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NOVEL METAL ION SURFACE MODIFICATION TECHNIQUE

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ABSTRACT

We describe a method for applying metal ions to the near-surface region of solid materials. 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. We report two simple demonstrations of the method: implantation of yttrium into a silicon substrate at a mean energy of 70 keV and a dose of 1×10^{16} atoms/cm^2, and the formation of a titanium-yttrium multilayer structure with ion beam mixing to the substrate.

A wide spectrum of methods has been developed for the modification of material surfaces by the application of externally generated beams of atoms, ions, or plasma [1-4]. Ion implantation is used to energetically inject ions to depths of hundreds or thousands of Angstroms below the surface, while a surface film can be deposited onto the substrate by an intense low energy flux of neutral or ionized species. In recent years hybrids of these various methods have been investigated, such as ion beam mixing [5] and ion beam assisted deposition (IBAD) [6]. Thus, for example, a condensible (eg, metal) species deposited onto the surface at low energy can be driven into the substrate material by knock-on collisions with energetic ions. Much progress has been made in a number of means of implementation of this recoil implantation technique.

At the same time, a unique means of carrying out ion implantation has been developed, principally by Conrad and co-workers [7,8] and also by others [9-12], in which the object 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. This technique has been called plasma source (or plasma immersion) ion implantation (psii or piii). PIII with a gaseous plasma has been shown to be an effective tool for both metallurgical [7-9] and semiconductor [10-12] ion implantation.

For the case when the plasma in which the object is immersed is a metal plasma, the plasma condenses and remains on the substrate as a film, and qualitatively new and different consequences follow: other features can then be added to the basic 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 (piii stage) with respect to the plasma pulse (low energy plasma deposition stage); and finally all of these parameters can be tailored throughout the duration of the surface processing operation to fabricate a wide range of surface structures at the atomic level.

In the preliminary experiments described here, plumes of highly ionized metal plasma are generated by vacuum arc plasma guns and the low energy (approx 50 eV directed energy) plasma is directed toward a silicon substrate. For a part of the time (about a half, here) that the metal plasma impacts the surface, the substrate is pulse biased to a high negative potential so as to accelerate ions and implant them into the substrate. The result is a combination of low energy ion deposition, direct ion implantation, and recoil ion implantation.

The experiments were carried out in a vacuum vessel pumped cryogenically to a pressure of about 1×10^{-6} Torr. The pulsed metal plasma source was a miniature metal vapor vacuum arc

plasma gun of the kind we have developed and used previously for metallic thin film and multilayer fabrication [13]. Cathode materials were yttrium and titanium; in the first experiment we simply implanted yttrium into silicon and in the second experiment we fabricated an yttrium-titanium multilayer structure with ion beam mixing at some of the interfaces. Previous work [14,15] has shown that the metal plasma generated in this way is multiply ionized, with mean charge state $\overline{Q}$ of 2.3 for yttrium and 2.1 for titanium. Thus, when implanted, the mean ion energy is greater than the applied pulse voltage by this factor. The substrate was a small piece of silicon wafer cleaned in hydrofluoric acid and water; silicon was used for experimental convenience. The silicon substrate was located a distance of approximately 5 cm in front of the pulsed yttrium plasma gun. Prior to implantation (repetitive application of the high voltage pulse), the plasma ion current collected by the substrate during each pulse was measured by biasing the substrate to -200 V and measuring the ion saturation current in the usual way [16]. The ion saturation current pulse was typically 2 μsec wide and 2 Amps in magnitude. A schematic representation of the set-up is shown in Figure 1.

For the first experiment the plasma gun was operated with yttrium. A negative high voltage pulse of magnitude 30 kV and width 1 μsec was applied to the substrate, timed for the maximum of the plasma pulse, and the system was repetitively pulsed. The equivalent time-averaged ion implantation current was approximately 40 μA. For an yttrium ion mean charge state of 2.3, the 30 kV voltage pulse corresponds to a mean ion energy of 70 keV. 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 samples were analyzed by 2.0 MeV He^+ Rutherford Backscattering Spectrometry (RBS) and the results are shown in Figure 2. The RBS resolution 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. With the pulse biasing, 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. A nominal depth of the implanted region (half width of the profile, with an ad-hoc correction for the RBS resolution) is approximately 500 A, which can be compared with the TRIM-calculated [17] range for 70 keV Y into Si of 470 A. The RBS-measured dose is 1.0×10^{16} atoms/cm^2, in 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.

For the second experimental demonstration of the method two plasma guns were used, containing 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/cm^2, followed by a low energy (about 50 eV; no high voltage pulse applied) 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 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 x 10^{15} atoms/cm^2, then 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 A, corresponding to a deposited particle density of approximately 1.4 x 10^{17} atoms/cm^2 for Y and 2.5 x 10^{17} atoms/cm^2 for Ti.

These results demonstrate that the surface modification method described here - plasma immersion ion implantation for the case of a condensible 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 configuration used here is particularly simple and the method can be extended in a variety of ways. For example, many metal plasma guns could be used and the compositional structure of the layer can be tailored. Following the initial recoil implantation phase, the low energy deposition phase could 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; in this case the film adhesion would be excellent. 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. We plan to explore these avenues in future work.

