REVIEW OF SCIENTIFIC INSTRUMENTS VOLUME 70, NUMBER 11 NOVEMBER 1999

Pure high dose metal ion implantation using the plasma immersion technique

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(Received 5 May 1999; accepted for publication 18 August 1999)

High energy implantation of metal ions can be carried out using conventional ion implantation with a mass-selected ion beam in scanned-spot mode by employing a broad-beam approach such as with a vacuum arc ion source, or by utilizing plasma immersion ion implantation with a metal plasma. For many high dose applications, the use of plasma immersion techniques offers a high-rate process, but the formation of a surface film along with the subsurface implanted layer is sometimes a severe or even fatal detriment. We describe here an operating mode of the metal plasma immersion approach by which pure implantation can be obtained. We have demonstrated the technique by carrying out Ti and Ta implantations at energies of about 80 and 120 keV for Ti and Ta, respectively, and doses on the order of 1×10^{17} ions/cm^2. Our experiments show that virtually pure implantation without simultaneous surface deposition can be accomplished. Using proper synchronization of the metal arc and sample voltage pulse, the applied dose that deposits as a film versus the part that is energetically implanted (the deposition-to-implantation ratio) can be precisely controlled. © *1999 American Institute of Physics.* [S0034-6748(99)03911-8]

I. INTRODUCTION

Ion implantation is an established technique for the surface modification of materials[1–3] and it provides a means for adding a wide range of dopant species to the near-surface region of the implanted material. Metal ion beams of high intensity have traditionally been somewhat more difficult to produce than beams of gaseous ions, and research and development of ion implantation applications using metal ion species has been hampered. Metal vacuum arc ion sources or metal vacuum vapor arc (MEVVA) sources[4–6] have filled this need in recent years and have provided a tool for high dose ion implantation of virtually all of the metal species in the periodic table in broad-beam, repetitively pulsed operational mode.

Plasma immersion ion implantation (PIII)[7–9] is an alternative to conventional beamline ion implantation in which the object to be implanted is immersed in a plasma of the desired ion species and repetitively pulse biased to high negative voltage. A high voltage sheath forms at the substrate boundary and plasma ions are accelerated through the sheath drop and into the substrate. If the pressure is low enough, collisionless conditions are satisfied, thereby accomplishing implantation of the plasma ions at an energy determined by the bias voltage. The voltage is repetitively pulsed until the desired implantation dose is accumulated. Because of the surface retention of the condensed metal plasma, the PIII process in a metal plasma is different from that in a gaseous plasma, and qualitatively new and different consequences result.[10–12] In the ‘‘voltage-off’’ part of the applied substrate bias pulse, the metal plasma ions can deposit on the surface as a film, while during the ‘‘voltage-on’’ part of the pulse, the plasma ions are accelerated into the substrate, undergoing both direct ion implantation as well as recoil implantation with previously deposited neutral metal atoms. Thus, the implantation depth profile of the metal plasma immersion process is different from the usual shifted Gaussian-like shape and extends approximately uniformly from the surface down to the maximum range, including a surface film. This kind of surface modification, called metal plasma immersion ion implantation and deposition (MePIIID), can be attractive for some applications. It provides a surface film that is atomically mixed into the substrate.[10–15] However, if pure implantation with no surface film is required, the conventional metal plasma immersion process may not be acceptable.

The deposition of low energy metal ions on the surface can be avoided if, for that period of time during which the substrate is exposed to the metal plasma, the substrate bias is always at high (negative) voltage. Since it is usual that vacuum arc metal plasma sources are operated in a repetitively pulsed mode, the high voltage bias may be maintained without adverse effects such as breakdown between the substrate and the grounded vacuum vessel. This is the approach adopted in the work described here. Furthermore, by fine control of both the lengths and the phases of the two critical timing pulses involved in the operation, namely, the plasma pulse and the high voltage bias pulse, one can fine-tune the process to achieve either pure implantation or a controllable hybrid process containing a fraction of deposited surface film.

