

THIN FILM DEPOSITION USING PVD

Altin Gjevori

Polytechnic University of Tirana, Albania, altingjevori@yahoo.com

Neset Izairi

State University of Tetova, Republic of North Macedonia, neset.izairi@unite.edu.mk

Fadil Ajredini

State University of Tetova, Republic of North Macedonia, fadil.ajredini@unite.edu.mk

Shefket Dehari

State University of Tetova, Republic of North Macedonia, shefket.dehari@unite.edu.mk

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 vacuum arc deposition and plasma immersion ion implantation, are available.

This work presents how the 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.

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 report, an attempt is made to give an introduction into deposition technologies involving energetic ions with kinetic energies in the range from 0.1 to 10 keV. 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. 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.

All the thin film properties presented in this manuscript 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. As long as no single crystalline films or amorphous films are obtained, the texture, i.e., the distribution of crystallographic orientations of a polycrystalline film, can be influenced by the ion bombardment during deposition, as well as the intrinsic mechanical stress.

Keywords: PVD; thin films; vacuum arc deposition; ion implantation; nanostructures

1. INTRODUCTION

In the last decades, thin film deposition evolved into a ubiquitously present technology, penetrating all major industries. Besides semiconductors, optoelectronics, optics and aerospace, the whole machine tool industry depends on coatings. 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.

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 [31], for ionized physical vapor

Anders, A. (2010) A structure zone diagram including plasma-based deposition and ion etching. *Thin Solid Films*, 518, 4087-4090.

deposition [32] or stress generation and relief processes [33]. In this manuscript, an attempt is made to give an introduction into different deposition technologies involving energetic ions with kinetic energies in the range from 0.1 to 10 keV.

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. 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.

2. MATERIALS AND METHODS

Physical vapor deposition (PVD) is an established technology to obtain individually tailored surface coatings on various substrates [34]. For growth of epitaxial semiconductors, molecular beam epitaxy (MBE) or hyperthermal ion beam assisted MBE (IBA-MBE) is the method of choice, 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). For pulsed laser deposition (PLD), similar ion energies compared to arc process are encountered, while ion beam assisted deposition (IBAD) or plasma immersion ion implantation and deposition (PIIID) leads to even higher average particle energies (see Figure 1 for a schematic overview of the typical energy ranges).

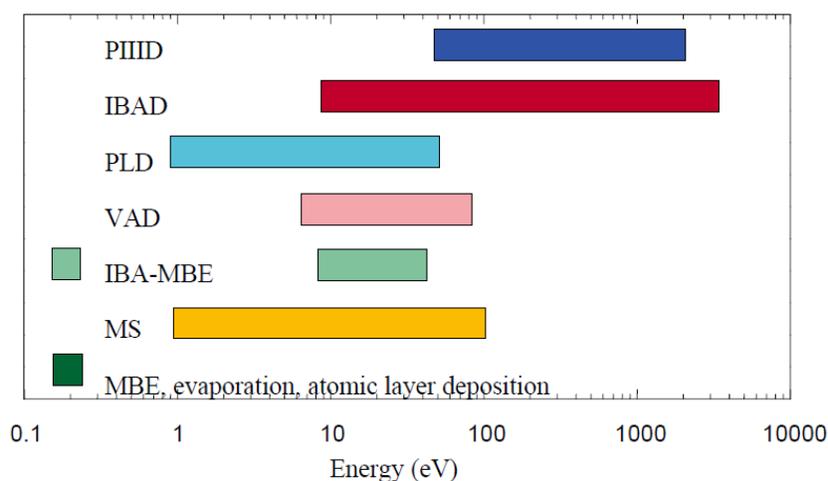


Figure 1. Typical energy ranges for different PVD processes. PIIID = plasma immersion ion implantation and deposition; IBAD = ion beam assisted deposition; PLD = pulsed laser deposition; VAD = vacuum arc deposition; IBA-MBE = ion beam assisted molecular beam epitaxy; MS = magnetron sputtering; MBE =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

Vacuum Arc Deposition

A cathodic vacuum arc is characterized by plasma production at micrometer-size cathode spots which are rapidly moving across the cathode [35].

Helmersson, U.; Lattemann, M.; Bohlmark, J.; Ehiasarian, A.P.; Gudmundsson J.T. (2006) Ionized physical vapor deposition (IPVD): A review of technology and applications. *Thin Solid Films*, 513, 1-24.

