The Characteristics of Cu_2O Thin Films Deposited Using RF-Magnetron Sputtering Method with Nitrogen-Ambient

Seong Hyun Lee, Sun Jin Yun, and Jung Wook Lim

We investigate the characteristics of Cu_2O thin films deposited through the addition of N_2 gas. The addition of N_2 gas has remarkable effects on the phase changes, resulting in improved electrical and optical properties. An intermediate phase ($6CuO{\cdot}Cu_2O$) appears at a N_2 flow rate of 1 sccm, and a Cu_2O (200) phase is then preferentially grown at a higher feeding amount of N_2. The optical and electrical properties of Cu_2O thin films are improved with a sufficient N_2 flow rate of more than 15 sccm, as confirmed through various analyses. Under this condition, a high bandgap energy of 2.58 eV and a conductivity of 1.5×10^{-2} S/cm are obtained. These high-quality Cu_2O thin films are expected to be applied to Cu_2O-based heterojunction solar cells and optical functional films.

Keywords: Cuprite, nitrogen, Cu_2O, high energy gap, sputter.

I. Introduction

Cu_2O (cuprite or cuprous oxide) is a *p*-type semiconductor material with a direct bandgap (bulk 2.17 eV) and has been studied for a long time owing to its relative non-toxicity, low material cost, and abundance. Although the fabrication of high-quality Cu_2O thin films is essential for the realization of Cu_2O-based devices, practical applications using a Cu_2O thin film have not been reported much because it is difficult to control the electrical and optical properties of Cu_2O thin films [1]. Researchers have fabricated Cu_2O films using various deposition methods [2]. Among the deposition techniques, RF-magnetron reactive sputter deposition is one of the most promising methods because the composition of a Cu_2O thin film can be easily controlled by varying the deposition parameters, such as the working pressure, flow rate of ambient gas, and substrate temperature. In particular, among these parameters, many groups have varied the flow rate of ambient gas, such as O_2, to improve the structural and electrical properties of Cu_2O thin films [3].

In the case of a reactive sputtering process for a Cu_2O thin film, the phases of thin films change from Cu-rich oxide to Cu_2O and then from Cu_2O to CuO (tenorite or cupric oxide) with an increment of the flow rate of O_2 (ambient gas) [4]. In this manner, it is possible to control the structural phase of a Cu_2O thin film by varying the flow rate of O_2 gas. However, it is difficult to obtain stoichiometric Cu_2O films, owing to the high reactivity between Cu and O_2. At a high deposition temperature, in addition, a single phase of Cu_2O cannot be formed easily because of the increment of mixing entropy and high reactivity [5]. In this study, we therefore try to make a stoichiometric and single phase Cu_2O, with the addition of N_2 gas. It was reported that oxygen radical densities in the O_2-N_2 plasma condition can be controlled by the ratio of O_2-N_2 gases, which may have an influence on the reactivity between Cu and O atoms [6]. Thus far, another group has tried to use N_2 gas as a *p*-type dopant gas, but there are no reports of a phase change caused by adding N_2 gas during the deposition process [7].

In this study, we investigate the effect of the addition of N_2 gas on the structural, electrical, and optical properties of Cu_2O films using various analysis methods. By adding N_2 gas, we

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can obtain high-quality Cu_2O thin films that can be applied to various fields, such as Cu_2O-based heterojunction solar cells, optical functional films, and antireflection thin films.

II. Experiment

Cu_2O thin films are deposited on a glass substrate (boro 33 glass) at 200°C using the RF-magnetron sputtering method with a copper target (99.99% purity). During the process, Ar is used as a sputtering gas, and O_2 and N_2 are used as reactive gases. The Ar and O_2 flow rate are fixed at 50 sccm and 4.8 sccm, respectively. The N_2 flow rate is varied from 0 sccm to 45 sccm. The working pressure is 43 mTorr, and the thicknesses of the samples range from 430 nm to 500 nm. The structural properties are characterized using X-ray diffraction (XRD) in θ-2θ mode. The sheet resistance is measured using a four-point probe, and the film thicknesses are measured using a depth profiler and scanning electron microscopy (SEM). Auger electron spectroscopy (AES) is used to analyze the composition of the Cu_2O films. The chemical bonding state is measured through X-ray photoelectron spectroscopy (XPS). The transmittance is measured using a UV-Vis spectrophotometer, and the bandgap energy is calculated from the transmittance data (λ=300 nm to 1,500 nm) using a Tauc plot.

