# Surface Modification: Advancing the Functionality of Materials

## The Pollock Memorial Lecture in Mathematics and Physics

MARCELA M.M. BILEK

## INTRODUCTION

The surface properties of materials are most commonly optimised for their applications by coating with a layer of a material that has the required surface properties. Surface modification allows us to mix and match surface and bulk properties to optimise materials for their applications. For example, base metal door knobs can be made to shine like gold for decorative purposes, the surfaces of steel cutting tools can be hardened by a layer of titanium nitride, and skeletal prosthetic implants can be made more biocompatible by doping with magnesium (Bilek et al. 2000).

A good coating needs to be both contiguous and well adherent. Physical vapour deposition is a flexible coating technique with advantages over wet chemical methods such as electroplating, especially in minimising hazardous waste. The problems of porous films with voids have been solved by the use of techniques in which a fraction of the surface reacting species impinges with elevated energy. The downside of these techniques is that they often lead to significant amounts of intrinsic compressive stress in the films produced. This stress limits the thickness to which films can be grown and often causes films to delaminate exposing parts of the original surface. This is a particularly serious problem in applications where even small exposures of the original surface cannot be tolerated, such as in corrosion protection and biomaterials. In prosthetic implants, the delaminated material presents an even greater problem because it will be released into the body.

In this paper we describe a new generation of methods that offer solutions for the problem of intrinsic stress in surface modifying coatings.

The physics behind their ability to alleviate intrinsic stress is presented together with experimental results. The paper concludes with a discussion of further work necessary to develop the techniques to a stage where they can readily be used to coat complex and varied shaped components used in real world applications, with particular reference to the field of biomaterials.

## GROWTH MODES AND STRESS

Figure 1 shows schematically the types of microstructures produced as impact energy varies across a variety of thin film deposition techniques. Films deposited at thermal energies (a fraction of an electron volt) tend to grow as columns with voids in between. This is because the atoms have very low surface mobility and the voids are shadowed from incoming ions by the columns just as the floor of a gorge is shadowed from sunlight. 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. 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 (ie coatings without voids or pores) are readily produced by a range of energetic ion assisted deposition techniques, such as sputtering and plasma enhanced chemical vapour deposition (PECVD). In all of these techniques a fraction of the species condensing on the surface to form the coating layer are ionised. The substrates are usually biased negatively so that the ionised species arrive at the

substrate with energies of 50 to a few hundred electron volts. The energies of these impacts are sufficient to burry the ions a few atomic layers beneath the surface of the growing film and provide some mobility for minor atomic re-arrangements. 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 increases.
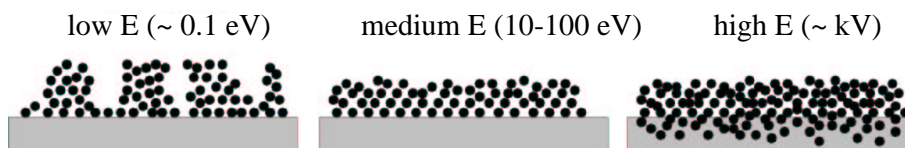


**Figure 1**: Schematic diagram showing film microstructures that result from various levels of ion bombardment. The low surface mobility in the low energy case leads to columns separated by voids, leading to tensile stress. Higher levels of ion energy result in ions being buried below the top few atomic layers, this results in densification and compressive stress. Very high energies produce a mixing layer at the substrate interface and appear to reduce the level of compressive stress.
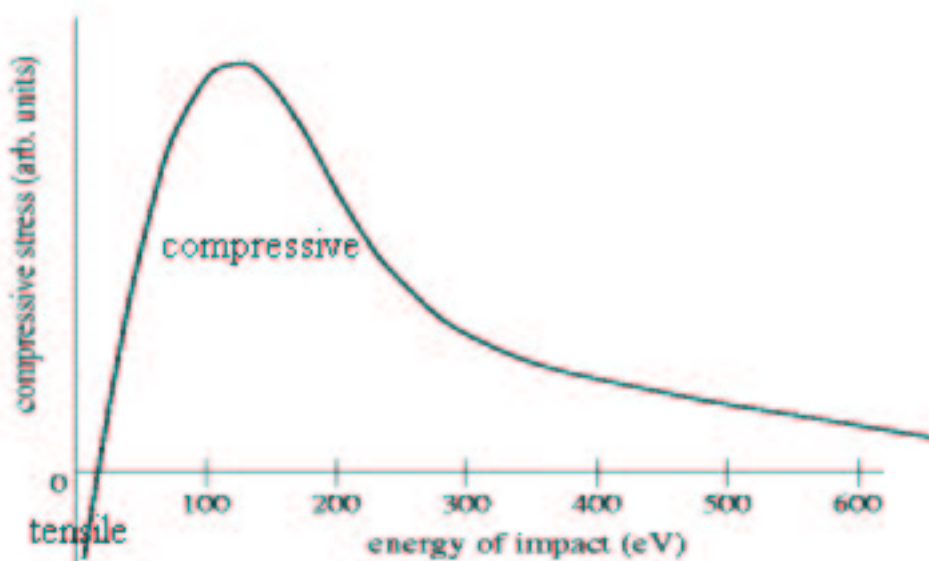


**Figure 2**: Schematic diagram of the generally observed relation between impact energy and intrinsic film stress.

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 (ie substrate and underside of film).

