Characteristics of p-Cu_2O/n-Si Heterojunction Photodiode made by Rapid Thermal Oxidation

Raid A. Ismail

***Abstract*—Transparent Cuprous oxide film was deposited by rapid thermal oxidation (RTO) of Cu at 500 °C/45s condition on textured single-crystal n-Si substrate to form Cu_2O/n-Si heterojunction photodiode. The Hall effect measurements for the Cu_2O films showed a p-type conductivity. The photovoltaic and electrical properties of the junction at room temperature were investigated without any post-deposition annealing. I-V characteristics revealed that the junction has good rectifying properties. The C-V data showed abrupt junction and a built-in potential of 1 V. The photodiode showed good stability and high responsivity in the visible at three regions; 525 nm, 625-700 nm, and 750 nm denoted as regions A, B, and C, respectively.**

***Index Terms*—Cuprous oxide, thin film, rapid thermal oxidation, heterojunction**

I. INTRODUCTION

Cuprous oxide (Cu_2O) film is a p-type semiconductor having a direct band gap of 2.1 eV and cubic crystal structure with lattice constant of a = 4.27 Å [1]. It offers the potential advantages of non-toxicity, low cost production processing, and abundant raw material [2]. Several studies showed the potential use of Cu_2O for gas sensing [3], photo-degradation of dye molecule [4], CO oxidation [5], and solar cells [6]. Thin films of Cu_2O had been grown by many techniques, such as electrodeposition [7], spraying [8], CVD [9], thermal oxidation [10], MBE [11], plasma based ion implantation and deposition [12] and reactive sputtering [13]. The potential application of Cu_2O-based heterojunctions film in electronics requires understanding its physical properties and transport mechanism. Cu_2O/Si heterojunction is one of the important structures, although very little data had been reported on it. Drobny and Pulfrey fabricated Cu_2O/Si heterojunction solar cells by reactive sputtering [14]. In their study of the photoelectrochemical properties of the Cu_2O/n-Si, Yoon and Choi confirmed its good rectifying properties. In the present study, the fabrication and characterization of anisotype Cu_2O/Si heterojunction photodiode prepared by RTO is presented and analyzed.

II. EXPERIMENT

The substrate used was (111)-textured n-type, Cz single crystal silicon with a resistivity of (1-3) Ωcm. Random pyramid texturing was made on the silicon surface using KOH solution containing a small amount of isopropyl, as wetting agent, for 10min. High purity (99.99%) Cu thin film was deposited on the textured Si substrate by thermal evaporation at 10^{-7} torr. A 200 nm thick Cu_2O thin film was grown on Si by rapid photothermal oxidation of deposited Cu film using a halogen lamp 500 °C for 45s in static air. The experimental set-up and details are given elsewhere [15]. The ohmic contacts of the photodiode were made by depositing a thick film of In-Ga on the back surface of the silicon and Al thick film on the Cu_2O film through special mask. The planar photosensitive area of the photodiode was around 16 mm^2. Fig. 1 shows a cross-section of Cu_2O/Si heterojunction structure.

The conductivity type of the film and its mobility were investigated using Hall measurements. The white light response of the photodiode was tested by placing it under

Manuscript received Feb. 14, 2009; revised Mar. 10, 2009.
School of Applied Science / University of Technology / Iraq
(Ministry of Science and Technology)
35010 Baghdad, Iraq
E-mail : raidismail@yahoo.com

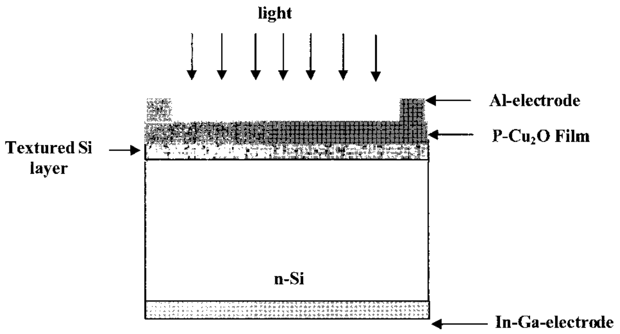


Fig. 1. Cross-sectional view of Cu_2O-Si p-n heterojunction photodiode.

illumination of a 100 W tungsten filament lamp, placed 15 cm away. The J-V characteristics were measured using a DC power supply and Keithley electrometer. The spectral responsivity of the photodiode was measured for the spectral range (450-900) nm using a calibrated monochromator. C-V measurements at a frequency of 25 kHz were made using an (hp) LCZ meter. All measurements were carried out at room temperature.

III. Results and Discussion

Fig. 2 revealed the optical micrograph of textured silicon surface; it is obvious from this figure that the pyramids are formed on the silicon surface. In textured silicon surface some light rays will be reflected from one angle surface merely to strike another, resulting in an improved probability of absorption, and therefore reduced reflection comparing to the non-textured silicon surface.

