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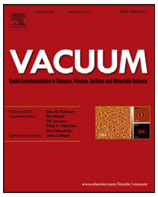

Reactive magnetron sputtering deposition and characterization of niobium carbide films

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ABSTRACT

Niobium carbide thin films have been deposited on Si(100) substrates by direct current reactive magnetron sputtering using CH_4 as a carbon source. With increasing F_{CH_4} from 4 to 22 sccm, the carbon content for the film increases from 32.7 to 68.7 at.% gradually, accompanying with a phase transition from hexagonal-Nb_2C to cubic-NbC, and at the highest carbon content, the film exhibits a typical nanocomposite structure consisting of NbC nanocrystallites embedded in an amorphous hydrocarbon (a-C:H) matrix. The morphology, mechanical properties and tribological behavior for the films exhibit a significant dependency on the amount of the amorphous carbon in the nanocomposite structure. The film surface becomes smooth with increasing the carbon content, corresponding to a transition from columnar crystallites to free of columnar features. In addition, the increase in carbon content for the films leads to an increase in the compressive stress for the well-crystallized film, but the excessive amorphous phase partially relaxes the stress. The NbC_x film with 53.9 at.% carbon content shows the maximum hardness 25.0 GPa. Both friction coefficient and wear resistance are improved by increasing the content of the surplus amorphous carbon.

1. Introduction

Transition metal nitrides and carbides have been attracting much attention, owing to their characteristics such as high hardness, high melting points, high chemical stability and excellent wear resistance, and have been applied for protective coatings in cutting tools and decorative coating [1–10]. As a potential material for protective coating, carbides have previously been shown to substantially increase contact fatigue life when applied to steel substrates and have also shown lower coefficient friction compared with nitrides [11,12]. Up to now, only a few carbide coatings like titanium carbide, tungsten carbide, titanium carbon nitride, titanium carbide/amorphous carbon and WC/a-C:H have been investigated extensively [13–19].

Among the transition metal carbides, niobium carbide (NbC) has attracted considerable attention because it possesses excellent comprehensive properties. In addition to the high melting point (3610 °C) [20], excellent chemical stability [21], high toughness and Young's modulus [22], the NbC also exhibits a higher hardness than other transition-metal carbides [23], high conductivity with a normal resistivity of 4.6 $\mu\omega{*}$cm and superconductivity at 12 K [24]. Until now, a few investigations have been reported on the NbC films. Ma et al. [20] have prepared nanocrystalline NbC using the reaction of metallic magnesium powders with niobium pentoxide and basic magnesium carbonate, showing a good thermal stability and oxidation resistance. Thummler and Gustfeld [25] have reported a significant increase in the wear resistance of sintered steels reinforced with NbC, as compared to the same steels reinforced by TiC, TiN, Al_2O_3 and VC. Nedfors et al. [23] have obtained the Nb–C coatings using dual non-reactive DC magnetron sputtering. These reports on the NbC films concentrate on their optical properties [26], electrical properties and hardness [23], anticorrosive and biocompatible qualities [27]. Nevertheless, it is worth noting that as a potential protective coating in machine industry, the tribological behavior for NbC films has received relatively little attention, and only very few reports [28] involve in the mechanical properties and tribological behavior for niobium carbide. In previous work [22], we have studied the structure and tribological behavior for NbC films at different substrate bias voltage. While the chemical and physical properties of the NbC films depend on the chemical composition. No systematic study has yet been carried out to establish the correlation between the film composition and

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tribological behavior. Moreover, the NbC film is considered as a promising candidate protective coating in electrical friction contacts owing to its metallic conductivity and resistance to wear, and in order to achieve large-scale production it is expected to deposit with relatively low cost and low substrate temperature. Thus there is a need for a systematic study on the relationship between process parameters, phase composition and properties for NbC films deposited at a low growth temperature.

In this work, the NbC_x films have been prepared on Si(100) substrates using direct current (DC) reactive magnetron sputtering in discharging a mixture of CH_4 and Ar gas, and the deposition rate, chemical bonding, phase composition, microstructure, intrinsic stress, hardness and tribological behavior as a function of the flow rate of CH_4 for the obtained films have been investigated. The motivation of this work is to establish a correlation between the microstructure, stress, hardness, and tribological behavior for the niobium carbide film, which will lay a solid foundation for its future applications.

