Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 24
ISSUE 1
September
2007

Electrical resistivity of copper oxide thin films prepared by reactive magnetron sputtering

A.A. Ogwu [a,*]
co-operating with
T.H. Darma [b], **E. Bouquerel** [c]
[a] Thin film centre, School of Engineering and Science, Paisley University, High street, Paisley PA1 2BE, Scotland, United Kingdom
[b] Physics Department , Bayero University, Kano, Nigeria
[c] CERN, Geneva, Switzerland
* Corresponding author: E-mail address: oqwu-ph0@paisley.ac.uk

Received 03.04.2007; published in revised form 01.09.2007

Properties

ABSTRACT

Purpose: Investigation the effect of varying r.f. power and oxygen flow rates during deposition on the electrical properties of copper oxide thin films prepared by reactive magnetron sputtering
Design/methodology/approach: The films were characterised by AFM, XPS, four point electrical resistivity probe measurements and spectrophotometry.
Findings: The electrical sheet resistance of the films was found to vary from greater than 4 x 105 ohms/square for films prepared at 200W r.f. power to as low as 20 ohms/square for films prepared at 800W r.f. power. The variation in the electrical resistivity of the films with deposition conditions has been explained in terms of stoichiometric changes induced by copper or oxygen ion vacancies and neutral defects.
Practical implications: The formation of these defects depends on the sticking coefficient, nucleation rates and the migration of impinging copper and oxygen species on the substrate during deposition.
Originality/value: This information is expected to underlie the successful development of copper oxide films for solar windows and other semi-conductor applications including gas sensors.
Keywords: Electrical properties; Magnetron sputtering; Thin films

1. Introduction

Cuprous oxide (Cu_2O) is a metal deficient semi-conductor of p-type conductivity which shows a varying optical behaviour because of stoichiometric deviations arising from it's preparation methods and parameters [1-3]. It has been reported that many of the growth methods for cuprous oxide result in a combined growth of copper (I) oxide Cu_2O and copper(II) oxide CuO, i.e. Cupric oxide [1-5]. A range of direct optical band gap energies have also been reported for Cu_2O [6-13] and CuO [10,13] semiconductor films in the literature, depending on the method of fabrication and stoichiometry. The reported direct optical band gap energy values for Cu_2O range from 2.10-2.6 eV [6-13], whilst values of 1.3-2.1 eV [10, 13] have been reported for CuO . Cu_2O oxide films are reported to have high transparency, with a slightly yellowish appearance and absorb usually at wavelengths below 600nm, whilst CuO absorbs strongly throughout the visible spectrum and is black in appearance[2] .The current potential application areas of copper oxide thin films include solar cells and electro-chromic devices [1,2] . Copper oxide films have been reported to have band gap energy values, which make them suitable for application as windows for solar energy conversion [1,9]. Richardson [14] has also highlighted the potential of copper oxide films as spectrally selective variable reflectance coatings for radiant energy control in architectural and aerospace applications. The two basic requirements for materials to be used as solar cell windows are a high optical transmittance in the visible and low

electrical resistivity. Despite it's high optical transmittance in the visible, cuprous oxide is known to have a high electrical resistivity which varies with the method of preparation [1,15]. Thermal preparation methods result in resistivities in the range 10^2-10^4 Ω cm and electro-deposition produces films with resistivities in the range 10^4-10^6 Ω cm [1,15]. There are several practical difficulties with the substitutional doping of Cu_2O films [1]. Several attempts have been made in the literature to develop alternative fabrication methods that will produce Cu_2O films with lower resistivities. Drobny and Pulfrey and other researchers in the literature [15] have attempted to prepare copper oxide films by reactive sputtering, which had the potential to produce a range of films with stoichiometries varying from Cu-rich Cu_2O to Cu_2O and finally CuO by changing the deposition parameters. Drobney and Pulfrey [15] prepared copper oxide films by both D.C. and rf. reactive sputtering and found out that they could vary the resistivity of the prepared films by varying the oxygen partial pressure. Copper oxide films with resistivities as low as 25Ω cm was reported by these authors [15]. However, all the reported resistivity measurements by Drobny and Pulfrey on copper oxide films [15], was conducted at a fixed forward power of 200W.

