



Effects of substrate bias voltage on the microstructure, mechanical properties and tribological behavior of reactive sputtered niobium carbide films

Kan Zhang, M. Wen, Q.N. Meng, C.Q. Hu, X. Li, C. Liu, W.T. Zheng*

Department of Materials Science, Key Laboratory of Mobile Materials, MOE, and State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, People's Republic of China

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ABSTRACT

Niobium carbide films have been deposited on Si(100) substrates using direct current reactive magnetron sputtering in discharging a mixture of CH₄ and Ar gas. The effects of substrate bias voltage (V_b) and methane flow rate (F_{CH_4}) on the phase structure, composition, morphology, mechanical properties and tribological behavior for NbC films have been explored. For the film grown at $F_{CH_4} = 6$ sccm, a phase transition from a mixture of hexagonal-Nb₂C and cubic-NbC phases to cubic-NbC phase occurs with increasing the absolute value of V_b and no C–C bonding appears. In contrast, for the film deposited at $F_{CH_4} = 16$ sccm, only the cubic-NbC phase is observed with increasing the absolute value of V_b and the C–C bonding appears. If F_{CH_4} is fixed at either 6 or 16 sccm, as the absolute value of V_b is increased, the growing film surface becomes smoother, and the compressive stress increases. This can be attributed to the increase in the carbon ion bombarding energy, which leads to promoting the diffusion of adsorbed atoms and more carbon species' occupying the interstitial positions. It is found that the hardness (H) increases first, and then decreases after reaching a maximum value with increasing the absolute value of V_b . The friction coefficient for the film obtained at $F_{CH_4} = 16$ sccm is lower than that at $F_{CH_4} = 6$ sccm, which may be ascribed to the presence of either graphite or amorphous carbon in the film grown at $F_{CH_4} = 16$ sccm. Furthermore, a high stress results in a poor wear resistance.

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1. Introduction

Transition-metal carbides possess excellent properties, such as high melting points, high hardness, and good chemical stability, enabling these carbides for potential applications as wear-resistant coatings, diffusion barriers, and field emitters [1–3]. Especially, the transition-metal carbides with high hardness and low friction play important parts in surface engineering [4–6]. The emergence of these transition-metal materials provides a wider range of selection to meet different machining requirements in extreme environments. With respect to the other transition-metal carbides, niobium carbide (NbC) film has attracted considerable attention because it possesses excellent comprehensive properties. For example, the NbC shows not only a much higher electrical conductivity than either TiC or ZrC, but also a higher hardness than other transition-metal carbides [7–9]. Meanwhile, good tribological behavior coupled with chemical inertness and high melting point makes NbC film as a suitable material for protective coating. In addition, compared to the Group IV metals (Ti, Zr and Hf), Nb alloyed with C can form two phases: Nb₂C and NbC, which provides an opportunity to investigate a structural evolution with changing the experimental parameters [10].

To date, there are many routes to deposit protective coatings such as chemical vapor deposition (CVD) [11] and physical vapor deposition (PVD) [12]. Among these techniques, the advantage of PVD is that the compound films can be deposited at relatively lower substrate temperatures [13], while reactive sputtering is one of the typical PVD techniques to deposit films, because it is an industrial process applicable to large-area deposition, and the high quality films can be obtained. In reactive sputtering, the influence of deposition parameters on structure and properties for films has been widely reported in TiC [14,15], VC [4,16], WC [17,18] and ZrC systems [19]. Among the deposition parameters, the substrate bias voltage (V_b) is a very important factor. Some investigations have reported that the microstructure of NbC films deposited by reactive sputtering was strongly dependent on the V_b [10,20]. However, the relationship between V_b and the mechanical properties such as hardness for NbC films has not been well understood yet so far. Meanwhile, the carbon content in NbC films could change significantly, which leads to remarkably varying the structure and properties for NbC films [7,21]. Therefore, in addition to understanding the influence of V_b on the structure and mechanical properties for NbC films, it is also necessary to explore how the C content in NbC film influences its structure and mechanical properties. It is also worth noting that as a potential protective coating in machine industry, the tribological behavior for NbC films has received relatively little attention in the past. In this work, we try to explore the influence of both V_b and C content on the structure and mechanical properties, as well as tribological

* Corresponding author. Tel./fax: +86 431 85168246.

E-mail address: WZzheng@jlu.edu.cn (W.T. Zheng).

behavior of NbC films deposited using direct current magnetron sputtering, in which the CH_4 flow rate (F_{CH_4}) of 6 and 16 sccm, respectively, is chosen to obtain the NbC film with a low and high C content, respectively. The relationship between the microstructure, stress, hardness, and tribological behavior for the NbC films has been investigated.

2. Experimental details

The NbC films were deposited on Si(100) wafers by direct current (DC) reactive magnetron sputtering in discharging a mixed Ar (99.999%) and CH_4 (99.999%) gas. The pure Nb target (99.95%) was a disk with a diameter of 60 mm and a thickness of 3 mm. N-type Si(100) substrates were degreased in acetone, alcohol and distilled water for 20 min, respectively. The chamber was evacuated by a turbomolecular pump to 4×10^{-4} Pa prior to sputtering, in which the pumping speed was fixed at a value of 1000 L s^{-1} for all experiments. The Nb target was pre-sputtered in discharging a pure Ar gas for 10 min to remove the surface Nb_2O_5 layer, and then in discharging a mixed Ar and CH_4 gas for 10 min to achieve a steady-state reaction between Nb and C. During the deposition, the applied current on the Nb target, substrate temperature and total pressure for all samples were kept at 0.3 A, 500°C and 0.8 Pa, respectively. The flow rate of Ar and CH_4 was accurately controlled by mass flow controllers. The flow rate ratio of Ar: CH_4 was held at 80:6 and 80:16 sccm (sccm denotes cubic centimeter per minute at STP), respectively. Different V_b ranging from floating to -200 V was applied to the substrate during deposition.

