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Randomly oriented rectangular shaped structures of CuO on NiO/ITO surfaces

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ABSTRACT

Metal oxide materials are one of the promising materials for low power consumption devices due to their unique size and dimensionality dependent physical and chemical properties. Low cost of production is also a key component in micro/nanoscale devices. Cupric oxide (CuO) nanostructures are of particular interest because of their interesting properties and promising applications in solar cells, bio and gas sensors, batteries, super capacitors, catalysis, photo detectors, energetic materials and removal of organic pollutants from waste water. An attempt has been made to synthesize randomly oriented rectangular shaped nanostructures of CuO, via hydrothermal synthesis at low temperature (~70 °C) on top of NiO porous structured film. The film was deposited using chemical bath deposition method at room temperature using ITO coated glass plate as a substrate. One can observe that the CuO growth on NiO/ITO substrate not only filled the porous structures of NiO but also formed the long rectangular shaped nanostructures which were randomly oriented on top of NiO surface. The CuO rectangular nanostructures have the dimensions in order of $(6\pm 2.0) \ \mu m \ x \ (2.0\pm 0.5) \ \mu m$. The randomly oriented rectangular structure can assist the charge transport in between the different semiconducting layers. These rectangular shaped nanostructures can also be used in nanoelectronic devices, or as a p-type conducting wires in future electronic device applications. The present study is limited to the surface morphology studies of the nanostructured thin layers of NiO/CuO composite materials. Structural and absorption measurements of the CuO/NiO hetero junction have been studied using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), UV spectroscopy. The energy band gap of both layers NiO and CuO have been calculated using UV spectroscopy and discussed further. Therefore, the present rectangular structure of CuO could be helpful for the purpose of designing novel function nanostructures for efficient energy harvesting. Copyright © 2016 VBRI Press.

Keywords: Nickel oxide (NiO); copper oxide (CuO); thin film; structural and optical properties.

Introduction

In our modern day-to-day life, environmental and energy resource concerns have been increasing, due to which the greater stress has been placed on development of renewable energy resources, especially on solar energy based photovoltaic cells. The economic feasibility of this relies on efficient collection, retention, and utilization of photons. Over the past decade, solar cell research has become hot topic with in science and engineering community [1-3]. The need for higher solar cell efficiencies at lower cost has become apparent, and at the same time synthetic control of nanostructures using topdown/bottom-up approaches have improved such that the high performance electronic devices are becoming possible [4, 5]. In organic nanostructures [6] with tailored geometry over its organic counterparts are expected to play significant roles for the next-generation nanoscale electronic, optoelectronic, electrochemical and electromechanical devices [7-10].

Copper oxides (CuO and Cu₂O) are p-type semiconductors, have been studied for numerous reasons such as: the natural abundance of copper, starting material; easy to prepare by solution process able methods; their non-

toxic nature and the reasonably good electrical and optical properties exhibited by both of them. At the same time, they are suitable materials for high efficiency solar cells due to their band gap lying between 1.3 and 2.0 eV, respectively which are close to the ideal energy gap for solar cells. Particularly, CuO has been intensively studied for photovoltaic/sensing devices due to its rich family of nanostructures and promising electrochemical and catalytic properties it possesses at nanoscale level [11-13]. CuO nanostructures can be grown either on a Cu substrate using a thermal oxidation process or synthesized through wet chemical routes especially using hydrothermal method on any supporting substrates. One of the concerns regarding the growth of CuO nanostructures (NS) by wet chemical method is that it shows poor adhesion to the substrates [13]. The important features of copper oxide semiconductors are their high optical absorption coefficient, non-toxicity and low fabrication cost [14, 15].

