Flexible CuO–ZnO nano-bulk junction with photovoltaic response

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Abstract
Nano-Bulk junction grown over flexible Cu substrate demonstrating photovoltaic response has been developed. The structure of the device fabricated by us is Cu/CuO/CuO-ZnO/ZnO/Ag with the entire device fabrication sequence taking place at a temperature lower than 330 K. A nano-crystalline p-type CuO layer was deposited on Cu substrate using chemical bath deposition at 300 K. The n-type ZnO was solution grown and spin coated over the blend of CuO-ZnO deposited as a buffer between p-type CuO an n-type ZnO layer. The optimized device exhibited an open circuit voltage of 0.25 V, a short circuit current density of $2 \times 10^{-6}$ A cm$^{-2}$, a fill factor of 8% and efficiency of 0.11%. A space charge limited conduction mechanism was identified for the best device structure. The optimized cell structure had a diode ideality factor of 2.11 and work function of 3.28 eV.

1. Introduction
Solar cells based on heterojunction between solution processed inorganic semiconductors comprising of bulk/nano-crystalline layer of hole transporting material and electron transporting nano-crystalline complementary material have been envisaged recently [1]. It has opened up a platform for development of nano-composite materials with tailored photovoltaic properties. For solar cell application the primary choice of the material is based upon its solar energy harnessing capacity. Another critical parameter is the carrier lifetime and ease of charge separation across the junction such that efficient drift and diffusion of the photo-generated charges to the electrodes occurs. The need to absorb maximum amount of incident solar radiation makes a low band gap material sought-after for solar cell fabrication. On the other hand the need to have a large built in electric field makes a wide band gap material attractive.

As a compromise an ideal hole transporting candidate resonating to the former requirement is CuO. Its features include high optical absorption coefficient, non toxicity, low raw material cost, low thermal emittance and a band gap of 1.35 eV [2]. Theoretically CuO based photovoltaic devices may deliver conversion efficiency upto 30% [3]. A large built in voltage can cause electrons to move easily towards a negative surface, where they become available to the external electrical circuit. A material suitable to the later requirement is ZnO. A wide band gap of 3.3 eV, non-toxicity, high stability, ease in synthesis makes it’s a widely used conducting window layer material in solar cells.

A solar cell architecture that permits the use of the least contingent processing tools and conditions, minimal requirement of state of the art tools, eco-friendly and non hazardous materials and process temperature less 373 K envisaged us to undertake a research on a solution grown first layer of CuO over flexible Cu sheets, followed by a second layer growth achieved by spin coating wet synthesized ZnO nano particles. Peng Wang el al reported CuO/ZnO junction, in which ZnO layer was drop casted over CuO layer deposited by thermal oxidation of copper foil. They reported a power conversion efficiency of 0.1% [4]. Zhao et al reported on the junction between drop-cast grown ZnO and thermal oxidized CuO layer with an open-circuit voltage of 0.445 V, short-circuit current density value of 0.89 mA cm$^{-2}$ and power conversion efficiency 0.17% [5]. Chemical bath deposition and Spin coating are both simple and cost effective thin film deposition techniques. In our work we report on the growth of a photovoltaic device using the above two techniques. First a CuO p-type material is grown using chemical bath deposition over flexible Cu substrates and subsequently a blend of the CuO and ZnO.
was spin coated. Finally the n-type ZnO is spin coated over the blend layer. The effect of variation of the blend layer thickness and n layer thickness on the photovoltaic response is investigated.

2. Experimental section

Facile formation of CuO nanostructures on copper substrate was carried out by the oxidation of copper foil in alkaline solution. For this first a Copper foil was cleaned in diluted nitric acid solution and then it was washed with deionised water and dried at 40 °C. Cleaned copper foil of this kind were left immersed vertically in a solution containing 1 M KOH solution. Optimized film formation was complete at the end of 144 h. ZnO nanoparticles were synthesized using reported sol-gel method \[6\]. Blends of CuO and ZnO were prepared by mixing desired amount of CuO powder with ZnO solution. The device was fabricated by spin coating blend solution over the CuO layer followed by spin coating of the grown ZnO nano-particles. The samples were named based on the number of spin coated layers as CuOB4Z4- which contained 4 blend layers and 4 layers of ZnO. Similarly samples CuOB6Z6- and CuOB8Z8- were prepared. Ag paste was applied on the n-type ZnO and cured at 323 K to obtain the front contact. The second contact was taken from the Cu substrate.

