Effect of CH_4 partial pressure on the microstructure and mechanical properties of magnetron sputtered TiC films

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TiC thin film has become one of the most frequently used hard coatings because of its high hardness (26–31 GPa), good wear resistance, low coefficient of friction against steel, and other excellent properties [1]. It can be deposited by chemical or physical vapor deposition (CVD or PVD). TiC films manufactured by PVD have the advantages of low deposition temperature, high quality, and high deposition speed, etc. [2]. Reactively sputtered TiC films are deposited by using gases which contain carbon such as CH_4 and C_2H_2. Compared with using highly active C_2H_2, the processing is better controlled by using CH_4. In this paper, TiC thin films were deposited with reactive magnetron sputtering method at different CH_4 partial pressures and the effect of CH_4 on their phase, microstructure, and mechanical properties was investigated.

TiC films were deposited on silicon substrates by using radio frequency (RF) magnetron sputtering at room temperature. The substrates were ultrasonically cleaned in acetone and alcohol and then mounted on the substrate holder in the vacuum chamber. To improve the adhesion, a metallic Ti layer with a thickness of approximate 200 nm was deposited prior to the deposition of the ceramic TiC films. The TiC films were deposited from a pure Ti target (99.99%) in an Ar and CH_4 mixture atmosphere. The Ar partial pressure was kept at 0.3 Pa, while the CH_4 partial pressure varied from 0.01 to 0.08 Pa. (The CH_4 partial pressure was 0.01, 0.02, 0.04, 0.06 and 0.08 Pa; specimens were numbered from 1 to 5 respectively). During this study, the target power was kept at 200 W and the deposition time was 120 min for each specimen.

The phase formation and microstructure of films were investigated by X-ray diffraction (XRD) using a Dmax-rC diffractor and transmission electron microscopy (TEM) using a JEM-100CX TEM. The morphology of films was observed using a Nanoscope IIIa atomic force microscope (AFM). Mechanical property measurements of TiC thin films were carried out using a Fischerscope HV100 microhardness tester and the results were checked by AFM.

The XRD spectra of the TiC films deposited at different CH_4 partial pressures are shown in Fig. 1. It can be seen that at the CH_4 partial pressure of 0.01 Pa, the film mainly contains metallic Ti. When CH_4 pressure increases from 0.02 to 0.04 Pa, the films are single phase fcc TiC. When the CH_4 partial pressure is higher than 0.04 Pa, the fcc TiC disappears and the films exist in an amorphous state.

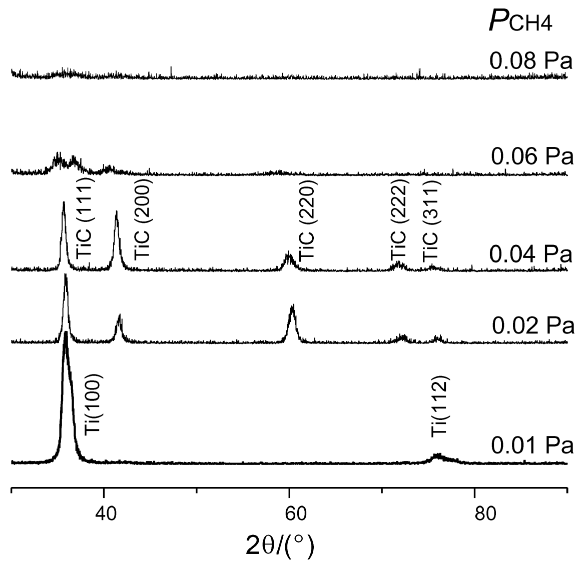

Figure 1 XRD spectrum of TiC thin films deposited at different CH_4 partial pressures.

Fig. 2 is the TEM bright field (B.F.) image and electronic diffraction (E.D.) patterns of TiC films at a CH_4 partial pressure of 0.04 Pa. From the B.F. image (a), it can be seen that the crystallite size of TiC films is small, about 20 to 30 nm. The E.D. patterns of TiC films (Fig. 2b) show continual and broadened polycrystalline diffraction patterns, in which TiC was indexed as fcc crystal structure, matching the XRD results well.

