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STRUCTURAL, PHOTO-FUNCTIONAL AND SEMICONDUCTOR PROPERTIES OF COPPER OXIDE THIN FILMS PREPARED BY DC REACTIVE METHOD UNDER VARIOUS THICKNESSES

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ABSTRACT

Cuprous oxide (Cu_2O) has been formed on glass substrates by dc reactive magnetron sputtering method, whereas pure target of the solid copper was sputtered with a mixture of plasma for argon gas and oxygen gas was used to form these films. Under vacuum chamber pressure of 1.2×10^{-5} Pa, thin film thickness was changed from 100 nm to 300 nm while other deposition parameters were fixed. The influence of changing the thickness of thin films on the electrical and the optical properties was investigated in this study. X-ray photoelectron spectroscopy (XPS), X-ray Diffractions system XRD, Atomic Force Microscopy (AFM), hall effect measurement system, UV–VIS spectrophotometer were employed to determine the characteristic of the deposited thin films. Thin film of 200 nm has observed low resistivity of 60.63 Ω cm and direct band gap of 2.5eV. This study has demonstrated that the thickness has direct influence on electrical and optical properties.

KEYWORDS: optical properties; Atomic Force Microscopy; spectrophotometer; copper oxide

دراسة تأثير تغيير سمك الفلم على الخصائص الكهربائية والضوئية لغشاء Cu2O بطريقة الترسيب الفيزيائية

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الملخص

تم تكوين غشاء CU2O باستخدام طريقة الترسيب الفيزيائية ,حيث تم وضع ضغط الجهاز على 5 -10×1.5 بار و قذف ذرات CU مع بلازما متكونة من غاز الأوكسجين و الاركون وتكوين الفلم على شرائح زجاجية . وبعد ذلك تم فحص التركيب البلوري للأفلام بواسطة جهاز رسم حيود الأشعة السينية (XRD), اما بالنسبة لتركيب مكونات الأغشية تم استخدام تقنية الأطياف الضوئية للأشعة السينية (XPS) ولفحص الخواص الكهربائية مثل تركيز الناقلات والمساحية للسطح والمقاومة الكهربائية قد استخدم جهاز تأثير طاقة الفجوة (HALL EFFECT SYSTEM). أما في ما يخص قياس فجوة فقد استخدم جهاز نظام الطيف الضوئي UV–VIS تحت طول موجي يتراوح ما بين 300 نانومتر إلى 900 نانومتر. جهاز مجهر القوة الذرية (AFM)استخدم لقياس خشونة الأغشية.

تم تكوين الأغشية الرقيقة CU2O بطبقات مختلفة السمك تتراوح من 100نانومتر الى 300 نانومتر. زيادة السمك إلى 200 نانومتر تبين تحسن التركيب البلوري بشكل ملحوظ مع انخفاض كبير للمقاومة الكهربائية حيث انخفضت الى 60.63 اوم/سم وضيق في فجوة الطاقة المباشرة. كان محصلة هذا البحث هي تكوين غشاء رقيق من أفلام CU2O بواسطة تغيير سمك الفلم و دراسة التأثير المباشر لتغير السمك على الخواص الكهربائية والضوئية للأغشية الرقيقة لهذه الأفلام.

