Nickel copper oxide \( (\text{Ni}_{1-x}\text{Cu}_x)\text{O}) \) thin films, where the Cu content \( x \) was changed in the range from 0 to 1, were prepared by pulsed laser deposition. The copper content of the thin films was determined by energy-dispersive X-ray analysis with scanning electron microscopy. Transmission electron microscope observations of the thin film with \( x=0.52 \) revealed that the unit cell was distorted from cubic to tetragonal according to the Jahn-Teller effect by Cu\(^{2+}\) ions dissolved in the NiO lattice.

Key words: (Ni,Cu)O, Jahn-Teller effect, tetragonal, pulsed laser deposition, crystal structure

1. INTRODUCTION

Transition metal oxides show various physical phenomena such as the metal-insulator transition, high temperature superconductivity, and enormous magnetic resistance.\(^{5,7}\) The main origin of these properties is the \( d \) electrons of transition metal ions. Historically, the starting point of research on \( d \) electrons was a series of studies on Mott insulators including charge-transfer-type insulators. According to band theory, transition metal oxides should show metallic electrical conduction properties, but some of them are insulators because their \( d \) electrons are localized at each transition metal ion by a repulsive force between electrons. Among transition metal oxides, nickel oxide (NiO) is a charge-transfer-type insulator.\(^9\) It has a NaCl-type (B1) structure and exhibits antiferromagnetism below the Néel temperature (\( T_N = 523 \) K). These properties of NiO have been exploited in a variety of applications. It is known that NiO thin films are suitable for use in magnetoresistance sensors, electrochromic devices, transparent conducting films, and chemical sensors.\(^{9-11}\) Various attempts have been made to add alloying elements into NiO. For example, it has been reported that in the Ni-Li-O system, hole carriers are introduced into NiO by substituting Li atoms for Ni since Li is ionized to Li\(^+\).\(^{12}\) A Ni-Li-O phase has been used as a negative-temperature-coefficient thermistor. A Ni-Fe-O phase shows ferromagnetism caused by double-exchange interaction at room temperature, and is anticipated to be suitable for use in diluted magnetic semiconductor (DMS) applications.\(^{13,14}\) The Ni-Nb-O system includes a phase being regarded as a promising catalyst used to substitute Ni\(^2+\) for Ni\(^3+\).\(^5\) In the Ni-Zn-O system, the addition of Zn into NiO has been observed to alter the electron structure and cause excitation from O(p) \( \rightarrow \) Ni(d) to O(p) \( \rightarrow \) Zn(s) as a result of Zn\(^2+\) substitution.\(^{16}\) Studies on NiO are expected to lead to new DMS and catalytic applications.

In the present study, we attempted to add Cu\(^{2+}\) ions into NiO. It is well known that Cu\(^{2+}\) ions (d\(^9\)) in an octahedral environment cause lattice distortion brought about by the Jahn-Teller effect.\(^{17}\) The common coordination environment of Cu\(^{2+}\) is a distorted octahedron with four short and two long bonds. In Cu\(_2\)F\(_2\) (distorted rutile structure), the distortion is fairly small (four Cu-F bonds with 1.93 Å, two with 2.27 Å). It is larger in CuCl\(_2\) (four Cu-Cl bonds with 2.30 Å, two with 2.95 Å) and extreme in tenorite, CuO, which is effectively a square planar (four Cu-O bonds with 1.95 Å, two with 2.87 Å).\(^{17}\) The importance of the Jahn-Teller effect in Cu\(^{2+}\) compounds is seen by comparing the structures of the oxides of the first-row divalent transition metal ions. All members of the oxide series Mo \( (M^{2+}) \) can be Ti, V, Mn, Fe, Co, Ni, and Cu have the B1 structure with regular octahedral coordination, apart from CuO, which contains the above-mentioned distorted CuO\(_6\) octahedra.\(^{17}\) Another example of distorted octahedral coordination due to the Jahn-Teller effect is CuFe\(_2\)O\(_4\); Bertauthas reported that the Cu\(^{2+}\)-occupied octahedra are tetragonally deformed in the same way, with an axis ratio c/a of 1.06.\(^{18}\)

