Controlled growth and properties of p-type cuprous oxide films by plasma-enhanced atomic layer deposition at low temperature

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Various copper oxide films were successfully grown by plasma–enhanced atomic layer deposition (PEALD) at a low temperature of 100°C. X-ray diffraction analysis of the films indicated that phase-controlled deposition of CuO x phases (0 ≤ x < 1) was possible by controlling the number of Cu deposition steps during one PEALD cycle with a fixed oxidation step. When Cu deposition was executed in one step, an amorphous CuO x (x = 0.9) film with a smooth surface (RMS roughness of 0.97 nm) was obtained. On the other hand, when the number of Cu deposition steps was increased to three, a CuO x (x = 0.6) thin film with a polycrystalline phase (grain size: 25 nm) was obtained. The as-deposited CuO 0.6 film showed p-type conductivity (Hall mobility ~37 cm²/V·s and hole concentration ~5.4 × 10¹⁴ cm⁻³). Moreover, p-type CuO 0.6/n-type ZnO heterojunction diodes fabricated on a flexible polyethylene terephthalate substrate exhibited electrical rectification with a threshold voltage of 1.2 V.

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1. Introduction

Cuprous oxide (Cu₂O or CuO₀.₅) – a p-type semiconductor with a band gap of 2.3 eV – has attracted significant interest for application in solar cells and sensors owing to its high light absorption, non-toxicity, and low-cost production [1–5]. Recently, the fabrication of thin-film transistors (TFTs) using Cu₂O has been attempted for realizing p-channel oxide semiconductor devices [6]. Several deposition techniques such as anodic oxidation, [7] thermal oxidation, [8–10] electrodeposition, [11] reactive sputtering, [12,13] chemical bath deposition, [14] and evaporation [15] have been used to prepare Cu₂O thin films. Cu-based oxides have low values of hole mobility, and p-channel TFTs with Cu₂O films exhibit poor performance. Since stable region of Cu₂O in pressure versus temperature equilibrium phase diagram is narrow, Cu₂O easily is changed to two different valence states of Cu⁺ and Cu²⁺ [15]. In most of these processes, post-annealing above 180°C was necessary to obtain high-quality Cu₂O films. Fortunato et al. reported that p-channel device operation was realized after annealing at 200°C for 10h [13]. On the other hand, Yao et al. recently obtained p-channel TFTs fabricated on a sputtered Cu₂O film prepared at room temperature without post-annealing [16]. Meanwhile, K. Akimoto et al. reported that nitrogen doping in Cu₂O film increased hole density by acting as an acceptor, in order to improve the electrical conduction, influenced by point defect concentration [17,18].

Atomic layer deposition (ALD) appears to be a very promising technique for the microelectronic industry owing to its simplicity, reproducibility, high conformality, and self-limiting growth behavior. Therefore, it is expected that high-quality Cu₂O thin films could be prepared by the ALD process. However, to the best of our knowledge, Cu-based oxide semiconductor films deposited by ALD have not been investigated so far. Even though Waechtler et al. adopted a thermal ALD process for depositing copper oxide nucleation layers applicable to electrochemical Cu metallization, they focused only on the growth kinetics on different substrates and did not investigate the electrical properties of Cu₂O films [19].

In this paper, we report Cu₂O thin films deposited by the PEALD process in which the deposition cycle involved two chemical reaction steps – (1) the formation of elemental Cu by using hydrogen plasma as a reducing agent and (2) the subsequent oxidation by using oxygen plasma. The stoichiometry of the deposited films could be easily controlled by changing the number of Cu deposition
Fig. 374 J.-D. Ar

Fig. 1. Schematic diagram of the PEALD cycle for deposition of copper oxide films.

steps; moreover, the phase-controlled deposition of Cu oxide films was also possible. The electrical properties and band alignment of p-type Cu₂O films were investigated. Furthermore, the rectification behavior of a p-type copper oxide/n-type zinc oxide heterojunction was also examined.

