Investigation of Cu_2O films sputtered with ceramic target: effect of RF power

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High purity Cu_2O films were obtained under room temperature by using Cu_2O target. The thickness of Cu_2O films increased from 376 nm to 1110 nm when the RF power was varied. A band gap narrowing was observed which caused by the increase of film's thickness, and the value was 2.18-2.10 eV. From PL spectra, it can be seen that all samples have a very strong peak located at ~618 nm which was attributed to the radiative recombination of band excitons. A weak broaden peak located at ~750 nm was also observed in some samples and it has been considered deriving from the defect of V_O.

(Received November 27, 2017; accepted August 9, 2018)

Keywords: Cu_2O, Sputtering, Transmittance, Photoluminescence

1. Introduction

Cu_2O is an old p-type semiconducting material. Currently, there is renewed interests on Cu_2O with respect to solar-cell applications due to its high absorption coefficient, non-toxicity and the abundance of its composing elements even despite of the relatively large band gap (2.17eV) [1]. Up to now, there have been many reports on various Cu_2O-based solar cell fabricated using Cu_2O as the active layer [2,3,4]. The SQL predicts the efficiency for Cu_2O-based solar cell is about 20%, but the current experimental data is only about 6.1% [5,6]. So, there is a lot of room for improvement.

Further more, large number of researchs indicated that the photoelectric properties of devices based on Cu_2O are mainly related to the quality of each laminated film and its interface [7,8,9]. High quality Cu_2O films with minimal surface roughness are the key to increase the efficiency of solar cells. And the inhibition of CuO phase is one of the difficulties must to be solved for preparing high purity Cu_2O films. In addition, the structure and properties of Cu_2O films depend not only on the preparation technique but also on the experimental parameters. At present, various methods have been used for the synthesis of Cu_2O. Such as thermal oxidation [10], electrochemical deposition [11], RF-magnetron sputtering [12,14-16], chemical vapor deposition [13]. Among them, the RF-magnetron sputtering is widely used because of its high deposition rate, good adhesion and large area deposition. Most of researchers used Cu targets in a mixed atmosphere of oxygen and argon to growth the Cu_2O thin films [14]. While, the variation of O_2/Ar may lead to CuO phase appeared. To solve this problem, li et al adopted CuO target in a mixed atmosphere of nitrogen and argon and pure Cu_2O films were obtained [15]. More, their results indicated that the N doping can inhibited the appearance of CuO during the deposition of Cu_2O. In addition, Cu_2O ceramic target also have been used and Cu_2O films with high mobility and low hole concentration can be obtained under that conditions [16]. While, that reports pay more attention on the electrical properties of Cu_2O films. And few researchs focus on the variation of structure, band gap and optical properties for Cu_2O films along with the RF power. In this work, Cu_2O target was adopted, high purity and good crystal quality Cu_2O films can be obtained conveniently under room temperature. A band gap narrowing which caused by the thicker thickness of Cu_2O films can be observed. So, the effect of RF power on the structure, band gap and optical properties of Cu_2O films were investigated as followings.

2. Experimental

All samples were deposited by RF magnetron sputtering system with a Cu_2O target (99.99%, purity). 1cm×1cm Quartz glasses were used as substrates. Before loading into reaction chamber, substrates were cleaned in an ultrasonic cleaner using acetone, ethanol, and deionized water for 20 min, and dried with nitrogen gas. The base vacuum level was 6.0×10^{-4}Pa, and the pressure during deposition was 0.5Pa. For all samples, the flow rate of Ar was kept at 20 sccm, and the RF power was varied from 80 to 150 W. In order to remove the oxide on the surface of the Cu_2O target, the sputtering target was pre-sputtered in a pure Ar atmosphere for 5 min. During deposition, the substrates were not heated intentionally. The deposition time was 30min.

