Thin Solid Films 518 (2010) 7509–7514

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Tribological properties of Cr–Si–N nanocomposite film adherent silicon under various environments

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ARTICLE INFO

Available online 10 May 2010

Keywords:
Nanocomposite thin films
Pulsed DC magnetron sputtering process
Cr–Si–N films
Tribological property

ABSTRACT

Chromium nitride thin films have good corrosion resistance and mechanical properties. However, their hardness is slightly lower than that of other hard coatings. The concept of nanocomposite thin films is employed by adding silicon to form Cr–Si–N thin films with enhanced hardness and wear resistance. In this study, Cr–Si–N films with various Si contents were coated on silicon wafer to enhance the tribological properties and anticorrosion by a bipolar symmetry pulsed DC reactive magnetron sputtering process. The tribological properties were studied by a pin-on-disk tester. The tests were conducted with the same operating condition under three different environments. They were performed in the ambient atmosphere (in 55% humid air), DI water, and 0.01 M NaCl aqueous solution, respectively. The wear tests revealed that, as the silicon content was increased, even though the Cr–Si–N films had a better anticorrosion property they had an inferior performance on wear resistance. The results were concluded to be mainly due to Cr–Si–N films' microstructures and adhesion to the Si substrate rather than their hardness and toughness.

1. Introduction

Chromium nitride (Cr–N) thin film has been widely applied in molding industries to prolong service life due to its excellent corrosion resistance and mechanical properties [1]. It also exhibits rather good adhesions when deposited on general steel substrates [2]. The Cr–N coating has also been noted for its good oxidation resistance up to 800 °C [3]. At higher temperatures, the formation of Cr_2O_3 on the surface can further promote the coating's wear resistance and its capability as a diffusion barrier. This is beneficial to the improvement of die casting molds [4,5]. According to the concept of superhard nanocomposite hard coatings proposed by Veprek et al. [6], the addition of silicon to the Cr–N thin film to form amorphous silicon nitride phase has been adopted to improve the mechanical properties and oxidation resistance [7–14]. It has been observed that CrN crystalline and amorphous Si_3N_4 phase are two major contributors in the Cr–Si–N nanocomposite thin film [8,14]. Lee and Chang [14] evaluated the mechanical properties of the Cr–Si–N films by microhardness as well as micro wear tests of atomic force microscopy (AFM). The antiwear capability and microhardness of the composite films were increased with Si contents of up to 12 at. %. The corrosion resistance of each thin film was evaluated by a potentiostat in 3.5 wt.% NaCl aqueous solution in our previous report [15], showing that it was enhanced directly by the amount of Si content of the composite film. Microwear tests in a corrosive environment (a NaCl solution) by AFM were also implemented to investigate the possible wear-corrosion synergism. It has been shown that the best wear resistance under the corrosive environment is obtained with Cr–Si–N films with a concentration of Si of 10.1 at.%, which also yields the maximum hardness of Cr–Si–N coatings. In this work, the same asymmetric bipolar pulsed DC reactive magnetron sputtering technique [15] was adopted to deposit Cr–Si–N thin films with different silicon contents on p-type (100) silicon substrates. The tribological properties of the coated samples rather than the composite thin films themselves were studied by a pin-on-disk tester. The tests were conducted with the same operating condition under three different environments to investigate the wear resistance and tribological behavior of Cr–Si–N coatings on Si substrates.

2. Experimental details

2.1. Deposition of nanocomposite films

Cr–Si–N thin films were coated on a p-type (100) silicon wafer by using a bipolar asymmetry pulsed DC reactive magnetron sputtering system. Two DC power suppliers with a pulse controller (SPIK 2000A, Shen Chang Electric Co., Taiwan) were used to supply controlled power to Cr and Si targets, respectively. To obtain Cr–Si–N films with various Si contents, the powers supplied to Si target

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0040-6090/$ – see front matter
doi:10.1016/j.tsf.2010.05.035

Table 1
Elemental compositions of Cr–Si–N nanocomposite thin films produced by various pulse powers supplied to Si target.

Code of silicon specimen	Cr target power (W)	Si target power (W)	Element content (at.%)		
			Cr	N	Si
A1	300	224	53.1	34.1	12.8
A2	300	160	52.1	38.9	9.0
A3	300	95	55.5	38.4	6.1
A4	300	65	58.0	38.1	3.9

were kept at four values: 224, 160, 95, and 65 W, while, that to Cr target was fixed at 300 W. The purity and diameter of Cr and Si targets were both 99.99 wt.% and 76.2 mm. The pulse frequency was kept at 20 kHz with 100% reversed voltage and an 80% duty cycle during the sputtering process. A substrate bias of −300 V was applied with a pulse unit (Sparcle V, Advanced Energies Industries, USA) with 80 kHz frequency, 15% reversing voltage and a 60% duty cycle. The base pressure, 5.6×10^{-6} Pa, was achieved before sputtering. All substrates were sputtered clean for 10 min at 2.7 Pa argon pressure with a substrate bias of −500 V. A Cr–Si mixed film was deposited as an adhesion interlayer with around 150 nm thickness onto the substrate under 5×10^{-3} Pa in pure Ar atmosphere. The flow rates of Ar/N_2 mixture at a ratio of 1:1 were monitored by individual mass flow controllers. The pressure in the chamber during deposition was 8.0×10^{-1} Pa. The deposition time was 165 min. All substrates were heated to 300 °C during the sputtering process. They were placed 100 mm from both targets and fixed to a holder which rotated continuously in order to obtain uniform nanocomposite thin films.

