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Photocurrent generation in Cu_xO thin films deposited by radio frequency sputtering

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Copper oxides (Cu_xO) thin films were deposited using radio frequency (RF) sputtering on glass substrates. By tuning the argon (Ar) partial pressure during deposition, cuprous oxide (Cu_2O), cupric oxide (CuO), or their mixed phase could be achieved. Drastic variations in the Hall mobility, hole density, and resistivity of the samples were observed due to the presence of different phases in the films. Kelvin probe studies indicate that the photo-generated carriers have lower recombination rate in pure Cu_2O phase. This was further validated by transient absorption measurements, where the estimated carrier lifetime for Cu_2O was much larger than other phases. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4788680>]

In recent years, copper oxide (Cu_xO) has attracted much interest for its potential applications for solar energy scavenging since it is a p-type semiconductor with high absorption coefficient in visible spectrum.^{1–4} Cupric oxide (CuO) and cuprous oxide (Cu_2O) are the two main phases of copper oxide with narrow bandgaps. Cu_2O thin film deposition is quite versatile owing to the possibility of depositing it through various methods like sputtering,⁵ pulsed laser deposition,⁶ plasma evaporation,⁷ and chemical vapor deposition.⁸ CuO is an indirect bandgap material with bandgap varying from 1.3 to 2.1 eV,^{9–12} while Cu_2O is a p-type direct bandgap material with a bandgap of 2.0–2.6 eV.^{9–11,13,14} It has been predicted that Cu_2O is promising for photovoltaic applications, with a theoretical energy conversion efficiency of 20%.^{15,16} Thin-film-type polycrystalline p- Cu_2O /n-ZnO solar cells prepared on glass substrates have also been demonstrated.^{4,17,18} However, it was found that despite the ideal bandgap (1.3–2.1 eV) for solar light absorption, the efficiency of the CuO solar cells is quite low. On the other hand, CuO is easier to form compared to Cu_2O , where the latter needs a more reducing or oxygen deficient atmosphere to form. Therefore, thorough understanding of the structural and electronic properties of Cu_2O is necessary to understand the adaptability of CuO as a future solar cell absorber material.

Here we report the optoelectronic properties of radio frequency (RF) sputter-deposited p-type Cu_xO under varying partial pressure of Ar gas. By tuning the Ar partial pressure, the Cu_xO can be tuned from single-phase Cu_2O to single-phase CuO with mixed phase for intermittent Ar pressures. Using Kelvin probe force microscope (KPFM), the local surface potential variation at the grain boundary under dark and illuminated conditions has been studied. A negative surface potential variation is observed only for single-phase Cu_2O , indicating rapid exciton annihilation in other samples. This

was confirmed with the exciton lifetime estimates using transient absorption measurements.

Cu_2O thin films were deposited by means of reactive radio-frequency (rf) magnetron sputtering using a Cu_2O target at various Ar partial pressures in the sputtering chamber. The Ar partial pressures were varied from 4 to 30 mTorr. The substrates were kept at room temperature during deposition. With a fixed deposition time of 30 min the yielded film thickness was typically 400 nm. The crystallinity of the films was investigated using X-ray diffraction (XRD), for which a Bruker D-8 diffractometer was employed ($\text{Cu K}\alpha$ radiation with wavelength 1.5406 Å). The optical bandgaps of the materials were estimated using films deposited on quartz substrates and were measured using a double beam spectrophotometer (Shimadzu UV-3600). The resistivities of the Cu_2O thin films were measured with a four-point probe. The surface potential studies were carried out using an Asylum Research MF3PD AFM system using commercially available platinum-coated Si cantilever (Olympus AC240 TM). The transient absorption measurements were performed on a commercially available nanosecond flash photolysis system (LKS80 Laser Flash Photolysis Spectrometer, from Applied Photophysics Ltd, United Kingdom). The kinetic traces were collected with long pass filters between the white probe light (Xe lamp, pulsed mode) and the sample, which cut off the part of the probe light above the bandgap of the sample. The pulse width of the q-switched Nd:YAG laser after the second and third harmonic generator elements (Brilliant B, from Quantel, France) was less than 10 ns.