Structural analysis was done using x-ray diffraction (XRD) with a Rigaku (D.Max.C) x-ray diffractometer, having Cu K\(_\alpha\) (\(\lambda = 1.5405 \text{ Å}\)) radiation and Ni filter operated at 30 kV and 20 mA. Optical absorption and transmission studies were carried out using UV–vis-NIR spectrophotometer (Shimatzu UV 1800). Photoluminescence studies were performed using a spectro-fluorometer (JASCO FP8600). Electrical measurements were conducted using a source measure unit (Aglient B2900). The illuminated current voltage characteristics were measured under an illumination of 0.1 W m\(^{-2}\) using a halogen light source. The area of the cell was \(3.75 \times 10^{-4} \text{ m}^2\).

3. Results and discussion

Figure 1 shows the XRD spectra of CuO thin film grown on flexible Cu sheet substrate. The preferential diffraction peaks were identified to the \((11-1)\) and \((111)\) planes of CuO phase as per JCPDS file no: 96-101-1149. In addition to this diffraction peaks along the \((20-2)\) and \((-113)\) planes corresponding to CuO were also identified as per JCPDS file No: 96-101-1149. Some of the planes were identified to the Cu substrate also. The average crystallite size was obtained as \(\sim 19 \text{ nm}\) using Scherrer equation \[7\].

![Figure 1. XRD spectrum of CuO thin film.](image-url)
where $\lambda$ is the wavelength of the x-rays, $\theta$ is angle of diffraction and $\beta$ is the full width half maximum of the diffraction peaks.

Figure 2 shows the UV–vis absorption spectrum of spin coated ZnO on a glass substrate. The film exhibits room temperature exciton absorption in the UV region with a sharp absorption edge at 358 nm. The sharp rise in the absorption spectra indicates absence of defect states near the band edge which contribute to absorption tail. The room temperature photoluminescence spectrum of the deposited ZnO thin films using an excitation wavelength of 300 nm and 358 nm are shown in figures 3(a) and (b) respectively. The PL spectrum consists of emissions at 396 nm, 426 nm, 466 nm and 558 nm. Based on earlier reports the emission at 396 nm may be assigned to the near band edge emissions while emissions at 426 nm, 466 nm and 558 nm may be assigned to the transitions from Zinc interstitial levels (Zn$_i$) to valence band edge, conduction band edge to Oxygen interstitial levels (O$_i$) and oxygen deficiency respectively [8–10].

The characteristic curves generated by plotting the current density $J$ against $V$ for the grown junctions under dark and illuminated conditions are shown in figure 4. The light has the effect of shifting the I-V curve down into
the fourth quadrant where power can be extracted from the junction and demonstrates that it behave as a solar cell. This J-V curve is most often shown reversed, with the output curve in the first quadrant, and can be mathematically represented by the relation

\[
I = I_L - I_0 \left( \frac{e^{V}}{\exp(nV/kT)} - 1 \right)
\]

Where \( I_0 \) represents the current across the junction without illumination, \( n \) is the diode ideality factor and \( I_L \) is the light generated current. A plot of \( \frac{dV}{d \ln(I)} \) against current density \( J \) under dark and illuminated conditions yields a straight line which may be fitted using the relation

\[
\frac{dV}{d \ln(I)} = \frac{A_{\text{eff}}}{n} \frac{R}{J} + \frac{n}{n \beta}
\]