Recently, Hosseini et al. has demonstrated an inexpensive, high yielding, and eco-friendly route for synthesis of sphere-like CuO, NiO and CuO-NiO nanoparticles through emulsion route. They have shown

that CuO-NiO (1:1) nano particles show more catalytic activity than CuO and NiO NPs [16]. Whereas GuO et al. have used the Cu-Ni bimetallic organic framework to synthesis unique CuO/NiO microsphere with three-layer ball-in-ball hollow structure. They have utilized the facile microwave-assisted production of the Ni organic framework spheres as a template for inducing the morphology control of bimetallic oxides [17]. Further to it, Hassanpour et al. have evaluated the photocatalytic behaviour of CuO/NiO nanocomposites using the degradation of methyl orange under ultraviolet light irradiation. They have synthesized via a fast microwave method in a short period of time and demonstrated that the nanocomposites have applicable magnetic and photocatalytic performance [18]. For sensing application, Ibrahim et al. have deposited the thin film of copper oxide nanoparticles mixed with different concentration of nickel oxide wt % and deposited on Si and PS substrates. After annealing at 400 °C, the film was utilized for nitrogen dioxide gas sensor. The variation of operation temperature of gas sensors which fabricated from the prepared samples on sensor sensitivity and response time have been studied, the maximum sensitivity was about 53.3 % for 20 mA current [19]. Whereas, for nanowire arrays application [20] Huang et al. have shown the synthesis of a novel nanoscale core/shell heterostructure with CuO nanowires as the core and NiO nanoparticles as the shell directly grown on copper foam by a two-step solution method. The heterostructures indicate that the secondary growth of NiO nanoparticles around CuO nanowires leads to the creation of CuO/NiO hetero-hierarchical core/shell nanowire arrays. The wettability of the CuO/NiO core/shell nanowire arrays after being modified by trichloro silane is also studied. The CuO/NiO core/shell nanowire arrays on copper foam present promising super hydrophobic properties with high water contact angles up to $164 \pm 2^{\circ}$. Interestingly, Chen H. et al. have utilized the CuO-NiO nanocomposites with high surface areas, as anode materials for Lithium-Ion Batteries (LIBs), the nanocomposite was prepared by a facile wetchemical method. The CuO-NiO nanocomposites composed of CuO microspheres and NiO nanosheets possess a high surface area of 158.0 m²g⁻¹. When the CuO-NiO nanocomposites are used as anode materials, they show an initial discharge and charge capacity of 886.7 and 638.8 mAhg⁻¹. A high capacity of 562.5 mAhg⁻¹ at 0.1 C was observed after 50 cycles, which is higher than CuO (345.9 mAhg⁻¹ at 0.1 C after 50 cycles) and NiO (334.4 mAhg⁻¹ at 0.1 C after 50 cycles), demonstrating that the CuO-NiO nanocomposites with high surface area show a better cycling performance than pure CuO and NiO. Therefore, the CuO-NiO nanocomposites materials have a great potential application in LIBs [21]. The optical and luminescent properties of NiO-CuO composites were studied by J. Gajendiran et al. [22], have synthesized the nanocomposite via precipitation method, the optical absorption spectra exhibit that the band gap energies of the NiO-CuO nanocomposite decrease with the increase in the calcination temperature, which can be attributed to the improvement in the crystallinity of the NiO-CuO nanocomposite. The PL intensity of the NiO-CuO nanocomposite peaks which decreased with the increase in the calcinations temperature was observed from the PL spectra; it was due to the lesser oxygen vacancy defects that

occurred. Similarly, Mwhmadi M. et al. [23] have synthesized the NiO and CuO nanostructures via simple and fast microwave approach. Olive oil was chosen as surfactant for stabilizing nanostructures. Different parameters such as microwave time and power and olive oil concentration were investigated on product size and morphology. Whereas, Gao P. et al. [24] have utilized the copper oxide nanostructure to detect the hydrogen peroxide. They have synthesized the grass-like CuO nanostructure via a simple hydrothermal reaction at 100 °C for 6 h without using any surfactant. The as-prepared sample was further calcined at 500 °C for 1 h in nitrogen atmosphere for comparison. It was found that the sample prepared after calcinations in a nitrogen atmosphere exhibited better electrochemical catalytic performance for the determination of H.