It may be possible to overcome this limitation by using even higher impact energies. Re-

cent experimental evidence shows that impact energies of a few kilo-electron volts or greater introduce enough energy to the atoms near the impact site to allow for significant atomic rearrangement and the relaxation of local stress and strain. For all materials studied to date, the stress versus impact energy behaviour has been found to be as sketched in Figure 2. 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 Figure 1. The diffuse interface provides for improved adhesion. The next section describes the new techniques for deposition with high-energy bombardment and the physics behind their success in eliminating stress.

## PLASMA BASED ION IMPLANTATION AND THE THERMAL SPIKE

Plasma based ion implantation (PBII) also known as plasma immersion ion implantation (PIII) is a technique in which 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 to 1 ns), the electrons are accelerated out of the region surrounding the biased work-piece. This establishes a charged region with high electric field around the work-piece across which virtually the entire voltage difference between the work-piece and the plasma drops. This region, often called the ion matrix sheath, shields the plasma from the high-voltage of the work-piece. At greater time scales (given by the inverse ion plasma frequency, usually over 100 times longer than the time scale of electron motion) the more massive and less mobile ions start to accelerate across the sheath towards the surface of the biased work-piece. As the ions accelerate and implant beneath the surface of the work-piece the ion density in the sheath is reduced and it is no longer able to completely shield the plasma from the bias on the work-piece. Electrons at

the edge of the sheath feel an electric field and they are repelled further into the plasma and thus the sheath expands. The sheath will continue to expand until a steady state ion density profile is established across it or until the plasma is depleted of ions. In order to avoid plasma depletion it is usually necessary to apply the high-voltage bias in pulses.
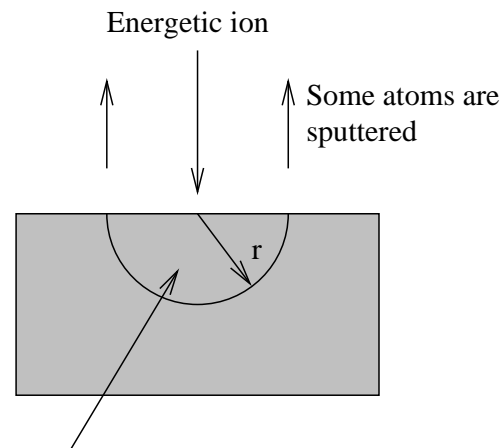


Quench time depends on radius

Figure 3: Schematic diagram of the thermal spike or high mobility region produced immediately surrounding the site of an energetic ion impact.

In some ways ion impacts on the surface of a film are a microscopic version of meteor impacts on a planet. In both cases the size of the affected area is dependent on the energy of the impact. For a meteor this is determined by its size and velocity. For the impact of an ion, it is also determined by the mass and energy of the impacting ion. The effected region is often referred to as a thermal spike and is shown schematically in Figure 3. It can be approximated as a hemispherical region with radius r ($r \propto \sqrt[3]{E}$) around the impact site. As with a meteor impact some material may be ejected in the form of sputtered surface atoms, but most of the energy is transferred to vibrational energy of the surrounding material. The energy is then gradually dissipated to the rest of the film as heat. It can be shown (Marks, 1997) that as the energy of the impact and hence the radius

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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 are an ideal way to relieve intrinsic stress during the growth process.

## SOME RECENT EXPERIMENTAL RESULTS

Figure 4 shows scanning electron microscope (SEM) images (Tarrant et al. 2001) of films deposited using a cathodic arc carbon plasma (~50 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 ms 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. Figure 5 shows a cross-sectional SEM image (Tarrant et al. 2001) of a 11.4 $\mu$m thick film. Conventional cathodic arc deposition can achieve no more than a few hundred nanometers before the film spontaneously delaminates.

