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Synthesis of Cu_2O from CuO thin films: Optical and electrical properties

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Hole conducting, optically transparent Cu_2O thin films on glass substrates have been synthesized by vacuum annealing (5×10^{-6} mbar at 700 K for 1 hour) of magnetron sputtered (at 300 K) CuO thin films. The Cu_2O thin films are p-type and show enhanced properties: grain size (54.7 nm), optical transmission 72% (at 600 nm) and Hall mobility 51 cm^2/Vs. The bulk and surface Valence band spectra of Cu_2O and CuO thin films are studied by temperature dependent Hall effect and Ultra violet photo electron Spectroscopy (UPS). CuO thin films show a significant band bending downwards (due to higher hole concentration) than Cu_2O thin films. © *2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4919323]

Copper being multivalent, it forms several oxides; among them, CuO and Cu_2O thin films are well known p- type semiconductors; their reported optical band gaps are 1.3 eV - 2.1 eV for CuO and 2.1 eV – 2.6 eV for Cu_2O.[1,2] The recent review articles on copper oxide[3,4] clearly bring out the present state of understanding on the optical and electrical properties and the applications of the oxides of copper. The p - type conductivity in these oxides arises from the existence of negatively charged Cu vacancies.[5,6] The CuO and Cu_2O thin films are widely used in several device applications such as thin film transistors, photovoltaics, smart windows, IR detector, optical limiters etc.[7–11] Apart from the conventional methods like pulsed laser deposition,[1] CVD,[12] magnetron sputtering,[4] etc., the Cu_2O thin films can be synthesized from vacuum annealing of CuO thin films. Different annealing conditions yield mixed phases of copper oxide with varying physical properties. There are several reports on annealing of CuO in air or vacuum. Recent reports show that (i) annealing CuO in vacuum (at 500 °C to Cu_2O) improves the optical (transmittance 55% in the visible part of the spectrum) and electrical (mobility 47 cm^2/Vs) performances[13] and (ii) annealing Cu_2O in air (in the temperature range 180 – 320°C) shows an increase in the transmittance (~ 60%) in the visible region.[14] All the efforts in preparing Cu_2O thin films are focused for achieving better electrical and optical properties. Growth of Cu_2O thin films on transparent substrates (like glass) with reasonable optical transparency and high hole mobility (as required in transparent electronic applications) is still a challenge.

In the present work, we report the synthesis of Cu_2O thin films on glass substrates by vacuum annealing (at 623 K and 700 K for one hour) of magnetron sputtered CuO thin films. Vacuum annealing of CuO show enhanced electrical and optical properties for Cu_2O thin films. The band bending at the surface of copper oxide thin films have been predicted by temperature dependent Hall effect studies and UPS measurements.

The CuO thin films of thickness 250 (± 5) nm have been prepared on cleaned borosilicate glass substrates by reactive DC magnetron sputtering technique. The vacuum chamber was initially

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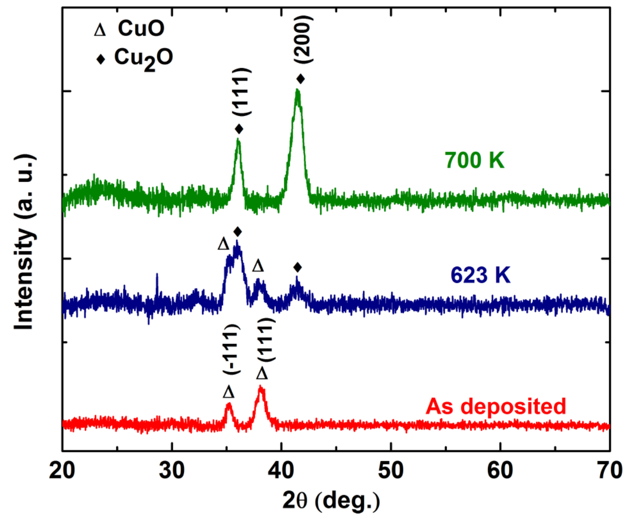

FIG. 1. X- ray diffraction of copper oxide thin films: "as deposited", annealed in vacuum at 623K, and annealed in vacuum at 700 K.

evacuated to $8x10^{-6}$ mbar. Pure Argon and oxygen were introduced into the chamber at flow rates of 9 sccm and 6 sccm (Unit Mass flow controllers) respectively; depositions were conducted at room temperature (300 K) and at a chamber pressure of 3 x 10^{-3} mbar. The target is pure (99.9%) copper (66 mm dia and 3 mm thick). The target is powered to 1.4 W/cm^2 by Advanced Energy Power Supply. The "as deposited" CuO thin films have been vacuum annealed at $5x10^{-6}$ mbar at 623 K and 700 K for 1 hour.