To the best knowledge of the present authors, no systematic study of the combined effect of the rf power and oxygen flow rate during deposition, on the electrical resistivity and optical properties of copper oxide films prepared by magnetron sputtering has been reported in the literature. We report the result of our investigation into how the rf power in the range 200W-800W and oxygen flow rate in the range 4sccm to 10sccm, during the magnetron sputtering process, affects the electrical resistivity, optical transmission and optical band gap of copper oxide films.

2. Experimental investigation

2.1. Film deposition conditions

A cryo-pumped vacuum chamber (CVC) magnetron sputtering unit was used for the thin film deposition. The starting materials were a solid copper target (99.99 at% pure) and two gases namely, Oxygen and Argon. The deposition chamber was evacuated to a base pressure of 0.01mTorr. High purity argon and oxygen were used as sputtering and reactive gases. The investigated deposition parameters are indicated in Table 1.

2.2. Film characterisation (EDAX and XPS)

Chemical characterisation was conducted on the films using the EDAX facility on the scanning electron microscope.A Hitachi S-4100 scanning electron microscope with EDAX was used for the investigation. The EDAX analysis revealed the presence of copper and oxygen and other elements from the glass substrates as shown in fig.1 . The gold traces arise from the gold coatings applied to enhance the SEM imaging. The SEM images were smooth and no features were revealed, indicating that the films could be amorphous. Chemical compositional analysis on the copper oxide films was carried out by x-ray photoelectron spectroscopy using a VG Escalab 200D electron spectrometer.Mg K_α X- radiation was used for the examination, at a source excitation of 15KeV and emission current of 20 mA.

Table 1.
The deposition conditions of the prepared copper oxide films

Argon flow rate	50 sccm
Oxygen flow rates	4, 6, 7, 8, 9, 10 sccm
Forward rf power (input)	200, 400, 600, 800 W
Reflected power	< 5W
Target	Copper
Substrate	Glass
Deposition time	30 seconds
Substrate temperature	Room Temperature

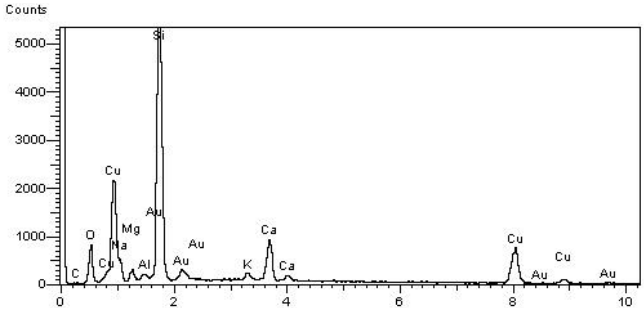

Fig. 1. Elemental composition of the copper oxide films and glass substrates

2.3. Optical transmission measurement

The optical transmittance of the copper oxide films was studied in the wavelength range 400-850nm and in more detail in the green (550 nm wavelength) using a Hitachi U-3501 model spectrophotometer. This equipment consists of a deuterium discharge tube used to produce UV light and an iodine tungsten lamp used for the production of visible and near –infrared light. All measurements were made in the laboratory in air and at room temperature. The results were presented using a computer software package on a computer interfaced to the spectrophotometer in the form of percentage of transmitted light intensity against wavelength.

2.4. Bandgap measurement

Optical transition in the prepared copper oxide films was characterised for transitions between extended band states. The absorption coefficient α near the absorption edge was determined from the optical transmission measurements at various wavelengths using the relationship of Sunds [16,17], given by

$$\alpha = 1/d \ln (I_0/I) \quad (1)$$

where d is the film thickness, and I_0 and I are the intensities of the initial and transmitted beams respectively. In order to determine the direct optical band gap, we used the Tauc relationship [18] as follows,

$$(\alpha h\nu) = A (h\nu - Eg)^{1/2} \quad (2)$$

where h = Plancks constant, v = photon frequency, Eg = optical band gap

An extrapolation of the linear region of a plot of the graph of $(\alpha hv)^2$ on the y-axis versus photon energy (hv) on the x-axis, gives the value of the optical band gap Eg, since Eg = hv , when $(\alpha hv)^2 = 0$ [6,10].

