

## Mechanical Properties and Oxidation Behavior of Cr-N-O Thin Films Prepared by Pulsed Laser Deposition

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Chromium oxynitride (Cr-N-O) thin films have been successfully prepared by using pulsed laser deposition (PLD). Oxygen content in the thin films ( $x$ ) was controlled by changing experimental conditions. From the results of Rutherford backscattering spectroscopy (RBS) and X-ray diffraction (XRD), the structure of the thin films was B1 (NaCl) type up to  $x = 35$  at. %, above which it changed to chromium oxide ( $\text{Cr}_2\text{O}_3$ ) type. This fact indicated that phase transition from B1 to  $\text{Cr}_2\text{O}_3$  types occurs in the  $x$  ranging from 35 to 43 at. %. The Cr-N-O thin film with  $x = 35$  at. % exhibits maximum Vickers hardness (HV) over 3000, which was approximately HV = 1000 harder than the thin film with  $x = 3$  at. %. Friction coefficient ( $\mu$ ) of the thin films with  $x = 3$  and 35 at. % was found to be  $\mu = 0.5$ . In oxidation tests, since the Cr-N-O thin film heat-treated at 800 °C in atmospheric air contained B1 phase, the hardness of such thin film was clarified to maintain the high hardness of approximately HV = 3000.

Key words: chromium oxynitride, hardness, friction coefficient, oxidation, pulsed laser deposition

### 1. INTRODUCTION

Chromium nitride (CrN), which has excellent properties in hardness, oxidation resistance and chemical stability, has been used as coating materials for cutting tools [1]. However, other coating materials for high-speed cutting tool have been demanded to have the properties more than those of CrN.

Titanium nitride (TiN) having same structure as CrN (B1 type) is possible to substitute oxygen atoms for partial nitrogen ones. The titanium oxynitride (Ti-N-O) thin films maintained B1 structure when the oxygen content in the thin film ( $x$ ) was ranging from 0 to approximately 50 at. % [2]. In addition, the hardness of the Ti-N-O thin films was harder than that of TiN thin film. The fact can be explained by solid solution hardening induced by dissolved oxygen atoms.

Until now, the structure of chromium oxynitride (Cr-N-O) thin films was B1 type at  $x < 50$  at. % [3,4], whereas hardness, friction coefficient and oxidation behavior of such thin films has not been clarified. The authors have prepared the Cr-N-O thin films by using pulsed laser deposition (PLD). This investigation was undertaken to reveal the hardness, friction coefficient and oxidation behavior of the Cr-N-O thin films.

### 2. EXPERIMENTAL SETUP

Figure 1 shows schematic illustration of the apparatus used for preparing thin films. Thin films were prepared by the irradiation of the third harmonic of a Nd: yttrium aluminum garnet (YAG) (355 nm) laser beam onto a target. The laser was electrooptically Q switched by a Pockels cell to produce an intense short pulse width (7 ns). A laser beam was concentrated by lens, and the energy density

( $F$ ) was adjusted from 1 to 10 J/cm<sup>2</sup> on the target. The deposition time was for 1 hour at a pulse repetition rate of 10 Hz. A plate of 99.9 % pure chromium (Cr) is used as the target. The laser beam was focused on the area of 1 mm<sup>2</sup> on the target. The chamber was evacuated using a rotary and a cryo pump. The thin films were synthesized to ablate Cr metal in ammonia ( $\text{NH}_3$ ) or nitrogen ( $\text{N}_2$ ) gasses. In deposition, the pressure in the chamber as base ( $p_b$ ), ammonia ( $p_{\text{NH}_3}$ ) and nitrogen ( $p_{\text{N}_2}$ ) was changed to control the oxygen content in the thin films ( $x$ ). The deposition area was more than 4 cm<sup>2</sup> when a single-crystal (100)-oriented silicon substrate was placed at a distance ( $d_{\text{TS}}$ ) of 10, 15 and 20 mm from the target. The substrate temperature ( $T_s$ ) was controlled using a heater and a thermocouple.