The positive sign of Hall coefficient obtained confirms the p-type conductivity of the Cu_2O. Film mobility was estimated to be 12.4 $cm^2 V^{-1}s^{-1}$. This result agrees well with that for Cu_2O film prepared by magnetron sputtering [16]. The dark semi-log J-V characteristics of the photodiode heterojunction in the forward and reverse directions are depicted in Fig. 3. It demonstrates good rectification characteristics. The turn-on voltage observed from forward curve is approximately 1 V. Soft breakdown was noticed at a reverse voltage of 4 V. The ideality factor (β) was calculated as follows:

$$\beta = \frac{q}{KT} \frac{\Delta V}{\ln \frac{\Delta J}{J_o}} \qquad (1)$$

The saturation current density J_o of the heterojunction was obtained from extrapolating the linear part of the forward curve to zero applied voltage. It was found to be as low as 2 μA/cm^2.

The high value of leakage current density of the photodiode can be ascribed to interface defects resulting from high mismatch of lattice constant between Cu_2O and Si (-21.4%) [17].The value of ideality factor was found to be 1.5, indicating that the current transport mechanism is a mixture of trap-assisted tunneling and thermoionic emission. Shown in Fig. 4 is the reciprocal of square capacitance versus reverse bias voltage plot deduced from C-V characteristics (inset of Fig. 4). The linear relationship of I/C^2-V curve suggests that the junction is abrupt type, and the interception of $1/C^2$ with voltage is the diffusion potential which found to be 1 V within Cu_2O side. This value is close to that of the turn-on voltage obtained from I-V characteristics. Fig. 5 exhibits dark and illuminated semi-log J-V characteristics of the heterojunction photodiode. The photodiode exhibited good photo-response with a photocurrent density of 10 mA/cm^2 and a dark current density of 0.15 mA/cm^2, measured at -2 V reverse bias.

By varying the incident white light power density, an

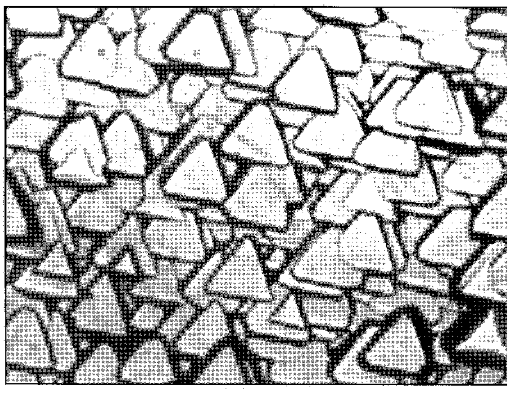


Fig. 2. Optical micrograph of textured silicon surface (X300).

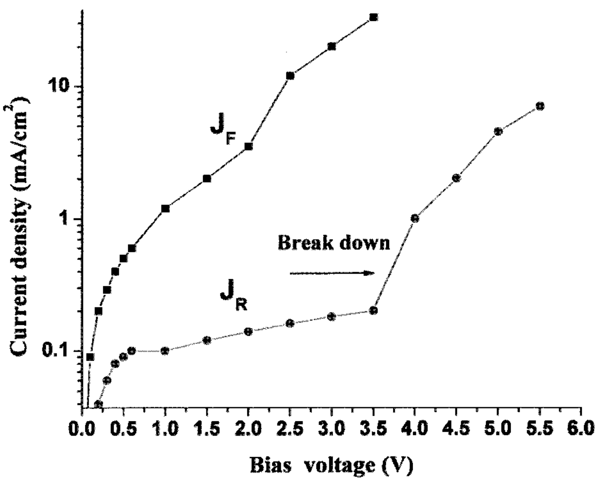


Fig. 3. Dark semi-log J-V characteristics of Cu_2O/Si diode.

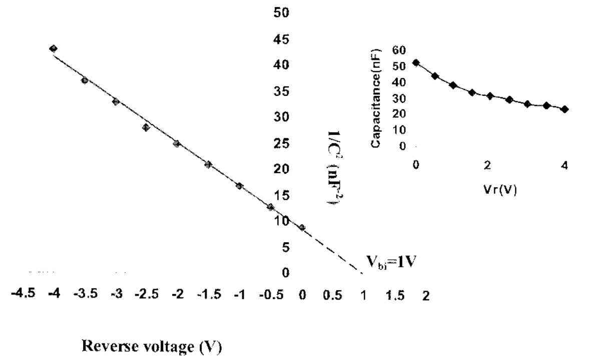


Fig. 4. $1/C^2$-Vplot of p-Cu_2O/n-Si heterojunction.Inset on the right shows C-V characteristics.