Because the thickness values of TiC films deposited at different CH_4 partial pressures are widely variable, the measurement of their mechanical properties is difficult. Large penetration loads will bring in the influence of the substrates, while small loads cannot avoid the noise caused by surface roughness, oxidation, and other factors. To measure the films precisely, a two-step penetration method was used [3].

Firstly, a large load (200 mN) indentation test was carried out to demonstrate the influence of substrate deformation on the universal hardness (HU) [4] of coating/substrate composite. Secondly, a smaller applied load (15 mN) was then selected according to the first-step result for the penetration test. The computer-controlled microhardness tester can give an indentation

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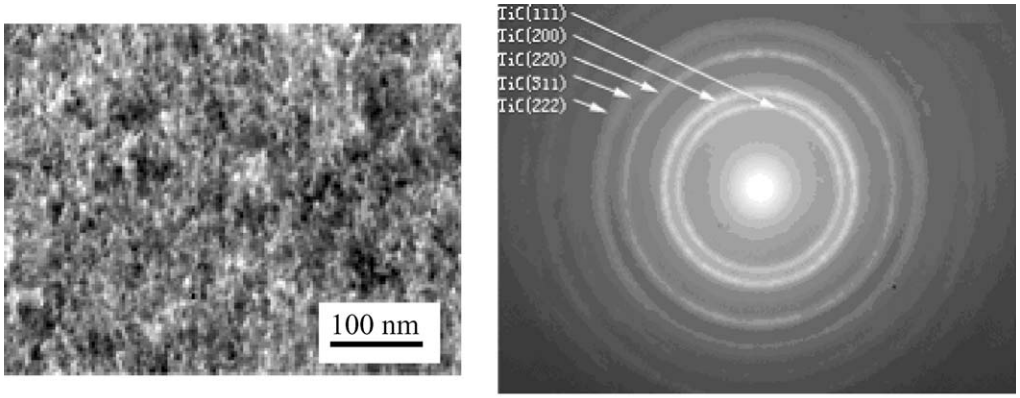

(a) (b)

Figure 2 TEM image (bright field) (a) and E.D. patterns (b) of TiC film deposited at a CH_4 partial pressure of 0.04 Pa.

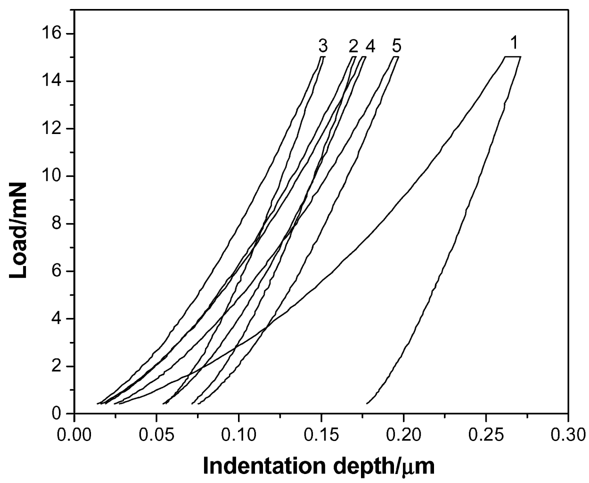

Figure 3 Load-indentation depth curve of TiC films (15 mN).

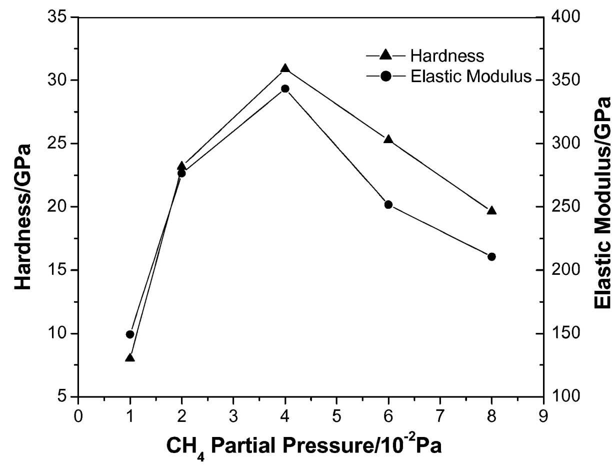

Figure 4 Hardness and elastic modulus of TiC films vs. CH_4 partial pressure.

