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P-type semiconducting Cu_2O–NiO thin films prepared by magnetron sputtering

Toshihiro Miyata · Hideki Tanaka · Hirotoshi Sato · Tadatsugu Minami

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Abstract P-type semiconducting thin films consisting of a new multicomponent oxide composed of Cu_2O and NiO were deposited on glass substrates by r.f. magnetron sputtering using Cu_2O–NiO mixed powder targets. The multicomponent oxide thin films deposited in an Ar atmosphere with a Ni content (Ni/(Cu + Ni) atomic ratio) in the range from 0 to 100 at.% were found to be p-type semiconductors. As the Ni content was increased in the range from 0 to about 30 at.%, the energy bandgap of the resulting films gradually increased as well as the obtained resistivity increased from 70 to $4 \times 10^4\ \Omega$ cm, a consequence of decreases in both the Hall mobility and the hole concentration. The films prepared with a Ni content of about 30–50 at.% exhibited a relatively constant resistivity and energy bandgap. The resistivity and the energy bandgap of films prepared with a Ni content above about 60 at.% considerably increased as the Ni content was increased. Furthermore, a pn thin-film heterojunction prepared by depositing undoped *n*-ZnO and *p*-multicomponent oxide (Ni content of 50 at.%) thin films exhibited a rectifying I–V characteristic.

Introduction

Recently, polycrystalline oxide thin films that exhibit p-type semiconducting have attracted much attention in various device applications. Sato et al. reported the preparation as well as application of p-type transparent conducting NiO thin films deposited on glass substrates by r.f. magnetron sputtering [1]. In addition to their preliminary report, Kawazoe et al. have also proposed device applications and new p-type semiconducting oxide materials [2]. In addition, many experimental and theoretical investigations to obtain p-type ZnO have also been attempted in recent years [3–5]. Up to now, many examples of the preparation and application of p-type semiconducting thin films using newly developed oxide materials have been reported. Nevertheless, from a viewpoint of applications for large area devices, this paper will be focused on polycrystalline semiconducting oxide thin films. Recently, the preparation of p-type polycrystalline semiconducting thin films deposited on glass substrates using new oxide materials such as Ag_2O–In_2O_3 [6], $CuAlO_2$ [2], $CuY_{1-x}Ca_xO_2$ [7], $CuCr_{1-x}Mg_xO_2$ [8], $CuScO_2$ [9], $CuGa_{1-x}Fe_xO_2$ [10], $AgCoO_2$ [10], $CuNi_{2/3}Sb_{1/3}O_2$ [10], $NiCo_2O_4$ [11] and Cu_2O–CoO [12] has been reported. In particular, p-type semiconducting thin films consisting of multicomponent oxides, whose electrical and optical properties can be controlled by varying the chemical composition, have been gaining importance in applications for optoelectronic devices.

In this paper, we describe the preparation of p-type semiconducting thin films consisting of new Cu oxide–Ni oxide material multicomponent oxide (Cu–Ni oxide) thin films. The Cu–Ni oxide thin films were prepared by r.f. magnetron sputtering using Cu_2O–NiO powder targets.

Experiment

The films were deposited by conventional r.f. planar magnetron sputtering using a powder target in an Al holder

T. Miyata (✉) · T. Minami
Optoelectronic Device System R&D Center, Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan
e-mail: tmiyata@neptune.kanazawa-it.ac.jp

