-33], depending on the material class considered.

The energy distribution of an effusive (free-molecular) flux of atoms toward the substrate is

$$f_{\text{effusive}}(E) = \frac{E}{(k_B T_{\text{source}})^2} \exp\left(-\frac{E}{k_B T_{\text{source}}}\right) \quad (6)$$

where T_{source} is the temperature of the vapor source (the evaporant in the crucible), and the most probable energy in the flux is $k_B T_{\text{source}}$. Considering that 1 eV corresponds to 11605 K, typical evaporation sources deliver atoms with energies less than 0.2 eV. This low value needs to be put in relation as we consider other, often plasma-based deposition methods.

As the coatings technology expanded from deposition by evaporated material to deposition by sputtering in 1970s, the concept of a structure zone diagram needed expansion considering the most important new parameter: the gas pressure. Thornton added this variable as a new axis [30, 34] (Fig. 4).

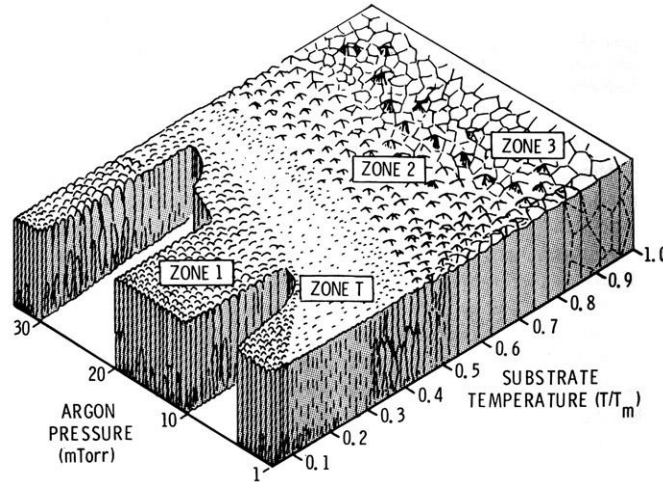


Fig. 4. Structure zone diagram for sputter deposition. In addition to the substrate temperature, T , normalized by the melting temperature of the coating material, T_m , Thornton introduced the gas pressure as a variable, which is a proxy for the kinetic energy of the arriving atoms. The cutouts on the left side of the figure are done to show the structure of the coating (from [30], with permission of AIP Publishing).

The new variable, pressure, should be interpreted as a proxy for the kinetic energy of atoms arriving at the substrate surface, namely, due to absence or presence of collisions of sputtered atoms on their way to from the target to the substrate, lower pressure corresponding to higher energies, and vice versa. In the absence of collisions, sputtered atoms have a Thompson energy distribution [35],

$$f_{\text{Thompson}}(E) \propto \frac{E}{(E + E_{SB})^3}, \quad (7)$$

which is the result of atoms leaving the surface of the sputtering target due to ion-induced collision cascades; E_{SB} is the surface binding energy. The distribution (7) is not dependent on temperature (assuming the target is not evaporating) and features an energy peak that is typically in the range of a few electron volts, much higher than the energies (6) related to evaporation, and a tail that scales with E^{-2} up to the energy of primary ions. At low pressure, sputtered atoms can deliver their kinetic energy to the growing film. As the pressure is increased, sputtered atoms increasingly collide with gas atoms, lose their energy until they are thermalized. The resulting coating structure at high sputtering pressure is therefore similar to the structure observed in deposition using a flux of evaporated material.

Besides the typical eV-range of sputtered atom as described by the distribution (7), sputtering also involves very energetic particles not captured by (7), namely backscattered atoms, i.e., ions that were neutralized upon contact with the target and scattered back due to a direct knock-on collision with a

surface atom. Their energy can be as high as the ion energy upon target impact, often several 100 eV. This is especially relevant when the sputtering gas contains relatively light ions and the target is composed of relatively heavy atoms. For example, in a study on tungsten (atomic mass 183.84) sputtering with argon (atomic mass 39.95), it was shown that the microstructure of the deposited tungsten film was largely determined by the effect of backscattered argon [36].

As this example shows, a word of caution is needed when interpreting structure zone diagrams. They are not comprehensive because there are other parameters in the deposition process that are not included. For example, Barna and Adamik [32] studied the role of contaminants and additives and found that not only surface and bulk diffusion are responsible for the microstructure but that contaminants and additives promote or inhibit the structure-forming phenomena of diffusion and defect evolution. All conditions and events leading to the promotion or interruption of local epitaxial growth and renucleation are of importance. Therefore, structure zone diagrams, while useful in giving orientation, cannot fully illustrate complex real systems.

Let us complete the discussion on structure zone diagrams by explicitly including the kinetic and potential energies that ions bring to the surface in plasma-based deposition (and etching) processes. As early as 1984, Messier and coworkers [37] distinguished “thermal- and bombardment-induced mobility”. They consequently replaced the sputtering pressure as the axis label by the kinetic energy of bombarding particles (they write “bombarding particles”, not ions, since they still investigate sputtering, not yet plasma-based deposition). The concept of distinguishing thermal- and bombardment-induced mobility is even more important for plasma-based deposition, such as high power impulse magnetron sputtering (HiPIMS), where a large fraction of the sputtered atoms is ionized on their way from the source (sputtering target) to the substrate [38, 39]. For cathodic arc deposition (CAD) or pulsed laser deposition (PLD), the plasma is generally fully ionized and, in most cases, contains multiple ion charge states, and therefore bias techniques are highly effective.

A generalized structure zone diagram was developed where kinetic and potential energies of ions arriving the growing film are taken into account (Fig. 5).

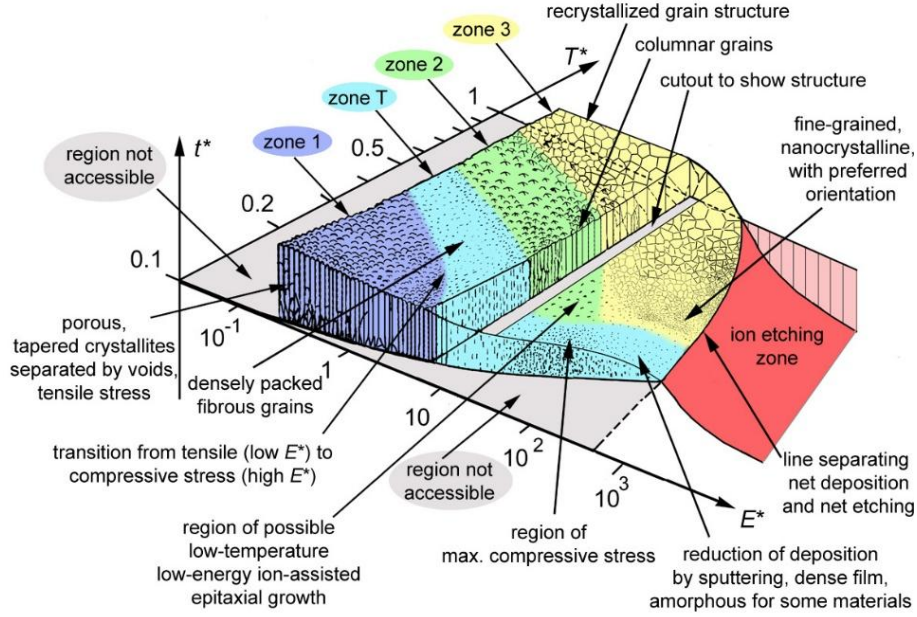


Fig. 5. Structure zone diagram for deposition with energetic particles, where T^* is a generalized temperature; E^* is the normalized kinetic energy, and t^* represents the net film thickness, which can be negative (ion etching). The boundaries between zones are gradual and for illustration only. The numbers on the axes are for orientation only — the actual values depend on the film material and many other conditions and therefore the reader should avoid reading specific values or predictions (from [40] with permission by Elsevier).

Compared to Thornton's structure zone diagram (Fig. 4), the following main changes are made [40]:

(i) The linear homologous temperature T_{hom} axis is replaced by a generalized temperature T^* that takes the process heat by the incoming particle flux into account. In the original work [40], the contribution of the potential energy of incoming particles, especially ions, was emphasized at this point. Deviating from the original interpretation [40], the axis parameters T^* can be interpreted as an effective (global) film surface temperature. It is the result of the global homologous temperature, as provided by conventional substrate heating, plus a (global) temperature shift of the surface, $\Delta T_{\text{process}}$, resulting from the accumulation of many individual temperature spikes, leading to

$$T^* = T_{\text{hom}} + \Delta T_{\text{process}} / T_m. \quad (8)$$

As estimated by equation (4), thermal spikes are isolated. However, as the thermal energy spreads away from impact locations, the surface temperature around each impact is enhanced. Now one can use the heat conduction equation (1) and consider much longer times than the spike time until the heat fluxes from neighboring impacts overlap. This will give a (global) surface temperature enhancement determined by the deposition process. The energy leading to heating in equation (1), labeled as E_{heat} , is not simply the ion's kinetic energy or the sum of its kinetic and potential energies, but only the part which is available to become process heat, i.e., the sum of kinetic and potential energy reduced by the energies taken by

defect generation, strain, and secondary effects such as photon emission, secondary electron emission, sputtering, impact-stimulated desorption, etc.,

$$E_{heat} = E_{kin} + E_{pot} - E_{defects} - E_{strain} - E_{secondary} . \quad (9)$$

(ii) The linear pressure axis is replaced by a logarithmic axis for the normalized kinetic energy, E^* , is the kinetic energy of bombarding particles normalized by a characteristic material energy. The kinetic energy results from the initial kinetic energy ions had in the plasma, E_0 , plus the kinetic energy change due to acceleration in the sheath, hence

$$E_{kin} = E_0 + QeV_{sheath} \quad (10)$$

where Q is the ion charge state number, and V_{sheath} is the voltage drop between plasma and substrate surface. E^* captures the effects associated with the non-equilibrium nature of energetic deposition, i.e., those associated with subplantation, thermal spikes and the short-living, impact-specific processes of mobility enhancement, surface and sub-surface diffusion, bond-breaking and annealing, grain refinement, renucleation, etc.

