Fabrication of p-CuO/n-ZnO heterojunction diode via sol-gel spin coating technique

Rajeev R. Prabhu a,⇑, A.C. Saritha a, M.R. Shijeesha a, M.K. Jayaraja a,b

a Nanophotonic and Optoelectronic Devices Laboratory, Department of Physics, Cochin University of Science and Technology, Kochi 682 022, India
b Centre for Advanced Materials, Cochin University of Science and Technology, Kochi 682 022, India

ABSTRACT

We report a facile all-solution approach for the growth of nanostructured p-CuO and n-ZnO thin films. The influence of annealing temperature on the physical properties of CuO and ZnO thin films was examined. XRD and Raman spectra depict the structural and phase purity of solution grown CuO and ZnO films. The electrical as well as the optical properties of thin films were also studied. The average optical transmission of CuO and ZnO thin films in the visible spectral region was found to be above 80 and 95% respectively. Band gap energy variations on annealing temperature were investigated for CuO as well as ZnO films. Surface morphology analyzed by FESEM shows that the films are very smooth. All solution grown p-n heterojunction using p-CuO and n-ZnO films was fabricated in the structure ITO/n-ZnO/p-CuO/Au which showed rectification behavior with a turn on voltage of 2.5 V and an ideality factor of 3.15.

1. Introduction

In recent years, much effort has been devoted for preparing transparent semiconducting oxide (TSO) thin films owing to their wide applications in electronics, optoelectronics, solar cells, surface-acoustic wave devices, electromechanical devices etc. Amorphous and/or crystalline TSOs are becoming the material of choice for most of the optoelectronic device applications. Currently the industry standard TSOs are IGZO, ZnO, SnO2, ITO, FTO, SnO, CuO etc [1–6]. Among these CuO and ZnO form an important pair to fabricate heterojunctions for solar cell and photodetector applications.

Copper oxide is a TSO material that has been considerably investigated for applications in diverse fields. Copper oxide exists in two different crystalline phases viz. cuprite or cuprous oxide (Cu2O) and tenorite or cupric oxide (CuO). CuO has a monoclinic structure and a band gap of 1.2–1.9 eV [7–9] while Cu2O has a cubic crystal structure and a band gap of 2.1–2.6 eV [10–12]. As an exceptional family of p-type semiconductors, copper oxide in any form has high optical absorption coefficient in the visible and near infrared regions due to its direct band gap [13]. CuO having a band gap of ~1.5 eV can attain an ultimate solar cell efficiency of almost 30%, considerably higher than a maximum limit of 20% for Cu2O that have a band gap value of ~2 eV [13–16]. CuO is a non-toxic material and the mostly inexpensive production means make it a suitable substitute to silicon, which is basically used in conventional solar cells. CuO can be used in field emitter [17], gas sensing medium [18,19], magnetic storage media [20,21], electrode material in lithium-ion batteries [22,23], optical switches [24], as a co-catalyst for hydrogen evolution [25] and also as an active material for fabricating thin film photodetectors [7,15,26–29]. To make use of the properties of CuO in various applications, several methods have been developed to prepare different morphologies of CuO nanostructures which include thermal evaporation [30], RF-sputtering [23,31], pulsed laser deposition (PLD) [32], microwave assisted deposition [33], ultrasonic spray pyrolysis [34], solvothermal [35], hydrothermal [36], electrodeposition [37], SILAR [8] and chemical bath deposition (CBD) methods [38].

Likewise, zinc oxide (ZnO) is an n-type transparent semiconductor with a direct wide band gap of about 3.37 eV and a large excitonic binding energy of about 60 meV at room temperature. As an important functional oxide semiconductor, ZnO nanostructured thin films have attracted significant attention for its applications related with "ultraviolet" based photonic devices, of which the performance is strongly influenced by the presence of structural defects [39]. RF-magnetron sputtering [40], electron beam evaporation [41], PLD [42] and atomic layer deposition technique [43] have been employed to fabricate high quality ZnO films. Chemical synthesis is another important method for the
fabrication of ZnO films, where the expense is very low and film quality is comparable to that of other sophisticated vacuum deposition techniques. A few reports on CBD technique for the growth of ZnO and CuO films are also available in literature [38,44]. But the main drawback of CBD technique is the wastage of the chemically prepared solution after every deposition. The more simple method of sol-gel spin coating has a lot of benefits compared to CBD such as, cost effectiveness, minimum material wastage, lower crystallization temperature, economical way of large-area deposition under atmospheric conditions etc.

