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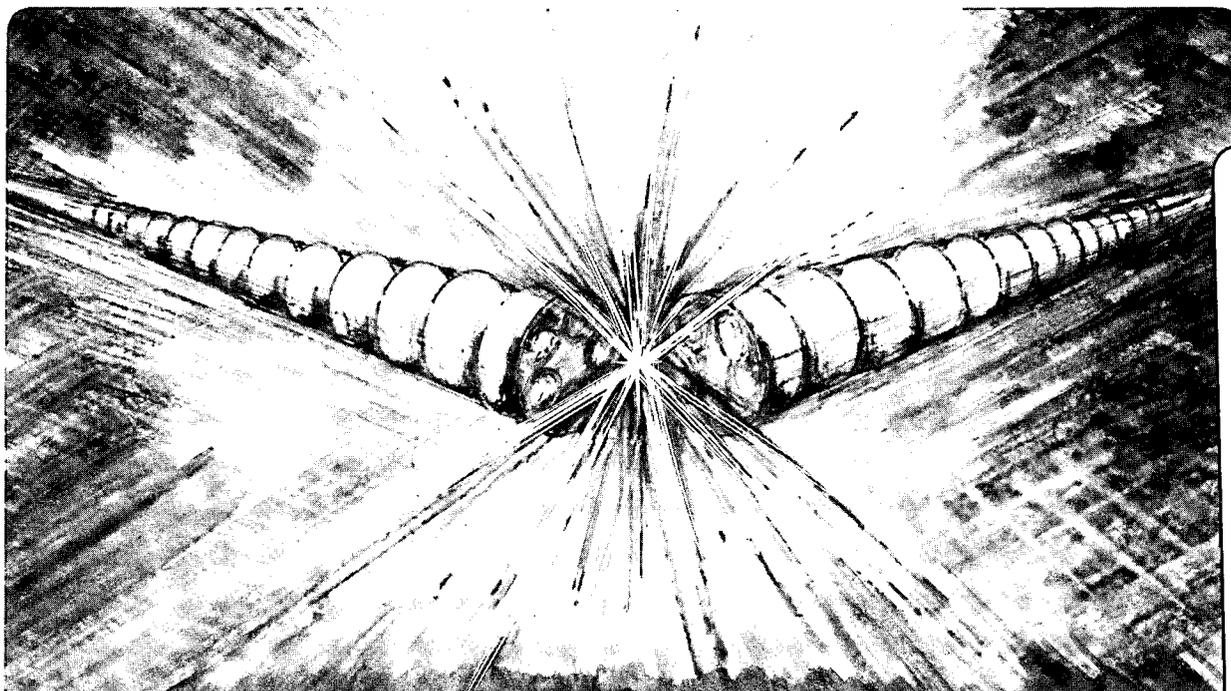
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Plasma Immersion Surface Modification with Metal Ion Plasma

I.G. Brown, X. Godechot, and K.M. Yu

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I. G. Brown, X. Godechot* and K. M. Yu

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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I. G. BROWN, X. GODECHOT* and K. M. YU

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

ABSTRACT

We describe here a novel technique for surface modification in which a metal plasma is employed and by which various blends of plasma deposition and ion implantation can be obtained. The new technique is a variation of the plasma immersion technique described by Conrad and co-workers. When a substrate is immersed in a metal plasma, the plasma that condenses on the substrate remains there as a film, and when the substrate is then implanted, qualitatively different processes can follow, including 'conventional' high energy ion implantation, recoil implantation, ion beam mixing, ion beam assisted deposition, and metallic thin film and multilayer fabrication with or without species mixing. Multiple metal plasma guns can be used with different metal ion species, films can be bonded to the substrate through ion beam mixing at the interface, and multilayer structures can be tailored with graded or abrupt interfaces. We have fabricated several different kinds of modified surface layers in this way.

INTRODUCTION

Wide application has been made of plasma and ion beam techniques for the synthesis and modification of material surfaces. Methods have been developed which make use of the implantation of high energy ions to some depth below the surface, and the deposition of low energy plasma fluxes on top of the surface. A wide range of ion and plasma species has been employed, and the energy range used spans many orders of magnitude, from thermal up to multi-MeV. Many hybrid techniques have also been explored, some of which have been highly successful and are used industrially. These techniques have been widely addressed in the literature [1-6]. In ion implantation, energetic ions that impinge on the solid surface at high energy, typically of order 100 keV, are buried to depths typically several hundred Angstroms; and because of the relative technological simplicity of gaseous ion sources compared to metal ion sources, gaseous ion species, particularly N^+ for metallurgical implantation and O^+ for semiconductor implantation, have mostly been used rather than metallic ion species. For low energy deposition, on the other hand, it has been more common that metal ion (or plasma or atomic) species be used in order that the impinging flux condense and remain on the substrate surface rather than simply recombine and evaporate as a gas.

