Ion Plating and Beyond: Pushing the Limits of Energetic Deposition

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ABSTRACT

Ion plating has been introduced about four decades ago, and recently much progress has been made in deeper understanding of ion beam assisted and self-ion assisted deposition techniques. A variety of energetic deposition processes have been developed which involve either plasmas, or low-energy ion beams, or both. Of particular interest are hybrid processes such as plasma immersion techniques that have several energy and species "knobs" to tune and tailor properties of coatings, graded layers, and multilayers. These processes will be briefly reviewed. Increasing the energy of condensing species leads to the formation of intermixed layers, usually accompanied with improved adhesion. Energetic deposition often leads to high compressive stress; however, stress relief can be obtained under certain conditions, especially when using high-energy ions at low duty cycle. The choice of energy and duty cycle of the high-energy particle fraction is dictated, among other factors, by the average power limits, temperature tolerance of the substrate, and the effect of re-sputtering from the growing film.

INTRODUCTION

It is well known that the properties of coatings depend on the substrate conditions (e.g. precleaning, temperature, etc.) as well as on the complex characteristics of the flow of condensing vapors. This article will focus on the latter, where "vapor" in a more general sense includes neutral atoms, ions, and energetic beams of particles. Already in the 1960s, Mattox [1] introduced "ion plating" as a method to obtain highly adherent metal coatings on substrates at relatively low temperature. Sputtering of the substrate by ions was a central part of the original deposition concept [2]. In his handbook, Bunshah [3] defines ion plating as "a process in which a proportion of the depositing material from an evaporation, sputtering, or chemical vapor source is deliberately ionized; once changed this way, the ions can be accelerated with an electric field so that the impinging energy on the substrate is greatly increased, producing modifications of the microstructure and residual stresses of the deposit." First applications have been reported as early as 1973, ref. [4].

There have been a number of excellent handbooks and reviews about ion plating and related techniques, e.g. [3, 5, 6]. More recently, ion plating can be associated with what is sometimes called "energetic condensation" [7, 8], i.e., a deposition process that is characterized by hyperthermal energies of the condensing species. Other terms for a similar approach are "plasma immersion deposition" and "plasma immersion processing." The common ground and the specifics of these coating techniques will be discussed below, with some emphasis on highly or even fully ionized arc plasmas such as obtained by filtered cathodic arc plasma sources.

ION PLATING

Coating by evaporation is characterized by very high deposition rates, translating into low cost per deposited area and thickness, which makes this technique very attractive from an economics point of view. The coatings obtained, however, may show poor adhesion; they have a characteristic columnar structure and a density smaller than the corresponding solid bulk material. By ionizing a part of vapor prior to condensation, i.e. forming a partially ionized plasma, and attracting the ions by negative substrate bias, film adhesion can be significantly improved and film density can be enhanced. Figure 1 shows a simplified schematic of an ion plating setup.

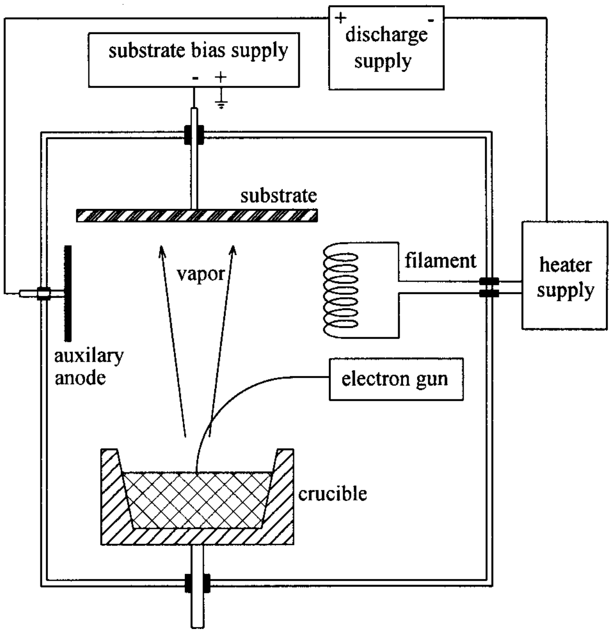

Figure 1: Simplified schematic of an ion plating setup.