III. Results and Discussion

Figure 1 shows the XRD data of Cu_2O thin films with an increasing N_2 flow rate (0 sccm to 45 sccm). For a Cu_2O thin film without N_2 gas, a Cu_2O (200) peak appears. As the flow rate of N_2 gas is added to 1 sccm, new peaks of the $6CuO{\cdot}Cu_2O$ (paramelaconite) phase are observed. In general, the $6CuO{\cdot}Cu_2O$ phase is known to be an intermediate phase between Cu_2O and CuO and is formed by a higher oxygen flow rate than needed to form a Cu_2O phase during the supttering process [3], [4]. In this work, however, the addition of a small amount of N_2 gas seems to affect the formation of an intermediate phase. This result can be explained by the fact that the addition of a small amount of N_2 under an O_2 plasma condition significantly increases the oxygen radical density, owing to the collision of metastable nitrogen molecules and oxygen molecules [6]. Thus, more oxygen would be involved in the film formation at a small N_2 flow rate (1 sccm). At a N_2 flow rate of 5 sccm, Cu_2O (111) and (200) phases newly appear, whereas the intermediate phase disappears. When the flow rate of N_2 gas increases from 10 sccm to 45 sccm, the preferred orientation growth of Cu_2O (200) is observed. Therefore, we find that N_2 gas has a strong influence on the phase change of Cu_2O films.

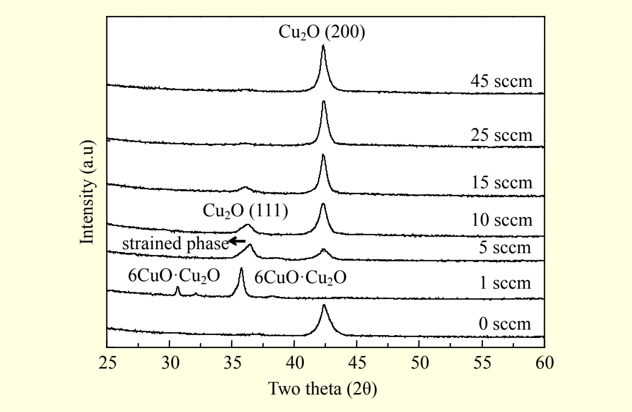

Fig. 1. XRD peak intensity of Cu_2O thin films with various N_2 flow rates (0 sccm to 45 sccm) at 43 mTorr.

Table 1. Cu/O atomic percent ratio and N atomic percent as function of N_2 flow rate.

N_2 (sccm)	Cu/O ratio (AES)	N atomic percent
0	2.22	< 0.1
1	1.82	< 0.1
15	2.08	< 0.1
25	2.02	< 0.1

Table 1 shows the atomic percentages of Cu_2O thin films with various amounts of N_2 gas analyzed by AES. An abrupt reduction of Cu content is observed (the value of Cu/O ratio is 1.82) at a N_2 flow rate of 1 sccm, which is due to the formation of oxygen-rich $6CuO{\cdot}Cu_2O$ phases. In addition, the value of the Cu/O ratio is close to 2 with an increment of the N_2 flow rate, which seems to play an important role in forming stoichiometric Cu_2O films. It was reported that the oxygen radical density rapidly increased with the addition of a small amount of N_2 gas in O_2 plasma and then decreased with a large amount of N_2 gas [6]. In addition, sputtered Cu ions seem to be scattered by N_2 gas in plasma. This may suppress the reaction probability between Cu and O, which leads to a decrease in the deposition rate of Cu_2O thin films forming stoichiometric films.

Another noticeable point is that the atomic percentages of nitrogen are below the detection limit in thin films, as shown in Table 1; that is, in spite of a considerable change in the phase of film, nitrogen is rarely involved in such films. This may be due to the low deposition temperature (200°C) compared to other reports (over 400°C), where nitrogen is largely incorporated in Cu_2O films as a *p*-type dopant [7]. If we fabricate Cu_2O films at a higher temperature, the quality of the films can be improved.