Many authors have reported the deposition of CuO and ZnO thin films by sol-gel spin coating method. Lim et al. have reported the deposition of Cu2O and CuO thin films by sol-gel spin coating for photocatalytic water splitting application [45]. A study by Akgul et al. has demonstrated the preparation of CuO thin films by facile sol-gel method and its subsequent photodetector application [46]. In 2013, Park et al. fabricated a highly transparent heterojunction photodiode using ZnO and NiO thin films by sol-gel spin coating method and observed a good photoresponse and quantum efficiency under UV illumination [47]. A self-powered UV photore sponsive property with excellent stability and reproducibility have been reported by Zhang et al. from a CuSCN/ZnO nanorods heterojunction prepared by sol-gel spin coating method [48].

In general, a multi-layer configuration with complementing n- and p- type TSQs could lead to high performance devices. Heterojunction made of p-CuO and n-ZnO thin films has been fabricated by many research groups for various optoelectronic applications [49-51]. In the present study, transparent and conducting CuO and ZnO films were deposited on glass substrates by sol-gel spin coating technique. The grown films were characterized by studying the structural, electrical and optical properties. A completely solution-processed transparent (>60%) p-n heterojunction diode in the structure ITO/(n-ZnO/p-CuO)/Au has been fabricated and performance of the device under dark and UV illumination conditions are investigated.

2. Experimental

2.1. Growth of CuO thin films

Copper oxide (CuO) thin films were prepared by dissolving 0.2 M copper acetate and monoethanolamine in a 1:1 M ratio in 20 ml of 2-methoxyethanol solvent. Acetic acid was added drop wise to achieve a homogeneous solution. The above stock solution was vigorously stirred at 80 °C for 120 min. The Cu aqueous solution was filtered through a 0.2 μm poly-tetrafluoroethylene membrane (Whatman make) and was aged for 24 h. The colour of the solvent became dark green. The precursor solution was uniformly deposited on clean glass substrates by spin coating technique at a spin speed of 2000 rpm for 60 s. The coating process was repeated to attain the desired thickness. The films were annealed at 100 °C for 5 min after each layer deposition.

2.2. Growth of ZnO thin films

The precursor solution for fabricating zinc oxide thin films were prepared by dissolving 0.3 M zinc acetate and monoethanolamine (MEA) in a 1:1 M ratio in 20 ml of 2-methoxyethanol solvent. MEA was added as a stabilizer to ameliorate the solubility of the precursors. Acetic acid is then added to achieve a homogeneous solution. Above mixture was stirred at 70 °C for one hour. After stirring, the Zn aqueous solution was aged for 24 h. The colour of the solvent then became yellowish orange. The precursor solution was uniformly deposited on clean glass substrates by spin coating technique at a spin speed of 2000 rpm for 60 s. The coatings were repeated to achieve the desired thickness. After each coating the films were baked at 95 °C for 5 min.

The CuO and ZnO films were finally air annealed at various temperatures ranging from 150 °C to 350 °C for three hours. The organics used in the sols for depositing the films were easily removed or evaporated at temperatures less than 125 °C. Each layer was characterized by studying structural, electrical and optical properties. Glancing angle X-ray diffraction analysis of the films was performed with PANalytical XPerT PRO system. The thickness of the thin films was measured by a stylus profiler (Dektak 6 M). Surface morphology of the film was studied by ZEISS FESEM. Optical transmittance measurements were performed with Jasco V-570, UV–vis-NIR spectrophotometer. Micro-Raman measurements were performed at room-temperature using a Horiba Jobin-Yvon Lab Ram Micro-Raman spectrometer with a 10 mW power, 514.5 nm wavelength Ar+ laser as excitation source. Transport properties of the charge carriers were studied by Hall effect measurement in the van der Pauw geometry (Ecopia, HMS-3000). Electrical characterization of the resistive thin films and current voltage characteristics of p-n junction were performed at room temperature using Keithley 4200-SCS semiconductor parameter analyzer equipped with Suss MicroTec microprobe station.

