Characterization of Cu$_2$O thin films prepared by evaporation of CuO powder

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Abstract. Among the potential photovoltaic devices based on semiconductor oxides as active layer is cuprous oxide (Cu$_2$O). This oxide semiconductor shows many attractive characteristics useful for solar cells production such as low cost, nontoxicity, high mobility and diffusion length of minority carriers, high absorption coefficient and direct energy gap. In this work we report our results of optical and structural investigations of Cu$_2$O thin films fabricated by thermal vacuum evaporation of CuO powder. The effects of the deposition velocity on structural and optical properties of Cu$_2$O films were investigated. The X-ray investigations have shown that at low deposition velocity the films consist only of Cu$_2$O phase without any interstitial phase and have a nano-grain structure. The grains have an average dimensions about (25-30) nm and all these grains showed (200) preferential crystallographic orientation. Optical investigations have shown that the absorption edge of prepared films is due to a direct allowed transition. The value of determined optical band gap is 2.05 eV which corresponds to band gap of bulk Cu$_2$O.

1. Introduction
Thin films technologies allow developing next and more efficient generation of solar cells. Among the potential photovoltaic devices based on semiconductor oxide as active layer is cuprous oxide (Cu$_2$O). The theoretical energy conversion efficiency of Cu$_2$O solar cell is about 20% [1]. This oxide semiconductor shows many interesting characteristics useful for solar cells production such as low cost, nontoxicity, good mobilities, fairly high minority carrier diffusion length, high absorption coefficient and direct energy gap.

Cu$_2$O is spontaneously a p-type semiconductor since it contains negatively charged copper vacancies and probably interstitial oxygen [2]. A large number of elements were tested as doping impurities. Up to now n-type conductivity is not demonstrated conductivity and a possible explanation for this negative result is based on the self-compensation mechanism [3] or the low solubility of the tested doping impurities [4].

Although the theoretical limit of Cu$_2$O solar cell efficiency is about 20% the highest efficiency obtained up to now is 2% [5]. This is due to a limited amount of work devoted to this semiconductor and only during last a few years PV device composed of p-Cu$_2$O and n-ZnO has received broadens attention as a real candidate of next generation thin film solar cells [6-9]. Only recently, conversion efficiency 3.83% has been obtained in ZnO/Cu$_2$O heterojunction solar cells [10].
The optimization of Cu$_2$O solar cell is slowed down by the lack of clear understanding of the electrical and crystalline structure properties of this material and defects arising on heterojunction, as well as limited technological methods applied up to now.

Several methods of deposition have been used in attempts to obtain thin films of Cu$_2$O, such as an electro-deposition [11,12], a chemical methods [13,14], sputtering method [15,16] and method of Cu$_2$O powder thermal evaporation [17]. The thermal oxidations of Cu sheets and sputtering methods have attracted much attention because up to now these two methods provide high mobility and structure performance of Cu$_2$O.

The objective of the present paper is to fabricate Cu$_2$O thin films by thermal evaporation of small portions of CuO powder and investigate the dependence of structural and optical properties of these films on deposition conditions.

2. Experimental

Thin films of Cu$_2$O were fabricated by continuous thermal evaporation of CuO small particles. Schematic view of vacuum evaporation setup presented in figure 1. CuO particles have different size from 100 to 500 micrometers. These particles were prepared by crushing of pallet which was obtained by pressing commercially available CuO powder (99.9% purity) and sintering at 700$^\circ$C in air 1 h. The vacuum chamber before evaporation was pumped to a base pressure of 1.5$\times$10$^{-5}$ mm Hg. The thermal evaporation was carried out by dosed supply of CuO particles to the molybdenum boat heated to the temperature 1300$^\circ$C. Process of CuO particles evaporation occurred as follows. After contact to boat the particles of CuO in process of their heating at first convert to Cu$_2$O by the reaction:

$$4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2 \quad (1)$$

and then convert to Cu by the reaction:

$$2\text{Cu}_2\text{O} \rightarrow 4\text{Cu} + \text{O}_2 \quad (2)$$

Since the temperature of boat was above the temperature of Cu evaporation (1260$^\circ$C) after thermal decomposition of Cu$_2$O to Cu and O$_2$ a full evaporation of Cu was occurred. This method of evaporation provides in average the same flows of copper and oxygen atoms due to different temperature of evaporating particles.