2. Experimental details

2.1. Sample deposition

The NbC_x films were deposited on Si(100) wafers using a pure Nb target (99.95%) by DC reactive magnetron sputtering medium of Ar (99.999%) and CH_4 (99.999%) gas. The distance between the target and the substrate holder was fixed at 8 cm, and the chamber was evacuated by a turbomolecular pump to 4×10^{-4} Pa prior to sputtering. The Si(100) substrates were rinsed with acetone, alcohol and distilled water in an ultrasonic bath for 20 min, respectively. The target was pre-sputtered by Ar^+ for 10 min to remove the surface oxide layer, and then in discharging a mixed Ar and CH_4 gas for 10 min to achieve a steady-state reaction condition. When pre-sputtering, the substrate was covered by a shutter. During the deposition, work pressure was kept at 0.8 Pa, the flow rate of Ar and CH_4 (F_{CH_4}) was accurately controlled by a mass flow controller, wherein F_{CH_4} was fixed at 4, 6, 10, 14, 18, and 22 sccm (sccm denotes cubic centimeter per minute at STP), respectively, while that of Ar was kept constant at 80 sccm. And the applied current on the Nb target and the DC bias voltage for all samples were kept at 0.3 A and −60 V, respectively. In our case, the substrate temperature was measured by a thermal couple, which was fixed in the center of the sample holder. During the deposition, the substrate was not intentionally heated. However, the temperature of the substrate increased with the sputtering time due to the self-heating, yielding a substrate temperature from 25 to 55 °C. Since the heat flow from the center of the sample towards the metallic substrate holder should be worse than from the border zone to the substrate holder, higher substrate temperatures in the center are expected [29]. In order to compare their structure and properties objectively, all the characterizations were carried out on the center of the samples after deposition. The deposition rates for the niobium carbide films, deposited at different CH_4 flow rates, are listed in Table 1. And the thickness of all films was about 2 μm by adjusting the deposition time.

2.2. Microstructure, composition and morphology

The chemical composition of the films was determined by X-ray photoelectron spectroscopy (XPS) using ESCALAB-250 with an Al Kα as an X-ray source. In order to remove the surface oxides and exclude sputter damages, the samples were cleaned by Ar ion for 10 min prior to XPS analysis with energy of 1 keV [30]. The microstructure for each sample was characterized by X-ray diffraction (XRD) using a Bragg–Brentano diffractometer setup (D8_tools) in the θ–2θ configuration with a Cu Kα line at 0.15418 nm as an X-ray source. The microstructure of the film was also observed by a high resolution transmission electron microscope (HRTEM) (field emission JEOL 2100F) operated at 200 kV. The morphology of the film was examined from fractured cross-section images obtained by scanning electron microscopy (SEM) (JEOL JSM-6700F), while the surface morphology and surface roughness were investigated by atomic force microscope (AFM, Dimension Icon, Veeco Instruments/Bruker, Germany).

Table 1
Deposition rate, grain size calculated by Scherrer's equation (*D*), composition, cell parameters calculated from XRD, *x* in NbC_x calculated from XPS for niobium carbide films deposited at different flow rates of CH_4 (F_{CH_4}).

F_{CH_4} (sccm)	Deposition rate (nm/min)	D_1 (nm)	Cell parameters (Å)	Composite (at.%)			NbC_x
				Nb	C	O	
4	18.5	22.2	3.120	66.2	32.7	1.1	$NbC_{0.49}$
6	17.2	40.6	4.473	57.3	41.8	0.9	$NbC_{0.53}$
10	16	35.1	4.482	55.0	44.0	1.0	$NbC_{0.54}$
14	15.1	22.7	4.487	45.9	52.3	1.8	$NbC_{0.56}$
18	15	11.0	4.494	45.0	53.9	1.1	$NbC_{0.59}$
22	12.4	3.9	4.503	29.4	68.7	1.9	$NbC_{0.75}$

2.3. Mechanical properties and tribological behavior

The curvature of the sample was measured by a surface profiler (Veeco Dektak 150), and the total residual stress (IS) was calculated using Stoney equation [31]:

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

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 film hardness was evaluated by MTS Nanoindenter XP with continuous stiffness measurements (CSM) mode. The films were indented by a Berkovitch type pyramidal diamond tip to a maximum depth of 1000 nm, and at least six indentations at different places on the film surface were made. Constant stiffness data measurements were obtained by oscillating the tip during indentation with a frequency of 45 Hz and amplitude of few nanometers. The tribological properties of the films were measured on a CSM ball-on-disk tribometer in ambient air (temperature 295 K, humidity 70%) using WC ball ($Ø = 6$ mm) as a sliding counterpart under a 2 N load at velocity $v = 0.05$ m/s. The feature of the wear track was observed by an optical microscope.

3. Results and discussion

3.1. Composition and chemical bonding

To deduce the relative elemental composition of the films and to study the chemical bonding of each element, all samples were investigated by XPS. Table 1 shows the carbon, niobium and oxygen content at different F_{CH_4} for NbC_x films. The carbon content increases linearly with increasing F_{CH_4} from 32.7 to 68.7 at.%, which indicates that the incorporation of carbon is approximately proportional to the F_{CH_4}, similar to the other reports [4,9,32,33]. Our XPS results also show the presence of 1–2% oxygen in the NbC_x films, and this oxygen contamination is likely to be either from residual oxygen in the deposition chamber or from the atmosphere after the sample is taken out of the chamber.