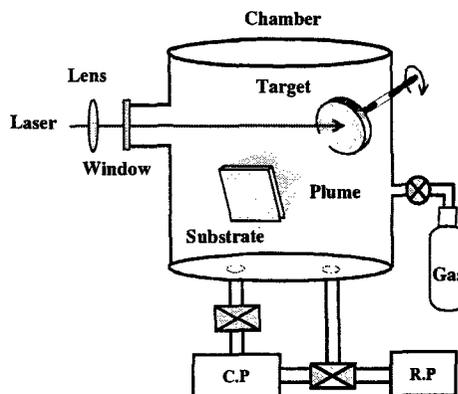


Fig. 1 Schematic illustration of the apparatus used for preparing thin films.

The composition of the thin film was determined by Rutherford backscattering spectroscopy (RBS). The crystal structure of the thin film was studied by X-ray diffraction (XRD) using Cu  $K\alpha$  radiation of 0.15418 nm under the operating conditions of 50 kV and 300 mA. The hardness of the thin film determined using a Vickers hardness tester at a load of 5 gf. The hardness measurements was carried out for 7 times, and the hardness was evaluated to take out minimum and maximum values. Friction coefficient was measured with the tester of ball-on-disk type. The conditions for the friction coefficient measurement were as follows; ball of 6 mm in diameter: SUJ2 (Fe - 1 % C - 1.3 % Cr), load: 2 N, rotation speed: 50 mm/s and sliding distance: 100 m. In oxidation tests, the thin films were heat-treated in an electrical furnace. The heat-treatment conditions were as follows; temperature ( $T$ ): RT to 900 °C, gas: atmospheric air, pressure: 0.1 MPa and holding time: 1 hour.

### 3. RESULTS AND DISCUSSION

Figure 2 shows a typical spectrum obtained by RBS of Cr-N-O thin film deposited on carbon substrate. It was prepared under the condition of  $F = 5 \text{ J/cm}^2$ ,  $p_b = 1.3 \times 10^{-3} \text{ Pa}$ ,  $p_{\text{NH}_3} = 110 \text{ Pa}$ ,  $d_{\text{TS}} = 15 \text{ mm}$  and  $T_s = 500 \text{ °C}$ . In Fig. 2, dots and the solid line indicate the results of measurement and simulation, respectively. From the result of simulation, the composition of the thin film having chromium, nitrogen and oxygen atoms was found to be  $\text{Cr}_{0.47}\text{N}_{0.37}\text{O}_{0.16}$ . This result suggested that the composition of cation (Cr) and anions (N and O) in the thin film becomes approximately equal. Chromium and nitrogen atoms in the thin film were provided from the chromium target and ammonia gas, whereas oxygen atoms seem to be incorporated from residual gas in the deposition chamber. Table I shows the composition of the thin films prepared by changing experimental conditions by RBS. As a result, oxygen content in the thin films ( $x$ ) was clarified to be controlled in the range from  $x = 3$  to 43 at. % by changing the experimental conditions.

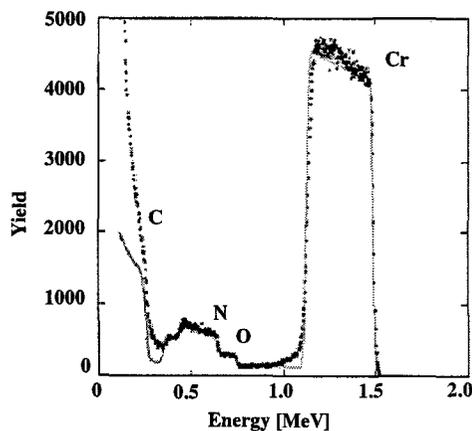


Fig. 2 A typical spectrum obtained by RBS of Cr-N-O thin film deposited on carbon substrate.