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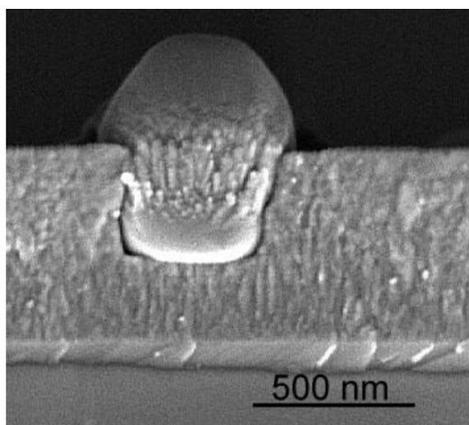


Figure 2. Cross section of TiO_2 thin film with prominent macroparticle, subsequently partially coated at later stages of the deposition process.

A small, dense plasma cloud with plasma and power density of up to 10^{26} m^{-3} and 10^{13} Wm^{-3} respectively is generated by evaporation processes at the spot surface. Within a small space charge layer of 5–10 nm, a high electric field is accelerating ions towards the surface and emitting electrons—either by thermionic emission or field emission—towards the plasma ball, despite a rather low voltage drop of only about 50 V. Within the plasma ball, the electron beam is stopped by collisions and the vapor is heated and ionized, with thermal ionization dominating over direct impact ionization. This central main plasma of the arc spot has a typical diameter of about 5–20 μm . Here, a local thermodynamic equilibrium is reached—albeit with the ion temperature lower than the electron temperature. Beyond this spot plasma, expansion of the plasma in the direction towards the anode is favored by the influence of the anode potential. While the ions are accelerated, the plasma density is rapidly decreasing, reducing the collision rate and freezing the plasma at a distance of less than 100 μm from the spot plasma. As a result, a supersonic ion flux with velocities of $1\text{--}2 \times 10^4 \text{ m/s}$ and average charge states of $2^+ \text{--}3^+$, depending on the cathode material is observed. It has to be noted that a parallel transport of ions and electrons towards the anode is occurring, with typically 10% of the total current as ions and 110% as electrons. A minimum current of about 50–75 A is necessary to allow these collective processes to occur, with an upper limit—in the pulsed mode—of several kA only due to the power supplies.

The plasma ball exerts a considerable pressure on the partially molten surface, reaching up to 40–50 bar and ejecting molten droplets, leading to macroparticles within the plasma stream. The presence of these macroparticles in deposited films, as shown in Figure 2, is a major obstacle for the broad application of cathodic arc deposition for high quality defect-free functional coatings.

Normally, elevated temperatures of at least 200–300 $^\circ\text{C}$ are employed to improve adhesion properties while additionally influencing the morphology and properties of the coatings themselves [36].

Plasma Immersion Ion Implantation and Deposition

The restrictions of a direct line of sight process can be overcome, at least partially, using a biased substrate. In PIID, a condensable plasma—normally created by a cathodic arc—is combined with high voltage pulses of 1–10 kV applied directly to the substrate. Thus, a combination of low energy ion deposition with high energy ion implantation is obtained [37].

However, for non-planar substrates a complex situation is encountered, as shown in Figure 3. The flow of the condensable metal plasma can be described by magnetohydrodynamics, similar to a fluid moving around an obstacle in fluid mechanics. However, when encountering a surface, the metal ions will stick to it [38]. Without high voltage pulses, the plasma sheath is very small, less than 100 μm , thus the local deposition rate closely follows the plasma flow. In contrast, its width can reach between 1 and 10 cm during the pulses, depending on the orientation in the plasma stream.

Gjevori, A., (2014), Phase Formation of Photoactive TiO_2 Thin Films by Metal Plasma Immersion Ion Implantation and Deposition, *Engelsdorfer Verlag, ISBN 978-3-95488-746-0, Leipzig, Germany*

Anders, A. (2000), Handbook of Plasma Immersion Ion Implantation and Deposition; *Ed.; Wiley-VCH: Berlin, Germany*

Mändl, S., Manova, D., (2019) Modification of metals by plasma immersion ion implantation, *Surface and Coatings Technology Volume 365, Pages 83-93*

On the upstream side, no plasma presheath is present as the Bohm criterion is over-fulfilled, while it is re-established on the downstream side where the ions move away from the substrate, with a drop in the plasma density by a factor of 5–10. As a result of this, a very strong decrease of the layer thickness on areas not exposed to the plasma stream is observed. A further complication is the existence of high energy ions producing defects deep in the bulk which will not be annealed for lower temperature deposition processes.