A novel technique for the energetic implantation of gaseous ion species into a substrate has been described and developed by Conrad and co-workers [7-10], and this technique is also being actively pursued by others [11-16]. The method has been called plasma source ion implantation (psii) or plasma immersion ion implantation (piii). In this technique the substrate to be implanted is immersed in a plasma and repetitively pulse-biased to high negative voltage, thereby accelerating ions across the plasma sheath into the substrate. High implantation doses of the species of which the plasma is composed can rapidly be accumulated. This method has several advantages over the more conventional method of implantation in which a traditional ion source is employed to create a directed energetic ion beam, and it has been shown to be an effective tool for both metallurgical [7-12] and semiconductor [13-16] ion implantation. However, it has to-date been the case that only gaseous plasmas have been used.

When the plasma in which the substrate is immersed is a metal plasma, the plasma condenses and remains on the substrate as a film, even at low energy and in the absence of the high voltage pulsing. When the high voltage bias pulse is applied, the metal plasma ions are

accelerated across the sheath and bombard the substrate with its metallic overlayer of previously-condensed plasma. If now the plasma is applied in a pulsed mode with a time structure comparable to the high voltage pulse biasing, then we have a situation in which a wide range of new surface structures can be synthesized. Other features can also be added to this basic metal plasma immersion pulse biasing technique, such as: multiple metal plasma guns, perhaps of different metal species; variation of pulse length of the metal plasma pulse; phasing of the ion acceleration pulse (pulse biasing phase) with respect to the plasma pulse (low energy plasma deposition phase); and finally all of these parameters can be tailored throughout the duration of the surface processing operation to fabricate a very wide range of surface structures at the atomic level. The added species can be energetically implanted below the surface or built up as a surface film with an atomically mixed interface with the substrate; the metal ion species can be the same as the substrate species or different from it, and more than one kind of metal species can be applied, either simultaneously or sequentially. Surface structures can be fabricated, including coatings and thin films of single metals, tailored alloys or metallic multilayers, and they can be implanted or added onto the surface and ion beam mixed.

Here we describe the configuration we have used to test the concept and the results of some experiments demonstrating the versatility of the method. A preliminary account of a part of this work has been reported elsewhere [17].

DESCRIPTION OF THE METHOD

In the experiments described here we have used miniature pulsed metal vapor vacuum arc plasma guns to provide highly ionized metal plasma that is directed toward a suitable substrate located within a vacuum vessel cryogenically pumped to a base pressure of about 1×10^{-6} Torr. These kinds of plasma guns have been developed in our laboratory and their use for the deposition of metallic thin films and multilayers has been described in the literature [18]. A very wide range of metal species can be generated; we have demonstrated operation [19,20] with 48 different metallic elements of the periodic table (ie, nearly all of them), and the plasma species generated can be changed simply by replacing a small cylindrical metallic cathode. In general the ions produced by the vacuum arc are multiply ionized with a charge state distribution having a mean in the range $\bar{Q} = 1+$ to $3+$. This provides an advantage in that the mean energy acquired by the ions when they are accelerated across the plasma sheath by the high voltage pulse is greater than the applied voltage by a factor equal to the mean charge state. The directed energy of the plasma stream generated by the plasma gun is of order 50 eV. For a part of the time that the metal plasma impacts the substrate surface (about a half, here) the substrate is pulse biased to several tens of kilovolts so as to accelerate ions and implant them into the substrate. Thus the metal plasma ions impact the substrate with an energy that is approximately 50 eV during the deposition part of the cycle, or many tens of keV during the implantation part of the cycle.

The small (approximately 1 cm square) substrate was located about 5 cm in front of the pulsed plasma gun(s). The substrate materials used were carbon, silicon or aluminum, and the cathode materials and thus metallic ion species used were yttrium, titanium or platinum. For the experiments reported here the plasma pulse length was either 2 or 5 μ s, and the high voltage bias pulse length was either 1 or 2 μ s (respectively). For some of the work we wanted to build up a film of several thousand Angstroms thickness, and in this case the plasma pulse was 250 μ s long. Pulse repetition rate was varied between 10 and 70 pulses per second, and the total number of pulses accumulated was from several thousand up to as high as 200,000. The ion current collected by the substrate during a plasma pulse was measured by biasing the substrate to -200 V and monitoring the ion saturation current [21]. The ion saturation current was typically 2 Amps in magnitude. A schematic representation of the set-up is shown in Figure 1.