1. INTRODUCTION

Copper oxide-based materials have been considered is one of the distinctive and attractive semiconductor that leading it to apply in many technological fields (Derin and Kantarli, 2002). Among these fields, Cu_2O have employed in different fields of applications such as oxygen and humidity sensors (Murayama, 1998), alternative electrochromic, photoelectrochemical and an attractive absorption material in heterojunction solar cells (Balamurugan and Mehta, 2001). Furthermore, of Cu_2O have many features such as a low industrial cost, no toxicity and high optical absorption coefficient (Paretta et al., 1996). Cu_2O have direct optical band gap energy of 2.0eV to 2.6eV, yellowish appearance, high transparency, and absorption usually at wavelengths of 600 nm (Balamurugan and Mehta, 2001). Cu_2O is considered as a semiconductor which has various characteristics behavior because of the harmonious results emerging from its formation technology (Derin and Kantarli, 2002; Murayama, 1998). Various preparation methods for the thin film such as thermal evaporation (Sharma, 1997; Richardson et al., 2001), activated reactive evaporation (Minami et al., 2004), molecular beam epitaxial (Wautelet, 1990), electro deposition (Fernando and Wetthasinghe, 2000), solution growth (Kamimura et al., 2004), sol-gel process (Yin et al., 2005), reactive RF magnetron sputtering and reactive DC magnetron sputtering (Huang et al., 2004; Ogwu et al., 2003) were employed for preparing Cu_2O thin films. DC reactive magnetron sputtering method have been chosen to prepare Cu_2O thin films, which considered as one of the best techniques to form a semiconductor thin film because of the useful of appropriate control on the structure of the thin films, perfect for the deposition, lower temperature during the formation, providing regular thickness on large substrates region and easier to control over the composition of the characteristics for the films (Reddy et al., 2005). In this method, the electrical and photofunction properties of the prepared films critically depend on the sputtering parameters such as oxygen flow rate, argon flow rate, substrate temperature and sputtering power (Richardson, 2000). In this study, Cu_2O thin films with various thicknesses have fabricated by reactive magnetron sputtering, the results expected for this study is summarized to prepared Cu_2O by changing thickness and improved the optical and electrical characteristic of these films.

2. EXPERIMENTAL METHOD AND MEASUREMENTS

2.1. Experimental Method

Cu_2O thin films were fabricated by a vacuum chamber (PVD), dc reactive magnetron sputtering method. These thin films have been sputtered on a substrate of corning glass (#1737) and mirror finishing stainless steel (304ss). The deposition chamber was evacuated by turbo molecular pump and rotary pump combination to obtain for a base pressure of 1.2×10^{-5} Pa. Under this pressure, a pure solid copper target, O_2 and Ar were employed to form the main plasma. To clean the surface of the target from the oxide layers, each thin film was sputtered in pure argon atmosphere for 10 min. Table 1 shows the deposited rates at the deposition, Cu_2O thin films were formed at a various thickness ranged from 100nm to 300nm while the other remaining deposition parameters such as oxygen flow rate, argon flow rate, substrate temperature, sputtering power and sputtering pressure have remained constant. The sputtering rate and the deposition time at 30W were used to determine the thickness of thin films as shown in Table 2. Whereas, the sputtering rate at 30W was 0.044 nm/sec. This sputtering rate have been measured by shedding 30W on solid copper target under same base pressure of 1.2×10^{-5} Pa without adding any gases.

Table 1. The depositions parameters of prepared copper oxide thin films.

Deposition parameter	Copper (99.99% pure)
Sputtering power (W)	30
Film thickness (nm)	100~300
Oxygen flow rate (sccm)	10
Argon flow rate (sccm)	15
Substrate temperature (°C)	300
Base pressure (Pa)	1.2×10^{-5}
Sputtering rate(nm/sec)	0.044

Table 2. Deposition times at various thickness.

Thickness (nm)	Sputtering rate (nm/sec)	Deposition time
100	0.044	100/0.044=40min
200	0.044	200/0.044=1h:20min
300	0.044	300/0.044=2h:00min

2.2. Measurement Methods

Composition of the films have been examined by X-ray photoelectron spectroscopy (XPS:Shimadzu Co., Ltd.) with Mg Kα (1253.4eV) radiation. XRD diffractions (XRD: MAC science. Co., Ltd) with Cu Kα (0.154 nm) radiation at an incident angle of 0.3 degree was used to determined a crystal structure form of the thin films. The surface morphology for films was measured by Atomic Force Microscopy (AFM: SPM-9500 Shimadzu Co., Ltd.) device. Electrical properties such as the resistivity, mobility and carrier concentration were measured by employing hall effect measurement system. The optical energy band gaps of the films have been determined by a UV–VIS spectrophotometer at wavelength range of 300~900.