H. Tanaka · H. Sato
Research and Development Center, Gunze Limited, 163 Morikawara, Moriyama, Shiga 524-8501, Japan

with a diameter of 80 mm [1]. A mixture of Cu_2O and NiO powders (purity, 99.99%) calcined at 1000°C in an Ar or air atmosphere for 1 h was used as the target: Ni content (Ni/(Cu + Ni) atomic ratio) in the range from 0 to 100 at.%. The powder target with thickness of about 1 mm was lightly pressed. The powder in the target was completely replaced for every deposition. After presputtering for 10 min, sputtering deposition was carried out with a power of 80 W at a sputter gas pressure of 0.2–2.0 Pa in an Ar or O_2 atmosphere. Substrates (20 × 100 mm) of OA-2 glass (Nippon Electric Glass Co. Ltd) were placed parallel to the target surface. The distance between the target and substrate was about 30 mm. The substrate temperature was varied from 200 to 500°C. The film thickness was varied from 0.1 to 1 μm. The thin-film deposition rate was dependent on target powder composition, powder calcination condition and sputtering atmosphere. For example, the deposition rates in Ar using Cu_2O and NiO powder targets calcined in Ar were 47.0 nm/min and 21.6 nm/min, respectively. Film thickness was measured using a conventional surface roughness detector with stylus. The crystallinity of deposited films was investigated by X-ray diffraction (XRD) using a conventional X-ray unit (Rigaku Ultima 2100) with a copper anode. The chemical composition (Ni content) of deposited films was analyzed by energy dispersive X-ray (EDX) spectroscopy. The electrical properties were measured using the van der Pauw method (Accent HL-5500PC). The electrical properties presented in the following description were measured at the center of the substrate surface, corresponding to the center of the target, except for those concerning the location dependencies of the substrate surface. The carrier type was established by measurement of both the Hall voltage by the van der Pauw method and the Seebeck voltage induced by a temperature gradient. The optical transmission through the film on glass substrate was measured using a spectrophotometer (Hitachi U-3500). The optical absorption and the refractive index were measured using spectroscopic ellipsometry (J.A.Woollam Co. Inc. HS-190).

Results and discussion

Deposition condition dependence

It was found that the electrical, optical and crystallographical properties of the Cu–Ni oxide thin films were strongly dependent on the deposition conditions as well as the Ni content and the calcination conditions of the powder targets used. In order to determine the optimal deposition conditions of Cu–Ni oxide thin films, we investigated the preparation condition dependencies of Cu oxide and Ni oxide thin films, i.e., a Ni content of 0 and 100 at.%, respectively. As an example, Fig. 1 shows the optical transmission spectra of Cu oxide and Ni oxide thin films deposited in either a pure Ar or O_2 atmosphere at a pressure of 0.4 Pa. These films were prepared on substrates at 500°C using a Cu_2O powder or NiO powder target calcined in a pure Ar atmosphere. The main composition of Cu-oxide thin films deposited in pure Ar and O_2 atmospheres were identified as Cu_2O and CuO, respectively, as evidenced from their optical absorption edges [13] and XRD analyses. The Ni oxide film deposited in an Ar atmosphere exhibited a generally higher average transmittance over the measured wavelength region and was identified as NiO [1, 14]. It should be noted that the obtained electrical resistivity of Ni oxide films deposited in an Ar atmosphere was higher than that of films deposited in an O_2 atmosphere. Typical electrical properties obtained in these films are summarized in Table 1. Accurate Hall measurements were difficult to obtain for NiO thin films because of the ferromagnetism in Ni atoms. Similar to Ni oxide films, the resistivity of Cu oxide films deposited in an Ar atmosphere was higher than that of films deposited in an O_2 atmosphere. This effect is attributed to the decrease of carrier concentration being larger than the increase of Hall mobility. It should be noted that the obtained resistivities and/or Hall mobility in NiO and Cu_2O thin films prepared in an Ar atmosphere approximately agree with those of the NiO [1, 15–17] and Cu_2O [18–20] films, as reported previously; the obtained resistivities and Hall mobility were considerably affected by the film preparation method and condition.

