High specific heterocontacts of p-CuO/n-ZnO thin film composites for enhanced sunlight absorption

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Abstract. This study is focused on investigating the heterocontacts development between p-CuO and n-ZnO semiconductor composite for enhancing its sunlight absorption. CuO and ZnO are chosen as precursors due to their many potentials. High absorption of sunlight is one of the most important criteria in photovoltaic (PV) device. However poor crystal structure and low contact surface between the p and n semiconductors limits the light intake and is due to several factors. To carry out intensive study on the mechanism of the heterocontact growth, CuO:ZnO thin film is synthesized by mechanical alloying process using high energy ball mill (HEBM) followed by sol gel technique. Three parameters were studied; sol-gel’s surfactant to solvent ratio, annealing temperature and annealing duration. The homogeneity and compounds’ distribution of the composite is analysed by EDS analysis and structural characterization is done with XRD analysis. The UV-VIS analysis is done to determine the light absorbance and the bandgap of the composite. The initial mechanical centrifugation HEBM has aided the process for homogenizing the composite and boost the heterointerface between the semiconductors by mechanochemical effects such as phase transformations and solid-state reactions. EDS analysis reported that annealed specimen giving the lowest percentage of ratio gap than others temperature and the heterocontact surface between molecules of material also increased. Uv-Vis analysis also agrees with EDS, showing the specimen having highest absorbance spectra. However, bandgap narrowing occurred in the specimen, as resulted by the coexistence of transitional metal Cu in the composite system. XRD analysis shows a near single oriented crystal growth which promotes clean growth of crystal structure and hypothetically reduce the presence of unwanted voids and large boundaries.

1. Introduction

The photovoltaic cell (PVD) which is an electric device that converts the energy of light directly into electricity by photovoltaic effect which is physical and chemical situation. In PV device terminology, semiconductor are combination of insulator and metal. Silicon semiconductor available in homojunction and this is achieved by same material with opposite polar. When two different materials are combined, heterojuctions is formed. Because of the difference in nature, they will have different energy bandgaps, the energy of band will have a discontinuity at the junction interface [2].

Semiconductors can be engineered to change from narrow bandgap to a wide bandgap material by considering the synthesis techniques and parameters. There are a few factors need to be considered upon in fabricating PV materials. Firstly, indirect band gap materials have photons absorption ability which depends to the wavelength. Short wavelengths are very energetic and photons are being absorbed close to the top surface while long wavelengths are less energetic [1]. The wide-band-gap semiconductors possess many advantages for optoelectronics and electronics applications. The nature of wide-band-gap energy is suitable for to absorb or emit ultraviolet (UV) light in applications of
optoelectronic devices. It normally possesses a chemically and mechanically stable structure which provides a higher electric breakdown field and may sustain under harsh environments [3]. The utilization of UV light is crucial for applications in sustainable energy and solid-state lighting. In actual, wider bandgap is particularly important for allowing devices that use them to operate at much higher temperatures, on the order of 300 °C [3]. On the other hand, semiconductor photocatalysis begins when an electron from the valence band is activated to the conduction band by optical excitation, creating an electron in the conduction band and a hole in the valence band. Bandgap is one of the critical properties of a semiconductor. However, the larger the band gap, the greater the resistivity for the valence electrons to jump to the conduction band [4]. This explains the poor electrical conductivity of non-metals (insulators). Lower bandgap materials have been studied to complement it; and the most encountered pairing candidate to n-type ZnO is 1.4 eV p-type semiconducting CuO. Thus, the efficiency limit for CuO is about 10%, the maximum efficiency realized using oxidized metal foils [5] is significantly below the limit. This comes from a variety of factors including limited heterocontacts between the p and n junction which led to poor collection of minority carriers, unoptimized band structure in the device structure, and high surface recombination. During growth of crystalline process, there are defect such as some voids of space between molecules of materials used and grain boundaries so the absorption of light is low because the defect will block the light penetration into it. Then, it will affect the light absorption. The good contact surface between the main precursors is allowed maximum values of absorption light without waste of bouncing light back.

2. Experimental methods

FTO coated glass was used as a substrate and was cut into dimension 2cm x 1cm. Microstructural refinement and solid-state reactions of the starting materials which is ZnO (99% purity, molecular weight 81.40, Sigma Aldrich) and CuO (99% purity, molecular weight 79.54, Sigma Aldrich) were mechanically centrifuged by high energy ball milling (HEBM). This is to promote high surface contact between individual CuO and ZnO particles. The starting materials were mixed together (1:1 by weight, maintaining nearly the same molar ratio, total weight 8 g) underwent HEBM process (Planetary Milling, 300 rpm, steel balls, 10 mm diameter, ball-to-powder weight ratio (BPR) was 10:1). The milling was carried out for 2 hours. A solution was prepared from the ball-milled powder was made using a mixture of Triton X-100 and acetic acid. The total mixture is 10ml with ratio surfactant 1:6 and added 1g of mixing of CuO and ZnO powder. The sol-gel solution has been aged in room temperature for 24 hours after it was prepared before coating on substrate. Then the sol was coated on fluorine tin oxide (FTO) coated glass substrates by doctor’s blade technique to give the form of a thin film and was dried on the hot plate at temperature 80°C for 3 minutes. Crystal regrowth of the thin film was realized by annealing process, and were varied by three different temperatures; 300°C, 400°C and 500°C for 40 minutes. The samples were put on a ceramic boat before inserted into furnace. After annealing, the specimens were left in the chamber to self-cool.