To investigate the effect of N_2 addition on the surface

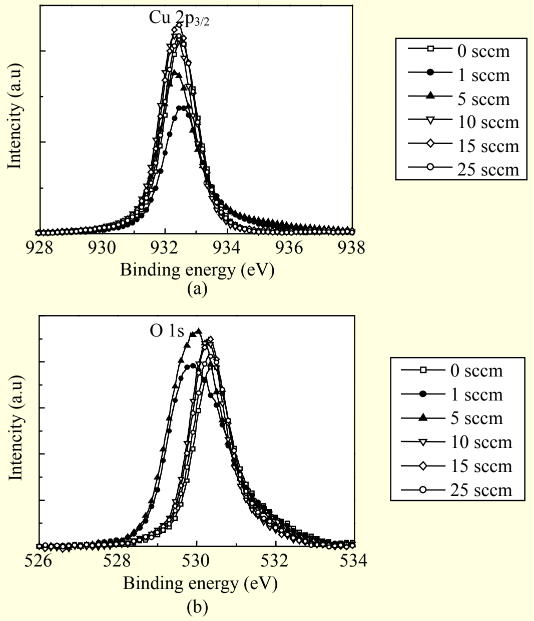

Fig. 2. XPS spectra of (a) Cu $2p_{3/2}$ and (b) O 1s as function of N_2 flow rate.

chemistry of Cu_2O thin films, an XPS analysis is carried out. Figures 2(a) and 2(b) exhibit the XPS spectra of Cu $2p_{3/2}$ and O 1s, respectively. The copper 2p level is spilt into two sublevels (Cu $2p_{3/2}$ and Cu $2p_{1/2}$). In the case of Cu $2p_{3/2}$, spectra observed under all conditions except N_2 flow rates of 1 sccm and 5 sccm are analogous. In the case of O 1s, as shown in Fig. 2(b), the spectra curves shift to a lower binding energy at 1 sccm and 5 sccm compared with the other samples. This result supports the advent of an intermediate phase and the formation of a stoichiometric phase of Cu_2O films, as suggested by XRD and AES data.

To analyze the bonding states of the thin films in more detail, the XPS spectra are deconvoluted into two components. In other reports, the binding energies of Cu $2p_{3/2}$ for Cu_2O and CuO were observed at around 932.4 eV and 933.6 eV, respectively. In addition, the binding energies of O 1s for Cu_2O and CuO were observed at around 530.4 eV and 529.8 eV, respectively [8]. In both cases of our study, $2Cu^{+1} - O^{-2}$ and $Cu^{+2} - O^{-2}$ bonding states exist in thin films, simultaneously, at N_2 flow rates of 1 sccm and 5 sccm. In particular, although the intermediate phase is not shown in the XRD data at a N_2 flow rate of 5 sccm, the evidence for the existence of an intermediate phase is clearly revealed in the XPS data shown in Fig 2. In other deposition conditions, however, only a $2Cu^{+1} - O^{-2}$ binding state is formed. From various analysis methods, to obtain stoichiometric Cu_2O films and growth at a (200) preferred orientation, which lead to high-quality Cu_2O films, it is necessary to introduce a N_2 flow rate of more than 15 sccm.

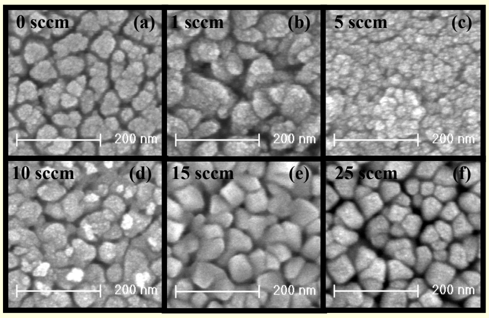

Fig. 3. SEM images with various N_2 flow rates (0 sccm to 25 sccm).

We also carry out an SEM analysis to explain the microscopic change of film growth and surface. Plain SEM images are shown in Figs. 3(a) through 3(f). At a N_2 flow rate of 0 sccm, granular surfaces with void gaps are observed. At 1 sccm, however, the surface of the film is considerably irregular, and different sizes and shapes (peanut-shaped) of grains, which are somewhat larger than those of 0 sccm, can be observed in Fig. 3(b). These results indicate the formation of intermediate phases, which are shown in the XRD data. As the N_2 flow rate increases to 5 sccm, smaller grains are observed, and the shape is considerably different from those obtained with a smaller N_2 flow rate, which is due to the advent of strained phases of Cu_2O (111) and (200). As shown in Fig. 3(d), a larger grain can be observed, and grain boundaries are clearly shown in the sample with 10 sccm. Figures 3(e) and 3(f) exhibit a quadrangular surface with a clearer grain boundary, that is, it seems that (200) phases are preferably grown as expected by the XRD results. Interestingly, a tendency of the variation in the grain sizes of SEM images between (a) and (f) corresponds with that in the estimated full-width half-maximum (FWHM) values of the Cu_2O (200) phase in the same samples.