Figure 1(a) shows the XRD patterns of the copper oxide thin films deposited on quartz at different argon pressures varied from 4 mTorr to 30 mTorr. The diffraction peaks located at $2\theta = 36.67^\circ$ correspond to (111) plane of Cu_2O (deposited at 4 mTorr). It can be seen that the intensity of the (111) peaks increases with increasing argon pressure. Further increase in Ar pressure to 10 mTorr causes a reduction in the grain size to 11 nm. When the pressure increases further to 20 mTorr, other peaks located at 32.3° and 35.3° start to

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FIG. 1. (a) XRD patterns of copper oxide films prepared at the oxygen pressure of (a) 4 mTorr, (b) 6 mTorr, (c) 10 mTorr, (d) 20 mTorr, (e) 30 mTorr, respectively; (b) the bandgaps of the films deposited on quartz, estimated from UV-Vis absorption spectrometry.

appear as shown in spectrum (d), which correspond to (110) and (-111) planes of CuO. Upon increasing the argon pressure further, the films contain the phase of pure CuO with (110), (-111) , and (111) planes indicated by the signature peaks at 32.3° , 35.3° , and 38.6° .

The effect of higher argon pressure for the formation of CuO phase can be understood by the simple reaction

Since this reaction needs extra oxygen and there is no oxygen in the sputtering system, CuO phase must be coming from the sputtered O atoms from the target itself. As the argon gas pressure increases, the ratio of oxygen/copper ions sputtered increases, because being lighter than Cu, more oxygen ions are sputtered from the target, resulting in the formation of CuO on the glass substrates. Therefore, controlling the Ar pressure in the sputtering chamber is crucial for achieving Cu₂O in the film even when the film is sputtered from a Cu₂O target. In the case of tungsten-oxide films deposited on glass substrates from a metal-oxide target, similar dependence on Ar pressure has been reported.¹⁹

The optical bandgaps of pure phase Cu₂O and CuO thin films were estimated using optical absorption spectra of four typical samples deposited at 4 mTorr, 6 mTorr, 10 mTorr, and 30 mTorr on glass substrates. The values of direct bandgaps $E_{g,dir}$ are determined to be 2.14 eV, 2.26 eV, and 2.27 eV, respectively. The films, being CuO, deposited at 30 mTorr has an indirect bandgap. The variation of the estimated bandgap as a function of the Ar pressure in the chamber is

shown in Fig. 1(b). These bandgap values are similar to other reports on cuprous and cupric oxide films.^{10,11,14}

Employing Hall measurements with electrodes in Van der Pauw configuration,²⁰ the majority carrier (hole) mobility, resistivity, and the carrier density were estimated. Fig. 2(a) shows the measured mobility and the resistivity of the sample, and Fig. 2(b) is the carrier concentration in these films. The Hall coefficients of the samples deposited at 4 mTorr, 6 mTorr, 10 mTorr, and 30 mTorr are $+5110 \text{ m}^2/\text{C}$, $+247 \text{ m}^2/\text{C}$, $+6100 \text{ m}^2/\text{C}$, and $+344 \text{ m}^2/\text{C}$, respectively. The positive Hall coefficients confirm that all these copper oxide films are p-type semiconductors. The p-type conduction in copper oxides is attributed to the holes generated by Cu vacancies.²¹ As the pressure decreases from 10 mTorr to 6 mTorr, the resistivity of cuprous oxide Cu₂O reduces from 4337 to 345.6 $\Omega \text{ cm}$. As evident from XRD studies, the films deposited at 10 mTorr also is Cu₂O phase but has a lower crystallinity compared to the film deposited at 6 mTorr. This is reflected in the drastic fall in Hall mobility of 10 mTorr film. On the contrary, the CuO film formed at 30 mTorr pressure has a much smaller grain size and poor crystallinity, but has a relatively large mobility of $1.23 \text{ cm}^2/\text{V s}$ and the lowest resistivity of 208 $\Omega \text{ cm}$ among the deposited films. While these results are in agreement with the early reports on hole mobility of Cu₂O and CuO thin films,^{4,20–22} it is still not evident why CuO is not the favorable phase for photovoltaic applications.

In order to understand the photoelectric properties of the films, the combination of surface topography imaging together with surface potential mapping has been carried out. The work-functions of the sputtered Cu_xO deposited at

FIG. 2. (a) Mobility and resistivity of the films from Hall measurements as a function of the deposition pressure. (b) Carrier (hole) density of the films as a function of the deposition pressure.

