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Synergetic effect for improved deposition of titanium nitride films

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ABSTRACT

It is known that cathodic arc deposition (CAD) has been widely used in industry for high quality thin film coatings. An extremely high current density (~10^{12} A/m^2) was created to evaporate and ionize the target material rapidly. However, the CAD also produces macroparticles or droplets along with the deposition process leading to the degradation of the film properties. Magnetic filters with different designs were therefore adopted to reduce the macro particles or droplets. However, the macroparticles still cannot be fully eliminated. Lately, a newly developed PVD process known as high power impulse magnetron sputtering (HiPIMS) was found to have the capability of yielding highly ionized flux of both gas and sputtered materials by applying a high power in short pulses to the target. High plasma density in the order of 10^{17} to 10^{19} m^{-3}, which is three orders of magnitude higher than that of the conventional dc magnetron sputter (dcMS), can therefore be achieved from the large fluxes of energetic ions in a HiPIMS process. As a result, a smoother and denser thin film with better adhesion to the substrate can be obtained, leading to enhanced mechanical, electrical, and optical properties. However, it was also found the deposition rate of the HiPIMS process was much slower than that of the conventional dcMS and CAD process. Therefore, a hybridized deposition system combining CAD and HiPIMS was studied in this paper. Titanium nitride (TiN) films were deposited to investigate their microstructures, physical, chemical, and mechanical properties. The macroparticles were reduced in the HiPIMS system while thin films with enhanced hardness was obtained in the CAD system.

1. Introduction

It is known that cathodic arc deposition (CAD) has been widely used in industry for depositing protective coatings. However, the emission of micro-sized macroparticles or droplets due to the interaction between the plasma and the cathode spots becomes the major obstacle for the widespread of the CAD process [1,2]. In order to combat the macroparticle problem, several approaches have been proposed to suppress the macroparticles emission or to prevent the macroparticles from landing on the growing film. For suppressing the macroparticles emission, steered arc, current-controlled arc, distributed arc, and shunting arc were used to prevent overheating of the cathode spot [1,3]. However, macroparticle elimination is limited. For preventing the macroparticles from landing on the growing film, various kinds of magnetic and electromagnetic filters were designed to remove the droplets from the plasma [2,4]. However, this leads to a lower deposition rate due to the reduced plasma transport efficiency. Other alternative approaches such as increasing the partial pressure of the reactive gas [5], increasing the negative DC potential on the substrate [6,7], and applying high-frequency short-pulse negative bias to the substrate have been investigated to reduce the number of macroparticles [8–11].

Hybridized coating processes combining CAD and sputter deposition have also been developed to deposit coatings having complex structures and/or composition for improved coating performance [12–20]. In these studies, macroparticle-free TiC containing diamond-like carbon coatings were investigated using a CAD and middle-frequency magnetron sputter deposition hybridized system [21]. In this study, a hybridized deposition system combining CAD and high power impulse magnetron sputtering (HiPIMS) was studied to deposit titanium nitride (TiN) films. Compared to the CAD technique, the HiPIMS process is capable of yielding highly ionized flux of both gas and sputtered materials, thus leading to a smoother, denser, and macroparticle-free thin film with better adhesion to the substrate. Therefore, HiPIMS technique has been used not only as a major deposition process but also used for interface pretreatment [22,23]. However, it was also found the deposition rate of the HiPIMS process was much slower than that of the

