Applied Surface Science 435 (2018) 305–311

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Pulsed-laser-deposited, single-crystalline Cu_2O films with low resistivity achieved through manipulating the oxygen pressure

Xiaohui Liu[a], Meng Xu[a], Xijian Zhang[a], Weiguang Wang[a], Xianjin Feng[a,*], Aimin Song[a,b]

[a] Center of Nanoelectronics and School of Microelectronics, Shandong University, Jinan, 250100, China
[b] School of Electrical and Electronic Engineering, University of Manchester, Manchester, M13 9PL, United Kingdom

ARTICLE INFO

Article history:
Received 23 July 2017
Received in revised form
13 November 2017
Accepted 14 November 2017

Keywords:
Copper oxide
PLD
Epitaxial
Oxygen pressure

ABSTRACT

Low-resistivity, single-crystalline Cu_2O films were realized on MgO (110) substrates through manipulating the oxygen pressure (P_{O2}) of pulsed-laser deposition. X-ray diffraction and high resolution transmission electron microscopy measurements revealed that the films deposited at P_{O2} of 0.06 and 0.09 Pa were single phase Cu_2O and the 0.09-Pa-deposited film exhibited the best crystallinity with an epitaxial relationship of Cu_2O (110)‖MgO (110) with Cu_2O (001)‖MgO (001). The pure phase Cu_2O films exhibited higher transmittances and larger band gaps with an optical band gap of 2.56 eV obtained for the 0.09 Pa-deposited film. Hall-effect measurements demonstrated that the Cu_2O film deposited at 0.09 Pa had the lowest resistivity of 6.67 Ω cm and highest Hall mobility of 23.75 $cm^2 v^{-1} s^{-1}$.

1. Introduction

Depending on the crystal bonding and structure between the metal cation and oxygen, metal oxides show quite different functional properties. Metal oxides could exhibit magnetic, insulating, conducting and semiconducting properties [1]. Metal oxide semiconductors were applied to fabrication of various devices such as light emitting devices, thin film transistors (TFTs) and solar cells [2]. Cuprous oxide (Cu_2O) is a well-known p-type semiconductor. It has a direct band gap (E_g = 2.0–2.6 eV) [3–7] and can exhibit a hole mobility exceeding 100 $cm^2 v^{-1} s^{-1}$ at room temperature [8]. Cu_2O is also regarded as one of the promising functional materials for its abundance, nontoxicity and large optical absorption coefficient [9]. There are many reports on Cu_2O-based solar cells and thin film transistors [10–14]. However, the highest reported energy conversion efficiency of Cu_2O solar cells was only around 6.1% with the Cu_2O active layer formed through oxidation of Cu sheets [12] even though the maximum theoretical conversion efficiency is 20% [15]. For Cu_2O thin film transistors, the performance is also unsatisfactory. Yao et al. demonstrated a p-type TFT formed by sputtered Cu_2O, showing a field effect mobility of ~2.40 $cm^2 v^{-1} s^{-1}$ and an on/off current ratio of $\sim 3.96 \times 10^4$ [13]. Using the atomic layer deposition method, Maeng's group fabricated a p-type Cu_xO TFT with a field effect mobility of 5.64 $cm^2 v^{-1} s^{-1}$, an on/off current ratio of 1.79×10^5, and a subthreshold swing of 0.75 V/decade [14]. Because the film crystal orientation and microstructure as well as the electrical properties could not be well controlled in most of the previously reported Cu_2O films, Cu_2O-based functional devices have not shown good performance. It is therefore necessary to obtain high quality Cu_2O films with good electrical properties (high Hall mobility, proper resistivity) in order to further improve the performance of Cu_2O-based functional devices [16].

