INVESTIGATION OF THIN FILM PROPERTIES PRODUCED BY ENERGETIC IONS DEPOSITION

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ABSTRACT

One important recent trend in deposition technology is the continuous expansion of available processes towards higher ion assistance with the subsequent beneficial effects to film properties. Nowadays, a multitude of processes, including laser ablation and deposition, vacuum arc deposition, ion assisted deposition, high power impulse magnetron sputtering and plasma immersion ion implantation, are available. However, there are obstacles to overcome in all technologies, including line-of-sight processes, particle contaminations and low growth rates, which lead to ongoing process refinements and development of new methods. Concerning the deposited thin films, control of energetic ion bombardment leads to improved adhesion, reduced substrate temperatures, control of intrinsic stress within the films as well as adjustment of surface texture, phase formation and nanotopography.

***Keywords**: PVD; thin films; ion assisted deposition; ion implantation; nanostructures*

INTRODUCTION

In the last decades, thin film deposition evolved into a ubiquitously present technology [1], penetrating all major industries. Correspondingly, a large variety of thin film deposition methods is available, ranging from paints and varnishes often employed for corrosion protection, dip or spin-coating commonly used for sol-gel processes, anodic oxidation for decorative consumer goods, for different vacuum processes. By avoiding the presence of a background gas at low and very low pressures, both incorporation of impurities and scattering processes of particles are avoided, or at least minimized, in the latter group. Consequently, kinetic energies beyond the thermodynamic equilibrium are realized across several orders of magnitude.

While a large amount of literature is available describing the different processes and methods, with a different set of literature detailing the film properties and applications, a short and concise overview of processes and feasible influences on film properties, including recent advances in nanotechnology, can seldom be found. Current overviews could be consulted on more specific details of selected aspects, e.g., for the microstructural evolution during film growth detailing the influence of temperature, reactive species and ion irradiation, for ionized physical vapor deposition or stress generation and relief processes. In this paper, an attempt is made to give an introduction into different deposition technologies involving energetic ions with kinetic energies in the range from 10 to 10,000 eV, corresponding to temperatures of tens of thousands of Kelvins for the lower range.

Non-equilibrium processes are expected to dominate in the ion-surface interactions encountered during these energetic deposition processes, including ion mixing, surface sputtering and the formation of metastable phases, effects which all can be employed in modern functional coatings [2]. The understanding of the phenomenology and mechanisms is necessary to develop new structures and applications in a fast and efficient way, in contrast to the empirical exploration of a vast parameter space.

MATERIALS AND METHODS

Physical vapor deposition (PVD) is an established technology to obtain individually tailored surface coatings on various substrates [3]. For growth of epitaxial semiconductors, molecular beam epitaxy (MBE) or hyperthermal ion beam assisted MBE (IBA-MBE) is the method of choice [4], while optical coatings are mainly produced by magnetron sputtering. Hard and wear resistant

coatings with very high deposition rates are obtained from either magnetron sputtering (MS) or vacuum arc deposition (VAD) [5]. For pulsed laser deposition (PLD), similar ion energies compared to arc process are encountered [6], while ion beam assisted deposition (IBAD) [7] or plasma immersion ion implantation and deposition (PIIID) [8] leads to even higher average particle energies (see Figure 1 for a schematic overview of the typical energy ranges).