where \( A_{\text{eff}} \) is the effective area of the junction, \( R \) is the series resistance and \( \beta \) is reciprocal of thermal voltage i.e. \( \frac{q}{kT} \). From the fit the value of series resistance \( (R) \) and diode ideality factor \( (n) \) were obtained. Similarly rearranging equation (1) using a function \( H(J) \) defined as

\[
H(J) = V - \frac{n}{\beta} \ln \left( \frac{J}{A_{\text{eff}} T^2} \right)
\]

can be used to plot a graph between \( H(J) \) versus \( J \) which yields straight line. This plot was fitted by using the relation

\[
H(J) = A_{\text{eff}} R J + n \phi
\]

which gives the value of \( R \) and work function \( \phi \) from the slope and intercept respectively. The numerical values obtained for these electrical parameters based on the theoretical fitting are tabulated in Table 1. The J-V characteristic shows a very small shift towards the forth quadrant which represents the short circuit current density of the device indicating that transport of minority carriers is being effected across the junction as a result of illumination.

The room temperature dark current-voltage characteristic for the CuOB6Z6 was used to evaluate the ideality factor and series resistance since this device showed the highest open circuit voltage \( (V_{oc}) \) of 0.25 V and short circuit current density of \( 2 \times 10^{-6} \) A cm\(^{-2} \) under illuminated condition. A semi-log plot as shown in figure 5 between log \( (I) \) and voltage was used to extract the behavior of dark current across the junction. The plot shows an unusual curve with the dark saturation current \( I_0 \) changing. This characteristic of the dark I-V has been explained earlier by Zhao et al as due to change in recombination velocity at the rear surface [12]. For our device the rear surface is metallic which has a lower resistance and is supportive of the explanation. For the device, the
Figure 5. Semi-log plot between log (I) versus voltage for the sample CuOB6Z6 using dark J-V data.

Figure 6. Plot between log (I) and log (V) in the forward bias condition for the sample CuOB6Z6.

Table 1. Electrical parameters obtained from theoretical fitting of the J-V characteristics using relations 3 and 5.

| Samples        | R, Ω (from dV/dln(I) - J graph) × 10^6 | R, Ω (from H(I) - J graph) × 10^6 | Work function (φ) eV |
|----------------|---------------------------------------|----------------------------------|---------------------|
|                | Dark | Illumination | Dark | Illumination | Dark | Illumination |
| CuOB4Z4        | 452  | 104          | 1.51 |            | 425  | 106          | 3.35     | 2.51 |
| CuOB6Z6        | 98   | 37           | 1.13 |            | 91   | 37           | 3.36     | 3.57 |
| CuOB8Z8        | 24   | 40           | 2.11 |            | 27   | 43           | 3.28     | 3.21 |
relation between \( \log(I) \) and \( \log(V) \) in the forward bias condition is shown in figure 6. A space charge limited conduction mechanism is evident from the graph as there is no Ohmic region in the plot.

The maximum power output of the cell can be graphically extracted from the area of the largest rectangle that can be fitted under the I-V curve. Theoretically at the maximum power output point

\[
\frac{dP}{dV_{mp}} = 0
\]  

(6)

Thus from the plot of \( dP \) versus \( dV \) as shown in figure 7, the maximum power output point can be taken as the intercept along the \( x \)-axis. From the inset of figure 7 we obtained \( V_{mp} = 0.1 \) \( V \). The current corresponding to this \( V_{mp} \) was obtained as \( I_{mp} = 4.13 \times 10^{-7} \) \( A \). The fill factor which is a measure of the junction quality and series resistance of the cell was found to be 8\% using the relation

\[
FF = \frac{V_{mp}I_{mp}}{V_{oc}I_{sc}}
\]  

(7)

Ideally, the fill factor in cases where no parasitic resistance losses occurs, is a function of open circuit voltage only and can be approximately calculated as [13]

\[
FF = \frac{V_{oc}}{V_{oc} + 0.72}
\]  

(8)

where

\[
V_{oc} = \frac{V_{oc}}{nKT} \frac{q}{q}
\]  

(9)

Using equations (8) and (9) we obtained \( FF = 0.52 \). This proves that the device performance may be improved by optimization of the parasitic resistance losses [14, 15]. Using the relation

\[
\eta = \frac{P_{max}}{G \times A}
\]  

(10)

where \( G \) is the irradiance in \( W \text{ m}^{-2} \), \( A \) the surface area of the solar cell and \( P_{max} \) the output power at its maximum power point the efficiency is found to be 0.11\%. This is a promising start to the novel deposition process we are optimizing for growth of flexible solar cells.