X-ray diffraction (XRD) studies (PANalytical X'Pert Pro with Cu-K_α radiation) on "as deposited" films show CuO phase (Fig. 1(a)) with preferential planes: (-111) and (111). Samples annealed in vacuum at 623 K have shown XRD peaks corresponding to both CuO (with preferential orientation along (-111), (111)) and Cu_2O (with preferential orientation along (111), (200)) phases. The samples annealed in vacuum at 700 K have shown a single phase of Cu_2O; the observed XRD peak intensities are comparatively higher indicating that the Cu_2O thin films have enhanced crystalline nature or larger grains. Using Debye – Scherrer empirical formula, $d = \frac{0.9\lambda}{B\cos\theta_B}$, (where d is the particle size, λ the wavelength of X-ray radiation, B the full-width at half-maximum value of θ_B, and θ_B diffraction angle[15]), the grain sizes of CuO and Cu_2O are calculated as 12.8 nm and 58.4 nm respectively.

The optical transmission data have been acquired using a Jasco (V-570) double beam spectrophotometer. The average optical transmittance in the visible part of the spectrum (at 600 nm) in the "as deposited" CuO film is ~ 15% and after annealing at temperatures 623 K and 700 K, it increases to 40% and 72% respectively (Fig. 2(a)). The direct optical band gap (Eg) is evaluated by Tauc plots (Fig 2(b) and Table I): $\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}}$, where A is a constant α is the absorption coefficient, h is Planck's constant and ν is the photon frequency.[16] The band gap energies are 2.0 eV (CuO - "as deposited"), 2.2 eV (CuO + Cu_2O - vacuum annealed at 623 K) and 2.4 eV (Cu_2O – vacuum annealed at 700 K). These band gap values match with the reported values.[1,13] The optical transmission for the Cu_2O thin films (grown on glass substrates) observed in the present study is 72% at 600 nm.

X ray photon spectroscopy (XPS) studies on these copper oxide thin films have been conducted to find out the valence state of copper. Al kα line (1486.6 eV) generated in a synchrotron radiation source is the probe (INDUS 1, Inter University Consortium, Indore, India). The "as deposited" CuO (Fig. 3(a)) shows a $2p_{3/2}$ binding energy peak at 933.5 eV and 934.2 eV (corresponding to Cu^{2+}). After annealing CuO in vacuum at 700K, the Cu_2O phase is formed; the $2p_{3/2}$ binding energy peak is observed at 932.5 eV (corresponds to Cu^+ ions).[17]

The SEM micrographs (Fig. 3(c)) show that annealing in vacuum at 700 K enhances the crystallinity (CuO phase to Cu_2O) and the grain size (from 11.2 nm for CuO films to 54.7 nm for Cu_2O

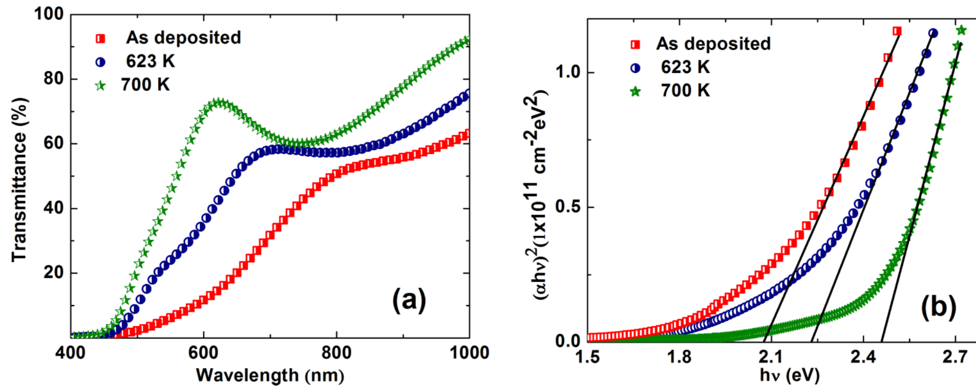

FIG. 2. (a) Optical transmission spectra of 250 nm thick copper oxide thin films. (b) Tauc plots of copper oxide thin: as deposited, 623 K vacuum annealed and 700 K vacuum annealed.

films); the grain sizes calculated using Scherrer's equation are consistent with these values. Thus it confirms that annealing in vacuum changes the structure and composition of copper oxide thin films.

