Novel plasma immersion ion implantation and deposition hardware and technique based on high power pulsed magnetron discharge

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A novel plasma immersion ion implantation technique based on high power pulsed magnetron sputtering (HPPMS) discharge that can produce a high density metal plasma is described. The metal plasma is clean and does not suffer from contamination from macroparticles, and the process can be readily scaled up for industrial production. The hardware, working principle, and operation modes are described. A matching circuit is developed to modulate the high-voltage and HPPMS pulses to enable operation under different modes such as simultaneous implantation and deposition, pure implantation, and selective implantation. To demonstrate the efficacy of the system and technique, CrN films with a smooth and dense surface without macroparticles were produced. An excellent adhesion with a critical load of 59.9 N is achieved for the pure implantation mode. © 2011 American Institute of Physics. [doi:10.1063/1.3565175]

I. INTRODUCTION

Plasma source ion implantation or plasma immersion ion implantation (PIII) first proposed in 1987 (Refs. 1 and 2) was operated with gaseous plasmas such as nitrogen, oxygen, and BF3 in the early days. To extend the applications and obtain thicker films, alternative techniques featuring non-gaseous elements such as metallic elements and carbon had been developed.3–5 The process typically involves both deposition and implantation phases. That is, film deposition occurs in the interval between successive high-voltage (HV) pulses applied to the sample and ion implantation occurs during the pulses. As a result, plasma immersion ion implantation and deposition (PIII&D) has been widely utilized to produce various types of films with different compositions and thicknesses that exhibit good adhesion to samples and industrial components such as tools, molds, pistons, punches, and drills.6, 7

The most widely used device for metal PIII&D was introduced by Brown et al.4, 8 In this technique, a pulsed cathodic arc plasma source is used to produce a metal plasma and metals ions, sometimes combined with gaseous ions, are implanted when high-voltage pulses are applied to the samples. However, because of the dynamic process during plasma formation, droplets are produced from the cathodic arc spots.9 These droplets having sizes of 0.1–10 μm are often referred to as macroparticles. Macroparticles are not acceptable in most applications and must be removed from the samples. A common method to eliminate macroparticles from the drifting plasma is to use a curved magnetic filter,10–12 but the curved magnetic filters decrease the plasma flux and consequently deposition efficiency. For instance, an S-shaped filter has a transport efficiency of 6% with no detectable macroparticles.13 In addition to macroparticles, filtered arc plasmas are difficult to scale up because the plasma is produced from small and nonstationary cathodic spots, and multiple targets and power supplies are required in industrial applications.14 Therefore, there is a need for scalable, reproduceable plasmas for ion-based surface modification and film deposition. In 1999, high power pulse magnetron sputtering (HPPMS) was proposed by Kouznetsov and co-workers15 and a high plasma density of more than 1018 m−3 and ionization rate of about 90% have been reported.16, 17

In this paper, a novel metal plasma immersion implantation and deposition method, high power pulsed magnetron sputtering discharge plasma immersion ion implantation and deposition (HPPMS-PIII&D) is described. The metal plasma is produced by HPPMS using a common magnetron sputtering target instead of ionizing atoms from a pulsed cathodic arc plasma source. This method combines the advantages of PIII and HPPMS, and there are very few macroparticles in the high density plasma. Since the target used to produce the plasma is a common magnetron sputtering target, it is easy to scale up to process large samples. The principle and efficacy of the hardware and technique are demonstrated by depositing smooth and dense CrN films without macroparticles.

II. DESIGN PRINCIPLES

High power pulsed magnetron sputtering discharge plasma immersion ion implantation and deposition was conducted using a magnetron sputtering source as the metal plasma source. The discharge was triggered by pulsed high voltage or combined pulsed and direct current (dc) voltages. Negative high-voltage pulses with a repetition frequency equal to or being a multiple of that of the HPPMS pulse were applied to the samples during (in-duration mode), before (before-duration mode), or after (after-duration mode) firing
of the HPPMS pulses by adjusting the pulse width and relative phase. If the pulse repetition frequency of both pulses is the same, pure ion implantation, pure deposition, or implantation combined with deposition can be achieved by adjusting the relative pulse widths.

