Preparing CuO, Cu_2O thin films at various argon gas by using reactive dc magnetron sputtering method

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المستخلص

تم تكوين غشاء Cu_2O باستخدام طريقة الترسيب الفيزيائية ,حيث تم وضع ضغط الجهاز على 1.5×10^{-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 CuO, Cu_2O بتغير كمية غاز الاركون 5-15sccm المضافة في التجربة . حيث تم تكوين افلام CuO الرقيقة بكمية اركون 5 sccm وبحزمة طاقة 1.8 eV وقطبية سالبة , بعد زيادة غاز الاركون بدء الفلم بالتحول من خصائص Cu Oالى خصائص Cu_2O حتى تم الحصول على خصائص الثابتة الى Cu_2O عنده كمية الاركون 15 sccm وبقطبية موجبة وحزمة طاقة 2.7 eV. كان ملخص البحث هو, باستخدام طريقة الترسيب الفيزيائية تم تكوين خصائص لعنصرين وبقطبيتين مختلفة وذلك بتغيير احد عناصر التجربة غاز الاركون وتثبيت جميع المتغيرات الاخرى.

Abstract

Copper oxide (Cu_2O, CuO) has been formed by dc reactive magnetron sputtering method of glass substrates, whereas pure target of the solid copper was sputtered with a mixture of plasma for argon gas and oxygen gas which are used form these films. Under vacuum chamber pressure on 1.2×10^{-5} Pa, Ar was varying from 5 to 15 sccm while other deposition parameters were fixed. X-ray photoelectron spectroscopy, XRD diffractions system, Atomic Force Microscopy (AFM), hall effect measurement system, and UV–VIS spectrophotometer were used to calculate the characteristic of the deposited thin films. Thin film at 5 sccm has investigated n-type of CuO thin film with direct band gap of 1.8eV and p-type of Cu_2O at 15 sccm with direct band gap of 2.7eV. The influence of changing the Ar on the electrical and the optical properties was investigated in this study, furthermore in this study approved that the reactive dc magnetron sputtering method is suitable to prepare two type of semiconductors by change only one condition.

Keywords: Sputtering magnetron, Thin Films, Cu_2O, Cu,CuO and Photo-function.

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 [1]. Among these materials, benefit of high optical absorption coefficient combined with no toxicity and low cost abundance [2], Cu_2O films have employed in varied field of uses like oxygen and humidity detection [3], electro chromic devices and absorber sheet in hetero junction thin film solar cells [4]. Cu_2O has direct optical band gap energy of 2.0eV to 2.6eV, slightly yellowish appearance, high transparency, and absorption usually at wavelengths below 600nm [3]. Cu_2O is considered as a semiconductor which has a varying electrical and optical behavior because of the stoichiometric deviation arising from its fabrication methods [1, 2]. Different thin film deposition techniques such as thermal evaporation [5, 6], activated reactive evaporation [7], molecular beam epitaxial [8], electro deposition [9], solution growth [10], sol-gel process [11], reactive RF magnetron sputtering and reactive DC magnetron sputtering [12, 13] were employed for preparing Cu_2O thin films. Among these methods, dc reactive magnetron sputtering method has chosen to prepare Cu_2O thin films, which considered one of the best techniques to form a semiconductor thin film because of the advantage of proper control on the chemical composition, high deposition rates, low substrate heating during the deposition, providing uniform thickness on large substrates area and easier to control over the composition of the electrical and optical characteristic of the deposited films [14]. In this method, the physical properties of the fabricated films highly depend on the sputtering parameters such as oxygen flow rate, argon flow rate, substrate temperature and sputtering power [15]. In this study, Cu_2O thin films with various argon flow rat were prepared by reactive magnetron sputtering, the relation between the changing of the Ar and the characteristic of copper oxide thin films were demonstrated.