The phase structure for the obtained films were characterized by X-ray diffraction (XRD) using a Bragg–Brentano diffractometer (D8_tools) in the θ – 2θ configuration with a Cu $K\alpha$ line at 0.15418 nm as an X-ray source. The composition and chemical bonding states for NbC films were determined by X-ray photoelectron spectroscopy (XPS) using ESCALAB-250 with an Al $K\alpha$ as an X-ray source, in which the NbC films were cleaned by Ar ion for 10 min prior to XPS measurement in order to clean the surface from adventitious contamination. The surface morphology and surface roughness were investigated by atomic force microscope (AFM) using ScanAsyst mode in air (Dimension Icon, Veeco Instruments/Bruker, Germany).

The radius curvature of the wafer before and after deposition was determined by a surface profiler (Veeco Dektak 150), and the residual stress was calculated using Stoney equation [22]:

$$\sigma = \frac{E_s}{6(1-\nu_s)} \frac{t_s^2}{t_f R} \quad (1)$$

where E_s , ν_s and t_s are Young's modulus, Poisson's ratio, and thickness of Si substrate, respectively, while t_f and R are the thickness and radius curvature for the film. The hardness and elastic modulus of niobium carbide were evaluated by MTS Nanoindenter XP with continuous stiffness measurements (CSM) mode. A Berkovich-type pyramidal diamond tip indented the films to a maximum depth of 1000 nm . Constant stiffness data measurements were obtained by oscillating the tip during indentation with a frequency of 45 Hz and amplitude of few nanometers, and hardness values were taken at approximately 100 – 200 nm depth to avoid the surface effect and the substrate effect. At least six indentations at different places on the film surface were made to minimize the deviation of the results after rejecting few extreme values. The tribological properties of the films were performed on a CSM ball-on-disk tribometer using WC ball (with a diameter of 6 mm) as a sliding counterpart in air (temperature 298 K , humidity 40 – 50%). The sliding speed was selected as 50 mm/s and the load was fixed as 2 N . The feature of the wear traces was observed by an optical microscope.

3. Results and discussion

3.1. Microstructure, composition and morphology

Fig. 1(a) shows the XRD patterns in symmetric θ – 2θ configuration for the niobium carbide films deposited at $F_{\text{CH}_4} = 6 \text{ sccm}$ with different V_b (floating, -40 , -80 , -120 , -160 , and -200 V), from which a mixture of hexagonal- Nb_2C and cubic-NbC phase appears when the absolute value of V_b is smaller than or equal to 80 V . As the absolute value of V_b further increases from 120 to 200 V , only a cubic-NbC phase with a mixed texture of (111) and (200) appears. It is noted that a phase transition from a mixed phase of carbon-poor $\text{Nb}_2\text{C} + \text{NbC}$ to a cubic-NbC occurs with increasing the absolute value of V_b , indicating that V_b has an important influence on the C content in NbC film. For dc plasma system, the ion energy (E) has been determined taking into account V_b and V_p [23]:

$$E = -e(V_b - V_p) \quad (2)$$

where e is constant, the V_p was estimated by measuring the voltage directly on the substrate for a reference sample in identical plasma conditions but without external V_b . In this work, V_p is 4.6 V . Thus, E

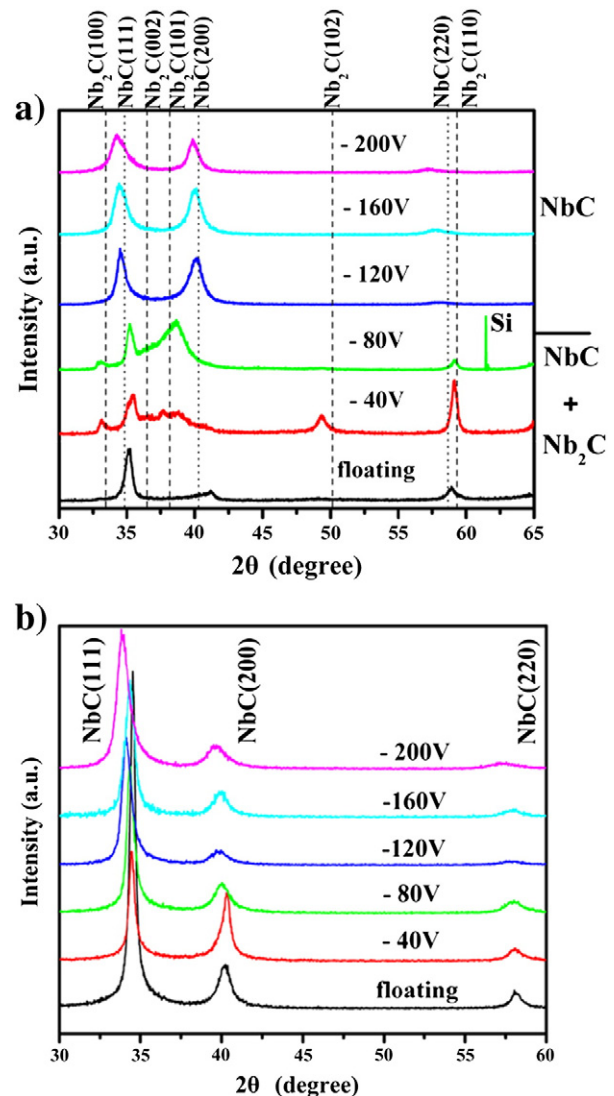


Fig. 1. XRD patterns for niobium carbide films grown at different V_b and a constant of either $F_{\text{CH}_4} = 6$ (a) or 16 sccm (b).

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