A $\Phi 50 \text{ mm} \times 6 \text{ mm}$ Cr target ($\sim 99.99\%$ purity) was mounted on the magnetron cathode. The substrate was a rectangular stainless steel plate ($8 \times 6 \text{ cm}^2$) located in front of the target at a distance of 16 cm. Figure 1 shows the schematic of the HPPMS-PIII&D system. A special pulsed matching circuit was developed to modulate the HPPMS and HV pulses such that the pulse width and phase could be adjusted independently.

The HPPMS pulses were applied to the magnetron sputtering target, while the HV pulses were applied to the sample. Two digital oscilloscopes were used to monitor the target voltage, target current, HV pulse voltage, and substrate current. The signal to trigger the HV pulse was also sent to the matching circuit and after being modulated by two 1/2 CD4098 chips, it was output to trigger the HPPMS pulse. This matching circuit provided the same pulse repetition frequency as the HV pulse, but the pulse phase could be adjusted to meet the operation requirement. The pulse widths of the HPPMS and HV pulses could be adjusted independently in order to conduct the PIII&D experiments in different modes.

The various matching modes of the HPPMS and HV pulses, e.g., pure implantation (mode A), simultaneous implantation and deposition (mode B), and selective implantation (mode C), are shown in Figs. 2(b)–2(d), respectively. The HPPMS discharge had a pulse amplitude of 920 V, pulse repetition frequency of 50 Hz, and pulse width of 200 $\mu$s. HPPMS of Cr in an Ar atmosphere at a working pressure of 0.5 Pa was performed while the hybrid dc discharge was also operated at a current of 0.2 A. The substrate was biased by a negative HV with an amplitude of 10 kV, repetition frequency of 50 Hz, and pulse width of 250 $\mu$s.

The substrate currents for different HV pulse amplitudes with the three modes were measured and displayed in Figures 2.
Figs. 3(a)–3(c), respectively, which also shows the substrate current in the dc magnetron discharge mode at the same power as HPPMS for comparison. Here, the average target pulse current was kept constant in the HPPMS discharge. As the HV pulse amplitude was increased, a substantial increase in the substrate current was observed. For example, take the pure implantation mode. The substrate current peak was 10.28 A for the HV with a pulse amplitude of $-10$ kV and went up to 15.01 A if the HV was raised to $-20$ kV. In comparison with HPPMS discharge, the substrate current in dc discharge was low with a peak of only 1.12 A. The average substrate currents were calculated to be 8.37 mA in dc discharge and 555.80 mA in HPPMS discharge for a single $-20$ kV pulse.

III. FILM DEPOSITION BY HPPMS-PIII&D

CrN films were produced on Si(100) and SU201 stainless steel substrates using the pure implantation mode (mode A), simultaneous implantation and deposition mode (mode B), and selective implantation mode (mode C) of HPPMS-PIII&D, respectively. The discharge parameters for HPPMS and dc were the same as those mentioned in Sec. II, except that the HV pulse amplitude increased to 18 kV as shown in Fig. 2. The films were fabricated under a constant pressure of 0.5 Pa (mixed Ar and N$_2$ with the Ar/N$_2$ flow ratio of 5/2). Figure 4 depicts the SEM micrographs of the CrN films deposited on Si(100) substrates achieved by HPPMS-PIII&D with mode A and using CA (Cathodic Arc) plasma source filtered by a φ20 mm × 40 mm straight-tube magnetic filter. As a result of ion bombardment and implantation, a very smooth and dense surface was obtained by HPPMS plasma source. More importantly, no defects (macroparticles) could be observed on the film surface, and the results were superior to those produced by conventional cathodic arc plasma sources with plasma filtration.$^{18-20}$

