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Materials Science and Engineering A 423 (2006) 111–115

MATERIALS SCIENCE & ENGINEERING A

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Texture development in Ti–Si–N nanocomposite thin films

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Received 8 July 2005; received in revised form 15 September 2005; accepted 30 September 2005

Abstract

Nanocomposite thin films of titanium silicon nitride were deposited by sputtering on *R*-plane sapphire substrates. The effects of silicon addition and negative substrate bias on the texture development of the films were studied systematically by varying the bias voltage in the range −20 to −200 V. The accompanying changes in the microstructure and growth morphology of the phases in these films were investigated in detail using X-ray diffraction and a atomic force microscopy. In addition, the effect of texture on the mechanical properties of the films was also investigated using nanoindentation technique. Pure TiN films deposited without Si exhibit a strong (1 1 1) preferred orientation, while with addition of Si, the orientation of the films changes from (1 1 1) to (2 0 0). Meanwhile the surface morphology of these films changed from a pronounced columnar microstructure to a dense, fine-grained structure. The effect of negative substrate bias voltage applied during deposition also resulted in a similar change of film orientation and microstructure and leads to the increase in hardness of the films from 21 to 40 GPa, respectively.

Keywords: Texture; Nanocomposite; Thin films; Ti–Si–N films

1. Introduction

Hard coatings with tailored properties are increasingly important for applications in many different areas of engineering and industry such as coatings for cutting tools under dry and high speed machining conditions protective coatings for turbine blades and engine parts to improve their durability [1–5]. A nanocomposite coating comprises of at least two phases: a nanocrystalline phase and an amorphous phase, or two nanocrystalline phases. The addition of the second phase not only prevents grain growth but also suppresses grain boundary sliding (for grain size <10 nm), and hence improve the mechanical properties [6–10]. The hardness of these coatings can be tailored depending on the design and application.

Thin films with preferential crystallographic orientation are desirable for particular applications because of their anisotropic nature. For example, the mechanical behaviour of TiN films is governed by the preferred growth orientations, since TiN is an anisotropic material with $E_{1\,0\,0} > E_{1\,1\,1}$ (where $E_{1\,0\,0}$ and $E_{1\,1\,1}$ are the elastic moduli along the [1 0 0] and [1 1 1] crystallographic directions, respectively) [11]. The preferred orientation of TiN films may be dependent upon the competition between the surface free energy and the strain energy [12]. By assuming that the strain energy in the film increases linearly with thickness, it has been postulated that, when the film thickness is sufficiently small, the film orientation is the result of minimization of surface energy (observed to be (1 0 0) for TiN films) [12]. However, in other work [13], an increase in internal stress from 0.3 to 2 GPa as a result of increased substrate bias voltage during film growth, resulted in a change in preferred TiN orientation from (1 1 1) to (2 0 0), also in Ref. [14] the orientation changes to (2 0 0) from (1 1 1) by varying the incident ion/metal flux ratio from 1 to ≥5 keeping N_2^+ ion energy constant at ∼20 eV which suggests that the strain energy might not be the main cause for the (1 1 1) preferred orientation.

In this paper $Ti_{1-x}Si_xN$ thin films were deposited by ionised magnetron sputter deposition (IMSD). The variations of film structure and properties as a function of Si addition and substrate bias voltage were investigated.

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doi:10.1016/j.msea.2005.09.132

2. Experimental

Titanium silicon nitride (Ti_{1-x}–Si_xN) films were deposited by IMSD, using separate Ti (99.96%) and Si (99.999%) dc magnetron targets (55 mm × 35 mm × 2 mm). Film stoichiometry, Ti_{1-x}:Si_x (where x is the atomic fraction of Si: x = Si/[Ti + Si]) could be precisely controlled with the power to each target. The target power was typically set at 5.2 W/cm^2 for Ti and 1.8 W/cm^2 for the Si. A three-turn rf coil between targets and substrates generated an additional plasma, through which the depositing flux passed. The base pressure of the deposition chamber was 10^{-8} Pa, and the depositions were carried out in 1.4 Pa Ar/N_2 (50:50): the gases both of 99.9999% purity were pre-mixed in a reservoir and bled into the system via a leak valve. By setting the leak and gate valve to the main pump, gas flow rate and pressure were controlled. Substrates rested on a platinum strip heater and the dc substrate bias was varied over the range of 0 to −200 V. Further details of the deposition system have been reported elsewhere [15].