On the other hand, the transmittance and crystallinity of these films prepared using targets calcined in Ar were always improved, in contrast to the transmittance and crystallinity of films prepared using targets calcined in air. It was also found that the transmittance in the visible wavelength range and the crystallinity of Cu_2O and NiO films showed a tendency towards improvement as the

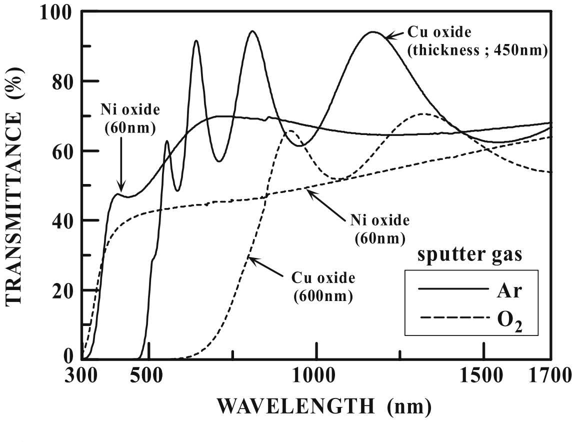

Fig. 1 Optical transmission spectra of Cu oxide and Ni oxide films deposited in an Ar or O_2 atmosphere

Table 1 Typical electrical properties of Cu oxide and Ni oxide films deposited in an Ar or O_2 atmosphere

Target	Gas supply	$\rho[\Omega\ \text{cm}]$	$p[\text{cm}^{-3}]$	$\mu[\text{cm}^2/\text{Vs}]$
Cu_2O	Ar	96	4.6×10^{15}	1.4×10^{1}
	O_2	1.8	2.1×10^{19}	1.6×10^{-1}
NiO	Ar	8.2×10^{5}		
	O_2	2.5		

substrate temperature was increased in the range from 200 to 500°C. From the results described above, it can be concluded that the sputter deposition of Cu–Ni oxide thin films being produced by varying the Ni content should be carried out at a substrate temperature of 500°C and a sputter gas pressure of 0.4 Pa in an Ar atmosphere using Cu_2O–NiO powder targets calcined in an Ar atmosphere. In other words, in order to obtain Cu–Ni oxide thin films with higher transmittance in the visible range and better crystallinity, film preparation consisting of low grade oxides of Cu and Ni is necessary; for example, Cu_2O films containing univalent copper rather than CuO containing divalent Copper. The oxidization is mainly affected by the content and chemical activity of oxygen gas in the chamber as well as the substrate temperature; when using a pure Ar gas as the sputter atmosphere, oxygen gas in the chamber is provided by sputtering the target.

Electrical and crystallographical properties

Because the electrical, optical and crystallographical properties of deposited Cu–Ni oxide thin films were strongly dependent on the deposition conditions as well as the Ni content and the calcination conditions of the powder targets used, the following depositions were carried out under the optimized conditions described above. Figure 2 shows resistivity (ρ), carrier concentration (n) and Hall mobility (μ) as functions of Ni content for Cu–Ni oxide thin films prepared under the optimal conditions. The films were prepared with a thickness of 320–400 nm. The metal element content (Ni/(Ni + Cu) atomic ratio) of deposited films was measured by EDX spectroscopy and found to be approximately equal to that in the targets used. It should be noted that accurate Hall measurements were difficult to achieve for Cu–Ni oxide thin films deposited with a Ni content above about 60 at.% because of the ferromagnetism in Ni atoms. All the prepared Cu–Ni oxide thin films were found to exhibit positive hole conduction, as evidenced from Hall measurements and/or the Seebeck effect: The multicomponent oxide thin films prepared with a Ni content in the range from 0 to 100 at.% were all found to be p-type semiconductors with a resistivity that was increased by increases in the Ni content. As can be seen in Fig. 2, the resistivity of Cu–Ni oxide thin films increased markedly as the Ni content was increased up to about 30 at.%, remained relatively constant in the range from about 30 to 60 at.%, and then increased markedly with further increases of Ni content.

