Insulator surface charging and dissipation during plasma immersion ion implantation using a thin conductive surface film

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Plasma immersion ion implantation of insulating materials is inherently problematic due to charge accumulation on the insulator surface. Surface charge can be removed by the application of an ultrathin conductive film, which is essentially transparent to the incident ions. The minimum thickness of the film is determined by its capability to effectively conduct away the implanted charge. We present a model for charge accumulation on insulators during plasma immersion ion implantation and use this to study the plasma sheath width and voltage, with and without an ultrathin metal film. Charge accumulation occurs more quickly when the plasma has a directed velocity greater than the Bohm velocity, which is the case for a cathodic arc plasma. We show that for both cases the effectiveness of plasma immersion ion implantation is improved with the application of an ultrathin conductive film. © 2002 American Institute of Physics. [DOI: 10.1063/1.1503149]

INTRODUCTION

In recent years plasma immersion ion implantation (PIII) has been proven to be an effective method of modifying surface properties of materials. It has an advantage over conventional line-of-sight ion implantation in that it is possible to uniformly implant complex shaped objects subject to certain limitations. The basic principle of PIII involves the immersion of the substrate or target to be implanted in a plasma, and the application of high negative potential pulses to the substrate (typically many kilovolts). Electrons in the plasma are repelled by the negative potential and a sheath of ions is formed around the substrate. The positive ions are accelerated toward the substrate and implanted into the surface. When the substrate to be implanted is an insulator, a common approach has been to place the insulator on a conductive substrate holder and apply the negative potential pulses to the holder. The voltage across the sheath is then reduced by an amount equal to the voltage drop across the insulator due to dielectric capacitance and charge accumulation on the insulator surface.

A number of authors have indicated that the application of PIII to insulators is limited to short pulses, thin substrates, and low plasma densities. In a recent paper we presented results showing that the reduction in the sheath voltage due to charge accumulation could be made negligible by the application of a very thin conducting layer on the surface of the insulator prior to PIII processing. Ions from the plasma penetrate the surface layer and implant into the underlying insulator. Obviously the thinner the surface layer, the more transparent it will be to incident ions. The limit of film thickness is determined by its capability to effectively conduct away the charge implanted during a PIII pulse.

The focus of this article is to study the PIII sheath dynamics for an insulating substrate in a cathodic vacuum are plasma. A model describing the effect of charge accumulation on the sheath voltage will be presented. The model will be utilized to predict the charging effects in a cathodic arc plasma for pulsed voltages applied to the substrate holder. The effects of adding a thin conductive layer to the insulator will then be investigated. Implications for PIII of insulators will be discussed in light of previous experimental results and observations. We will show that even very thin conducting layers can remove the deposited charge on insulating substrates to reduce the problem of charge accumulation.

SHEATH DYNAMICS IN PIII

The dynamics of sheath evolution in PIII have been described by Lieberman and Lichtenburg. In the initial stage of the high voltage pulse electrons are expelled from the area surrounding the substrate on a timescale of order the inverse electron plasma frequency and an ion matrix sheath is formed. Ions from the matrix sheath are subsequently accelerated by the electric field in the sheath and implant into the substrate on a timescale of order the inverse ion plasma frequency. After depletion of the matrix sheath a quasistatic Child law sheath forms.

As the ions are removed from the matrix sheath, the sheath boundary begins to expand due to the reduced ion density. Ions uncovered by the moving boundary are accelerated toward the substrate and implanted. Eventually, equilibrium occurs between the implanted ion current and the replenishment of ions due to ions approaching the sheath boundary at the Bohm velocity. In this case a stationary Child law sheath is said to have formed. The Child–Langmuir law, which holds for both the quasistatic and stationary cases when the applied voltage, $V_0$, is much greater than the electron temperature, gives the current density, $j$, crossing the sheath boundary as

$$j = A \frac{V_0^{3/2}}{x^2},$$  \hspace{1cm} (1)$$

where $x$ is the sheath width and...
\[ A = \frac{4 \epsilon_0}{9} \left( \frac{2 e}{M} \right)^{1/2}, \]

where \( \epsilon_0 \) is the permittivity of free space, \( e \) is the electron charge, and \( M \) is the ion mass. The current density drawn by a planar substrate is given by

\[ j = en \left[ u + \frac{dx}{dt} \right], \]

where \( u \) is the directed ion velocity and \( n \) is the ion density at the sheath boundary. Equating Eqs. (1) and (3) gives the basic equation for the model of sheath dynamics in PIII. If the plasma ion velocity is subsonic a presheath will be established to satisfy the Bohm sheath criterion. The ion density at the sheath boundary will then be determined by the Boltzmann relation and will be approximately \( 0.6n_0 \).

