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Advances in Thin Film Technology through the Application of Modulated Pulse Power Sputtering

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Abstract. High power pulsed magnetron sputtering (HPPMS) is an emerging thin film deposition technology that generate high ionization plasma by applying a very large amount of peak power to a sputtering target for a short period of time. HPPMS is also known as High Power Impulse Magnetron Sputtering (HiPIMS). However, HPPMS/HiPIMS exhibits decreased deposition rate as compared to continuous dc magnetron sputtering. Modulated pulse power (MPP) magnetron sputtering is an alternative HPPIMS deposition technique that overcomes the rate loss problem while still achieving a high degree of ionization of the sputtered material. In the present work, the principles and some important characteristics of MPP technology were presented. Technical examples of CrN coatings were deposited using MPP and continuous dc sources. The positive ion mass distributions were characterized using an electrostatic quadrupole plasma mass spectrometer. The structure and properties of MPP and dc CrN coatings were characterized using x-ray diffraction, scanning electron microscopy, nanoindentation tests, and ball-on-disc wear test. It was found that the MPP CrN coating exhibits denser microstructure and improved mechanical and tribological properties as compared to the dc CrN coating.

Introduction

The advantage of magnetron sputtering is that ions present in the plasma are abundantly available to the deposition process. However, the chemistry at the substrate is usually dominated by the ions of the inert sputtering gas while ions of the sputtered material are rare. There has been some considerable interest in developing high power and density plasmas to improve the quality of thin films. In the last 10 years, a new type of power has been developed for sputter deposition. It uses high energy-high ionization techniques generally referred to as high power pulse magnetron sputtering (HPPIMS), which is also known as high power impulse magnetron sputtering (HiPIMS). The basis of HPPMS technique is to apply a very large amount of peak power to a sputtering target for a short period of time [1,2,3,4]. In the conventional dc magnetron sputtering (dcMS), the degree of metal ionization is low (<10%) which is due to the low power density (e.g. 3 Wcm^{-2}) limited by the target overheating from the ion bombardment. In HPPMS, typical peak powers for the HPPMS are in 1-3 kW/cm^2 range, however the pulse width is only 100-150 µs, therefore the average thermal load on the target is low due to the very low duty cycles (1%~10%) and long off times, and therefore the total heat load to the substrate can be very significantly lower than in dcMS.

The advantage of HPPMS is that there can be a very high degree of ionization of the sputtered material. With the high peak power on the target, a considerably large fraction of ionized target metal species can be created by the dense plasma created in front of the target. This degree of ionization is dependant on the peak power and material sputtered [5]. It is well known that it is a challenge to coat complex shaped substrate/components in most PVD processes due to the line-of-sight limitation. However, as the deposited species are largely metal ions in the HPPMS/HiPIMS plasma, it is possible to control the metal ion trajectory by biasing the substrate. Alami [6] has compared Ta films on a Si substrate placed along the wall of a 2 cm deep and 1 cm wide trench by dcMS and HiPIMS and found improved homogeneity of the coating achieved by HiPIMS.

However there is a disadvantage to the HPPMS/HiPIMS technique. The deposition rate is typically only 25-30% of the DC rate for an equivalent amount of power. A model explaining the loss in deposition rate has been developed by Christie [7], which explained that the drop of the deposition rate was mainly because that the ions will be attracted back toward the target by the high negative peak voltage on the target.

Chistyakov has developed an alternative HiPIMS deposition technique known as modulated pulse power (MPP) that overcomes the rate loss problem while still achieving a high degree of ionization of the sputtered material [8,9,10,11]. The difference between the HPPMS and MPP techniques is that the pulse length with the MPP technique is in the 2-3 ms range, and there are multiple steps in the pulse. The pulse is repeated periodically to produce an average power that is typical for sputtering operations. With the longer pulse, it has reported that the MPP deposition rate can actually exceed the DC rate for an equivalent amount of power, and in several cases the MPP deposition rate is twice the DC rate [8,9]. In MPP, the maximum pulse width is 5000 µs, the pulse frequency can be adjusted from 4 to 1000 Hz. MPP can generate a pulsed plasma with controllable peak power (>200 kW) and peak current (>300 A) on the target.

The development of MPP and HPPMS technique opens new approaches in the engineering and design of film materials with high deposition rate, improved microstructure and properties, and low residual stress by using highly ionized and high density plasma. In the present work, the principles, and some important characteristics of MPP technology were discussed. The positive ion mass distributions in the MPP and dc discharged plasma were characterized using an electrostatic quadrupole plasma mass spectrometer (EQP). Technical examples of CrN coatings were deposited using MPP and dc techniques. The structure and properties of CrN coatings were characterized using x-ray diffraction, scanning electron microscopy, nanoindentation tests, and ball-on-disc wear test, and further compared with that synthesized using dcMS.