Although the phase diagram of the Ni-Cu-O system has been reported by Zilber et al., it is an incomplete diagram.\(^{19}\) In addition, Turkyl has synthesized NiO-CuO samples that can be used for catalytic applications.\(^{20}\) However, the NiO-CuO system that they investigated was prepared under equilibrium conditions so that the amount of CuO was about 3 at.%. The substitution of supersaturated Cu\(^{2+}\) into NiO causes lattice distortion brought about by the Jahn-Teller effect, and there is a possibility that novel properties such as electrical properties and magnetism could be induced. Preparation of thin films in a nonequilibrium state can be realized by physical vapor deposition techniques, and we have succeeded in the synthesis of various metastable materials by pulsed laser deposition (PLD).\(^{21-23}\) In previous research\(^{24}\), it was clarified that both interplanar distances and lattice constants increased with increasing copper content, and the \( (\text{Ni}_{1-x}\text{Cu}_x)\text{O}) \) phase with \( 0<x<0.27 \) has a B1 structure. The purpose of the present investigation was to prepare supersaturated (Ni,Cu)O thin films with \( x>0.27 \) by PLD, to determine the crystal structure of the (Ni,Cu)O thin films, and to discuss a crystal distortion factor by Cu\(^{2+}\) solution into NiO.
2. EXPERIMENTAL

The thin films were deposited by irradiating a target with a Nd:yttrium aluminum garnet (λ= 355 nm) laser beam. The laser was electro-optically Q-switched using a Pockels cell to produce intense pulses of short duration (7 ns) with a repetition rate of 10 Hz. The laser beam was concentrated by a lens, and the fluence was adjusted to 5 J/cm² on the targets. Plates of 99.9% pure Ni and 99.96% pure Cu were used as targets. The cation composition of the thin films was controlled by changing the irradiated area of the Ni (S_Ni) and Cu (S_Cu) plates. The surface area ratio of the targets (S_R) is expressed as S_R = S_Cu/(S_Ni+S_Cu). The deposition chamber was evacuated to 3 Pa using a rotary pump. Experiments were carried out under an oxygen pressure of 66 Pa. A single-crystal (100)-oriented silicon (Si) substrate was placed at a distance of 20 mm from the target surface. In this study, the Si substrate surface was washed with acetone. However, hydrogen termination such as HF treatment was not carried out. (This implies that the thin films were deposited on a thin silicon oxide layer covering the substrate surface.) The substrate temperature was set at 673 K.

The macroscopic composition of the thin films prepared by changing S_R was measured using an energy-dispersive X-ray analysis (EDX) system equipped on a scanning electron microscope (SEM). The crystal structure of the thin films was determined by X-ray diffraction (XRD) analysis. Diffraction patterns were recorded using CuKα radiation of 0.15418 nm wavelength under 50 kV and 300 mA operating conditions. Microstructural characterization was performed on a transmission electron microscope (TEM; JEOL JEM 2000FX) operated at an accelerating voltage of 200 kV. The intensity of the characteristic X-rays from the sample was calibrated using those from a standard sample of cupronickel.

The thin films were abraded using a diamond cutter and then placed on a molybdenum (Mo) mesh. The composition in the abraded grains was measured using another EDX system equipped on the TEM.

3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the thin films prepared by changing the copper content (x). The peaks due to B1-111 and B1-200 are referred to as diffraction peaks I and II, respectively. Since the difference in ionic radius between Ni²⁺ (0.69 Å) and Cu²⁺ (0.72 Å) is relatively small, Ni²⁺ can be replaced with Cu²⁺. The diffraction peaks of the thin films with x=0 to x=0.27 appeared at the positions attributed to B1-NiO. For the thin films with x=0.72 to 1, diffraction peaks were located at positions attributed to CuO. All the thin films were observed to contain a small amount of Ni phase. The thin films with x=0 to 0.37 had a strong 111 orientation. Both diffraction peaks I and II, which were observed from x=0 to 0.63, shifted to lower angles with increasing x.