Hall effect measurements at 300 K (Lakeshore HMS7604) shows that all the copper oxide thin films are p- type (Table II). It is observed that the vacuum annealing at 700 K (resulting in Cu_2O) enhances the Hall mobility from 0.26 to 51 cm^2 (V s) $^{-1}$, and decreases the hole density from 7.4×10^{19} to 1.5×10^{15} cm^{-3} (Table II). The Hall mobility of Cu_2O films is comparable to that of single crystal Cu_2O.[18,19] It may be noted that for the Cu_2O film prepared by annealing in vacuum at 700 K, the Hall mobility is higher compared to the corresponding values reported in the literature (Table II). The enhanced values of Hall mobility, observed in the present investigation, may be attributed to the reduced number of grain boundary density due to the enhanced crystallization after annealing in vacuum at 700 K; this observation is also confirmed by the SEM and XRD studies (Fig. 3(b)).

The temperature dependent (15 K to 300 K) Hall effect (with a closed cycle refrigeration system controlled by Lakeshore Model 340 temperature controller) measurements have been conducted to investigate the (bulk) valence bands in these oxide thin films. The temperature dependence of hole density P (T) is given by, [20,21]

$$\mathrm{P\,(T)} = \left(\frac{2\mathrm{m}^*\mathrm{kT}}{\mathrm{h}^2}\right)^{\frac{3}{2}}\left[\frac{N_a}{N_d}-1\right]e^{\left(\frac{-E_a}{kT}\right)} \tag{1}$$

where the effective mass m* is $0.58m_0$[22] for Cu_2O and $7.9m_0$[23] for CuO; k is the Boltzmann constant, h is the Planck constant, N_a is the acceptor density, N_d is the donor density, and E_a is the activation energy (acceptor levels to Fermi level energy gap).[19,20] The acceptor level E_a can be obtained by fitting eq. (1) to the data shown in Fig. 4(a), in which the straight lines were determined by the least squares method. The activation energy E_a evaluated from the experimental observation of P (T) vs 1/T (Fig. 4(a) and Fig. 4(b)) is: 0.09 eV for CuO and 0.21eV for Cu_2O. These values of

TABLE I. Electrical and optical properties of copper oxide thin films.

	Carrier type	Resistivity (Ω cm)	Hall Mobility (cm^2/Vs)	Carrier(hole) concentration (cm^{-3})	Optical bandgap (eV)	Acceptor level (eV)
As deposited (CuO)	p	0.26	0.12	7.4×10^{19}	2.0	0.09
Vacuum annealed at 700 K (Cu_2O)	p	149.00	51.00	1.5×10^{15}	2.5	0.21

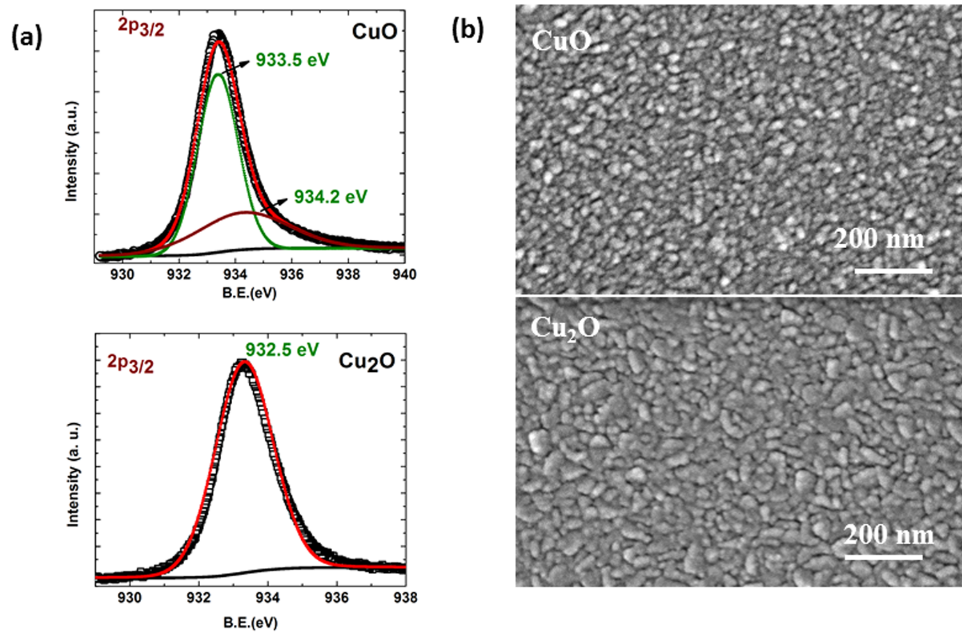

FIG. 3. (a) XPS spectra of "as deposited" CuO thin films and CuO thin films annealed in vacuum at 700 K (Cu_2O). For CuO the main 2p3/2 peaks are coming at 933.5 eV and 934.2 eV. For Cu_2O it is at 932.5 eV. (b) SEM images of as deposited CuO and annealed in vacuum at 700 K (Cu_2O).

