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Tuning the structure and preferred orientation in reactively sputtered copper oxide thin films

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ABSTRACT

Binary copper oxide (Cu_2O, Cu_4O_3 and CuO) thin films have been selectively deposited on glass and silicon substrates by magnetron sputtering at room temperature from a metallic copper target in various Ar–O_2 reactive mixtures. The influence of oxygen flow rate and total pressure on the film structure and its preferred orientation has been studied. A schematic deposition diagram, which describes the film structure as a function of O_2 flow rate and total pressure, is depicted by combining X-ray diffraction and Raman spectrometry. The oxygen flow rate process windows for Cu_2O or Cu_4O_3 single phase synthesis are narrow, while that for CuO is wider. Between two single phase domains, biphase films are systematically deposited. It is found that the deposition total pressure is a relevant parameter to control the texture and the morphology of pure Cu_2O and Cu_4O_3 films. Low total pressure favors the growth of planes with high surface energy ((1 0 0) for Cu_2O and (1 0 1) for Cu_4O_3) parallel to the substrate. On the other hand, high total pressure facilitates the growth of planes with low surface energy ((1 1 1) for Cu_2O and (1 0 0) for Cu_4O_3). The oxygen flow rate is effective to control the preferred orientation of CuO thin films that evolves from ⟨1 1 1⟩ to ⟨$\bar{1}$ 1 1⟩ with the increase of oxygen flow rate. These results are supported by transmission electron microscopy observation in cross section.

1. Introduction

The copper abundance and its non-toxicity have attracted much attention to the synthesis of p-type copper oxides semiconductors, Cu_2O, Cu_4O_3 and CuO, that exhibit high potential applications in energy conversion and storage [1–5]. Among these three oxides, the stable Cu_2O (cuprite) phase with an optical band gap of 2.38–2.51 eV at room temperature [6], has been intensively studied for application in low-cost solar cells during the past two decades [2,3,7], due to its theoretical conversion efficiency of about 20% [8]. Besides, Cu_2O has also been considered as a promising photocatalyst for direct water splitting into H_2 and O_2 under visible-light irradiation [9]. The stable CuO (tenorite) phase is of interest for Li-ion battery electrodes due to its low-cost, high stability, environmental friendliness and high theoretical capacity (674 mAh g^{-1}) [10–12]. On the other hand, the metastable Cu_4O_3 (paramelaconite) phase, an intermediate compound between Cu_2O and CuO, has received less attention and its properties are still unclear [13–15]. More recently, Cu_4O_3 has also been found to be attractive for Li-ion batteries due to its unique lithium storage behavior at low voltage range and superior electrochemical performance [5]. In addition, the presence of Cu_4O_3 in a binary copper oxide (Cu–O) light absorber of photovoltaics can enhance the photovoltaic activity significantly, indicating its potential solar cell applications [4].

For scientific research or technological applications, it is of great interest to fabricate binary copper oxide thin films with high quality. Up to now, most of the usual deposition methods have been used to grow Cu_2O and CuO thin films, including magnetron sputtering [14,15], molecular beam epitaxy [16], pulsed laser deposition [17,18], electrochemical deposition [19,20], and sol–gel [21]. Since it is difficult to stabilize Cu^{2+} and Cu^{+} ions simultaneously via conventional aqueous chemistry, it is hard to synthesize pure Cu_4O_3 by electrochemical deposition and sol–gel methods. The synthesis of pure Cu_2O phase by pulsed laser deposition or molecular beam epitaxy usually requires high temperature that limits its wide applications [16–18]. Among the various thin film deposition technologies, reactive magnetron sputtering is a good choice to grow binary copper oxides, as it allows the selective deposition of the

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three copper oxides, including Cu_4O_3 [14,15], and is a highly versatile technique for large area deposition at low cost.

The crystal growth orientation of thin films has great impact on the microstructure and properties of films. Since the Cu_2O preferred orientation may change the interface states and the photon absorption efficiency at the interface, it strongly influences the efficiency of solar cells [22,23]. Similarly, {1 1 1} surfaces of Cu_2O exhibit a higher photostability than other planes, indicating the dependence of the photocatalytic properties on the growth orientation [9]. Besides, the texture and microstructure of CuO Li-ion battery electrodes are found to be tightly related to the performance [24]. Thus, it is interesting to grow copper oxide thin films with tunable preferred orientation. Several parameters may be used to control the film growth in magnetron sputtering processes such as oxygen partial pressure, total pressure, substrate orientation, substrate temperature, and the use of a buffer or seed layer [25–28]. Although lattice-matched substrates and high substrate temperature have typically been employed to tune the growth orientation, the harsh conditions are undesirable for large scale applications at low cost. Hence, controlling the growth orientation using conventional substrates with random orientation at room temperature will extend the application range of copper oxide thin films.

In this work, we have investigated the selective growth of the three copper oxide thin films by reactive magnetron sputtering on glass and silicon substrates at room temperature. The influence of the oxygen flow rate and total pressure on the phase structure, growth orientation, morphology and microstructure of thin films have been studied.

2. Experimental details

Copper oxide thin films were deposited on glass substrates (microscopy slides) and (1 0 0) silicon substrates by magnetron sputtering in various $Ar–O_2$ reactive mixtures. During the deposition, no intentional heating was applied to the substrates, and the deposition temperature was close to room temperature. The argon flow rate was fixed at 25 standard cubic centimeter per minute (sccm), while the oxygen flow rate varied in the 7–25 sccm range. Thin films were deposited at different total sputtering pressures (0.5, 1 and 2 Pa) by changing the pumping speed via a throttle valve. A pulsed-DC supply (Pinnacle+ Advanced Energy) was used to sputter the copper target (50 mm diameter and 3 mm thick with a purity of 99.99%). The current applied to target was fixed to 0.3 A, the frequency and the off-time were 50 kHz and 4 μs, respectively. The distance between the substrate and the target was fixed at 60 mm.

