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Effect of negative substrate bias on the microstructure and mechanical properties of Ti–Si–N films deposited by a hybrid filtered cathodic arc and ion beam sputtering technique

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ABSTRACT

A hybrid cathodic arc and ion beam sputtering method was employed to synthesize Ti–Si–N films. The influence of negative substrate bias on the structure and mechanical properties was investigated by using XRD, XPS, HRTEM, nanoindentor and so on. With the increasing of negative bias there is a decrease in the TiN crystallite size from 36 nm to 10 nm. Negative substrate bias promoted the conformation of nc–TiN/a–Si_3N_4 nanocomposite structure with complete phase separation and uniform crystallite size. Superhard TiSiN films with a maximum hardness of 46 GPa were successfully synthesized under 100 V negative bias. Severe oxidation occurred in films deposited under 200 V and 300 V negative substrate bias due to the decreasing of deposition rate, which led to the hardness of films reduced to the value of 26 GPa and 22 GPa respectively.

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1. Introduction

Recently, Ti–Si–N films have been extensively studied due to their superior mechanical, thermal and other properties. Ti–Si–N films containing approximately 7–10 at.% Si were reported to have exceptionally high hardness values, i.e. 40 GPa [1–5]. Moreover, the film hardness was reported to remain stable even after annealing at 900–1000 °C [6]. Veprek et al. [7,8] have attributed these novel properties to a unique microstructure, which is a nanocomposite consisting of nanocrystal TiN embedded in a thin layer of amorphous Si_3N_4 matrix. Firstly, plasma assisted chemical vapor deposition (PACVD) technique was used to prepare Ti–Si–N films [1,9]. Due to the usage of aggressive chemicals as metal sources and high deposition temperature for CVD, physical vapor deposition (PVD) technique is considered to be more suitable for industrial-scale synthesis of these films. Various PVD techniques, such as magnetron sputtering [10–14], ion beam assisted deposition [4], cathodic ion plating [15,16] and some hybrid cathode arc techniques [17–19] have been applied. Arc evaporation provides a relatively simple and efficient method. Alloy target of Ti and Si was used because silicon is relatively difficult to arc evaporate in a pure elemental state. Alloy target restricted the range of the Ti:Si ratio of films [16]. For hybrid cathode arc techniques, separate sources of silicon were supplied through magnetron sputtering [18,19] or by bubbling silicon-based liquid precursor into a cathodic arc process [17]. In the current work we used a novel technique combining magnetic filtered cathodic arc (MFAC) and ion beam sputtering, in which a cathodic arc evaporator is used to supply the flux of titanium ions and a ion beam sputtering is used to produce the flux of silicon atoms. Ion beam sputtering presented Si source and flexible controllability for preparation of Ti–Si–N films based cathodic arc technique. The effect of Si content on the film properties synthesized by this method has been studied systematically [20]. The results indicated that without substrate bias and heating system the energy of deposition ions produced from cathodic arc was insufficient for formation of super-hard Ti–Si–N nanocomposite films with Si content range of 3.2–15.5%.

In the present work, in order to enhance deposition ion energy, we synthesized Ti–Si–N films using the hybrid cathodic arc and ion beam sputtering technique under different substrate bias. The influence of substrate bias on films growth, microstructure and properties was investigated systematically.

2. Experimental details

2.1. Thin film deposition

The deposition system used in this study is shown in Fig. 1. Single crystal Si (400) wafers were used as substrate, which were ultrasonically cleaned for 20 min in acetone followed by 10 min

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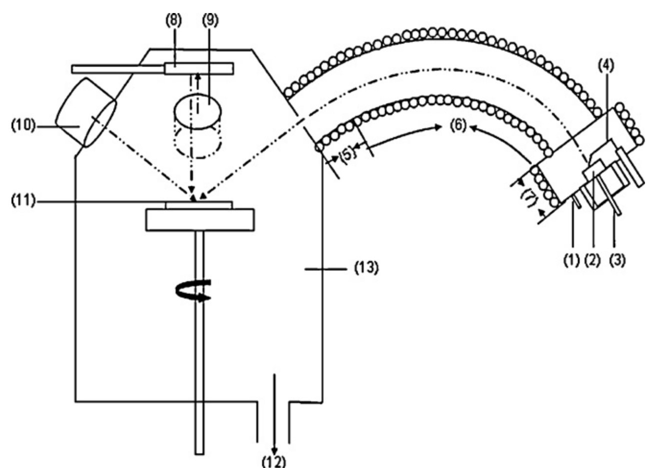

Fig. 1. (1) gas admission hole of cathodic, (2) cathodic target, (3) cathodal electrode, (4) arc striker, (5) outlet coil, (6) filtered coil, (7) source coil, (8) ion beam sputtering target, (9) kaufman ion gun, (10) ICP ion source, (11) substrate, (12) pump and (13) vacuum chamber.