2. Experimental method and measurements

2.1 Experimental method.

In this paper Cu_2O thin film organized by a vacuum chamber (PVD) dc reactive magnetron sputtering unit. The thin films have been sputtered on a substrate of corn glass (#1737) and mirror finishing stainless steel (304ss). The deposition chamber is 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, oxygen gas and argon gas are employed to form the main plasma. To remove oxide layers from the surface of the target, each thin film is sputtered in pure argon atmosphere for 10 min. Table.1

shows that the deposited rates of the deposition, Cu_2O, CuO thin films are formed at a various Ar from 5 to 15 sccm while the other deposition parameters such as oxygen flow rate, argon flow rate, substrate temperature, sputtering power and sputtering pressure have remained constant.

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

Deposition parameter	Copper (99.99% pure)
Sputtering power (W)	30
Film thickness (nm)	200
Oxygen flow rate (sccm)	10
Argon flow rate (sccm)	5-15
Substrate temperature (°C)	300
Base pressure (Pa)	1.2 10^{-5}
Deposition rate(nm/sec)	0.044

2.2 Measurement methods

Composition of the films has decided by X-ray photoelectron spectroscopy (XPS: Shimadzu Co., Ltd.) with Mg Kα (1253.4eV) radiation. The XRD diffractions (XRD: MAC science. Co., Ltd) with Cu Kα (0.154 nm) radiation at an incident angle of 0.3 degree is used to decide a crystal structure form of the thin films. The surface morphology for films is observed by Atomic Force Microscopy (AFM) device. The thickness measurement of the films is carried out with a Dektak profilometer and checked for accuracy by AFM step-height analysis using a Digital instrument (Nanoscope III) atomic force microscopes. Electrical properties such as the resistivity, mobility and carrier concentration are measured by employing Hall Effect measurement system. The optical energy band gaps between the films have been determined by an UV–VIS spectrophotometer at wavelength range of 300~900.

3. Film characterization

3.1 Films structure

Fig.1 shows x-ray diffraction patterns results of the deposited films at various argon gas flow rate, low rate of argon gas at 5 sccm showed single-phase CuO thin film that has strong pecks at $2\theta = 35.44°$,38.73 ° and 48.76 ° , corresponding to (1 1 1), (111) and (202) orientation of CuO, respectively. While, the thin films at 10 sccm shows Cu_2O with composite orientation of Cu_2O/CuO, by increasing the gas flow rate the peaks value of CuO have decreased, and also new peaks that related to Cu_2O orientation of (1 1 0), (111), (200), (311) and (222) at 2θ=29.55°, 36.41°, 42.29°, 73.52° and 76.64° have investigated. Thin film at 15 sccm shows pure single phase Cu_2O with strong peak of the main orientation (111) at 2θ=36.41°. These results attributed to the argon gas flow rate that have been changed during the sputtering. Whereas, increasing of argon gas lead to increase the bombed Cu atomic from the target to the vacuum chamber, therefore increasing in the argon gas flow rate lead to change the crystal structure form CuO to Cu_2O. The proportion of the ions of oxygen to copper atoms and atomic oxygen to copper atoms were determined the stability of phase which regime for Cu_2O and CuO[16, 17]. The formation of these films is based on the reaction,

$$Cu_2O + O \rightarrow 2CuO \qquad (1)$$

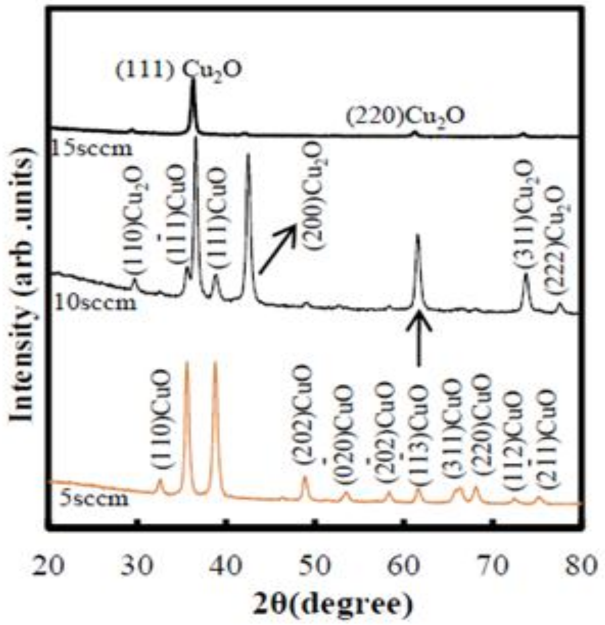


Fig.1 XRD patterns of copper oxid thin film under various Ar.