We then investigate the optical and electrical properties of a Cu_2O thin film strongly related with the structural properties. Figure 4 describes the variation of the optical bandgap and FWHM of peaks of the Cu_2O (200) phase, as shown in Fig. 1. Here, the bandgap energies are calculated using the Tauc plot from the transmittance data (data not shown). With the increment of the flow rate of N_2 gas, an increasing tendency in the bandgap energy is observed, whereas a decreasing tendency is obtained in FWHM. In the film growth, the lower value of FWHM indicates a higher crystallinity and improvment in the preferred orientation. Therefore, we find that the preferred growth of the (200) phase enhances the bandgap energy in Cu_2O films. From other reports, it can be inferred that the reason for the bandgap widening may be due to the smaller d-d interaction between the Cu atoms of the Cu_2O (200) than that of the Cu_2O (111) [9].

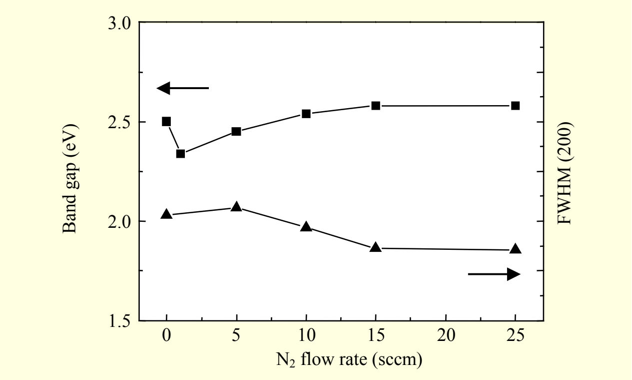

Fig. 4. Variation of optical bandgap energy and FWHM value with increasing flow rate of N_2.

Table 2. Electrical properties (conductivity, carrier concentration, and type) as function of N_2 flow rate analyzed through Hall measurement.

N_2 (sccm)	Carrier type	Carrier concentration (cm^{-3})	Conductivity (S/cm)
0	*n*	-1.4×10^{20}	2.19
1	-	-	6.1×10^{-4}
10	*p*	2.8×10^{17}	1.2×10^{-2}
15	*p*	3.2×10^{17}	1.2×10^{-2}
25	*p*	3.3×10^{17}	1.2×10^{-2}
45	*p*	4.8×10^{17}	1.5×10^{-2}

It is also expected that the preferred growth of the (200) phase affects the electrical properties. The carrier types and conductivities of Cu_2O thin films measured by a Hall measurement and a four-point probe are shown in Table 2. Unlike other samples, the film without a N_2 addition shows a relatively high conductivity and *n*-type conduction. This may be explained by the formation of Cu-rich phases. In spite of the high conductivity of the films, they seem to be porous and defective, as shown in the SEM data in Fig. 3(a). Therefore, to obtain higher quality Cu_2O films, a sufficient amount of N_2 should be supplied in the film growth. Moreover, the polarity of the carrier is changed to positive when the N_2 flow rate exceeds 10 sccm, as listed in Table 2. This result demonstrates that stable *p*-type conduction properties are obtained by the addition of a sufficient amount of N_2. Another noticeable point is that the carrier concentration slightly increases with the increment of N_2 flow rates from 10 sccm to 45 sccm. Since it was reported that the conduction of Cu_2O films is due to holes generated by Cu vacancy in films [10], N_2 gas may play an important role in generating a Cu vacancy in a forbidden gap in this work. Accordingly, the high conductivity of a Cu_2O thin film, 1.5×10^{-2} S/cm, is obtained at a N_2 flow rate of 45 sccm.

IV. Conclusion

We fabricated Cu_2O thin films using an RF-reactive sputtering method with the addition of N_2 gas. We found that the N_2 gas has a strong effect on the structural, electrical, and optical properties of Cu_2O and that high-quality Cu_2O films are obtained with a N_2 addition of more than 15 sccm. We expect that our stable Cu_2O thin films can be promisingly used in various applications, such as Cu_2O-based heterojunction solar cells, optical functional films, and antireflection thin films, owing to their superb electrical properties and increased bandgap, which is mainly caused by the preferred orientation of the Cu_2O (200) phase.

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