Plasma-based ion implantation utilising a cathodic arc plasma

M.M.M. Bilek*a, D.R. McKenziea, R.N. Tarranta, S.H.M. Limb, D.G. McCullochb

aApplied and Plasma Physics Department (A28), School of Physics, University of Sydney, Sydney, NSW 2006, Australia
bDepartment of Applied Physics, RMIT University, Melbourne, Victoria 3001, Australia

Abstract

Plasma-based ion implantation (PBII) is usually carried out with isotropic gaseous plasmas, such as a discharge in nitrogen. More recently, it has been applied using drifting plasmas, such as those produced by cathodic arcs, in order to allow efficient implantation of metallic species. The condensable nature of a cathodic arc plasma allows for the deposition of ion-stitched thin film coatings, as well as surface modification by ion implantation. In this paper the promising results for biomaterial fabrication are discussed in light of current limitations of the technique. The use of PBII to control preferred orientation in titanium nitride films is also discussed, together with implications for the physical mechanisms involved in the development of preferred orientations in thin films. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cathodic arc; Ion implantation; Stress relaxation; Adhesion; Preferred orientation; Biomaterials

1. Introduction

Plasma-based ion implantation is a technique developed in the late 1980s. The principle of operation is that the object to be ion-implanted is immersed in a plasma and biased with a high-voltage power supply. A sheath forms around the object and ions are accelerated across the sheath into the surface of the immersed object. The bias is usually pulsed to allow the plasma to replace depleted ions between the pulses. It has been extensively applied using plasma sources such as glow discharges, which produce a more or less isotropic low-density plasma from a gas. The ions generally do not condense on the surfaces being treated, so that the treatment involves only the implantation of high-energy ions into the surface.

More recently, the technique has been adapted to a cathodic arc plasma [1]. This is a drifting plasma plume produced from the material of a conducting solid. The arc is usually ignited by an electric discharge between a trigger electrode and the cathode. The metallic ions have energy ranging from 20 to 100 eV and condense on the surface being treated during times between high-voltage pulses, resulting in the deposition of a thin film which is ion implanted during the on time of the pulses.

This paper describes the material properties of thin films deposited in this way. In particular, the stress in the film is dramatically reduced compared to that observed in films deposited in the cathodic arc without simultaneous PBII. This reduced stress allows the deposition of much thicker films with better adhesion than would otherwise be possible. These properties are particularly important for demanding applications, such as in the field of biomaterials. The paper outlines a model that can be used to explain the reduction in intrinsic stress and the improved adhesion and to describe results obtained with carbon and titanium nitride coatings. In the case of titanium nitride, a change in the preferred orientation of the film crystallites is also observed. This effect is described, together with its implications for models describing the development of preferred orientation in thin films. The article concludes with some problems that need to be overcome in further developing this surface modification technique for biomedical applications.

2. The effect of ion energy

Fig. 1 schematically shows the types of microstructures produced as impact energy varies across a variety of thin-film deposition techniques. Films deposited at thermal energy values (a fraction of an eV) tend to grow as columns with voids in between. This is because
the atoms have low surface mobility and the voids are created by shadowing effects. The high points shadow their surroundings from incoming ions and develop into columns with crack-like voids between \[w^2x\]. In an attempt to reduce the very high surface energy of this structure, van der Waals’ forces between the columns result in a tendency for the film to try to contract—a tensile stress. Vacancies and vacancy clusters may also play a role in generating tensile stress. The forces on the substrate, shown by the arrows in the diagram, are directed inwards. The integrity of these coatings and their usefulness in protecting a surface are compromised by the presence of the voids.

Contiguous coatings (i.e. coatings without voids or pores) are readily produced by a range of energetic ion-assisted deposition techniques. The substrates are usually negatively biased, so that the ionised species arrive at the substrate with energy of 50 to a few 100 eV. In the case of the cathodic arc, the native ion energy values in the plume fall in this range. The energy of these impacts is sufficient to bury the ions a few atomic layers beneath the surface of the growing film and provide some mobility for minor atomic rearrangements. This densifies the structure and prevents the formation of columns and voids. A secondary effect of the buried ions is to cause a tendency for the deposited material to swell and try to expand laterally. This creates a significant compressive stress in the film, which results in strain and forces on the substrate, as shown by the arrows in the diagram. As the thickness of the film increases, the stress and stored strain energy increase.