Park, S. H. et al. [25] have explored the hierarchically mesoporous CuO/carbon nanofiber coaxial shell-core nanowires (CuO/CNF) as anodes for lithium ion batteries which were prepared by coating the $Cu_2(NO_3)(OH)_3$ on the surface of conductive and elastic CNF via electrophoretic deposition (EPD), followed by thermal treatment in air. The CuO shell stacked with nanoparticles grows radially toward the CNF core, which forms hierarchically mesoporous three-dimensional (3D) coaxial shell-core structure with abundant inner spaces in nanoparticle-stacked CuO shell. The CuO shells with abundant inner spaces on the surface of CNF and high conductivity of 1D CNF increase mainly electrochemical rate capability. The CuO/CNF nanowires deliver an initial capacity of 1150 mAhg⁻¹ at 100 mAg⁻¹ and maintain a high reversible capacity of 772 mAhg⁻¹ without showing obvious decay after 50 cycles. Jeyarani W. J. et al. [26] have reported the synthesis of CuO nanoparticles with varying concentrations of the organic modifier glucose as capping agent by the facile and versatile sol-gel route. SEM results revealed that with increase in the molar concentration of the capping agent CuO nano-powder tends to become more homogeneous and thus well prevented the agglomeration of the nanoparticles. Also the particle size was observed to decline with increasing capping agent concentration. Band gap calculations made employing the Tauc's plot method indicate a consistent increase in the band gap with increase in concentration of capping agent corresponding to the reduction in particle size. The photoconductivity of the CuO nanoparticles showed a decrease in the dark and photo current values with the increase in molar concentration of the capping agent which could be attributed to the increase in the optical band gap. Thus the particle size and hence the band gap of nanoparticles could be tuned effectively by altering the concentration of the capping agent.

Tadatsugu M. *et al.* [27] have described the significant improvements of the photovoltaic properties that were achieved in Al-doped ZnO (AZO)/n-type oxide semiconductor/p-type Cu₂O heterojunction solar cells fabricated using p-type Cu₂O sheets prepared by thermally oxidizing Cu sheets. In most of the Cu₂O-based heterojunction solar cells using multicomponent oxides composed of combinations of various binary compounds, the obtained photovoltaic properties changed gradually as the chemical composition was varied. However, higher conversion efficiencies (η) as well as a high open circuit voltage (V_{oc}) were obtained by using a relatively small amount of MgO or Al₂O₃, a high V_{oc} of 0.98 V and η of 4.82% were obtained. At the same time, Mahmoud Abdelfatah *et al.* [**28**] have first time demonstrated the fabrication of a p-Cu₂O/ZnO/AZO flexible heterojunction solar cell by electro-deposition of Cu₂O thin film on a plastic substrate and sputtering of ZnO:Al layer. The Atomic Layer Deposition (ALD) has been employed to insert 5 nm ZnO as buffer layer. The solar cell device exhibits a power conversion efficiency of 0.897 ± 0.005% with an open circuit voltage of $V_{oc} = 300 \text{ mV}$, a short circuit current density of $J_{sc} = 6.819 \pm 0.048 \text{ mA cm}^{-2}$ and a fill factor of FF = 0.439.

Whereas, Biswas, P. et al. [29] have reported the lowtemperature solution-processed p-CuO nanorods (NRs)/n-ZnO NRs heterojunction light emitting diode (LED), ZnO NRs were synthesized at 90 °C by using hydrothermal method while CuO NRs were synthesized at 100 °C by using microwave reaction system. The current-voltage characteristic of the heterojunction showed a significantly high rectification ratio of 10^5 at 4 V with a stable current flow. A broad orange-red emission was obtained from the forward biased LED with a major peak at 610 nm which was attributed to the electron transition from interstitial zinc to interstitial oxygen point defects in ZnO. A minor shoulder peak was also observed at 710 nm, corresponding to red emission which was ascribed to the transition from conduction band of ZnO to oxygen vacancies in ZnO lattice. This study demonstrates a significant progress toward oxide materials based, defect-induced light emitting device with low-cost, low-temperature methods.

Zheng, X. *et al.* [**30**] have used the facile method to oxidize p-type Zinc Selenide (ZnSe) nanowires into n-type Zinc Oxide (ZnO) through a 700 °C annealing process in air. Single crystal ZnSe nanowires, with a hole concentration of 0.805×10^{18} cm⁻³ and a negative photoconductivity, were oxidized into polycrystalline ZnO nanowires with an electron concentration of 4.88×10^{18} cm⁻³ and a positive photoconductivity. Both the as-synthesized ZnSe nanowires and the post-oxidized ZnO nanowires presented excellent optoelectronic properties. This method can be used to construct radial p–n junctions or other nano-devices based on a single NW through a region-selective oxidation process.

to realize the three important characters including color contrast, switch speed and cycling durability, it requires the electrochromic layer to possess different microstructures or crystalline properties. Thus there is still difficulty in designing a suitable structure for NiO film to have excellent electrochromic performance. Here, Xin Zhang et al. have prepared a nano-crystalline modified nano-comb novel NiO structure by a simple chemical process. This novel microstructure shows highly multiple channels, high surface areas and good crystallinity. All of these characters produce a good electrochromic performance including fast switch speed (around 2s), high color contrast (69.4 %) and good cycling durability (more than 1000 cycles).

