PROPERTIES OF TiN, Ti(C,N), TiC FILMS PREPARED BY ARC ION PLATING

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abstract

Ti(C,N) films were deposited on SUS 304 substrate by arc ion plating method using a reactive gas of N_2/C_2H_2 changed from 100/0 to 0/100 in the mixing ratio. Ti(C,N) films prepared at a bias voltage of -400V had a strong (111) preferred orientation and the crystallite size was very small (about 8-10 nm). The Vickers microhardness of these Ti(C,N) films increased from 2082 (TiN) to 3879 kg/mm^2 (TiC) with increasing carbon atomic percentage in the film. Ti(C,N) film prepared at N_2/C_2H_2 = 80/20 maintained after the oxidation test at 623K about the same hardness value (about 2800 kg/mm^2) as that of room temperature. Even at 773K, the hardness of the film was a comparatively high value of 1951 kg/mm^2.

1.INTRODUCTION

Recently, Ti(C,N) films, which have the characteristics of TiN and TiC film, have been applied to the protective coatings on cutting tools, steel molds, and so on. These coated parts are greatly improved as to the mechanical properties such as hardness, friction coefficient and corrosion resistance. Ti(C,N) films deposited by magnetron sputtering, hollow cathode discharge ion plating (H.C.D.), activated reactive evaporation ion plating (A.R.E.) and plasma chemical vapor deposition have been studied with respect to mechanical properties by several authors [1-5]. But there have been few detailed reports on Ti(C,N) films deposited by arc ion plating, especially oxidation resistance properties of Ti(C,N) films which is one of the most important factor for determing the life of cutting tools etc.[6.7]. Arc ion plating method has the advantage of high ionization degree of the metal vapor (about 80%) caused by a random arc spot on the cathode target. This degree of ionization is higher than that in other ion plating and sputtering processes. Therefore, it is expected that high reactivity between Ti vapor and N_2-C_2H_2 mixed gas and high film density can be attained. The purpose of the present study is to investigate the various properties, especially oxidation resistance of each films which varies with the

C/N atomic ratio in Ti(C,N) films.

2.EXPERIMENTAL DETAILS

Ti(C,N) films were deposited onto SUS 304 using the arc ion plating apparatus showed in Figure 1. Ti metal ions were generated by vacuum arc discharge on the cathode target, then reacted with N_2 and C_2H_2, and were deposited onto SUS 304 substrate as Ti(C,N) films. The cathode target was cylindrical pure Ti block (99.90%). Pure N_2 (99.999%) and pure C_2H_2 (99.5%) were used as reactive gases. The polished substrates were ultrasonically cleaned in acetone, then mounted just under the target. The cathode-substrate distance was 165mm. The reactive chamber was evacuated to a background pressure of 2×10^{-5} Torr, and all the deposition runs were carried out at the total pressure of 5×10^{-3} Torr. The composition of the gas mixture was controlled through the each mass flow controllers, and the gas ratio of N_2/C_2H_2 was changed from 100/0 to 0/100. The arc discharge current for Ti target was 50A. The negative d.c. bias voltage was applied to the substrate during the deposition of films, which was varied between 0 and -400V. Typically the bias voltage was set at -400V and the substrate temperature was 573K.

The film thickness for oxidation test was about 1.5μm, which was controled by coating time. The oxidation test was conducted as follows : the specimens were set in the electric furnace with oxygen atomosphere,and were heated in the range of 623-973K for 1 hour.

The chemical structure of films was determined by X-ray diffraction and X-ray photoelectron spectroscopy. The composition of films was determined by electron probe microanalysis. The morphology of films was observed by atomic force microscopy. The microhardness of films was measured by microhardness tester with a max load of 0.05gf.