Although strain energy is not a problem for many applications, it cannot be tolerated in situations where coatings need to be thick and completely free of cracks, such as in biomaterials. The classical Griffith criterion tells us that a crack will propagate and a film will delaminate if the strain energy relieved is greater than the total surface energy of the two new surfaces created by the delamination (i.e. substrate and underside of film).

It may be possible to overcome this limitation by using even higher impact energy values. Recent experimental evidence shows that impact energy of a few keV or greater provides enough energy for a sufficiently long time to enable the atoms near the impact site to undergo significant atomic rearrangement, and for the relaxation of local stress and strain to occur. For all materials studied to date, the stress vs. impact energy behaviour has been found to take the form sketched in Fig. 2. In the schematic curve of Fig. 2, other parameters affecting stress, such as the ion/neutral ratio, are held constant. High-energy impacts also provide an additional benefit in the mixing of the substrate–coating interface, because the first energetic impacts implant atoms under the surface of the substrate, as shown in Fig. 1. The diffuse interface provides for improved adhesion. The next section describes techniques for deposition with high-energy bombardment and the physics surrounding the elimination of stress.

3. Plasma-based ion implantation and the thermal spike

Plasma-based ion implantation (PBII) includes the techniques known as plasma immersion ion implantation (PIII) [3,4] and variations that also allow for deposition, known as plasma immersion implantation and deposition (PIID) [1,5]. In these techniques, a high negative voltage is applied to the component being treated while it is immersed in a plasma. On short time scales, of the order of the inverse plasma electron frequency (typically 0.01–1 ns), the electrons are accelerated out of the region surrounding the biased workpiece. This establish-
Ion impacts on the surface of a material have been analytically studied using the assumption of an isotropic medium by Marks [6]. The thermal spike was defined by a hemispherical region with a temperature of 5000 K. Marks found that the time taken for the energy to be dissipated to the rest of the film, that is the lifetime of the spike, is proportional to the square of its radius. As the energy of the impact, and hence the radius of the thermal spike increases, the time it takes for the region to be quenched back to the initial temperature also increases. If the thermal spike endures for long enough, there will be sufficient time for significant atomic movements and relaxation corresponding to local annealing. Thus, high-energy impacts, which produce thermal spikes with a lifetime greater than the relaxation time of the material being treated, are an ideal way to relieve intrinsic stress during the growth process.

4. Ion dose required for stress relief

The relief of stress by energetic bombardment requires a sufficient fluence of ions during the film deposition to ensure that all parts of the film have been subject to the effects of at least one, and preferably many, annealing thermal spikes. To calculate this fluence, we first need to calculate the coverage of a surface as a function of the number of randomly placed circles, assuming each thermal spike produces a circular region of annealing of a constant radius \( r \propto \sqrt{E} \).

An upper bound to the coverage, assuming no overlap of the circles, is simply given by \( n \pi r^2 \), where \( n \) is the fluence, that is the number of energetic impacts per unit area. A lower bound can be found by subtracting the areas of overlaps between any two overlapping circles. Such simple overlaps are referred to as type A overlaps. Fig. 4 shows a surface with some randomly placed circular impacts. In addition to type A overlaps, a more complex overlap is shown in which three type A overlaps themselves overlap. This situation is referred to as a type B overlap; type B and higher-order overlaps become important at high coverages.

We can calculate the loss of treated area resulting from type A overlaps as follows: The loss of coverage

\[
\text{Type A overlap}
\]

Fig. 4. Schematic diagram showing the thermal spikes produced by random impacts on a surface.
caused by a single type A overlap is given by:

$$A(b) = \int_{-a}^{a} \sqrt{r^2 - x^2} \, dx - ab \tag{1}$$

Overlap occurs if the distance, $b$, between the two adjacent impact centres is between 0 and $2r$. The distribution of nearby impacts is random and the same on average for each impact site. Thus, the number of adjacent impacts with distances between $b$ and $b + db$ is $n^2 \pi b \, db$. We multiply this by $n$ to account for each and every impact site, and also multiply by $A(b)$ to account for area lost when impacts land a distance $b$ apart. This expression is then integrated between 0 and $2r$ to sum over all possible impact pairs that result in lost area. The total area of overlaps of type A per unit surface area is then given by:

$$2 \pi r^2 \int_{0}^{2r} b A(b) \, db = \frac{1}{2} \pi^2 n^2 r^4 \tag{2}$$

Subtracting this from the sum of areas of all the impacts per unit area gives:

$$n \pi r^2 - \frac{1}{2} \pi^2 n^2 r^4 \tag{3}$$

That this expression is a lower bound for the covered area can be observed by noting that, for overlaps of type B, we subtract three-fold the area of overlap of all three impacts, whereas we should only be subtracting it once. This error, and errors from higher-order overlaps, will become important at large $n$. Hence, the actual area covered will always lie somewhere between the upper and lower bounds, $n \pi r^2$ and $n \pi r^2 - \frac{1}{2} \pi^2 n^2 r^4$, shown on the graph in Fig. 5.

We can now use the above result to estimate what proportion of the incoming atoms or ions need to be highly energetic in order to relieve the intrinsic stress in the growing film. Using the lower bound, we can calculate the minimum ratio of energetic to non-energetic flux required. The region over which the thermal spike has an effect extends to a depth $r$, and hence contains $N r$ atoms per unit area, where $N$ is the atomic number density of the film. We do not have to achieve complete coverage of this layer with thermal spikes in order to relieve the intrinsic stress. It is sufficient to have enough impacts so that the regions treated form a connected network across the film. Hence, we can assume that a coverage of over 50% is required. The density per unit area of energetic impacts required to ensure this minimum coverage can be found by setting the minimum coverage expression Eq. (3) equal to 0.5 and solving for $n$. The solution is $n = 1 / \pi r^2$, so the proportion of impacts required to be energetic for stress relieve is given by:

$$n = \frac{1}{N r} \frac{1}{N \pi r^3} \tag{4}$$

assuming that the thermal spike has an average temperature of 5000 K (as in [6]). This is equivalent to saying that each atom in the spike volume has an energy of 0.43 eV, so the relationship between the spike radius and the impact energy, also in eV, of the incoming ion that created it is:

$$E_i = 0.43 N \frac{2}{3} \pi r^3 \tag{5}$$

Rearranging this equation gives the following expression for the proportion of energetic impacts required to ensure stress relief as a function of the impact energy:

$$n = \frac{1}{N r} \frac{1}{N \pi r^3} \frac{0.86}{3 E_i} \tag{6}$$

For an impact energy of 1 keV, this corresponds to only 0.03% of the incoming flux. Assuming a typical HV pulse on-time of 1% and that the bombardment by ions and neutrals is in proportion to their number density in the plasma, this means that the plasma must have an ionisation level of at least approximately 3% for intrinsic stress relief to be achievable. To ensure that there are enough ions per high-voltage pulse, it is therefore
preferable to use a highly ionised plasma, such as that produced by the cathodic arc.

5. Surface treatments achieved with PBII using a cathodic arc plasma

5.1. Carbon

Fig. 6 shows scanning electron microscope (SEM) images [7] of films deposited using a cathodic arc carbon plasma ( \( \sim 50\text{-eV ions} \) ), (a) without high-voltage pulsing of the substrate and (b) with high-voltage pulsing. The high-voltage pulsed power supply delivered 20 kV pulses lasting 20 \( \mu \text{s} \) at a frequency of 500 Hz. There is a dramatic reduction in cracking and delamination around the test scratch mark for the film deposited with the high-voltage ion impacts. The reduction in intrinsic stress has allowed the deposition of extremely thick carbon layers. Fig. 7 shows a cross-sectional SEM image [8] of a 11.4-\( \mu \text{m} \)-thick film. Conventional cathodic arc deposition can achieve no more than a few 100 nm before the film spontaneously delaminates.