Experimental details

CrN coatings were sputtered from elemental Cr target in Ar+N_2 atmosphere using continuous dc and MPP power sources in a two magentron closed field unbalanced magnetron sputtering (CFUBMS) system. Fig. 1 shows the schematic drawing of the setup of the deposition system and the EQP probe. The deposition system is a cylinder chamber (640 mm in diameter and 940 mm in height) which contains two unbalanced magnetrons of reversed magnetic polarities installed vertically to form a closed magnetic field. Ar and N_2 were introduced into the system using MKS mass flow controllers controlled by a MKS 146 pressure and flow control unit. AISI 304 stainless steel coupons and (100) Si wafers were used as the substrates. The substrates were ultrasonically degreased in denatured acetone and alcohol for 20 minutes respectively and then were placed 140 mm away from the Cr target. After evacuating the chamber to a base pressure of 1.2×10^{-4} Pa, the substrates were firstly cleaned by Ar^+ plasma etching with a substrate bias of -450 V pulsed at 100 kHz and 90% duty cycle to remove the surface contaminates. The working pressure is 0.5 Pa and the N_2 flow is of about 25 sccm, which was set about 50% of the total flow rate. A floating substrate bias was used for MPP CrN coating depositions, while a -50 V dc substrate bias was used for dcMS in the present study.

MPP generates high density plasma by using multiple steps within one pulse [8,9,12]. The pulse width in MPP used in the present work was fixed at 1500 µs, which contains 500 µs weakly ionized and 1000 µs strongly ionized periods. The pulse frequency was fixed at 30 Hz. The target peak power and peak current were set at 4.5 kW and 12 A respectively during the weakly ionized period. During the strongly ionized period, MPP generate a peak power of 135 kW and a peak current of 189 A on the target in a pure Ar atmosphere by controlling the the pulse shape and pulse width. However, a peak power of 180 and a peak current of 250 A were achieved when 50% N_2 was introduced into the system using the same pulse condition. For the continuous dc sputtering, the target power was fixed at

1.0 kW. The target peak power, current and deposition parameters for MPP and dc conditions are summarized in Table 1.

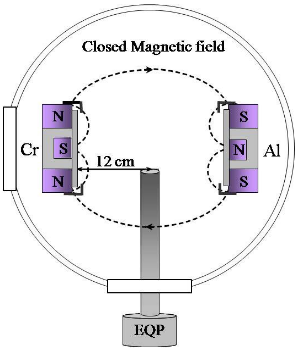

Fig. 1 Schematic drawing showing the setup of the CFUBMS system and the EQP probe.

A Hiden Analytical Ltd EQP was used to characterize the positive ion mass distributions in the discharged plasma. The EQP axis was placed exactly along the middle line between two targets. The distance between the target surfaces to the EQP probe is of about 120 mm as shown in Fig 1. The diameter of the orifice in front of the EQP is 100 μm. The same tuning parameters were applied for all plasma measurements in an effort to keep a consistent comparison for the IED.

The structure of the coatings were studied by grazing incident angle X-ray diffraction (GIXRD) using 2^{o} incident angle scaned from 30 to 70^{o}. The Cu Ka radiation with wavelength of 1.54056 Å operated at 45 kV and 30 mA was used as the X-ray source. The microstructure of the coatings were examined using a JSM-7000F field-emission scanning electron microscope (SEM). The hardness of the coatings was measured by a nanoindenter (NanoIndenter XPTM, MTS Systems Corporation) equipped with a Berkovich diamond indenter using depth sensing method from the load displacement curve. The wear resistance of the coatings were evaluated by a ball on disk microtribometer (Center for Tribology, Inc) under lubricant free sliding conditions. The wear tests were carried out along a circular track of 12 mm diameter under a load of 3 N for the duration up to 5000 cycles. A WC-6 wt.% Co ball of a diameter of 1 mm was selected as the counterpart.