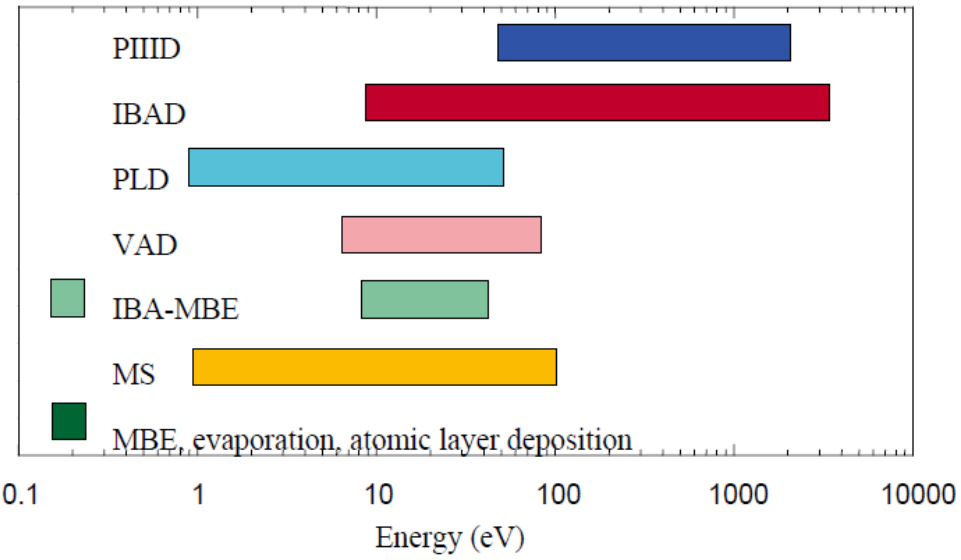

Figure 1. Typical energy ranges for different PVD processes. PIIID = plasma immersion ion implantation and deposition; IBAD = ion beam assisted deposition; PLD = pulsed laser deposition; VAD = vacuum arc deposition; IBA-MBE = ion beam assisted molecular beam epitaxy; MS = magnetron sputtering; MBE = molecular beam epitaxy.

One of the most important parameters is the average energy per incoming particle where higher values lead to an increased surface mobility [9]. With increasing the deposited energy per particle, a higher (transient) mobility of the atoms impinging on the surface is obtained, thus increasing the apparent surface temperature [10]. At identical deposition rates, the larger mobility will lead to a higher diffusivity, thus allowing a further transport from the original arrival site and earlier coalescence [11].

RESULTS AND DISCUSSION

All the thin film properties presented in this section depend on the provision of additional energy, preferably kinetic energy or potential energy from multiple charged cluster ions. However, additional factors such as chemical affinity, cohesive energy, orientation dependent surface energy and potential barriers encountered in volume, grain boundary or surface diffusion processes, always play a very important role. Hence, the mobility, respective ion damage, has to be seen in this light.

Radiation damage is the natural result of ion bombardment, which can be partitioned in nuclear and electronic energy loss. The former process describes momentum and energy transfer from the implanted particle towards nuclei of substrate atoms, while the latter is used to depict inelastic interactions with the electron system, leading to excitations on a timescale of less than 100 fs. In the energy range of 0.1–10 keV, the elastic nuclear energy loss dominates as long as projectile atoms with a mass equal or larger than carbon are used. For longer times, the excited volume increases from a few atoms towards several thousands of atoms while the average energy or—more precise the temperature of this region—translates to a few thousand or, at later stages, of several hundred K, returning to thermal equilibrium within less than a millisecond.

A multitude of parameters is experimentally (and theoretically) accessible, including the atomic structure of the interface to the substrate, important for electronic defects and adhesion, morphology and phase formation, which have to be looked upon separately.

Morphology

The morphology of the growing film, tending towards polycrystalline at lower temperatures and faster deposition rates under consideration here, can vary significantly, depending strongly on substrate temperature, ion current and ion energy. A convenient way to depict general tendencies is a structure zone diagram [12]. In the presented form by Anders, it is extended and now proposed to cover any energetic deposition from cathodic arc deposition, HIPIMS, and other forms of PVD.

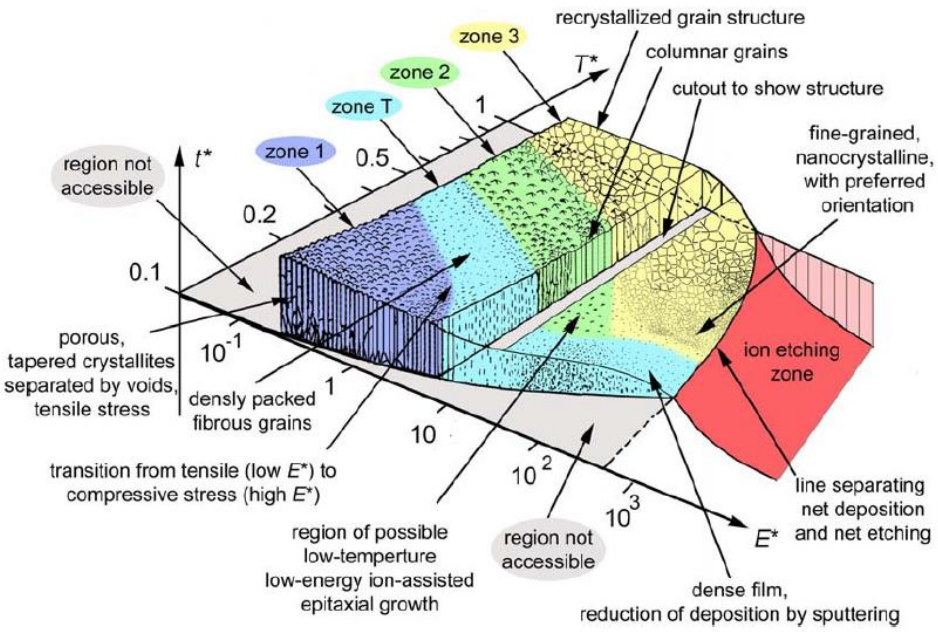

Figure 2. Structure zone diagram applicable to energetic deposition as a function of the generalized temperature *T* and the normalized energy flux *E*; *t* represents the net thickness. The boundaries between zones are gradual and for illustration only.