Vequizo, J. J. et al. [32] have shown the FeO based semiconductor for solar cell fabrication. They have successfully fabricated the Cu₂O/Fe–O heterojunction solar cells by electro-deposition method. The deposited and annealed FeO films showed *n*-type conductivity with approximated band gap of 2.1-2.3 eV. All the fabricated Cu₂O/Fe–O heterostructures exhibited photovoltaic characteristics (open circuit voltage, $V_{OC} = 38-108$ mV and short circuit current density, $J_{SC} = 0.74 - 1.58 \text{ mA/cm}^2$), although no appreciable differences were found on their solar cell parameters. Wee, S. H. et al. [33] have reported epitaxial growth of Cu₂O films on low cost, flexible, textured metallic substrates. Cu₂O films were deposited on the metallic templates via pulsed laser deposition under various processing conditions to study the influence of processing parameters on the structural and electronic properties of the films. The (00l) single-oriented, highly textured, Cu₂O films deposited under optimum temperature conditions exhibit excellent electronic properties with carrier mobility in the range of 40–60 $\text{cm}^2 \hat{V}^{-1} \text{s}^{-1}$ and carrier concentration over 10^{16} cm⁻³. Whereas the power conversion efficiency was only 1.65 % is demonstrated. Moreover, Zhu, Z. et al. [34] have reported the preparation of CuO nano-flower using hydrothermal method, which exhibited good performances in gas-sensing. Four different morphologies have formed a flower-like shape with a diameter of 1-3 µm by varying the reaction time. The CuO nanostructures were composed of abundant aggregative nanobelts. The prepared CuO properties in gas-sensing were also measured.



Fig. 1. Different applications of metal oxides thin films, (1) solar cell; (2) photocatalyst; (3) PEC cell.

Zhang, X. *et al.* [**31**] have utilized NiO for electrochromic devices. Nickel oxide thin films have been widely applied as an optical anodic layer due to its ability to adjust the optical properties by ion exchange. Generally,

Synthesis of nano-materials using hydrothermal method has come up as a cost effective method for producing the CuO nanostructures on flexible substrates [**35**]. By applying the hydrothermal approach one can have the precise control over the synthesis of the nano-structured CuO at low temperature and variation in the temperature (40 to 90 °C) can produce the different nanostructures of CuO material. Recently, Joshi et al. have prepared the thin films of complex oxides (NiO/CuO/ZnO) using layer by layer growth and studied the surface morphology as well as absorption properties of each individual layer. They have demonstrated the formation of nanostructures of NiO, CuO, ZnO layers individually using hydrothermal method at elevated temperatures. The composite structure can be used for photovoltaic application [**36**].

As Li et al. [13] has already claimed the poor adhesion on the direct growth of CuO nanostructures on Si or ITO/glass substrates using wet chemical method. Therefore, one needs to modify the substrate, in order to have a proper growth and good adhesion of CuO nanostructures for enhancing the life time of these nanostructures. The present work in this paper shows the growth of CuO nanostructures on porous structured NiO film coated on ITO/glass substrate. Reasons of using NiO layer could be first to provide better surface interface interaction with CuO laver. this will not only improve the adhesion property of CuO layer on modified substrate (NiO/ITO/glass) but also the electronic device aspect since NiO layer can also be considered as hole transporting layer too. The schematic side view layer structure has shown in Fig. 2. For any device application further, any n-type layer can be deposited to form the pn-junction. At the same time, it will also be a cost effective solution towards affordable electronics too.



Fig. 2. Schematic diagram of composite layers used for Photovoltaic properties, prepared by Chemical bath deposition and hydrothermal methods on top of ITO coated glass plate.