Table 1. Summary of the conditions for the dc and MPP depositions and the properties of CrN coatings.

coating	Average power [kW]	Peak power [kW]	Peak current [A]	Bias [V]	N_2 flow%	Hardness [GPa]	Young's modulus [GPa]	COF
dc CrN	1.0	1.0	N/A	-50	50	24	289	0.52
MPP CrN	4.2	180	250	floating	50	26	310	0.38

Results and Discussion

MPP and dc plasma properties. A comparison of the positive mass scan of the ion species within the discharged plasma generated using continuous dc, and MPP techniques for sputtering metal Cr in pure Ar at an average target power of 2 kW is shown in Fig. 2. It can be seen that the intensity of the metal Cr^{+} ions is very low in the dc discharge compared to the gas Ar^{+} ions, indicating low target material ionization fraction in the discharged plasma. On the other hand, significant increased number of Cr^{+} ions was identified in the MPP discharge generated at the same average target power (2 kW) but with a peak power of 90 kW and a peak current of 122 A (not shown in Table 1), confirming that a large fraction of the target Cr atoms were ionized in the MPP process due to the high peak power and peak current on the target. Additionally, a small fraction of double ionized Cr+ ions was also revealed in the MPP plasma, which was not observed in the dc discharged plasma, as shown in Fig 2. A detailed study of the MPP plasma diagnostics can be found in reference [12].

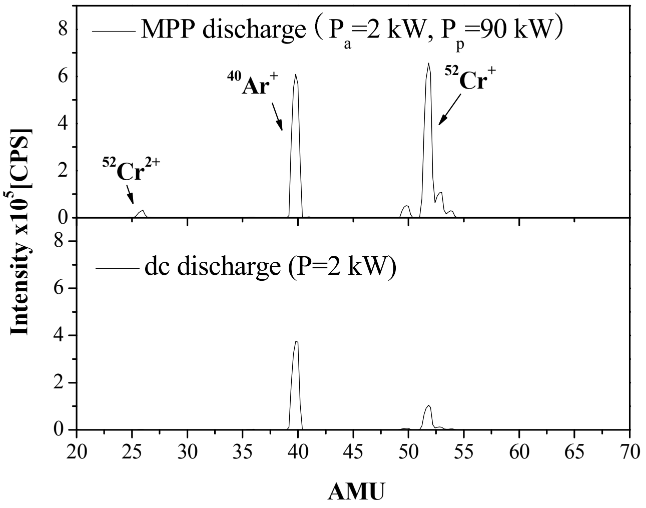

Fig 2. Comparison of the positive mass distribution within the discharged plasma generated in dc and MPP discharges during Cr coating deposition in a closed magnetic field magnetron sputtering system at average target power of 2 kW

Microstructure of MPP CrN coatings. XPS composition analysis confirmed both dc and MPP CrN coatings exhibit near stoichimetric concentrations deposited with 25 sccm N_2 flow rate. Fig. 3 shows the GIXRD patterns of dcMS and MPP sputtered CrN coatings (-50V bias in dc and a floating bias in MPP conditions). It can be seen that both dc and MPP sputtered CrN coatings exhibit a NaCl-type structure, where the diffraction peaks (111), (200) and (220) can be observed. The diffraction intensities of MPP CrN coating is higher than those in the dc CrN coating, which is probably because of the larger thickness of the coating obtained in the MPP condition.

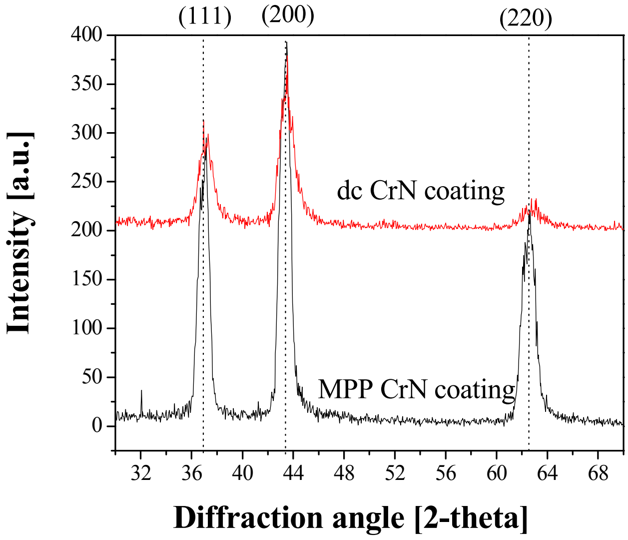

Fig. 3 GIXRD patterns of CrN coatings synthesized using dcMS and MPP at 50% N_2 flow rate and -50V bias in dc condition and a floating bias in MPP condition

Fig. 4 shows the cross-sectional SEM micrographs of CrN films grown by dcMS and MPP depositions with 25 sccm N_2 flow rate. It can be seen that the CrN coating grown by dcMS at -50 V bias contains typical long columnar grains with the grain size in the range of 50-100 nm (Fig. 4a). However, a very dense and large columnar free structure was revealed in the MPP sputtered CrN coating deposited using floating substrate bias. From the plasma diagnostic study (Fig 2) [12], it has demonstrated that MPP plasma exhibits significant increases in the number of both target material (Cr) and gas (Ar) ions than continuous dc plasma. Therefore, the highly ionized MPP plasma provides enhanced ion bombardment from the low energy ion species, which leads to the interruption of the columnar grain growth and the improved the coating structure and density even without using the aid of the substrate bias (Fig.4b).