As the Ni content was increased in the range from 0 to 30 at.%, the obtained resistivity in the resulting Cu–Ni oxide thin films increased from 70 to $4 \times 10^4\ \Omega$ cm, resulting from decreases in both the Hall mobility and the hole concentration. In contrast, the Cu–Ni oxide thin films prepared with a Ni content in the range from 30 to 50 at.% exhibited a relatively constant resistivity on the order of $10^4\ \Omega$ cm. However, the electrical properties of the Cu–Ni oxide thin films prepared by r.f. magnetron sputtering exhibited a spatial distribution on the surface of the glass substrates. As an example, the spatial distribution of electrical properties shown in Fig. 3 was exhibited by a film prepared on a glass substrate with a Ni content of 30 at.%. The distance of 0 cm and around 2–3 cm in the figure indicate locations on the substrate that correspond to the center and the erosion area of the target, respectively. It should be noted that an area of increased resistivity, attributed to an decrease of carrier concentration, exists around the center of the substrate surface in p-type semiconducting Cu–Ni oxide thin films.

Figure 4 shows the Ni content dependence of XRD patterns for the Cu–Ni oxide thin films shown in Fig. 2.

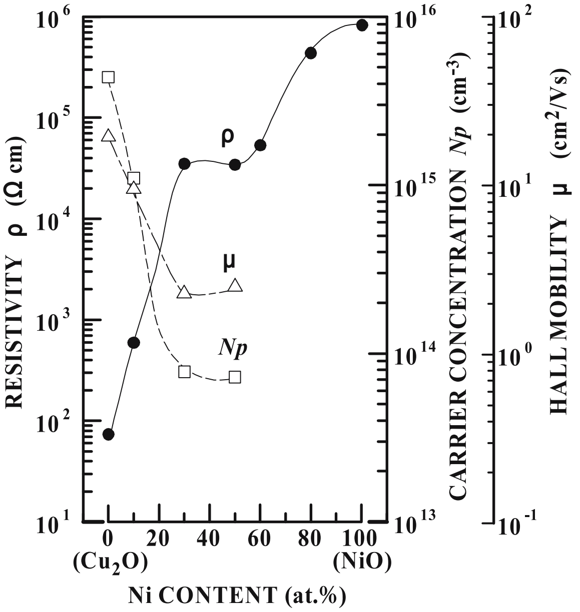

Fig. 2 Electrical properties as functions of Ni content for Cu–Ni oxide films

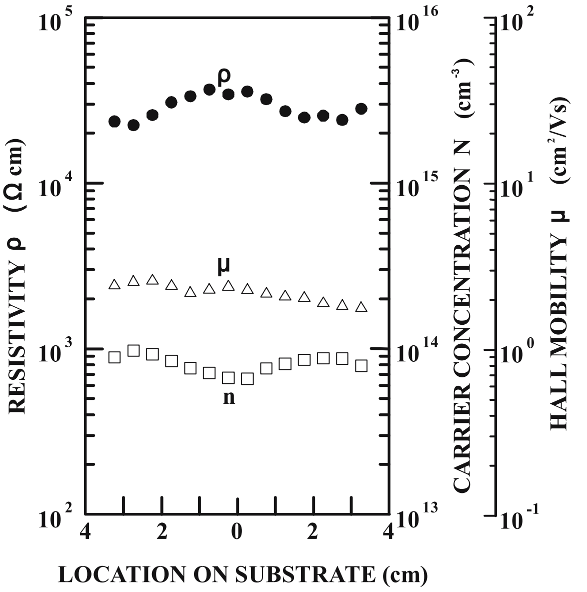

Fig. 3 Distribution of electrical properties across the substrate surface of a Cu–Ni oxide film deposited with a Ni content of 30 at.%