plotting as shown in Fig. 3. The final Vicker's hardness (*HV*) and elastic modulus (*E*) of TiC films can be calculated according to Oliver's formula [5]

$$HV = \frac{P}{C \bullet h_c^2} \quad \text{and}$$

$$E = (1 - \nu^2) \Big/ \left(\frac{2\sqrt{A}}{S\sqrt{\pi}} - \frac{1 - \nu_{\mathrm{Dia}}^2}{E_{\mathrm{Dia}}} \right),$$

where HV is the hardness, P is the indenter load, C is a constant (26.43 for Vicker's indenter), h_c is the vertical distance along which contact is made (also called contact depth), E and ν are elastic modulus and Poisson's ratio for the specimen, E_{Dia} and υ_{Dia} are the same parameters for the indenter (1200 GPa and 0.25 respectively for diamond), A is the projected area of the elastic contact and S is the experimentally measured stiffness of the upper portion of the unloading data.

Fig. 4 shows the hardness and elastic moduli of TiC films. It can be seen that at low CH_4 partial pressure, the hardness and elastic modulus is low because of the Ti in the films caused by insufficient CH_4. With the increase of CH_4 partial pressure, the hardness of TiC films reaches the maximum values of 30.9 GPa at CH_4 partial pressure of 0.04 Pa. From the XRD and TEM, it can be seen that at that pressure, the films are fcc TiC. When the CH_4 partial pressure is higher than 0.04 Pa, the hardness and elastic modulus decrease due to the excessive carbon in the films.

The AFM technique is also used to check the correctness of the hardness measurement, and to observe the morphology of TiC films. Fig. 5 shows the morphology (a) and profile image (b) of the indentation of TiC film deposited at 0.04 Pa CH_4 partial pressure. A cellular structure with surface fluctuation of 15 nm can be observed on the surface of TiC film. In order to measure the hardness correctly, the depth of the indent was measured, as shown in Fig. 5b, in which the horizontal line is the surface average position. The diagonal of the indent is approximately 918 nm, and then the hardness can be calculated to 33.6 GPa, which corresponds well with the value detected from the microhardness tester.

In summary, by using the reactive magnetron sputtering method on silicon substrates at room temperature, nanocrystalline TiC films were deposited and they processed a high hardness (30.9 GPa) and elastic modulus (343 GPa). The CH_4 partial pressure shows an obvious effect on the phase, microstructure, and mechanical properties of TiC films. Single phase TiC films can be prepared at the CH_4 partial pressure of 0.04 Pa. Either high or low CH_4 partial pressure will cause the decrease of hardness and elastic modulus.

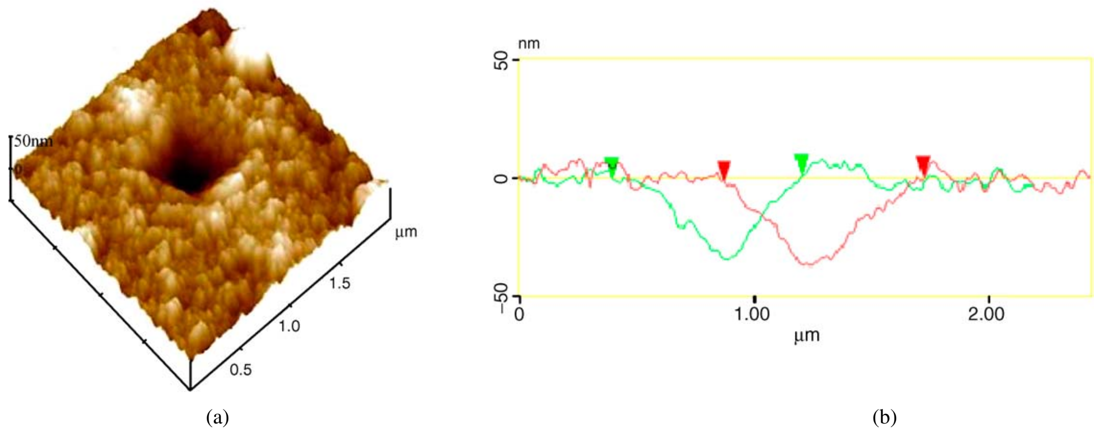

Figure 5 AFM morphology (a) and profile image (b) of the indentation on TiC thin film.

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