3. FILM CHARACTERIZATION

3.1. Films Structure

Fig. 1 indicates to the results of X-ray diffraction patterns of Cu_2O and Cu_2O/CuO thin films deposited at various thickness. The film deposited at low thickness 100 nm showed single-phase Cu_2O thin film with peaks at 2θ= 36.42°, 42.3°, 61.4°, 73.5° corresponding to (1 1 1), (200), (220) and (311) orientation of Cu_2O, respectively, at this thickness, the rate of Cu atomic was sufficient to active reaction with the obtainable oxygen atoms to form pure crystal structure of Cu_2O films. However, thickness of 200 nm showed stable and uniform Cu_2O crystal structure of main orientation (111). In addition to others orientation of (1 1 1), (200), (220) and (311) of Cu_2O, thin films at 300 nm showed a peak at 2θ=61.5° corresponding to (113) orientation of CuO. The existence of the CuO at this thickness attributed to long deposition time as shown in Table 2, whereas the CuO formation needs long time to connect the bonds between O_2 and Cu.

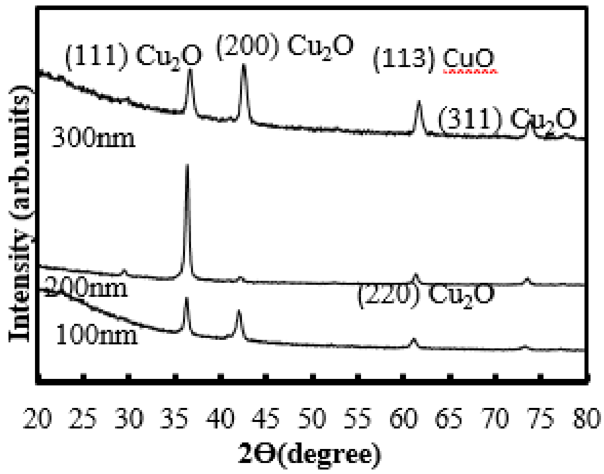

Fig. 1. XRD patterns of copper oxide thin film for different thickness.

3.2. Films Composition

Fig. 2 shows the composition of the deposited thin films which measured by X-ray photoelectron spectroscopy XPS ($Cu2p_{3/2}$), this measurements have determined the binding energy of each of the materials [Cu_2O]-[CuO] in the composite films. Fig. 2 was investigated the binding energies of 932.7eV relating to Cu_2O and 933.6eV relating to CuO. Changing the composition of these films attributed to the range of separation of the initial oxygen molecules through deposition into atomic oxygen, therefore providing the stability phases for the prepared films by controlling on the rates of oxygen ions to copper atoms and atomic oxygen to copper atoms (Feietsch et al., 2000; Samarasekara et al., 2006).

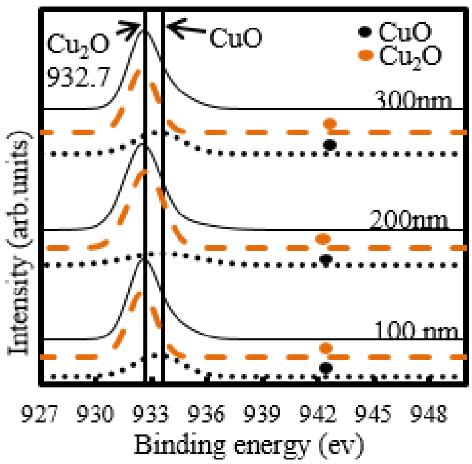

Fig. 2. Spectra of binging energy for $Cu2p_{3/2}$. at various thickness.

3.3. Surface Morphology Measurement

Fig. 3 shows the surface morphology of the deposited Cu_2O and Cu_2O/CuO thin films under various thickness. Thin film at 100 nm showed low roughness of Ra=4.3 nm with external appearance slant to the yellow and showed small numbers of spherical shaped for Cu_2O and nano-particles with non clear grain boundaries. The thickness of 200 nm demonstrated uniform surface with clear spherical granules that is lead up to increase the roughness to Ra=8.4 nm. Cu_2O thin film that formed at thickness of 300 nm showed large number of spherical shaped granular and high roughness of Ra=12.8 nm, this indicates that the films prepared at 300 nm are composite films of Cu_2O\CuO (Sameer et al., 2016; Kumar, 2013). XRD results already revealed that the films have formed at 300 nm was composite films from Cu_2O and CuO.