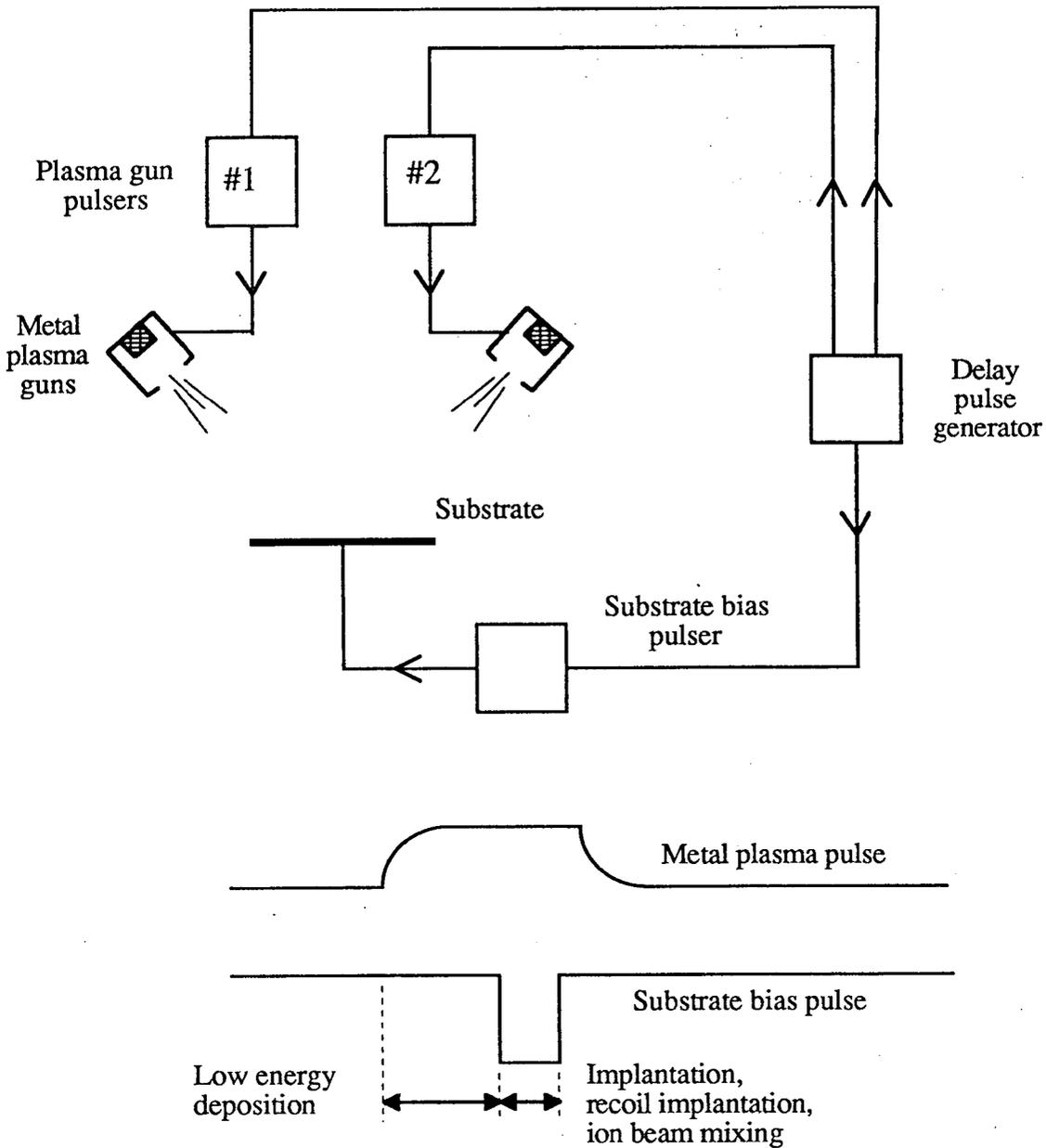


Fig. 1 Schematic of the experimental configuration used here. (XBL 9010-3414)

RESULTS

We have demonstrated the technique by synthesizing several different surface structures. Surfaces showing metal ion implantation, thin film deposition with atomic mixing at the interface ("ion stitching"), and metallic multilayer fabrication with several interfaces atomically mixed, have been fabricated and analyzed with 2 MeV He⁺ Rutherford Backscattering Spectrometry (RBS). These several experiments are summarized in the following.