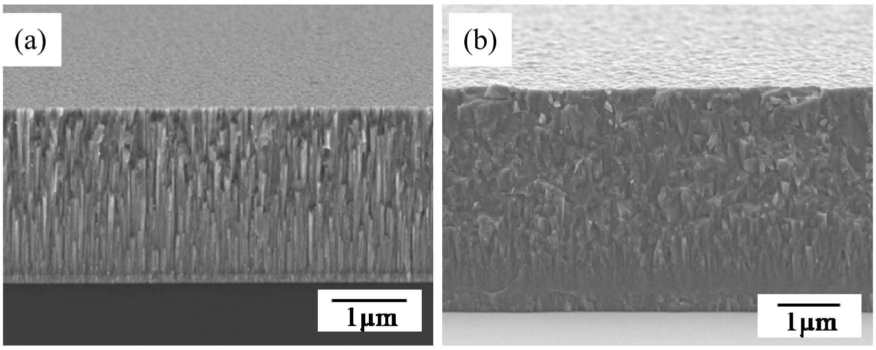

Fig. 4 Cross-sectional SEM micrographs of CrN coatings deposited at 50% N_2 flow rate using (a) continuous dc at 1 kW at -50 V bias and (b) MPP at 4.2 kW at floating substrate bias

Mechanical and tribological properties. The mechanical properties and sliding coefficient of friction (COF) of dc and MPP sputtered CrN coatings were summarized in table 1. The dc CrN coating showed a hardness of 24 GPa by applying -50 V substrate bias to assist the deposition. On the other hand, a higher hardness of 26 GPa was obtained in the MPP CrN coating deposited with floating substrate bias voltage. A lower sliding COF of 0.38 was achieved in the MPP CrN coating than in the dc CrN coating (Table 1). Fig. 5 shows the optical micrographs of the wear track morphologies of CrN coatings at the end of the wear tests. The MPP CrN coating exhibits a narrow wear track with shallow grooves, indicating smaller amount of coatings being removed (Fig. 5a). EDS analyses show that there was no apparent failure of the coatings at the end of the tests. However, the dc CrN coating exhibits more intensive abrasion wear. At the end of the test, the wear track exhibits a very rough morphology with larger width (Fig. 5b), indicating extensive tribochemical reactions during the wear test. The corresponding EDS analysis confirms that the some parts of the coating were almost worn out and the substrate peaks were revealed. It is believed that the improved hardness and wear resistance in the MPP CrN coating are mainly because of the improved density of the coating by the significant increased low energy ion flux bombardment from the more intense MPP plasma.

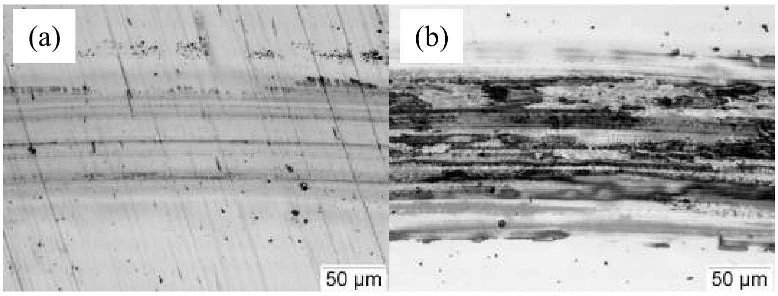

Fig. 5 Optical micrographs of the wear track morphologies of (a) MPP and (b) dcMS CrN coatings after sliding against WC-Co ball at 3 N load.

Conclusions

Modulated pulse power (MPP) magnetron sputtering is an alternative HPPIMS deposition technique which is an emerging thin film deposition technology that generates high ionization plasma by applying a very large amount of peak power to a sputtering target for a short period of time. In the current study, plasma diagnostics showed that single and double ionized Cr ion species were identified in the MPP plasma in the pure Ar atmosphere condition. Significant increases in the number of both target material (Cr) and gas (Ar) ions in MPP plasma than continuous dc plasma were demonstrated, suggesting significant increased target material ionization fraction was achieved in the MPP condition. In the present work, CrN coatings were deposited using MPP and dc techniques using the same working pressure and N_2 flow rate, but with different bias voltages and peak target powers. The MPP CrN coatings deposited using a floating substrate bias exhibit denser microstructure and improved mechanical and tribological properties as compared to the dc CrN coatings deposited using a -50 V dc substrate bias.

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