3. Results and discussions

3.1. CuO thin films

The X-ray diffraction (XRD) patterns of copper oxide thin films annealed at different temperatures are illustrated in Fig. 1a. The observed XRD patterns match well with monoclinic phase of CuO (JCPDS 45-0937) [8,9]. No peaks corresponding to metallic Cu or Cu2O phases were detected in the XRD patterns. Annealing the CuO films in air at various temperatures shows an improvement in crystallinity. The average crystallite size of the CuO films was determined using the Scherer equation,

\[ d = \frac{k \lambda}{\beta \cos \theta} \tag{1} \]

where, \( d \) is the crystallite size, \( k \) is the shape factor lying between 0.95 and 1.15 depending on the shape of the crystals and in the present study the value is assumed to be 1, \( \beta \) is the full width at half maximum (FWHM) of the diffraction peak in radians, \( \theta \) is the Bragg angle of the diffraction peak and \( \lambda \) is the wavelength of X-rays [52]. The average crystallite size as calculated from XRD are found to be 8, 9, 10, 12 and 15 nm respectively for the CuO films annealed at 150, 200, 250, 300 and 350 °C (Fig. 1b).

The electrical properties of the films were found to depend strongly on the annealing temperatures and duration of annealing. Annealing of the films for one hour and two hours at the temperatures ranging from 150 °C to 350 °C did not result in conducting films. On the other hand CuO film annealed at 150 °C for three hours showed n-type conductivity and the nature of conductivity changed to p-type on annealing above 150 °C for three hours. This change in nature of conductivity is due to the presence of mixed phases of copper oxides in the film [53]. Fig. 2 shows the electrical parameters of CuO films obtained from Hall measurement. Carrier concentration of n-type CuO film which is annealed at 150 °C was 1.66 × 10¹⁰ cm⁻³. The carrier concentration and mobility increased as the annealing temperature is increased. The highest mobility of 4.5 cm² V⁻¹ s⁻¹ was obtained for films annealed at 250 °C in air for 3 h. The decrease in mobility on annealing above 250 °C and the decrease in carrier concentration above 300 °C need further investigation. The observed low conductivity for the films annealed at lower temperatures can be due the lower crystallinity and the presence of large number of smaller grains and associated grain
boundary scattering. The presence of a number of defects such as structural disorders, dislocations and surface imperfections can also play an imperative role in decreasing the conductivity as reported earlier [54,55].

The optical properties of the films were studied by measuring the transmission in the visible region. Fig. 3 shows the transmission spectra of CuO thin films annealed at various temperatures for a duration of three hours. The average transmission of CuO thin films was found to be above 80% in the visible spectral region.

The absorption coefficient \(a\) and band gap \(E_g\) of the material are related by the equation [13]

\[
a = \frac{A h v}{(h v - E_g)^n}
\]

where \(n = \frac{1}{2}\) for allowed direct transition and \(n = 2\) for allowed indirect transition. The absorption coefficient is calculated from the transmission spectra using the relation \(I = I_0 e^{-at}\). The optical energy band gaps \(E_g\) of CuO thin films can be estimated using Tauc equation (Eq. (2)). The allowed direct band gap of CuO is found from the Tauc plot (Fig. 3a) [13].

The straight line intercept on energy axis at \((ahv)^2\) equal to zero in the \((ahv)^2\) versus hv plot will give the direct band gap of CuO films (Fig. 3a). While the indirect band gap is estimated from the plot \((ahv)^{1/2}\) versus hv (Fig. 3b). The direct and indirect band gap of CuO films are observed to decrease with annealing temperature (Fig. 4). From Figs. 1b and 3c, it is observed that as the annealing temperature increases the grain size as well as the film thickness increases. The decrease in the values of band gap energy with increase in grain size is attributed to the increase in crystallinity of CuO phase in the films [56,57].

