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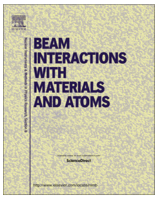

Effect of pulsed bias voltage on the structure and mechanical properties of Ti–C–N composite films by pulsed bias arc ion plating

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ABSTRACT

The influence of pulsed bias voltage on the structure and mechanical properties of Ti–C–N composite films prepared by pulsed bias arc ion plating was systematically investigated. The microstructure, surface morphology and bonding structure of the films were evaluated with grazing incidence X-ray diffraction, high resolution transmission electron microscopy, Raman and X-ray photoelectron spectroscopy, and scanning electron microscope. The mechanical properties such as hardness and elastic modulus were measured by nano-indentation. A composite structure consisting of nanocrystallites Ti(C,N) and amorphous carbon is observed. The surface morphology indicates that the size and amount of macroparticles at the film surface decrease with the increase of bias voltage. Applying a bias voltage of −300 V in Ti–C–N films induces strong crystalline characteristic. However, other bias voltages cause a tendency to a lower degree of crystallinity and an enhanced fraction of amorphous phase. With increasing the bias voltages from −100 V to −700 V, the corresponding hardness and elastic modulus increase firstly and then decrease, reaching a maximum value of 32.5 GPa and 367.4 GP at the bias voltage of −300 V.

1. Introduction

In recent years, Ti–C–N films have been investigated extensively due to their excellent mechanical properties [1,2]. The Ti–C–N films are already known to have a structure evolution from solid solution to nanocomposite [3]. It is worth noting that Ti–C–N nanocomposite films might exhibit higher hardness and lower friction by optimizing the phase fractions of nanocrystallites TiN or Ti(C,N) and amorphous carbon. The amorphous carbon phase fraction affects significantly the mechanical properties of nc-Ti(N,C)/a-C:H nanocomposite films [4]. The effects of nitrogen content on phase composition, structure and mechanical properties of Ti–C–N films are also reported [5,6]. Among deposition conditions, bias voltage applied to the substrates could significantly change film structure and mechanical properties due to the enhancement of adatom mobility and the effects of low energy ion bombardment during deposition process. Therefore, an understanding of bias voltage effects on the structure of Ti–C–N films is necessary to improve the mechanical properties for industrial applications.

At present, numerous advanced methods for synthesis of Ti–C–N films such as magnetron sputtering, pulsed laser deposition, cathodic vacuum arc deposition, etc. have been reported [7–9]. Due to its high ionization rate, high adhesion, low deposition temperature, macro-particle cleaning and low residual stress, pulsed bias arc ion plating (PBAIP) becomes a preferable technique widely used to deposit hard protective coatings [10,11]. In the previous works [12,13], we described a successful deposition of Zr–C–N and V–C–N composite films using PBAIP system. The present paper focuses on the variation of the bias voltage and investigates the effect of a pulsed bias voltage on the structure and mechanical properties of the Ti–C–N films prepared by PBAIP.

2. Experimental details

Ti–C–N films were deposited on silicon(100) and $W_6Mo_5Cr_4V_2$ steel substrates in a PBAIP system as described in detail elsewhere [14]. Circular graphite and Ti cathodes (55 mm in diameter) were symmetrically installed on the opposite side of the chamber wall. A rotational substrate holder was positioned in the center of the chamber with a rotation speed of 15 rpm and a target-substrate distance of 600 mm. The steel substrates were polished to an average roughness (*Ra*) value below 50 nm by diamond paste. All substrates were ultrasonically cleaned in acetone and alcohol for 15 min before loading them into the deposition chamber.

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Before introducing the working gas, the chamber was firstly evacuated to less than 5×10^{-3} Pa. Then the preheating procedure was carried out and maintained at 150 °C to remove tiny liquid contaminants and solid pollutants. Prior to the deposition, all substrates were sputter-cleaned by Ar^+ ion bombardment from an Ar plasma using a negative bias voltage of −900 V under Ar atmosphere of 2.0 Pa for 10 min. A thin Ti interlayer about 50 nm in thickness was deposited to improve the adhesion. During the deposition of Ti–C–N films, nitrogen gas was introduced into the chamber with a gas flow of 70 sccm by mass flow controller and the working pressure maintained at 0.5 Pa. The arc currents of graphite and Ti targets were fixed at 50 and 100 A, respectively. A pulsed bias source with pulse frequency f = 40 kHz and duty ratio D = 40% was connected to the substrate holder to apply the negative pulsed bias voltage. The effect of bias voltage on the microstructure and other properties of Ti–C–N films were investigated by varying the bias voltage from −100 to −700 V. The total deposition time of all films was 1 h.