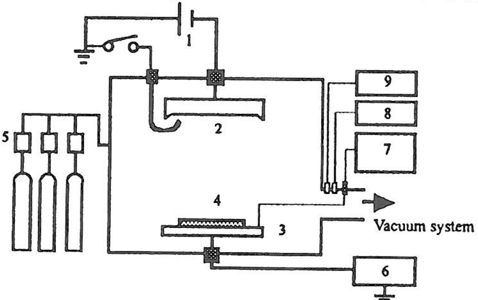


Fig.1 Schematic illustration of the arc ion plating apparatus.
1 arc power supply, 2 Ti target, 3 holder, 4 substrate, 5 mass flow controller, 6 bias power supply, 7 c.a. thermocupple, 8 pirani vacuum gage controller, 9 ionization vacuum gage controller

3.RESULTS AND DISCUSSION

3-1 Phase and structure

Fig. 2 shows the X-ray diffraction patterns of Ti(C,N) films deposited at a substrate bias voltage of -400V with different reactive gas ratios of N_2/C_2H_2. All films were consisted of only single phase of Ti(C,N) which has a face-centered cubic lattice structure with a strong (111) preferred orientation. The preferred orientation does not depend on gas ratio of N_2/C_2H_2, but on the value of substrate bias voltage.The diffraction peaks of films were shifted to lower angle with increasing the C_2H_2 concentration. The relationship between C/N atomic ratio in the film and the lattice constant is shown in Fig. 3. The lattice constant of films was calculated with peak of (111), and the atomic composition of films was determined by electron probe microanalysis (shown in Table 1). The lattice constant of films was linearly increased from 0.4281 nm (TiN) to 0.4386 nm (TiC) with increasing carbon atomic percentage. This result suggested that Ti(C,N) films were obtained as continuous solid solution between TiN and TiC. The lattice constant of TiN and TiC films were larger than the ASTM values, respectively. This seems to be due to compressive stress in films. The relationship between the reactive gas ratio of N_2/C_2H_2 and the crystallite size at different d.c. bias voltages is shown in Fig. 4. The crystallite size was calculated by the Scherrer formula as shown here under.

$$t = K\lambda / B \cos\theta_B \qquad (1)$$

where t = crystallite size, K = Scherrer's

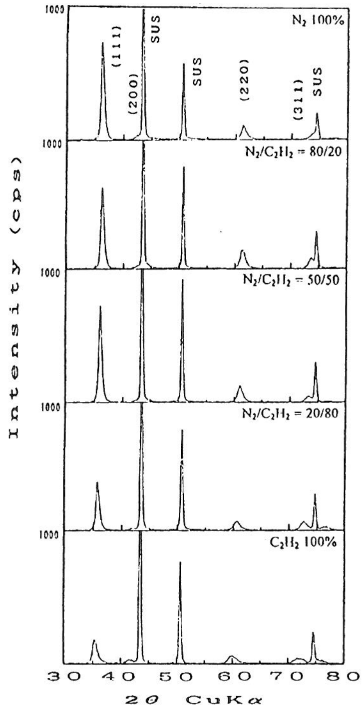


Fig.2 XRD patterns of films deposited with different reactive gas ratio of N_2/C_2H_2 (bias voltage: -400V)

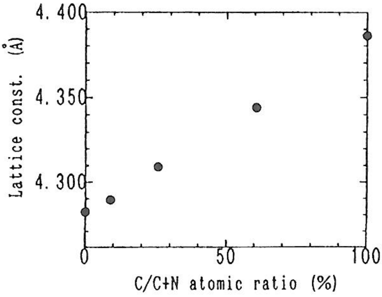


Fig.3 The relationship between C/C+N atomic ratio in the film and the lattice constant