During the past years, in order to obtain high quality Cu_2O films, many methods such as sputtering [5], thermal oxidation [10], evaporation [17], molecular beam epitaxy [18], and electrodeposition [19] have been used. Due to the high kinetic energy of the ionized and ejected species in the laser produced plasma, pulsed-laser deposition (PLD) technique could deposit highly oriented crystalline films at low substrate temperatures [20,21]. Furthermore, PLD is very suited to stoichiometric growth due to its operating far away from equilibrium [22]. However, until now, there are only a few reports on Cu_2O films prepared by PLD and the influence of oxygen pressure (P_{O2}) during the deposition on the film properties was especially rarely studied [23,24]. Moreover, the reported pulsed-laser deposited Cu_2O films usually had high electrical resistivities in the range of 10^2–10^5 Ω cm [24–26], which are not suitable to be used in both solar cells and thin film transistors. It is well-known that the optimum resistivity for the absorber layer in a solar cell is around 0.1–1 Ω cm [27]. While for high performance thin film transistors, the typical carrier concentration of the channel layer is usually in the range of 10^{16}–10^{17} cm^{-3} [28,29] with a Hall mobility

* Corresponding author.
E-mail address: xianjinfeng@sdu.edu.cn (X. Feng).

https://doi.org/10.1016/j.apsusc.2017.11.119
0169-4332/

higher than 10 $cm^2 v^{-1} s^{-1}$ (normally the higher the better), leading to a resistivity value lower than 10^2 Ω cm.

In this work, copper oxide films were prepared on MgO (110) substrates by PLD and the structural, optical and electrical properties of the films as a function of P_{O2} were investigated in detail. MgO (110) was chosen as substrate because the lattice mismatch between MgO and Cu_2O is very small (~1.4%), and the Cu_2O (110) plane has relatively lower surface free energies than other planes making it easier to be epitaxially grown [30]. High quality single-crystalline Cu_2O film with a low electrical resistivity of 6.67 Ω cm and a high Hall mobility of 23.75 $cm^2 v^{-1} s^{-1}$ was obtained through manipulating the oxygen pressure, which may have promising applications in solar cells and thin film transistors.

2. Experimental

High vacuum PLD system with a KrF excimer laser (wavelength: 248 nm, pulse duration: 20 ns, pulse frequency: 20 Hz) and a ceramic Cu_2O target (4N purity) was used to deposit the copper oxide thin films. MgO (110) single crystals substrates were mounted 8 cm away from target in the PLD chamber with a base pressure under 10^{-4} Pa. The laser energy density was ~6 J/cm^2 at the target surface. Growth condition was varied in the range of P_{O2} = 0.02–0.12 Pa at a fixed substrate temperature of 600 °, where Cu_2O is the stable phase in a phase equilibrium diagram [31].

The out-of-plane θ-2θ and in-plane Φ and $2\theta\chi$-scans were measured using respectively the Rigaku and Philips X'Pert PRO X-ray diffractometers (XRD) to determine the crystalline quality and epitaxial relationship. A FEI Nova NanoSEM 450 field emission scanning electron microscope (SEM) was used to observe the surface morphology. The atomic arrangements across the substrate-film interface were observed using high resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) with a Tecnai F30 transmission electron microscope operated at 300 kV. The chemical composition was measured by the X-ray photoelectron spectroscopy (XPS) using an ESCALAB MK II multi-technique electron spectrometer. A TU-1901 double-beam UV–vis-NIR spectrophotometer was used to measure the optical transmittance. The electrical properties were measured by Van der Pauw method.

3. Results and discussion

The crystallinity of the as-grown copper oxide films was investigated by XRD. Fig. 1(a) shows typical patterns of θ-2θ scan for the copper oxide films deposited under representative oxygen pressures. Besides the substrate diffraction peak of MgO (220) located at 62.4° (JCPDS No. 65-0476), five other peaks located respectively at 29.5°, 42.1°, 43.6°, 60.8° and 73.5° can be seen at 0.02 Pa, which are identified as Cu_2O (110), Cu_2O (200), Cu (111), Cu_2O (220) and Cu_2O (311) (JCPDS No.65-3288 for Cu_2O, No.04-0836 for Cu), indicating the presence of a mixed phase of Cu_2O and Cu. With the increase of P_{O2} to 0.06 Pa, the Cu (111) peak disappears, indicating the existence of single phase Cu_2O. For the sample fabricated under P_{O2} of 0.09 Pa, only the Cu_2O (110) and (220) peaks can be observed in addition to the substrate peak, indicating that a single orientation along the Cu_2O (110) direction is obtained. With the further increase of P_{O2} to 0.12 Pa, the CuO (020) and (310) peaks (JCPDS No. 48-1548) as well as the Cu_2O (200) peaks are visible, indicating a mixed phase of Cu_2O and CuO and the degradation of film crystalline quality. It should be noticed that, due to the close 2θ values of CuO (221) and Cu_2O (311) reflections, the peak at around 73.5° is hard to distinguish for the 0.12 Pa-deposited sample and therefore it may be considered as a combined peak of these two reflections. While for the 0.02 and 0.06 Pa-deposited samples, considering the pure Cu_2O phase of the film grown at 0.09 Pa, it is reasonable to assign this peak to Cu_2O (311) rather than CuO (221) for the films prepared at such lower oxygen pressures.