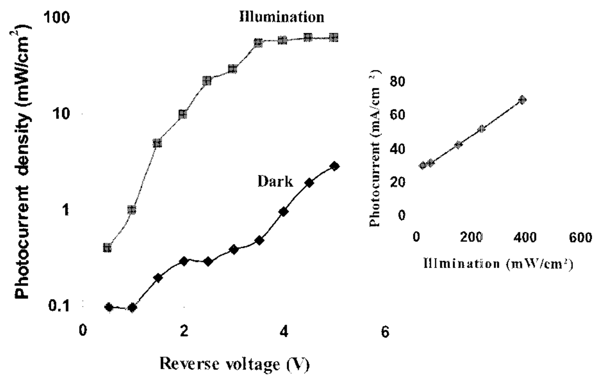


Fig. 5. Illuminated reverse semi-log J-V characteristics of the photodiode. Inset on the right shows the photo-detector linearity characteristics under white light illumination.

approximately linear variation of photocurrent was obtained as shown in the inset of Fig. 5. The responsivity R as function of wavelength of the photodiode at -2 V reverse bias (photoconductive mode) is depicted in Fig. 6. The responsivity can be calculated from the following relationship:

$$R = I_{ph} / P_{inc} = \eta \frac{q}{h\nu} (A/W) \quad (2)$$

Where I_{ph} is the photocurrent, P_{inc} is the incident power, and q, h, ν are the electron charge, Planck's constant, and the frequency of incident photon, respecttively. Responsivities of 0.22 A/W, 0.27 A/W and 0.28 A/W (denoted by regions A, B, and C, respectively in Fig. 6) were obtained for the wavelengths 525 nm, 625 nm and 750 nm, respectively. These values of responsivites correspond to quantum efficiency (QE), represented by η, of 54.3%, 53.6%, and 46%, respectively. The high absorption at 625 nm is due to the effective band gap of Cu_2O (2.04 eV). Also, the peak located at the wavelength 750 nm is mainly due to band edge absorption in silicon substrate[18,19]. The values of responsivity and corresponding

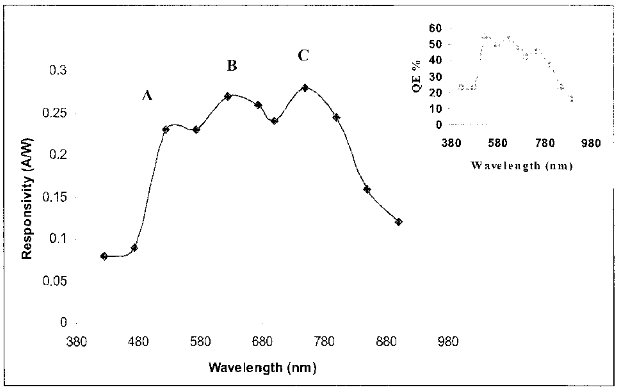


Fig. 6. Responsivity as function of wavelength for photodiode at reverse bias voltage of – 2 V. Inset shows the QE versus wavelength.

quantum efficiency are competitive to those for common ZnO/Si heterojunction photo-detectors [19,20]. The low value of the photodiode responsivity in the absence of bias voltage may be due to the recombination defects occurring at the depletion region and/or at the junction interface. The measurements were repeated after three months of storing in normal environment and no remarkable degradation was observed.

IV. CONCLUSIONS

P-Cu_2O/n-Si heterojunction photodiode was fabricated by rapid thermal oxidation after depositing an undoped Cu_2O thin film on (111) textured silicon substrate without a buffer layer. The photodiode exhibited good rectifying characteristics and the turn-on voltage was around 1 V. The C-V measurements showed an abrupt type junction and a diffusion potential of 1 V. The photodiode operated in photoconductive mode demonstrated good photoresponse in visible and near infrared regions. The responsivity of the photodiode exhibited three distinct regions around the wavelengths 525 nm, 625 nm and 750 nm. The responsivity and quantum efficiency for these regions were 0.22 A/W and 54.3%, 0.27 A/W and 53.6% and 0.28 A/W and 46%, respectively. The technique of growing Cu_2O layer by rapid photothermal oxidation for optoelectronic devices is relatively new, simple, cheap, and reliable. We are in the process of improving the performance of photodetector by postoxidation annealing of Cu_2O and /or by deposition of buffer layer.

REFERENCES

[1] B. P. Rai, "Cu_2O solar cells : A review," *Solar Cells*,

25, 265, 1988.

[2] A.E. Rakshani, "Preparation, characteristics and photovoltaic properties of cuprous oxide- A review," *Solid State Electron*, 29, 7, 1986.

[3] J. Zhang, J. Liu, Q. Peng, X. Wang, and Y. Li, "Nearly monodispers Cu_2O and Cu nanospheres : preparation and applications for sensitive gas sensors," *Chem. Mater.*, 18, 867, 2006.

