Construction of internally stacked Cu$_2$O:CuO layers in Cu$_2$O:CuO/Gr/ZnO heterojunctions for solar cells applications

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Abstract. The present work shows the construction of CuO grains on the electrodeposited Cu$_2$O layer through annealing method and the photovoltaic effect of Cu$_2$O:CuO/ZnO heterojunctions with graphene buffer layer is also discussed. The annealing temperature of Cu$_2$O layer is varied from 100 to 300 ℃. The graphene monolayer was deposited by chemical vapor deposition method. The morphology, structural and electrical properties of Cu$_2$O layer were characterized by using Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (HR-TEM), X-ray Diffractometry (XRD) and I-V measurement, respectively. The Cu$_2$O grains size increase as the annealing temperature increased and the CuO grains could be observed at 300 ℃. The graphene monolayer was successfully inserted in between Cu$_2$O:CuO/ZnO heterojunction. The Cu$_2$O:CuO/Gr/ZnO heterojunction shows high electrical rectification with threshold voltage of 0.5 V.

1. Introduction
Solar energy is one of the most promising renewable energy. The need for sustainable power generation has encouraged research into a variety of photovoltaic systems, which have the potential to cope with the global energy crisis in the future. Copper oxide (Cu$_x$O) is a perspective material for solar cells. Generally, two phases of copper oxide compound, cuprite oxide (CuO) and cuprous oxide (Cu$_2$O) are used to fabricate solar cells. Both CuO and Cu$_2$O are p-type semiconductors with the band-gap energy of 1.4 and 2.1 eV, respectively [1,2] have received broad attention as a light-absorbing layer in a photovoltaic device, because of its non-toxicity, abundance, and theoretical conversion efficiency of 26% and 20% [3].

The CuO and Cu$_2$O layers have been prepared by several methods of thermal oxidation [4] and solution process [5]. Thermal oxidation offers several advantages over solution process and gas phase processes such as higher electrical properties i.e. electron mobility and carrier concentration as demonstrated by the preparation of thermal oxidation of copper (Cu) sheet [4]. Due to its excellent electrical properties, Cu$_2$O/CuO bilayers prepared by solution processes followed by annealing were also reported, but nanopores and defect introduced during annealing showed undesirable effect for photovoltaic (PV) performance [6]. Insertion of graphene (Gr) monolayer in between Cu$_2$O/CuO
bilayers and zinc (II) oxide (ZnO) could improve this problem due to its excellent electrical properties [7].

Thus, in this study, we report the fabrication of internally stacked CuO layer on the electrodeposited Cu₂O layer as well as the electrical properties of Cu₂O:CuO/Gr/ZnO heterojunctions.

2. Experimental section

2.1. Preparation of Cu₂O:CuO/Gr/ZnO heterojunctions

Pure copper sheet with dimension of 20 × 10 × 1 mm (length × width × thickness) was used as a substrate. Prior to electrodeposition process, the copper substrate was polished with #2000 SiC sandpaper and then immersed in acetone for 2 minutes and rinsed with deionized water, followed by drying with pressurized air. The Cu₂O layer was deposited potentiostatically at 0.5V referenced to Ag/AgCl electrode on the Cu substrate at a constant electric charge of 1.7 C/cm² with a potentiostat in an alkaline aqueous solution containing a 0.4M copper(II) acetate monohydrate (Cu(CH₃COO)₂) and 3M of lactic acid (C₃H₆O₃) (Kanto Chemical, Co., Inc.) at temperature of 328K. The solution was prepared with 500ml of deionized (DI) water with a resistivity of 18 MΩ·cm and potassium hydroxide (KOH) was added for the pH adjustment to 12.5. A platinum (Pt) plate was used as the counter electrode. Annealing of the electrodeposited Cu₂O layer was performed at 100°C, 200°C and 300°C for 2 hours in air condition using a heating furnace.