While many primary parameters such as target current, voltage, pressure or substrate distance will affect growth processes, they are impractical for comparison or for fundamental analysis. Hence—even for a qualitative presentation as in Figure 2 – the parameters directly controlling the film growth process must be displayed. Thus, a generalized temperature *T** (on a logarithmic scale) including the substrate temperature and any shift caused by the potential energy of particles arriving on the surface, together with a normalized energy *E** (also on a logarithmic scale) describing displacement and heating by the kinetic energy of bombarding particles, is used. Additionally, an effective thickness including consequences of densification and sputtering, even up to dominating etching effects, is presented on the third axis.

With increasing substrate temperature, a transition from a porous phase (zone 1), towards densely packed fibrous grains (zone T), followed by columnar grains (zone 2) and finally a recrystallized grain structure (zone 3) or a zone of single crystals, is observed. As a result of ion bombardment, thermal energy is replaced by kinetic energy, allowing a similar morphology at different combinations of energy and temperature, leading to competing processes of defect generation, annealing, grain nucleation and crystallite growth. Thus the different zones 1, T, 2, and 3

are delimited by approximately diagonal lines. However, as mentioned previously, an excessive ion bombardment leads to a domination of sputtering processes, thus reducing the effective, remaining film thickness. Additionally, texture effects and nanocrystalline grains may be encountered at high ion fluences. However, additional phase formation processes, especially of compounds with widely differing melting temperatures may complicate the picture in reality.

Mechanical stress

In addition to morphology, the film stress is determined by the deposited energy (as shown in Figure 3). At low energies, the films are found to be porous with a large void fraction and tensile intrinsic stress [13]. With increasing the average energy per particle to a few tens of eV, there is a transition to compressive stress as the material is densified by the impinging ions. Increasing the deposited energy even further, a maximum value for the stress is observed, ideal for the formation of cubic BN [14] and diamond-like carbon (DLC) coatings with a high sp^3/sp^2 ratio. Beyond that value, stress relaxation by thermal spikes is proposed, accompanied by a slight reduction in density, which can be observed in several different materials, e.g., t-a:C or AlN.

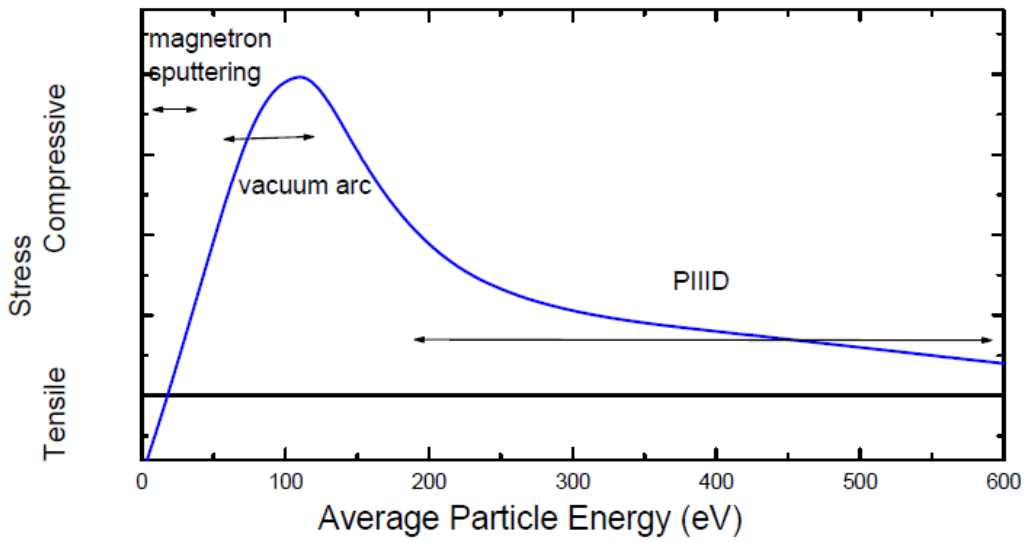

Figure 3. Evolution of intrinsic stress as a function of deposited energy. Typical energy regions for different processes are indicated.