The estimated band gap values of CuO thin films for direct and indirect transitions in the present study are consistent with the reported \(E_g\) values of copper oxide thin films [12,13,15,56]. Several authors have reported both direct and indirect transitions involved in CuO thin films [13,15]. The calculated indirect energy gap (1.17–1.08 eV) may be due to the absorption involving defect states present in the CuO thin films [13]. Also the band gap determination from Tauc plot for the films annealed at lower temperatures may not strictly follow the relation \((ahv)^{1/2}\) versus hv, because of higher amorphous content. It is reported that amorphous semiconductors have subgap states and these subgap absorption can be found more clearly in log \(a\) versus hv plot [58].

Micro-Raman spectrum of CuO thin film annealed at 250 °C is displayed in Fig. 5. CuO having a monoclinic crystalline structure belongs to the space group \(C_{2h}^5\) with two formula units in each primitive cell.

\[
\Gamma_{opt} = 4A_a + 5B_a + A_g + 2B_g
\]

where \(A_a\) and \(B_a\) are IR modes, while \(A_g\) and \(B_g\) are Raman modes. There are three acoustic modes \((3A_g + 4B_g)\), six infrared active modes \((3A_a + 3B_a)\), and three Raman active modes \((A_g + 2B_g)\) [59]. Raman spectrum of CuO thin film shows peaks at 155, 299, 345, 565/610 and 1100 cm\(^{-1}\) which correspond to the \(A_g\), multi-phonon 2\(A_g\), B\(_{1g}\), B\(_{2g}\) and a multi-phonon 2\(B_g\) modes respectively, and the values

Fig. 1. (a) X-ray diffraction patterns of spin coated CuO thin films annealed at different temperatures and (b) Plot of grain size versus annealing temperature of CuO thin films.

Fig. 2. Variation of carrier mobility, carrier concentration and resistivity of CuO thin films with annealing temperature.
are in good agreement with that of reported ones for tenorite or cupric oxide \[8,12,60–64\] indicating that the sample is composed of CuO phase. Observation of broad peaks and the red-shift of the Raman peaks compared to the bulk counterpart of CuO indicate the formation of nanocrystalline CuO thin film\[13\]. The absence of peaks at 219, 415 and 631 cm\(^{-1}\), corresponding to cuprite or cuprous oxide, rules out the possibility of presence of Cu\(_2\)O phase in the CuO thin film annealed at 250 °C \[12\].

3.2. ZnO thin films

The XRD patterns of ZnO thin films annealed at different temperatures are shown in Fig. 6a. The diffraction peaks correspond to the wurtzite ZnO having hexagonal structure (JCPDS No. 36-1451) \[65\]. The crystallinity of the films increases with annealing temperature. The average crystallite size as calculated from XRD by Scherer equation (Eq. (1)) \[52\] is found to increase on annealing (Fig. 6b). The average crystallite size was found to be 7, 9, 10, 17 and 24 nm respectively for the ZnO films annealed at 150, 200, 250, 300 and 350 °C. It is also observed that the thickness of the ZnO films is increased from 120 nm to 160 nm when the annealing temperature was raised from 150 °C to 350 °C (Fig. 6b).

The room temperature electrical characterization of ZnO thin films were carried out by four point method in van der Pauw

---

**Fig. 3.** Optical transmission spectra of spin coated CuO thin films annealed at different temperatures (arrow indicates the increasing order of annealing temperature). Inset shows the Tauc plots \( (zh\eta)^2 \) versus \( h\eta \) showing direct band gap, \( (zh\eta)^{1/2} \) versus \( h\eta \) showing indirect band gap of CuO films and (c) Plot of film thickness versus annealing temperature of CuO thin films.

**Fig. 4.** Plot shows band gap energy versus grain size of spin coated CuO thin films.

**Fig. 5.** Micro-Raman spectrum of spin coated CuO thin film annealed at 250 °C.
All the ZnO films were n-type and the film annealed at 250 °C showed a better mobility (2.817 cm²/V s) of charge carriers (1.243 x 10¹⁵ cm⁻³). All the films have an optical transmission about 95% in the visible region.

