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Comparison of chromium carbide thin films grown by different power supply systems

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ABSTRACT

The potential use of chromium carbide thin films has been a great interest to academia and industry due to their outstanding properties such as chemical stability, low coefficient of friction, adequate hardness and high wear resistance. In this study, the chromium carbide thin films were fabricated by a magnetron sputtering using different power supply systems, including direct-current (DC), pure high power impulse magnetron sputtering (HiPIMS), and superimposed HiPIMS- middle frequency (MF). The Cr target poisoning status was controlled using a plasma emission monitoring (PEM) system by adjusting the gas flow ratios of Ar and acetylene (C_2H_2). The morphology and microstructure of thin films were evaluated by scanning electron microscope (SEM) and transmission electron microscope (TEM). The crystallinity of films was studied using an X-ray diffractometer (XRD). The electron probe micro analyzer (EPMA) and X-ray photoelectron spectroscope were used to determine the chemical compositions and binding structures of thin films, respectively. The hardness and residual stress were explored. The results showed that the thin film sample prepared by the superimposed HiPIMS-MF power supply can obtain the maximum hardness of ~27.5 GPa at a PEM set point of 30%, i.e., the target poisoning degree of 70%. The hardening mechanism may be caused by the formation of nanoscale CrC crystallites incorporated into the amorphous CrC_x matrix in the thin film, which can be attributed to the Hall-Petch strengthening effect.

1. Introduction

Amorphous carbon (a-C) films with sp^3 and sp^2 bonds have been studied for years due to their good mechanical properties as well as excellent wear and corrosion resistances. The a-C films are very suitable for the molding die surface and other low friction applications because of its outstanding properties. The major challenges in these coatings are poor adhesion to substrates, high internal stresses and poor thermal stability. To overcome these issues, an alternative approach was used to deposit the a-C films by introducing the carbide-forming metals, such as Mo, W, Ti, Nb and Cr [1–3] in the coating.

Among the metal carbide coatings, CrC_x films show good adhesion behavior. For example, an adhesion class of HF1 by the Rockwell-C DB adhesion test was reported by Tillmann et al. [4]. The hardness of CrC films is varied from 3.6 to 48 GPa depending on the deposition processes and power supply systems, such as reactive magnetron sputtering [5–7], cathodic vacuum arc deposition [8,9] and high power impulse magneton sputtering (HiPIMS) [4], etc. The mechanisms of hardness enhanced of CrC_x films reported in the literatures were influenced by different sp^3/sp^2 bonding ratios of the hydrogenated graphite-like amorphous carbon (a-C:H) and chromium carbide fractions [7]. The appearance of small amount of nanocrystalline CrC_x phase embedded in the a-C:H also enhances the hardness and elastic modulus [7]. Meanwhile, the coatings with Cr_3C_2 phase also show the highest hardness up to 22–25.5 GPa [8,9].

The HiPIMS system has benefits of providing high peak current, high peak power density, and high plasma density during sputtering. These characteristics are essential to achieve unique film properties such as dense microstructure, high hardness and good adhesion [10–13]. However, its low deposition rate limits the application of HiPIMS system in industries. Recently, the deposition rate of HiPIMS process was greatly improved without the sacrifice of coating mechanical properties by superimposing the middle-frequency (MF) pulses during off-time of HiPIMS pulsing [12], and by a combination of direct

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current (DC) magnetron sputtering with HiPIMS [14]. Accordingly, it is expected that the pure HiPIMS and superimposed HiPIMS-MF apparatus can be used to fabricate chromium carbide films with improved film properties. In the work, CrC_x thin films were prepared by DC, pure HiPIMS, and superimposed HiPIMS-MF power supplies, respectively. Effects of Cr target poisoning rate (PEM set points) on the chemical composition, microstructures, crystal phases, bonding status, and mechanical properties of thin films are studied. In addition, the influence of three different power supply systems on the properties of grown chromium carbide thin films were also compared.

2. Experimental procedure

Twelve chromium carbide thin films were prepared by DC, pure HiPIMS and superimposed HiPIMS-MF power supply systems in this study. The rectangular (127 × 304.8 × 6 mm) Cr target (99.99% in purity) was used in a chamber size of Φ 660 mm × 600 mm (LJ-UHV Technology Co., Ltd., Taiwan). The Cr target was connected to a power supply system (SIPP2000USB Dual, MELEC GmbH, Germany), which can output its power at DC, pure HiPIMS and superimposed HiPIMS-MF modes, respectively, at 1000 W. The values of frequency and duty cycle of HiPIMS and MF are 200 Hz and 2%, and 25,000 Hz and 50%, respectively. A plasma emission monitoring (PEM) system using an optical emission spectrometer (OES, PLASUS EMICON, Germany) to feedback control the flow rate of reactive gas, C_2H_2, in the deposition process was utilized to control the poison status of Cr target in this study. The OES detector of the PEM system was located parallel to the Cr target surface for analyzing the plasma signals from the Cr target directly, which was reported in our previous work [12]. The plasma emission spectrum of Cr^o at 520.8 nm was monitored and to feedback control the flow rate of reactive C_2H_2 gas by a piezoelectric valve. The chromium carbide coatings were deposited on the hardened AISI420 stainless steel disks, AISI304 stainless steel plates and P type (100) Si wafer substrates. Prior to chromium carbide film deposition, the substrates were etched by Ar plasma for 15 min at a DC substrate bias of −850 V in the chamber. Before the growth of CrC_x film, an interlayer of pure Cr layer with a thickness around 170 nm was deposited to obtain good adhesion with substrates. After the interlayer deposition, CrC_x coatings were subsequently deposited at a working pressure of 0.67 Pa. The Ar gas flow rate was fixed at 20 sccm while C_2H_2 gas flow rate was controlled by PEM system to obtain the target poisoning status of 10%, 30%, 50%, and 70% using DC, pure HiPIMS and superimposed HiPIMS-MF power supply systems, respectively. A DC substrate bias of −600 V was employed during the growth of Cr interlayers and CrC_x films for all deposition processes. The deposition temperature was measured by a thermocouple placed around 10 cm away from the substrate holder. During the pure HiPIMS and superimposed HiPIMS-MF depositions, a digital oscilloscope (Keysight InfiniiVision DSO-X 2024A, Agilent Technologies, USA) was used to measure the voltage and current waveforms of Cr target. The peak current was the maximum current in the on-time of HiPIMS or MF pulse. The peak power density of Cr target for each sputtering process was calculated by multiplying the peak current and target voltage, and divided by the ion-eroded target area of 200 cm^2. The designation of twelve samples and the parameters of sputtering processes are listed in Table 1.