[4] H. Xu, W. Wang, and W. Zhu, "Shape evolution and size-controllable synthesis of Cu_2O octahedral and their morphology-dependent photocatalytic properties," *J. Phys. Chem. B.*, 110, 13829, 2006.

[5] B. White, M. Yin, A. Hall, D. Le, S. Stolbov, T. Rahman, N. Turro, and S. Brien, "Complete CO oxidation over Cu_2O nanoparitcles supported on silica gel," *Nano Lett.*, 6, 2095, 2006.

[6] R. N. Briskman, "A study of electrodeposited cuprous oxide photovoltaic cells," *Sol. Energy Mater. Sol. Cells*, 27, 361, 1992.

[7] Y. Liu, Y. Liu, R. Mu, H. Yang, C. Shao, J. Zhang, Y. Lu, D. Shen, and X. Fan, "The structural and optical properties of Cu_2O films electrodeposited on different substrates," *Semicond. Sci. Technol.*, 20, 44, 2005.

[8] Y. C. Zhou and J. A. Switzer, "Glavanostatic electrodeposition and microstructure of copper(I) oxide film," *Mater. Res. Innovat.*, 2, 22, 1998.

[9] T. Maruyama, "Copper oxide thin films prepared from copper dipivaloylmethanete and oxygen by chemical vapor deposition," *Jpn. J. Appl. Phys.*, 37, 4099, 1998.

[10] V. Figueiredo, E. Elangovan, G. Gonçalves, P. Barquinha, L. Pereira, N. Franco, E. Alves, R. Martins, and E. Fortunato, "Effect of post-annealing on the properties of copper oxide thin films obtained from the oxidation of evaporated metallic copper," *Applied Surface Science*, 254, 3949, 2008.

[11] R. Kita, K. Kawaguchi, T. Hase, T. Koga, R. Itti, and T. Morishita, "Effect of oxygen ion energy on the growth of CuO films by molecular beam epitaxy using mass-separated low energy O+ beams," *J. Mater. Res.*, 9, 1280, 1994.

[12] Xinxin Ma, Gang Wang, Ken Yukimura, and Mingren Sun, "Characteristics of copper oxide films deposited by PBII&D," *Surface and Coatings Technology*, 201, 6712, 2007.

[13] F. Drobny and D. Pulfrey, "Properties of reactively-sputtered copper oxide thin films," *Thin Solid Films*, 61, 89, 1979.

[14] F. Drobny, and D. Pulfrey, "The photovoltaic properties of thin copper oxide films," *13th IEEE Photovoltaic Specialists Conference- 1978*, Washington, DC, USA, 180, 1978.

[15] R. Ismail, I. Ramadhan, and A. Mustafa, "Growth and characterization of Cu_2O films made by rapid thermal oxidation," *China Physics Letter*, 2, 2977, 2005.

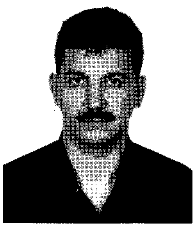
[16] S. Koynov, M. Brandt, and M. Stutmann, "Black nonreflecting silicon surfaces for solar cells," *Appl. Phys. Lett.*, 88, 203107, 2006.

[17] J. Switzer, R. Liu, E. Bohannan, and F. Ernst, "Epitaxial electrodeposition of crystalline oxide on single –crystalline silicon," *J. Phys. Chem. B.*, 106, 12369, 2002.

[18] L. Chen and C. Pan, "Photosensitivity enhancement of ZnO/Si photodiodes through use of an ultrathin oxide interlayer," *Eur. Phys. J. Appl. Phys.*, 44, 43, 2008.

[19] L. Mandalapu, F. Xiu, Z. Yang, D. Zhao, J. Liua, "P-type behavior from Sb –doped ZnO heterojunction," *Appl. Phys. Lett.*, 88, 112108, 2006.

[20] R. Ismail, "Studies on fabrication and characterization of a high -performance Al-doped ZnO/n-Si (111) heterojunction photodetector," *Semicon. Sci. Technol.*, 23, 075030, 2008.



Raid A. Ismail received the B.Sc degree in physics from Al-Mustansiriyah university, Iraq in 1986 and M.Sc and Ph.D degrees in Applied Physics from University of Technology, Iraq in 1991 and 1996 respectively.

From 1998 to 2002, he worked as assistant professor in applied science department University of Technology. From 2003 to 2005, he worked as professor in Applied Science department. From 2006 till now he is professor of physics at university of Hadhramout. His research interest includes fast laser detectors, heterojunctions, thin films and solar cells. He published more than 95 papers in local and international journals and 30 M.Sc and Ph.D thesis carried out under his supervision. He is member of editorial board of many peer review scientific journals.