activation energy match well with the reported values.[21,24] The activation energy for CuO (0.09 eV) corresponds to Vcu^{1-}/ Vcu^{2-} transition.[8] In Cu_2O the activation energy (0.21 eV) evaluated, corresponds to the reported Vcu vacancy at 0.23 eV.[9] In Cu_2O thin films, the copper vacancy has the lowest formation energy leading to p type conduction. This activation energy evaluated from the temperature dependent Hall effect measurements indicate that the (bulk) Fermi level lie above the valence band maximum (VBM).

The Valence band spectra (VBS) have been studied on these CuO and Cu_2O thin films using 100 eV photons (Ultra-violet photo electron Spectroscopy: UPS) from synchrotron source: INDUS-1 (RRCAT, Indore, India). Calibration has been carried out with Au $4f_{7/2}$ of sputter cleaned Au foil. This valence band spectra measures the position of the maximum of valence band at the surface with respect to Fermi level. The positions of the (surface) valence band edges have been determined (standard procedure) by extrapolating the leading edge of valence band to its intersection with back-ground counts near the Fermi level.

UPS analysis shows that the valence band maximum is at 0.62 eV for CuO thin films and it is at 0.5 eV for Cu_2O thin films with respect to the Fermi level (Fig. 4(c)). The value of valence band onset in Cu_2O (0.5eV) matches with reported values.[25,26] The difference between the bulk valence band (Hall effect measurements) and the surface valence band (UPS) shows the downward band bending at the surface. The bending is more for CuO: which is due to its higher carrier concentration.

TABLE II. Comparison of Hall mobilities of Cu_2O thin films prepared by annealing methods.

Synthesis conditions	Annealing Temperature (K)	Substrate used	Hall Mobility (cm^2/Vs)	Carrier (hole) Concentration (cm^{-3})	Reference
Vacuum annealing	773	Silicon	47.5	2.95×10^{14}	13
annealing in Air	593	Glass	7.6	8.3×10^{16}	14
Vacuum annealing	700	Glass	51	1.5×10^{15}	Present work

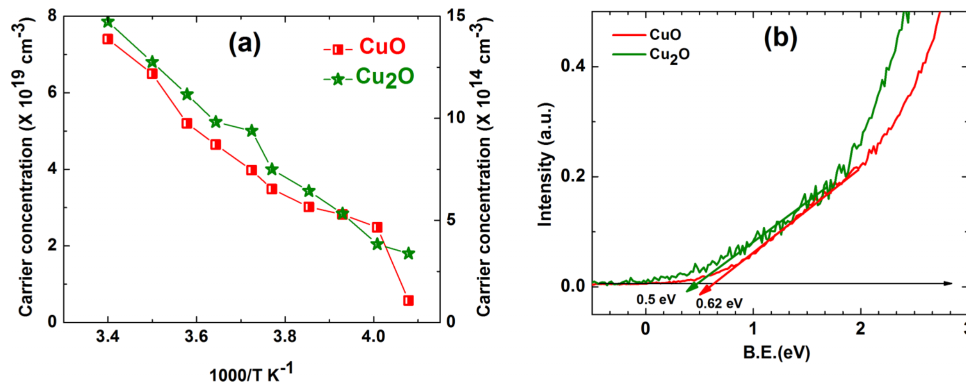

FIG. 4. (a) Temperature-dependent carrier (hole) density of copper oxide films; "as deposited" CuO thin film and annealed in vacuum at 700 K (Cu_2O thin films); (b) represents the VBS CuO and Cu_2O respectively.

The important conclusion of the present study is: magnetron sputtered CuO thin films (prepared at room temperature on cleaned borosilicate glass substrates) when annealed in vacuum at 700 K for one hour gives Cu_2O thin films; this Cu_2O thin films have a higher optical transmission of 72% at 600 nm and a higher Hall mobility of 51 cm^2/Vs on a transparent glass substrate. With information from VBS and electrical transport measurements, we estimated the downward band bending (p - type) at the surface of the copper oxide thin films: CuO and Cu_2O.