Gr layer was synthesized by chemical vapor deposition (CVD) method. Thin Cu foil (thickness 0.025 mm) is used as a catalyst substrate for the growth of Gr layer. The furnace was heated to 1000 °C with the 10°C/min ramping and dwelling of 3 min. Synthesis started when the temperature reached 1000°C. High quality of pure methane (CH₄) gas at a rate of 50 ml/min was supplied into the chamber together with the continuous supply of hydrogen (H₂) gas at a rate of 164 ml/min and nitrogen (N₂) gas at a rate of 100 ml/min, all at the constant pressure of 2 bar after 30 minutes. The gas controller valve for CH₄ and H₂ was closed after 3 min of CH₄ supply. The Gr layer deposited on Cu foil was then etched with 1.0 M of ferric chloride (FeCl₃) solution until the Cu layer was thoroughly dissolved. The suspended graphene layer was scooped on Cu₂O:CuO layers. Later, the ZnO layer was deposited on the Gr layer by sol gel method as explained in our previous work [8]. Prior to current-voltage (I-V) testing, aluminium (Al) electrode was deposited on the top of the heterojunction film using HHV Thermal Evaporator Auto 306.

2.2. Characterization of analysis

Structural characterization was carried out by X-ray Diffractometer (XRD BRUKER D2 PHASER), operated at 30kV and 10mA using Cu Ka radiation (wavelength of Ka₁=1.5406Å) that linked with DIFFRAC.SUITE EVA Software with scan rate at 0.1s/step. The surface of the sample was observed using the JEOL JSM 6460 LA SEM Machine with the magnification of 30k. High resolution transmission electron microscopy (HRTEM- JEOL ARM 200 F cold FEG) was used for imaging materials on the atomic scale for graphene analysis. The electrical properties of PV device were characterized by measuring the relationship between voltage (V) and current (I) under simulation of sunlight. The (I-V) curve under the illumination AM1.5 with 100 mW/cm² in power was recorded using a solar simulator Xenon Lamp Main Power Supply XPS-1600 with Keithley SMU 2400 source meter.

3. Result and Discussion

3.1. Morphology of Cu₂O:CuO layers

Fig. 1 shows the SEM images of the obtained Cu₂O layers annealed at different temperatures. The surface of the as-deposited Cu₂O layer was composed of continuous well-faced grains with pyramidal shape which is favourable to reduce the optical reflection [9]. The observed three-sided pyramidal grains
correspond to the corner of a cubic, indicating that the Cu$_2$O layer had a (111) preferred orientation. The SEM images revealed the changes of grain sizes depending on the annealing temperature.

![SEM images of Cu$_2$O annealed at different temperatures](image)  

**Figure 1** SEM image of Cu$_2$O annealed at different temperatures (a) as-deposited Cu$_2$O layer on Cu substrate, and Cu$_2$O layer on Cu annealed at (b) 100ºC, (c) 200ºC and (d) 300ºC

The size of the grain increased with increase of annealing temperature from 100ºC to 200ºC but decreased when annealed at 300ºC due to precipitation of a new oxide layer. The formation of a new oxide layer on the surface of Cu$_2$O annealed in air was also reported elsewhere [10]. The Cu$_2$O layer annealed at 300ºC for 2 hours exhibited the co-existence of the CuO layer when the pyramid-like structure of the Cu$_2$O layer was covered completely by a compact irregular structure of CuO grains. The grain size of Cu$_2$O layer was about 201.206 nm at 200ºC while the grain size of CuO layer was approximately 173.440 nm at 300ºC.

3.2. **Structural properties of Cu$_2$O:CuO layers**

Fig. 2 shows the XRD patterns for as-deposited Cu$_2$O layer and annealed Cu$_2$O layer at different temperatures from 100ºC until 300ºC. The as-deposited Cu$_2$O layer revealed single orientation which was indexed to (111) at diffraction peak of 36.43°. The Cu$_2$O orientation corresponding to cubic Cu$_2$O pattern (PDF 01-071-3645) and the intensity increases as the annealing temperature increased up to 300ºC. No obvious peak of CuO layer could be seen as the Cu$_2$O layer was annealed in air at 200ºC and 300ºC, irrespectively with the changes in the microstructure. However, the peak of CuO layer became visible in the diffraction pattern when the annealing temperature was slightly increased to 350ºC [11]. It was clear that the CuO layer could be constructed by annealing of Cu$_2$O layer in air at temperature as low as 300ºC [12].