Titanium nitride films deposited with high voltage pulsing are also quite different from the gold coatings produced by a titanium cathodic arc operating in a nitrogen atmosphere. When high-voltage pulsing is used the colour of the films becomes purple. There is also a distinct change in the preferred orientation of the crystallites in the film. For the usual arc fabricated material a $< 111 >$ direction perpendicular to the plane of the film dominates, whereas with high-voltage pulsing the preferred direction becomes $< 200 >$. This is the crystal orientation observed in low stress material where minimisation of surface energy determines the orientation (Pelleg et al. 1991). The minimisation of bulk strain energy on the other hand leads to the $< 111 >$ orientation (McKenzie et al. 1999) in highly stressed material deposited using a cathodic arc without high-voltage pulsing.

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 (Yap et al. 1998). Lower intrinsic stress in the deposited film also reduces the tendency to delaminate.
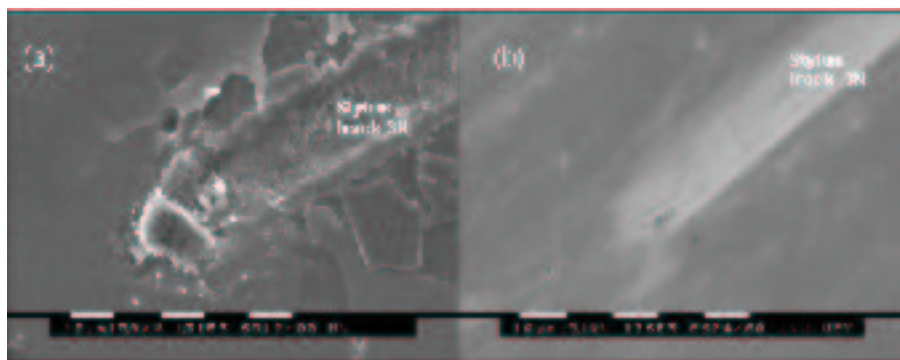


Figure 4: Scanning electron microscope images of scratched surfaces of 200 nm carbon films on silicon substrates produced (a) with no ion implantation and (b) with 20 keV ion implantation.
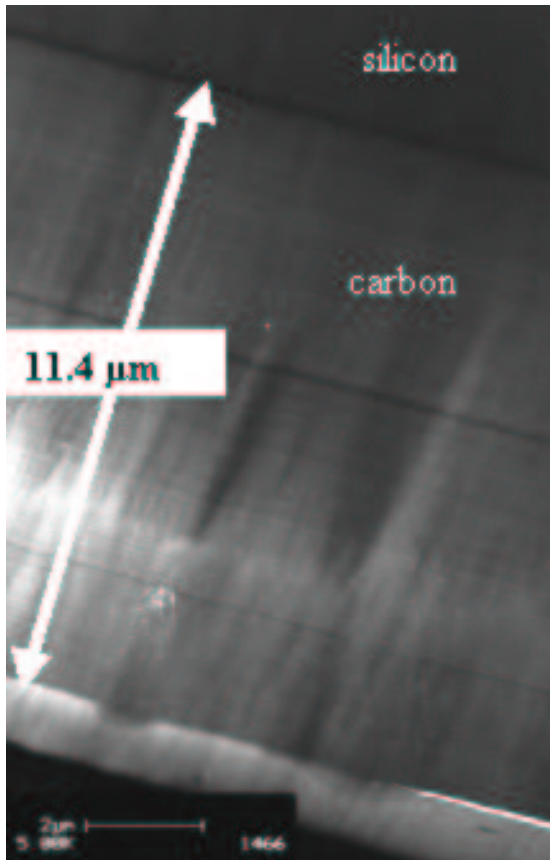
Figure 5: Scanning electron microscope image of an 11.4 micrometer thick carbon film on a silicon substrate produced with 20 keV ion implantation.

Skeletal prosthetic implants are bonded to the skeleton most effectively when there is a 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 treatment of the titanium alloy coating on a cobalt-chromium substrate achieves almost the same recruitment of adhered bone cells as does the titanium alloy (Howlett et al. 1999). The implantation of magnesium without concurrent film deposition into an alumina substrate was also found to increase the recruitment of bone cells (Bilek et al. 2000).

## THE TREATMENT OF COMPLEX SHAPES FOR BIOMATERIALS 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 there is thinner than it is near a flat approximately planar part of the substrate (Bilek 2000). 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 which 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 work-piece 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. Because the drift maintains a higher plasma density on the side of the work piece facing into the plasma beam the sheath on this side will be thinner than that on the wake side. Further work is required to study experimentally and theoretically the development of the sheath around complex substrates and develop control strategies suitable for reliable plasma based implantation of the devices used in the medical industry.

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## CONCLUSION

Plasma based ion implantation with energies 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. These advances are of special significance in the field of biomaterials, where even minor delamination cannot be tolerated. The next step in the application of the 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.

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Marcela M.M. Bilek
Applied and Plasma Physics Group
A28, School of Physics,
University of Sydney,
NSW 2006.