2.5. Electrical resistivity measurement

The sheet resistance of the prepared films was measured by the four point probe. The sheet resistance was determined by measuring the ratio of the voltage drop (V) from the two inner probes to the applied current (I) measured from the two outer probes. The result was multiplied by a geometric correction factor that depends on the probe geometry, given by the relationship,

$$R_s = k\left(\frac{V}{I}\right) \quad (3)$$

where R_s is the sheet resistance and k is a geometric factor, which is 4.53 for a semi-infinite thin sheet. The sheet resistance R_s is the ratio of the resistivity (ρ) of the films to their thickness (t).

3. Results and discussion

The optical transmittance of copper oxide films prepared at 200W, 600W and 800W rf power and 4sccm flow rate of oxygen gas is shown in fig 2. As shown in fig.2, the optical transmittance of the films showed a strong dependence on the applied rf power during deposition; the optical transmittance decreased with an increase in rf power during deposition. This behaviour was observed for all the film deposition conditions we investigated. Fig.3 summarises the inter-relationship between the rf power, oxygen flow rate and the optical transmission at 550nm wavelength in the amorphous copper oxide films. The predominant factor controlling the optical transmission seems to be the input rf power.

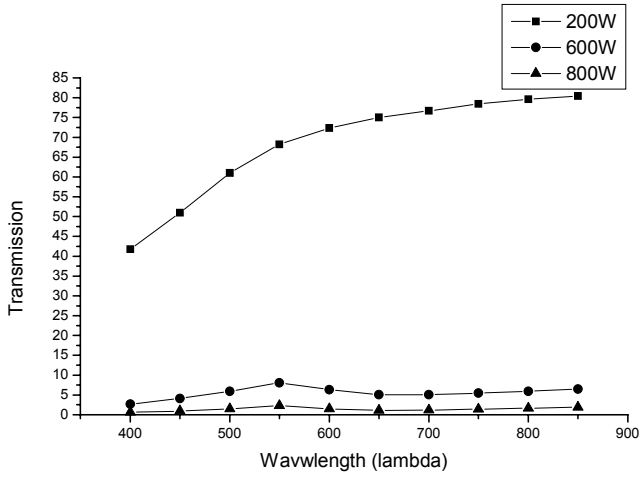

Fig. 2. Percentage optical transmission against wavelength of copper oxide films prepared at 200W, 600W and 800W rf power and 4 sccm oxygen flow rate

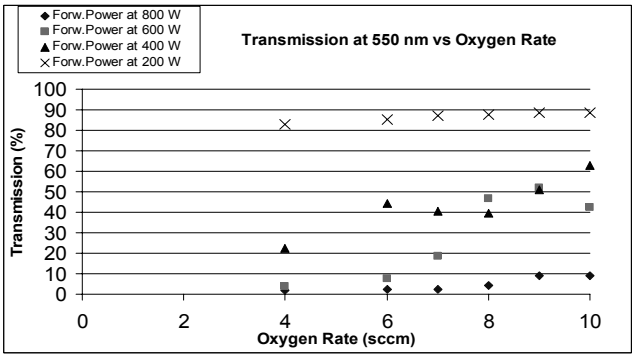

Fig. 3. The combined effect of oxygen flow rate during deposition and rf power on the optical transmission of the investigated copper oxide films