![Figure 1. Schematic representation of the experimental setup.](image)

The films were deposited on sapphire substrate. The temperature of substrates was 700$^\circ$C. During the evaporation process the base pressure in vacuum chamber was changed from base pressure 1.5$\times$10$^{-5}$
mm Hg to the partial pressure of oxygen 1·10-4 mm Hg. After the film deposition the substrate was cooled to the room temperature during 1 hour with the chamber pressure 6·10-6 mm Hg. The film thickness and duration of deposition were typically 1-3 micrometers and 3 hours.

The structural properties of samples were studied by X-ray diffractometer URD-6 in the 0-20 mode using Cu - Kα radiation as well as by optical Olympus microscope with magnitude 500. Transmittance and reflectance, over the wavelength from 300 to 1000 nm were measured using double beam Specord M-50 spectrophotometer.

3. Results and discussion

3.1. Phase formation
We have investigated the characteristics of films depend on the deposition velocity at the temperature of substrate 700°C. Figure 2 shows the photo of surface morphology of two films series A and B which differ from each other by the velocity of deposition. For low deposition velocity less than 5 nm/min the films of series A consist of smaller size grains than the films of series B (figures 2a and 2b).

![Figure 2. The photo of surface morphology of (a) films series A, and (b) films series B (500°).](image)

3.2. Structural analysis (XRD)
Angular XRD patterns of films series A and B are shown in figure 3. For films series A, there is one strong XRD peak at 2θ = 42.4°, corresponding to the (200) crystal plane of Cu$_2$O (figure 3a). This XRD pattern indicates that films series A is single phase Cu$_2$O film with crystalline structure. These films consist of nano-size grains and all these grains have identical orientation. Full width of half maximum (FWHM) of the XRD peak was used to estimate the grain size of the films series A. The values of the grain size calculated using Scherrer’s formula [18]:

$$D = \frac{0.9 \lambda}{d \cdot \cos \theta}$$

where $\lambda$ is the x-ray wavelength, $\theta$ is the Bragg diffraction angle, and $d$ is full-width at the half-maximum (FWHM) of the peak corresponding to $\theta$.

For the peak corresponding to the (200) plane of Cu$_2$O, the resultant grain size is 25 nm. The XRD pattern for films series B presented in figure 3b contains one Cu$_2$O - related diffraction (111) peak (2θ =36.38°) and two Cu - related diffraction peak (111) (2θ=42.9°) and (200) (2θ=49.8°).
Figure 3. XRD patterns of (a) films series A, and (b) films series B.

The composition of deposited layer formed due to reaction between copper and oxygen. Figure 4 shows the equilibrium phase diagram of the Cu-O system [19]. The partial pressure and temperature of substrate corresponding to the films deposition conditions are shown in figure 4 (point A). At low velocity of deposition Cu atoms have enough time in order to completely react to oxygen. This time determined by the time of kinetic reaction for formation Cu$_2$O phase. In this case the composition of deposited film determined by the equilibrium Cu-O phase diagram. It is confirmed by XRD pattern of films series A where observe only Cu$_2$O - related diffraction peaks. We believe that at high velocity of deposition Cu atoms have not enough time to completely convert in Cu$_2$O phase (figure 3b).

Figure 4. The cooper-oxygen equilibrium phase diagram.
3.3. Optical properties

The transmission and absorbance spectra were taken to obtain information on the optical properties of the copper oxide thin film. In the fundamental absorption region, the optical absorption coefficient (\( \alpha \)) can be calculated from the transmittance and reflectance data by the equation,

\[
\alpha = \frac{1}{d} \ln \left( \frac{1 - R}{T} \right)
\]

where \( d \) is the thickness of the film.