Table I The composition of the thin films prepared by changing experimental conditions.

Sample	Experimental conditions						Composition		
	$F$ J/cm <sup>2</sup>	$p_b$ Pa	$p_{\text{NH}_3}$ Pa	$p_{\text{N}_2}$ Pa	$d_{\text{TS}}$ mm	$T_s$	Cr	N	O
A	5	$1.3 \times 10^{-4}$	110	-	15	500	53	44	3
B	5	$1.3 \times 10^{-3}$	110	-	15	500	47	42	11
C	5	$1.3 \times 10^{-3}$	40	-	15	500	47	37	16
D	1	$2.7 \times 10^{-4}$	53	-	20	500	50	30	20
E	1	$2.7 \times 10^{-4}$	27	-	20	500	50	20	30
F	3	$5.3 \times 10^{-4}$	27	-	20	500	45	22	33
G	3	$5.3 \times 10^{-4}$	27	-	20	500	50	15	35
H	10	$1.3 \times 10^0$	-	6.7	10	400	44	13	43

Figure 3 shows XRD patterns of Cr-N-O thin films with  $x = 3, 16, 35$  and 43 at. %. The Cr-N-O thin films with  $x = 3, 16$  and 35 at. % were primarily B1 phase, although thin films with  $x = 3$  and 16 at. % have small peaks for Cr phase. Although  $\text{CrO}_2$ ,  $\text{CrO}_3$  and  $\text{Cr}_2\text{O}_3$  have been known as typical chromium oxides, only  $\text{Cr}_2\text{O}_3$  can be stably present under the condition above  $T_s = 400 \text{ °C}$ . However, the thin films with  $x = 3, 16$  and 35 at. %, which were prepared above  $T_s = 400 \text{ °C}$ , did not contain  $\text{Cr}_2\text{O}_3$  phase. This result seems to be due to the substitution of oxygen atoms for partial nitrogen ones in B1 phase. On the other hand, in the Cr-N-O thin film with  $x = 43$  at. %, the only diffraction peaks attributed to  $\text{Cr}_2\text{O}_3$  were observed. Therefore, the solubility limit of oxygen atoms for CrN was found to be in  $x$  ranging from 35 to 43 at. %.

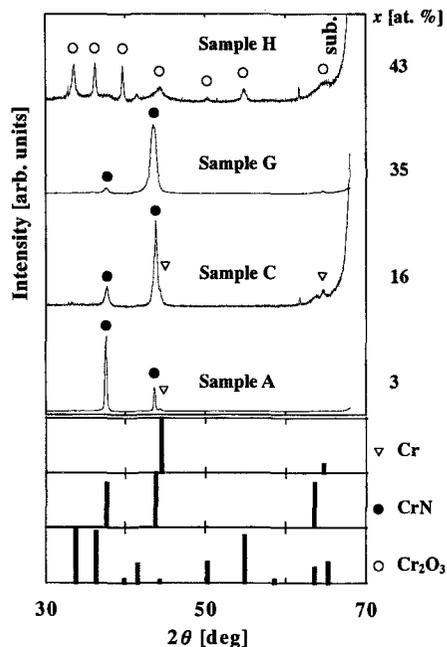


Fig. 3 XRD patterns of Cr-N-O thin films of samples A, C, G and H with  $x = 3, 16, 35$  and 43 at. %, respectively. JCPDS data for Cr, CrN and  $\text{Cr}_2\text{O}_3$  phases were also shown for comparison [5-7].

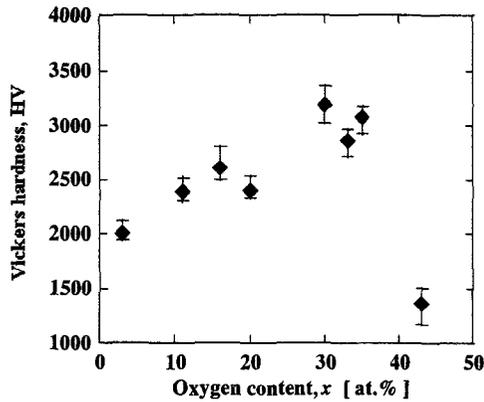


Fig. 4 Vickers hardness of Cr-N-O thin films as a function of oxygen content.