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Partial ionization of the vapor can be achieved by various discharge approaches, including thermionic arcs where electrons are emitted from a hot filament, hollow cathode discharge, or radio-frequency (RF) discharge. The degree of ionization is defined as $\alpha = n_i/(n_i + n_0)$, where n_i is the ion density and n_0 is the density of neutral atoms or molecules. In early work, the degree of ionization was on the order of 0.1%, but even this small fraction made a remarkable change in coatings properties. Originally, bias was applied in constant-current (DC) mode. RF self-bias was shown to be advantageous especially when ion plating was performed in a reactive gas environment such as to form compound coatings (reactive ion plating) because charge-up of the insulating surface can be minimized. Yet other, more advanced techniques are (DC) pulsed bias, and bipolar pulsed bias.

SCALE-UP OF ION PLATING

Ion plating can be scaled up in different ways, e.g. focussing on the rate of deposition, area, film quality, extension to new materials, and combinations thereof. New developments are often given new names in order to distinguish them from previous achievements, and also to be able to stake patent claims in uncharted territory; however, one can find a continuous thread and combining themes in these developments.

One extension of ion plating has been named “rod cathode arc-activated deposition” [9] or the “RAD” method. In this technique, the evaporant serves as the anode of a thermionic arc discharge; the cathode is not a filament but a hot tungsten rod operating in the spotless (thermionic) mode, and no auxiliary anode is used (Figure 2). The arc current of 100-500 A is heating the evaporant and partially ionizing the vapor flux. The power levels demonstrated are impressive: up to 300 kW for the electron beam gun and up to 50 kW for the thermionic arc discharge. It is claimed that the degree of ionization may be up to 50%, although no specific measurement was reported to confirm this high number.

The “RAD” method is best suited for metals of low melting point and high vapor pressure. If applied to refractory metals such as W, Mo, and Ta, the deposition rates are low. In these cases, another hot electrode approach is better suited, namely when the evaporant is used as a cathode operating in the spotless arc mode. The spotless arc mode is known for decades and has been investigated primarily for use in plasma discharge lamps [10]. More about arc modes can be found in [11]. Schiller and co-workers called this approach “spotless arc deposition” or “SAD” [12]: The location of electron emission for the spotless arc is controlled by the impact of the electron beam from the high-power electron gun (Figure 3).

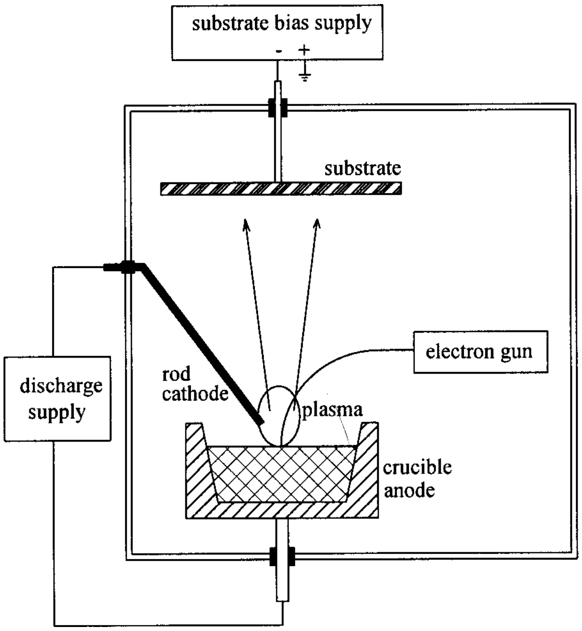

Figure 2: Simplified presentation of rod cathode arc-activated deposition (RAD).

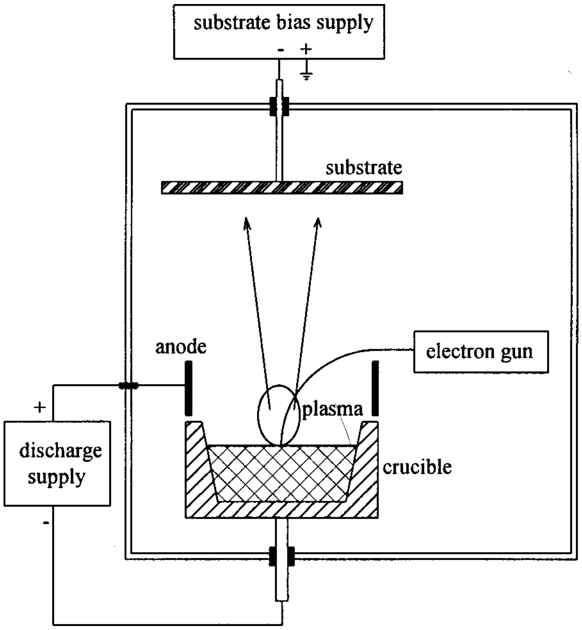

Figure 3: Simplified presentation of spotless arc deposition (SAD).