Crystallinity of obtained films was analyzed by X-ray diffraction using a D-MAX/γA system with Cu*K*α radiation λ=0.154178nm in the range of 20^0~80^0. Optical transmittance was measured using a UV/vis spectrometer (Hewlett-Packard 8453). The thickness was observed by a model JEOL-JSM-6700F field emission scanning electron microscope (FESEM). The photoluminescence of Cu_2O films were collected using a laser micro-Raman spectrometer (Renishaw in Via-Reflex) equipped with a YAG laser light source which excited the samples at 532 nm.

3. Results and discussion

3.1. Structure

First, the structure was investigated. The XRD patterns for Cu_2O films deposited at different RF power are shown in Fig. 1. Three diffraction peaks which derived from (111), (110) and (200) planes of Cu_2O located at 36.4^0, 29.2^0 and 42.2^0 respectively. And these strong peaks indicate a single phase of Cu_2O. None of the other phases such as Cu or CuO were detected .When the RF power is 80W, there are two peaks located at 29.2^0 and 36.4^0 respectively, and the intensity of the peak located at 36.4^0 is much stranger that of the peak at 29.2^0. This indicated that the obtained Cu_2O films have a highly preferred (111) orientation. Along with the increase of RF power, the intensity of (111) diffraction peak increased, while the (110) peak weakened and disappeared when the RF power was increased to 120W. This indicated that the crystal quality was optimized along with the increased of RF power. However, unexpected, another peak located at 42.2^0 appeared when the RF power was increased furtherly. It is means that the 120W is the most appropriate condition.

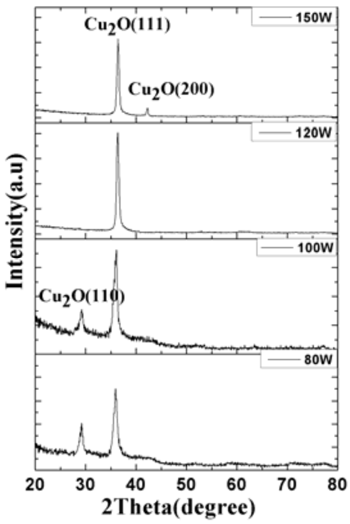

Fig. 1. XRD patterns for the Cu_2O films deposited at different RF power in the range of 80-150W