In this article, we describe the plasma and high voltage

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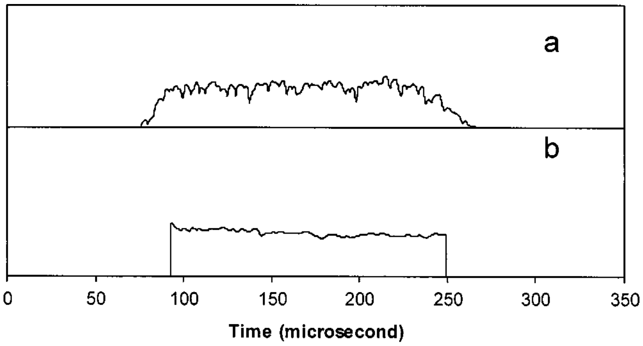

FIG. 1. Synchronization of the sample and metal arc voltage pulses: (a) ion current of one cathode arc pulse collected on the plane collector plate. (b) Negative high voltage pulse on the plate. The phase and duration of the pulse shown in (a) can be adjusted to cover almost the entire ion flux pulse shown in (a).

experimental configuration used as a demonstration of the approach, and summarize the results obtained for two processes employing Ti and Ta plasmas. We show that energetic, high-dose, metal ion implantation can be done in a short processing time.

II. EXPERIMENT

The metal plasma was generated by a filtered vacuum arc plasma gun of the kind that has been discussed in the literature[16,17] and our particular setup has been described in detail previously.[18] The plasma source used a 1 cm diam cathode of either Ti or Ta and a stainless-steel 2 mm mesh anode positioned about 16 mm in front of the cathode. The plasma gun was located at the entrance to a 45° magnetic duct consisting of a vacuum elbow 8 cm in diameter and 50 cm long, around which a solenoid was wrapped to establish the duct magnetic field. For the experiments reported here, the arc current pulse was 150 A and the duration was about 200 μs with a repetition rate of 33 pulse/s. The duct magnetic field was 320 G. An aluminum electrode (Bilek bias plate) was positioned at the duct wall and biased at about $+15$ V to increase plasma transport through the duct.[19–22]

A plane collector plate to which silicon samples were affixed was positioned about 15 cm from the duct exit in the vacuum chamber. Hence, the samples were positioned within the stream of filtered metal plasma transported through the duct and into the main vacuum chamber. The plate with the silicon samples was connected to a high voltage, high current pulser whose pulse amplitude could be varied from 0 to -40 kV and had a pulse width of 0–160 μs. The bias pulse was adjusted to be in phase with the timing of the plasma pulse at its arrival at the substrate location (Fig. 1). The Ti and Ta implantation times were about 10 min. Because of the relatively slow rise and fall times of the plasma pulse, the 160 μs bias pulse was able to envelope most of the plasma pulse. The substrate pulse voltage and current were monitored. There was no suppression of secondary electrons produced by impact of the ions with the collector plate, and thus the current monitored was a sum of the bombarding ion current and the secondary electron current. We took the monitored current signal as only a semi-quantitative current indicator. The vacuum chamber pressure was typically about 5 $\times 10^{-3}$ Pa (4×10^{-5} Torr). A simplified schematic of the experimental configuration is exhibited in Fig. 2.

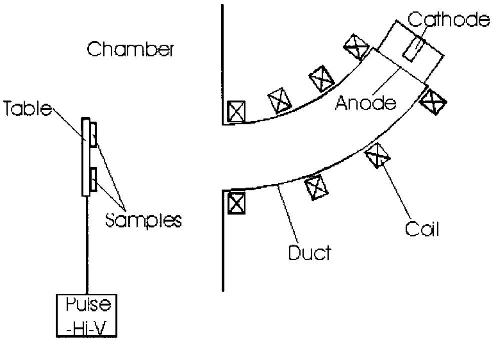

FIG. 2. Schematic of the metal plasma immersion ion implantation setup.

III. RESULTS AND DISCUSSION

The implanted samples were characterized using 1.8 MeV He ion Rutherford backscattering spectrometry (RBS), and the data were deconvoluted using the RUMP code. The depth profile obtained for the case of Ta implanted into Si at 40 kV is displayed in Fig. 3(a). For this sample, the ion implantation dose was 4.1×10^{16} ion/cm^2, and the measured range (depth below the Si surface of the peak of the concentration distribution) was about 240 Å . Similar data obtained for the case of Ti are depicted in Fig. 3(b). There, the dose was 7.9×10^{16} ions/cm^2 and the range was about 450 Å.