In yet another configuration, which actually is very close to the original ion plating concept, electron beam evaporation is combined with a hollow cathode arc discharge through the vapor flow, and thus the vapor is partially ionized (Figure 4). Although this is clearly ion plating, the developers named it “hollow cathode activated deposition” or ”HAD” [12].

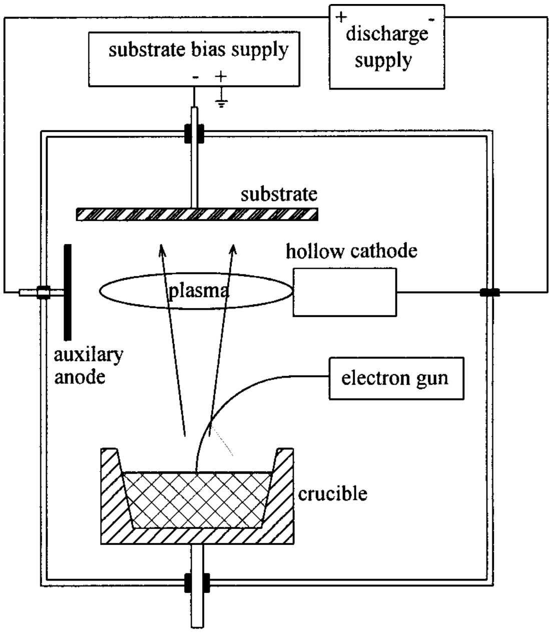

Figure 4: Simplified presentation of hollow cathode activated deposition (HAD).

INCREASING THE DEGREE IONIZATION

Besides going for larger areas and higher deposition rate, enhancing the degree of ionization of the condensing vapor is a crucial goal of process development. The degree of ion ionization determines the fraction of condensing particles whose kinetic energy can be influenced. The electric field created by substrate bias acts only on charged particles, and the neutral atoms of the vapor "ignore" the presence of bias. As shown in the early work, even a degree of ionization of only 0.1% can make a difference in coatings properties. The bias is usually several hundred volts or even kilovolts, and the energy of impacting ions is therefore much larger than the surface binding energy (which is typically 2-8 eV), and displacement energy (which is typically 10-40 eV), and therefore each energetic ion will influence a large number of atoms near the surface. High voltage bias is often not desirable because it may lead, among other issues, to electrical breakdown and substrate arcing. If the degree of ionization is high, lower bias voltage can be used because many more condensing particles are accelerated to hyperthermal energies.

Using a large current of arc discharge electrons (like in the HAD, RAD, and SAD methods mentioned above) will lead to ionization of the vapor. The degree of ionization will depend on the current intensity, the vapor density, and cross section of ionization of the specific vapor integrated over the electron energy distribution function.

The degree of ionization can qualitatively be associated with the power density in the ion production region. An extremely high power density is automatically obtained in cathodic arcs, where the current at the cathode surface is concentrated in micron-size cathode spots. Current densities of order 10^8 A/cm^2 have been observed [13, 14], and when taking a cathode fall voltage of order 10 Volts one obtains an areal power density of about 1 GW/cm^2! The resulting explosive phase transition [15] from the solid to the plasma delivers a fully ionized plasma that often contains even multiply charged ions [16].

ION PLATING WITH FILTERED CATHODIC ARC PLASMAS

The cathodic arc processes do not only lead to a very high degree of ionization, they are responsible for ion acceleration to supersonic velocities, which are in the range 4700-23100 m/s, corresponding to 19-142 eV, depending on the material [17]. Therefore, even in the absence of substrate bias, cathodic arc plasmas enable ion plating or energetic condensation.