Figure 2(a) shows the interplanar distances obtained from diffraction peaks I and II. In Fig.2(a), the solid and dashed lines represent the interplanar distances of B1-NiO. Both interplanar distances increased with increasing copper content. The amount of deviation from the ICDD card data for diffraction peak II was larger than that for peak I. Figure 2(b) shows the lattice constant calculated from the two interplanar distances shown in Fig.2(a), where the crystal structure was assumed to be cubic. In Fig.2(b), the dashed line represents the lattice constant of B1-NiO. Both calculated lattice constants increased with increasing copper content. Figure 2(c) shows the ratio of the above two lattice constants. This ratio was approximately equal to 1.0 for x<0.27. Thus, the thin films obtained for 0<x<0.27 had a B1 structure. For x>0.27, the ratio increased with increasing x.

In order to clarify the details on the crystal structure of the (Ni₀.₄₈Cu₀.₅₂)O thin film, TEM observations were performed. The thin films were abraded using a diamond cutter and then placed on a molybdenum (Mo) mesh. The composition in the abraded grains was measured using another EDX system equipped on the TEM.
carried out. Figure 3(a) shows bright field image, and Fig.3(b) shows the EDX spectrum of the (Ni,Cu)O thin film (x=0.52) obtained with the electron beam focused on area A in Fig.2 (a). Three peaks due to NiKα, CuKα, and O Kα were observed. In a different energy region, peaks attributable to MoLα and C Kα appeared owing to scattered electrons in the TEM measurement from the Mo mesh and microgrid. According to EDX measurements carried out in the TEM, the copper content x of this crystal grain was 0.52. It was found that this grain was a single crystal of the (Ni0.47,Cu0.52)O phase, composed of Ni, Cu, and O.

Figure 4 shows selected-area diffraction (SAD) patterns and the intensity profile, obtained with the electron beam focused on area A in Fig.2 (a). The [200] direction was defined as the a axis, and the [002] direction was defined as the c axis. The angle between the two diffraction spots for 200 and 002 was not 90° but 89.81°. The interplanar distance (d value) of the 002 spot was clearly larger than that for the 200 spot. The two lattice constants along the a and c axes calculated from the interplanar distance were a=4.20 Å and c=4.44 Å. From the results of Fig.3 and Fig.4, it was proven that the crystal structure of (Ni1-x,Cux)O thin film appeared to have been distorted as a tetragonal phase according to the Jahn-Teller effect by Cu2+ ions dissolved in the NiO lattice.

In the case of a material showing the Jahn-Teller effect, the degree of distortion would be increased with decreasing temperature, since the entropy term would be stronger than the Jahn-Teller distortion at elevated temperatures. In this work, XRD measurement at 93K was carried out. In Figure 5, the axial ratio c/a at 93K and 303K of the (Ni,Cu)O thin films with x=0, 0.19 and 0.52 was compared. Though the c/a ratio of (Ni,Cu)O with x=0 and 0.19 was almost constant when the XRD measurement accuracy was considered, the ratio for x=0.52 at 93K was larger than that at 303K. This increase in the c/a ratio at low temperature was thought to be evidence of the Jahn-Teller effect in the (Ni,Cu)O thin film.
4. CONCLUSIONS

Using PLD, (Ni,Cu)O thin films were prepared from Ni and Cu targets. The ratio of the lattice constants, calculated from two interplanar distances of 111 and 200, was approximately equal to 1.0 for $x<0.27$. For $x>0.27$, the axial ratio $c/a$ increased with increasing $x$. Thus, the thin films for $x=0.52$ had a tetragonal phase, according to the Jahn-Teller effect, by Cu$^{2+}$ ions dissolved in the NiO lattice.

REFERENCES


(Received December 27, 2009; Accepted February 28, 2010)