In the first experiment we simply implanted yttrium into silicon. We used an yttrium plasma, for which the mean ion charge state is $\bar{Q} = 2.3$. Thus the negative high voltage pulse of magnitude 30 kV implies a mean ion energy of 70 keV. The high voltage bias pulse width was 1 μ sec, timed for the maximum of the 2 μ sec long plasma pulse, and the system was repetitively pulsed; the equivalent time-averaged ion implantation current was several tens

of microamperes. Another sample was prepared under identical conditions except that the high voltage implantation pulse was not applied, thus providing a non-implanted sample for comparison. The RBS results are shown in Figure 2. The resolution of the RBS is indicated by the Gaussian-shaped profile obtained from the film that is deposited on the surface of the silicon when the pulse biasing is not applied. When the pulse biasing is applied, the depth profile extends below the surface and has a shape that is qualitatively as expected for a combination of conventional ion implantation, recoil implantation, and surface deposition. The nominal depth of the implanted region (half width of the profile, with an ad-hoc correction for the RBS resolution) is approximately 500 Å, which can be compared with the TRIM-calculated [22] range for 70 keV Y into Si of 470 Å. The RBS-measured dose is 1.0×10^{16} atoms/cm², in good agreement with the dose expected from the accumulated number of pulses. Note that the RBS Y profile for the sample with the pulse biasing shows a long tail extending into the substrate, indicating recoil implantation.

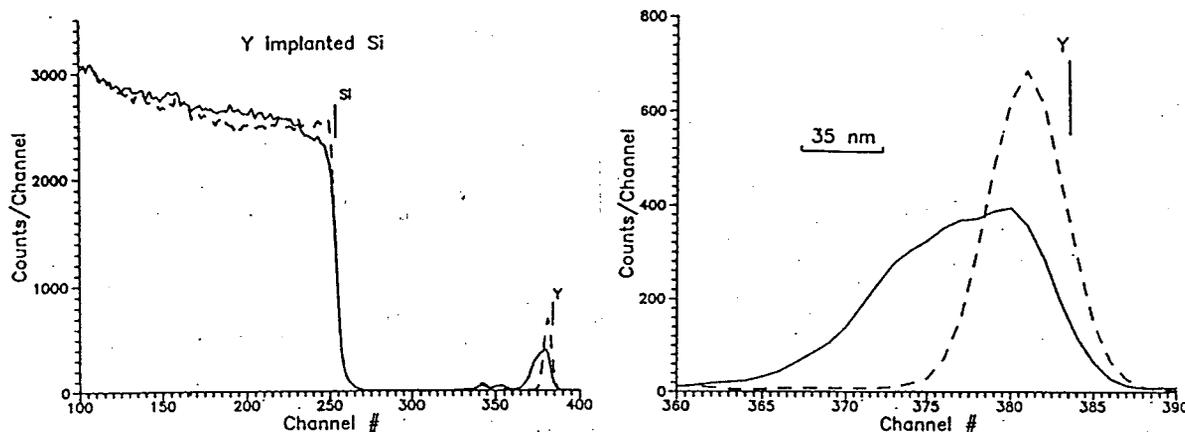


Fig. 2 Rutherford Backscattering spectra for Yttrium into Silicon. The dashed curve is from the sample without pulse biasing and the solid curve from that with pulse biasing. The depth of implantation is approximately 500 Å and the dose is 1×10^{16} cm⁻². (XBL 9010-3415) The second curve shows the detail of the Y distribution. (XBL 9010-3416)

In the second experiment we fabricated an yttrium-titanium multilayer structure on silicon with ion beam mixing at some of the interfaces. Two plasma guns were used, with yttrium and titanium cathodes. The sequence of operations was: yttrium was implanted into the substrate at an energy of 70 keV and a dose of 1×10^{16} atoms/cm², followed by low energy deposition of yttrium to build up a layer of thickness several hundred Angstroms (the pulse length of the yttrium plasma pulse was increased from 2 μsec up to 250 μs for this film fabrication phase); then successive layers of Ti-Y-Ti-Y-Ti were added, each of several hundred Angstroms thickness; the final Ti layer was started out by implanting Ti into the underlying Y layer at an energy of about 50 keV and a dose of about 1×10^{15} atoms/cm², followed by the low energy, longer pulse length part of the final Ti phase. The RBS data are shown in Figure 3. The multilayer structure is evident; the layers have a thickness of approximately 400 Å, corresponding to a deposited particle density of approximately 1.4×10^{17} atoms/cm² for Y and 2.5×10^{17} atoms/cm² for Ti.