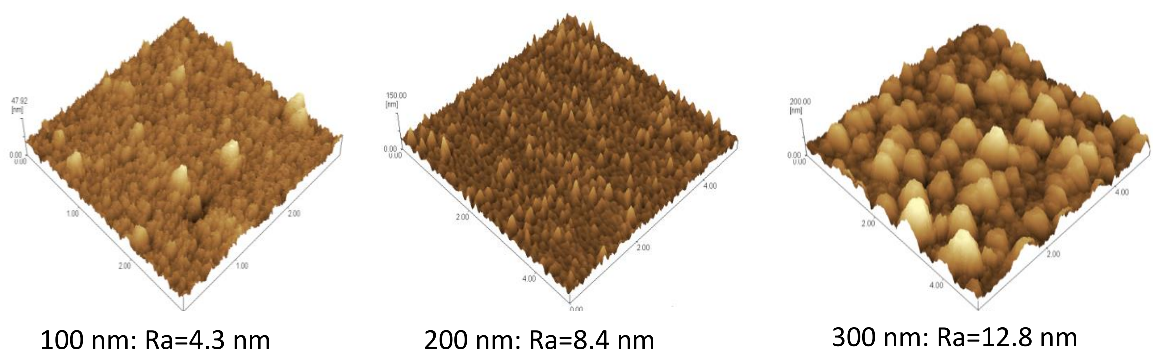

Fig. 3. Surface morphology of copper oxide at various thickness.

3.4. Semiconductor Properties Measurement

Fig. 4 shows the electrical properties of Cu_2O and Cu_2O/CuO under various thickness. The films at thickness of 100 nm observed resistivity of 700.4 Ω cm and carrier concentration 7.02E+13 cm^{-3}. However the film at 200 nm have investigated decreasing in the resistivity to the 60.63 Ω cm and increasing the carrier concentration to the 7.66 E+15 cm^{-3}, each results of 100 nm and 200 nm were for p-type Cu_2O semiconductor. The thickness of 300 nm showed increasing in the resistivity to the 70.5 Ωcm again and the carrier concentration decreased to 9.9 E+14 cm^{-3}. There are two reason to explain the higher resistivity at 100 nm, the first attributed to the poor structure crystalline as shown in XRD results, whereas the initial Cu_2O films prepared at thickness 100 nm is non-stoichiometric (Ogwu et al., 2007), the second attributed to the carrier concentration with Cu atoms was insufficient to obtain low resistance. Thin film at 200 nm have demonstrated significant decreasing in the resistivity due to, the films became near to the full stoichiometry, also the sufficient numbers for proportional of Cu atoms in the film. Increasing the resistivity at 300 nm, due to the appearance of n-type CuO thin film along with Cu_2O (Mohd et al., 2011).