The diffraction peak from the Cu oxide thin film (prepared with a Ni content of 0 at.%) is identified as coming from a cuprous (Cu_2O) lattice; the peak from the Ni oxide thin film (prepared with a content of 100 at.%) is identified as coming from a NiO lattice. In the case of Cu–Ni oxide thin films prepared with a Ni content below about 10 at.%, only diffraction peaks from the Cu_2O lattice were exhibited. The diffraction peak from the Cu_2O lattice was observed in films prepared with a Ni content below about 60 at.%, while the diffraction peak from the NiO lattice was observed in films prepared with a Ni content above about 30 at.%. Consequently, in films prepared with a Ni content in the range from about 30 to about 60 at.%, the diffraction peaks are identified as coming from both the binary compounds, Cu_2O and NiO. Although this diffraction peak from the Cu_2O lattice was not observed in the film prepared with a Ni content of 80 at.%, two weak diffraction peaks identified as coming from the metal Cu lattice were present. The approximately constant resistivity of films prepared with a Ni content in the range from about 30 to about 60 at.% may be related to the formation of a multicomponent oxide, Cu_2O–NiO. When the Ni content was raised above about 60 at.%, the observed increase of resistivity may be related to the increase of diffraction peaks from the NiO lattice. Therefore, the change of resistivity in films resulting from an increase in Ni content from 0 to 100 at.% may be related to a change in the crystallographical properties.

Optical properties

Figure 5 shows the Ni content dependence of the optical transmission spectra for the multicomponent oxide (Cu_2O–NiO) thin films shown in Fig. 2. The absorption edge of the Cu_2O–NiO thin films was shifted to shorter wavelengths by increasing the Ni content. However, the blue-shift of the absorption edge in films prepared with a Ni content in the range from 0 to about 50 at.% was relatively small. In contrast, the absorption edge of films prepared with a Ni content above 60 at.% exhibited a considerable blue-shift. In order to understand in detail the optical properties of these films, the optical absorption and the refractive index were also measured using spectroscopic ellipsometry. The spectral responses of the extinction coefficient and the refractive index as functions of Ni content are shown in Figs. 6 and 7, respectively, for the Cu_2O–NiO thin films shown in Fig. 2. Since the increase of absorption with decreasing wavelength is attributable to band-to-band transition, the energy bandgap of Cu_2O thin films (Ni content of 0 at.%) [13, 22] is smaller than that of NiO thin

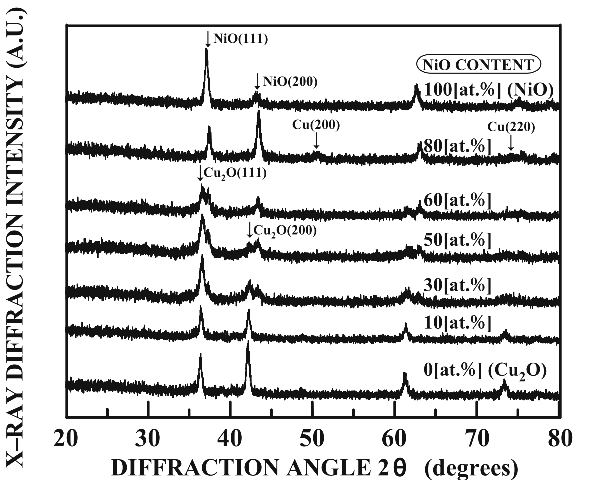

Fig. 4 X-ray diffraction patterns of Cu–Ni oxide films as a function of Ni content

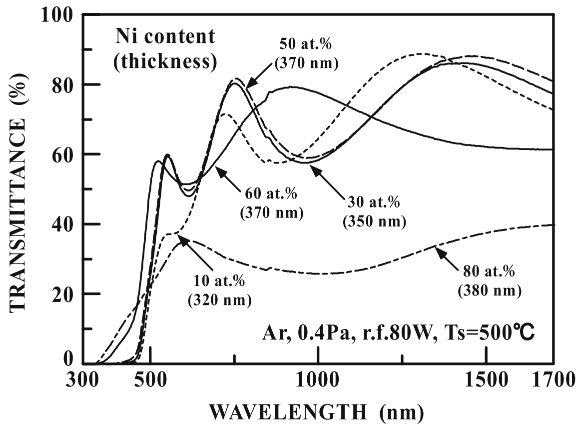

Fig. 5 Optical transmission spectra of Cu–Ni oxide films deposited with various Ni contents

