Effects of N2/Ar gas ratio on phase formation and tribology of Ti–Si–N composite coatings prepared by hybrid PVD

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Ti–Si–N hard coatings have been fabricated at different N2/Ar gas ratio (N2:Ar = 1:1, 1:2, or 1:3) sputtering conditions by the hybrid Physical Vapor Deposition (PVD) method, which consists of sputtering and arc ion plating (AIP). The pure silicon and titanium targets were selected for reactive sputtering and the AIP process, respectively. Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDS) analysis has shown that the Ti/Si ratio increased as the Ar gas flow rate increased. Moreover, it found that the main growth plane of Ti–Si–N film was changed from (111) plane to (220) plane with increasing Ar gas flow from the results of X-ray diffraction (XRD) analysis. The wear rate of composite films was found to be lower than that of monolithic TiN with different friction coefficients at the initial running-in stage.

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1. Introduction

Multi-compositional nanostructured hard coatings for tools, molds and dies, and precision components in the industry of transportation vehicles and optical parts have been intensively studied for their outstanding mechanical stability under severe working conditions.1–3 Recently, they were found to be synthesized by hybrid vacuum coating techniques with multi-deposition sources.4)

Ti–Si–N is one of the prospective nanocomposite coatings of interest for its high hardness, excellent wear properties, and good chemo-mechanical stability based on multi-composition with nanoscale structures. Representatively, Hayashi et al.5) Shizhi et al.6) and Veprek et al.7,24) reported the microstructure and mechanical property of Ti–Si–N films as a form of embedded nanocrystalline TiN in an amorphous SiNx matrix prepared by Plasma Assisted Chemical Vapor Deposition (PACVD). Diserens et al.9,30) also reported the synthesis of Ti–Si–N films using a sputtering-based PVD method. Methodologically, Haug et al.10) and L. Le Brizoual et al.19) used a hybrid PVD process including an arc-combined sputtering method to deposit Ti–Si–N films in their research report. Mostly, the previous experiments focused on improvement of the mechanical properties of films, such as hardness and wear resistance, which can be obtained by controlling the grain size and boundary phases induced from the variance of silicon or nitride content in Ti–Si–N coatings.11,12)

Furthermore, in the hybrid PVD process, which consists of AIP and sputtering, induced power and gas conditions, including reactive and sputtering gases for a sputter source, are key factors for promoting sputtering yield and related phase-forming behavior that result in changing the film properties.20,21) There were also several studies regarding the effect of nitrogen species in the gas mixture of nitrogen and argon on the film properties of reactively sputtered Ti–Si–N films.19,22) In these cases, the investigation focused mostly on the effect of pressure and the flow rate of nitrogen gas on the Si or nitride contents and related phase evolution accompanied by microstructural changes resulting in film properties such as hardness, electrical resistivity, and wear properties.

In this study, we investigated the effects of the N2/Ar ratio on growth behavior, microstructure, and related mechanical properties of Ti–Si–N films deposited by the arc bond reactive sputtering method while controlling the Ar gas flow for the sputtering of Si. In addition, the tribological properties of Ti–Si–N films at the running-in stage were studied.

2. Experimental procedure

All of the film samples were fabricated using a laboratory-designed hybrid PVD system (J＆L Tech., Korea). Figure 1 shows the schematic design of the vacuum chamber of a coating system. This system is equipped with a magnetron-installed cathodic arc source (5" diameter) and an unbalanced magnetron (UBM) target size of 5" in diameter. The silicon target (5N, Applied Materials, Korea) for sputtering and the Ti target for the arc source (3N, Applied Materials, Korea) were used as coating sources. The argon and nitrogen gases are controlled by mass flow controllers and supplied individually in relation to each corresponding target. The Ar flow rate varied from 20 to 80 sccm, with a fixed N2 flow of 20 sccm for corresponding samples. The base pressure was 5.3 × 10−2 Pa, and the practical working pressure was kept at approximately 1.1 Pa for all deposition processes. The Ti–Si–N composite films were grown on metal substrates (SCM415) by a hybrid process using simultaneous operation of the arc ion plating (60 A) and the magnetron sputtering driven by DC power supplies (400 V). Before the deposition, the metal substrates were polished to a mirror-face surface using diamond paste (dia. 1 μm). After that, all of the specimens
were cleaned with acetone, methanol, and deionized water in an ultrasonic container for 30 min and dried in an oven prior to being loaded in the vacuum chamber.

The substrates were mounted on a rotating substrate holder (5 rpm) and heated to approximately 400°C by radiation heaters. Before coating, all of the targets were cleaned by Ar sputtering (5 rpm) and heated to approximately 400°C by radiation heaters. The substrates were cleaned with acetone, methanol, and deionized water in an ultrasonic container for 30 min and dried in an oven prior to being loaded in the vacuum chamber.

Before coating, all of the targets were cleaned by Ar sputtering for 10 min. Afterward, argon gas was added to initiate sputtering of the Si target. At the same time, argon and nitrogen gases were flowed into the arc target during arc evaporation. The deposition time was fixed to 20 min, which resulted in layers with a thickness range of 1.2 to 1.9 μm. Details of the deposition conditions are shown in Table 1.