2. Experimental

Cu oxide films were prepared on Si(1 0 0) and soda-lime glass substrates at a deposition temperature of 100 °C by the PEALD [Lucida M100, NCD Technology] technique. One PEALD cycle consisted of a Cu deposition step and an oxidation step, as shown in Fig. 1 and Table 1. Hexaflouroacetylacetonate Cu(I) (3,3-dimethyl-1-butene) [(hfac)Cu(I)(DMB)] was used as a Cu precursor and was delivered to the reactor by Ar carrier gas flowing at 40 sccm. For a uniform supply, the temperature of the canister containing (hfac)Cu(I)(DMB) was maintained at 40 °C. In one PEALD cycle, the Cu deposition step consisted of a (hfac)Cu(I)(DMB) pulse of 1 s, a purge pulse of 10 s with 100 sccm Ar, a H₂ plasma pulse of 5 s with 100 sccm H₂, and a purge pulse of 3 s with 100 sccm Ar flow. One oxidation step in the PEALD cycle consisted of an O₂ plasma pulse of 5 s with 100 sccm O₂ flow and a purge pulse of 3 s with 100 sccm Ar flow. The plasma power was maintained at 100 W. In each step, H₂ plasma was used as a reducing agent for depositing Cu and O₂ plasma was as an oxidizing agent for Cu. By varying the number of Cu deposition and oxidation steps in one PEALD cycle, the phase of the deposited copper oxide films was controlled. Table 1 shows a schematic of the PEALD cycle for the deposition of various copper oxide films. Four samples labeled as S1–S4 were used. Letters “a” and “b” denote the number of Cu deposition and oxidation steps, respectively. For the fabrication of p-n-heterojunction diode devices, n-type ZnO (50 nm) was grown on a 100-nm-thick sputtered ITO polyethylene terephthalate (PET) substrate at a deposition temperature of 100 °C by PEALD using diethyl zinc (DEZ, Zn(C₂H₅)₂) and oxygen plasma. Next, without breaking vacuum, a 50-nm-thick Cu₂O film was deposited on the n-type ZnO films/ITO substrate.

To measure the electrical, chemical, optical, and physical properties of Cu₂O (0 ≤ x ≤ 1) films, the thicknesses of the PEALD films were fixed to 40 nm, excluding p-n-heterojunction diode devices (50-nm-thick S1 and S2 films). The film thickness was measured using field-emission scanning electron microscopy (FESEM), and the microstructure of the films was determined by X-ray diffraction (XRD) using Cu-Kα radiation at 1.5405 Å. Further, the film composition was measured by 2.43-MeV He⁺ Rutherford backscattering spectrometry (RBS). The surface morphological properties of the films were analyzed by atomic force microscopy (AFM). Moreover, the resistivity, Hall mobility, and hole density of the films were measured by the van der Pauw method by using a HMS 3000 ECOPIA system at room temperature. The band gap values of the films were measured by spectroscopic ellipsometry (SE) in the energy range 0.75–6.4 eV with incident angles of 65°, 70°, and 75°. The oxidation state of Cu species and the valence band structure of the films were examined by X-ray photoelectron spectroscopy (XPS) performed using a monochromatic Al-Kα (1486.6 eV) source with a pass energy of 20 eV. Finally, the current voltage (I–V) characteristics of p-type copper oxide/n-type zinc oxide heterojunction diodes were measured using a semiconductor parameter analyzer (2636A, Keithley) at room temperature.