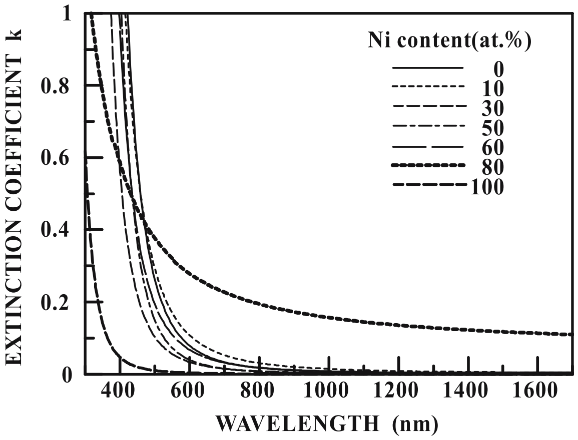

Fig. 6 Spectral response of the extinction coefficient for Cu–Ni oxide films deposited with various Ni contents

films (Ni content of 100 at.%) [1, 14]. It should be noted that a film prepared with a Ni content of 80 at.% exhibited the largest overall absorption in an extended wavelength region. The anomalous optical property of the film prepared with a Ni content of 80 at.% may be attributable to the presence of Cu in the film, as evidenced by the XRD analyses described above. It should be noted that the refractive index of films prepared with a Ni content in the range from 0 to about 60 at.% was relatively independent of the Ni content, as shown in Fig. 7. Although the reflection of incident light at the film surface is affected by the refractive index, the high refractive index of the film prepared with a Ni content of 80 at.% may be attributed to the large absorption.

The energy bandgap of the Cu_2O–NiO thin films was determined using the absorption coefficient estimated from the spectral responses of the extinction coefficient shown in Fig. 6. It was found that the energy bandgap (Eg) can be estimated from the photon energy (hν) dependency of the absorption coefficient (α) for direct transition, i.e., the relationship between $(\alpha h\nu)^2$ and hν [21]. The estimated energy bandgap as a function of Ni content is shown in Fig. 8 for the Cu_2O–NiO thin films. The energy bandgap increased as the Ni content was increased from 0 to about 30 at.%, it slightly decreased as Ni was with increased up to about 60 at.%, and it again increased as the Ni content was increased further.

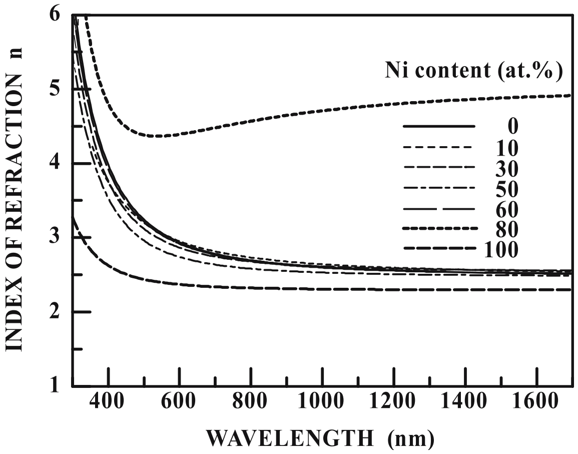

Fig. 7 Spectral response of the index of refraction for Cu–Ni oxide films deposited with various Ni contents