Brown et al. have described an extension of the model for sheath behavior in a drifting plasma, like that encountered in a cathodic vacuum arc. In this case the ions approach the sheath boundary at a directed velocity greater than the Bohm velocity. As a consequence the formation of a presheath is not required to satisfy the Bohm criterion. Experimental observations suggest that this is indeed the case.

Using such a model, Emmert and Linder and Cheung have investigated the sheath dynamics of dielectric insulating substrates on a conducting holder in an isotropic plasma. The substrate surface and conducting holder can be modeled as a capacitor and calculating the time to charge the capacitor to the experimental conditions are presented in Ref. 3.

The minimum thickness of the conductive film is determined by its capability to effectively conduct away the surface charge accumulating during the PIII pulse, thereby retaining the voltage across the sheath for the duration of the pulse. For a circular thin film, radius \( r \), thickness \( t \), uniformly implanted with current density \( j \), the total incident ion current is \( j \pi r^2 \). As charge is deposited it will be attracted to the contact at the edge of the circular film. In the steady state the total implanted current will equal the current through an area at the film edge equal to \( 2 \pi r t \). For a film of conductivity \( \rho \), the voltage drop across a ring element of width \( dr \) is

\[ dV_f = \frac{\rho dr}{2 \pi r^2} j \pi r^2, \]

\[ V_f(r) = \int_0^r \frac{\rho j r}{2t} dr, \]

\[ V_f = \frac{\rho j r^2}{4t}, \]

where \( V_f \) is the voltage profile across the film surface. Thus the magnitude of the sheath voltage, \( V_0 \), in Eq. (1), at the center of the circular conducting film, will be equal to \( V_0 - V_f(R) \), where \( R \) is the radius of the annular holder.

A parabolic potential profile will be established across the film surface, reaching equilibrium when the current implanted is equal to the current conducted away. Our model assumes the equilibrium condition is established on a time scale that is short compared with the time steps in our calculation. The time to establish the equilibrium condition can be estimated by considering the thin film, dielectric substrate, and substrate holder as a polymer–electrode sandwich capacitor and calculating the current across the gap of the material. The sheath voltage, replacing \( V_0 \) in Eq. (1), is then

\[ V_f = V_0 - \frac{nedx/(\epsilon_0 \kappa)}{1 + [(4d)/3x \kappa]}. \]

However, Emmert neglected the current due to secondary electrons and as a consequence vastly underestimated the charge accumulation on the substrate surface. Linder and Cheung included the secondary electron current and also the electron flux to the substrate due to Boltzmann electrons from the plasma. This provides a more complete model of the sheath dynamics for insulating substrates. In our model we have omitted the electron flux due to Boltzmann electrons since this flux is negligible at high voltages. As a consequence the simulated surface potential can reach zero when in reality it would tend toward the plasma floating potential, typically a few volts.

Under certain conditions, charge accumulation on insulating substrates during the implantation pulse can be enough to extinguish the sheath voltage and facilitate the collapse of the sheath. Additionally the implant energy of the ions is nonuniform if the sheath voltage is reducing during the pulse. This limits the effective pulse lengths applicable to PIII of insulators. In a recent paper we presented experimental results of PIII of polymeric substrates utilizing a sacrificial conductive surface layer. Very thin copper and carbon films, of the order of 10 nm, were first deposited on polycarbonate substrates using a dc filtered cathodic vacuum arc. The films were then contacted to the high voltage supply by placing a biased metal annulus around the edge of the substrate. The samples were then treated with metal ion PIII in a cathodic arc plasma. TRIM simulations showed that the majority of the ions would penetrate the metal film and implant into the underlying substrate. Cross-sectional transmission electron microscope images showed an implanted polymer surface layer of the order of 100 nm thick. Four-point probe conductivity measurements of 20 and 50 \( \mu \)S implantation pulse widths showed that the applied pulse was not being extinguished by surface charge accumulation. Details of the experimental conditions are presented in Ref. 3.
We used these equations to write a program in MATLAB™ to model the sheath width and voltage as a function of time for dielectrics in isotropic and streaming plasmas, with and without a thin conductive film.

RESULTS AND DISCUSSION

For the case of an isotropic, neutral plasma a presheath is established to maintain the continuity of the ion flux. This accelerates the ions at the sheath edge to the Bohm velocity, \( u_B \), and the plasma density at the sheath edge is approximately 0.6 times the bulk plasma density, \( n_0 \).