3. Results and discussion

Fig. 2 shows the XRD patterns of as-deposited copper oxide films with the number of Cu deposition steps in one PEALD cycle recorded by 2θ scanning. The XRD patterns of all 40-nm-thick copper oxide films were recorded to exclude the effect of thickness on grain growth. Even at a low deposition temperature of 100 °C, all the films except for sample S1 were well-crystallized as identified from their distinct XRD peaks. However, the film phases underwent a drastic change as the number of Cu deposition steps in one PEALD cycle increased. When the number of Cu deposition step in one PEALD cycle was 1, the film (sample S1) contained monoclinic CuO phases. With an increase in the number of Cu deposition steps, however, CuO films sequentially changed to cubic Cu₂O (sample S2), Cu₂O–Cu₂O+ Cu₂O–Cu (sample S3), and cubic-Cu (sample S4) films. Thus, phase-selective deposition of CuO, Cu₂O, Cu₂O+Cu, and Cu films was possible by controlling the number of Cu deposition steps in one PEALD cycle. Samples S1 and S2 were prepared on a carbon substrate to identify their composition by RBS analysis. The composition of sample S1 (CuO,0,9 by RBS) showed the presence of CuO—a phase that is oxygen-deficient in comparison with the theoretical stoichiometry of copper(II) oxide (cupric oxide). However, the composition of sample S2 (CuO,6,0 by RBS) showed the presence of Cu₂O—a phase that is oxygen-rich in comparison with copper(I) oxide (cuprous oxide). It is necessary to define the chemical composition of the deposited copper oxide films by analyzing their XPS spectra. However, the oxidation states of Cu²⁺ and Cu⁰ cannot be differentiated by analyzing the XPS core-level spectra of Cu.

Table 1

Summary of PEALD cycle design for preparing copper oxide films. Samples S1, S2, S3, and S4 denote that the number of Cu deposition steps is 1, 3, 5, and 7, respectively.

<table>
<thead>
<tr>
<th>Samples (a,b)</th>
<th>Number of each step in Cu–O cycle for Cu deposition Step</th>
<th>Oxidation Step</th>
</tr>
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<tbody>
<tr>
<td>S1 (1,1)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>S2 (3,1)</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>S3 (5,1)</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>S4 (7,1)</td>
<td>7</td>
<td>1</td>
</tr>
</tbody>
</table>
2p_{1/2} because the binding energies of these states are superimposed [19–21].

Thus, high-resolution XPS spectra of Cu LMM of samples S1, S2, and S3 were investigated, as shown in Fig. 3. The kinetic energy of a Cu LMM peak was obtained by subtracting the binding energy from the X-ray incident beam energy (1486.6 eV) of aluminum. The spectrum was referred to the Au 4f_{9/2} core level (83.98 eV) of a sputtered gold standard. All the samples showed deconvoluted Cu LMM peaks centered at 918.5, 917.7, and 916.7 eV that were assigned to metallic Cu (Cu^0), Cu^{2+}, and Cu^{+}, respectively [21]. The uncertainty of the deconvoluted peaks was ±0.1 eV. Figure 3(d) shows the area ratios of peak with Cu^0, Cu^{2+}, and Cu^{+} per total area. As the number of Cu deposition steps increased, the area ratio for the Cu^{2+} state decreased from 53 to 13% while the area ratios for Cu^0 and Cu^{+} increased from 27 to 60% and from 20 to 27%, respectively. This observation implies that with an increase in the number of Cu deposition steps, the amount of Cu-rich phases such as CuO or Cu increased more than that of cupric oxide. The area ratios of Cu and CuO phases indicated that they constituted nearly half of sample S1 for single-step Cu deposition, even though the XRD spectrum for S1 showed a monoclinic CuO phase. During a Cu deposition step, [[hfac]Cu(1)(DMB)] was adsorbed onto the CuO substrate, and the Cu precursor was then exposed to hydrogen plasma to form elemental Cu. However, in this step, the hydrogen plasma could reduce CuO to Cu or CuO because the Cu precursor did not fully cover the CuO substrate owing to the steric hindrance of the Cu precursor [22]. Therefore, the presence of an oxygen-deficient phase (CuO_{0.9}) can be attributed to the subsequent phase transformation of CuO to Cu or CuO under exposure to the hydrogen plasma. In the case of sample S2, the use of oxygen plasma for obtaining CuO in the oxidation step might have resulted in the formation of an oxygen-rich phase (CuO_{0.6}) by subsequent transformation of Cu or CuO to CuO. To investigate the surface morphological properties of as-deposited copper oxide films, the samples were subjected to AFM analysis. Fig. 4 shows the AFM images of as-deposited copper oxide films with the number of Cu deposition steps. When the number of Cu deposition step in one PEALD cycle is 1, CuO_{0.9} (sample S1) showed a very low root mean square (RMS) value of 0.97 nm for the surface roughness. However, upon increasing the number of deposition steps to 3 (sample S2), 5 (sample S3), and 7 (sample S4), the RMS values of surface roughness of the films gradually increased to 1.04, 1.14, and 4.29 nm, respectively. Generally, Cu films obtained by ALD have been reported to be rough because of a low number of nucleation sites and a strong agglomeration tendency, depending on substrates such as silica, refractory metals, or refractory metal nitrides [23,24]. This fact implies that the surface morphologies of copper oxide films would be strongly related to the ALD growth rates owing to the varying density of adsorption sites and different modes of chemisorption on the substrate. Interestingly, the variations in the morphologies of the films may be in agreement with the PEALD growth rate, showing that the growth rate for samples S1, S2, S3, and S4 in one PEALD cycle was 0.08, 0.086, 0.11, and 0.15 nm/cycle, respectively.