(iii) The z-axis is labeled net film thickness, t^* , resulting from the arrival and departure of particles. This approach allows us to maintain the familiar qualitative illustration of the Thornton diagram while including thickness reduction by densification and sputtering, including “negative thickness” when the removal of particles is larger than their arrival, i.e., we include ion etching in this presentation of a structure zone diagram.

Each ion delivers significant kinetic and potential energies leading to what has been called *atomic scale heating* (ASH) [41]. In case the film is primarily grown by deposition of ions from the plasma phase, such as in pulsed laser deposition (PLD), cathodic arc deposition, or HiPIMS, each of the atoms in the growing film was several times subject to ASH, namely, once when it arrived, and again when neighboring atoms arrived. Musil [42] pointed out that ASH can replace conventional heating and produce dense films via enhanced surface mobility at generally low bulk temperature. The accumulated energy delivered by ASH gives rise to temperature elevation of the substrate surface and the growing film as a whole [43]. If the substrate is attached to a heat sink, the film bulk may stay close to the preset, original temperature, in some cases even close to room temperature. In that way, plasma-based deposition can lead to dense and even crystalline films [44, 45] which is of special interest when dealing with temperature-sensitive substrate materials where the substrate temperature is generally limited due to decomposition, melting or degeneration (e.g., polymers).

If we consider the zone boundary lines in Figs. 4 and 5, we see that they are not parallel to the pressure axis (Fig. 4) or kinetic energy axis (Fig. 5). They are tilted relative to the E^* axis, which is the manifestation of non-equilibrium heating, indicating that non-equilibrium heating can be used to reduce conventional heating.

However, the assistance of film growth by energetic particles is not fully equivalent to conventional heating. While conventional heating drives the system always toward equilibrium, non-equilibrium heating involves competing effects of defect generation and annealing; it is complex and enables the formation of metastable, non-equilibrium phases. The ratio of defect generation and

annealing is determined by the global temperature, the momentum transfer from the arriving particle to atoms of the growing film, strain, and materials properties.

In particular, subplantation inserts atom under the surface, enables mobility under the surface and results in phases not attainable under equilibrium conditions [46]. Examples of early realization include subplantation of Ta into Cu [47] and more recently the synthesis of the cubic phase of $\text{Ti}_{0.31}\text{Al}_{0.69}\text{N}$ and $\text{Zr}_{0.48}\text{Al}_{0.52}\text{N}$ with a high Al content outside the equilibrium-predicted range [48]. The concept can be extended to other material systems [49].

There are plenty of examples that show that energetic bombardment allows us to reduce the global substrate temperature to obtain a similar but not equal microstructure. Namely, energetic bombardment leads to grain refinement and continuous renucleation, which is evident by observations of smaller grains and smoother surfaces under bombardment conditions. Depending on the application, this can be a desired or undesired effect. The structure zone diagrams for sputtering (Fig. 4) and plasma-based deposition (Fig. 5) illustrate that energetic deposition can lead to dense films with smooth surfaces at relatively low substrate temperature [43, 50]. A smooth surface, however, does not imply that the interface to the substrate is smooth, quite contrary, the subplantation mechanism leads to intermixing of substrate and film material, which has been shown in experiments [51-53] and simulations [54, 55] (Fig. 6).

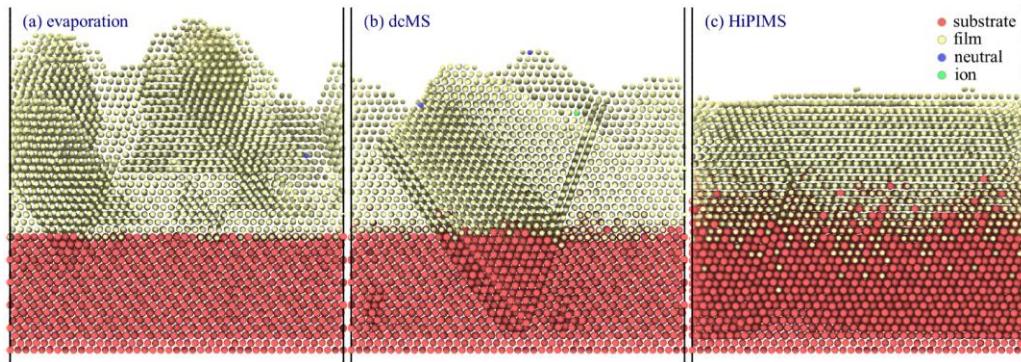


Fig. 6. Atomistic simulation of different deposition processes (a) deposition by evaporation, (b) deposition by DC magnetron sputtering, (c) deposition by high power impulse magnetron sputtering. The substrate and film atoms are colored as indicated in the legend (from [55], with permission by AIP Publishing).

Of great interest for many applications is deposition within a certain energy window, namely when the arriving particles have enough energy to promote high adatom mobility but do not cause bulk atom displacements (“ion damage”) to the growing film. That window of kinetic energy of arriving particles is typically in the range 1-20 eV, resulting in dense films or multilayers with sharp interfaces. At higher energies, we deal with energetic deposition that includes sub-surface processes, hence interface mixing occurs. Collision with process gas may be used to reduce the energy of incoming particles and shift the most likely energy to the desired energy window [56]. This is used, for example, in the emerging field of magnetron sputtering epitaxy [57, 58].

We consider now the high energy end when using a high negative substrate bias voltage of -1000 V or higher such that the sputter yield will exceed unity (Fig. 7). The removal of material by sputtering

from the substrate surface exceeds the incoming flux of ions and atoms and therefore no film is deposited. This is the regime of ion etching. The ion etch regime is often used as a pre-coating surface cleaning step. When argon is used, the gas diffuses out and represents a gas source, which in some cases can be very substantial [59]. Some argon atoms, a few percent of the composition, remain in the near-surface layer leading to reduced film adhesion [51]. This problem has been addressed by using metal ions instead, preferably of the elements used in the coating [60].

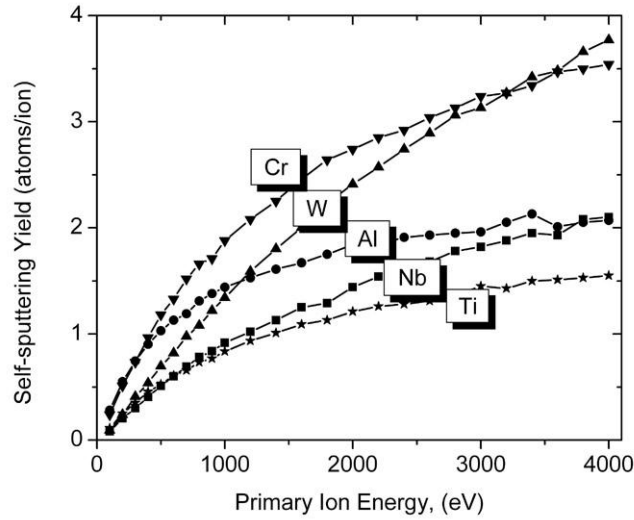


Fig. 7. Self-sputtering yield for selected metals as a function of ion energy calculated by T-DYN Monte Carlo code (the apparent scatter of data points is due to the statistics). A self-sputter yield greater than unity indicates the ion etch regime (from [7], Chapter 8, with permission by Springer Nature).

5. Non-equilibrium heating by the kinetic and potential energies of ions

When ions approach the substrate surface, they bring kinetic and potential energies that lead to highly localized, non-equilibrium heating. We assume that there is a sheath between plasma and substrate in which the sheath voltage

$$V_{sheath} = V_{plasma} - V_{surface} \quad (11)$$

drops. In most cases, the surface is negative relative to the plasma potential, which implies acceleration of positive ions of charge states $Q = 1, 2, 3, \dots$ from the plasma toward the surface. A general formula that describes the different contributions to heating the surface region may be written as

$$E_{heat}(Q) = \underbrace{E_{kin,pl}}_{[1]} + \underbrace{QeV_{sheath}}_{[2]} + \underbrace{f_{ion}}_{[3]} \left(\underbrace{E_{ion}^{cum}(Q)}_{[4]} - \underbrace{Q\phi}_{[5]} \right) + \underbrace{f_{cap}f_{exc}}_{[6]} E_{exc} + \underbrace{(E_{coh} - \Delta E_{defects})}_{[7]} - \gamma_{sputter} (E_{SB} + E_{kin,a}) - \gamma_{SE}^i (\phi + E_{kin,SE}) \quad (12)$$

This is a more complete description than the simplified equation (9). The symbols and the meaning of the terms are explained as follows.