Fig. 7a shows transmission spectrum of a ZnO thin film annealed at 250 °C. The optical energy band gap (Eg) of ZnO thin films was 3.32 eV (inset of Fig. 7a) as estimated from Tauc plot (Eq. (2)). Fig. 7b shows a plot of the variation in band gap energy with annealing temperature and it is observed that as the annealing temperature increases the band gap energy of ZnO decreases. The decrease in the values of band gap energy with annealing temperature is attributed to the increase in crystallinity and grain size of ZnO films [57].

Fig. 8 shows the micro-Raman spectrum of ZnO thin film annealed at 250 °C. Having a hexagonal-wurtzite structure ZnO belongs to the space group C₆ᵥ with two formula units per primitive cell, where all atoms occupy C₃ᵥ sites. At the centre of the Brillouin zone group theory predicts six optical phonons modes as

\[ \Gamma_{opt} = 1A_{1} + 2B_{1} + 1E_{1} + 2E_{2} \]  (4)

where A₁ and E₁ are polar modes and are both infrared and Raman active, the E₂ mode is non polar and only Raman active, while B₁ mode is a silent mode which is neither infrared nor Raman active. The non polar E₂ modes have two wave numbers, specifically, E₂ (high) and E₂ (low) related with the motion of oxygen and Zn sub lattice respectively [66].

A Lorentzian fit was applied to the Raman spectrum of ZnO thin film (Fig. 8) and was deconvoluted into four different possible peaks at 213, 437, 547 and 645 cm⁻¹. It is found that a peak at 437 cm⁻¹ is attributed to ZnO non-polar optical phonons of E₂ (high) mode [67–69]. The A₁ (LO) peak at ~547 cm⁻¹ is associated from smaller scattering cross sections [70] while the Raman peak at ~213 cm⁻¹ represent the phonon scattering from 2E₂ (low) mode [66,70] and that of ~645 cm⁻¹ is the acoustic overtone with A₁ symmetry [71]. The absence of the E₁ (LO) peak at about 591 cm⁻¹ in Raman spectrum imply a low defect density in our ZnO thin films [68].
3.3. Fabrication of p-CuO/n-ZnO thin film device

A p-n heterojunction was fabricated using solution-processed n-ZnO and p-CuO layers with glass/ITO/n-ZnO/p-CuO/Au structure. ITO coated glass substrate was used for the fabrication of the p-n heterojunction. The thickness of the ITO layer was 150 nm. The n-ZnO layer having a thickness of 150 nm was deposited over ITO by spin coating of Zn-precursor solution followed by air annealing process at 250 °C for 3 h. A 180 nm thick CuO layer, was deposited above the ZnO layer by spin coating of Cu-precursor solution which is again followed by air annealing at 250 °C for 3 h. Au electrode, having thickness 50 nm was deposited by thermal evaporation technique through a shadow mask of diameter 1.5 mm, completing the device structure of ITO/n-ZnO/p-CuO/Au. The ohmic contacts to the p-CuO and n-ZnO layers were gold (Au) and ITO respectively [72]. The n-ZnO film showed a mobility of 2.817 cm² V⁻¹ s⁻¹ and a carrier concentration of 1.243 × 10¹⁵ cm⁻³. The mobility and carrier concentration of p-CuO film were 4.42 cm² V⁻¹ s⁻¹ and 2.609 × 10¹⁴ cm⁻³ respectively. The schematic diagram of p-n heterojunction fabricated with structure glass/ITO/n-ZnO/p-CuO/Au is shown in Fig. 9.

The cross sectional FESEM image of the junction and the top-view FESEM images of the individual layers are shown in Fig. 10. From the cross sectional FESEM, the individual layers of the device can be distinguished and the thickness of the solution grown ZnO and CuO layer was found to be ~150 nm each. Top-view FESEM image of ZnO film annealed at 250 °C for 3 h showed a nanostructured grain, porous surface distributed throughout the film area (Fig. 10b). The CuO thin film annealed at 250 °C for 3 h has a continuous and homogeneous surface as observed in top-view FESEM image (Fig. 10c).