Figure 4 shows Vickers hardness of Cr-N-O thin films as a function of oxygen content. The hardness of the Cr-N-O thin films increased gradually up to approximately  $x = 30$  at. % above which it decreased rapidly. The maximum hardness of HV = 3200 was obtained for the Cr-N-O thin film these composition is close to the solubility limit. The maximum hardness was approximately HV = 1000 higher than that of CrN thin film. One of the reasons to explain the high hardness maybe the pinning of dislocations by distortion associated with the dissolved oxygen atoms in the lattice.

Figure 5 shows friction coefficient of Cr-N-O thin film with  $x = 3, 11, 16$  and  $35$  at. %. The friction coefficient of the thin films was approximately  $\mu = 0.5$  over the whole  $x$  range. Friction coefficient seems to strongly depend on hardness and surface roughness of the thin films. In friction test, friction force was caused due to adhesion induced by plastic deformation. Thus, the friction coefficient of the thin film was considered to decrease with hardening in such thin film. However, the thin film with  $x = 35$  at. % was approximately 1.5 times harder than the thin film with  $x = 3$  at. %, whereas the friction coefficients of these thin films was almost same. On the other hand, the surface roughness of the thin films with  $x = 3$  and  $35$  at. % was conjectured to differ, since the composition of the thin films was controlled by changing experimental conditions. Thus,

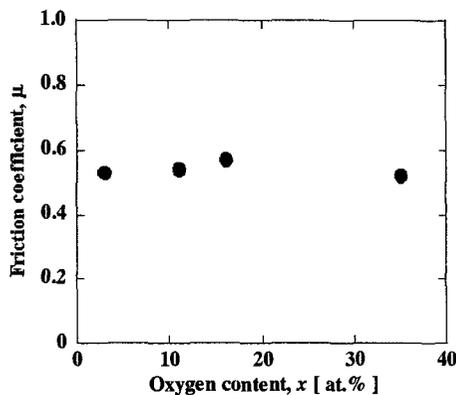


Fig. 5 Friction coefficient of Cr-N-O thin film with  $x = 3, 11, 16$  and  $35$  at. % samples A, B, C and G, respectively.

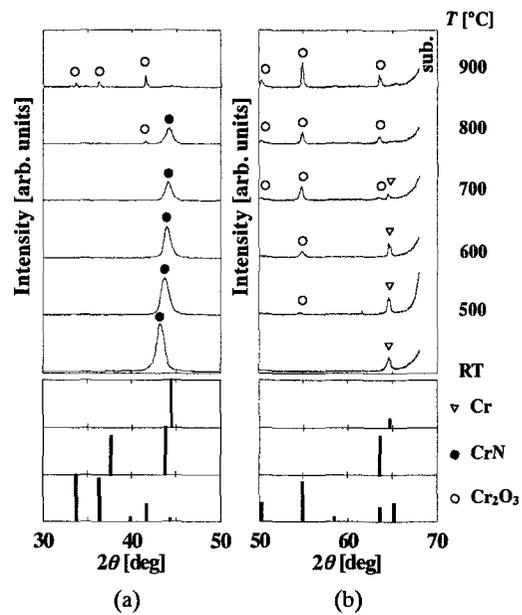


Fig. 6 XRD patterns of Cr-N-O thin films with  $x = 30$  at. % sample E heat-treated in the  $T$  ranging from RT to  $900$  °C. JCPDS data for Cr, CrN and  $Cr_2O_3$  phases were also shown for comparison. (a):  $2\theta = 30-50^\circ$ , (b):  $2\theta = 50-70^\circ$ . Intensity of patterns in (b) is multiplied by those in (a).

in the Cr-N-O thin films, surface roughness may be more effective for reducing in friction coefficient, compared with hardness.