However, for films deposited at 400 and 600W power, there are clear indications of variations in the optical transmission due to changes in the oxygen flow rate during deposition. We have also observed a gradual colour change from transparent slightly yellowish appearance for films deposited at 200W power to a more yellowish less transparent film at 400W and dark absorbing non-transparent films at 800W power for all oxygen flow rates investigated. The changes in the colour of the films with input power can be associated with the production of Cu_2O rich films with a transparent yellowish appearance [2] at a low input rf power of 200W and black absorbing CuO rich film at a forward rf power of 800W. A co-deposition of Cu_2O and CuO is also produced for input powers of between 400 and 600W as already reported in the literature for other deposition methods [1-5] based on observed colour changes and our x-ray photoelectron spectroscopy investigation**.** We observed bonding changes in the copper atoms in the copper oxide films based on Cu $^2P_{3/2}$ peak binding energies that ranged from 933.6 ev to 932.4ev. The film prepared at 600W was found to be a mixture of Cu_2O and CuO as suspected from the optical transmission measurements. The films are observed to be either Cu_2O rich or CuO rich depending on if the rf power was less than or greater than 600W. The details of the photoelectron line energies, Auger line energies and XPS satellites observed in the copper oxide films will be the subject of a future publication.

The kinetics of the formation of oxides of copper during thin film deposition is dependent on a number of factors [19-21], namely

1) The nucleation rates of Cu, Cu_2O and CuO during the deposition process
2) The sticking coefficient / sticking probability of the particles reaching the substrate
3) Re-evaporation and migration by the impinging copper and oxygen species
4) The different growth rates of the nucleated species

All of the above factors will depend on the rf power and gas pressure in the deposition chamber during the sputtering process. The effective sticking probability, S (P), is defined by the relationship [22],

$$S(P) = \Gamma(P, depo) / \Gamma(P, in) \quad (4)$$

where Γ (P, depo) = actual deposited particle flux of particles of element P, Γ (P, in) = incident particle flux of particles of element P.

The importance of the two parameters Γ(P, depo) and Γ(P, in) used to determine the effective sticking probability during the thin film deposition process has been highlighted by Kawaguchi et al [20] and Muthe et al [21] for copper oxide thin films. Kawaguchi et al [20], observed that the growth of Cu_2O films under molecular beam epitaxy (MBE) conditions is achieved by maintaining a ratio of oxygen ions $[O^+]$ to copper atoms i.e $[O^+]$ / [Cu] flux ratio of approximately 1.7. They further observed that a $[O^+]$ / [Cu] ratio of 10 was necessary for CuO film formation, whilst a flux ratio of 0.6 was found to lead to the formation of a mixed phase of Cu and Cu_2O. Muthe et al [21] also investigated the stoichiometric changes in copper oxide films as a function of the ratio of atomic oxygen to copper fluxes during deposition. Muthe et al [21] observed that the type of oxide formed i.e. Cu_2O or CuO depended on the oxygen to copper flux ratio, but not on the individual flux values during deposition. They observed the formation of pure Cu films at a flux ratio of ~ 0.16, a mixture of Cu and Cu_2O films at flux ratios of between 0.16 and below 0.8, pure Cu_2O phases above a flux ratio of 0.8 and a predominantly CuO film at flux ratios above 3.0. Muthe et al [21] also observed that the kinetics of CuO formation was much slower than that of Cu_2O. They further proposed that CuO formation is based on the reaction,

$$Cu_2O + O \rightarrow 2CuO \quad (5)$$

Since the extent of dissociation of the starting oxygen molecules during deposition into atomic oxygen and oxygen ions depends on the applied rf power during deposition, the ratios of oxygen ions to copper atoms and atomic oxygen to copper atoms, which determine the phase stability regime for Cu_2O and CuO formation [20, 21], will depend on the rf power applied during deposition. As already mentioned we obtained transparent slightly yellowish films of Cu_2O rich films at 200W rf power during deposition and dark absorbing non-transparent CuO rich films at 800W rf power for the same oxygen flow rate during deposition. An increase in rf power during deposition will increase the energy and flux ratio of the species in the particle flux as explained above and this will lead to a change in film stoichiometry from Cu_2O to CuO.

Also contrary to reports in the literature that Cu_2O is strongly absorbing for wavelengths below 600nm [2], we have observed transmissions of between 40% and 80% for the films prepared at a low forward rf power of 200W in the wavelength range 400-850nm for all oxygen flow rates investigated. A typical relationship between the input rf power and the absorption coefficient (α) for the prepared films is shown in fig 4. The absorption coefficient is found to increase with an increase in rf power. This indicates a likely dependence of the optical transmittance, structure as well as stoichiometry of the deposited films on the input power during deposition. In order to better understand the changes in optical transmittance as a function of deposition parameters, we computed the direct optical bandgap values using results based on the optical transmission measurements in the wavelength range 400-850nm.