The chemical composition and phase analysis of coatings were carried out using a field emission electron probe microanalyzer (FE-EPMA, JXA-8500F, JEOL, Japan) and a grazing angle X-ray diffractometer (GA-XRD, PANalytical, X'pert, Netherlands), respectively. An X-ray photoelectron spectroscope (XPS, Sigma Probe, Thermo VG-Scientific, UK) analysis was carried out to understand the binding status of alloying elements in CrC_x films. The X-ray source energy of XPS was Al Kα 1486.6 eV, and the energy resolution was 0.1 eV. All XPS spectra were referenced to the C 1s line of hydrocarbon-type carbon at an energy of 284.8 eV [15]. Each specimen was sputter-cleaned for 10 s by an Ar^+ ion beam of 3 keV before the XPS analysis. The cross-sectional microstructures and thickness of the CrC_x thin films were observed by a field-emission scanning electron microscope (FE-SEM, JSM-6701, JEOL, Japan). A transmission electron microscope (TEM, JEOL, JSM-2100, Japan) was employed to analyze the microstructure and phase constituents. The nanoindenter (TI-900, TriboIndenter, Hysitron, USA) was used to analyze the hardness and elastic modulus of the films. Residual stresses of deposited films were determined by substrate curvature measurements according to Stoney's equation [16].

3. Result and discussion

3.1. Characteristics of HiPIMS-MF discharge and plasma emission characteristics of Cr

In order to precise control the plasma emission for Cr deposition process, the OES intensity of Cr^0 line at the wavelength of 520.8 nm was used to control the C_2H_2 gas flow through a fast response mass flow controller in PEM system. Before deposition, the effect of C_2H_2 flow rate on the hysteresis behaviors of Cr target under DC sputtering, pure HiPIMS, and superimposed HiPIMS-MF process were obtained to define the target poison performance, as shown in Fig. 1. It is noticed that the emission intensities of OES of DC, pure HiPIMS, and superimposed of HiPIMS-MF are based on the same integration time. This slowly decreasing OES intensity with respect to the increasing acetylene gas flow rates implies the presence of target poisoning status. During the reverse of the hysteresis loop, the target surface was kept at poisoned regime when the C_2H_2 flow rate gradually decreased. Four PEM set points, 70%, 50%, 30% and 10%, were chosen to be the experimental parameters, which represented the Cr target poisoning degree were 30%, 50%, 70%, and 90%, respectively.

Fig. 2 depicts the typical OES spectra during sputtering of Cr target using pure Ar gas and powered by DC, pure HiPIMS, and superimposed HiPIMS-MF, respectively. It is obvious that the emission intensity obtained from superimposed HiPIMS-MF is the highest, whereas the intensity of DC is the lowest one. The Cr lines at 520.7 nm show maximum intensities in each sputtering process. Meanwhile, the Cr^+ and Ar^+ lines are also observed in the spectra in three sputtering processes.

In this study, the MF pulses were superimposed during the off-time of HiPIMS pulsing to Cr target. Fig. 3(a) shows the temporal evolutions of the target voltage and current waveforms of Cr target powered by a superimposed HiPIMS-MF sputtering at a PEM set point of 30% in one superimposed cycle. The waveforms of a HiPIMS pulse and five MF pulses introduced during the off-time of HiPIMS are depicted in Fig. 3(b) and (c), respectively. The MF pulses were superimposed into the HiPIMS by simply adjusting the “dwell time” to be ~2500 μs before and after HiPIMS pulses. The target voltage, peak current and peak power density of pure HiPIMS and superimposed HiPIMS-MF using four different PEM set points, including 10%, 30%, 50%, and 70%, are listed in Table 2. The target voltage values of pure HiPIMS at different PEM set points are kept at a narrow range around 701 to 724 V, whereas these of superimposed HiPIMS-MF processes are varied greatly from 786.3 to 866.5 V. The peak power density and peak current of HiPIMS power supply increased with decreasing PEM set points, i.e., increasing target poisoning degree. For the pure HiPIMS and superimposed HiPIMS-MF process, the maximum peak current of HiPIMS, 159 A, can be found for H10 coating, whereas the maximum peak power density of 586.8 W/cm^2 is discovered for S10 coating.

3.2. Chemical composition, phases and microstructure of CrC_x thin films

The chemical compositions of various CrC_x films analyzed by EPMA measurements are listed in Table 3. The Cr content of the samples deposited by the DC sputtering, HiPIMS, and superimposed HiPIMS-MF are increased from 18.2 to 52.7, 30.9 to 55.5, and 32.8 to70.8 at.%, respectively, while the PEM set point from 10% to 70% (target poison degree decreased from 90% to 30%). The corresponding C contents of