3.2 Films composition

X-ray photoelectron spectroscopy XPS ($Cu2p_{3/2}$) have been used to determine binding energies of Cu_2O,CuO as shown at Fig.2. Fig.2 obviously demonstrated the binding energies of 530.5eV relating to Cu_2O at Ar of 15sccm and 529.6eV relating to CuO at 5sccm. The peak have been shown at 10sccm related to the composite film Cu_2O/CuO. These results boosted the result of XRD.

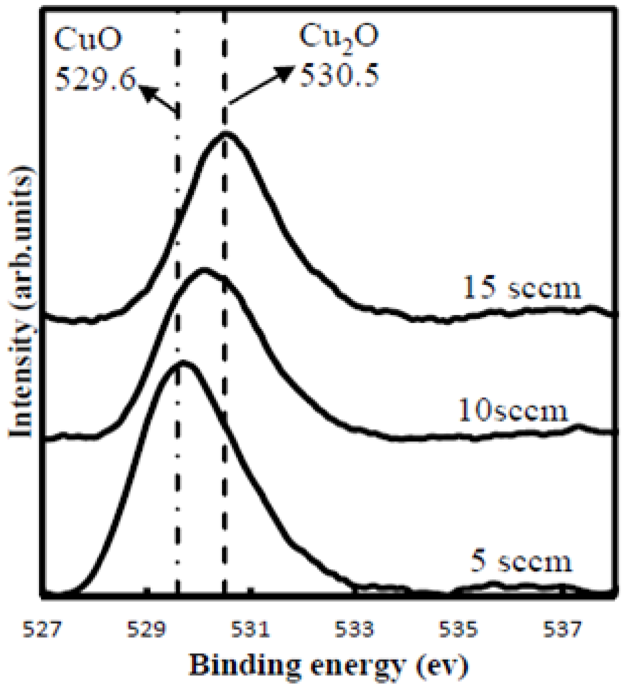
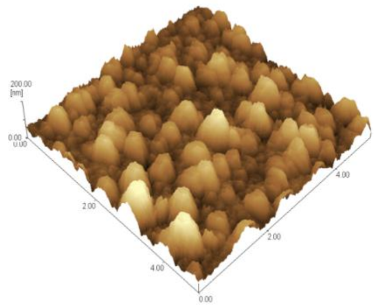


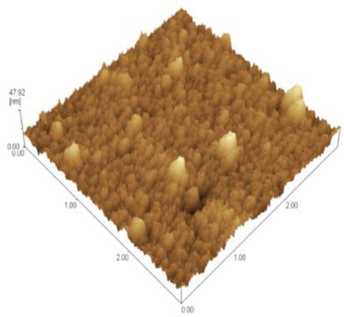
Fig.2 Binging of Energy for $Cu2p_{3/2}$ at various Ar.

3.3 Surface morphology measurement

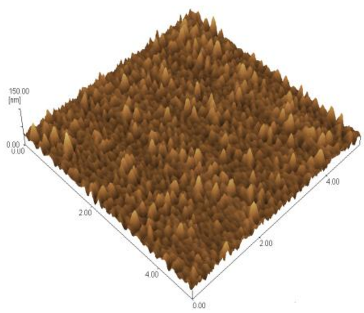
Fig.3 shows the surface morphology of the deposited Cu_2O, CuO and Cu_2O/CuO thin films by various Ar. Thin film of 5sccm demonstrated high roughness of Ra=12.8 nm with black external appearance and large numbers of spherical shaped for CuO and nano-particles with clear grain boundaries, due to atoms of O^+ in the films. At 10sccm the atoms of O^+ decreased sufficiently to lead up the roughness to decrease into Ra=8.4 nm. The characteristics of surface morphology for Cu_2O have investigated at 15sccm, whereas the films showed small numbers of spherical shaped granular and low roughness of Ra=4.3 nm. [19, 20] also have indicated to the similar results.