Figure 8 shows the cross-sectional SEM analysis for the best device fabricated. The image clearly shows the interface formation between the different layers. The demarcation between the individual layers is non homogenous. The thickness of the layers was estimated be 3.4 \( \mu \text{m} \), 2.08 \( \mu \text{m} \) and 0.74 \( \mu \text{m} \) for the CuO, blend and ZnO layers respectively. The poor interface formation between the blend and the p-type CuO is clearly visible. In
some regions the interface between the p-type layer and the blend is absent. A clear interface between the blend and the n-type ZnO is clearly formed. In order to fabricate a better device a strategy to achieve a better interface is to be evolved.

4. Conclusions

We have fabricated a solar cell using chemical bath deposition and spin coating technique sequentially. The entire device fabrication process has been achieved at a temperature lower than 330 K which demonstrates the feasibility of optimizing the process sequence for a better device. The p-type CuO layer was deposited on Cu substrate and was identified to have nano-crystalline nature. The blend of CuO–ZnO which was applied as a buffer between p-type CuO an n-type ZnO layer was critical in optimizing the present device performance. The optimized device presently exhibited an open circuit voltage of 0.25 V, a short circuit current density of $2 \times 10^{-6}$ A cm$^{-2}$, fill factor of 8% and efficiency 0.11%. The theoretical fitting to the J-V characteristic identified the optimized cell structure to be having a diode ideality factor of 2.11 and work function of 3.28 eV. A space charge limited conduction mechanism was identified for the best device structure. We conclude that device performance may be improved by optimization of the parasitic resistance losses.

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Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

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References

[1] Rath A K, Bernechea M, Martinez I, Pelayo Garcia de Arquer F, Osmond J and Konstantatos G 2012 Nat. Photonics 6 529–34
[2] Park J W, Baeg K J, Ghim J, Kang S J, Park J H and Kim D Y 2007 Electrochem. Solid-State Lett. 10 H340
[3] Shockley W and Queisser H J 1961 J. Appl. Phys. 32 510
[4] Wang P, Zhao X and Li B 2011 Opt. Express 19 11271–9
[5] Zhao X, Wang P, Gao Y, Xu X, Yan Z and Ren N 2014 Mater. Lett. 132 409–12
[6] Liu D and Kelly T L 2014 Nat. Photonics 8 133
[7] Chatterjee S, Saha S K and Pal A J 2016 Sol. Energy Mater. Sol. Cells 147 17–26
[8] Mishra S K, Srivastava R K, Prakash S G, Yadav R S and Panday A C 2010 Opto-Electron. Rev. 18 467–73
[9] Morkoç H and Özgür Ü 2009 Optical Properties (New Jersey: Wiley-Blackwell) 131–244 Chapter 3, pages 978-3-527-62395-2
[10] Ramya E, Rao M V, Jyothi L and Rao D N 2018 J. Nanosci. Nanotechnol. 18 7072–7
[11] Khatib T, Elmenreich W and Mohamed A 2017 Sustainability 9 657
[12] Zhao J, A. W, Dai X, Green M A and Wenham S R 1991 22nd IEEE PV Specialists Conference. pp 399–402
[13] Green M A 1982 Sol. Cells 7 337–40
[14] Wu J-K, Chen W-J, Chang Y H, Chen Y F, Hang D-R, Liang C-T and Lu J-Y 2013 Nanoscale Res. Lett. 8 387
[15] Hussain S, Cao C, Nabi G, Khan W S, Tahir M, Tanveer M and Aslam I 2017 Optik 130 372–7