Figure 6 shows XRD patterns of Cr-N-O thin films with  $x = 30$  at. % heat-treated in the  $T$  ranging from RT to  $900$  °C. Fig. 6 (a) and (b) indicate the measurement results in the ranges of  $2\theta = 30-50^\circ$  and  $50-70^\circ$ , respectively. Furthermore, the intensity of Fig. 6 (b) is 10 times higher than that of Fig. 6 (a). It was due to that the intensity of diffraction peaks attributed to  $Cr_2O_3$  is very low in the  $2\theta$  ranging from  $50$  to  $70^\circ$ . From the results of Fig. 6 (a) and (b), the diffraction peak attributed to  $Cr_2O_3$  appeared at  $T = 500$  °C. Thus, the oxidation temperature of the Cr-N-O thin films was clarified to be approximately  $T = 500$  °C. This oxidation temperature was approximately  $100$  °C lower than that of CrN thin film [8]. In addition, the diffraction peak attributed to B1 phase, which was located at approximately  $2\theta = 43^\circ$ , was shifted to a higher angle with increasing  $T$  up to  $800$  °C. Such a peak shift seems to be due to the composition change induced by oxidation process. In the thin film heat-treated at  $T = 900$  °C, a large part of the Cr-N-O thin film was conjectured to change to  $Cr_2O_3$  phase, since the only diffraction peaks attributed to  $Cr_2O_3$  were observed. Therefore, the Cr-N-O thin films with  $x = 30$  at. % were revealed to maintain B1 phase up to  $T = 800$  °C.

Figure 7 shows Vickers hardness of Cr-N-O thin films with  $x = 30$  at. % heat-treated in the  $T$  ranging from RT to  $900$  °C. The hardness of the thin films was approximately HV = 3000 in the  $T$  ranging from RT to  $800$  °C. This fact may be a result of the existence of B1

phase in the thin films, as shown in Fig. 6. In contrast, since the Cr-N-O thin film heat-treated at  $T = 900\text{ }^{\circ}\text{C}$  did not contain B1 phase, the hardness of such thin film was clarified to decrease abruptly.

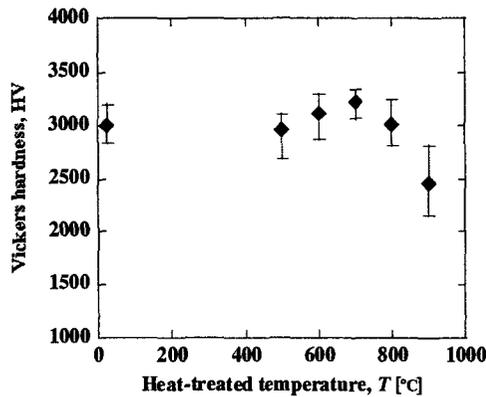


Fig. 7 Vickers hardness of Cr-N-O thin films with  $x = 30$  at. % heat-treated in the  $T$  ranging from RT to  $900\text{ }^{\circ}\text{C}$ .

#### 4. CONCLUSIONS

From these experimental results, the authors have obtained the following conclusions.

- 1) Cr-N-O thin films have been successfully prepared by using the PLD method.
- 2) Oxygen content in Cr-N-O thin films could be controlled in the  $x$  ranging from 3 to 43 at. % by changing experimental conditions.
- 3) The maximum hardness of  $\text{HV} = 3200$  was obtained for Cr-N-O thin films with  $x$  ranging 35 to 43 at. %, which was close to the solubility limit.
- 4) The friction coefficient of Cr-N-O thin films was approximately  $\mu = 0.5$  over the whole  $x$  range.
- 5) Cr-N-O thin film heat-treated at  $T = 800\text{ }^{\circ}\text{C}$  where contained B1 phase had  $\text{HV} = 3000$ .

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