



The improvement of hole transport property and optical band gap for amorphous Cu₂O films



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ARTICLE INFO

Article history:

Received 18 February 2015
Received in revised form
16 June 2015
Accepted 17 June 2015
Available online 20 June 2015

Keywords:

Amorphous Cu₂O
Hole transport behavior
Density of states
Blue shift

ABSTRACT

This work presents an interesting observation that the suppression of crystallization for p-type Cu₂O facilitates the transition of transport behaviors from variable-range-hopping (VRH) to Arrhenius-like mechanism and further lead to a great reduction of thermal activation energy. Raman spectroscopy analysis shows a distortion of symmetrical O–Cu–O crosslink structure in the amorphous Cu₂O. The disruption of symmetry is revealed to increase dispersion of upper valence band and reduce Fermi as well, which results in possible intrusion of the Fermi level into a band tail state adjacent to the upper valence band level. Meanwhile, the amorphous Cu₂O film shows an optical band gap of 2.7 eV, much larger than 2.0 eV for the crystalline counterparts. The blue shift is consistent with the variation of energy band structure with the film changing from crystalline to amorphous state, suggesting that the O-mediated d–d interaction can be weakened with the nonsymmetrical structure in amorphous phase.

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1. Introduction

Transparent conductive oxides (TCOs) continue to be attractive due to their great potential for the applications of solar cells, flat-panel displays and other optoelectronic devices [1–3]. However, those applications in the visible electronic devices based on transparent pn junction are rather restricted due to absence of high performance p-type TCOs. For example, the well-known p-type cuprous oxide (Cu₂O) is naturally poor conductive, which is caused by the localization of positive holes around the negatively charged oxygen ions [4,5]. Nonetheless, the oxide remains promising due to its abundance in nature and environmental friendliness. Therefore, much effort has been made on investigating the effects on its conductivity of pressure, sputtering temperature, crystal orientations as well as doped elements [6–10], in an attempt to improve the conductive performance. Doped Cu₂O is one of the promising ways for increasing the conductivity. Firstly, the doping leads to formation of Cu^(I)-based delafossite group, resulting in modification of the energy band structure and thereby weakening the localization behavior of holes [11,12], which, however, needs high-quality crystalline oxide and raises requirements for the related fabrication process control [9,13]. Secondly, the doping may

increase hole concentrations while keeping the cuprite structure of Cu₂O nearly unchanged. However, the doped oxide is often accompanied with reduction of mobility, thereby hardly leading to an improvement of the conduction.

Recently, several amorphous oxides were reported to have larger hole mobility and hole concentration with respect to their crystalline counterparts [14–16]. In our previous work, we also observed that the cuprous oxide in an amorphous state shows several orders of magnitude larger conductivity than crystalline Cu₂O and even comparable to some of the delafossite oxides which need complex and expensive fabrication technologies [9,17]. In addition, with the capability of uniform and large-area deposition at room temperature, the amorphous oxides have attracted a growing interest as a promising choice for large-area optoelectronic applications [18,19]. Thus, it is of scientific interest and practical significance to understand physical origin underlying the enhancement of hole conduction in the amorphous Cu₂O, especially from the perspective of energy band variations.

On the other hand, Cu₂O has a narrow band gap with the theoretical value of only 2.17 eV [20], which is another limitation for its practical applications in the related transparent devices. Up to date, doping of some third elements into Cu₂O has been reported to broaden the band gap [21]. From the theoretical study by M. Nolan et al. [22], the doping brings about distortion of O–Cu–O network and in turn reduces the Cu–Cu interaction, leading to the increase

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of optical band gap. In this respect, it can be anticipated that the optical band gap of amorphous phase might be increased as compared to that of the crystalline due to the distorted lattice structure of the former.

In this work, p-type amorphous Cu_2O film with cuprite structure was prepared using magnetron sputtering method. Temperature dependent conductivity has been investigated, together with the theoretical calculation and experimental measurement of energy band structure. The suppression of crystallization is observed to result in Arrhenius-like transport characterization as well as the widening of optical band gap.