X-ray diffraction (XRD) patterns were recorded using a conventional X'Pert Philips diffractometer (generator current and voltage 40 mA and 40 kV, respectively). The average grain size was calculated using Scherrer equation [16]. The titanium to silicon ratio in the deposited films was measured using a energy dispersive X-ray analysis (EDX) and was found to be $Ti_{0.84}Si_{0.16}N$. The surface morphology of the films was observed by atomic force microscopy (AFM), in tapping mode. Film thickness (measured by profilometry of a step on a masked substrate) was typically 3–3.5 μm. Film hardness, H, was measured with nanoindentation (Nanotest 600, Micro Materials Ltd., Wrexham, UK, fitted with Berkovich indenter: a three-sided pyramid with the same area-to-depth ratio as a Vickers indenter). The intrinsic mechanical properties of these films were measured at indentation depths between 200 and 330 nm, which is less than 10% of the film thickness, and averaging over a total of five indents. The influence of the mechanical properties of the substrate on the measurement is therefore avoided. A test load of 30 mN was typically used and the loading and unloading speed was kept at 0.8 nm s^{-1}. The Oliver–Pharr method was used to analyze the loading and unloading curves [17]. To minimize creep and thermal drift effects the hold period was kept at 10 s at maximum depth and 60 s during unloading at 20% of the maximum load.

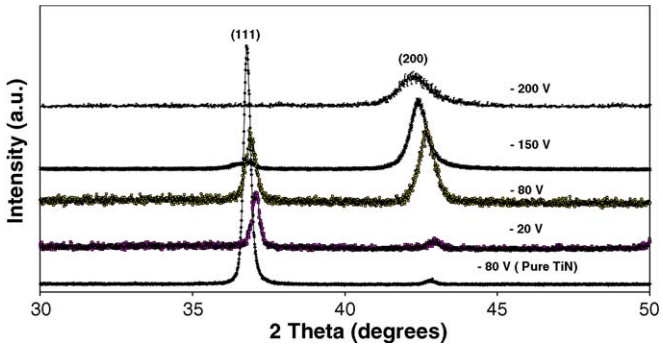

Fig. 1. XRD patterns of $Ti_{1-x}Si_xN$ films deposited at various substrate bias voltages along with the pure TiN film.

3. Results and discussion

Fig. 1 shows XRD spectra of the $Ti_{1-x}Si_xN$ films deposited at 400 °C with varying negative substrate bias voltages, V_b, from −20, to −200 V (along with a reference TiN film prepared with a bias voltage of −80 V). Only diffraction peaks assigned to crystalline TiN are observed, with no indication of the presence of crystalline Si_3N_4 or titanium silicide phases. These observations are in agreement with earlier findings from nc-TiN/a-Si_3N_4 films deposited by PVD [18–21], suggesting that the silicon is present in an amorphous phase. The undoped TiN film shows strong preferred (1 1 1) orientation and a narrow line width corresponding to a grain size of approximately 30 nm. For the $Ti_{1-x}Si_xN$ films, an increase in negative substrate bias gradually changes the preferred film orientation of TiN (in $Ti_{1-x}Si_xN$) from (1 1 1) to mixed, and finally to (2 0 0), with broadening of the peaks. Peak broadening is generally attributed to reduction in the coherent

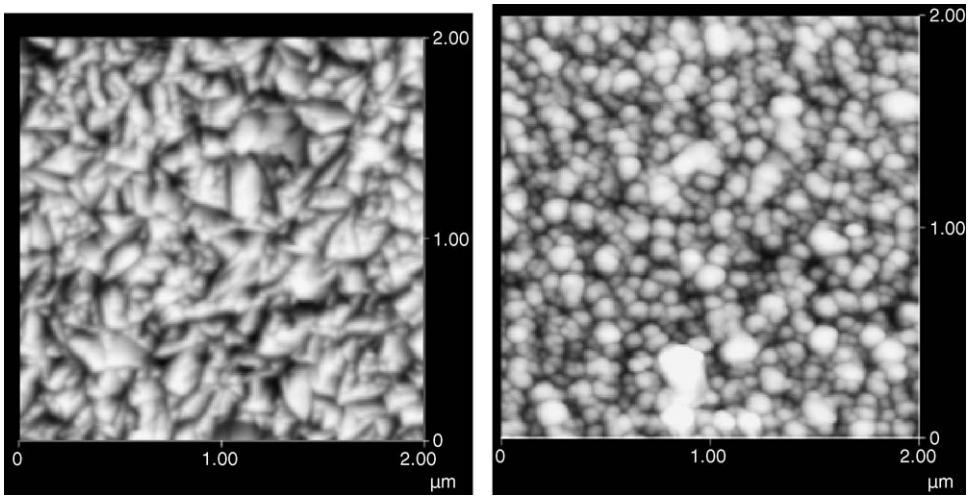

Fig. 2. AFM images of (a) TiN and (b) $Ti_{0.84}Si_{0.16}N$ film at bias voltage of −80 V.