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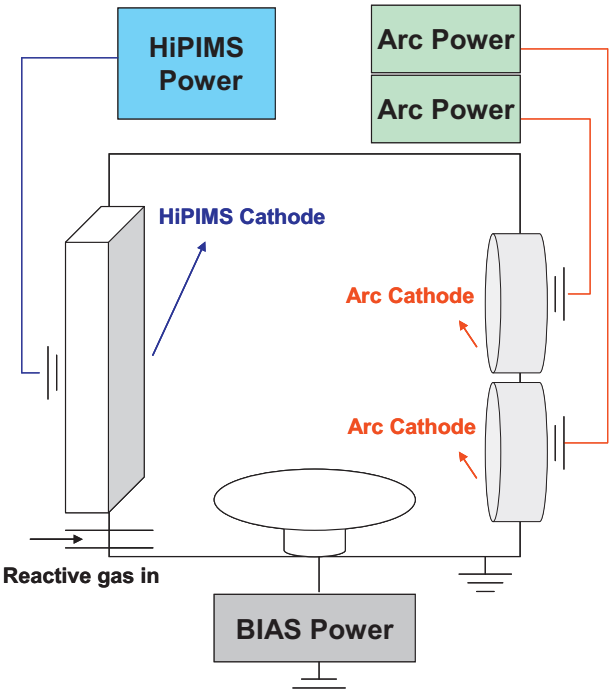

Fig. 1. A schematic of the hybridized deposition system.

CAD process. Using such a hybridized process combing CAD and HiPIMS, TiN films were deposited and the film microstructure, physical, chemical and mechanical properties were investigated. The synergetic effect was discussed.

2. Experimental

A hybridized deposition system combining CAD and HiPIMS, as shown in Fig. 1, was used to deposit TiN thin films. A rectangular Ti target (size 255 × 525 mm^2) and two round Ti targets (diameter 152 mm) were powered by the HiPIMS and CAD, respectively. A mixture gas of argon and nitrogen was used. The deposition was performed under various schemes, as shown in Fig. 2. For the deposition, an Ti interlayer, deposited using either the HiPIMS or CAD process, was used. The deposition of TiN was done under pure HiPIMS (A-0 and B-1 in Fig. 2), CAD (A-1 and B-0), or the combination of the two techniques (A-2 and B-2). Before the deposition, the deposition rate was determined to control the thickness of the TiN layer. The deposition rate is 5.6 nm/min for the HiPIMS-TiN (H-TiN) and was 18.5 nm/min for the CAD-TiN (C-TiN). The deposition time was adjusted to have a Ti interlayer and a TiN layer with thickness in the ranges of 100–150 nm and 1500–2000 nm, respectively. Between two processes, the power of the proceeding process was first turned off and the gas was evacuated. This was then followed by feeding the gas to the required working pressure and turning on the power of the subsequent process. The deposition condition for the HiPIMS was a dc input power of 2.4 kW, a duty cycle of 4.5% (on-time 50 μs), a substrate bias of −60 V, a working pressure of 3 × 10^{-3} Torr, a Ar flow rate of 120 sccm for Ti interlayer, and a N_2/Ar flow rate ratio of 5/120 for TiN layer. The obtained peak current and peak voltage in the HiPIMS process were 170 A and 425 V, respectively. The deposition condition for the CAD was a target current of 70 A, a substrate bias of −100 V, a working pressure of 2 × 10^{-2} Torr, a Ar flow rate of 150 sccm for Ti interlayer, and a N_2 flow rate of 400 sccm for TiN layer. Besides, the substrate temperature for both deposition techniques was fixed at 400 °C and the substrate rotation was 2 rpm.

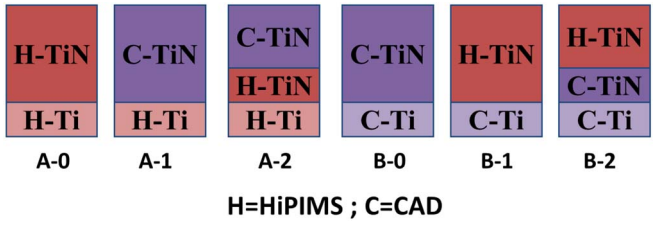

Fig. 2. A schematic showing six layer structures.

