Effects of Oxygen Flow Rates on the Physical Characteristics of Magnetron Sputtered Single-Phase Polycrystalline Cu$_2$O Films

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The single-phase polycrystalline copper oxide (Cu$_2$O) films were prepared on sapphire substrates by radio frequency (RF) magnetron sputtering technology which was characterized by low cost and high efficiency. The influences of oxygen flow rate on physical characteristics of the prepared films were investigated. The XRD results showed that the single-phase Cu$_2$O film exhibited a (110) preferred orientation through the analysis of texture coefficient. The AFM images exhibited that the prepared Cu$_2$O film had the highest surface roughness with a distinctive quadrangular surface morphology. The optical transmittance of the single-phase Cu$_2$O film was under 35% and the band gap energy was calculated to be 2.30 eV, the absorption spectra included the peak wavelength of solar radiation and the high absorptivity made it to be a suitable absorbing material. The Hall measurement indicated that all the samples exhibited p-type conductivity. The resistivity, mobility and carrier concentration of the single-phase Cu$_2$O film was 4625 Ω·cm, 1.87 cm$^2$/V·s and 7.227×10$^{14}$ cm$^3$, respectively.

Keywords: Magnetron sputtering; Cu$_2$O films; Oxygen flow rate; P-type semiconductor.

1. Introduction

Cuprous oxide (Cu$_2$O) is a kind of p-type semiconductor material with cubic structure and direct band gap [1]. Compared with the other inorganic p-type semiconductor materials [2-6], it has been widely used in photo catalysis [7] and humidity sensors [8] due to its characteristics of rich sources, non-toxic, low preparation cost and high optical absorption coefficient [9]. Furthermore, it is also an attractive absorber layer for heterojunction solar cells because of a band gap energy of 2.1–2.6 eV [10,11]. Meanwhile, according to the calculation of the Shockley-queisser theory, the theoretical photoelectric conversion efficiency of the single-junction solar cell can reach 20% [12].

At present, the technologies for preparing semiconductor thin films include vacuum evaporation [13], chemical vapor deposition [14], electrochemical sedimentation [15], sol–gel [16], electron beam evaporation [17], solution growth [18], molecular beam epitaxy [19] and magnetron sputtering. Among them, RF magnetron sputtering has become one of the optimal methods to deposit Cu$_2$O films due to its advantages of high deposition rate and strong controllability of the chemical composition and deposition of uniform films on large area substrates [20,21]. The various properties of Cu$_2$O thin films prepared by magnetron sputtering were mainly depended on substrate temperature, oxygen partial pressure, sputtering power and substrate self-bias, etc. Among them, the oxygen partial pressure (oxygen flow rate) could affect the stoichiometric ratio of copper and oxygen in the preparation of the film samples, which would be accompanied by the generation of Cu and CuO. Eventually, the physical properties of film samples will be deteriorated [22,23]. In order to prepare single-phase Cu$_2$O thin films, Li et al. [24] have adopted CuO ceramics as the sputtering target by magnetron sputtering method under the mixed atmosphere of nitrogen and argon gas. It is found that the nitrogen doping can efficiently suppress the formation of CuO phase to obtain the single-phase Cu$_2$O films. Zhu et al. [25] fabricated Cu$_2$O porous nanostructured films on glass slide substrates by magnetron sputtering system and the effects of electrons and argon ions on the deposition process were studied by quantitative calculation, a new model of tip charging effect was further proposed to account for the film forming mechanisms. In this work, we adopted a pure Cu as the target and the single-phase Cu$_2$O films were obtained by adjusting the oxygen flow rate. In order to further explore the effect of deposition parameters on the single-phase Cu$_2$O films, the surface morphology, crystal structure, optical and electrical characteristics of the thin films were investigated in detail.