5.1. Kinetic energy before acceleration in the substrate sheath

Ions have kinetic energy before they are accelerated by the electric field of the sheath. The first term describes thus the kinetic energy at the boundary between plasma and sheath, the sheath edge. Depending on the type of plasma, the kinetic energy at the sheath edge is

$$E_{kin,pl} = \begin{cases} (k_B T_e / m_i)^{1/2} & \text{if ions are subsonic in the plasma} \\ m_i v_{pl}^2 / 2 & \text{if ions are supersonic in the plasma} \end{cases} \quad (13)$$

For example, in an equilibrium plasma, ions have a temperature associated with subsonic velocities, and acceleration to the ion sound velocity (Bohm velocity) occurs in the presheath [61, 62]. In contrast, plasmas produced by explosive-like processes such as laser ablation plasmas and cathodic arc plasmas have supersonic ions when reaching the sheath; their most likely velocity is in a relatively narrow range of $v_{pl} = (1-3) \times 10^4$ m/s [27]. The corresponding most likely kinetic energy, i.e., the peak of the kinetic energy distribution, depends on ion mass and is in the range 20-150 eV [27]. That is a lot of energy as measured by the energy needed to affect film nucleation growth processes.

5.2. Kinetic energy gain by acceleration in the substrate sheath

If $V_{sheath} = V_{plasma} - V_{surface} > 0$, positive ions are accelerated when passing through the sheath. The ion charge state Q is a multiplier for the kinetic energy gain, as already described in equation (10). We assume here that there are no collisions in the sheath, otherwise the energy gain is reduced. Biasing is the most forward approach to changing the kinetic energy of ions, especially since it can be pulsed, tailored, or shaped.

5.3. Cumulative ionization energy of ions reduced by work function to neutralize them

Each ion carries potential energy in the form of its ionization energy. The ionization energy $E_{ion}(Q)$ is defined as the energy needed to remove a bound electron from an atom (charge state $Q = 0$) to form an ion of charge state $Q + 1$ [63, 64]. Multiply charged ions carry therefore the cumulative ionization energy,

$$E_i^{cum}(Q \geq 1) = \sum_{Q'=0}^{Q-1} E_{i,Q'} \quad (14)$$

which is the sum of the energies needed to produce the first ionization state from a neutral, the second ionization state from the first ionization state, etc., until charge state Q is reached. The cumulative ionization energies are high energies in the context of film growth, even if only a fraction f_{ion} of that energy heats the growing film and the rest is lost by photons and Auger electrons [65] due to the stepwise reduction of Q near the surface, which is discussed below.

The issue of delivering the cumulative ionization energy to a surface is well studied for highly charged ions (for example for Xe with charge states up $Q = 40$, where that energy is extremely high [65]).

The contribution is much more modest in the case of ions commonly used in plasma-assisted deposition. Still, learning from studies with highly charged ions, one can state that the ionization energy is released in two steps. The first step is above the surface via radiation and Auger processes, and the second step is in the solid. Before arriving on the surface, the ion is stepwise neutralized, and therefore Q electrons need to be emitted, which requires the work function energy $Q\phi$. Therefore, we see in expression 3 of equation (12) the term $-Q\phi$. Part of the cumulative ionization energy is transferred to the solid via electronic excitation [66] followed by electron-phonon coupling, which leads to local heating of the lattice. The timescale to reach equilibrium between electron and lattice temperature is of the order 1 ps [67]. In the remainder of this work, we will occasionally use the nomenclature O(1 ps) to describe the order of magnitude as opposed to a specific value. Quenching of the lattice heat spike by thermal conduction is much slower, O(100 ps). On that timescale, surface and near-surface atoms can readily move and contribute to the formation of the film's microstructure.

A closer look at the stepwise reduction of the charge shows that approaching ions generates an image charge of equal amount but opposite sign (Fig. 8).

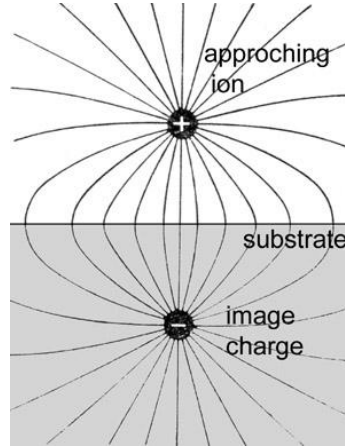


Fig. 8. Schematic presentation of the formation of an image charge due to a redistribution of charges in the substrate or growing film (from [7], Chapter 8, with permission by Springer Nature)

Ions gain an additional small amount of kinetic energy, E_{ic} , by image charge acceleration, however, this gain in kinetic energy will not contribute to heating. One argument is that the gain in kinetic energy is just a redistribution of energy since it takes energy to produce the image charge. Therefore, there is no image charge term in (12).

When the ion is within few nanometers of the surface, which for now we assume to be a metal, an image charge of opposite polarity exerting the Coulomb force

$$F = (eQ)^2 / (4\pi\epsilon_0 (2z)^2) \quad (15)$$

on the ion, where z is the distance between the ion and the surface. This force causes acceleration toward the surface and therefore provides a small “kick” to the approaching ion, slightly enhancing its

kinetic energy. Image charge acceleration has been measured [68] and discussed [69]. Equation (15) is only valid and relevant in a narrow range of a few nanometers from the surface: At larger distances, the force is negligibly small and the potential is distorted/shielded by the presence of other charges, and when the distance is smaller than about 0.3 nm, the approximation of a flat, continuum substrate fails and must be replaced by a more sophisticated, quantum mechanical theory (like density functional theory, DFT) that involves the electron structure of arriving ion and surface atoms.

With decreasing distance from the surface, the electric field associated with the image charge reduces the effective work function. Electrons near the Fermi edge of the metal can transfer resonantly into an excited level of the incident ion when the potential barrier between metal and the ion reaches the Fermi level, i.e., when the transfer becomes classically allowed (classical “over-the-barrier” (COB) model [69]). Electron transfer occurs at a critical distance [69]

$$d_c(Q) \approx a_B E_H / \phi \sqrt{8Q+2} , \quad (16)$$

where a_B is the Bohr radius, E_H is the ionization energy of hydrogen and ϕ is the work function. After the transfer, the ion charge and the image charge are reduced and the barrier height is increased. In the case of a multiply charged ion, a second, shorter critical distance exists where a second electron transition is classically allowed. Multiply charged ions reduce their charge stepwise in a staircase fashion. In the staircase approximation, the kinetic energy gain by image charge is [69]

$$E_{ic}(Q) = \frac{\phi}{2} \sum_{i=0}^{Q-1} \frac{2(Q-i)-1}{\sqrt{8(Q-i)+2}} . \quad (17)$$

For example, a gold ion of charge state $Q=3$ approaching a gold surface ($\phi \approx 5.4$ eV) will gain $E_{ic} \approx 5.4$ eV kinetic energy by image charge acceleration. The energy gain is about 2-3 eV for charge state $Q=2$, ref. [68], an amount that is generally negligible compared to the other kinetic energy terms, and it cancels out when also considering the associated potential energy changes.

The physics of image charge acceleration is different when the ion approaches an *insulating* surface because there is no conduction band in which electrons can freely move, and thus the rearrangement of electrons of the substrate is impeded and determined by localized surface charge [70, 71]. One may consider an effective image charge $Q_{eff} = \chi Q$ where χ is a dielectric response function [72] with $0 < \chi < 1$. The energy gain is determined by the image energy gain at the distance d_{c1} of the *first* electron capture

$$E_{ic,insul}(Q) = \chi(d_{c1}) \frac{e^2 Q^2}{4d_{c1}} . \quad (18)$$

After the first electron has been captured, the surface is locally positively charged. Image charge acceleration is partially offset by deceleration by the newly formed surface charge and thus no further kinetic energy gain occurs [72].

5.4. Excitation energy

A fraction f_{exc} of the arriving (now neutralized) ions can be in an excited state, and therefore the additional energy E_{exc} they carry should be mentioned. Usually one would determine f_{exc} based on a Boltzmann distribution, giving $f_{exc} \sim \exp(-E_{exc}/k_B T_e)$, however, in the vicinity of the surface, electronic

excitation is likely greatly affected by the capture of secondary electrons leading to the reduction of the ion's charge state. This complicated process is further discussed in the context of secondary electron emission and image charge acceleration.

5.5. Cohesive energy reduced by defect energy

The cohesive energy E_{coh} of a solid is the energy required to decompose the solid into separate and independent atoms, or, from an atomistic point of view, it is the energy to take an atom from the bulk and bring it to a large distance where no interaction occurs. In the reverse process, when the solid is formed from its constituents, the cohesive energy becomes available as heat. The cohesive energy can be used in calculations when the (neutralized) ion penetrates the substrate or growing film, establishes bonds and becomes part of the bulk. For very low energy ions that do not penetrate but stick to the surface, the surface bonding energy should be used, which is generally less than the cohesive energy because of reduced coordination at the surface.

In the sputtering and ion implantation community, however, the surface binding energy is generally assumed to be the same as the cohesive energy or heat of sublimation because real-world surfaces are often rough and polycrystalline [73, 74]. In fact, it has been found that the surface binding energy even exceeds the cohesive energy by 30-40% which can be associated with the role of defect creation and annealing [75, 76]. For example, step-edge formation on Cu(111) costs about 0.25 eV per step-edge atom. Removing one terrace atom on a hexagonal (111) terrace produces a small “vacancy island” with a six-atom perimeter, so the added step energy is about $6 \times 0.25 \text{ eV} = 1.5 \text{ eV}$ [77].

To illustrate the complication introduced by defects, different scenarios will explain the situation.