3.3. **Morphology of graphene buffer layer**

Fig. 3 shows the HR-TEM images of Gr monolayer inserted between Cu$_2$O:CuO/ZnO layers. It can be seen that the synthesized Gr comprises of continuous monolayer with an evident edge layer with low defect density. The evident Gr layer edges also confirm that the grown film comprises of epitaxial single-crystalline film induced by wetting transparency associated with Gr [13]. The epitaxy of the layered two-dimensional (2D) material is motivated by the weak Van der Waals reciprocities and at the same time, permits facile layer detachment from seeding surfaces [14].
Figure 2 (a) XRD patterns of the (a) Cu substrate, (b) electrodeposited Cu$_2$O layer and annealed Cu$_2$O annealed at (c) 100°C, (d) 200°C and (e) 300°C.

Figure 3 HR-TEM image of monolayer Graphene inserted between Cu$_2$O:CuO/ZnO layers.

3.4. Structural properties of Cu$_2$O:CuO/Gr/ZnO heterojunctions

The Gr monolayer and ZnO layer were deposited on the Cu$_2$O:CuO layers to form the p-n heterojunction. Fig. 4 shows the XRD patterns of Cu$_2$O:CuO/Gr/ZnO heterojunction. A well-defined crystallinity of synthesized Cu$_2$O layer with preferred orientations of (111) corresponding to ICDD card no. 01-071-3645 was observed (Fig. 4(a)). The crystallinity of the materials decreased marked by the decrease and broadening of peak indicated by the increase of FWHM (not shown) with incorporation of ZnO (Fig. 4(b), with preferred orientation of (002) corresponding to ICDD card no. 00-036-1451. The reduction in crystallinity could be explained by the small lattice mismatch between Cu$_2$O:CuO and ZnO. The interaction of Cu$_2$O and ZnO is assumed to be heteroepitaxial with structural mismatch of 7.6% [15]. The XRD profile of the Cu$_2$O:CuO/Gr/ZnO heterojunction is shown in Fig. 4(d). In the structural perspective, it can be observed that insertion of Gr buffer layer between Cu$_2$O:CuO and ZnO improves the interfacial aspects between the p and n material by initial crystallinity improvement as observed in the (111) and (200) peaks increase.
Figure 4 XRD patterns of copper oxide-based heterojunction with different configuration; (a) Cu$_2$O:CuO (b) Cu$_2$O:CuO/ZnO (c) Cu$_2$O:CuO/Gr and (d) Cu$_2$O:CuO/Gr/ZnO.

Figure 5 I-V characteristics of Cu$_2$O:CuO/Gr/ZnO heterojunction in the dark and the inset of schematic illustration of Cu$_2$O:CuO/Gr/ZnO heterojunction.