Experimental

All chemicals used for this study were analytical reagent grade and used without further purification. The preparation methods and conditions for depositing the NiO and CuO layers are almost same as mentioned in our previous work. [**36**] After depositing the Nickel oxide (NiO) layers using Chemical Bath Deposition (CBD) technique on pre-cleaned Indium Tin oxide (ITO) coated glass plates. The obtained thickness of film varies between 75 ± 10 nm.

Next, the rectangular shaped randomly oriented nanostructures of CuO layer was synthesized on top of porous NiO layer/ITO/glass using hydrothermal method. The average thickness measured using AFM is 400 ± 50 nm. The method has been given in detail in our previous work [**36**]; except of the temperature, all other parameters were same and for present case after transferring the copper solution in a beaker to the laboratory oven, the temperature was set at 70 °C for 4 hours. After the growth of black CuO structure on NiO/ITO/glass substrate, the vessel was further cooled down to room temperature (RT) and washed several times with de-ionized water.

The microstructures of the NiO and CuO thin layers were investigated by state-of-the-art techniques like X-ray diffractometer (XRD, Brucker D₂ Phaser system) with Cu K α radiation operating at 30 kV and 10 mA having wavelength (λ) of 0.154 nm under out-of-plane geometry. For the morphological analysis, Scanning Electron Microscopy (SEM, Phenom Desktop SEM, Phenom World, Netherland, 5 KV acceleration voltage) was carried out for nanostructure analysis of such inorganic layers. The optical transmission/absorption spectra of the samples were obtained in the ultraviolet (UV)/Visible/near infrared (nir) region up to 1100 nm using Shimazdu UV-VIS spectrophotometer (Model: UV - 3600).

Results and discussion

Fig. 3 shows the SEM micrographs of NiO thin film deposited at RT on ITO coated glass plate. AFM measurement indicates the thicknesses of such thin layers are between 75 ± 10 nm as shown in Fig. 4.



Fig. 3. SEM images of NiO porous nanostructure deposited using chemical bath deposition on top of ITO coated glass plate.

It is observed that the NiO film is highly porous in nature with some overgrown clusters observed having nano-sized Ni crystallites. One can observe the uniformly distributed porous structure over entire ITO/glass substrate. This over growth could be due to the nucleation and coalescence process. Similar porous structures growths of NiO have been reported also in earlier literature. [**37-40**].



Fig. 4. AFM Height profile for NiO thin film prepared on ITO/glass substrate.

Similarly, **Fig. 5** shows the top view of SEM micrographs of CuO nanostructured layer of (400±5nm on top of NiO/ITO substrate at different magnification values (**Fig. 5a - d**). From **Fig. 5**, one can conclude that the

presence of thick rectangular shape structure, are randomly oriented and distributed along the whole NiO film and even penetrated into the NiO surface, indicating the good contact or better NiO-CuO interface. The structures show the average dimensions (6±2.0) μ m x (2.0±0.5) μ m. Similar morphologies have been reported, such as nanosheets, nanobelts, wires etc. [41-45].



Fig. 5. SEM images of CuO rectangular randomly oriented structure deposited using hydrothermal method on top of NiO/ITO coated glass at 70 $^\circ$ C.

Next, X-ray diffraction studies of NiO thin film on top of ITO layers were performed, particularly, out-of-plan geometry using θ -2 θ scan taken in to account for all the measurements for NiO and CuO layers. Under out of plane scan, X-ray detector moves along surface normal direction with respect of the sample surface, therefore cutting all the crystal planes oriented parallel to the surface. Fig. 6 indicates the presence of NiO (111), NiO (200), NiO (220) as well as NiO (311) peaks, where NiO (111) and NiO (200) are the pronounced peaks. At the same time some buried peaks of ITO have been observed too, which indicates that the NiO film is thin as well as porous too. After exploiting Debye-Sherrer formula (Size of crystallites = $0.9\lambda/(B*\cos\theta)$, Where B is peak width in radian) as well as Inter-planar distance [D spacing = $\lambda/(2^* \sin\theta)$], it has observed that all the three peaks (111), (200) and (220) have similar size of crystallites along the surface normal direction. Whereas in terms of combined Intensity (area), NiO (111) peak has the highest area compared to (200) and (220) NiO peaks. It can be interpreted as NiO (111) orientation is dominating in the NiO film along the depth of the film (Table 1). Similar measurements were also observed by Joshi et al. [36].