2. Experimental and theoretical methods

The oxide films were deposited at room temperature by reactive magnetron sputtering method. Impulse and radio frequency power supplies were applied to adjust the crystallization of the films. A detailed description of the deposition can be seen elsewhere [17]. The $\text{Cu}_2\text{O}_{\text{c1}}$ and $\text{Cu}_2\text{O}_{\text{c2}}$ are crystalline films with different grain sizes, while the $\text{Cu}_2\text{O}_{\text{c}+\alpha}$ is two phase structure with grains existing in amorphous phase and the $\text{Cu}_2\text{O}_{\alpha}$ is in an amorphous state, which were confirmed using X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) [17]. Temperature dependence of electrical property was investigated in the range from 100 to 300 K by using physical property measurement system (Quantum Design PPMS - 9T). Raman spectroscopy measurement was made on the oxide films using Renishaw inVia-Reflex with 532 nm line emitted from an argon ion laser in the wave number ranging from 50 to 1000 cm^{-1} . Valence band structure for $\text{Cu}_2\text{O}_{\text{c2}}$ and $\text{Cu}_2\text{O}_{\alpha}$ films was studied by XPS (AXIS UTLTRADLD SHIMADZU Multifunctional X-ray Photoelectron Spectroscopy) using a monochromatic Al-K α (1486.6 eV) source with a pass energy of 20 eV. The optical band gap was derived from UV–Vis transmission measurement (Perkin–Elmer Lambda 950) with the wavelength in the range of 250–2000 nm.

Electronic structure of the crystalline and amorphous films were calculated on the basis of density functional theory (DFT) package of Cambridge Serial Total Energy Package (CASTEP) codes [23], using the plane wave ultra-soft pseudo potential method with the generalized gradient approximation (GGA) within Perdew–Burke–Ernzerh of (PBE) function. The supercell model for the crystalline one in this work was set to be comprised of $2 \times 2 \times 3$ unit lattice cells, in which O atoms constituting bcc lattice and Cu atoms lie in the vertices of a tetrahedron around each of the O atoms. While for the amorphous film, the simulation model is based on the continuous random network (CRN) structure [24,25] containing the same number of Cu and O atoms as those of crystalline counterpart.

3. Results and discussion

The crystalline $\text{Cu}_2\text{O}_{\text{c1}}$ film was highly resistive and beyond the measurement range of PPMS. For $\text{Cu}_2\text{O}_{\text{c2}}$, $\text{Cu}_2\text{O}_{\text{c}+\alpha}$ and $\text{Cu}_2\text{O}_{\alpha}$ films, temperature dependent resistivity in the range of 100–300 K is characterized by semiconductor behaviors, as displayed in Fig. 1 (a). The films exhibit a monotonous reduction of resistivity with decreasing the temperature below room temperature. The negative temperature coefficients of resistance start to increase as the film changes from crystalline to amorphous phase. The $\ln(\rho)$ is plotted as a function of $T^{-1/4}$, as shown in Fig. 1 (b). The linear relationship of $\ln(\rho) \sim T^{-1/4}$ for the $\text{Cu}_2\text{O}_{\text{c2}}$ indicates that the conduction is dominated by variable-range-hopping (VRH) mechanism, as often observed in crystalline cuprite oxide [26,27]. The transport behavior is associated with the localized state caused by the strong