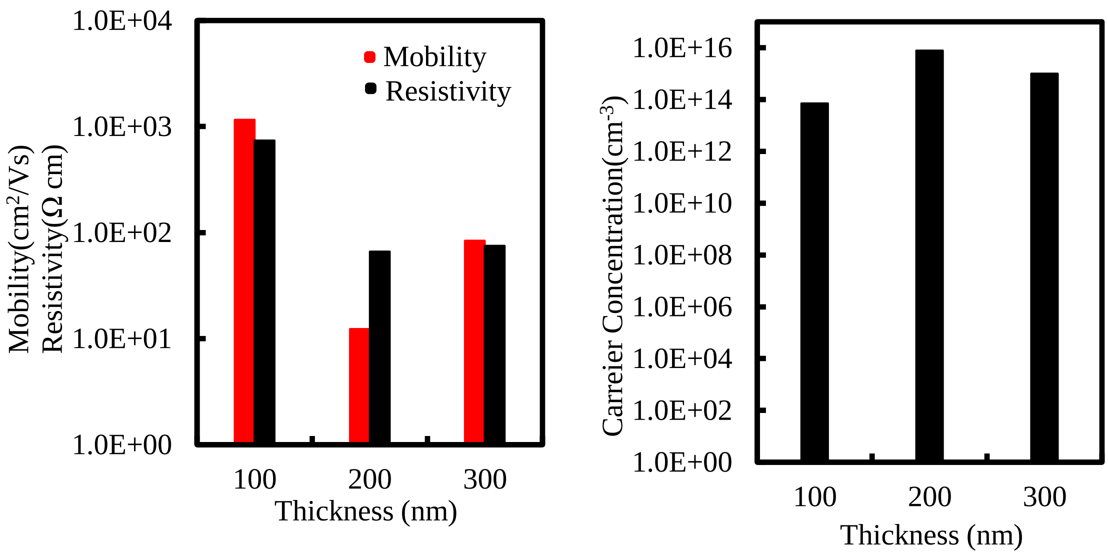

Fig. 4. Electrical properties of Cu_2O for different thickness.

3.5. Optical band gap measurement

Fig. 5 demonstrates the direct optical band gaps for Cu_2O and Cu_2O/CuO thin films at different thicknesses. The photon energy (hv) were calculated by Lamia, (2006):

$$E = hv = \frac{hc}{\lambda} \qquad 2$$

Where h = Planck's constant (6.626×10^{-23}), c is speed of light (3×10^{8}), λ is the wavelength. The optical transition is controlled by the optical band gap energy (E_g) for the semiconductor which is related to the optical absorption coefficient (α) and the indicated photon energy (hv) by using Tauc equation:

$$(\alpha hv) = A\,(hv - Eg)^{n} \qquad 3$$

where v = photon frequency, Eg = optical band gap, n=1/2.

The results of this measurements demonstrated optical band gaps of 2.7eV, 2.6eV, 2.5eV related to the thicknesses of 100 nm, 200 nm, 300 nm, respectively. All the deposited films were in the rang that related to Cu_2O except a slight difference attributed to composition of the film. Whereas, the films at 300 nm observed decreasing in the band gap due to presence of CuO along with Cu_2O (Sameer et al., 2016).

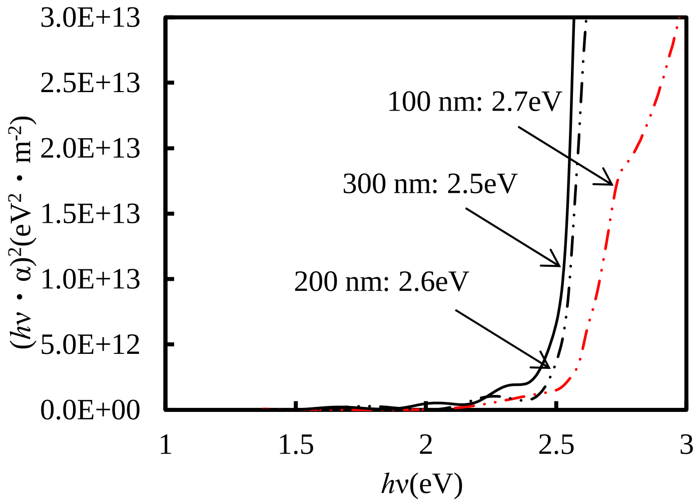

Fig. 5. The direct band gap of Cu_2O at various thickness.

4. CONCLUSION

Cu_2O thin films were prepared at various thicknesses by using dc reactive magnetron sputtering method. The films were formed on a substrate of corning glass (#1737) and mirror finishing stainless steel (304ss) with 99.99% copper target. This study have investigated the ability to form Cu_2O at slight thickness of 100 nm and short time. The film structure has improved by increasing the thickness to the 200nm and the resistivity also improved from 700.4 Ω cm to 60.63 Ω cm. When the thickness was raised above the 200 nm, the CuO thin film was shown along with Cu_2O, that is cause to increase the resistivity. These results suggest the possibility of enhancing on the electrical properties of Cu_2O by the control on the thickness of thin films. The thickness has directly influence on the optical properties, where the direct optical band gap were decreased by increasing the thickness. Crystal structure also has changed with changing the thickness, whereas single phase of Cu_2O have been obtained at thickness 200nm,100nm and composite crystal structure of Cu_2O\ CuO at thickness 300nm.

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