 Table 1. Different calculated values corresponding to Ni (111) and Ni (220) pronounced peaks observed in XRD scan of NiO/ITO sample (Fig. 6).

| Peaks | FWHM (degree) | Position (degree) | Area (Arb.) | D spacing (nm) | Size of Crystallites (nm) |
|----------|------------------|----------------------|----------------|-------------------|------------------------------|
| Ni (111) | 0.653 | 37.18 | 48 | 0.241 | 14 |
| Ni (200) | 0.929 | 41.31 | 32 | 0.218 | 10 |
| Ni (220) | 0.829 | 45.06 | 30 | 0.201 | 11 |



Fig. 6. XRD scan of NiO film deposited using chemical bath deposition method on ITO glass, ITO peaks also noticed.

Fig. 7 shows the XRD curve of nanostructured CuO thin film deposited on NiO/ITO substrate using hydrothermal method. One can observe multiple peaks which correspond to random orientation of CuO crystallites, of which (002) phase is dominating in terms of intensity and indicates the maximum number of such crystallites present in CuO thin films along the surface normal direction. Whereas CuO (200)/(111) is the second highest in intensity.



Fig. 7. XRD scan of CuO thin film on top of NiO/ITO substrate deposited using hydrothermal method on ITO glass, some of ITO and NiO peaks are also noticed.

 Table 2. Calculated values corresponding to some of the CuO

 pronounced peaks observed in XRD scan of CuO/NiO/ITO sample

 (Fig. 7).

| Peaks | FWHM (degree) | Position (degree) | Area (Arb.) | D spacing (nm) | Size of Crystallites (nm) |
|-----------------|------------------|----------------------|----------------|-------------------|------------------------------|
| CuO (-110) | 0.277 | 30.18 | 496 | 0.30 | 32 |
| CuO (002) | 0.415 | 35.03 | 1464 | 0.26 | 22 |
| CuO (111)/(200) | 0.510 | 38.10 | 1286 | 0.24 | 18 |
| CuO (-202) | 0.527 | 48.11 | 425 | 0.19 | 18 |

All the peak values here calculated using Debye-Sherrer and interplanar distances formula and summarized in **Table 2**, one can observe that due to least FWHM value of CuO (-110) peak (0.277°), the biggest size of crystallites observed is of CuO (-110) of 32 nm. Similarly, CuO (002) has the size of crystallites of 22 nm along surface normal

direction. Whereas the size of crystallites for CuO (200) and CuO (-202) are same, 18 nm each.

UV spectroscopy has been explored to study the optical properties of thin NiO/CuO film. Figure 8 shows the transmittance spectra of porous NiO thin film on ITO/glass substrate. **Fig. 8** shows that the transmittance value is increasing with the wavelength, the curve is smooth and continuous and there is no sharp peak in between the whole range (300-1100 nm). Considering the absorption part of the curve, it indicates that under UV region the sample has the absorption peak at 280 nm and absorbs the UV light, whereas under the visible region (400-750 nm) the sample becomes more transparent towards higher wavelengths.



Fig. 8. UV transmission and absorbance curve of NiO film deposited on ITO substrate using Chemical Bath Deposition process.

The CuO layer UV curve is shown in **Fig. 9**. From **Fig. 9** it is clearly visible that except of low wavelengths (250-375 nm) the absorption is increasing toward higher wavelengths, which is opposite to NiO layer property. In between the visible range (400-750 nm), the maximum absorption is obtained around 700 nm.



Fig. 9. UV transmittance and absorbance curve of CuO film deposited on NiO/ITO substrate using hydrothermal method.

This shows that the film is highly active towards the higher wavelengths. Even the film is also active within near infrared region too. The energy band gap (E_g) was estimated by assuming a direct transition between valence and conduction bands from the expression $ahy = k(hv - E_g)^{1/2}$, where k is constant, E_g is determined by extrapolating the straight line portion of the spectrum to ahv = 0. Using this, the NiO, CuO band gap have found 2.82 eV and 1.30 eV, respectively.



Fig. 10. Energy level diagram of ITO/NiO/CuO multilayered system.

Based on calculated band gap values of NiO and CuO layers individually, the energy level diagram of multilayered structure (CuO/NiO/ITO) has been shown in **Fig. 10**. It shows the alignment of bands of CuO layer with respect to NiO that electrons flow from NiO to CuO and holes movement from CuO to NiO is well within alignment of their individual bands.