in ethanol, then set in vacuum chamber after blown by nitrogen. The background pressure of vacuum chamber was 3.0×10^{-4}Pa. Firstly, substrate was bombarded by Ar ion beam produced by ICP ion source for 20 min. The ICP ion source was operated at a power of 400 W and working pressure of 0.1 Pa. The Ti–Si–N films were co-deposited by ion beam sputtering and magnetic filtered cathodic arc. During the deposition, different negative substrate bias was applied. The power of ICP ion source was 400 W, and the Ar flow rate introduced into ICP ion source was 20 sccm. The cathodic arc source was operated at a DC arc current of 70 A. High purity Ti (99.95%) was used as cathodic target. Mixture of high purity nitrogen (purity 99.99%) and Ar (purity 99.99%) was introduced into arc source through mass flow control valve with the flow rates of 7 sccm and 21 sccm respectively. The current of source coil, filtered coil and outlet coil was 0.25 A, 3 A, 1.5 A respectively. High purity α-Si_3N_4 (99.99%) was used as ion beam sputtering target. Kaufman ion source was operated at 50 mA beam current, 1600 V plate voltage, 120 V accelerating voltage. The flow rate of high purity Ar was 8 sccm introduced into Kaufman ion source. The work pressure of whole process was 0.1 Pa. No intentional heating system was used. Separate temperature measurements by attached thermocouples inside the substrate holder showed that the deposition temperatures never exceeded 100 °C. The thickness of films deposited was about 300 nm.

2.2. Thin film characterization

The chemical bonding and element content of the coatings was investigated by an X-ray photoelectron spectroscopy (XPS) analysis using a Kratos–Axis spectrometer with monochromatic Al Kα (1486.71 eV) X-ray radiation (15 kV and 10 mA) and hemispherical electron energy analyzer. The reference peak used was C1s 248.8 eV. In order to avoid the effect of surface oxidation, prior to XPS analysis, the samples were etched using 5 keV argon ions for 3600 s, and the etched thickness was about 60 nm. The crystalline structure of the films was measured by X-ray diffraction (XRD) with a Cu Kα source using an X′ Pert Pro MPD (Phillips) diffractometer. To examine the microstructure, cross-section transmission electron microscopy (TEM) was carried out. The TEM observation was done using a JEM-2010 electron microscope. Cross-sectional TEM specimen was prepared by focused ion beam (FIB) milling using GATAN PIPS-691 Ion-Miller.

The magnitude of the residual stresses was calculated from the change in radius of curvature of silicon substrate measured by a

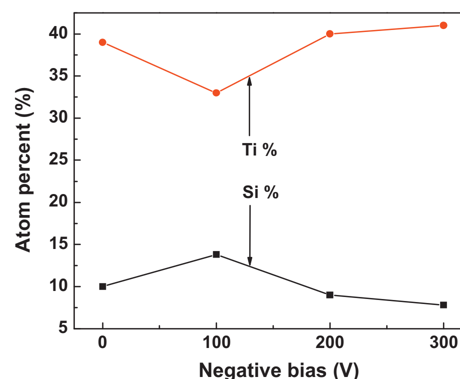

Fig. 2. The Si and Ti content in the Ti–Si–N films as a function of the substrate bias.

Tencor laser scanner before and after deposition using the Stoney's equation [21].

$$\sigma_f = \frac{E_S t_S^2}{6(1-\nu_s)t_f}\left(\frac{1}{R_2} - \frac{1}{R_1}\right)$$

where, the curvature radii R_2 and R_1 are the radii of silicon substrate before and after deposition, $E_s/(1-\upsilon_s)$ is the biaxial elastic modulus of the silicon substrate, t_s is the substrate thickness, t_f is the film thickness.

Coating hardness measurements were conducted in a Nanoindenter ((XP, MTS, Inc., USA)) with a Berkovich diamond indenter and determined by continuous stiffness measurement (CSM) technique. The indentation depths were set to 200 nm due to the instrument resolution limit to obtain the trend of hardness as a function of substrate bias or substrate bias ratio. On each sample, nine indentations were made in a 3×3 matrix with distance of 30 μm between each point and nine hardness values calculated for a mean value.

3. Results and discussion

3.1. Composition

Fig. 2 shows the content of Si and Ti in the Ti–Si–N films as a function of the substrate bias. It can be observed that Si content with a range of 7.8–13.8% reached peak value of 13.8% under 100 V negative bias, and then decreased with the increasing of substrate negative bias. Fig. 3 shows the deposition rate of TiN and TiSiN films. It can be observed that the deposition rate of TiN decreased sharply under 100 V negative bias, and decreased a little with the bias increased further. The ion beam of TiN with a diameter of 10 cm

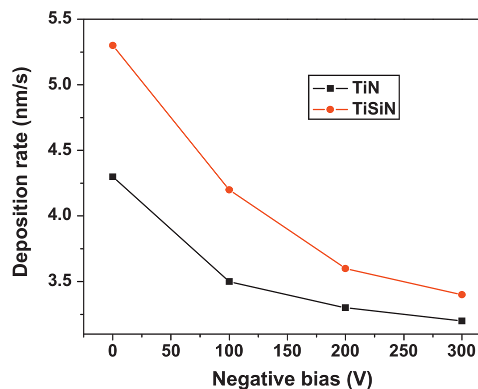

Fig. 3. The deposition rate of the TiN and TiSiN films as a function of the substrate bias.

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