Although the plasma obtained by the cathodic arc process appears to be advantageous, it has also a few undesirable features, including the contamination with "macroparticles," i.e. liquid and solid debris particles that are also produced at cathode spots. Particle contamination of cathodic arc films may be acceptable for some applications but has prevented the technology from being widely used in high-tech areas.

The most common and successful method of dealing with the macroparticle issue is plasma filtering using devices that prevent direct line-of-sight from the cathode to the substrate. The plasma is guided to the substrate by suitable curved magnetic fields. A typical example of such devices is the 90°-filter duct introduced in the late 1970s by Aksenov and co-workers [18]. Filter principles and devices have been reviewed, see for example [19]. Plasma filtering does not only remove macroparticles but also neutral atoms that may be present in the cathodic arc plasma (neutral atoms are mainly produced by evaporation from macroparticles and from the hot craters left by cathode spots). Ion plating with filtered cathodic arcs is energetic condensation where all condensing particles have considerable energy. The resulting coatings are dense, well adherent in most cases, and often characterized by high compressive stress [20].

METAL PLASMA ION IMMERSION IMPLANTATION AND DEPOSITION (MePIIID)

Once a fully ionized and condensable plasma is available, ions can be used for coatings and ion implantation. To understand the latter, let us consider an experiment by Adler and Picraux done in the early 1980s [21]. A substrate is placed in the flow of metal plasma by a pulsed cathodic arc discharge. The substrate is biased to high negative potential such that a high-voltage sheath forms between plasma and substrate. Ions entering the sheath are accelerated to high kinetic energy $E_{kin}=E_0+QV_s$ where E_0 is the kinetic ion energy gained at the cathode spot, Q is the ion charge state and V_s is the sheath voltage (determined by bias). If the bias is sufficiently high, the impacting ion will come to rest *under* the surface, i.e. the ion is implanted. The stopping power is about 100 eV/nm, or inversely, the depth is on the order of 10 nm/keV. For more precise predictions, Monte Carlo codes such as TRIM should be used [22]. The idea of ion implantation using substrate bias was adopted for gas plasmas and became known as plasma source ion implantation (PSII) [23] or plasma immersion ion implantation (PIII). It was extensively investigated for nitriding of steel and aluminum and later for a wide rage of applications [24].

By combining metal ion implantation and metal ion deposition (ion plating), Brown and co-workers [25] developed a flexible hybrid process. By choosing a specific ratio of pulsed bias and pulsed arc plasma production, a certain ratio of ion implantation (bias on) and ion deposition (bias off) can be achieved. To make this process more efficient, arc pulses can be made of arbitrary length, including DC operation, and a sequence of many bias pulses can be used. The general setup for this technique is shown in Figure 5. The technique is now sometimes called metal plasma immersion ion implantation and deposition (MePIIID, pronouced “me-pit”) [7, 26].

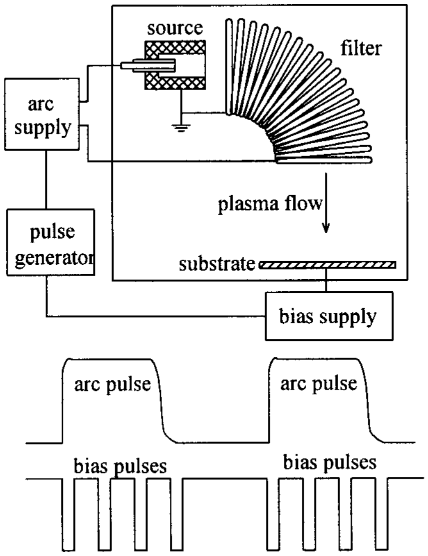

Figure 5: Simplified presentation of metal plasma immersion ion implantation and deposition (MePIIID).

MePIIID is very versatile technique for the formation of tailored films, multilayers, and graded structure because there are number of “knobs” that can be tuned to obtain the desired properties. Specifically, one can chose

- the bias pulse duration;
- the bias amplitude;
- the bias duty cycle;
- mono or bi-polar biasing;
- the arc current and associated plasma density;
- the cathode material and thus the kind of condensing species;
- the absence or presence of a reactive gas such as to form a metal or compound film, respectively;
- the pressure of reactive gas, if used, to affect film composition and texture;
- the substrate temperature to affect film properties such as texture;
- the use of more than one cathode material, e.g. by using several arc sources sequentially or simultaneously, to obtain multilayers or alloy films.