The thickness of ZnO layer as observed from FESEM is in good agreement with that estimated from stylus profiler while the thickness observed for CuO layer from FESEM is found to be 30 nm lesser than that estimated from stylus profiler. The CuO layer was spin coated over the porous surface of ZnO film. The Cu-precursor solution while spin coating would have deposited within a few nanometers inside the porous surface of ZnO film, which caused a decrease in the thickness of CuO layer. Moreover the annealing process at 250 °C might affect a few CuO atomic layers get diffused with the surface of the ZnO film. The transmission spectrum of the glass/ITO/n-ZnO/p-CuO device structure and the photograph of the transparent device are shown in the Fig. 11a. The device shows average transmission slightly greater than 60% in the visible region. The device is transparent to visible light which is confirmed by the back ground image visible though the device structure.
Current density-voltage (J-V) characteristic of ITO/n-ZnO/p-CuO/Au heterojunction were measured at room temperature and is shown in Fig. 12. The inset of Fig. 12 shows that the I-V characteristic for the ZnO/ITO and Au/CuO interface are both linear indicating ohmic nature of the contacts [73]. Fig. 12 shows that the n-ZnO/p-CuO junction exhibited nonlinear and rectifying J-V characteristics. From the J-V characteristics the forward threshold voltage or turn on voltage ($V_{on}$) of solution-processed n-ZnO/p-CuO heterojunction is found to be 2.5 V. The nonlinear J-V curve of n-ZnO/p-CuO junction is typical for any p-n heterojunctions [7,72] and therefore their rectification can be assumed to be originated at the interfaces of p-CuO and n-ZnO. The ITO/n-ZnO/p-CuO/Au heterojunction showed a rectification ratio of 7.02 at 3 V. The series resistance was found from I-V curve as 492 kΩ. The ideality factor ($n$) of the diode is calculated from the plot ln(I) versus V and is found to be 3.15 at low voltage region and 30.44 at high voltage region which are very much higher than the ideality factor of an abrupt junction. Kwon et al. [72] reported that the turn-on voltage for Cu$_1$O$_{0.9}$/ZnO heterojunction diodes fabricated by plasma-enhanced atomic layer deposition technique were in the range 2.4–3.7 V. The magnitude of the turn-on voltage depends on the Fermi levels of CuO and ZnO. A high turn-on voltage is expected in CuO based diodes if there is high oxygen content at the p-n junction interfaces.

The J-V characteristics of p-CuO/n-ZnO heterojunction under dark and UV illuminated conditions are shown in Fig. 13. Increased current was observed on UV exposure under both forward and reverse bias, signifying the photo responsive nature of the device. The device under UV illumination showed a rectifying behavior with a rectification ratio of 8.45 at 3 V and a turn on voltage of 2.22 V. These improved values indicate the absorption of incident UV light by the semiconducting layers and subsequent generation of photocarriers within the system by excitation of electrons from the valence band to the conduction band [74]. These results show the possibility of using the fabricated heterojunction for UV detector application. The all-solution-processed p-CuO/n-ZnO heterojunction fabricated by spin coating technique is transparent and this approach is supportive for the fabrication of inexpensive diodes for photodetector, solar cell and gas sensor applications.

4. Conclusions

Highly transparent and conducting p-CuO and n-ZnO thin films were prepared from sol-gel precursor solution. The XRD measurement confirms the monoclinic structure of CuO films and wurtzite structure of ZnO films. Raman spectral bands confirmed the phase purity of CuO and ZnO films. The band gap energy for CuO and ZnO films was found to decrease with annealing temperature. Surface morphology studies using FESEM revealed the smooth nature of the films. The all-solution grown p-n heterojunction fabricated in the device structure ITO/n-ZnO/p-CuO/Au showed a diode-like behavior with a knee voltage 2.5 V. The heterojunction device showed an average transmission above 60% in the visible region. The present study emphasize the applicability of all-solution grown p-CuO/n-ZnO heterojunctions for the development of efficient and low cost optoelectronic devices particularly photodetectors, solar cells and gas sensors.

Acknowledgements

The author Rajeev R. Prabhu acknowledges University Grants Commission (UGC), Government of India for granting a fellowship under UGC - Dr. D. S. Kothari Post Doctoral Fellowship Scheme. This work is also supported by Kerala State Council for Science, Technology and Environment (286/2014/KSCSTE), India.