The energy bandgap of a Cu_2O thin film prepared with a Ni content of 0 at.% is estimated to be approximately 2.7 eV as shown in Fig. 8. However, it is known that the energy bandgap of Cu_2O is about 2.2 eV [22]. It should be noted that using the data in Fig. 9 showing a considerable red-shifted of the absorption edge in the transmission spectra of Cu_2O as the film thickness was increased, the energy bandgap of a thick bulk Cu_2O is estimated to be approximately 2.2 eV. These thick Cu_2O sheets with thicknesses of 20, 90 and 180 μm were prepared by oxidizing Cu sheets with a heat treatment carried out in air at a temperature of 1000°C for 2 h [23]. Thus the absorption edge shift, i.e., the energy bandgap discrepancy described above, may be attributable to the band structure of Cu_2O. The conduction band of Cu_2O consists of two bands, Γ_1^+ (j = 1/2) and Γ_3^- (j = 3/2), separated by about 2.2 and 2.6 eV from the top of the Γ_5^+ (j = 1/2) valence band, respectively [24]. It should be noted that the transition from Γ_5^+ to Γ_1^+ is forbidden, but that from Γ_5^+ to Γ_3^- is allowed. Therefore, the absorption resulting from the transition between the Γ_5^+ and Γ_1^+ bands is only significantly observable in a thick layer of Cu_2O (i.e., a very long propagation distance of incident light), because of the low transition probability; absorption resulting from the Γ_5^+–Γ_1^+ transition with a high transition probability is

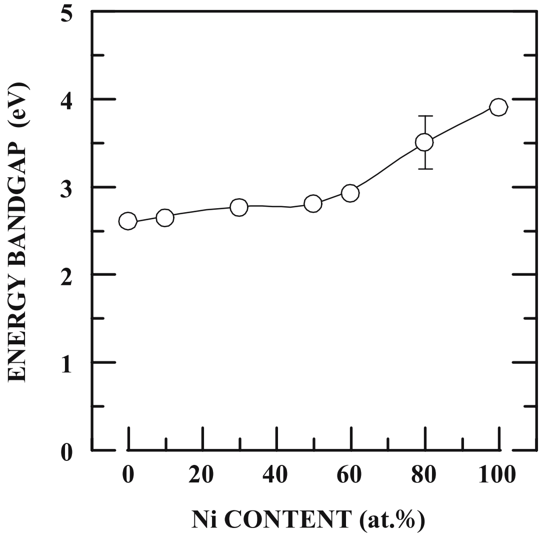

Fig. 8 Estimated energy bandgap of Cu–Ni oxide films deposited with various Ni contents

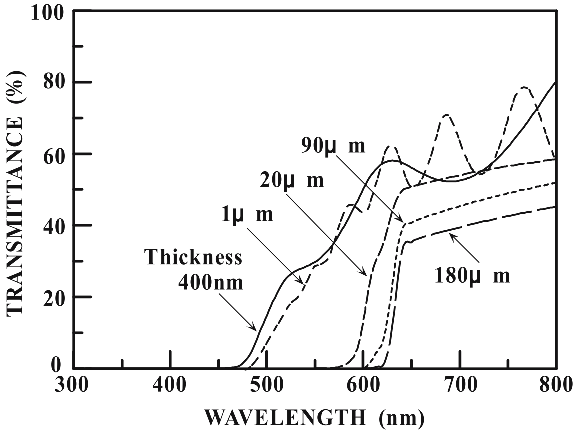

Fig. 9 Optical transmission spectra of Cu_2O films with various thicknesses

mainly observed in the spectral transmission measurement of thin films (i.e., a very short propagation distance of incident light), but that resulting from the Γ_5^+ to Γ_3^- transition is negligibly small.