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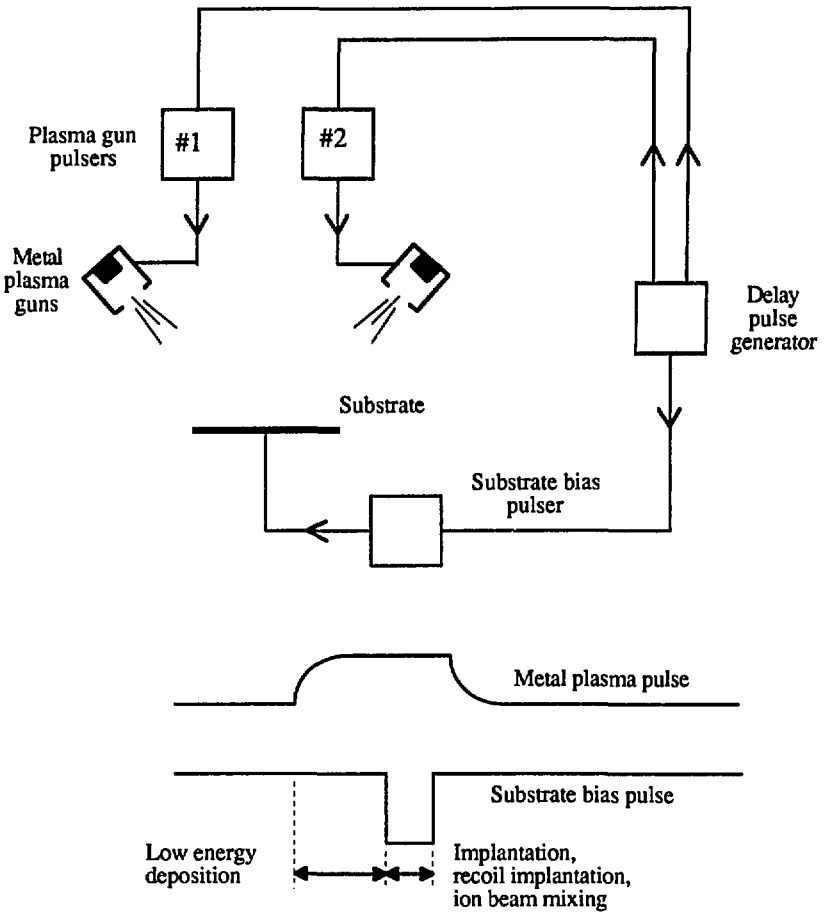

Fig. 1 Schematic of the experimental configuration used here.

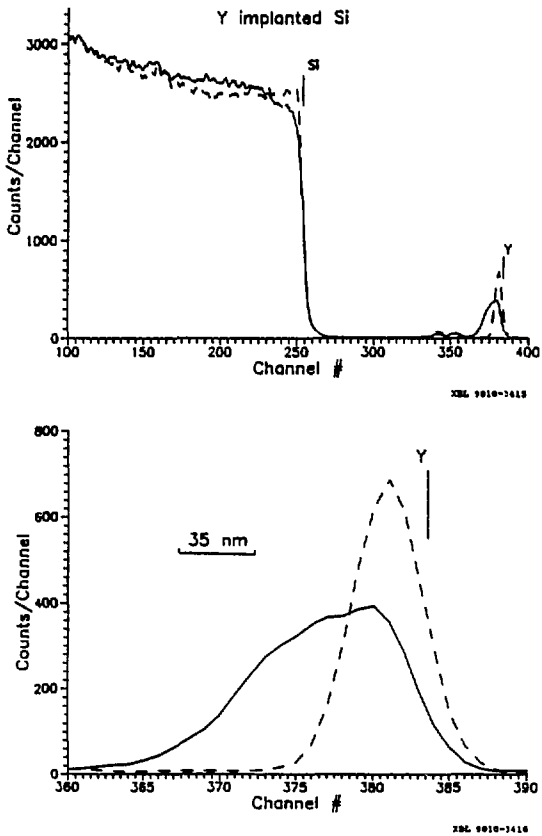

Fig. 2 Rutherford Backscattering spectra for Y into Si. The dashed curve is from the sample without pulse biasing and the solid curve from that with pulse biasing. The depth of implantation is approximately 500 A and the dose is 1 x 10^{16} cm^{-2}. The second curve shows the detail of the Y distribution .

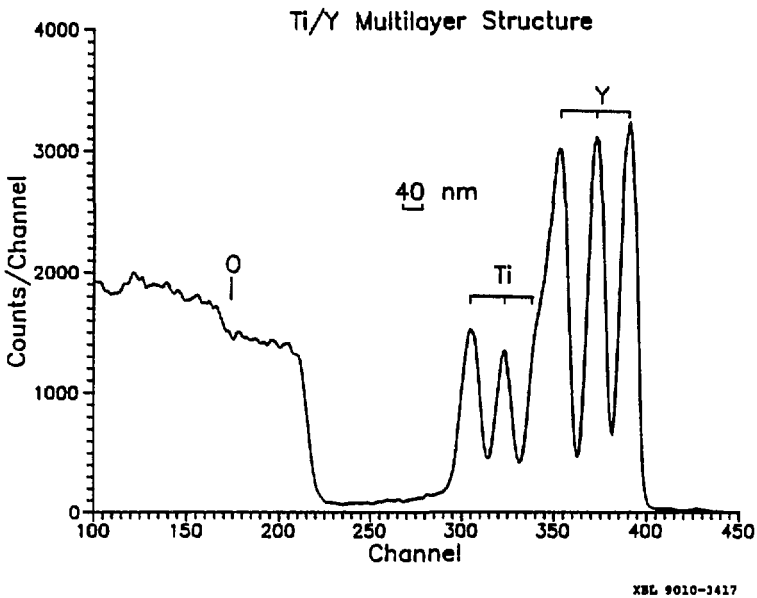

Fig. 3 Rutherford Backscattering spectra for a Ti-Y multilayer structure on Si with ion beam mixing at the first Si-Y and the final Ti-Y interfaces.