Controlling Oxygen Content by Varying Oxygen Partial Pressure in Chromium Oxynitride Thin Films Prepared by Pulsed Laser Deposition

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Cr(N,O) thin films were prepared by depositing Cr vapor in N2 or NH3 ambient gas with residual oxygen. However, the oxygen content control was difficult in this method. In the current work, an intuitive method using modification of the oxygen partial pressure (P02) for the precise oxygen content control is proposed. A highly reactive atmosphere of O2 mixed with N radicals is used in this method. Chromium oxynitride thin films prepared by reactive magnetron sputtering in N2/O2 reactive gases and effect of P02 on chromium oxynitride thin films were studied. However, preparation by PLD using O2 reactive gas has not been reported. Our goal in this study is to develop a highly precise control method of oxygen content and to obtain the maximum hardness in Cr(N,O) thin films.

2. Experimental

Figure 1 shows a schematic illustration of an apparatus used for preparing thin films. Ablation plasma was produced by irradiating an Nd: yttrium aluminum garnet laser (355 nm) onto a Cr target (99.9% purity). The laser was electro-optically Q-switched by a Pockels cell to produce intense pulses of a short duration (7 ns). The laser energy density was

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Fig. 1 Schematic illustration of the apparatus used for preparing thin films.
the deposition time was 5 h at a laser-pulse repetition rate of 10 Hz. The deposition surface area was 1 cm² on a single-crystal (100)-oriented silicon substrate placed at a distance of 45 mm from the target. The substrate temperature was controlled at 973 K using an infrared lamp heater. The deposited film thickness was approximately 100 nm in this condition.

The chamber was first evacuated to a pressure of $2.5 \times 10^{-5}$ Pa using a rotary pump and a turbo molecular pump, and the chamber was then filled with oxygen gas ($>$99.99995 vol% purity). The value of the vacuum gauge at this time was defined as $P_{O_2}$. After $O_2$ gas introduction, nitrogen plasma ($>$99.99995 vol% purity) from an RF radical source was supplied. Both continuous pumping and introduction of $O_2$ gas and N plasma were carried out during the deposition. In order to change the oxygen content of the thin films, $P_{O_2}$ was varied with changing the oxygen gas flow rate using a variable leak valve. The thin films were prepared under a fixed total pressure of $1.5 \times 10^{-2}$ Pa.

For composition analysis of the thin films, Rutherford backscattering spectroscopy (RBS) and electron energy loss spectroscopy (EELS) were utilized. In the EELS spectra, since $O$ K-edge and Cr L-edge are very close, only oxygen and nitrogen contents were measured by EELS. Cation and anion contents were calculated from RBS spectra. By these two spectroscopy results, compositions of thin films were precisely determined. The oxygen content was defined as x. The crystal structures of the thin films were studied by X-ray diffraction (XRD) using Cu Kα radiation (0.154 nm) in the Bragg–Brentano configuration. The chemical bonding state was estimated by Fourier transform infrared spectroscopy (FT-IR). The FT-IR spectrum for each sample was obtained after taking into account of the absorbance of the Si substrate. The film thickness measured in a scanning electron microscope (SEM) was approximately 100 nm. The hardness of the thin films ($H_{TT}$) was measured by nano-indentation testing under a load of 0.07 mN using a Berkovich indenter. The indentation depth was around 10 nm. The load was determined not to exceed the indentation depth more than 1/8 of the films thickness. The microstructures of the thin films were observed using a field emission transmission electron microscope (FE-TEM) with a 200 kV acceleration voltage. The TEM samples were made two methods, i.e., thinning by a focused ion beam (FIB) apparatus and by scratching with a diamond pen. The former was used for cross sectional observations in wide area to find initial growth layer among the thin films. The latter was chosen for plan view observations and compositional analysis to prevent the ion beam damage.

3. Results and Discussion

3.1 Oxygen content

From the results of RBS and EELS measurements, it was found that the thin films contained chromium, nitrogen and oxygen. Figure 2 shows the oxygen content of the thin films as plotted against $P_{O_2}$. As $P_{O_2}$ increased, $x$ increased monotonically from 0 to 62 mol%. The oxygen content of the Cr(N,O) thin film was thus successfully controlled by appropriately adjusting $P_{O_2}$. Figure 3 shows the composition of the thin films. In the thin film without oxygen, the chromium content was 47 mol%, which was close to the stoichiometric composition of CrN. In contrast, the chromium content of the thin films increased to that of Cr$_2$O$_3$ when the oxygen content was increased. As far as we know, there is no report on the chromium content in the Cr(N,O) thin films due to the increasing of the oxygen content. As we will describe later, the thin films have a B1 structure. Hence it is indicated that vacancy was formed in the Cr site by the replacement of N with O.