The surface and cross-sectional morphologies, and the thickness of the obtained TiN films on Si substrate were examined using scanning electron microscopy (SEM, JEOL-JSM7000F). Crystallinity and microstructure were investigated using X-ray diffractometry (θ–2θ, PANalytical-X'Pert PRO MRD). The X-ray source was a CuKα radiation (λ = 1.5418 Å) and operated at 45 kV and 40 mA. The cross-sections of the deposited films were observed using transmission electron microscopy (TEM, JEM-2100F). Surface chemistry of the obtained TiN films was examined using X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI-5000 VersaProbe) with a monochromatic Al Kα X-ray beam (energy = 1486.6 eV, power = 25 W, and beam size = 100 μm) without surface cleaning. The detecting angle is 45°with passing energy of 58.7 and 187.85 eV for detailed and survey spectra, respectively. The adhesion was measured using the Rockwell C indentation test (Wilson Wolpert Rockwell 500RA) with a 150 kgf diamond indenter. It classifies the coating adhesion to be from HF 1 to HF 6 according to the number of cracks or thin film coating delamination around the indent. The hardness of the TiN thin film was measured by a micro Vickers hardness tester (SHIMADZU-HMV-2) with a loading of 0.025 kgf. The wear behavior was investigated using a ball-on-disk tribometer (CSM Instruments Inc.) with a standard WC-Co ball having a diameter of 6 mm and 1 N loading against to the rotating disk. The rotational radius was 5 mm and the sliding speed was 300 mm/s. The corrosion behavior was also studied using Potentiostat (KEI-2000) in 1 M H_2SO_4 solution at room temperature. The TiN films deposited on 304 stainless substrates with a defined area of 1 cm^2 were polarized from +0.8 to −0.8 V with a scan rate at 1 mV/s. The potential was measured by a conventional three-electrode cell with a counter electrode of Pt and a standard calomel electrode (SCE) as a reference.

3. Results and discussion

The composition and chemical bonding of the A-0 and B-0 TiN films were first analyzed using XPS for comparison. Without any etching treatment of the TiN films, the N/Ti atomic ratio and the surface O concentration were found to be 1.084 and 16 at.%, respectively. For the B-0 TiN film, N/Ti atomic ratio is 1.058 and the O concentration is 15 at.%. Detailed Ti2p, N1s, and O1s XPS spectra after deconvolution are shown in Fig. 3. As seen in Fig. 3(A), the Ti2p spectra contain TiN, TiN satellite, TiON, and TiO_2 bonding. The peaks centered at 454.5 and 460.4 eV are assigned to the TiN bonding. TiN has typical satellite peaks at 457 and 462 eV. The peaks centered at 458 and 463.7 eV are assigned to the TiO_2 bonding. The splitting value varies with chemical states which is 5.9 eV for nitrides and 5.7 eV for oxides. Both the A-0 and B-0 TiN surface also contains TiON (oxynitride) bonding at 455.8 and 461.6 eV. As shown in Fig. 3(B), both the N1s spectra contain major bonding of TiN at 396.6 eV and the minor oxidized TiN bonding at 395.8 eV, and a satellite feature at 398.3 eV. In the O1s spectra, as shown in Fig. 3(C), the peaks at 529.6 and 531.3 eV are assigned to the TiO_2 and TiON bonding, respectively. Therefore, the XPS results confirm that the TiN films obtained from HiPIMS and CAD process exhibit similar compositions and bonding states. The hybrid layered structures of A-2 and B-2 TiN samples were examined using TEM, as shown in Fig. 4(A) and (B), respectively. Typical columnar structures were observed in HiPIMS and CAD TiN layers. The HiPIMS Ti interlayer, HiPIMS TiN, and CAD TiN in Sample A-2 have thicknesses of 133, 535, and 951 nm, respectively. The CAD Ti interlayer, CAD TiN, and HiPIMS TiN in Sample B-2 have thicknesses of 143, 533, and 1459 nm, respectively. The interface between the HiPIMS and CAD TiN layers was