Fig. 5 shows the plane-view TEM images and diffraction patterns of samples S1, S2, and S3. The grains and grain boundaries cannot be observed clearly in the image for sample S1. Moreover, the diffraction pattern for sample S1 exhibited shadowed fuzzy rings. These observations imply that sample S1 consisted of an almost amorphous phase. However, the high-resolution plane image of sample S1 showed its lattice structure and nanosized grains; this observation indicates that sample S1 had a nanocrystalline structure.
Fig. 4. AFM images of samples (a) S1, (b) S2, (c) S3, and (d) S4. The root mean square (RMS) roughness values for each sample are also indicated.

with an amorphous matrix. As the number of Cu deposition steps increased, the grain sizes of samples S2 and S3 increased to 20–30 and 40–60 nm, respectively. The diffraction pattern of sample S2 and S3 showed to coincide with ring pattern of cubic structured Cu2O thin film, and that of cubic structured Cu thin film. The growth in the grain size of the copper oxide films with an increase in the number of Cu deposition steps could be attributed to the strong agglomeration tendency such as the aspect of surface roughness. Among the deposited copper oxide films, CuO0.9 (sample S1) and CuO0.6 (sample S2) films were subjected to Hall measurement for investigating their semiconductor properties. The CuO0.6 film exhibited a p-type property with a Hall mobility of ~37 cm²/Vs and a carrier concentration of ~5.4 × 10¹⁴ cm⁻³; however, the properties of the as-deposited CuO0.9 film could not be measured (out of order, <10¹¹ cm⁻³). Although both CuO0.9 and CuO0.6 films are well-known p-type semiconductors [25,26], the as-deposited PEALD CuO0.9 film did not show the p-type property, which could have resulted from very low film crystallinity (Fig. 2). The electrical conductivity of the deposited films was measured by the transfer length method [27]. The conductivities of samples S1, S2,

Fig. 5. Plane-view TEM images and diffraction patterns for samples (a) S1, (b) S2, and (c) S3. (d), (e), and (f) show diffraction patterns for S1, S2, and S3.
S3, and S4 were $1 \times 10^{-6}$, $5.2 \times 10^{-3}$, $1.4 \times 10^{2}$, and $1.3 \times 10^{5}$ S/cm, respectively. As the number of Cu deposition steps increased, the conductivity of the films also increased, similar to the metal. On the basis of Hall measurement results and XRD spectra, the low conductivity ($1 \times 10^{-6}$ S/m) of the CuO0.9 film (sample S1) was attributed to its low carrier concentration and crystallinity.