constant (= 0.9), λ= wavelength of X-ray (CuKα), B = the full-width half maximum, θ_B = Bragg angle obtained maximum diffraction peak strength. In the bias voltage of -400V, the crystallite size of films were about 8-10 nm. The crystallite size had the max value at C_2H_2 gas ratio of 50%. This fact suggests that hydrogen in C_2H_2 combined with nitrogen, and then formed lots of NH radical species in plasma space, and so Ti^+ reacted more easily with NH radical species or carbon species. The crystallite size of films increased with increasing the bias voltage. But it can be expected that the crystallite size decreases with increasing the bias voltage, because the ion bombardment energy for films increases with an increase in the bias voltage. Accordingly, the result described above suggests that the thermal effect is larger than the ion bombardment effect under the bias voltage of over 100V, and so this thermal effect promoted the crystallization of films. Thus, all films consisted of nanometer crystallites. The surface morphology of the film deposited at N_2/C_2H_2 = 80/20, bias voltage = -400V is shown in Fig.5. This film took on a very smooth surface in which max height [Rmax] was 7.035nm. In this experiment, the surface of films prepared by arc ion plating was very smooth.

Table 1 Composition of films determined by EPMA (bias voltage -400V)

Reactive gas ratio (N_2/C_2H_2)	Atomic ratio (%)		
	Ti	C	N
100/0	53.08	-	46.92
80/20	52.60	4.18	43.22
50/50	51.70	12.40	35.90
20/80	50.53	29.98	19.49
0/100	51.47	48.53	-

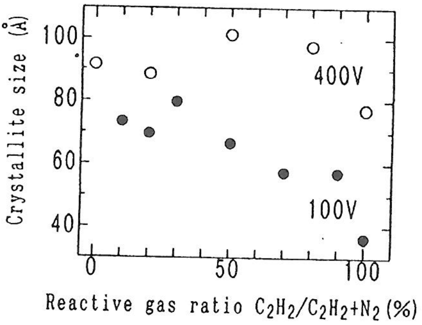


Fig. 4 The relationship between reactive gas ratio of N_2/C_2H_2 and the crystallite size at different d.c. bias voltages

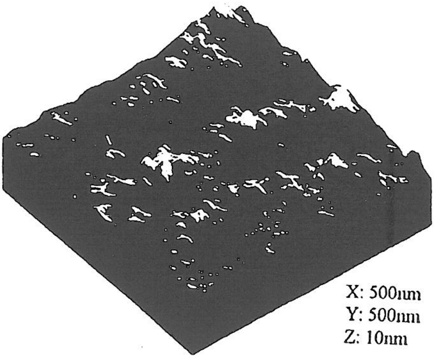


Fig.5 The surface morphology of the film deposited at N_2/C_2H_2 =80/20,bias voltage = -400V

3-2 Oxidation resistance of TiN, TiC and Ti(C,N) films

The relationship between the microhardness of films and oxidation temperature is shown in Fig.6. The penetration depth of indentor was about 70nm. At room temperature, the Vickers microhardness of films increased from 2082 (TiN) to 3879 kg/mm^2 (TiC) with increasing carbon atomic percentage in the film. The oxidation resistance of films depended on carbon concentration in films. The hardness of TiC film attained to the highest value of 3879 kg/mm^2 at room temperature, but it decreased to 2897 kg/mm^2 at 623K in oxygen atmosphere. At 773K in oxygen atmosphere, the hardness of TiC film decreased to 1212 kg/mm^2, because it was completely changed into TiO_2 (anatase) in the film, The film became powder-like and was partly peeled off from the substrate. To the contrary, the hardness of Ti(C,N) film prepared at N_2/C_2H_2 = 80/20 maintained after the oxidation test at 623K almost the same value (approximately 2800 kg/mm^2) as that at room temperatue. Even at 773K, the hardness of the film was a comparatively high value of 1951 kg/mm^2. At 973K in oxygen atmosphere, the hardness of all films had a low value of about 1000 kg/mm^2 because of formation of rutile.