5.2. Titanium nitride

Titanium nitride films deposited with high-voltage pulsing are also quite different from the gold-coloured coatings produced by a native-energy titanium cathodic arc operating in a nitrogen atmosphere. When high-voltage pulsing is used, the colour of the films changes to purple. There is also a distinct change in the preferred orientation of the crystallites in the film. For the usual arc-fabricated material, a \( \langle 111 \rangle \) direction perpendicular to the plane of the film dominates, whereas with high-voltage pulsing the preferred direction becomes \( \langle 200 \rangle \) [9]. This is the crystal orientation commonly observed in low-stress material [10]. The \( \langle 111 \rangle \) orientation, on the other hand, is usually associated with highly stressed material [11].
Gibbs free energy per unit volume can be expressed [12] as:

\[
G = G_0 - \frac{1}{2} \sigma^2 \left[ s_{11} - 2 \left( s_{11} - s_{12} - \frac{1}{2} s_{44} \right) \right] \times (\sigma'_1 \sigma'_2 + \sigma'_2 \sigma'_3 + \sigma'_1 \sigma'_3)
\]

where \( \sigma \) is the magnitude of the applied stress. The \( \sigma'_i \) are the components, projected onto the crystallographic axes, of the unit uniaxial tensor corresponding to the uniaxial stress tensor, which must be subtracted from a hydrostatic stress tensor to yield the biaxial stress present in the film. The direction of this tensor corresponds to the low-stress direction, i.e. the film normal. When this is aligned with the \( \langle 111 \rangle \) crystallographic axis \( (\sigma'_1 \sigma'_2 + \sigma'_2 \sigma'_3 + \sigma'_1 \sigma'_3) = \frac{1}{\sqrt{2}} \), whereas when it is aligned with the \( \langle 100 \rangle \) crystallographic axis \( (\sigma'_1 \sigma'_2 + \sigma'_2 \sigma'_3 + \sigma'_1 \sigma'_3) = 0 \). \( G_0 \) is the Gibbs free energy of the system under zero stress, which contains a component corresponding to the energy of the free surface. The \( s_{ij} \) are the components of the crystal’s elastic compliance tensor.

Substituting in the elastic compliance values for [13] TiN, the difference in bulk strain energy per unit volume between a TiN film with its \( \langle 111 \rangle \) direction oriented along the film normal and one with its \( \langle 100 \rangle \) direction along the film normal is given by:

\[
\Delta G = \frac{\sigma^2}{3} \left( s_{11} - s_{12} - \frac{1}{2} s_{44} \right) = -0.544 \times 10^{-3} \sigma^2 \quad (8)
\]

where both \( \Delta G \) and \( \sigma \) are in units of GPa. The difference in energy per unit area, in J/m², between the two films can then be written as:

\[
\Delta E = -0.544 \times 10^{-3} \sigma^2 + \Delta E_{surf} \quad (9)
\]

where \( t \) is the film thickness in nm and \( \Delta E_{surf} \) is the difference in energy of the free surface between the \( \langle 111 \rangle \)- and the \( \langle 100 \rangle \)-oriented films. A reasonable estimate of the surface energy difference \( \Delta E_{surf} \) is 1.2 J/m² based on surface energy calculations by Marlo and Milman [13] and an estimate that only approximately one-third of a \( \langle 111 \rangle \) surface actually terminates with a \( \langle 111 \rangle \) plane due to surface roughness effects; the remainder probably terminates with the lowest-energy (100) surface. Fig. 8 shows a graph of \( \Delta E \) for three film thickness values. When \( \Delta E \) is negative the \( \langle 111 \rangle \) orientation is favoured, and the \( \langle 100 \rangle \) orientation is preferred when it is positive. The transition from \( \langle 111 \rangle \) to \( \langle 100 \rangle \) orientation is predicted to occur at 8.6 GPa for a film 30 nm thick. This is at a larger stress than experimentally observed, but is within the correct order of magnitude. Further tests of the theory will rely on detailed studies of the termination of the surface.

5.3. Modification of polymers and biomaterials

Polymers have an attractive set of bulk properties. They combine lightness and strength with ease of fabrication. Their range of applications can be considerably enhanced by modifying their surface properties, to give them metallic lustre or scratch resistance for example. It is difficult to make a good adherent metal layer on a polymer, due to the lack of chemical bonds between the metal film and polymer surface. However, PBII allows interface mixing and improves the chance of chemical bonding between metal and polymer [14]. The lower intrinsic stress achieved by PBII treatment during deposition is important for the development of well adherent coatings, because it reduces the tendency for the film to delaminate.