Above the fundamental absorption edge the dependence of the absorption coefficient on the incident photon energy is given by Taue’s model [20]:

\[
\alpha \cdot h\nu = B \left( h\nu - E_g \right)^n
\]

where \( h\nu \) is the photon energy, \( E_g \) is the optical band gap and \( B \) is a constant and \( n \) is an exponent that depends on the type of optical transitions. As shown in figure 5 the best linear relationship is obtained by plotting \( (\alpha h\nu)^2 \) against photon energy \( (h\nu) \), indicating that the absorption edge in this film is due to a direct allowed transition. The linear portion of the curve is fitted using linear regression analysis. The value of optical band gap was determined from the value of intercept of the straight line at \( \alpha = 0 \). The value of determined optical band gap is 2.05 eV which corresponds to the band gap of bulk Cu\(_2\)O [21].

![Figure 5. Variation of \((\alpha h\nu)^2\) as a function of photon energy.](image)

4. Conclusion

The films of copper oxide were deposited on sapphire substrate by the continuous thermal evaporation of CuO small particles. The effects of deposition velocity on the structural and optical properties of Cu\(_2\)O films were investigated. It was shown that at deposition velocity less than ~ 5 nm/min the films deposited on the 700 °C substrate consist only of Cu\(_2\)O phase. These films have a nano-grain structure and all these nano-grains have (200) preferential crystallographic orientation with average dimensions about (25-30) nm.

It was found that the optical band gap of fabricated Cu\(_2\)O films is 2.05 eV which corresponds to the band gap of bulk Cu\(_2\)O.
Reference

[1] Olsen L C, Addis F W and Miller W 1982-1983 Solar Cells 7 247
[2] Porat O and Riess I 1995 Solid State Ionics 81 29
[3] Tsur Y and Riess I 1999 Phys. Rev. B 60 8138
[4] Tsur Y and Riess I 1998 Z. Phys. Chem. 207 181
[5] Mittiga A, Salza E, Sarto F, Tucci M and Vasanti R 2006 Appl. Phys. Lett. 88 163502
[6] Hsueh T J, Hsu C L, Chang S J, Guo P W, Hsieh J H and Chen I C 2007 Scr. Mater. 57 53
[7] Paul G K, Ghosh R, Bera S K, Bandyopadhyay S, Sakurai T and Akimoto K 2008 Chem. Phys. Lett. 463 117
[8] Wang R C and Lin H Y 2010 Sens. Actuators B 149 94
[9] Lv R, Zheng W, Lin L, Peng F, Huanf Z and Lai F 2011 Physica B 406 1253-1257
[10] Minami T, Nishi Y, Miyata T and Nomoto J 2011 Applied Physics Express 4 062301
[11] Hu F, Chan K C, Yue T M 2009 Th. Sol. Films 518 120–125
[12] Wijesundera R P, Hidaka M, Koga K, Sakai M and Siripala W 2006 Th. Sol. Films 500 241 – 246
[13] Necmi S, Tulay S, Seyda H and Yasemin C 2005 Semicond. Sci. Technol. 20 398–401
[14] Nair M T S, Guerrero L, Arenas O L and Nair P K 1999 Appl. Surf. Sci. 150 143–151
[15] Itoh T and Maki K 2007 Vacuum 81 904 –910
[16] Sheng H, Hong-Ying C, Lien-Teng K, Cheng-Hsien T 2008 Th. Sol. Films 517 1195–1199
[17] Al-Kuhaili M F 2008 Vacuum 82 623–629
[18] Klug H P and Alexander L E 1974 X-Ray diffraction Procedure for Polycrystalline and Amorphous Materials (New York: Wiley)
[19] Weichman F L and Reyeas J M 1980 Can.J.Phys. 58 325
[20] Tauc J 1970 Optical properties and Solids (Amsterdam: North-Holland)
[21] Nakamura N, Ishiwary S and Tanaka A 1998 Appl.Phys.Lett. 73 23-25