The film thickness was measured by a Talysurf tactile profilometer (see the supporting information). The phase structure and growth orientation of thin films were checked by X-ray diffraction (XRD, Brucker D8 Advance with Cu $K_{\alpha 1}$ radiation ($\lambda = 0.15406$ nm) in Bragg Brentano configuration). Micro-Raman spectrometry (Horiba LabRAM HR using a 532 nm laser) was also employed to indentify the phase structure. Transmission electron microscopy (TEM) investigation for the microstructure was performed by a JEOL ARM 200-Cold FEG (point resolution 0.19 nm) fitted with a GIF Quantum ER. For this investigation, the cross-section TEM samples of films deposited on silicon substrates were prepared using a focused ion beam (FIB)-scanning electron microscope (SEM) dual beam system (FEI Helios 600) using the 'in situ' lift-out technique. Final thinning was done with low voltage milling (5 kV) to reduce any possible preparation artifact. The morphology of thin films was observed by a FEI Helios 600 SEM. Films deposited on silicon and glass substrates showed the same structure, preferred growth orientation and morphology (see the supporting information). In this article, if there was no intentional specification, the X-ray diffractograms, Raman spectra and SEM images were obtained from films deposited on glass substrates, while the TEM images were acquired from films deposited on silicon substrates.

3. Results and discussion

3.1. Structure of copper oxide films

Fig. 1 shows the X-ray diffractograms of copper oxide thin films grown on glass substrate at 0.5 Pa total pressure with different oxygen flow rates (12, 16, 19, 21, and 22 sccm). Depending on the oxygen flow rate, the width of the diffraction peak is high, indicating the deposition of oxides with grain size at the nanometer scale. Furthermore, the use of a low deposition pressure (0.5 Pa) induces highly stressed materials and the position of the diffraction peaks may be affected by this stress. Finally, since the three copper oxide phases present diffraction peaks close to 36°, the assignment of the diffraction peak as a function of the oxygen flow rate is a hard task. The (1 1 1) diffraction peak of Cu_2O is located at 36.428° [JCPDS 04-007-9767], while (2 0 2) and (0 0 4) diffraction peaks of Cu_4O_3 are at 35.787° and 36.342°, respectively [JCPDS 04-007-2184]. Moreover, (0 0 2) and ($\bar{1}$ 1 1) diffraction peaks of CuO are located at 35.468° and 35.559° [JCPDS 04-007-1375]. However, the increase of the oxygen flow rate in the deposition chamber should induce an increase of the oxygen concentration of the deposited films, which may be a helpful indication to assign the X-ray diffractogram.

For an oxygen flow rate fixed at 12 sccm, the intense peak close to 42.3° has been assigned to the (2 0 0) diffraction peak of cuprite. This sample also exhibits a weak diffraction peak close to 36.3° that may be assigned either to the (1 1 1) diffraction peak of Cu_2O or to the (0 0 4) of Cu_4O_3. For the oxygen flow rate fixed at 16 sccm, the intensity of this peak strongly increases while that observed at 42.3° is still intense. If the oxygen flow rate is increased to 19 sccm, new diffraction peaks located at approx. 18°, 31° and 61.4° are detected. These peaks have been assigned to the paramelaconite Cu_4O_3. For the thin film grown at the oxygen flow rate of 21 sccm, the X-ray diffractogram shows an X-ray amorphous material (see Fig. 1(b)). Hence, it seems that the use of XRD as the only characterization method is not relevant to clearly distinguish the phase structures in these binary copper oxide polycrystal thin films.

Since Cu_2O, Cu_4O_3 and CuO have different Raman active vibrational modes [29], Raman spectrometry is a good complementary method to determine the film phase structure. Fig. 2 shows the Raman spectra of the copper oxide thin films previously characterized by XRD in Fig. 1. For films deposited at 19 sccm of oxygen, the E_g (311 and 505 cm^{-1}) and A_{1g} (531 cm^{-1}) Raman bands of Cu_4O_3 are clearly evidenced. This result is in agreement with that from XRD, indicating the use of 19 sccm in our deposition conditions leads to the synthesis of pure paramelaconite thin films. These two Raman bands are also evidenced for the films deposited at 16 sccm oxygen, accompanied by some new bands at approx. 93, 147 and 216 cm^{-1} that have been ascribed to defects, non-stoichiometry and resonant excitation in Cu_2O [30]. This demonstrates the formation of a biphase microstructure of $Cu_2O + Cu_4O_3$. Since the Raman bands of paramelaconite are not detected in the film deposited at 12 sccm anymore, this sample only contains the Cu_2O phase and the weak diffraction peak close to 36.3° is related to the Cu_2O (1 1 1) diffraction peak (Fig. 1(a)). Moreover, when the oxygen flow rate is increased to 21 sccm, Raman analysis shows besides the A_{1g} band of Cu_4O_3, the existence of a new band close to 288 cm^{-1} that corresponds to the CuO phase. Hence, this indicates the 21 sccm oxygen flow rate results in the deposition of an X-ray amorphous mixture of Cu_4O_3 and CuO. Here it should be pointed out that TEM analyses show a nanocrystalline character of this biphase thin film, rather than a real amorphous one. Finally, when the oxygen flow rate is fixed at 22 sccm, the Raman bands of Cu_4O_3 disappear and