3.2 Phase identification

Figure 4 shows XRD patterns of the thin films. Peak positions and relative intensities for CrN and Cr$_2$O$_3$ in International Centre for Diffraction Data (ICDD) are also included for comparison. It was found that all samples included a B1 phase based on CrN. In addition, only the sample formed with $P_{O_2} = 10 \times 10^{-5}$ Pa included the Cr$_2$O$_3$ phase. The peaks due to the B1 structure became broad with increasing $P_{O_2}$. Crystallite size effect and lattice strain are considered as a major cause for broadening of XRD peaks. However, as we will describe in the next paragraph,
crystallite size of the Cr(N,O) thin films did not change with increasing $P_{O_2}$. Hence it is suggested that the cause for this broadening is variations in the oxygen content in each crystallite. Figure 5 shows the lattice constants of the B1 phase of each thin film calculated from the peak positions from the (111) and (200) reflection. The lattice constant decreased with increasing $P_{O_2}$. The decrease in the lattice constant indicates solution of oxygen in the B1 phase. Transition metal oxides and nitrides which have the total valence similar to that of CrN include a lot of vacancies (ex. TiO, VO and TiN). These lattice constants change with increasing number of vacancies in the cation site. In Fig. 3, it is confirmed that the number of chromium vacancies increase with increasing the oxygen content. Hence it is considered that the cause for the decreasing of the lattice constant is formation of vacancies in the Cr site. Figure 6 shows the FT-IR spectra of the thin films. Reference data for CrN and Cr$_2$O$_3$ are also included. The absorption spectra of the samples formed with $P_{O_2}$ less than or equal to $7.5 \times 10^{-5}$ Pa showed a broad peak mainly at 390–430 cm$^{-1}$ due to the Cr–N bond. Absorption peaks due to Cr$_2$O$_3$ were not observed. On the other hand, the absorption spectra of the samples formed with $P_{O_2}$ greater than or equal to $8.5 \times 10^{-5}$ Pa show sharp peaks at 550 cm$^{-1}$, which is due to the Cr–O bond in the Cr$_2$O$_3$ crystal. From the results in Figs. 4 and 6, it was found that the thin films with only the B1-Cr(N,O) phase were prepared under $P_{O_2}$ less than or equal to $7.5 \times 10^{-5}$ Pa.

### 3.3 Microstructure and hardness

Figure 7 shows a bright field image (BFI) of the TEM sample prepared by focused ion beam (FIB) processing to keep the TEM sample thickness being less than 100 nm. According to this image, an initial growth layer was not observed. Figure 8 shows BFI, dark field images (DFI) and selected area diffraction patterns (SAD) for the prepared thin films. It was observed that all spots in the SAD pattern from all samples can be indexed for reflection from the B1 structure. The DFI were taken from the 200 diffraction of the SAD. From these DFI, it was found that crystallite size of the thin films was approximately 100 nm and did not change with increasing $P_{O_2}$. Rawal et al. reported that crystallite size of Cr(N,O) thin films prepared by reactive magnetron sputtering decreased with increasing oxygen partial pressure in the atmosphere. In our method, variation of $P_{O_2}$ ($10^{-5}$ Pa order) is far lower than the total pressure ($1.5 \times 10^{-2}$ Pa). Hence it is considered that varying $P_{O_2}$ do not affect crystal growth configuration of the Cr(N,O). Figure 9 shows the indentation hardness data for the thin films as a function of $P_{O_2}$. The
results of phase identification by XRD and FT-IR are also shown at the top of Fig. 9. The hardness of the thin films increased with increasing $P_{O_2}$ up to $7.5 \times 10^{-5}$ Pa. Above $7.5 \times 10^{-5}$ Pa, the hardness decreased. The thin films showed a maximum hardness value of 32 GPa, which was similar to the previous results. The maximum value was found around the solubility limit.

In general metallic materials, yield stress is related to crystallite size through Hall–Petch relationship. This relationship serves to demonstrate that the yield stress increases with decreasing crystallite size. In Cr(N,O), the crystallite size did not change with increasing the oxygen content. Hence it was found that high hardness was not achieved by the Hall–Petch relationship. The decreasing of hardness for $P_{O_2}$ above $7.5 \times 10^{-5}$ Pa related to the crystal structure of the thin films. In this zone, Cr$_2$O$_3$, which have the lower hardness value than that of CrN, exist as the second phase. It is considered that the hardness decreased due to increase of the volume fraction of Cr$_2$O$_3$.

4. Conclusions

From the above results, it was found that the oxygen content in the Cr(N,O) thin films was successfully controlled by varying $P_{O_2}$ in a pulsed laser ablation process using a RF radical source. The thin films had oxygen content up to
62 mol%. All the samples contained a phase with a B1 structure. In the thin films deposited under high $P_{O_2}$ ($\geq 8.5 \times 10^{-5}$ Pa), Cr$_2$O$_3$ existed as a second phase. The chromium content of the B1 phase decreased from 47 mol%, which was close to the stoichiometric composition of CrN, to 40 mol% when the oxygen content was increased. From TEM observations, it was found that crystallite size of the thin films did not change with increasing $P_{O_2}$. The hardness of the thin films increased with increasing $P_{O_2}$, and then decreased for $P_{O_2} \geq 8.5 \times 10^{-5}$ Pa. The thin films showed a maximum hardness value of 32 GPa around the solubility limit.

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