While a large number of groups, worldwide, are experimenting on laboratory scale, no commercialization of this processing method is known [39].

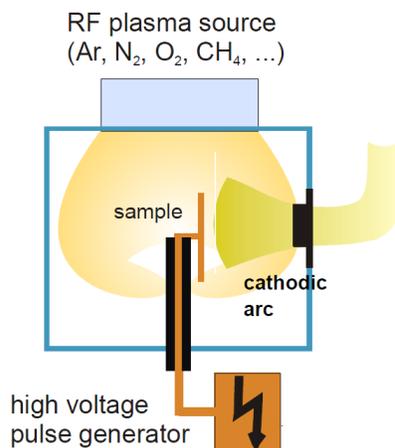


Figure 3. Presentation of a plasma immersion ion implantation and deposition (PIID) system with filtered cathodic arc, auxiliary plasma source and high voltage pulse generator.

3. RESULTS AND DISCUSSION

All the thin film properties presented in this manuscript 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. As long as no single crystalline films or amorphous films are obtained, the texture, i.e., the distribution of crystallographic orientations of a polycrystalline film, can be influenced by the ion bombardment during deposition, as well as the intrinsic mechanical stress.

Interface Mixing

The process initially active during the energetic deposition of functional coatings is ballistic ion mixing leading to atomic relocation of the substrate material induced by the energy loss during the stopping of incident ions. Besides an increased roughness of initial substrate surface, intermixing of the substrate and the grown film can occur, leading to an increased adhesion of the film on the substrate. An auxiliary process with a similar origin is surface sputtering, where the energy and momentum transferred to substrate atoms is sufficient for the secondary particle to be removed from the surface. However, additional, chemical effects will arise from the respective mixing energy, with miscible systems showing broader interfaces than immiscible systems. When depositing electronically active components, interface mixing has to be avoided as additional, unwanted interface states will arise. Next to reducing

the maximum particle energy, which reduces the transient particle energy within the collisions, chemical mixing effects have to be circumvented in these cases [40].

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 [1]. In the presented form, it is extended and now proposed to cover any energetic deposition from cathodic arc deposition, HIPIMS [41], and other forms of PVD.

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 4—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,

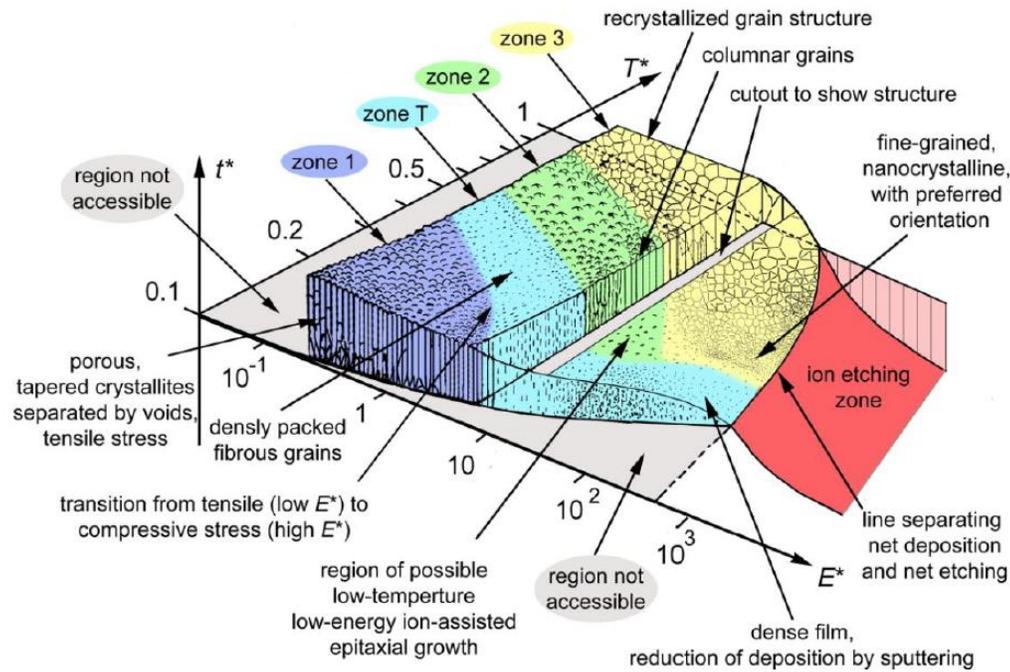


Figure 4. Structure zone diagram applicable to energetic deposition as a function of the generalized temperature T^* and the normalized energy flux E^* ; t^* represents the net thickness. The boundaries between zones are gradual and for illustration only.