It is well-known that the Cu-O phase is strongly influence by the thermodynamic conditions (substrate temperature and oxygen pressure). However, for the non-equilibrium physical vapor deposition process PLD, the increase of total chamber pressure i.e. the oxygen pressure in our study can also alter the plasma dynamics by changing the target-to-substrate transport from the ballistic to the diffuse regime, which in turn can result in the formation of different Cu-O phases [32]. Therefore, the Cu-O phase transition in our study could be attributed to the combination of pressure related kinetic and thermodynamic effects. The results of XRD measurement reveal that the film structure and crystallinity are strongly influenced by oxygen pressure and the 0.09 Pa-deposited film has the best crystalline quality.

Fig. 1(b)–(e) show the plan view SEM images of copper oxide films deposited under P_{O2} of 0.02, 0.06, 0.09 and 0.12 Pa, respectively. In Fig. 1(b), submicron particles can be observed on the surface of the 0.02 Pa-deposited film, for which metallic Cu that mainly exists at the surface of the particles is assumed to act as a catalyst of their growth [32]. Fig. 1(c) exhibits irregular grains and disordered grain edges due to the polycrystalline structure of this sample. In Fig. 1(d), a compact surface with regularly-shaped islands and well-defined boundaries could be observed, which corresponds to the best crystallization of the sample prepared at 0.09 Pa. A surface with ill-defined grain formation is observed for the film deposited under 0.12 Pa as shown in Fig. 1(e), due to the mixed phase of this sample as revealed by the XRD analyses. As mentioned above, the plasma dynamics and therefore the growth mode of the films in our study can be influenced by the different oxygen pressures. The variation of growth mode together with the Cu-O phase transition will result in the different observed film surface morphologies. The SEM analyses illustrate obviously that the oxygen pressure has a strong influence on the film morphology and crystallinity, which are consistent with the XRD results.

The off-specular Φ-scan of Cu_2O {111} planes (Ψ = 35.26°) for the 0.09 Pa-deposited film is shown in Fig. 2(a). Two diffraction peaks separated by 180° of the Cu_2O {111} planes indicate a good in-plane alignment inside the film. The {111} plane of Cu_2O is two-fold symmetrical along Cu_2O [110], which is consistent with Fig. 2(a), indicating a complete single-crystalline structure without any domains in the obtained film. Fig. 2(b) shows the off-specular Φ-scan of MgO {111} planes (Ψ = 35.26°) for the substrate, from which two diffraction peaks separated by 180° with the same Φ-angles as the Cu_2O {111} planes could be seen, indicating that the crystal lattices for both materials are aligned in-plane with an epitaxial relationship of Cu_2O (110)‖MgO (110) and Cu_2O (001)‖MgO (001). To further confirm that the peaks in Fig. 2(a) are really from the film and not the tail end of the substrate peaks, we have performed the in-plane $2\theta\chi$-scan of the sample at the fixed Φ and Ψ angles, as shown in Fig. 2(c). Only two distinct peaks of Cu_2O (111) and MgO (111) can be seen obviously, confirming the (111) reflections from the substrate and film are distinguishable. These results reveal that the Cu_2O film deposited under the P_{O2} of 0.09 Pa is epitaxial single crystal with no twins and the epitaxial relationship is Cu_2O (110)‖MgO (110) with Cu_2O (001)‖MgO (001).

The cross-sectional TEM measurements were performed to further study the atomic arrangements and microstructure of the sample deposited under P_{O2} of 0.09 Pa. From the low magnification TEM image as shown in Fig. 3(a), a compact film without any columnar structures inside as well as a clean and sharp interface between the film and the substrate are observed. The HRTEM image of the interface between the Cu_2O film and MgO substrate and the SAED pattern of the Cu_2O film are shown respectively in Fig. 3(b) and (c). The incident electron beam was parallel to the [10] direction