The determination of the direct optical bandgap of copper oxide films deposited at 4sccm oxygen flow rate and at 200W, 600W and 800W power, where we obtained the minimum optical transmission compared to other oxygen flow rates, for the range of rf power investigated, was carried out by linear extrapolation of the $(\alpha hv)^2$ versus hv curve as shown in figs 5, for the film prepared at 200W rf power. We obtained direct optical band gap values of 2.4eV for the film deposited at 200W power, 2.2eV for the 600W film and 2.05 eV for the film prepared at 800W power. On the basis of the previously reported direct optical band gap in copper oxide films in the literature [6-13], we infer that the copper oxide films prepared at 200W and 600W power and 4 sccm oxygen flow rate are Cu_2O rich films, whilst the film prepared at 800W power and 4sccm oxygen flow rate is a CuO rich film. We can confirm based on the low optical transmission in the film prepared at 600W for the wavelength range investigated (400nm-850nm), of the presence of a mixed Cu_2O / CuO phase. All of the above band gap correlations with reported values in the literature are in agreement with our XPS chemical phase determination.

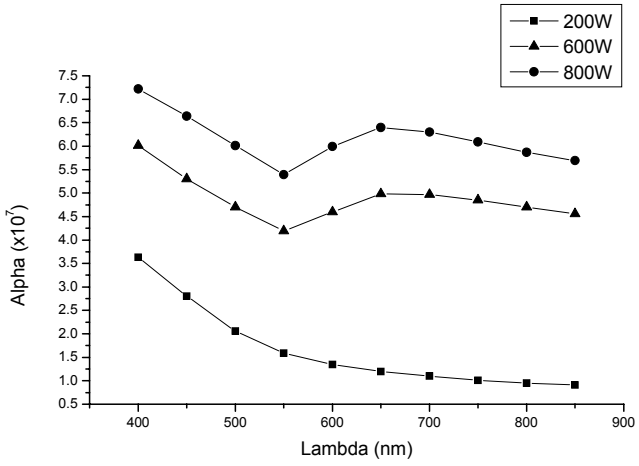

Fig. 4. Absorption coefficient (α) versus wavelength for copper oxide films prepared at 4 sccm flow rate

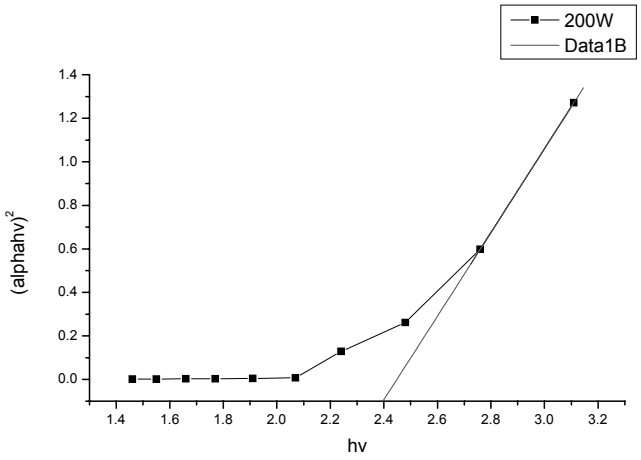

Fig. 5. $(\alpha hv)^2$ versus hv plot for copper oxide film prepared at 200W rf power and 4sccm oxygen flow rate

The effect of forward rf. power on the electrical sheet resistances of the films prepared at 4 sccm oxygen flow rate is shown in fig 6. The sheet resistance of the film prepared at 200W rf power identified as Cu_2O rich by our XPS measurement is quite high and in excess of 4.5×10^5 ohms/square.