- a) Suppose, hypothetically, the arriving particle becomes perfectly substitutional with no new defects created. For this to work, there must be step-flow growth to the surface with no energy spent. Then the heat that becomes available is E_{coh} . For example, if a copper atom becomes inserted into copper without defect creation, $E_{coh} = 3.5 \text{ eV}$.
- b) Suppose the arriving atom fills a pre-existing vacancy. In that case, not only the cohesive energy becomes available but also the vacancy formation enthalpy. For example, using copper as a test material, the available heat would be $E_{coh} + E_{vacancy} = 3.5 \text{ eV} + 1.2 \text{ eV} = 4.7 \text{ eV}$.
- c) Suppose the arriving atom becomes a self-interstitial (SI). Often, that results in a dumbbell defect, a point defect where two atoms share one lattice site because it is energetically more favorable. The energy available as heat is the cohesive energy reduced by the interstitial strain energy. Using again copper as an example, the lowest self-interstitial energy is the $\langle 100 \rangle$ dumbbell energy, which is almost as large as the cohesive energy, hence $E_{coh} - E_{SI} = 3.5 \text{ eV} - 3.3 \text{ eV} = 0.2 \text{ eV}$. Most of the energy is stored as strain energy. The barrier for migration of self-interstitials in copper is only $O(0.1 \text{ eV})$, so they tend to move, for example to the surface. This explains the mechanism of film growth “from below the surface”. The strain energy is released as heat when the defect anneals.
- d) Suppose the arriving atom creates a Frenkel pair (interstitial plus a vacancy). The energy that becomes available as heat is the cohesive energy minus the defect energy which is composed of a contribution

of interstitial and vacancy formation. For copper, for example, we have $E_{coh} - (E_{SI} + E_{vacancy}) = 3.5 \text{ eV} - (3.3 \text{ eV} + 1.2 \text{ eV}) = -1.0 \text{ eV}$, which means that the process is endothermic and actually requires energy, which is possible due to the kinetic, non-equilibrium nature of subplantation given the kinetic energy of the arriving atom.

These are not the only possible scenarios. For example, the arrival of rather energetic (neutralized) ions may result in extended defects such as interstitial loops or stacking fault tetrahedrons, especially when the initial ion energy was very high (keV to MeV) [78-80]. Many atoms are involved in these defects, and heat becomes available only when the defect anneals. That is interesting in the context of non-equilibrium heating and microstructure formation because not all transient processes need to be completed within O(100 ps) or faster.

Setting aside the reduction of heat by defect formation, let us now consider the cohesive energy (strictly speaking the enthalpy) for alloys and compounds. It may be calculated as the sum of the negative formation enthalpy of the solid and the formation enthalpies of the gaseous atoms related to the solid [81]. In the case of VN, for example, this reads

$$\Delta_{coh}H(VN, s) = -\Delta_fH(VN, s) + \Delta_fH(V, g) + \Delta_fH(N, g). \quad (19)$$

In such calculation, the unit kJ/mol is commonly used, where "mol" refers to a mole of the structural unit, which consists in the case of VN of two atoms, vanadium and nitrogen. Using formation enthalpy data from NIST [82]: $\Delta_fH(VN, s) = -217.15 \text{ kJ/mol}$ (at room temperature), $\Delta_fH(V, g) = 515.47 \text{ kJ/mol}$, $\Delta_fH(N, g) = 472.68 \text{ kJ/mol}$, we arrive at $\Delta_{coh}H(VN, s) = 1205.3 \text{ kJ/mol}$ which converts to 12.49 eV/(VN structural unit), which is in agreement with the value Ravi reported [83]. This is approximately 6.25 eV/atom when averaged of the two constituent atoms. This value is smaller than the (cumulative) ionization energies but still a significant fraction of the potential energy.

5.6. Reduction of heating by loss of surface atoms

If the arriving (neutralized) ion has sufficient kinetic energy, it causes a collision cascade that may lead to sputtering of surface atoms [84]. The sputtering yield $\gamma_{sputter} = \overline{N}_a / N_{primary}$ is defined as the average number of sputtered atoms per incident ion, which is found by observation of many events. For film deposition condition at a substrate, where the kinetic energy of ions is O(10-100 eV), we have $\gamma_{sputter} < 1$. Sputtering is substantial under ion etch conditions such as target sputtering with magnetrons [38] or with ion beams [85], where the yield can exceed unity. The latter is important for self-sustained or even gas-free magnetron sputtering [86, 87].

The energy needed to remove a surface atom is the surface binding energy E_{SB} . The kinetic energy of sputtered atoms can be described by the Thompson distribution, equation (7), which has a peak (the most likely energy) at about $E_{kin,a} \approx E_{SB}/2$ [35, 38, 88].

In the case of highly charged ions, the extremely high potential energy of the arriving ion can cause surface atoms to be emitted (potential sputtering) [65, 89]. This is mentioned for completeness but generally not relevant in the context of film deposition.

5.7. Reduction of heating by secondary electron emission

Besides causing sputtering, primary ions also cause the emission of secondary electrons, which reduces the heating effect of ions, hence we need to include term 7 in equation (12). One generally distinguishes kinetic and potential emission [90, 91]. Analogously to sputtering, one can define a yield of secondary electron emission by primary ion impact: $\gamma_{SE}^i = \overline{N_{SE}^i} / N_{primary}$, where $\overline{N_{SE}^i}$ is the average number of secondary electrons per incident ion. For coating situations with its relatively low kinetic ion energies, potential emission is dominant, and we find $\gamma_{SE} \sim O(0.01 - 0.1)$ [92]. However, the yield depends on the surface conditions and can exceed $O(1)$ [93]. It is long known that at least for the case of electron emission from a metal by noble gas impact, electrons are ejected by a process of Auger neutralization in which the interaction of two conduction electrons causes one electron to neutralize the ion in the ground state and the other to be excited into the continuum above the filled band [94]. The observed yield γ_{SE} is determined by the probability that these excited electrons escape from the metal.

For singly charged noble gas ion impact, Baragiola and coworkers [95] found the experimental fit

$$\gamma_{SE} = 0.032(0.78E_i - 2\phi) \quad (20)$$

where E_i is the ionization energy of the arriving ion. We see that equation (20) contains the ionization energy but not the kinetic energy of the arriving ion, which is typical for potential emission.

To complete the energy term 7 in equation (12) we need some information on the kinetic energy of the emitted secondary electron. This was measured to be low, $E_{kin,SE} \sim O(1 \text{ eV})$ [96]. For slow ions, the maximum energy that a secondary electron can have is the “excess energy” [97]

$$E_{SE,max} = E_i^{cum} - (Q+1)\phi \quad (21)$$

where E_i^{cum} is the cumulative ionization energy defined in (14). An ion of charge state Q needs to cause the emission of $Q+1$ electrons to become neutralized *and* to produce the secondary electron that escapes from the surface.

5.8. Simple examples

After we have discussed the seven terms in (12), let us consider two simple examples, the approach of a Cu^+ ion from a HiPIMS plasma and the example of a Cu^{2+} ion from a cathodic arc approaching the surface a growing copper film. Let's further assume, for the sake of this example, that the substrate is biased -100 V relative to the plasma potential. Using this reference circumvents the difficulties associated with the fact that the plasma potential may not be the same as the ground potential, the common practical reference potential. The terms in equation (12) deliver the contributions as shown in Table 1.

Table 1: Examples of the average effective heating energy brought to a surface, namely by one Cu^+ ion from a HiPIMS plasma, and the example of a Cu^{2+} ion from a cathodic arc plasma, both at substrate bias of -100 V.

Term number in (12)	Explanation	Example of Cu^+ from HiPIMS plasma	Example of Cu^{2+} from cathodic arc plasma
1	Most likely kinetic energy before acceleration in the sheath	20 eV [98]	57 eV [27]
2	Kinetic energy gain in the sheath of 100 V	100 eV	200 eV
3	Cumulative ionization energy minus Q -times the work function	3.1 eV [41, 99]	18.8 eV [41, 99]
4	Excitation energy. Uncertain. Negligible in comparison to other contributions	0	0
5	Cohesive energy minus defect energy (assuming a self-interstitial is formed) $E_{coh}(\text{Cu}) = 3.5 \text{ eV}$ minus $E_{SI}(\text{Cu}) = 3.3 \text{ eV}$	0.2 eV [84]	0.2 eV [84]
6	Reduction of heating due to loss of surface atoms, $\gamma_{\text{sputter,Cu}}(257 \text{ eV primary}) = 1.0$, $\gamma_{\text{sputter,Cu}}(120 \text{ eV primary}) = 0.5$, $E_{SB} \approx E_{coh} = 3.5 \text{ eV}$ plus the most likely kinetic energy $E_{SB}/2$	-2.62 [84]	-5.25 eV [84]
7	Loss of energy by secondary electron emission $\gamma_{SE}(\text{Cu}^{2+}) = 0.5$, $\gamma_{SE}(\text{Cu}^+) = 0$, $\phi = 4.6 \text{ eV}$, most likely kinetic energy $\sim 1 \text{ eV}$	0 [84]	-2.8 eV [84]
	total	$\approx 121 \text{ eV}$	$\approx 268 \text{ eV}$

We see that the majority of the effective heating energy stems from the kinetic energy contribution, in these examples about 99% and 96%, respectively. The relative contribution of the potential energy is higher if higher charge states are considered and less bias is applied.