Conclusion

Nanostructured CuO and NiO thin films have great potential for applications in the fields of optoelectronics and sensor devices. This research aims to study NiO, CuO and ZnO, which are low cost metal oxides abundant in the earth, for the purpose of designing novel function nanostructures for efficient energy harvesting. In the present study, we have explored the Chemical Bath Deposition (CBD) and Hydrothermal Deposition techniques for growing different nanostructures of NiO and CuO thin films. As the material size decreased to nanoscale, the electronic structure of any material differs from its bulk materials. These changes make them display some promising electronic properties, such as enhanced light absorption and prompt light response. At the same time, the partially or fully filled d-shells of metal oxides give them a variety of unique properties for all kinds of electronic device applications, like light emitting diode (LED), solar cells, thin film transistors (TFT), photocatalysts, photo-electrochemical cells, sensors. Some of the vital uses of such metal oxides thin films are - application for photo-catalysts, the narrow band gap of CuO makes it promising for photocatalytic applications. Various CuO nanostrucutres, i.e. nano-flowers, nanoribbons, were synthesized by the wet-chemical method to examine the effect of the morphology and exposed surfaces on

photocatalytic performance. Application in photocathodes to split water, CuO has a small band gap of 1.2 eV, which is suitable for all the visible light absorption. However, the drawbacks of CuO are low photocurrent density and instability in aqueous solutions. Cu₂O has a band gap of 2.0 eV, allowing for most of the visible light absorption. The conduction band edge of Cu₂O is 0.50 V higher than H₂ generation potential from water, making it a suitable photocathode candidate. The theoretical solar to hydrogen conversion efficiency was calculated to be 18 %, corresponding to a photocurrent density of 14.7 mA/cm²under AM 1.5. However, Cu₂O is unstable in aqueous solution and the photo-corrosion leads to photocurrent decay quickly. As a result, protection layers were always used as a strategy to improve the photocurrent density and stability. Whereas, application in solar cells, a semiconductor that can absorb solar radiation in visible and near infrared region is reported to be a good solar absorber [46]. Among the various semiconducting metal oxides, CuO is attractive as a selective soar absorber because of its high light absorbance efficiency and low thermal emittance. The theoretical power conversion efficiency (PCE) of CuO is around 30 % considering only radiative recombination [47]. In the present study, the structural, morphological and optical properties of both layers (NiO, CuO) have been studied using the techniques like SEM, XRD, AFM and UV-Vis spectrometer. CBD prepared NiO thin film reveals the porous structure in nature, whereas CuO layer has shown randomly oriented rectangular shaped like structure. By varying the one single parameter at a time like temperature, time of deposition, and annealing time one can judiciously manipulate these nanostructures as well as the mean ledge thickness of the NiO, CuO layers. The XRD and SEM techniques used to study the crystalline properties and growth direction of as-synthesized NiO, CuO nanostructures, confirm the presence of polycrystalline phase along the surface normal direction; it is also their most preferred direction of growth for CuO thin film structures. At the same time, the CuO nanostructures low temperature growth was visualized on top of 75 nm thin film of NiO. This indicates that NiO layer can be considered as an adhesion layer and provide the inductive growth to CuO nanostructures. The energy level diagram of both layers indicates that NiO/CuO could be one of the choices to consider for any electronic devices formation and the present layers' combination of NiO/CuO is completely open to put any n-type layer for application as a PN junction for photovoltaics, sensors applications. In present case, the obtained big rectangular structures of CuO films can make a difference in terms of device performance (charge transport), if used properly with suitable n-type materials. Further work of these structures towards solar cells and humidity sensors are in progress. To improve the efficiency, a better design and combination of materials at nanoscale level should be required. The present case is one of it. It can have several advantages in solar energy application, including reduced reflection, enhanced light absorption, improved band gap tunneling and longer exaction lifetime. Similarly, NWs with a high aspect ratio sufficiently allows sufficient light absorption in moderate thicknesses while providing short photo-excited carriers collection lengths. The short carrier collection lengths, as a result, improve the collection efficiency of photo-generated

carriers in the oxides with low minority diffusion lengths. Therefore, the surface morphology of presently grown CuO structure is promising for the applications of solar energy harvesting.

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