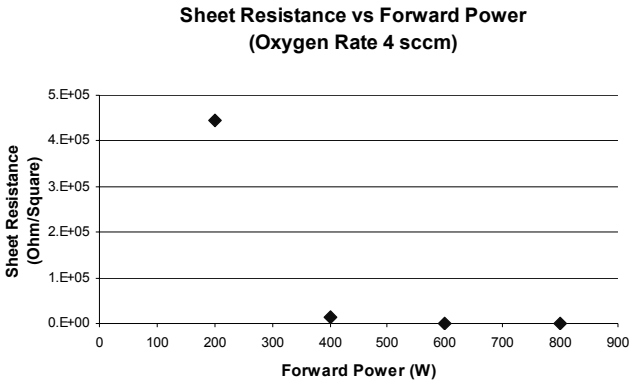

Fig. 6. Electrical sheet resistance versus forward r.f power during deposition for copper oxide films prepared at 4sccm oxygen flow rate

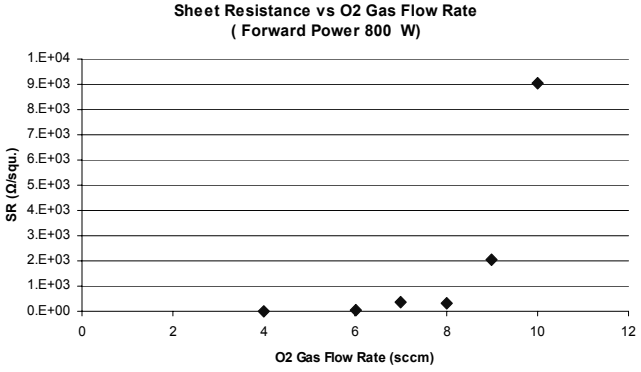

Fig. 7. Electrical sheet resistance versus oxygen flow rate for copper oxide films prepared at 800W r.f power

This sheet resistance is found to decrease steadily to a value of around 20 ohms/ square for the film prepared at 800W, which was identified by our XPS measurement as a CuO rich film. The effect of oxygen flow rate on the sheet resistance of the films is shown in figs 7,8 and 9, for films prepared at 800W, 600W and 400W rf power respectively. The sheet resistances increased with increasing oxygen flow rates. The observed sheet resistances are also found to decrease with increasing rf power for the oxygen flow rates considered. The sheet resistances of the films prepared at 200W rf power were found to be outside the measurement range of our four point probe equipment for oxygen flow rates greater than 4 sccm. The results of the electrical resistivity measurements by Drobny and Pulfrey [15] followed a similar trend to our present measurement of sheet resistances on copper oxide films in some cases. The phases identified by Drobny and Pulfrey [15] for the various oxygen flow rates they investigated are as shown in Table 2. They observed metallic like conduction on films produced at low oxygen partial pressures, which they attributed to a high copper content of the films produced under this condition.

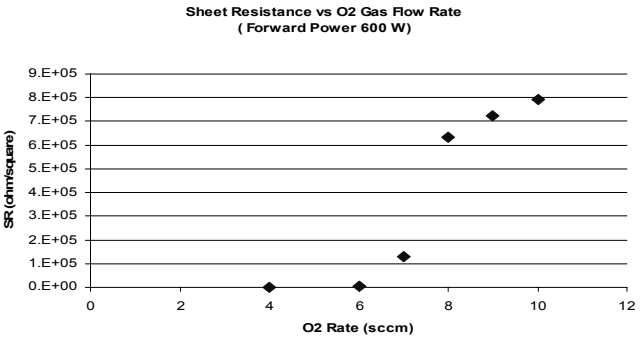

Fig. 8. Electrical sheet resistance versus oxygen flow rate for copper oxide films prepared at 600W r.f power

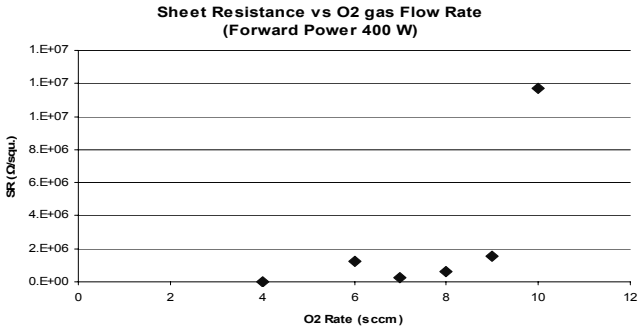

Fig. 9. Electrical sheet resistance versus oxygen flow rate for copper oxide films prepared at 400W r.f power