6. Heating by electrons

When an electron in a plasma-based deposition process arrives at a surface, it is very likely absorbed, and if that is the case, it contributes to heating. To discuss this in more detail, let us consider a metal where electrons in the conduction band are Fermi-distributed: they fill the “sea of Fermi electrons” up the Fermi level. If the arriving electron is captured, it falls into the Fermi sea and delivers the energy

$$E_e = \underbrace{E_{e0} - e(V_{plasma} - V_{surface})}_{\text{kinetic energy}} + \underbrace{\phi}_{\text{potential energy}} - \underbrace{\gamma_{SE}^e(\phi + E_{kin,SE})}_{\text{loss}} \quad (22)$$

where E_{e0} is the electron energy far from the surface (before the electron is affected by the sheath), the minus sign in front of the elementary charge e accounts for the fact that electrons are negative, and ϕ is the work function. The difference between plasma potential and the surface potential is the sheath voltage leading to deceleration of electrons if $V_{sheath} = V_{plasma} - V_{surface} > 0$ and acceleration in the opposite case. The labels “kinetic energy” and “potential energy” in (22) are valid for the moment when the electron reaches the surface: the distribution among the energy forms is different at other locations. The last term in (22) is the loss associated with the emission of secondary electrons, where the yield is γ_{SE}^e .

In the special and physically rather unlikely case that the surface is exactly at plasma potential, illustrated in Fig. 9, the second term of the kinetic energy in (22) is zero. In the framework of classical physics there is no barrier that hinders the capture of electrons: all electrons arriving at the surface will be captured. They deliver their kinetic energy E_{e0} and their potential energy ϕ when they drop into the sea of Fermi electrons. One can think of the reversal of thermionic emission: For electron emission, one needs to invest the work function ϕ , and in capture, this energy leads to heating of the capturing metal.

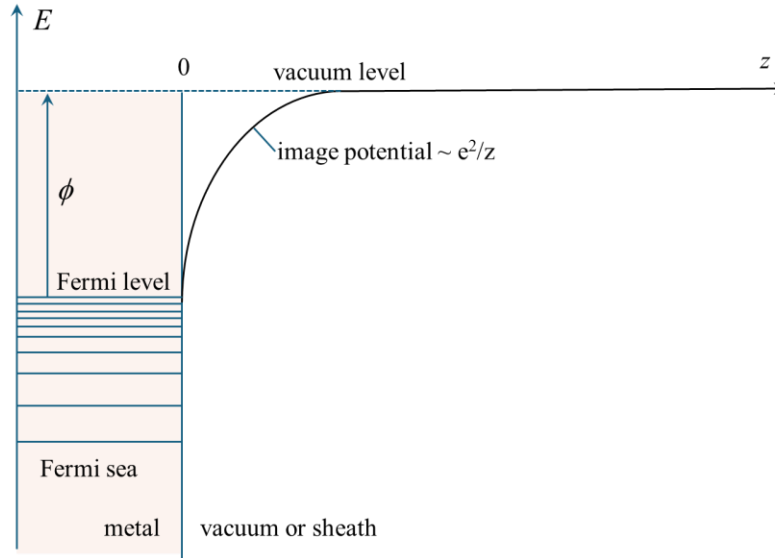


Fig. 9. Potential barrier for the situation when there is no external field present.

The potential energy curve is curved just before the electrons arrive. This is caused by the image charge acceleration due to the attractive force between the electron and image of opposite sign in the metal. In analogy to (15), the accelerating force is

$$F(d) = e^2 / (4\pi\epsilon_0 (2z)^2) \quad (23)$$

which is only applicable for distances shorter than the plasma's Debye length. The formula cannot be applied when the electron is very close to the surface. To avoid the unphysical singularity for $z \rightarrow 0$, one

introduces a near-surface matching point $z_0 \approx 0.1 - 0.3$ nm which regularizes the image charge term close to the surface. Regularization splices the asymptotic $1/z$ potential to a density functional theory (DFT) potential of the surface [100], and thus (23) should be written as

$$F(d) = e^2 / \left(4\pi\epsilon_0 (2(z + z_0))^2 \right). \quad (24)$$

The electron's potential energy as function of distance z from the surface can be written as

$$E_{pot}(z) = \phi - \frac{e^2}{16\pi\epsilon_0(z + z_0)} \quad \text{for } z > 0. \quad (25)$$

The reduction in potential energy close to the surface is accompanied by an equal increase in kinetic energy and therefore image charge acceleration does not constitute a separate energy gain. To illustrate the smallness of the image charge contribution, we can write

$$\Delta E_{image}(z_1 - z_2) = \frac{e^2}{16\pi\epsilon_0} \left(\frac{1}{z_1} - \frac{1}{z_2} \right) \quad (26)$$

which gives about 0.072 eV when the electron is 5 nm from the metal and about 0.36 eV when reaching 1 nm distance.

In practically all cases, there is an electric field, for example due to the presence of a sheath. Most often, the surface is negative relative to the plasma potential, decelerating electrons coming from the plasma. In the presence of the field $\mathcal{E}$, the potential energy as a function of distance from the surface can be written as

$$E_{pot}(z) = \phi - e\mathcal{E}z - \frac{e^2}{16\pi\epsilon_0(z + z_0)} \quad \text{for } z > 0 \quad (27)$$

which is illustrated in Fig. 10 (we use the symbol $\mathcal{E}$ for the field to distinguish it from the symbol E for energy).

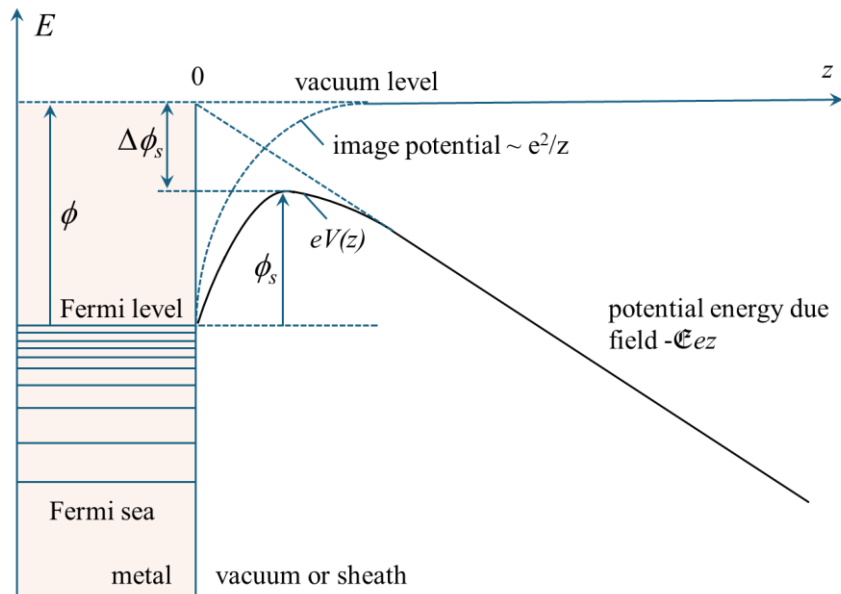


Fig. 10. Potential barrier for the situation when the surface potential is lower than the plasma potential, as it is typical for negatively biased substrates, i.e., a field associated with a positive space charge layer (sheath).

Under these conditions, the potential energy curve has a maximum at $dE_{pot}/dz = 0$, giving the distance of the maximum from the surface as

$$z_{\max} = \sqrt{\frac{e}{16\pi\epsilon_0\mathcal{E}}} \quad (28)$$

and the lowering of the height of the potential barrier as

$$\Delta\phi_S = \sqrt{\frac{e^3\mathcal{E}}{4\pi\epsilon_0}}, \quad (29)$$

which is known as the Schottky effect [101, 102]. The effective barrier height is reduced

$$\phi_{eff} = \phi - \Delta\phi_S. \quad (30)$$

This reduction allows more electrons from the plasma to reach the surface than without such reduction, their kinetic energy in the plasma in the direction of the surface need to satisfy the (reduced) condition

$$E_{e0} > eV_{sheath} - \Delta\phi_S. \quad (31)$$

If an electron overcomes the barrier and actually reaches the surface, it delivers the energy according to equation (22).

Now we consider the opposite field case, which can be realized for example through the application of a positive bias, so we have $(V_{plasma} - V_{surface}) < 0$. The electric field $\mathcal{E} = -\nabla V$ points from the plasma to the surface (Fig. 11).

In that case, there is no barrier, and all approaching electrons are accelerated and pushed into the Fermi sea. The potential energy is as before given by (27) and energy delivered to the surface by equation (22), just this time the electrons are accelerated before hitting the surface.

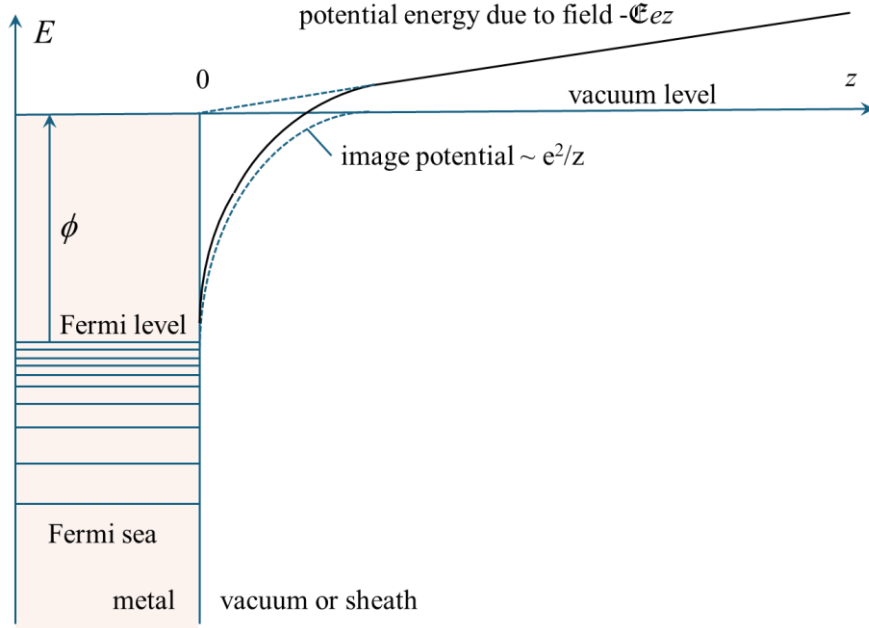


Fig. 11. Potential energy curve when the surface potential is higher than the plasma potential, as it is typical for positively biased substrates.