While a continuous adjustment of the average particle energy is possible in IBAD processes, e.g., by changing the current density, the higher kinetic energy and charge-states of ions employed in vacuum arc deposition leads to a rather high threshold in energy. Thus, when using PIIID with high voltage pulses in addition to the plasma stream from an arc, a stress value close to the maximum is observed even at low, additional ion bombardment during the pulses. By increasing the pulse frequency and voltage, a direct stress relaxation is possible. At a voltage of 5 kV, a duty cycle of 5% is sufficient for a reduction by more than 90%. Thus stress engineering can be used to obtain thick, well-adhering and relaxed c-BN or hard DLC coatings.

Phase formation

For pure ion implantation at elevated ion energies beyond 10 keV, stable or metastable phase formation especially favoring high pressure, high temperature phases is often observed, as enough compressive stress is created by the forceful insertion of ions into the original atomic structure. In contrast, during thin film deposition, and nucleation processes caused by ion bombardment are always accompanied by growth of grains or columns, making a direct distinction between both

processes very difficult. From a practical point of view, this question seems to be rather irrelevant. However, when facing the scaling up of a process or a transfer to a different substrate where a different balance between substrate temperature and ion bombardment may be necessary, different technology adjustments are required to maintain the functionality of the coatings.

As several distinct processes may be influential for the phase formation, a clear separation of causal links, which is deemed necessary, yet is not always possible. When returning to DLC or BN, the major factor determining the sp^2/sp^3 ratio, respective the nucleation of cubic or hexagonal BN, the major factor is creation (or absence) of compressive stress and not the transient increase of the temperature during the stopping of the incident ions.

Detailed results for investigations of interchanging temperature and ion bombardment without additional stress effects are available, e.g., for the system Ti-O, which has been and is extensively investigated. Beside widespread use of TiO_2 thin films in optics because of their high refractive index and their stability 48, TiO_2 is known as one of the most effective photocatalysts with its photocatalytic behavior extensively studied. In addition, photoinduced superhydrophilicity is reported for TiO_2 with the water contact angle decreasing from 72° in the dark towards values of less than 10° or even 0° under illumination [15]. A large amount of work employs high deposition temperature of around 200 °C or more or post annealing-steps after magnetron sputtering [16], thus precluding the use of temperature sensitive substrates such a polymers.

The phase formation itself shows a transition from amorphous via anatase at intermediate conditions towards rutile for high temperature, respective high particle energies [17], as schematically depicted in Figure 4.

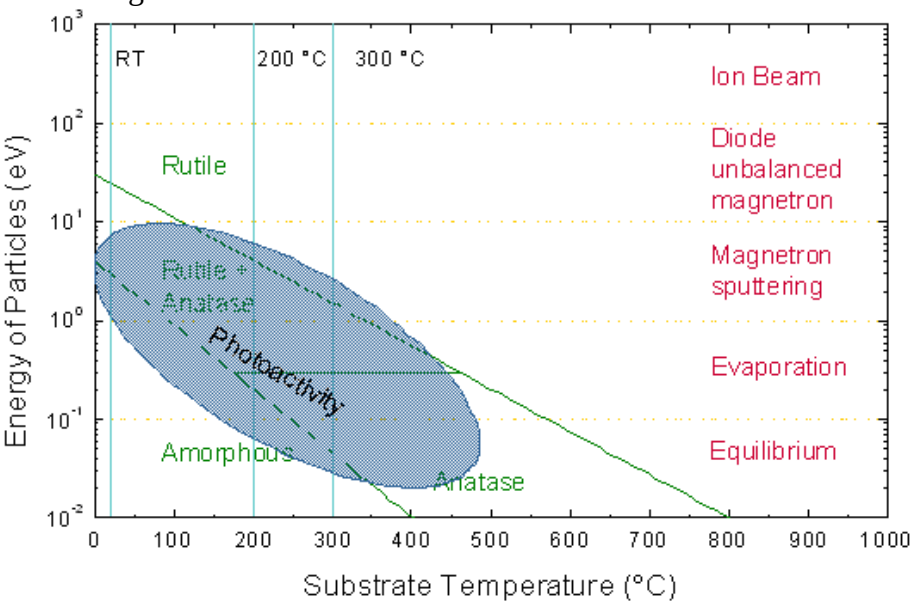

Figure 4. Identification of process window to obtain different phases as a function of substrate temperature and particle energy. Additionally, the region allowing photoactive thin films is indicated by the blue shaded region.