FIG. 3. (a) Topography image and (b) the corresponding Kelvin image for dark taken on the sample grown at 6 mTorr Ar pressure. The line-scan marked on topography image indicates the height distribution shown in (c) and the corresponding surface potential recorded under dark and illuminated conditions (d). Scan area of the image is $1 \mu\text{m} \times 1 \mu\text{m}$.

various pressures were estimated using KPFM. To understand the nature of the photocarrier generated under illumination, the surface potential of the samples were measured both in dark and under white light illumination. A typical surface potential image of the Cu_2O film deposited at 6 mTorr, measured in dark, is given in Fig. 3(b), together with the topography (Fig. 3(a)). The contact potential difference (ΔV_{sp}) measured in the KPFM can be translated to the work function of the sample, where $\Delta V_{sp} = \Phi_t - \Phi_s$, with Φ_t and Φ_s are the work functions of the tip and the sample, respectively. Work function of $5.3 \pm 0.05 \text{ eV}$ was obtained for the platinum tip when calibrated with a cleaned standard Pt sample. Fig. 3(c) shows the height profile of the grain boundary, and Fig. 3(d) is the Kelvin profile of the same line under dark and illuminated conditions. An abrupt drop in surface potential at the grain boundary is observed in dark and under illumination. This abrupt drop in potential or increase in the work function at the grain boundary indicates the presence of positively charged electric dipole accumulating at the grain boundaries. The p-type conductivity in Cu_2O is originating from the Cu cation vacancies, which have a low formation energy because of high energy of Cu^I (d^{10}) orbital with an activation energy as low as 0.28 eV above the valence band.²³ Upon illumination, an abrupt drop of 42.2 mV in surface potential on the grain is observed, while the difference at the grain boundaries is subtle.

Figure 4 shows the distribution of the surface potential of the sample deposited at 6 mTorr in dark and under illumination. The drastic change in the CPD distribution under illumination is noticeable; this reduction in surface potential shows the increase of work-function, which corresponds to a Fermi level shifting towards the valence band by 42.2 meV, due to the photo-generation of the holes. This Fermi level shift corresponds to a crude estimate of $2 \times 10^{20}/\text{cm}^3$ holes generated upon illumination. Interestingly, as Fig. 4 shows the work function of the samples deposited at 4 mTorr and 10 mTorr exhibit increase in the CPD (decrease in work

function), meaning that their Fermi levels are shifted up under illumination, which is in contrast with the work function increase for 6 mTorr sample. The extent of work function change varies in magnitude upon illumination; Cu_2O film grown at 4 mTorr shows a maximum change of 46.2 meV while at 10 mTorr the change of 39.3 meV. The increase in the Fermi level in 4 mTorr and 10 mTorr samples indicates that there are excess electrons than holes, which could be from either different phases existing in the film or from the larger annihilation rate of the holes. The increase in work function for 6 mTorr film upon illumination by an

FIG. 4. Histogram of surface potential value for the 6 mTorr sample observed at dark and illumination conditions. Comparison of Fermi-level shifting in samples deposited at 4 mTorr, 6 mTorr, and 10 mTorr from the KPFM images.

FIG. 5. Lifetime measurements of Cu_2O deposited at (a) 6 mTorr and (b) 30 mTorr Ar pressure, using pump-probe spectroscopy. Samples were excited using 519 nm laser and probed using 550 nm laser. The lines represent exponential fits to the data which give the lifetime of photo-generated carriers; (c) exciton lifetimes of samples prepared at different Ar pressure, derived from the exponential fitting of the transient absorption data.

extent of 42.2 meV indicates that the hole lifetime in Cu_2O is considerably larger than CuO samples.

In order to estimate the carrier lifetimes, transient absorption measurements using a pump-probe technique was carried out. The life times were extracted from an exponential tail fit of the data. Figures 5(a) and 5(b) show two typical transient absorption data for the samples deposited at 6 mTorr (having pure Cu_2O phase) and 30 mTorr (pure CuO phase). Samples were excited using 519 nm and probed using 550 nm lasers. Figure 5(c) shows the exciton lifetimes derived from the exponential fit of the transient absorption data of samples prepared at different Ar pressure. The data show that sample prepared at 6 mTorr, which is polycrystalline Cu_2O , has the highest lifetime of 515 ns, and the carrier lifetime is exponentially reducing with increasing CuO phase in the film. This is explained by the fact that the oxygen vacancies do not contribute to the annihilation of the holes generated by Cu vacancies in Cu_2O , and therefore the carrier lifetime should be larger in these films.²³