The image interaction always accelerates the electron toward the surface, but its contribution does not appear as an extra add-on in (22) because it is already accounted for. The image charge acceleration is just a redistribution of potential and kinetic energy. Therefore, equation (22) is applicable for all field directions and in the absence of a field. In the case of a decelerating field, the work function is reduced by the Schottky correction (29), which lowers the threshold for the kinetic energy of plasma electrons required to reach the surface. This reduction affects the flux of arriving electrons but not the energy each electron delivers.

In case of $(V_{plasma} - V_{surface}) < 0$, as shown in Figure 11, the effective secondary electron yield is $\gamma_{SE}^e = 0$ because all emitted electrons immediately return to the surface due to the electric field.

When the electron enters the metal, it causes first hot-electron excitations on a timescale $O(fs)$, followed by the thermalization of electrons and excitation of phonons (lattice vibrations), which happens on a timescale $O(1\ ps)$ [103]. The metal is non-linearly heated, not unlike the sub-picosecond electron-lattice heating observed in ultrafast (fs) laser ablation [104].

Now let us look at additional effects that affect heating of the metal by electrons. While there is no barrier to absorption in the classical picture, some slow electrons ($< 10\ eV$) are quantum-mechanically reflected (backscattered) by the abrupt potential change at the surface (quantum reflection/mismatch of wavevectors) [105]. Furthermore, (primary) electrons absorbed can cause secondary electron emission, especially when the primary kinetic electron energy upon impact is in the range 50-500 eV. Each escaping electron removes ϕ plus its kinetic energy, which is on average 2-5 eV [106, 107].

7. Heating by absorbed photons

In plasma processing, the surface of substrate or growing film is subject to more or less intense radiation of light which generally involves the entire spectrum from the infrared (IR), to the visible (VIS) and ultraviolet (UV) and even vacuum-UV (VUV) region. The spectrum is usually composed of a black body component and numerous spectral lines. Photons have the energy

$$E_{hv} = h\nu \quad (32)$$

where h is Planck's constant and ν is the frequency, which is related to the wavelength λ by $\nu = c/\lambda$, with c the speed of light in vacuum. UV photons are therefore particularly energetic. The arriving photon contributes to heating if it is absorbed in the growing film. Not all arriving photons are absorbed because, depending on the material, many can be reflected (typical for metal) or transmitted (typical for insulating materials with bandgap $E_{BG} > E_{hv}$). Much has been published about interaction of light with thin films and matter [108-113], and therefore only some key points in the context of film heating by photon absorption are summarized here.

We start with the microscopic picture looking at the absorption of individual photons. When an IR or VIS photon is absorbed by a metal, it will excite electrons of the conduction band (free carrier absorption, Drude model), while UV photons involve interband excitation. Hot conduction electrons rapidly thermalize within O(10-100 fs) and the heated electrons couple to the lattice by electron-phonon scattering, which occurs within O(sub-ps to few ps). The lattice hot spot quenches close to the general temperature O(100 ps). For metals, the photon electromagnetic field penetrates about the skin depth

$$\delta = \lambda / (4\pi\kappa) \quad (33)$$

where κ is the imaginary part of the complex refractive index

$$n(\lambda) = n(\lambda) + i\kappa(\lambda), \quad (34)$$

with a wealth of data in Palik's handbooks [114-116]. Ultrathin films (nm) have higher absorption than thicker films due to reduced reflectance, and additionally, plasmonic effects can occur when the "film" consists of conducting islands [117, 118]. Photoemission of electrons, if it occurs, reduces net heating. Photoemission is relevant only for UV photons with

$$h\nu > \phi \quad (35)$$

where ϕ is the work function, as used before in this article. The absorption mechanism of semiconductors include (i) band-to-band absorption when

$$h\nu > E_{BG}, \quad (36)$$

(ii) excitonic features near the band gap energy E_{BG} , (iii) sub-band gap absorption via Urbach tails and defects, and (iv) free-carrier absorption in IR that rises with doping. Most often electron-hole pairs recombine through non-radiative recombination producing phonons (heat).

The absorption of wide band-gap materials (transparent, insulators) is small and depends on defects and impurity bands. In the UV, $h\nu > E_{BG}$, absorption rises sharply.

Now we look at heating from a macroscopy viewpoint. The energy balance is split between absorptance $A(\lambda)$, reflectance $R(\lambda)$ and transmittance $T(\lambda)$ such that [112]

$$A(\lambda) + R(\lambda) + T(\lambda) = 1. \quad (37)$$

To quantify the situation, we need to take into account the absorbance of the film material. From the plasma we have the spectral angular irradiance $G(\lambda, \theta, \varphi)$ (in $\text{Wm}^{-2}\text{nm}^{-1}\text{sr}^{-1}$), where θ is the angle to the surface normal and φ is the azimuthal angle. The absorbed power per area is obtained by integrating $G(\lambda, \theta, \varphi)$ over the wavelength and angles. If the film is optically opaque, we have $T(\lambda) \approx 0$ and $A(\lambda) = 1 - R(\lambda)$. For a weakly absorbing film of thickness d , neglecting interference effects, we have

$$A(\lambda) \approx (1 - R(\lambda))(1 - \exp(-\alpha(\lambda)d)) \quad (38)$$

where

$$\alpha = \frac{4\pi\kappa(\lambda)}{\lambda} \quad (39)$$

is the absorption coefficient. These formulas may be good for estimates, but proper calculations should be based on Maxwell's equations and the complex Fresnel transfer matrix, where for example polarization and interference effects can be accounted for [113].

Since photons and plasma particles (ions, electrons) arrive at the growing film, parsing their effects is difficult and generally not done. We can however state that the absorption of individual photons cannot deliver more than the photon energy, which is generally O(1-10 eV) for our processing plasmas. The individual effects of photons to non-equilibrium heating are therefore much smaller than those of individual ions and even individual electrons. The effects of photon absorption are cumulative, contributing to enhancing the equilibrium temperature. In fact, one common way of establishing the desired (equilibrium) deposition temperature is through radiative heaters or heat lamps.

One important difference between heating caused by ion, electron and photon processes is the depth of penetration of the primary heat-generating particles. For ions with a kinetic energy of 1 keV or less, all processes happen in the near surface layer, typically at a depth of O(nm). The penetration of photons is dictated by the skin depth (33), which is very shallow (nm) in the case of metals, and can be much larger than the film thickness depending on the optical properties of the semiconductor or insulator under consideration.

8. Discussion

There is a vast literature on deposition using ions and electrons to utilize non-equilibrium heating for the tuning of density, microstructure, stress, and all resulting properties. No attempt is made here to capture this literature, rather, only a few points are made in this discussion to round up previous explanations.

8.1. Use of electron beams

In the general equation on heating by electrons, equation (22), the electron energy E_{e0} designated the average electron energy before the electron is affected by the electric field of the sheath. One may distinguish the cases where the electrons come from the processing plasma or where energetic electrons are supplied by a dedicated electron beam source, for example in electron beam evaporators where electrons have energies O(1-10 keV). Accordingly,

$$E_{e0} = \begin{cases} E_{e,beam} & \text{for energetic beam electrons} \\ k_B T_e & \text{for electrons coming from plasma} \end{cases} \quad (40)$$

For beam electrons, only the E_{e0} term is relevant in (22) because it is much larger than all others: they can be neglected. For an electron from a plasma, the term $E_{e0} = k_B T_e$ represents the average energy of an electron from a Maxwell distribution. Note that we considered the average energy contribution of an individual electron; if we take the flux of electrons into account, where energetic electrons arrive more frequently than slower electrons; averaging over the distribution in one direction gives $2k_B T_e$ [119].

8.2. Processing with bipolar pulses – the use of ions and electrons

Biasing is usually performed with negative polarity in order to accelerate positive ions. As a “side effect”, electrons are repelled. Ion acceleration is sometimes wanted to intentionally etch the surface before deposition, for example in the arc bond sputtering (ABS) process [120], which was later replaced by high power impulse magnetron sputtering (HiPIMS) ion etching before deposition [121].

We should recall that the physically relevant bias is always the potential difference between the substrate surface and the plasma as expressed in equation (11). This almost trivial statement deserves some thoughts.

First, in practice, one often uses earth ground as the reference, and the actual bias is therefore not exactly known. The plasma potential is generally close to the most positive element facing the plasma (such as an anode), and that is often good enough for practical purposes.

Second, by changing the relation between surface and plasma potential, one can switch from an ion acceleration to an electron acceleration regime and thereby utilizes the benefits of the respective heating process in controlled ways. This has become very popular in recent years, in particular in the context of bipolar HiPIMS [122-129] although the original motivation for bipolar pulsing was to enhance the deposition rate or to compensate for charge-up effects of insulating films. Bipolar bias techniques are usually asymmetric in voltage, current, and phase duration, and the process can be optimized by selecting these three parameters. Asymmetry allows us to account for the much smaller mass and higher mobility of electrons, compared to ions. When the surface does not show high conductivity, unipolar negative pulsed substrate bias can be sufficient with the argument that the sheath collapses in the bias-off time, and plasma electrons can reach the surface without the intentional positive bias because positive charge has accumulated during the negative pulse. To obtain the heating effect from electrons, the positive bias does not need to be applied in a bipolar mode; one may choose to use an extended electron-based

substrate heating phase before the main deposition starts [130]. The principle of heating by plasma electrons via positive bias can be broadly applied, for example to reduce film stress in the deposition of TiB_2 [131].