In the case of a streaming plasma, such as a cathodic arc plasma, the ion velocity is greater than the Bohm velocity and no presheath is established. The plasma density at the sheath boundary in this case is \( n_0 \). Figures 1 and 2 show the sheath voltage and width for the case where \( n_0 \) equals \( 1 \times 10^{10} \) cm\(^{-3} \). Titanium ions with an average charge state of 2.1 are used as the implanting species. We have assumed a Bohm velocity of \( 1 \times 10^3 \) ms\(^{-1} \) and a directed velocity of \( 1 \times 10^4 \) ms\(^{-1} \) for the streaming plasma. A secondary electron coefficient of 5 is assumed for all cases and the voltage applied is 10 kV. We have assumed that the risetime of the pulse is infinitesimal and that the matrix sheath implants instantaneously, since these timescales are short compared to the length of the pulse applied.

The dielectric constant of the polymer substrate was assumed to be 4.5 and its thickness 1 mm. For the thin conductive film case the film is 5 nm thick and the resistivity of the film is \( 3.5 \times 10^{-6} \) Ω m. This value was extrapolated from the measured values for ultrathin copper films down to 10 nm. The resistivity is higher than that of the bulk material due to increased scattering from the surfaces of ultrathin films. The distance from the high voltage contact to the center of the conductive film is 2.5 cm.

Figure 1 shows that for an isotropic plasma the sheath voltage will be negligible before the end of the applied pulse due to charge accumulation. For the streaming plasma case the pulse will be extinguished far more quickly due to the increased ion velocity and plasma density at the sheath boundary. In contrast, the application of a thin conductive film holds the sheath voltage very close to the applied voltage for the duration of the pulse for both plasma conditions. Expanding the voltage axis of the streaming plasma case over the same time period (Fig. 1, inset) shows that the voltage is initially reduced by around 50 V due to the high ion flux during the depletion of the matrix sheath. After a short period of time the voltage levels out to a value around 15 V below the applied voltage, \( V_0 \). In reality this initial reduction in voltage would not be so large since one of our assumptions in the model was that all the matrix sheath ions are implanted instantaneously. Another assumption was that the risetime of the pulse was infinitesimal when in reality it may take a few microseconds. This assumption would also tend to overestimate the initial voltage drop.

The main advantage of the conductive film method is to allow an increase in the effective pulse length. Without the film the sheath voltage is extinguished after around 2 \( \mu s \) for the streaming plasma and around 18 \( \mu s \) for the isotropic plasma. The conductive film maintains almost the entire applied voltage for the duration of the pulse. Additionally, it has been observed during experiments that breakdown across the sheath is reduced and often eliminated during the implantation process.

Whilst it is apparent that the sheath voltage is held relatively constant for the case of the thin conducting film, the ion implant energy is also more homogeneous than in the uncoated insulator case. Ions accelerated across the sheath potential will undergo collisions in the thin conductive film, lose energy, and consequently implant into the substrate with a range of energies. TRIM simulations show that for the conditions described above, over 80% of the incident ions are transmitted, and of these over 80% are transmitted with energy of greater than 50% of \( V_0 \). This is in contrast to the insulator case where the implant energy is equal to the product of the ion charge and the sheath voltage which is roughly...
evenly spread from just over 8 kV down to the floating potential of the plasma. Therefore, the thin conductive film method can reduce the energy spread of implanted ions and provide a greater effective pulse length, thereby reducing the processing time required.

In Fig. 2 the evolution of the sheath width is shown for the four cases described above. The dielectric insulator in the streaming plasma has a sheath that initially expands but quickly begins to contract as the sheath voltage is extinguished. In an isotropic plasma similar behavior is observed over a longer time period due to the reduction in charging rate. With a thin conductive film on the insulator surface the sheath does not contract since there is very little charge accumulation. Of note is the case for the thin conductor in the streaming plasma that quickly reaches a constant sheath width. This phenomenon is peculiar to plasma sources with a high directional velocity\textsuperscript{15} such as the cathodic arc. However this is only for the case of a planar substrate perpendicular to the direction of the direction of plasma flux. For three-dimensional objects in a cathodic arc plasma the sheath dynamics will be considerably more complicated.\textsuperscript{16}

**CONCLUSION**

We have extended the model for PIII of insulators to the case where the plasma is moving with a directed velocity, as is the case for a cathodic arc plasma. We have also developed a model for the change in voltage on the surface of a thin conductive film coated insulator during PIII. Using typical conditions for PIII we have used the model to simulate the time evolution of the sheath voltage and sheath width for insulating substrates with and without a thin conductive surface film. The sheath voltage is essentially maintained over the entire pulse duration for the conductive film coated insulator whereas the sheath voltage for the uncoated insulator is extinguished due to charge accumulation. The energy of the implanted ions is consequently more homogeneous for insulators with very thin conductive film coatings. A thin conductive surface film can therefore extend the effective pulse length that can be applied to insulating substrates, and improve control of the implantation energy and reduce the probability of breakdown across the sheath.

\textsuperscript{9} J. Ziegler, http://www.srim.org/.