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

Mattox, D. M., (2014) Handbook of Physical Vapor Deposition (PVD) Processing 2nd Edition, Cambridge University Press

Anders, A., (2017), Tutorial R-HiPIMS Data, JAP, May 2017

processes, especially of compounds with widely differing melting temperatures may complicate the picture in reality.

Texture

Especially for columnar growth modes assisted by energetic particles, the evolution of the film is always associated with a preferred orientation or crystalline texture and subsequent development of this texture during progressive growth. There is a strong correlation between the texture evolution and the process parameters such as ion energy, ion current density (ion/atom arrival ratio), film thickness, incident ion angle and substrate temperature. Different models exist to explain the preferred orientation in the film growth, where the channeling direction, preferential sputtering or deformation energy minimization are proposed to determine the final texture.

The Ti-N system has often been used to test the film growth models. Using PIIID, a controlled variation of the incident energy flux is possible. A {200} fiber texture develops for sufficiently high-ion energies, 3 kV pulses or higher in the presented experiment (at 9% duty cycle, repetition rate 3 kHz, pulse length 30 μ s), with the fiber axis parallel to the ion incident angle, i.e., normal to the surface [42]. This fiber texture can be identified from the ring structure seen in Figure 5b centered at a polar angle $\chi = 55^\circ$. A {110} texture was measured for a lower-pulse voltage of 1 kV, indicated by the smaller ring centered at $\chi = 35^\circ$ (see Figure 5a).

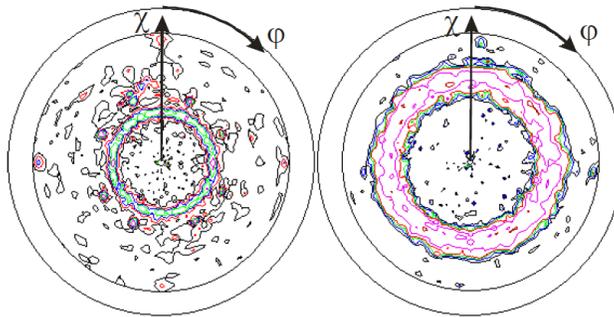


Figure 5. Depiction of TiN {110} and {200} fiber texture, as obtained from {111} pole figures, for plasma immersion ion implantation and deposition (PIIID) at different pulse voltages of (a) 1 kV and (b) 10 kV at fixed duty cycle of 9% .

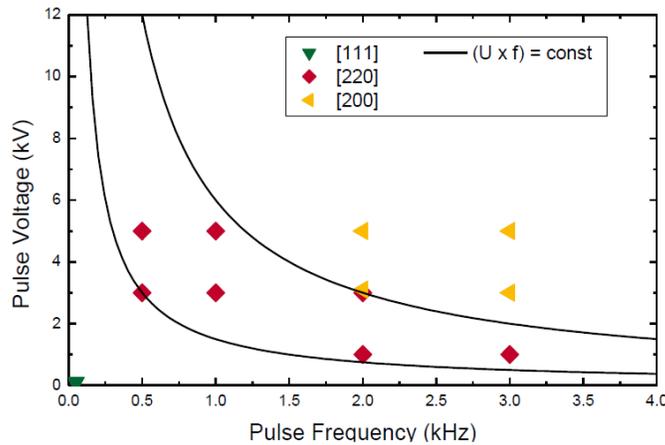


Figure 6. Observed texture evolution as a function of pulse voltage and frequency for the formation of TiN by PIIID. The data points show the measured texture for thin film produced at different voltage/frequency combinations, the thin lines show the approximate texture transitions boundaries when assuming that the average energy alone is the dominating factor to determine the texture.

Mändl, S.; Rauschenbach, B. (2003), Plasma stream homogeneity during metal plasma immersion ion implantation & deposition. *IEEE Trans. Plasma Sci.*, 31, 968-972.

Expanding the measurements to different pulse voltages and pulse lengths, i.e., a varying energy flux density towards the substrate, a good agreement between the product of voltage and frequency with the observed texture is obtained, as shown in Figure 6. Hence, variation of current density or ion energy is producing the same effect.

4. 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.

Whether it can supersede vacuum arc deposition, PIIID 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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