Temperature and ion energy seem to be interchangeable, however the plot apparently implies that an increase in the average particle energy by a factor of 10 leads to very similar results when increasing the temperature by 300 °C. This combination of logarithmic energy and linear temperature scale still necessitates further investigations.

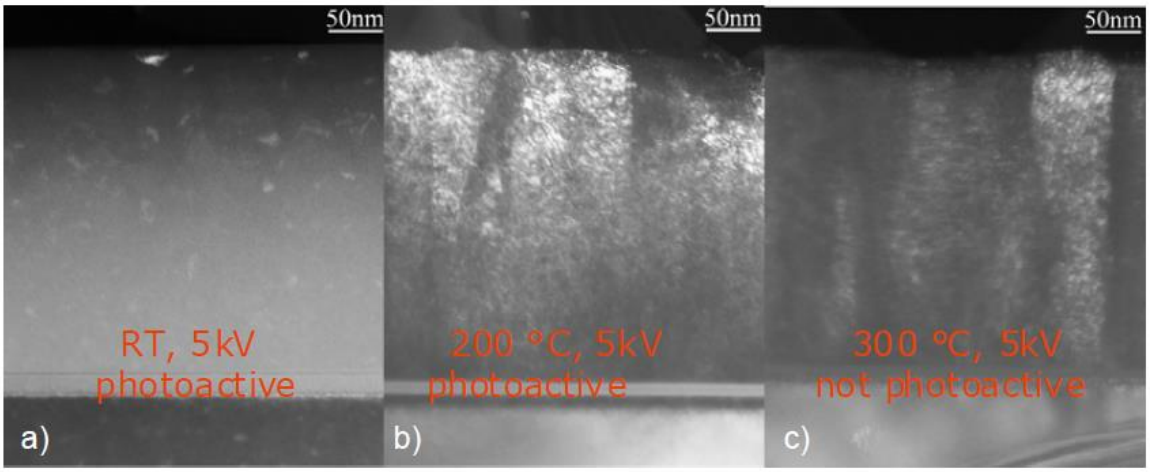

Figure 5. Transmission electron microscopy (TEM) dark field viewgraphs of three different samples, deposited at 5 kV pulse voltage at (a) room temperature, (b) 200 °C and (c) 300 °C.

Similar results on the phase formation have been observed for pure implantation of oxygen into chemically pure titanium, where the high temperature-high pressure phase rutile was found to nucleate even at a temperature of 265 °C [18]. However, at temperatures between 250 and 600 °C, anatase is the fast growing phase whereas rutile is growing very slowly. Thus, depending on growth rate and deposition time, different anatase/rutile mixtures can be encountered. Furthermore, unequivocal phase identification by either XRD or Raman spectroscopy of microcrystalline or nanocrystalline components is rather difficult [19]. However, a strong correlation of the phase composition—and not the morphology—with the photoactivity was observed, which can help in identifying the actual phase composition. Photoactivity was observed at room temperature and 200 °C, but not at 300 °C when applying 5 kV pulse voltages [20]. As can be seen in Figure 5, an amorphous phase with nanocrystalline rutile inclusions (indicated by the bright regions in the thin film in Figure 5a) was obtained at room temperature, while at higher substrate temperatures, columnar growth was observed.

CONCLUSIONS

Physical vapor deposition for formation of advanced functional coatings or nanostructured surfaces is a sizable field of technologies as no single method is dominating the field, neither in the laboratory nor in industrial applications. While fast deposition processes and the ability to coat complex shaped 3D substrates are desirable for low-cost, high-volume applications, thin films without defects and the ability to form nanostructures are the domain for technologically advanced coatings where energetic particles are employed for a multitude of adjustments, including morphology, texture and stress. For this class of applications IBAD processes are dominating for large and planar—or at least weakly curved substrates—with HIPIMS starting to create a huge amount of interest and research, due to a better control of the particle energy and less macroparticles. Whether it can supersede vacuum arc deposition, PIIIID or magnetron sputtering will be decided within the next years. The main problem for HIPIMS nowadays are low deposition rates and—compared to dual ion beam sputter deposition—no efficient way to control the particle, momentum and energy flux independently. Yet, here the verdict is still open with strong ongoing discussion and research efforts within the scientific community.

While a large amount of literature exists on the different phenomena and resulting thin film properties during deposition processes, the multitude of accessible effects leads to a large variability between different materials systems. However, no fundamentally new physics can be expected from energetic thin film deposition processes.

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