Reduced delamination is also very important for all biomaterial applications. We have tested a number of candidate treatments for skeletal prosthetic implants for biocompatibility. These devices are bonded to the skeleton most effectively when there is good compatibility between bone cells and the surface of the implant. The hospitalisation time of the patient is greatly reduced if the cells can be quickly recruited onto the new surface. Alloys of titanium have been found to be effective at bone cell recruitment, while alloys of cobalt and chromium have excellent mechanical properties. A well-bonded coating of the titanium alloy coating on a cobalt–chromium substrate achieves almost the same recruitment of adhered bone cells as does the titanium alloy surface [15]. The implantation of magnesium without concurrent film deposition into alumina substrates was also found to increase the recruitment of bone cells [16].
6. The treatment of complex shapes for biomaterial applications

The test samples reported on in the previous section were all small planar substrates; however, the shapes of real devices, particularly in the biomedical field, are much more complex, often having sharp points. Since the sheath controls the ion implanting process, it is essential to understand and to be able to correct for the behaviour of the sheath around complex objects. Solving the equations of sheath expansion near a curved surface of small radius shows that the sheath is thinner than it is near a flat, approximately planar part of the substrate [17]. This can be understood by realising that, as the ions are accelerated towards a pointed part of the substrate, they are also converging, so the reduction in density caused by their acceleration cannot be as great as that near a flat part of the substrate. Since it is the reduction in ion density in the sheath that causes it to expand, the sheath will always expand less near a sharp corner or curve than at a planar surface. In fact, in some situations it could conceivably even contract if the ion focusing is great enough.

If the sheath becomes too thin anywhere around the substrate, electric breakdown will occur between the substrate, electric breakdown will occur between the plasma source and the plasma. Such a breakdown causes substrate, so the reduction in density caused by their acceleration cannot be as great as that near a flat part of the substrate. Since it is the reduction in ion density in the sheath that causes it to expand, the sheath will always expand less near a sharp corner or curve than at a planar surface. In fact, in some situations it could conceivably even contract if the ion focusing is great enough.

The test samples reported on in the previous section were all small planar substrates; however, the shapes of real devices, particularly in the biomedical field, are much more complex, often having sharp points. Since the sheath controls the ion implanting process, it is essential to understand and to be able to correct for the behaviour of the sheath around complex objects. Solving the equations of sheath expansion near a curved surface of small radius shows that the sheath is thinner than it is near a flat, approximately planar part of the substrate [17]. This can be understood by realising that, as the ions are accelerated towards a pointed part of the substrate, they are also converging, so the reduction in density caused by their acceleration cannot be as great as that near a flat part of the substrate. Since it is the reduction in ion density in the sheath that causes it to expand, the sheath will always expand less near a sharp corner or curve than at a planar surface. In fact, in some situations it could conceivably even contract if the ion focusing is great enough.

If the sheath becomes too thin anywhere around the substrate, electric breakdown will occur between the substrate and the plasma. Such a breakdown causes ablation of material on the surface of the workpiece where it occurs and damages the surface. In a drifting plasma, such as produced in laser ablation or the cathodic arc, the sheath behaviour is further complicated by the plasma drift [18]. Because the drift maintains a higher plasma density on the side of the workpiece facing into the plasma beam, the sheath on this side will be thinner than that on the wake side. Further work is required to experimentally and theoretically study the development of the sheath around complex substrates in highly ionised, drifting plasmas, such as that of the cathodic arc or laser ablation methods. Control strategies suitable for reliable plasma-based implantation of the devices used in the medical industry can then be developed.

7. Conclusions

Plasma-based ion implantation with energy upwards of 1 keV and concurrent deposition using a cathodic arc plasma source has been found to produce good-quality films with significantly reduced stress. A further benefit of this surface modification technique is that it induces mixing at the interface. Interface mixing, together with stress reduction, leads to improved adhesion and the ability to deposit much thicker films than would be possible using the plasma source alone. A simple analysis enables the minimum fluence of energetic ions to achieve stress relief to be estimated. These advances are of special significance in the field of biomaterials, where even minor delamination cannot be tolerated. The effects of stress induced by ion impacts on preferred orientation in TiN films appear to be accounted for by a treatment in which energy is minimised. The next step in the application of the PBII technique to prosthetic implants of complex shape is the development of a process control strategy capable of ensuring a uniform treatment without electric breakdown across the plasma sheath.

References