2. Experiments

Cu$_2$O films were deposited on c-Al$_2$O$_3$ substrates by magnetron sputtering (JGP 300) equipment. Pure copper (99.999%) of 50 mm diameter and 3 mm thick was used as the sputtering target. The pure sputtering gas (argon, 40 sccm, 99.99%) and the reactive gas (oxygen, 99.99%) were used...
in the experiments, the oxygen flow rates value from 1 to 5 sccm were used to study the physical characteristics of the film samples. Before depositing, the substrates were placed in acetone, anhydrous ethanol and deionized water in sequence and respectively washed with ultrasonic for 5 minutes. Then the substrates were dried with high purity nitrogen and put into the vacuum chamber which was 350 mm high and 280 mm in diameter. Meanwhile, keeping the distance between the substrate plate and the sputtering target as 5 cm. The deposition parameters were as follows. The base pressure of the chamber was below 1×10⁻³ Pa using a turbo-molecular pump and a roots pump. The chamber pressure was maintained at 1.0 Pa, RF power was 120 W, and the sputtering temperature was 400 °C for 1 h for each group of experiments. The structure and orientation of the films were studied using X-ray diffraction (XRD, λCuKα1=1.5406 Å). The diffraction angle for scanning was started from 23 to 65 degrees continuously with a scan rate of five degrees per minute. The atomic force microscopy (AFM) was used to analyze the morphological feature on a Veeco Dimension 3100 scanning probe microscope and the sampling range kept at 5×5 μm². The optical properties of the films were recorded using UV-2600 Spectrophotometer where the uncoated sapphire substrate was used as a reference. The electrical properties of samples were studied by ACCENT HLS5500PC Hall system using the van der Pauw method. All characterizations were investigated at room temperature.

3. Results and Discussion

X-ray diffraction results of the samples formed at different oxygen flow rates were shown in Figure 1. It could be noted that the sample deposited at low oxygen flow rate of 1 sccm showed the obvious diffraction peaks at 2θ=29.41°, 2θ=38.83° and 2θ=61.08° related to the (110), (111) and (220) planes for cubic Cu₂O (JCPDS Card no.77-0199), respectively. Another peak observed at 2θ=43.44° corresponded to the (002) plane of monoclinic structured CuO (JCPDS Card no.80-1917) and (200) plane of CuO subphase (JCPDS Card no. 03-0879), respectively. Further increased the oxygen flow rate to 2 sccm. The diffraction peak of Cu₂O (200) disappeared and only CuO (111) diffraction with lower intensity was left. At the same time, the diffraction peak intensities of CuO (002) and (111) were further increased and a new peak of CuO (110) was generated instead of (202). Finally, single-phase CuO was obtained and both the intensities of CuO (110), (002) and (111) diffractions were increased because of more crystallites had been grown in the structure²⁸ as the oxygen flow rate was increased to 5 sccm.

In order to further characterize the crystal structure of single-phase CuO film. Orientation of the crystallites in the CuO film synthesized at the oxygen flow rate of 2 sccm is obtained by utilizing Harris texture analysis²⁹. The value of the texture is quantified by the direct comparison of the integrated peak intensities of a textured film with those of the standard JCPDS data. According to the following equation:

\[ C(hkl) = \frac{I_{hkl}(i)/I_{hkl}(0)}{(I/N)\sum_{i=1}^{N}I_{hkl}(i)/I_{hkl}(0)} \]  

where \( I_{hkl}(i) \) are the diffraction intensities of CuO powders from JCPDS Card no 77-0199. \( I_{hkl}(0) \) are the measured relative intensities of CuO diffractions from the XRD pattern, and \( N \) is the number of diffractions considered in the analysis. In addition, the standard deviation of all of the \( \sigma \) value is also calculated according to the following equation:

\[ \sigma = \sqrt{\frac{\sum_{i=1}^{N}(C_{hkl}(i)-\bar{C})^2}{N}} \]

Table 1 shows the values of \( C(hkl) \) for each plane and \( \sigma \) for the single-phase CuO film deposited at the oxygen flow rate of 2 sccm. A \( C(hkl) \) value above 1 and a \( \sigma \) value above 0 represent a preferential orientation of the \((hkl)\) plane³⁰. According to Table 1, the sample shows a very strong (110) texture with the values \( C_{(110)} = 2.053 \) and \( \sigma = 0.6197 \). The calculation results display that the film has...
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a Cu\(_2\)O (110) preferred orientation growth at the oxygen flow rate of 2 sccm.