The chemical composition and bonding structure of the films were determined by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA^{DLD}) with a monochromatic Al source. A field emission scanning electron microscope (FE-SEM, JEM2010) was employed to observe the surface morphology. The surface roughness was measured with a surface profiler (New View 5022). The crystalline structure and microstructure of the films were investigated using grazing incidence X-ray diffraction (GIXRD, D8 Discover) at an incidence angle of 1° combined with a parallel beam geometry and high resolution transmission electron microscopy (HRTEM, Tecnai G2 F30), respectively. A Raman spectrometer using excitation by a He–Ne laser with a wavelength of 632.8 nm (RENISHAW, in Via Raman) was used to evaluate the nature of carbon atomic bonds in the films. The hardness and elastic modulus of the films on steel substrates were measured by nano-indentation system (MTS, Nano-indenter XP) in a continuous stiffness measurement mode using a Berkovich diamond tip. The indentation depth was 250 nm in the present films, and the hardness was evaluated at about 10% of the film thickness in order to avoid a substrate effect.

3. Results and discussion

3.1. Composition and structure analysis

The chemical composition of the Ti–C–N films is summarized in Table 1. With increasing the bias voltage from −100 to −700 V, the C content of the films decreases from 31.2 to 24.1 at.%, while the Ti content firstly increases up to 44.2 at.% at −300 V, and then decreases linearly. The decrease of C content could be attributed to the carbon preferential resputtering caused by the high-energy ion bombardment. The weakly bonded and light carbon atoms would be more easily resputtered by incident ions during the film growth stage [15].

The dependence of film thickness and deposition rate on the bias voltage is presented in Table 1. As the bias voltage increases from −100 to −700 V, the film thickness and deposition rate reduces. At a bias voltage of −100 V, they reach maximum values with a thickness of 465 nm and a deposition rate of 7.7 nm/min. This phenomenon would be related to re-sputtering effect and densification of the film due to strong collision energy of ions [16].

Fig. 1 shows the grazing incidence X-ray diffraction patterns of Ti–C–N films deposited on steel substrates at various bias voltages. The Ti(C,N)(111), (200), and (220) diffraction peaks can be detected from XRD spectra. As the bias voltage increases from −100 to −300 V, the peak intensities increase indicating that the crystallinity of the film is enhanced. However, there is no distinct diffraction peak at higher bias voltage above −500 V. Because of difference between crystalline structures of Ti(C,N) and DLC, the normal crystalline structure of Ti(C,N) is disturbed by amorphous carbon phase. The film structure exhibits more amorphous-like Ti(C,N) containing DLC at bias voltage above −500 V. At low bias voltage of −100 V, ions of Ti cannot bond with ions of C due to low energy and quantity. Only if the energy and quantity of Ti and C ions increased to threshold, can Ti bonding with C form some nanocrystalline Ti(C,N) structure at −300 V. With the further increase of bias voltage above −500 V, the crystallinity deteriorates and the films show amorphous structure. The Ti-containing phase may remain as nanocrystalline but with an extremely small crystallite size.

In order to confirm the structure information, a cross-sectional HRTEM micrograph of the Ti–C–N film deposited at −300 V and the corresponding selected area electron diffraction (SAED) pattern in the inset are presented in Fig. 2. The HRTEM clearly reveals the presence of nanocrystallites with the size of about 10 nm embedded into amorphous matrix. Three strong diffraction rings corresponding to Ti(C,N) (111), (200) and (220) planes with an amorphous halo are observed in the SAED pattern, which are consistent with the XRD patterns. As a result, the as-deposited Ti–C–N film exhibits a typical composite structure with nano-sized Ti(C,N) crystallites surrounded by an amorphous carbon phase.

Raman spectroscopy is a very sensitive technique regarding carbon atoms. Fig. 3 shows the Raman spectra of the films deposited with various bias voltages. A broad peak ranging from 1100 to 1700 cm^{-1} reveals the amorphous carbon nature of the film and this broad peak can be fitted with two peaks, one around 1350 cm^{-1} (D band) and the other around 1560 cm^{-1} (G band) [17]. The G band is due to the bond stretching of all pairs of sp^2 atoms in rings and chains, while the D band is due to the breathing modes of sp^2 atoms in rings. As the bias voltage increases up to −300 V, the Raman intensity becomes weak, which might be related to the decrease of the amorphous carbon content inside the as-deposited films. Consequently, it is difficult to fit accurately the broad peak and calculate the intensity ratio of I_D/I_G at higher bias voltages in this study.

The bonding structure of carbon and nitrogen in the films was analyzed by XPS, yielding C 1s and N 1s high resolution spectra at different bias voltages as shown in Fig. 4. In Fig. 4(a), the C 1s spectra show a main peak at 284.8 eV and a shoulder peak centered at around 286.1 eV, which are assigned to C–C and C–N bonds, respectively [9]. The peak at low binding energy around 282.1 eV corresponds to the formation of C–Ti bonds [18]. Additionally, the presence of a weak peak at about 288.3 eV is attributed to C–O bonds due to oxygen contamination [19]. It is

Table 1
Summary of composition, thickness, deposition rate and roughness for all films.

Bias voltages (V)	Composition (at.%)			Thickness (nm)	Deposition rate (nm/min)	Roughness Ra (nm)
	Ti	N	C			
−100	35.8	33.0	31.2	465	7.7	10.96 ± 0.12
−300	44.2	29.7	26.1	375	6.3	10.48 ± 0.15
−500	41.1	34.3	24.6	352	5.9	10.89 ± 0.13
−700	38.4	37.5	24.1	343	5.7	11.15 ± 0.13