Third, one has the freedom to pick a reference potential. In most practical cases, one biases the substrate and uses earth ground as the reference. There may be situations where biasing of the substrate is technically not possible, for example when the substrate is handled by a grounded robotic system. In this case, one has the option to shift the plasma potential relative to the substrate potential. This *plasma biasing* (as opposed to *substrate biasing*) has been demonstrated for the deposition of diamond-like carbon [132, 133] and (V,Al)N films [45, 134]. It requires biasing of the plasma source including the related power supplies. Accordingly, floating output power supplies or isolation transformers to the mains power may be necessary. Furthermore, the inside of the grounded chamber may need to be protected by floating shields because shifting the plasma potential to very high positive values can have undesirable side effects, namely unwanted sputtering from all grounded components, desorption of adsorbed water vapor, and even arcing from the relatively negative components of the system.

Finally, it should be mentioned that it is possible to simultaneously shift both the substrate potential (negative with respect to ground) and the plasma potential (positive with respect to ground), which makes sense if the goal is to obtain an overall very high difference while keeping the high voltage equipment at modest cost [135].

8.3. Subplantation growth, non-equilibrium heating and stress evolution

Films obtained by deposition with ions of high kinetic energy usually exhibit high compressive stress. One generally distinguishes extrinsic and intrinsic stresses of a coating. The extrinsic or thermal stress is caused by the differences in thermal expansion between substrate and coating materials, and it develops when substrate and coating cool down from the deposition temperature T_{dep} to room temperature, T_{RT} . The extrinsic stress can be compressive or tensile, depending on the difference between the coefficients of thermal expansion, α_{sub} and α_{coat} [136],

$$\sigma_{extr} = -(\alpha_{sub} - \alpha_{coat})(T_{dep} - T_{RT}) \frac{Y}{1 - \nu}, \quad (41)$$

where Y and ν are the elastic (Young's) modulus and Poisson's ratio of the coating material, respectively. Extrinsic stress rarely exceeds 1 GPa [136, 137] and therefore we proceed to consider intrinsic or growth stress, which can reach much higher values.

Stress causes strain energy which can drive film delamination [138], especially when we consider growth by subplantation. Insertion of ions under the surface causes densification of the region where the ions come to rest. Densification (in the sense of atoms/volume) is related to compressive stress. If the material is a metal it can yield to stress by plastic deformation. If the material is covalently bonded, it will resist plastic deformation; it becomes metastable and tends to show a high coordination of bonds if more than one phase exists. Most famously, carbon establishes sp^3 bonds, diamond bonds, as opposed to the sp^2 bonds of less dense graphitic material.

For a thin film, stress σ is related to strain ε by [139, 140]

$$\sigma = \frac{Y}{1-\nu} \varepsilon . \quad (42)$$

Relating this to the kinetic energy E_i of arriving ions, one obtains [139]

$$\sigma(E_i) \propto \frac{Y}{1-\nu} \frac{E_i^{1/2}}{(\Gamma/j + \kappa E_i^{5/3})} , \quad (43)$$

where Γ is the net deposited flux, j is the ion bombarding flux, and κ is a material dependent parameter. This produced a characteristic curve (Fig. 12). Bilek and McKenzie [138, 141] point out that the time for energy removal from thermal spike volume around the point of insertion (the “quench time”) determines whether the material is densified (compressive stress increases), or atoms have time to rearrange their bonding structure, allowing the heated volume to expand toward the surface (stress is relieved). The quench time depends on the size of the heated volume, which in turn depends on the energy of the inserted ion.

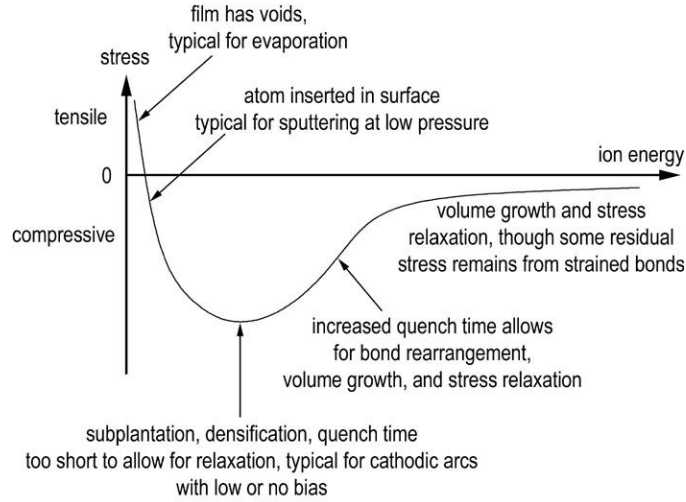


Fig. 12. Schematic presentation of stress evolution as a function of the kinetic energy of ions impacting the surface (from [7], Chapter 8, with permission by Springer Nature).

One could assume that the region affected by the thermal spike is spherical with the radius R_{th} (Fig. 13). Then the quench time is proportional to the square of the thermal spike or to the 2/3-power of the ion energy [142],

$$t_{quench} \propto R_{th}^2 \propto E_i^{2/3} . \quad (44)$$

For $E_i \sim 100$ eV, the quench time was calculated to be less than 1 ps, which is too short for significant rearrangement of atoms, rather, the atoms will use a high bond coordination with the available neighbors to *minimize the total system energy under constraints*.

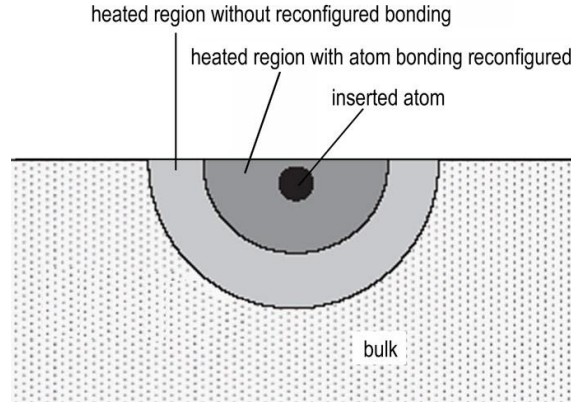


Fig. 13. Simplified geometry for developing a model for stress generation and relaxation by subplantation: the thermal spike volume is assumed to be spherical with the inserted atom in the center. The stress is accumulated in the light gray region, the size of which is proportional to $E_i^{2/3}$ (from [138] with permission by Elsevier).

The volume of the thermal spike is proportional to $\kappa(E_i - E_B) = (2/3)\pi R_{th}^3$, where E_B is the energy barrier for the ion to be inserted into the surface. The volume of the light gray region (Fig. 13) can be calculated as

$$V_{stressed} = 2\pi R_{th}^2 d\tau = 2\pi \left(\frac{\kappa}{2\pi} \right)^{2/3} E_i^{2/3} d\tau, \quad (45)$$

where $d\tau$ is the thickness of the interfacial region where atom movement is restrained by bonds to unaffected atoms in the bulk; the thickness $d\tau$ is about one bond length and remains that way even as the thermal spike volume grows at higher ion energies. The number of stressed sites is proportional to the volume $V_{stressed}$ and one can write a parametric equation for stress

$$\sigma = C(E_i - E_B)^{2/3}, \quad (46)$$

where C and E_B are material constants.

Looking now at ions inserted below the surface, with a kinetic energy clearly exceeding the 100-200 eV level, their effect on stress is quite different. An impacting ion creates a larger volume of a thermal spike, i.e., a transient melt shown in dark gray in Fig. 13, allowing the atoms of this temporary liquid to access many possible bonding configurations. Those atoms can remain in a thermodynamically preferred configuration in which the combined bond and strain energies are minimized. This is often not the phase of highest density, rather, the thermal spike volume can expand and raise the level of the free surface. The possibility of raising the surface, thereby minimizing the strain energy without constraint, is the basis for ion-induced stress relief by energetic ion bombardment. Experimentally it has been observed that only a small fraction of high energy ions is needed to relieve stress, and that saturation of such stress relief

occurs when the percentage of the energetic ions is still small. Saturation of stress relief occurs when the volume regions of unconstrained rearrangement start to overlap.