3.5. Electrical properties Cu$_2$O:CuO/Gr/ZnO heterojunctions

The schematic structures of the heterojunction assembly are illustrated in the inset of I–V curve profile shown in Fig. 5. The electrical properties of the Cu$_2$O:CuO/Gr/ZnO heterojunction was investigated in the dark at room temperature. To measure the I–V characteristics, Al electrode layer was evaporated on the top surface of the Cu$_2$O:CuO/Gr/ZnO to create ohmic contact. It is well established that the Cu$_2$O:CuO/Gr/ZnO heterojunction exhibited typical electrical rectification feature, indicating that a closed compact heterojunction has been formed between Cu$_2$O:CuO/Gr and ZnO layers. The threshold voltage (V$_{th}$) was deduced from the intersection of the linear section of the forward (I -V) linear plot. The threshold voltage is defined as the built-in potential that corresponds to a potential barrier the charges have to overcome to contribute to forward current. The threshold voltage is expected to be on within 0.5 ~ 1.1 V for Cu$_2$O/ZnO heterojunction [16], and the obtained threshold voltage is approximately 0.5 V which is in agreement of the reported value irrespective of the insertion of Gr buffer layer.
4. Conclusions
The Cu$_2$O:CuO/Gr/ZnO heterojunction was successfully fabricated by several methods. The internally stacked Cu$_2$O:CuO layer have been constructed by annealing of electrodeposited p-Cu$_2$O layer on Cu substrate in air at 300°C for 2 hours. The morphologies and structural result show the Cu$_2$O layer possess pyramid structure and polycrystalline nature with (111) preferred orientation, and covered by CuO layer when annealed up to 300°C. The Gr monolayer was inserted in between Cu$_2$O:CuO layers and ZnO layer by CVD method and was confirmed by HR-TEM image. Eventually, the Cu$_2$O:CuO/Gr/ZnO heterojunction was completely fabricated by depositing ZnO layer by sol gel method and the electrical rectification could be observed from I-V measurements. The I-V measurement exhibits an excellent electrical rectification with threshold voltage of 0.5 V. Although further enhancements are required, these outcomes demonstrate the viability of low cost and high-performance heterojunction for solar cells applications.

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References
[1] M. Zamzuri, J. Sasano, F. Binti Mohamad and M. Izaki. 2015 Thin Solid Films 595 136.
[2] Halla Lahmar, FatimaSetifi, AmorAzizi, GuySchmerber and AzizDinia. 2017 J. of Alloys and Comp. 718 36.
[3] M. Izaki, T. Ohta, M. Kondo, T. Takahashi, F. Binti Mohamad, M. Zamzuri, T. Shinagawa and T. Pauporte. 2014 ACS. Appl. Mater. & Interfaces 6 13461.
[4] T. Minami, Y. Nishi and T. Miyata. 2016 Appl. Phys. Exp. 9, 052301.
[5] M. Zamzuri, M. Hasnulhadi, Z. Nooraizedfiza, M. Marina, F. Mohamad, N. Hisyamudin and M. Izaki, 2017 IOP Conf. Ser.: Mater. Sci. and Eng. 226 012178.
[6] M. Izaki, K. Fukazawa, K. Sato, P.L. Khoo, M. Kobayashi, A. Takeuchi and K.Uesugi 2019 ACS. Energy Mater. 2 4833.
[7] R. Zan, Q. M. Ramasse, U. Bangert and K. S. Novoselov 2012 Nano Lett. 12 3936–40.
[8] S. Zainal, M. Zamzuri, M. Hasnulhadi, M. Marina, F. Mohamad, N. Hisyamudin and M. Izaki 2018 Ind. J. of Pub. Health Res. and Dev. 9 2620.
[9] Tran, M. H., Cho, J. Y., Sinha, S., Gang, M. G. and Heo, J. 2018 Thin Solid Films, 661 132–6
[10] T. Shinagawa. Y. Ida, K. Mizuno, S. Watase, M. Inaba, A. Tasaka and M. Izaki 2013 Cryst. Growth Des. 13 52.
[11] Du, F., Chen, Q. Y., & Wang and Y. H. 2017 J. of Phy. and Chm. of Solids 104 139.
[12] Zainal, S. M., Zamzuri, M., Hasnulhadi, M., Nooraizedfiza, Z., Marina, M., Mohamad, F., Hisyamudin, N. and Izaki, M. 2018 IOP Conf. Ser.: Mater. Sci. and Eng. 429 012097
[13] I. A. Kostogrud, E. V. Boyko and D. V. Smovzh 2017. Mater Today Proc. 4 11476–9.
[14] J. Kim et al. 2014 Nat. Commun. 5 1–7.
[15] K. Gregor Both 2019 Cu 2 O – ZnO p-n Junctions UNIVERSITY OF OSLO.
[16] S. Jeong and E.S. Aydil 2019 J. Cryst. Growth 311 4188.