Figure 2 showed the AFM image of samples deposited at various oxygen flow rates. The thin films showed the aggregating direction between the grains presented about 45 degrees with the X-axis and Y-axis. When the oxygen flow rate was increased from 1 to 5 sccm, the corresponding root mean square surface roughness of the thin films were 42.2, 58.2, 20.5, 6.89 and 14.4, respectively. As could be seen from Figure 2a, the surface of film showed a high surface roughness. Not only the grain size was inhomogeneity but there had some obvious gaps between the grains. Increasing the oxygen flow rate of 2 sccm, Figure 2b showed the grain size of the single-phase Cu\(_2\)O film had increased significantly due to the better crystallinity and the single component. The film had a distinctive quadrangular surface morphology with clear grain boundary, which was similar to the previous literature\(^3\). Figure 2c showed that the surface morphology of the film changed completely and the grain size decreased obviously, which caused the decrease of the film roughness. Increasing the oxygen flow rate to 4 sccm, the surface of the film was further refined with smaller grain size and minimum surface roughness. Then, the grains aggregated together as shown in Figure 2e as the oxygen flow rate was increased to 5 sccm. The increased grain size led to the film roughness increased again. This may be related to the formation of single-phase CuO with better crystalline quality of the film. Through the above analysis, it is found that the improvement of crystal quality and purity of the films will lead to the increase of grain size and the significant changes of surface texture.

According to the XRD results, the Cu ions could not fully react with oxygen when the oxygen flow rate was 1 sccm. This would lead to a low optical transmittance owing to the scattering of light by the metallic copper combined with Cu\(_2\)O. Therefore, this article do not take this sputtering condition into consideration in the representation of optical properties.

Figure 3a showed the optical transmittance of the samples deposited at different oxygen flow rates. The transmittance spectra of the samples were recorded in the wavelength range of 440-1050 nm. It could be found that the transmittance spectra of sample A did not appeared an absorption edge because of the quantum size effects (QSE)\(^2\). Shogo et al.\(^3\) also explained that such an indistinct absorption edge may be due to the band tailing caused by a mixture of Cu\(_2\)O crystalline phase and an amorphous phase. With the increasing of the oxygen flow rate, the absorption edge of the samples gradually exhibited red shift because of the proportion of CuO in the films was gradually increased. When the oxygen flow rate reached 5 sccm, the absorption edge of the film was approximately at 800 nm, which was conformed to the optical transmittance spectra of CuO. This result was consistent with the XRD conclusion. As a whole, the transmittance of both single-phase Cu\(_2\)O\(^3\) and CuO films\(^5\) were lower than that reported in previous literatures. This was probably due to the vast crystal defects in the crystal, resulting in more light scattering and internal recombination caused by reflection\(^3\).

It is this characteristic of high absorbance make the films to be a suitable semiconductor absorbing material\(^2\).

The direct optical band gap energy of the thin films can be estimated using linear extrapolation method by the following equation\(^3\):

$$E_g = \frac{1}{\frac{1}{E_{\text{g,exp}}} - \frac{1}{E_{\text{g,th}}}}$$

Table 1. The values of \(C_{(hkl)}\) for each plane and \(\sigma\) or the single-phase Cu\(_2\)O sample.