Assuming that film growth occurs with both low energy ions and atoms, and high energy ions of energy E_i , the volume V still untreated by a thermal spike is reduced exponentially [138],

$$\frac{V}{V_0} = \exp\left(-\frac{V_{spike} N}{V_0}\right), \quad (47)$$

where V_0 is the volume of a film slab under consideration, $V_{spike} = E_i / (E_A n_a)$ is the volume of each thermal spike, E_A is the average energy given to atoms of the thermal spike volume, $N = n_a V \delta$ is the number of high energy impacts before the slab is covered by more deposited atoms, n_a is the atom density of the slab, $\delta = w f$ is the duty cycle of high energy ions, produced by pulsed biasing, for example, with w being the pulse width of the bias and f the bias pulse repetition frequency. Alternatively, δ could be the fraction of energetic ions produced by other means such as an external ion source. While these considerations are developed with the plasma immersion technique [143] in mind, the underlying physics and derivations are rather general. Using the above expressions, (47) becomes

$$\frac{V}{V_0} = \exp\left(-\frac{E_i f w}{E_A}\right). \quad (48)$$

The stress can be assumed to vary with the volume fraction treated by high energy ions, from the as-deposited value, σ_0 , to the relaxed, residual value after ion treatment, σ_{res} , leading to

$$\sigma = \sigma_0 \frac{V}{V_0} + \sigma_{res}. \quad (49)$$

Using (48) gives

$$\sigma = \sigma_0 \exp\left(-\frac{E_i f w}{E_A}\right) + \sigma_{res}. \quad (50)$$

If we use (46) to express the stress generated by moderately energetic ions (those with energy E_G , inserted into or just below the surface), and replace the stress-relieving ion with energy $E_i = E_R$, one obtains

$$\sigma = C(E_G - E_B)^\chi \exp\left(-\frac{E_R \delta}{E_A}\right) + \sigma_{res}. \quad (51)$$

where the exponent χ could be 2/3, as suggested by (46), but other exponents such as $\chi = 1$ or $\chi = 1/2$ give also a good fit to experimental data for a number of materials such as TiN [144], AlN [139], BN [145], a-SiH [146], SiBCN [147], and hard amorphous carbon [148]. The different exponents can be interpreted to deviations from the idealized spherical shape of the thermal spike, for example, one could consider a cylindrical geometry of the thermal spike volume [149]. It turns out that the choice of the exponent χ is not very critical for the quality of the fit [138]. The approach will be illustrated by the special case of carbon, see next section.

8.4. The example of biasing to tune diamond-like carbon

While the focus of this review was on non-equilibrium heating effects by particle bombardment from a plasma, biasing is used to produce films of the desired composition, microstructure; in the case of diamond-like carbon, subplantation is the critical process to obtain high sp^3 content of the amorphous carbon film [9, 150, 151]. Carbon multilayer deposition is highlighted here because it shows the effect of ion energy in an illustrative way [152]. Using alternating substrate bias of -100 V and -2000 V, diamond-like carbon layers of different sp^3/sp^2 ratios were deposited (Fig. 14). It is known that subplantation with -100 V leads to material of maximum density and compressive stress.

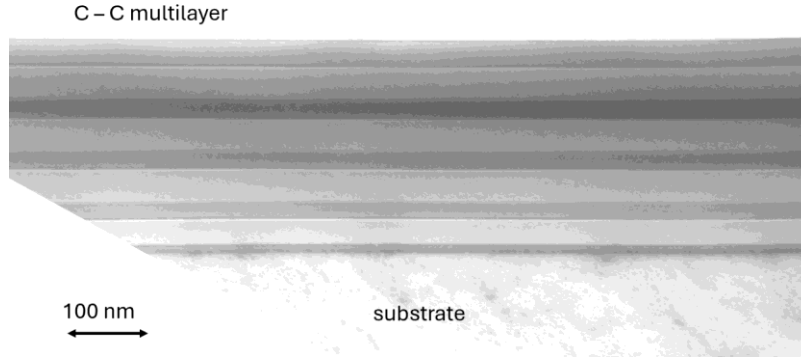


Fig. 14. TEM-cross-sectional image of a carbon-carbon multilayer deposited on silicon by filtered cathodic arc deposition under periodically alternating bias conditions: the dark layers are denser and of higher sp^3 content, deposited with pulsed bias of -100 V, while the lighter, less dense layers were deposited with pulsed bias of -2000 V. For more experimental details see [152].

8.5. Particle and energy flux diagnostics

The energy flux to a substrate was subject to investigations for many years. Due to the extremely transient and localized nature of non-equilibrium heating, all measurements of the energy flux from plasma particles and radiation effectively record only the cumulative effect of non-equilibrium heating but not the processes that occur on timescales $O(100 \text{ ps})$ and faster and areas of $O(10 \text{ nm}^2)$ and smaller. Still, various insightful techniques can be used to determine the average and cumulative energy flux to a substrate. They include, but are not limited to, (i) electrical probes (Langmuir probes, double probes, floating probes, emitting probes, etc.) [153-160], (ii) retarding field analyzers [161-163], (iii) plasma analyzers that measure ion energies/charge (for a selected mass) and ion mass/charge (for a fixed energy) [164-166], (iv) temperature measurements with thermocouples, sweeping probes, optical pyrometry and diffuse reflectance spectroscopy [167-170], and (v) calorimetric probes [163, 167, 171-175].

From the richness of these techniques, calorimetric probes are designed to directly evaluate heating effects. Figure 15 shows the principal design of such probe. The readout by a thermocouple from the backside a thick substrate illustrates that the cumulative temperature contribution by non-equilibrium

events to the resulting global temperature is measured but not the individual extremely fast and localized processes.

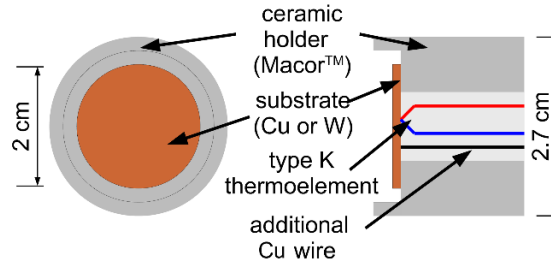


Fig. 15. Calorimetric probe based on thermocouple measurements; the readout is calibrated with a known energy source such as an electron beam (from [171], with permission by AIP Publishing).

One often tries to combine measuring techniques to gain information as comprehensively as possible [176]. For example, the thermocouple of a calorimetric probe can be “hidden” behind the grid system of a retarding field analyzer (Fig. 16) [163]. In this way, one can obtain the ion energy distribution and the energy flux density at a certain potential. Additionally, one can measure the power deposited by incoming fast neutrals when the appropriately biased grids keep away the ions [163].

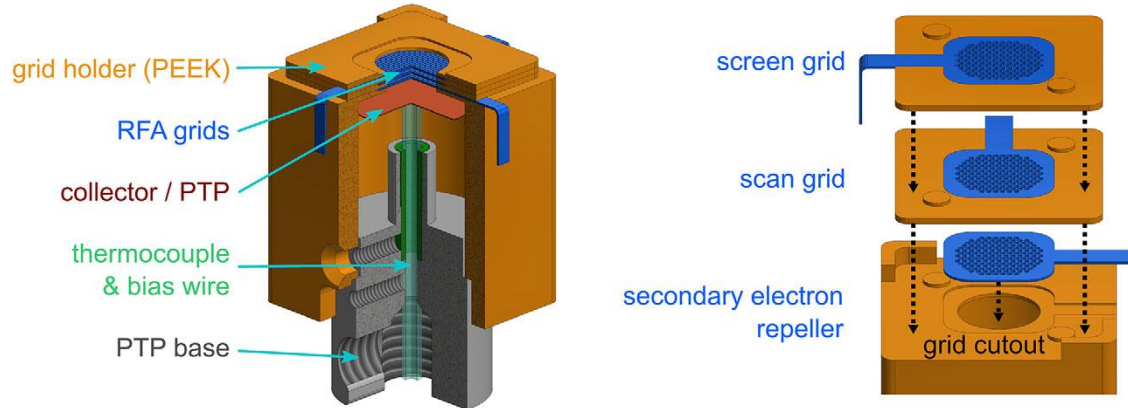


Fig. 16. Construction of a combined passive thermal probe (PTP) and a retarding field analyzer (RFA) for the measurement of ion and energy fluxes from a plasma (from [163], reuse under Creative Commons Attribution 4.0 International License).

9. Summary and Conclusions

In this review we distinguished between conventional “equilibrium” heating and extremely fast, highly localized, “non-equilibrium” heating. For the latter, the use of the term “temperature” can be questioned and in fact may not be applicable because we do not always have an atomic scale volume that

has enough particles where the underlying assumptions for heaving “temperature” of a particle assemble can be applied. The extremely fast heating events are primarily caused by energetic ions and to a lesser degree by electrons. Individual photons do not generally have enough energy to produce significant non-equilibrium events. All non-equilibrium heating effects accumulate and thereby contribute to elevating the global, equilibrium temperature. The substrate temperature results from the combined effects of intentional substrate heating and process heating composed of many individual non-equilibrium events. Non-equilibrium events caused by ions and electrons occur in the near-surface layer of the substrate and growing film. Since this is the location where the film microstructure is established, non-equilibrium heating is very effective. It allows surface and near-surface atoms to move while the rest of the substrate is not or only marginally affected.

The detailed atomistic description of ion and electron processes shows the contributions of kinetic and potential energies, where the kinetic energy usually represents a much greater fraction of the total energy contribution. The kinetic energy of ions and electrons is primarily determined by the sheath’s electric field. Hence the difference between plasma and surface potentials determines energy gain or loss. This implies that biasing the substrate and/or the plasma is the primary tool to effectively use non-equilibrium heating. An interesting window of deposition energy is the hyperthermal regime between 1 and 20 eV. In this window, particle-impact-based non-equilibrium heating effects exceed what could be possibly done by conventional heating while not yet reaching the subplantation regime where extensive defects are generated. In extension of that thought, a related field of research is to use less kinetic and more potential energy to further increase local heating while reducing the generation of defects. Keeping good control of the sheath voltage is critical, which implies the need for greater control of the plasma potential than usually done. The plasma potential, not ground, is the physically relevant reference potential.

Measurements of the energy flux, for example by calorimetric probes, are useful but capture only the cumulative part of non-equilibrium heating because the actual effects of individual impact events are too fast and too small to be registered. We see their effects in the microstructure of films, and we learn about them through modeling and simulation. This review is designed to give an overview, and future progress is likely due to extended modeling and simulation using density functional theory (DFT) and Monte Carlo (MC) methods, perhaps coupled with AI-supported validation using high resolution characterization of film materials.

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