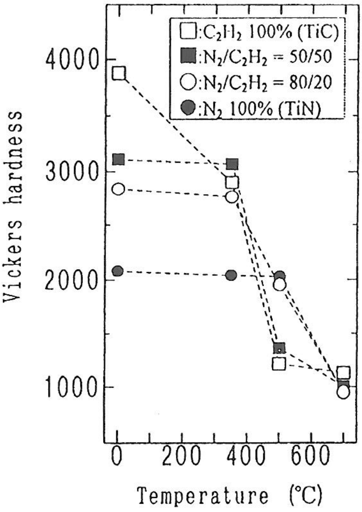
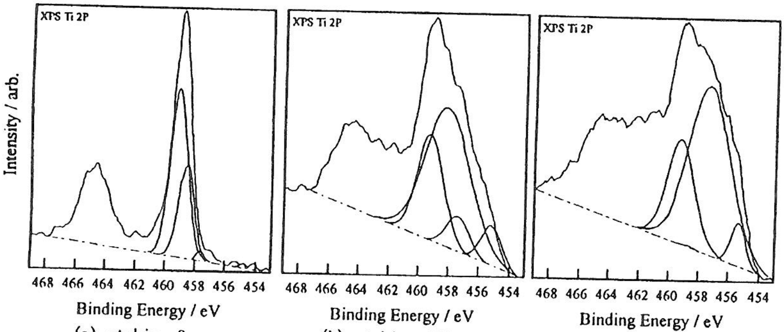


Fig.6 The relationship between microhardness of films and oxidation temperature

The Ti_{2P} spectra of the film prepared at N_2/C_2H_2 = 80/20 (oxidation temperature: 773K) were measured by XPS with different argon etching times. Fig.7 shows the result. The etching rate was 1 nm/min for SiO. Ti_{2P} spectrum of the film were separated into TiN (or TiO), Ti_2O_3, Ti_3O_5 and TiO_2. The detail data are shown in table 2. In non-etching, the layer was consisted of mostly TiO_2 (31.92%) and Ti_3O_5 (66.10%). After 180s etching, the layer was consisted of not only TiO_2 and Ti_3O_5, but also TiN(or TiO) and Ti_2O_3 which is a sub-oxide state. After 360s etching, TiO_2 spectrum extinguished. Therefore it was confirmed that progress of oxidation was suppressed at the position of several nm from the surface. The hardness of the film depended on its oxidation state and the grain size affected by release from compressive stress.

Table 2. Separated peak area ratio of Ti_{2P} spectrum in each etching times (N_2/C_2H_2 = 80/20, oxidation temp.: 773K)

Compound	Position (eV)	Etching time (sec.)		
		0	180	360
TiN(or TiO)	454.86-455.48	0.61(%)	7.71	6.11
Ti_2O_3	457.50-457.77	1.37	7.54	66.81
Ti_3O_5	459.24-459.39	66.10	26.22	26.97
TiO_2	458.27-458.69	31.92	58.53	0.11



(a) etching 0sec. (b) etching 180sec. (c) etching 360sec.

Fig. 7 Ti_{2P} spectrum of the film prepared at $N_2/C_2H_2 = 80/20$ (oxidation temperature : 773K)
(a) non-etching (b) after 180s etching (c) after 360s etching

4.CONCLUSIONS

Based on properties of Ti(C,N) films prepared by arc ion plating, following conclusions are derived: (1) The lattice constant of films is linearly increased from 0.4281 nm to 0.4386 nm with an increase in carbon atomic percentage in the film. The films prepared at a bias voltage of -400V have a strong (111) preferred orientation and the crystallite size is very small (8-10 nm). (2) The Vickers microhardness of films increases from 2082 to 3879 kg/mm^2 with increasing carbon concentration in the film. (3) Even at 773K in oxygen atmosphere, the hardness of Ti(C,N) film prepared at $N_2/C_2H_2 = 80/20$ has a comparatively high value of 1951 kg/mm^2. The hardness of films depends on its oxidation state and the grain size affected by release from compressive stress.

5.REFERENCES

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