2.2. Film characterization

The elemental compositions of the Cr–Si–N thin films were identified with a field emission electron probe microanalyzer (FE-EPMA, JXA-8500F, JEOL, Japan) with a ZAF-corrected program. The phases of the coatings were explored with a grazing incidence (1°) X-ray diffraction (XRD) equipped with a Cu target source. The surface roughness analysis was performed by an AFM system (D3100, Veeco). A silicon-based probe (NSC15/AIBS, Micko Mash) was used to scan a $50\times50\ \mu m^2$ area of the composite thin films to derive their roughness average (R_a) and maximum peak-to-valley height (R_{max}).

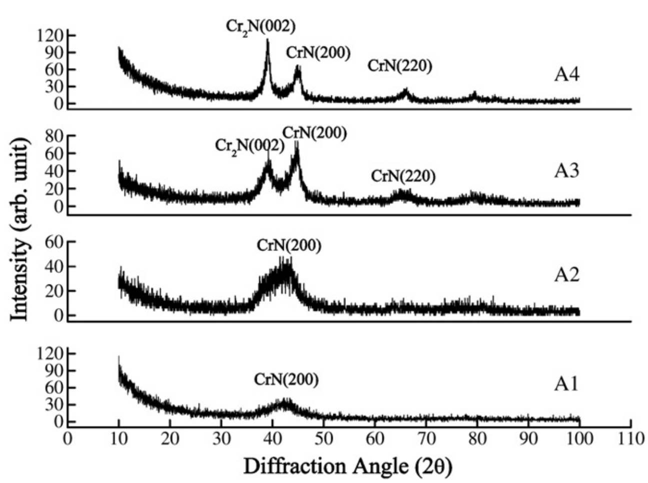

Fig. 1. XRD patterns of Cr–Si–N thin films deposited on Si substrates. (Note: A1: 12.8 at.% Si, A2: 9.0 at.% Si, A3: 6.1 at.% Si, and A4: 3.9 at.% Si).

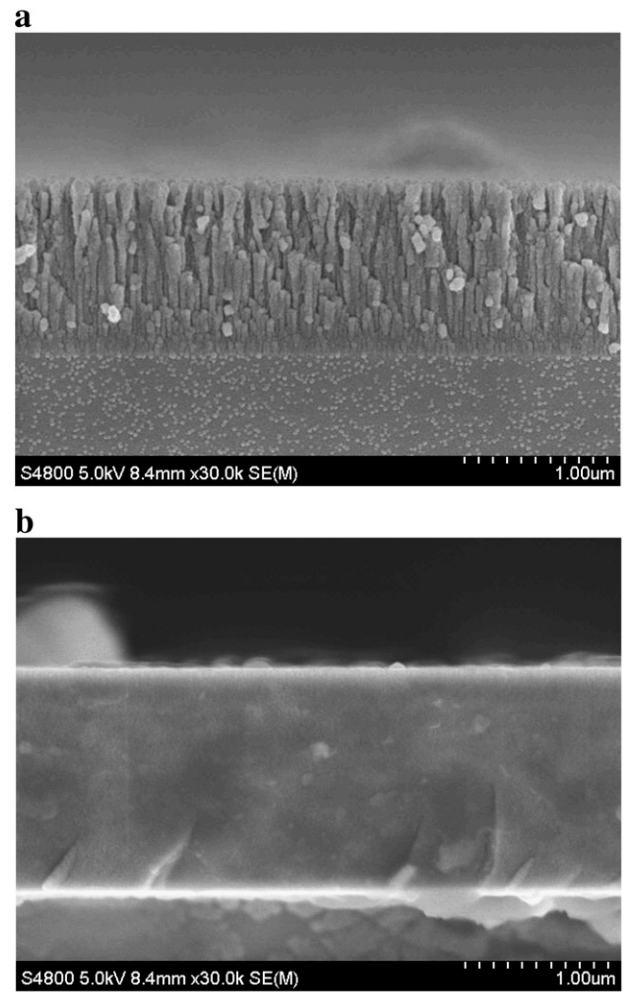

Fig. 2. Cross-sectional SEM images of Cr–Si–N coatings with (a) 3.9 at.% Si and (b) 12.8 at.% Si.

The mechanical properties, the hardness and reduced Young's modulus, were measured by micro indentation using a Triboindenter (Hysitron Inc.) equipped with a Berkovich pyramidal tip. The load–displacement curves were analyzed by applying the method of Oliver and Pharr [16]. The maximum load was 2.5 mN, applied at a loading–unloading rate of 1000 μN/s. Each specimen was tested more than three times.

2.3. Wear tests of Cr–Si–N samples

The wear coefficients were evaluated by means of pin-on-disk tests in three environments. They were conducted in the ambient atmosphere (in 55% humid air), DI water, and 0.01 M NaCl aqueous solution at room temperature. The counter parts were cemented tungsten carbide (WC with 6.0 wt.% Co) balls of 1/4″ (6.350 mm)

Table 2
Hardness (H), reduced Young's modules (E_r), and resistance to plastic deformation (H^3/E_r^2) of Cr–Si–N samples with different Si contents.

Code of silicon specimen	Hardness (H), GPa	Reduced Young's modulus (E_r), GPa	Resistance to plastic deformation (H^3/E_r^2), GPa
A1	15.31 ± 0.26	152.6 ± 2.1	0.15
A2	11.54 ± 0.35	147.6 ± 3.5	0.07
A3	13.85 ± 1.48	155.2 ± 7.4	0.11
A4	8.89 ± 0.43	131.4 ± 3.4	0.04