PLASMA IMMERSION PROCESSING (PIIP)

While all previously mentioned techniques represent developments that originated from simple physical vapor deposition (PVD), there is a whole different class of coating techniques relying on *chemical* decomposition of a precursor gas, i.e., chemical vapor deposition (CVD). If the precursor gas is at least partially ionized, one speaks of plasma-assisted CVD, or PACVD. The presence of ions in such plasmas allows us to utilize the above mentioned bias techniques, and so effects that were typical for plasma-assisted PVD, appear also in PACVD. If specifically *pulsed* bias is used, as it is typical of plasma immersion techniques, the CVD method has been called plasma immersion ion processing (PIIP) [27].

ION BEAM ASSISTED DEPOSITION (IBAD)

Ion plating and the derived developments are characterized by energetic condensation of at least a fraction of the condensing species. In this sense, all of these techniques are self-ion assisted deposition techniques. If one separates the ion assistance by providing an independent source of e.g. argon ions, such as a Kaufman ion source or end-hall ion source, one speaks about ion beam assisted deposition (IBAD) [6]. IBAD has advantages and disadvantages compared to self-ion assisted deposition. Among the advantages is the decoupling of ion energy and particle flux arriving at the substrate, and among the disadvantages is the generally unwanted incorporation of some gas into the growing film. IBAD is mentioned here only to relate it to advanced ion plating methods.

DISCUSSION OF ION PLATING AND ENERGETIC DEPOSITION

As already discovered in the early work, energetic impact of even a small fraction of arriving atoms and ions is important because it removes loosely bonded ad-atoms and contaminants from the substrate surface, increases surface mobility, introduces defects, and may lead to the formation of an intermixed layer. Since then, much understanding has been gained, filling entire books, e.g. [3, 6, 24, 28, 29].

One may approach energetic condensation in the hyperthermal range up to a few 100 eV of ion energy as an energetic deposition process, or as ion implantation at ultra-low energies, sometimes referred to as subplantation [30]. In the field of ion implantation, the term "thermal spike" is used to describe local melting of picosecond duration involving a volume that is determined by the collision cascade caused by the impacting ion. When going to a very low energy range, from an implantation point of view, the thermal spike shrinks to a small volume. The term "temperature" is becoming questionable because the number of atoms involved is small and the spike is rapidly quenched. One needs to keep this limitation in mind when considering "atomic scale heating" [31, 32].

Each ion arriving at the substrate surface delivers high energy that is mainly determined by the substrate bias. If the kinetic energy is "low" in the sense of ion assisted deposition, e.g. say 50 eV, energy contributions other than kinetic are important too. Each ion carries both kinetic and potential energy, and the latter can be significant especially if the ion is multiply charged because the potential energy can be of the same order as the kinetic energy. Each ion leads to local, atomic-scale heating of a volume around the impact location. The surface and subsurface processes are affected by thermal energy released *and* by the momentum associated with the kinetic energy of the impacting ion.

In the case of self-ion assisted deposition with fully ionized plasmas, e.g. filtered cathodic arc, each atom in the growing film is several times subject to atomic scale heating and momentum supply, namely, when this atoms was deposited, i.e., when the arriving ion became a film atom, and also when its neighboring atoms became part of the growing film. Each event may lead to atomic scale rearrangement of lattice neighbors and may affect their bond structure, and therefore each ion impact affects sputtering, stress, and texture even for substrates that are globally near room temperature. Energetic deposition is a method of achieving film properties for conditions that are far from thermodynamic equilibrium at the global substrate temperature.

OUTLOOK

Ion plating and other energetic deposition methods represent a growing part of the portfolio of deposition techniques. No single technique is a universal solution to all requirements, and so energetic deposition will not replace more traditional coatings technologies. There are preferred techniques for specific applications, taking quality and economic factors into account. One can anticipate that ion plating and its advanced forms will be perfected in several respects: larger areas, greater deposition rates, better uniformity, optimized energy for preferred textures, to name a few. Furthermore, surface science including computer simulation of energetic condensation and ion-assisted deposition will improve our understanding of the underlying elementary film growth processes.

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