Summarising the results, the stoichiometry and crystallinity of RF-sputtered Cu_xO thin films on glass substrate from Cu_2O targets depend on the Ar pressure in the sputtering ambient. A gradual phase change from Cu_2O to CuO phase was observed as the Ar pressure increases. XRD analyses of the thin films deposited at different Ar pressures indicate that Cu_2O with the largest grain size in this series was obtained at 6 mTorr Ar pressure. This is reflected in the Hall measurements also, where the least resistivity of Cu_2O was obtained for films deposited at 6 mTorr, with a modest carrier mobility. KPFM measurements reveal the photo-induced work-function enhancement occurring only in film deposited at 6 mTorr, indicating the photogeneration of holes, while films deposited at other Ar pressures exhibit work-function lowering, indicative of rapid hole annihilation process. Supporting this observation, transient absorption measurements show that Cu_2O deposited at 6 mTorr Ar pressure has the highest carrier lifetime. Since enhanced carrier lifetime is

crucial for photovoltaic applications to collect sufficient charges before their recombination, from charge carrier perspectives, Cu_2O phase is evidently more suitable than CuO for fabricating solar cells, as our observations demonstrate.

- ¹K. Akimoto, S. Ishizuka, M. Yanagita, Y. Nawa, G. K. Paul, and T. Sakurai, *Sol. Energy* **80**, 715 (2006).
- ²S. S. Jeong, A. Mittiga, E. Salza, A. Masci, and S. Passerini, *Electrochim. Acta* **53**, 2226 (2008).
- ³S. T. Shishiyuan, T. S. Shishiyuan, and O. I. Lupan, *Sens. Actuators B* **113**, 468 (2006).
- ⁴A. O. Musa, T. Akomolafe, and M. J. Carter, *Sol. Energy Mater. Sol. Cells* **51**, 305 (1998).
- ⁵T.-J. Hsueh, C.-L. Hsu, S.-J. Chang, P.-W. Guo, J.-H. Hsieh, and I. C. Chen, *Scr. Mater.* **57**, 53 (2007).
- ⁶W. Seiler, E. Millon, J. Perrière, R. Benzerga, and C. Boulmer-Leborgne, *J. Cryst. Growth* **311**, 3352 (2009).
- ⁷K. Santra, C. K. Sarkar, M. K. Mukherjee, and B. Ghosh, *Thin Solid Films* **213**, 226 (1992).
- ⁸T. Maruyama, *Sol. Energy Mater. Sol. Cells* **56**, 85 (1998).
- ⁹S. C. Ray, *Sol. Energy Mater. Sol. Cells* **68**, 307 (2001).
- ¹⁰A. A. Ogwu, E. Bouquerel, O. Ademosu, S. Moh, E. Crossan, and F. Placido, *J. Phys. D: Appl. Phys.* **38**, 266 (2005).
- ¹¹J. F. Pierson, A. Thobor-Keck, and A. Billard, *Appl. Surf. Sci.* **210**, 359 (2003).
- ¹²F. Marabelli, G. B. Parravicini, and F. Salghetti-Drioli, *Phys. Rev. B* **52**, 1433 (1995).
- ¹³T. Mahalingam, J. S. P. Chitra, S. Rajendran, M. Jayachandran, and M. J. Chockalingam, *J. Cryst. Growth* **216**, 304 (2000).
- ¹⁴B. Balamurugan and B. R. Mehta, *Thin Solid Films* **396**, 90 (2001).
- ¹⁵R. J. Iwanowski and D. Trivichdr, *Phys. Status Solidi A* **95**, 735 (1986).
- ¹⁶A. Mittiga, E. Salza, F. Sarto, M. Tucci, and R. Vasanthi, *Appl. Phys. Lett.* **88**, 163502 (2006).
- ¹⁷H. Tanaka, T. Shimakawa, T. Miyata, H. Sato, and T. Minami, *Appl. Surf. Sci.* **244**, 568 (2005).
- ¹⁸D. K. Zhang, Y. C. Liu, Y. L. Liu, and H. Yang, *Phys. B: Condens. Matter* **351**, 178 (2004).
- ¹⁹I. Riech, M. Acosta, J. L. Pena, and P. Bartolo-Perez, *J. Vac. Sci. Technol. A* **28**, 329 (2010).
- ²⁰O. Bierwagen, R. Pomraenke, S. Eilers, and W. T. Masselink, *Phys. Rev. B* **70**, 165307 (2004).
- ²¹N. Kikuchi and K. Tonooka, *Thin Solid Films* **486**, 33 (2005).
- ²²J. H. Hsieh, P. W. Kuo, K. C. Peng, S. J. Liu, J. D. Hsueh, and S. C. Chang, *Thin Solid Films* **516**, 5449 (2008).
- ²³H. Raebiger, S. Lany, and A. Zunger, *Phys. Rev. B* **76**, 045209 (2007).