The microstructures and silicon contents were identified by FESEM (including EDS, JSM-6701F, Jeol, Japan) and TEM (Tecnai F20, FEI, USA) analysis. For EDS measurement, the spectra of Ti and Si elements were measured using Kα line and the spectra do not overlap each other. The spectra were obtained from 5 different points of the same specimen. During the measurement, the spectrum of Ti from the TiN monolithic film specimen was also measured as a reference. The ratio of Ti and Si was obtained from the average value of the 5-point measurement of each specimen. For a cross-sectional analysis of each film specimen, all of the film specimens that were deposited on the metal substrate were machined to make them as thin as possible. Then the specimens were soaked in liquid nitrogen and fractured into several pieces. The growth behavior of the films was investigated by X-ray diffractometer (D/max-2500, Rigaku, Japan) with CuKα radiation under 20 kV and 100 mA. The hardness of the films was measured by nanoindentation with a Berkovich indenter with a maximum 10 mN load (Triboindenter, Hysitron, USA). The presented data were obtained by averaging 9 individual indents per sample. A typical pin-on-disk wear tester was used to characterize the tribological properties of Ti–Si–N films with different N2/Ar gas mixture conditions. Details of the wear test conditions are shown in Table 2.

3. Results and discussion

Based on the elemental analysis performed by FESEM-EDS, the relation between the Ar flow rate and Ti/(Ti + Si) compositional ratio was identified as shown in Fig. 2. From this, it was found that the Ti/(Ti + Si) ratio increased slightly as the Ar flow rate increased. Thus we can assume that the Si content in the Ti–Si–N film was approximately 0.5–1%, being reduced as the Ar gas flow increased. This result is the opposite of that reported in previous research.10,22 Many factors are involved in controlling the sputtering yield, such as the target power, vacuum levels, and gas flow.13 Presently, it seems that the increase of partial gas pressure for sputtering may unexpectedly cause the reduction of Si sputtering. This feature might be attributed to several possible causes. With the reduced mean free path of particles from the increased sputter gas, including neutrons, activated particles, and ions, the disturbance of effective sputtering (i.e., not enough Penning ionization/excitation) may occur due to the higher possibility of collisions in the plasma. Additionally, despite the target with shutters and an individual gas inlet configuration in the system, there might not be enough of a chance to effectively prevent cross-talk (target poisoning) in this multi-target system.13,20,21

Figure 3 shows the textured growing of films with the preferred orientations of TiN (111) and (220) planes parallel to
the substrate surface, which would be the first and/or the second strongest diffraction peak in the TiN film in literature.\textsuperscript{14)} The preferred orientation can often be affected by the substrate and deposition conditions.\textsuperscript{15)}–\textsuperscript{18)} Typically, when decreasing the N\textsubscript{2}/Ar ratio from TSN1 to TSN3, the intensity of the (111) plane is weakened, and the (220) peak is stronger, with a slight peak shift. In addition, there are no diffraction peaks assigned to silicon nitride or other titanium silicon crystalline phases. Such results suggest that Si may incorporate into the Ti–N structure or exist as an amorphous phase.\textsuperscript{10),11),23)}

Figure 4 shows cross-sectional SEM images of the TiN and Ti–Si–N coatings deposited on the metal (SCM415) substrates. No lateral or vertical cracks were observed for any of the films, even without any adhesive metallic interlayer. Film thicknesses were observed in the range of 1.2–1.9\,\mu m in all samples.

The coated TiN and T–Si–N series showed a columnar structure with a preferred orientation and well-crystallized behaviors. However, when comparing the TiN to TSN1, TSN2, and TSN3, it seems that the growing textures are slightly different. As we can see in the Ti–Si–N samples, the wider neighbored columns are observed to be unlike the case of TiN (TN), an integrated column structure. This may be due to the incorporation of even small amounts of Si.\textsuperscript{24)}

Figure 5 shows the hardness and removal rate after a wear test of the samples (1000 m). With respect to hardness, TiN appeared slightly lower than the Ti–Si–N composite films; however, there is no significant difference. From the TEM analysis of the cross-sectional view of TiN (TN) and TSN3 (Ti–Si–N) in Figs. 5(b) and 5(c), no remarkable difference in grain size can be found between the two samples in spite of Si incorporation in the Ti–N structure. However, the removal rate of the TiN film showed a much higher value, $1.8 \times 10^{-3} \, \text{m}^2/\text{N}$, than that of the other TSN film series, $\sim 10^{-4} \, \text{mm}^2/\text{N}$, even with similar hardness values. The friction coefficient of each sample is also shown in Fig. 6. As compared to the TiN coating, the Ti–Si–N samples showed lower friction coefficients and stable running-in modes at the initial stage of wear. As can be seen in Fig. 7, most of the Ti–Si–N coatings showed a typical sliding wear feature without remarkable
abrasive or adhesive wear traces inside the wear track. However, in the case of monolithic TiN (TN), as shown in Fig. 7(a), there are some traces of abrasive wear in the center area of the wear track (solid arrows). Additionally, some of the adhesives are found inside the wear track (hollow arrow). In the case of TSN1 in Fig. 7(b), small traces of rolling and adhesives are observed inside (hollow arrow) and outside (solid arrow) the wear track. Mostly, a small trace of adhesive is found inside the wear tracks of the TSN2 and TSN3 specimens in Figs. 7(c) and 7(d), respectively. The narrowest wear track is found in TSN3. From the results shown in Figs. 5, 6, and 7, it can be expected that the addition of small amounts (<1%) of Si into TiN can be effectively attributed to improve the tribological properties of the TiN coatings.

4. Conclusions

Ti–Si–N films were deposited on SCM415 steel substrates by a hybrid PVD deposition technique using individual Ti and Si targets under different N2/Ar atmospheres. Even with the small amounts of Si incorporation into TiN, it seems to make possible the effective contribution to the growing behavior of coatings with changes in surface textures and increased wear resistance of Ti–Si–N composite films. In addition to controlling sputtering gas flow, other deposition process factors need to be considered to obtain higher yields of sputtering material.

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