In order to investigate the band alignment in the band gap and the relative position of the Fermi level with respect to the valence band maximum ($\Delta E_{VB}$) of the CuO0.9 and CuO2.6 films, these films were analyzed by SE and XPS, as shown in Fig. 6. The optical band gap of the CuO0.9 film was 1.96 eV, which is higher than that of CuO (1.2 eV) [28]. This high optical band gap of the CuO0.9 film can be attributed to the energy gap confinement effect due to a quantum phenomenon [28]. For nanosized grains, a decrease in the distance between charged carriers increases the interaction energies, and this increase contributes to the high optical band gap. In addition, according to the XPS spectrum shown in Fig. 3, the incorporation of CuO could also have led to an increase in the optical band gap. The optical band gap (~2.47 eV) of the CuO0.6 film is almost equal to previously reported values (2.0–2.3 eV), and its Fermi energy position ($E_F$) is close to the valence band maximum, which directly confirms that the CuO0.6 film is a p-type semiconductor. Moreover, the $\Delta E_{VB}$ value (~0.29 eV) of the CuO film implied the compensated semiconductor with one acceptor level at 0.3 eV resulted from some defects (an oxide ion and a cation) in CuO0.6, as per the simple electronic model proposed by Brattain [29].

The thermal-equilibrium concentration ($p_0$) of holes in a p-type extrinsic semiconductor is given by the following equation [30].

$$p_0 = n_i \exp \left( \frac{E_F - E_F}{kT} \right)$$

where $n_i$ is intrinsic carrier concentration, $E_F$ is Fermi energy, $E_F$ is intrinsic Fermi energy, $k$ is Boltzmann constant, and $T$ is temperature. The value of ($E_F - E_F$) for the CuO0.9 film was 0.28 eV, which was less than that for the CuO0.6 film (0.95 eV). This low value for the CuO0.9 film implies a low hole carrier density that corresponds with the immeasurable results for this film in the Hall measurement (out of order, $<10^{11}$ cm$^{-3}$).

To investigate the electrical properties of p-type CuO (0.5 $\leq x < 1$) films, flexible and transparent heterojunction diodes were fabricated on a PET substrate with PEALD CuO0.6 and ZnO films at a low temperature of 100 °C. Fig. 7(a) shows the flexible and transparent heterojunction diodes with the following stacked structure: Au(50-nm-thick)/CuO(50-nm-thick)/n-ZnO(100-nm-thick)/ITO/Au (Fig. 7 (b)). As mentioned above, p-type CuO films showed wide band gap properties (over 2 eV) and were transparent under visible-region wavelengths (400–800 nm). Au disk electrodes were used to make an ohmic contact with the p-type Cu2O film. The fabricated diodes were not subjected to any additional post annealing and/or plasma treatment. Fig. 7(c) and (d) show the $I-V$ characteristics of p-type Cu1O0.9 (sample S1) and Cu2O1.25 (sample S2) heterojunction diodes, respectively. The $I-V$ characteristics of samples S3 and S4 are not shown because they
did not show any rectifying behavior (metallic behavior). Since the ohmic behavior of both Au/p-type CuOx and ZnO/ITO contacts were confirmed to be in the range –1.5–+1.5 V, it can be concluded that their rectification originated from the CuOx/ZnO heterojunction. Interestingly, the turn-on voltages for each diode were quite different in the case of CuOx/ZnO heterojunction. Therefore, CuOx/ZnO and Cu2O/ZnO heterojunction diodes were fabricated; these diodes exhibited excellent electrical rectification with a threshold voltage of 1.2 V without any post-annealing process. The observed properties of the Cu2O1.25 film and distinct rectification properties of the diodes suggest that PEALD can be a viable technique for constructing Cu2O-based semiconductor devices including diodes, photovoltaics, and complementary metal-oxide-semiconductor integrated devices.

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References