Figure 5(a) shows the cross-sectional SEM micrograph of the CrN coating deposited on a Si(100) substrate with mode A. The film exhibited a well-defined densely packed columnar structure with low surface roughness. Most of the columnar structures were broken and exhibited a discontinuous morphology. And the followed columns could be observed forming on top of existing columns due to a renucleation mechanism. These features as well as the high density of the coating microstructure showed that all stages of the coating growth occurred under conditions of highly energetic and highly ionized implantation and larger thermal diffusion induced by ion bombardment.$^{21}$ A different structure was observed for the Cr$_x$N$_y$ film deposited on a Si(100) substrate with mode B, as shown in Fig. 5(b). The film was mostly dominated by underdense columnar grains and most of the columnar grains continuously grew. For mode B, the ions were accelerated within the first 100 μs of the HPPMS pulse implying less ion bombardment during film deposition. The film microstructure achieved by mode C was similar to that achieved by mode A, as shown in Fig. 5(c). A dense columnar structure was also achieved. For mode C, the negative high voltage took effect during the latter 100 μs, which started 50 μs after the beginning of HPPMS pulse. Although negative high-voltage pulse was the same for both mode B and mode C, the effect of ion bombardment was greatly different. HPPMS discharges are featured by an initial pressure-dependent current peak followed by a second phase that is power and material dependent.$^{22}$ This suggests that the initial phase of a HPPMS discharge pulse is dominated by gas ions, whereas the latter phase has a strong contribution from self-sputtering, indicating the latter phase of a HIPIMS discharge pulse is dominated by metal ions.$^{22}$ In conjunction,
FIG. 4. SEM micrographs of the CrN films on Si(100) substrates with the simultaneous implantation and deposition modes using (a) HPPMS source and (b) CA source.

gas and metal ions have different behaviors when implanted. Metallic ions have a high bonding affinity and can be incorporated at lattice sites of the substrate as replacements. Thereby, the implantation effects of metal ions of mode C were more apparent than those of gas ions of mode B.

The adhesion strength of the CrN coatings on stainless steel was assessed by scratch tests and the micrographs of scratches with the three modes are displayed in Fig. 6. The coatings exhibited good adhesions and the highest critical load $L_c$ was up to 59.5 N for mode A. And the critical loads of the films for mode B and mode C were also up to 44.5 and 45.5 N, respectively. For comparison, better adhesion strength with a critical load of 85 N was accomplished by Ehiasarian and co-workers who deposited the CrN films on M2 high speed steel (HSS) substrate by HPPMS. In their work, the HSS substrates were bombarded by high energy metal ions (1200 eV) from a HPPMS discharge for 30 min before the CrN film was deposited. Substantial metal ion implantation and local epitaxial growth were observed in conjunction with efficient cleaning of the substrate. In addition, the substrates were heated to 250 °C to increase the mobility of deposited atoms. In our experiments, no plasma pretreatment and extra heating were applied. Hence, the high critical load originates from the high-voltage ion implantation effect. A gradient layer formed in the near surface of the substrate may reduce the stress induced by the different physical properties. In fact, the scratch results may somehow be affected by film thickness, but as reported, the effect is not significant even if hardly demonstrated exactly. Furthermore, from the data in Fig. 7 (demonstrated below), the hardness of deposited

FIG. 5. Cross-sectional SEM of the CrN films deposited on Si(100) substrates with different work modes: (a) pure implantation mode, (b) simultaneous implantation and deposition, and (c) selective implantation.

FIG. 6. (Color online) Micrographs obtained from the scratches on the CrN films deposited on stainless steels with different work modes: (a) pure implantation mode, (b) simultaneous implantation and deposition, and (c) selective implantation.
films deposited by magnetron sputtering. The Young's modulus arises from the single-phase CrN dense structures induced by ion bombardment. And the relative hardness improvement may be caused by the dense structures induced by ion bombardment. A lower hardness of 13.1 GPa was achieved by mode B. In contrast, both mode A and mode C led to a higher surface hardness. The hardness improvement may be caused by the dense structures induced by ion bombardment. And the relative low Young's modulus arises from the single-phase CrN film deposited by magnetron sputtering.

IV. CONCLUSION

A novel PIII&D technique has been developed. A magnetron sputtering target, driven by high-power pulse or high-power hybrid pulse, is used as the metal plasma source. A negative high-voltage pulse with the same repetition frequency is applied simultaneously to the substrate to conduct HPPMS-PII&D. A matching circuit is developed to enable experiments under different modes such as pure implantation, simultaneous implantation and deposition, and selective implantation. To demonstrate the hardware and efficacy, CrN films are prepared using the three work modes. A smooth and dense surface with no macroparticles is observed. The film has high surface hardness and adheres strongly to the substrate.

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