5sccm: Ra=12.8nm



10sccm: Ra=8.4nm



15sccm: Ra=4.3nm

Fig.3 Surface morphology of copper oxide at various Ar

3.4 Semiconductor properties measurement

The semiconductor properties of Cu_2O, Cu_2O/CuO and CuO thin films under various Ar have been showed at Fig.4. Films at Ar 5 sccm investigated resistivity of 1.09E+3 Ωcm and carrier concentration -3.49E+15 cm^{-3} attributed to a single phase of n-type CuO. A 5 sccm have considered turning point from characteristic of n-type at CuO to the characteristics of p-type at Cu_2O. Resistivity decreased from its maximum value 1.09E+3 Ωcm at 5sccm to the value of 1.38E+2 Ωcm at 10 sccm due to increase of Cu atoms by increasing the argon gas. A slight decreasing on resistivity was indicated at Ar of 15 sccm, also the number of carrier have showed increasing to 7.66E+15 cm^{-3} and the film characteristics have become single.

phase of p-type at Cu_2O as shown at Fig.2. The high carrier concentration that was observed at 15 sccm attributed to the pure structure of Cu_2O that have formed by the suitable number of Cu and O atoms. As shown in fig.4 the results of the mobility have provided the results of the surface morphology measurements in Fig.3. These results are consistent with the characteristics of CuO and Cu_2O[18].

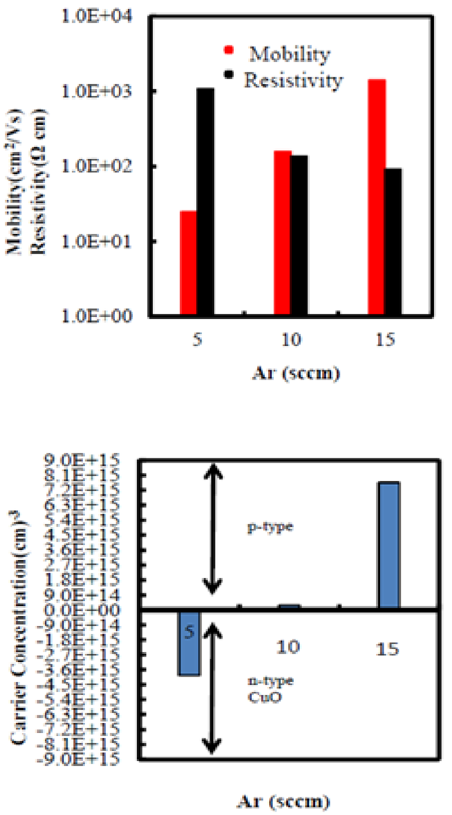


Fig.4 Electrical properties of Cu_2O at various Ar

3.5 Band gap measurement

Fig. 7 shows the optical band gap of copper oxide under various sputtering power. Optical band gap was determined by using UV-Vis absorbance spectrum and calculated by Tauc equation that shown in eq.2, where Eg is optical band gap, v is photon velocity, h = Planck's constant.

$$(\alpha hv) = \exp (hv - Eg)1/2 \quad (2)$$

Band gap of copper oxide was 1.8eV at 5 sccm, 2.5eV at 10sccm and 2.7eV at 15 sccm. In this result that the fabricated copper oxide showed a CuO properties at Ar of 5 sccm, while the band gap of Cu_2O thin films where observed at 10 sccm and 15 sccm.