Table 2.
The oxygen partial pressure ranges required for the deposition of various copper oxide compositions prepared by reactive sputtering. After Drobny and Pulfrey [15]

Phases	Oxygen partial pressure (mTorr), rf	Oxygen partial pressure (mTorr), D.C.
$Cu_2O + Cu$	< 0.3	< 0.26
Cu_2O	0.34-0.52	0.33-0.51
$Cu_2O + CuO$	0.57-0.92	0.62-0.89
CuO	> 1.0	> 1.06

They observed that a further increase in the oxygen partial pressure during deposition led to a peak in electrical resistivity value, which was identified with the formation of stoichiometric Cu_2O. As stated earlier we also observed our peak sheet resistance for films prepared at 200W rf power identified by XPS measurements as Cu_2O rich. Further increases in oxygen pressure during deposition was observed by Drobny and Pulfrey [15] to result in a lowering of the film resistance, which was explained as resulting from the doping of the films with excess oxygen i.e. effectively producing more copper ion vacancies and a p-type semiconductor Cu_2O. The measured resistivities were as low as 25-100 Ω cm. Padiyath et al [1] also reported measuring resistivity values as low as 10 Ω cm in Cu_2O, which they suggested could be due to ion bombardment induced doping of the films with oxygen, resulting in more copper ion vacancies and p-type semi-conductivity. As stated earlier, we did not observe this drop in resistivity with our Cu_2O rich films prepared at 200W

rf power and oxygen flow rates above 4 sccm. Instead, we observed an increase in sheet resistance in the films outside the measurement range of our equipment. The reason for this increase in resistivity with increasing oxygen flow rates is not fully understood, but we suspect that the initial Cu_2O films formed at 4sccm is non-stoichiometric, but approaches full stoichiometry with increasing oxygen flow rates during deposition, since the optical transmission also shows a slight increase in this regime as shown in fig.3.

Drobny and Pulfrey [15] also observed an initial increase in resistivity in films identified to be a mixture of Cu_2O + CuO. This initial increase in resistivity was associated with initial CuO sites acting as electrically neutral defects by replacing the electrically active copper ion vacancies present in Cu_2O films. Finally they obtained CuO films with quite low resistivity, similar to our current observation, which they associated with non-stoichiometry [1,15] .We have observed that the predominant factor controlling the observed optical and electrical properties of the copper oxide films is the input rf power during the film deposition process for all oxygen flow rates considered. However, the oxygen flow rate during deposition also had a significant effect on the electrical resistivity of the films as shown in figs 7 a-c. Our future investigations will be directed towards improving the electrical conduction in optically transparent Cu_2O films prepared at 200W rf power and below this value of input power, using surface plasma treatment and ion bombardment processes to alter the stoichiometry of the prepared films.

4. Conclusions

Copper oxide thin films were deposited on glass substrates by reactive rf sputtering from a copper target in an argon-oxygen atmosphere. The films were characterised by SEM, XPS, AFM, and optical transmission spectra. Our experimental investigation indicated that the rf power during film deposition has a significant influence on the optical transmittance and optical bandgap of the films. By varying the rf power during deposition from 200W to 800W, we were able to produce both Cu_2O rich and CuO rich films. The highest optical transmission was obtained for films prepared at a low rf power of 200W. Both the rf power and the oxygen flow rate during deposition affected the electrical sheet resistance of the prepared films. Our current investigation has revealed that the optical transmission of the films is likely to be further improved by considering rf power values below 200W during film deposition, whilst the electrical conductivity of the films under this condition might be improved by creating defects in the structure of the films through surface plasma treatment or ion bombardment processes.

References

[1] R. Padyath, J. Seth, S.V. Babu, Deposition of copper oxide films by reactive laser ablation of copper formate in an r.f. oxygen plasma ambient, Thin solid Films 239 (1994) 8-15.