The metal plasmas formed in a vacuum arc discharge typically have ion charge states greater than unity. The charge state distribution of the ions in vacuum arc plasmas have been well investigated,[5,12] and it is known that under a wide range of conditions the distributions remain basically constant. For our experiments, we can thus state that the charge state distribution for Ti is, within the uncertainty of

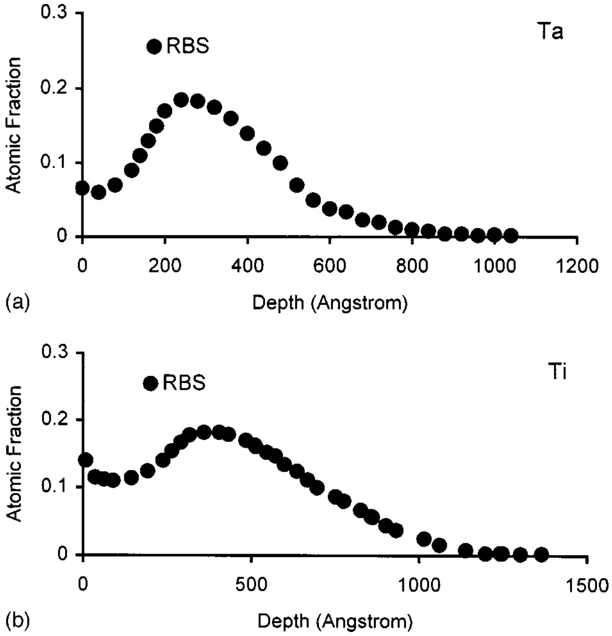

FIG. 3. Depth profiles derived from RBS data: (a) Ta ion implantation into Si, (b) Ti ion implantation into Si.

the experiment, 11:75:14 for charge states 1+:2+:3+, with a mean charge state of 2.1, and that for Ta is 2:33:38:24:3 for charge states 1+:2+:3+:4+:5+, with a mean charge state of 2.9. Here the fractional composition of the distribution is given in terms of particle current fractions, which is needed for consideration of implantation. Note that the particle current, i_p, is not the same as the electrical current, i_e, as measured by the Faraday cup, for example, and $i_p = i_e/Q$. The elevated ion charge states for Ti and Ta vacuum arc-produced plasmas are significant in that the ion implantation energy is given by $E_i = QV_{\text{bias}}$. For a 40 kV bias voltage used here, the mean implantation energies are thus approximately 84 keV for Ti and 116 keV for Ta.

We have performed a profile simulation by a TRIM Monte Carlo calculation[23] employing the actual ion energies involved and the dynamic TRIM (T-DYN)[24,25] which includes the effects of sputter erosion of the surface by the incident ions themselves. The TRIM-predicted ranges are 520 Å for Ta and 675 Å for Ti, and the T-DYN results are similar. While both TRIM and T-DYN in the present application provide good estimates of the Ti and Ta ranges expected, these values, ~650 and 500 Å, respectively, are greater than the RBS-measured depths. The discrepancy in the range is probably due to sagging of the substrate bias voltage due to loading of the pulse generator drawn by the high ion current and surface sputtering by the heavy metal ions. In fact, the measured profiles, especially for the Ti implanted sample, have a shape that would be expected for implantation over a wider energy spread. This points out the necessity of a pulse generator possessing a high slew rate and high deliverable current for this application.

The PIII configuration presented in this article can perform multiple functions: pure implantation of a metal ion, pure metal film deposition, a hybrid of dynamic surface film deposition and metal ion implantation, as well as gaseous ion PIII. The important advantages are the high-rate and large area implantation capability, making the process suitable for not only nonsemiconductor processes, but also semiconductor applications such as the synthesis of buried conducting layers (CoSi_x, IrSi_x, etc). Moreover, the process can synthesize surface and/or buried films containing different species. This is a valuable method to make advanced materials.

ACKNOWLEDGMENTS

This work was supported by Hong Kong RGC earmarked Grant Nos. 9040332 and 9040344 and by City University of Hong Kong Strategic Research Grant Nos. 7000964. The authors also acknowledge K. M. Yu for the RBS analysis.

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