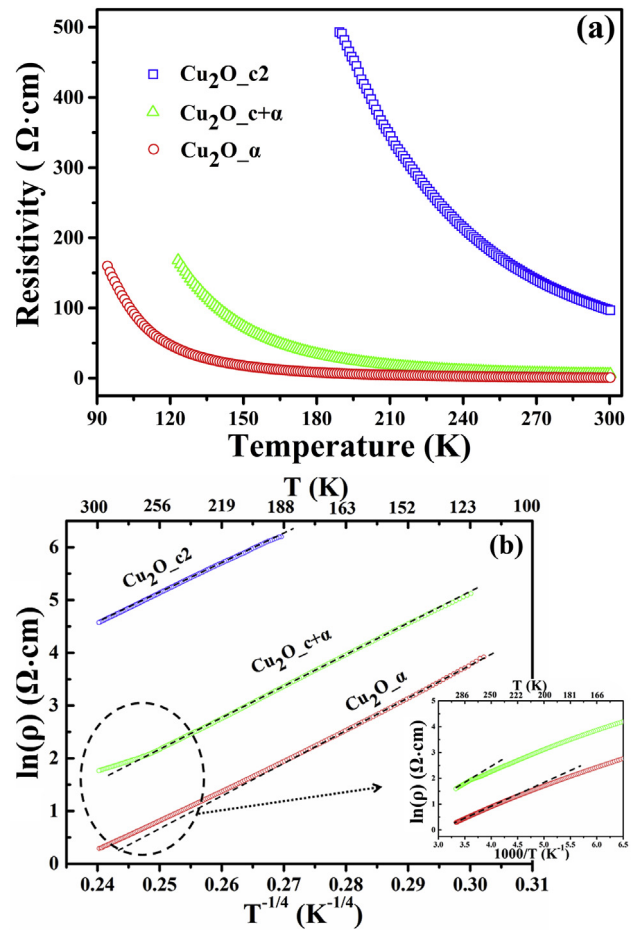


Fig. 1. (a) Temperature dependence of resistivity for $\text{Cu}_2\text{O}_{\text{c2}}$, $\text{Cu}_2\text{O}_{\text{c}+\alpha}$ and $\text{Cu}_2\text{O}_{\alpha}$ films in the temperature range of 100–300 K; (b) $\ln(\rho) \sim T^{-1/4}$ curves for the three films and $\ln(\rho) \sim 1000/T$ curves for $\text{Cu}_2\text{O}_{\text{c}+\alpha}$ and $\text{Cu}_2\text{O}_{\alpha}$ in the temperature range above 200 K (inset).

localization effect at oxygen 2p orbits [28]. However, the $T^{-1/4}$ linear dependence shows a deviation at 275 and 250 K for $\text{Cu}_2\text{O}_{\text{c}+\alpha}$ and $\text{Cu}_2\text{O}_{\alpha}$, respectively, reflecting transitions of the transport behavior at the temperatures. As shown in the inset of Fig. 1 (b), the films containing amorphous phase are characteristic of Arrhenius-like temperature dependence, following $\ln(\rho) \sim 1000/T$ relationship in the higher temperature region. Thermal activation energy is estimated to be 103 meV for $\text{Cu}_2\text{O}_{\text{c}+\alpha}$ and 79 meV for the $\text{Cu}_2\text{O}_{\alpha}$. The smaller thermal activation energy for the amorphous film is associated with a drop of its Fermi level which is shown below.

Raman spectroscopy has been investigated to reveal variations of the cuprite structure with decreasing the crystallization, as shown in Fig. 2(a). The Raman curves for $\text{Cu}_2\text{O}_{\text{c1}}$ and $\text{Cu}_2\text{O}_{\text{c2}}$ demonstrate characteristic phonon frequencies of crystalline cuprite oxide, resulting from the symmetric crosslink network configuration comprised of O–Cu–O three-dimensional crosslink in cuprite structure (see Fig. 2(b) left). The two weak peaks observed at 515 and 635 cm^{-1} are attributed to the Raman-allowed mode (Γ_{25}) and infrared-allowed mode, respectively, and have little influence on the structure variations [29], while the strong peaks at 96 cm^{-1} result from the inactive Raman mode (Γ_{15}) of the oxide [30]. The peak at 151 cm^{-1} may arise from Raman scattering from phonons of symmetry Γ_{15} , and the one at 220 cm^{-1} is assigned to the second-order Raman-allowed mode ($2\Gamma_{12}$) [31]. On the other hand, the characteristic peaks are very weak for $\text{Cu}_2\text{O}_{\text{c}+\alpha}$ and

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