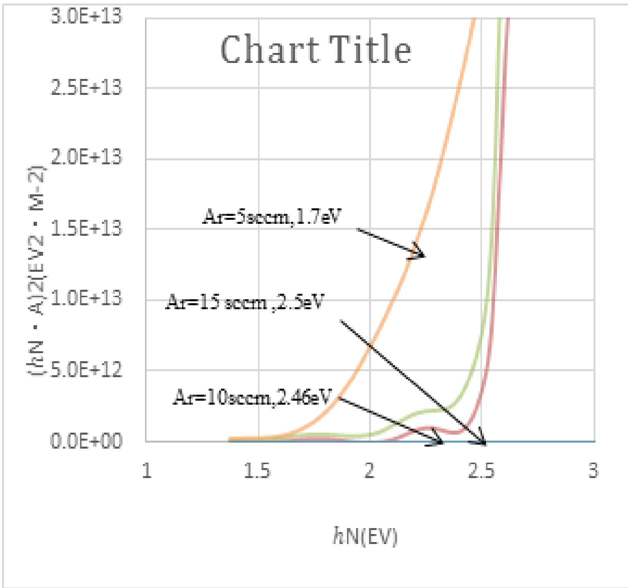


Fig.5 The direct band gap of Cu_2O at various thickness.

4. Conclusion

The copper oxide thin films were prepared under various argon gas by using the dc magnetron sputtering method. XRD, XPS results showed that the Ar had the main role in film structure. The copper oxides with an n-type of CuO phase were obtained under Ar of 5 sccm, while an p-type of Cu_2O phase was observed at 10 and 15 sccm. The Hall effect measurement and the calculated optical band gap showed that this film formation method could precisely fabricate copper oxcides with different characteristics.

References: -

[1]S.P. Sharma, J. Vac. Sci. Technol. 16 **(1979),** p. 1557.

[2]T.J. Richardson, J.L. Slack and M.D. Rubin, Electrochim. Acta.**46** (**2001**), p. 2381.

[3]T. Minami, H. Tanaka, T. Shimakawa, J. Miyata and H. Sato, Jpn. J. Appl. Phys. 43 (**2004**), p. 917.

[4] B. Balamurugan and B.R. Mehta, Thin Solid Films**396**(**2001**), p. 90.

[5] A AOgwu, E Bouerel, O Ademosu, S Moh, E Crossan and F Placido. Journal of Physics, Volume 38, Issue 2, pp. 266-271 (**2005**).

[6] Mugwang'a F.K, Karimi P.K, Njoroge W.K, Omayio O and Waita S.M,Int. J. Thin Film Sci. Tec. 2 No. 1, 15-24 (**2013**).

[7] T.Murayama, Sol Energ Mater Sol Cells 56 (**1998**),
P.85.

[8] J.F. Pierson, A. Thobor-Keck and A. Billard, Appl Surf Sci**210** (**2003**), pp. 359–367.

[9] B. Balamurugan and B.R. Mehta, Thin Solid Films**396** (**2001**), p. 90.

[10] S. Zhang, N. Ali, Nanocomposite thin films and coating, Imperial collage Press (2007), pp14.

[11] L.S. Huang, S.G. Yang, T. Li, B.X. Gu, Y.W. Du, Y.N. Lu and S.Z. Shi, J. Cryst. Growth **260** (**2004**), p. 130.

[12] B. Balamurugan, B.R. Mehta, D.K. Avasthi, F. Singh, A.K. Arora, M. Rajalakshmi, G. Raghavan, A.K. Tyagi and S.M. Shivaprasad, J. Appl. Phys. **92** (**2002**), p. 3304.

[13] I.L. Yubinetsky, S. Thevulhasan, D.E. Mc Cready and D.R. Baer, J. Appl. Phys.**94**(**2003**
), p. 7926.

[14] C.A.N. Fernando and S.K. Wetthasinghe, Sol. Energy Mater. Sol. Cells **63** (**2000**), p. 299.

[15] S.C. Ray, Sol. Energy Mater. Sol. Cells **68** (**2001**), p. 307.

[16] J. Morales, L. Sanchez, S. Bijani, L. Martizez, M. Gabas and J.R. Ramos-Barrado, Electrochem. Solid-State Lett.**8** (**2005**) (3), p. 159.

[17] A. Parretta, M.K. Jayaraj, A.D. Nocera, S. Loreti, L. Quercia and A. Agati, Phys. Status Solidi, A Appl. Res. **155**(**1996**), p. 399.

[18] K. Kawaguchi, R. Kita, M. Nishiyama, T. Morishita, Molecular beam epitaxy growth of CuO and CuO films with controlling the oxygen content by the flux ratio of Cu/O+, Journal of Crystal Growth 143 (**1994**) 221-226.