It is of considerable fundamental and technological interest to be able to form metallic thin films on metallic substrates, with film thickness of order a micron and with the film and substrate substantially atomically mixed at the interface. Such a thin film should have particularly good bonding to the substrate and the adhesion properties would be expected to be excellent. In Figure 4 we show RBS data for a 0.2 microns thick film of Pt that has been put down on an Al substrate with an atomically mixed interface layer. Firstly the pulse biasing was applied using a Pt plasma and a pulse energy of 20 keV so as to accumulate an implanted Pt dose of approximately 1×10^{17} cm⁻², followed by deposition at longer pulse length and lower energy. Note that in Figure 4 the low energy side of the Pt spectrum shows a reduced Pt signal. This indicates that the Pt/Al interface is well mixed by the ion stitching process. The mixed Pt/Al interface is estimated to be roughly 1500 Å thick with a nominal composition

[Pt]:[Al] = 1:3. The width of this region is greater than expected from the implantation energy; we will study this further. The mixed region at the interface can be very significant in the enhancement of adhesion of the film to the substrate.

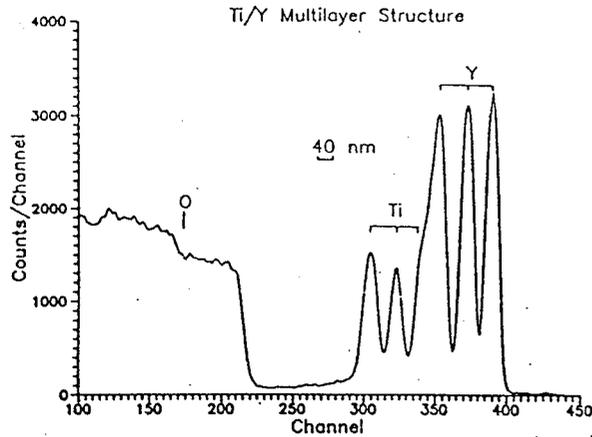


Fig. 3 Rutherford Backscattering spectrum for a Ti-Y multilayer structure on Si with ion beam mixing at the first Si-Y and the final Ti-Y interfaces. (XBL 9010-3417)

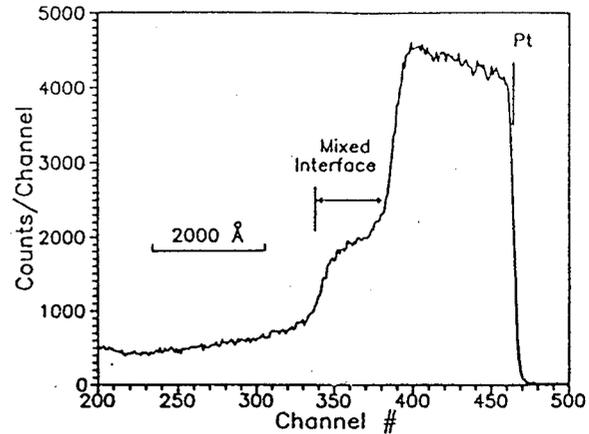


Fig. 4 Rutherford Backscattering spectrum for a Pt film on Al with ion beam mixing at the interface. The Pt film is approx. 0.2 microns thick. (XBL 914-871)

CONCLUSION

The surface modification method described here - plasma immersion ion implantation for the case of a condensable metal plasma, when the conventional 'pure implantation' is augmented by recoil implantation of the co-deposited metal film - can be used to form surface layers that could be of relevance to a number of fields. The experimental requirements are particularly simple and the method can be varied and extended in a variety of ways. For example a number of metal plasma guns having different metals can be used for tailoring the compositional structure of the surface being synthesized. Following the initial recoil implantation phase, the low energy deposition phase can be continued using dc vacuum arc plasma gun techniques to form a film of macroscopic thickness that is well bonded to the substrate through a deep, atomically-mixed zone. The bonding transition zone between substrate and film can be tailored widely to provide an optimum match between substrate and film properties, for example thermal expansion or lattice constant. Finally, the method is uncomplicated in principle and it is efficient, and by using numerous sources it can be scaled up to arbitrarily large size for the processing of large workpieces or for high material throughput rate. We plan to explore these avenues in future work.

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UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720