Fabrication of pn thin-film heterojunction diodes

For the device application of *p*-(Cu_2O-NiO) thin films, *n*-ZnO/*p*-(Cu_2O-NiO) thin-film heterojunctions were prepared by r.f. magnetron sputtering. First, a degenerated p-type semiconducting NiO–La_2O_3 thin film with a resistivity of 6×10^{-4} Ω cm and thickness of approximately 300 nm was prepared on a substrate glass. Subsequent to this deposition, a high-resistivity *p*-(Cu_2O–NiO) thin film prepared with a Ni content of 50 at.% and a thickness of 120 nm was deposited at a substrate temperature of 500°C and a sputter gas pressure of 0.8 Pa in an Ar sputter gas atmosphere. Then an *n*-ZnO (undoped) thin film with a thickness of 100 nm was deposited at a substrate temperature of 200°C and a sputter gas pressure of 0.8 Pa in an Ar + O_2 (20%) sputter gas atmosphere. Finally, a degenerated n-type semiconducting Al-doped ZnO (AZO) thin film with a resistivity of 8×10^{-4} Ω cm and a thickness of approximately 500 nm was prepared on the n-ZnO as a transparent electrode. The n^+-AZO thin films were prepared under the following deposition conditions: r.f. power, 50 W; sputter gas pressure, 0.8 Pa; atmosphere, Ar gas; and substrate temperature, 200°C. Figure 10 shows a typical current-voltage (I–V) characteristic of a fabricated n^+-AZO/*n*-ZnO/*p*-(Cu_2O-NiO)/p^+-(NiO–La_2O_3) thin-film heterojunction. It should be noted that the pn heterojunction exhibited a rectifying I–V characteristic. The turn-on voltage was approximately 0.15 V; the forward bias current was greater than the reverse bias current by a factor of approximately 6 at an applied voltage of ±1 V.

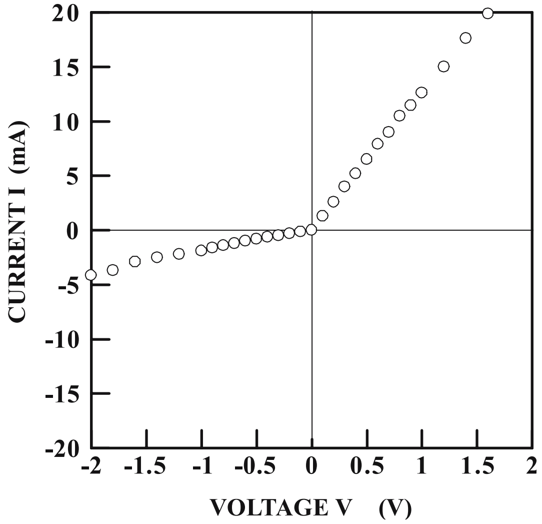

Fig. 10 Typical V–I characteristic of a pin heterojunction diode

Conclusion

P-type multicomponent oxide semiconducting thin films composed of Cu_2O and NiO were prepared by r.f. magnetron sputtering. The obtained electrical and optical properties of the resulting multicomponent oxide (Cu_2O–NiO) thin films prepared on glass substrates were strongly dependent on the deposition conditions as well as the Ni content (Ni/(Cu + Ni) atomic ratio) of the target. The sputter deposition was carried out in a pure Ar atmosphere using Cu_2O-NiO mixed powder targets calcined in an Ar atmosphere. The films prepared under these conditions with a Ni content in the range from 0 to 100 at.% were found to be p-type semiconductors with a resistivity and a energy bandgap that were increased by increases in the Ni content. For example, in Cu_2O–NiO thin films prepared with a Ni content that was increased from 0 to about 30 at.%, the obtained resistivity increased from 70 to 4×10^4 Ω cm, resulting from decreases in both Hall mobility and hole concentration. In contrast, films prepared with a Ni content in the range from about 30 to 50 at.% exhibited a relatively constant resistivity on the order of 3×10^4 Ω cm. In addition, the resistivity of films prepared with a Ni content above about 60 at.% increased markedly as the Ni content was increased. Furthermore, a pn thin-film heterojunction fabricated by depositing an *n*-ZnO thin film on a *p*-(Cu_2O–NiO) thin film prepared with a Ni content of 50 at.% exhibited a rectifying I–V characteristic.

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