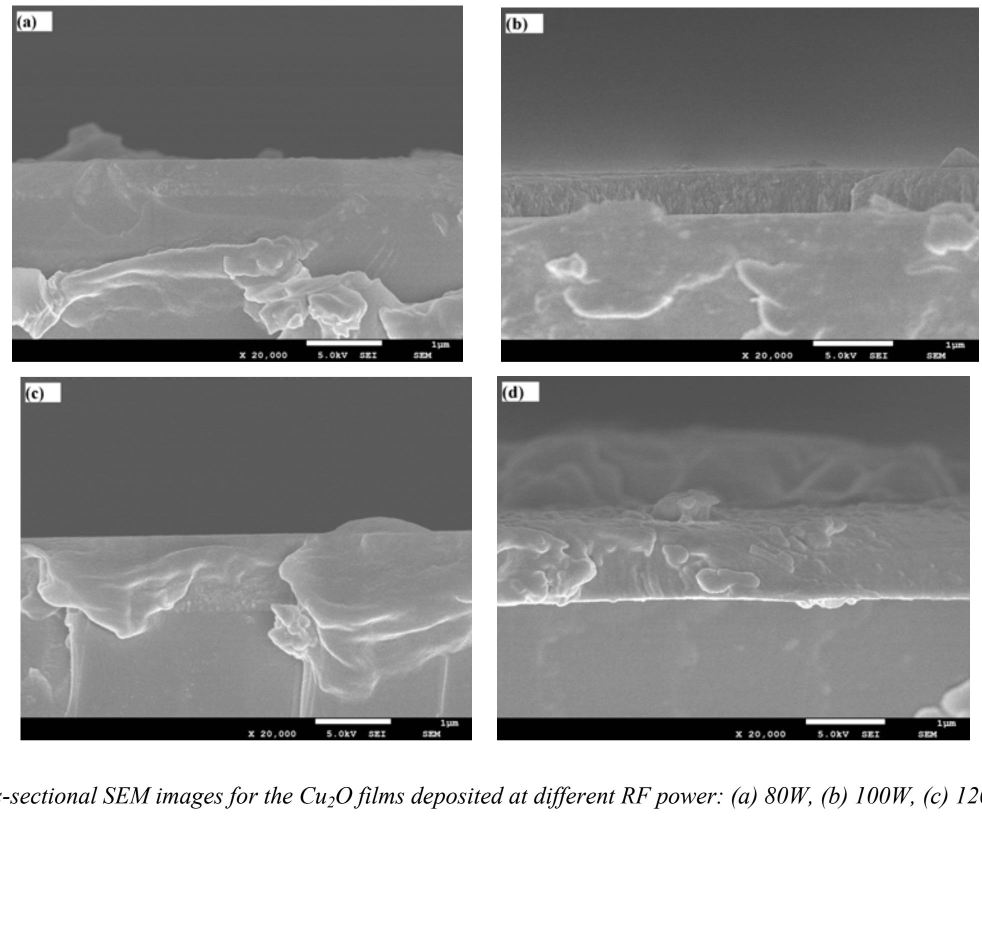

Fig. 2. Cross-sectional SEM images for the Cu_2O films deposited at different RF power: (a) 80W, (b) 100W, (c) 120W, (d) 150W

In order to examine the speed of deposition, cross-sectional SEM images for Cu_2O films were performed. Images were displayed in Fig. 2. It can be seen that, as the RF power was increased from 80W to 150W, the thickness of Cu_2O films was 376 nm, 566 nm, 892 nm and 1110 nm respectively. This indicated that the deposition rate increased obviously as the RF power was turned larger. Chih-Chieh Hsu also reported that when using Cu_2O target, the deposition rate is more sensitive to the RF power [16].

3.2. Optical properties

Fig. 3(a) and Fig. 3(b) show the transmittances and optical band gap energies of the Cu_2O films prepared at various RF power. The transmittance spectra show interference fringes, which indicate that the films are homogeneous. The average transmittance of the Cu_2O films in the visible spectral range slightly decreased with increasing the RF power. This is because that the thickness is increased as shown in cross-sectional SEM images. There is no obviously shift for the absorption edges except that for the Cu_2O film deposited as the RF power is 150W. To confirm the transmittances, the optical band gap energy were calculated using the Tauc model and the Davis and Mott model.

$$\alpha h\upsilon = A(h\upsilon - E_g)^{1/2}$$

Here, hν is the photon energy, α is the optical absorption coefficient. Eg is the optical band gap, and A is a constant [17]. The band gaps of Cu_2O films are extracted by plotting $(\alpha h\nu)^2$ versus hν and extrapolating the linear portion of this plot to the energy axis, as shown in Fig. 3 (b). When RF power is varied from 80W to 120W, the band gap energy of the Cu_2O films is about 2.18eV. And when the RF power increased to 150W, the band gap narrowed down slightly. This phenomenon may be attribute to the increase of film's thickness. It is consistent with the reports by O. Messaoudi and S. Korkmaz [18,19].