| Sample oxygen flow rate | Reflected plane(hkl) | Intensity (Expt.) | Intensity (JCPDS) | Texture coefficient(\(C_{(hkl)}\)) | Standard deviation(\(\sigma\)) |
|-------------------------|----------------------|------------------|------------------|----------------------------------|-----------------------------|
| 2 sccm                  | (111) 100            | 100              | 100              | 0.491                            | 0.6197                      |
|                         | (110) 22.6           | 5.4              | 2.053            |                                  |                             |
|                         | (200) 58             | 34.4             | 0.827            |                                  |                             |
|                         | (220) 33.8           | 26.4             | 0.628            |                                  |                             |

Table 1. The values of \(C_{(hkl)}\) for each plane and \(\sigma\) or the single-phase Cu\(_2\)O sample.
$\alpha h\nu = A(\nu - E_g)^{1/2}$  \hspace{1cm} (3)

where $A$ is a constant, $\alpha$ is the absorption coefficient and $h\nu$ is the photon energy. Figure 3b showed the plots of $(\alpha h\nu)^2$ versus photon energy of the samples deposited at different oxygen flow rates. The $E_g$ corresponded to the sample A, B, C and D were about 2.30, 1.88, 1.69 and 1.66 eV respectively, which presented a decreasing trend with the increasing of the oxygen flow rates. According to the curve of sample A, the $E_g$ of the single-phase Cu$_2$O film was 2.30 eV, which was in good agreement with the reported value of RF magnetron sputtered Cu$_2$O films. The decreasing value of $E_g$ was due to the generation of CuO phase, this phenomenon was similar with Alkoy and Prabu’s research work. Further, as has been described earlier, the observed change in $E_g$ is not only related to stoichiometry (x) of Cu$_x$O but nanocrystalline size in these films. From the AFM and XRD results, the particle size decreased due to the decline of crystal quality and the occurrence of non-stoichiometric ratio defects when the oxygen flow in excess of 2 sccm. The value of $E_g$ is expected to increase with the decrease in particle size given by effective mass approximation. In this work, the crystallite size reduction due to defects causes a smaller affect in the $E_g$ than what is expected from the decrease in stoichiometry value (X).

The electrical properties of samples deposited at different oxygen flow rates were studied at room temperature by Hall measurement using the van der Pauw method. The mobility and carrier concentration of the prepared samples were shown in Figure 4. It showed that the mobility and carrier concentration changed from 0.072 to 1.870 cm$^2$/v·s and 7.227×10$^{14}$ to 2.360×10$^{17}$ cm$^{-3}$, respectively. All of the films exhibited the p-type conductivity and the mobility of single-phase Cu$_2$O film reached 1.870 cm$^2$/v·s, which was the maximum of all samples. The characteristic of high mobility makes Cu$_2$O films are widely used in optoelectronic devices such as p-channel transistors to obtain a sufficiently large on-to-off current ratio. The resistivity of the samples at the oxygen flow rates from 1 to 5 sccm were 2557, 4625, 821.2, 367.3 and 1813 Ω·cm, respectively. The increasing resistivity of the films was due to the decrease of the conductive metallic copper when the oxygen flow rate was increased from 1 to 2 sccm. The subsequent sharp decline of the resistivity was due to the changing in crystallize quality and the formation of CuO phase, which causing the resistivity to be smaller than that of Cu$_2$O based on the original electrical properties.

4. Conclusion

In summary, the influences of oxygen flow rate on the physical properties of magnetron sputtered Cu$_2$O films had been explored. Each of samples showed a polycrystalline structure. The single-phase Cu$_2$O film with distinctive quadrangular surface morphology exhibited a strong Cu$_2$O (110) preferred orientation through the analysis of texture coefficient. The absorption edge was gradually formed and exhibited red shift to the wavelength of 800 nm as the oxygen flow rate was increased. Moreover, the electrical characteristics of the samples showed that all of the films exhibited p-type conductivity and the optimum conductivity and mobility of the films could be obtained at appropriate oxygen flow rate. These results in this article provide a reference value for the preparation of high-performance Cu$_2$O films by magnetron sputtering, and further promoting the extensive application of Cu$_2$O materials in the field of optoelectronics.

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