[2] T.J. Richardson, J.L. Slack, M.D. Rubin, Electrochromism of copper oxide thin films, Proceedings of the 4th International meeting on Electrochromism, Uppsala, 2000.

[3] H. Derin, K. Kantarli, Optical characterization of thin thermal oxide films on copper by ellipsometry, Applied Physics A Materials Science and Processing 75 (2002) 391-395.

[4] K.H. Yoon, W.J. Choi, D.H. Kang, Photoelectrochemical properties of copper oxide thin films coated on an n-Si substrate, Thin Solid Films 372 (2000) 250-256.

[5] P. Luzeau, X.Z. Xu, M.Lagues, N. Hess, J.P. Contour, M. Nanot, F.Queyroux, M. Touzeau, D. Pagnon, Copper oxide thin-film growth using an oxygen plasma source, Journal of Vacuum Science Technology 8/6 (1990) 3938-3940.

[6] J.F. Pierson, A. Thobor-Keck, A.Billard, Cuprite, paramelaconite and tenorite films deposited by reactive magnetron sputtering, Applied surface science 210 (2003) 359-367.

[7] L. Kleiman, K. Mudnick, Nitrogen states in Ga(As,P) and the long-range, short-range model: A systematic study, Physica Review B 21/8 (1980) 3478-3490.

[8] S. Ishizawa, T. Maruyama, K. Akimoto, Thin-Film Deposition of Cu_2O by Reactive Radio-Frequency Magnetron Sputtering, Japanese Journal of Applied Physics 39/2 (2000) 786-788.

[9] R. Chandra, P. Taneja, P. Ayuub, Optical properties of transparent nanocrystalline Cu_2O thin films synthesized by high pressure gas sputtering, Nanostructured Materials, 11/4 (1999) 505-512.

[10] S.C. Ray, Preparation of copper oxide thin film by the sol–gel-like dip technique and study of their structural and optical properties, Solar Energy Materials & Solar Cells 68\3-4 (2001) 307-312.

[11] A. Paretta, M.K. Jayaraj, A. Di Nocera, S. Loreti, L. Quercia, A. Agati, Electrical and optical properties of copper oxide films prepared by rf magnetron sputtering, Physic Status Solidi A155\2 (1996) 399-404.

[12] T. Murayama, The influence of rf power and oxygen flow rate during deposition, Solar Energy Materials & Solar Cells 56 (1998) 85-91.

[13] B. Balamurugan, B.R. Mehta, Optical and structural properties of nanocrystalline copper oxide thin films prepared by activated reactive evaporation, Thin Solid Films 396 (2001) 90-96.

[14] T.J. Richardson, New electrochromic mirror systems , Solid State Ionics 165 (2003) 305-308.

[15] V.F. Drobny, D.L. Pulfrey, Properties of reactively-sputtered copper oxide thin films, Thin Solid Films 61 (1979) 89-98.

[16] R.H. Sunds, Physica Review 99 (1955) 1222.

[17] E.A. Davis, N.F. Mott, Conduction in non-crystalline systems conductivity, optical absorption and photoconductivity in amorphous semiconductors, Philosophical Magazine 22 (1970) 903-922.

[18] J. Tauc, R. Grigorovici, A. Vancu, Physica Status Solid 15 (1966) 627.

[19] R. Kita, T. Hase, R.Itti, M.Sasaki, T. Morishita, S.Tanaka, Synthesis of cupric oxide films using mass-separated low-energy O+ beam, Applied Physica Letters 60 (1992) 2624-2630.

[20] 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.

[21] K.P. Muthe, J.C. Vyas, S.N. Narang, D.K. Aswal, S.K. Gupta, D.Bhattacharya, R. Pinto, G.P. Kothiyal, S.C. Sabharwal, A study of the CuO phase formation during thin film deposition by molecular beam epitaxy, Thin solid films 324 (1998) 37-43.

[22] J.W.A.M Gielen, Plasma beam deposition of amorphous hydrogenated carbon, PhD Thesis, Eindhoven University of Technology, 1996.