[1] A. Chen, H. Long, X. Li, Y. Li, G. Yang, and P. Lu, Vacuum **83**, 927 (2009).
[2] G. Papadimitropoulos, N. Vourdas, V. Em. Vamvakas, and D. Davazoglou, Thin Solid Films **515**, 2428 (2006).
[3] A. S. Zoolfakar, R. A. Rani, A. J. Morfa, A. P. O'Mullane, and K. Kalantar-zadeh, J.Mater. Chem. C **2**, 5247 (2014).
[4] B. K. Meyer, A. Polity, D. Reppin, M. Becker, P. Hering, P. J. Klar, Th Sander, C. Reindl, J. Benz, M. Eickhoff, C. Heiliger, M. Heinemann, J. Bläsing, A. Krost, S. Shokovets, C. Müller, and C. Ronning, Phys. Status Solidi B **249**, 1487 (2012).
[5] Y. Peng, Z. Zhang, T. V. Pham, Y. Zhao, P. Wu, and J. Wang, J. Appl. Phys. **111**, 103708 (2012).
[6] D. O. Scanlon, B. J. Morgan, and G. W. Watson, Phys. Rev. Lett. **103**, 096405 (2009).
[7] A. Chen, G. Yang, H. Long, F. Li, Y. Li, and P. Lu, Thin Solid Films **517**, 4277 (2009).
[8] A. Chen, G. Yang, H. Long, P. Lu, W. Zhang, and H. Wang, Materials Letters **91**, 319 (2013).
[9] S. B. Wanga, C. H. Hsiaoa, S. J. Changa, K. T. Lamb, K. H. Wenb, S. C. Hungc, S. J. Youngd, and B. R. Huange, Sens. Actuators, A **171**, 207 (2011).
[10] S. Nandy, A. N. Banerjee, E. Fortunato, and R. Martins, Rev. Adv. Sci. Eng. **2**, 1 (2013).
[11] P. Pattanasattayavong, S. Thomas, G. Adamopoulos, M. A. McLachlan, and T. D. Anthopoulos, Appl. Phy. Lett. **102**, 163505 (2013).
[12] T. Ghodselahi, M. A. Vesaghi, A. Shafiekhani, A. Baghizadeh, and M. Lameii, Appl. Surf. Sci. **255**, 2730 (2008).
[13] J. Sohn, S. H. Song, D. W. Nam, I. T Cho, E. S. Cho, J. H Lee, and H. I Kwon, Semicond.Sci.Technol. **28**, 015005 (2013).
[14] Y. Wang, P. Miska, D. Pilloud, D. Horwat, F. Mücklich, and J. F. Pierson, J. Appl. Phys. **115**, 073505 (2014).
[15] BD Cullitty, *Elements of X-ray Diffraction* (Addison Wesley, London, 1978).
[16] J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971).
[17] J. Ghijsen, L. H. Tjeng, J. van Elp, H. Eskes, J. Sesterink, G. A. Sawatzky, and M. T. Czyzyk, Phys. Rev. B **38**, 11322 (1988).
[18] E. Fortin and F. L. Weichman, Can. J. Phys. **44**, 1551 (1966).
[19] G. P. Pollack and D. Trivich, J. Appl. Phys. **46**, 163 (1975).
[20] Y. S. Lee, M. T. Winkler, S. C. Siah, R. Brandt, and T. Buonassisi, Appl. Phys. Lett. **98**, 192115 (2011).
[21] S. Ishizuka, S. Kato, T. Maruyama, and K. Akimoto, Jpn. J. Appl. Phys. **40**, 2765 (2001).
[22] J. W. Hodby, T. E. Jenkins, C. Schwab, H. Tamura, and D. Trivich, J. Phys. C **9**, 1429 (1976).
[23] F. P. Koffyberg and F. A. Benko, J. Appl. Phys. **53**, 1173 (1982).
[24] S. Suda, S. Fujitsu, K. Koumoto, and H. Yanagida, Jpn. J. Appl. Phys. **131**, 2488 (1992).
[25] M. Cantoni, D. Petti, R. Bertacco, I. Pallecchi, D. Marre, G. Colizzi, A. Filippetti, and V. Fiorentini, Appl. Phys. Lett. **97**, 032115 (2010).
[26] J. P. Hu, D. J. Payne, R. G. Egdell, P.-A. Glans, T. Learmonth, K. E. Smith, J. Guo, and N. M. Harrison, Phys.Rev. B **77**, 155115 (2008).