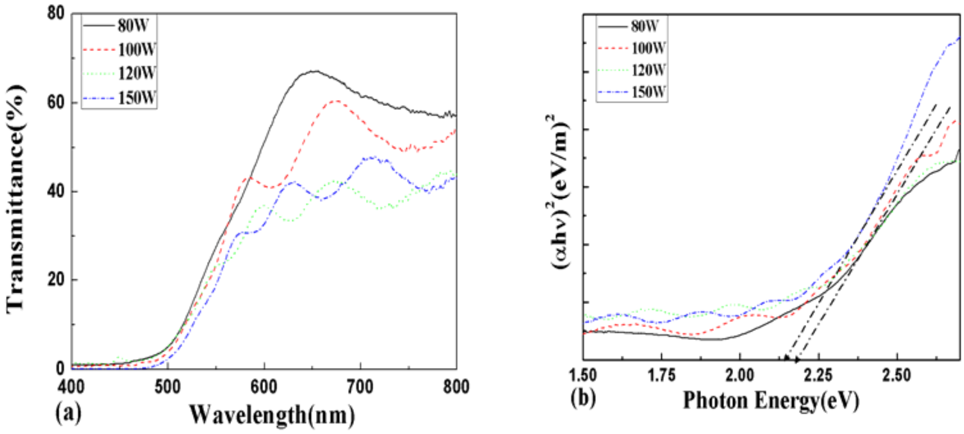

Fig. 3. (a) Optical transmittance for the Cu_2O films deposited at different RF power. (b)Plots of $(\alpha h\nu)^2$ versus hν for the Cu_2O films deposited at different RF power

3.3. Photoluminescence properties

Room temperature PL spectra of Cu_2O films which deposited when RF power varied from 80W to 150W were displayed in Fig. 4. It can be seen that all the spectra were dominated by a very strong peak located at ~618 nm (~2.00 eV). According to previous researchs, the PL spectra of Cu_2O films are generally contain two main signals extend from 450 to 650nm which are considered derive from the free excitons and bound excitonic region [20-22]. So the peak located at ~618 nm can be assigned to phonon assisted exciton transition [23]. More, the intensity of exciton transition peak rised as the RF power increased, reflecting the improvements in the crystal quality. While, when the RF power was increased to 150W, the intensity of exciton transition peak decreased, signifying the deterioration of the crystal quality. This variation tendency is consistent with the XRD results. In addition, the position of the exciton transition peak shift to long wavelength, reflecting the variation of band gap which has been shown in Fig. 3(b). Except the exciton transition, a broad emission peak located at ~750 nm which related to V_O also can be observed [24]. According to Junqiang Li's report that the concentration of V_O reveals no impact on the exciton transition [23]. So, here, the strong exciton emission was able to be observed simply because the prepared Cu_2O films have a high crystal quality. The formation of V_O may be due to the unbalance in the reaction chamber which be caused by too high RF power.

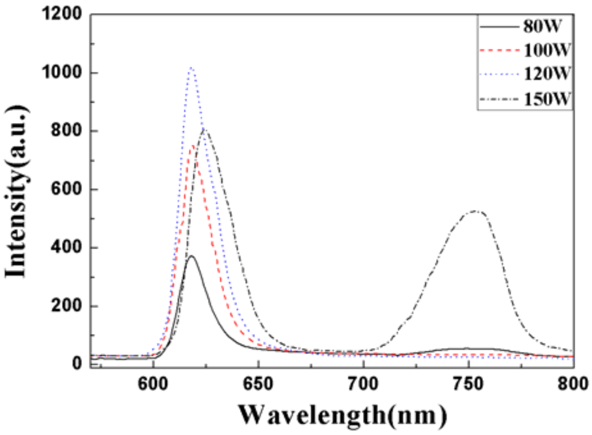

Fig. 4. PL spectra for the Cu_2O films deposited with the RF power varied from 80 to 150W

4. Conclusions

High preferred orientation Cu_2O films have been deposited by RF sputtering system with Cu_2O target. Effects of RF power on the structure, band gap and optical properties of Cu_2O films have been studied. XRD results indicated that high purity and good crystal quality Cu_2O films were obtained when the RF power was increased to 120W. Cross-sectional SEM displayed that the film's thickness was 376 nm, 566 nm, 892 nm and 1110 nm respectively when the RF power was turned from 80W to 150W. The average transmittances in the visible light range were 40-60%. The band gap of obtained Cu_2O films were ~2.18eV, and a little band gap shift was observed when the RF power was increased to 150W. PL spectra showed the emission peaks derived from the band excitons and defects of V_O respectively. This result demonstrated that the prepared Cu_2O films have a high crystal quality in another way. The above researchs are of great significance to the preparation of high quality Cu_2O films and then to improve the performance of Cu_2O-based optoelectronic devices.

Acknowledgements

The authors acknowledge the financial support from the NSF of China (Grant Nos. 51302128), and the NSF of Henan province (Grant Nos. 172102210398, 172102210401, 172102210404, 16A140012, 18B140008).

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