EDS analysis was carried out to observe the elements’ content. From this the ratio gap of the compositions is tabulated to determine the level of distribution uniformity of each specimens. Grain size analysis of the ZnO and CuO layer is carried out on the SEM. After the microstructure of the grain was detected, the Energy Dispersive Spectroscopy (EDS) analysis was carried out to observe the ratio gap of CuO and ZnO element in the sample. The ratio gap results of the Cu and Zn was observed the element composition yielded after the annealing process. The crystalline structure of the CuO and ZnO element in the sample were carried out by X-ray diffraction technique (Bruker D8 Advance machine) with CuKα radiation operating at 30kV, 10mA and scan range at 10°-90°. The XRD will give out information about on the crystalline components present in the sample. The XRD pattern were recorded on high resolution XRD in order to confirm the crystalline size, shape and phase transitions within the scanning range (2θ) of 20-80°. The higher the crystallinity, the better the probability that the charge carries can reach the surface without being trapped by the crystal defect. Whenever the particle size is small, the charge carriers have to travel only a short distance to reach the surface, and they will
reach the surface before recombination [10] The Uv-Vis spectrophotometer (UV-Vis) PERKIN ELMER LAMBDA 35 UV-Vis Spectroscope) was used to study the optical properties of the composite. The scanning was performed within range of 300-800 nm.

3. Results and discussion

3.1. Element Composition Ratio Evaluation (EDS)

The Energy Dispersive Spectroscopy (EDS) analysis was carried out to observe the ratio gap of CuO and ZnO element in the sample. The best uniformity of distribution was determined by the lowest different in percentage or ratio gap; as this reflects that equal amount of the elements yields better interface between the two semiconductors. The result of percentage of ratio gap CuO/ZnO was tabulated in Figure 1.

![Figure 1. Percentage ratio gap CuO/ZnO.](image)

From the graph it can be observed that specimen annealed at 500°C exhibits the lowest gap ratio between Zn and Cu at 3.5%. The detailed EDX result is illustrated in Figure 2.

![Figure 2. Percentage of CuO and ZnO (represented by Zn and Cu element together with their respective oxygen content) in the 500°C composite film.](image)

Smaller gap also is desirable as it also reflects that the presence of voids between CuO/ZnO is low. Thus, the area of heterocontact surface between CuO and ZnO also increased. This reveals that the annealing temperature has significant impact on the morphology of the synthesized composite.
3.2. Absorbance spectra
EDX analysis is performed to measure the absorbance spectra of the composite films. Uncoated substrate was also measured as reference. The light absorbance is measure by referring to the following Equation 1:

\[
\text{Å} = -\log (T) \\
\text{Å}_x = \text{Å}_n - \text{Å}_b
\]  

where \( \text{Å}_x \) is the absorbance spectra of CuO: ZnO composite; \( \text{Å}_n \) is the absorbance of each sample from graph and \( \text{Å}_b \) is the absorbance of blank sample from graph. The absorbance spectra of the specimens are shown in Figure 3.

![Figure 3. Absorbance spectra of CuO/ZnO samples.](image)

The spectra of 500°C annealed specimens were observed having the highest absorbance. Thin film composite having uniform distribution of the main materials; which is determined from the low ratio gap gets higher the absorbance spectra. According to Nalbant [8], from the UV–vis spectra, pure ZnO thin films have the absorption band near the UV-end of the electromagnetic spectrum (370 nm) and CuO has a strong absorption band at about 570 nm, which makes the thin films colour yellowish. Referring to Figure 3.3, at 370 nm of wavelength is happened change of graph due to occurring absorption band near the UV-end of the electromagnetic spectrum. On the other hand, crystallinity and crystalline size of the synthesized composite also believed to be influencer to the level of absorption of spectra [9]. On of the main factor that affects the crystal size is the initial particle size of precursors. Rohini Singh et al. [10] reported that sol-gel synthesized TiO\(_2\) nanopowder samples exhibits a narrow band gap due to reduced agglomeration and uniform particle size. The initially applied HEBM method was intentionally to homogenize the mixture and particle size.

3.3. Band gap
The synthesized composite can further be testified by the determination of band gap. Band gap, \( E_g \) is the distance between the valence band of electrons, and is represented by the following Equation 2:

\[
E_g = E_v - E_c
\]
$E_v$ is the conduction band, while $E_c$ represents the minimum energy required to excite an electron up to a state in the conduction band where it can participate in conduction. The lower energy level is the valence band, and thus if a gap exists between this level and the higher energy conduction band, energy input is required for electrons to become free [5]. For this, the optical absorption coefficient, $\alpha$ was evaluated using the following Equation 3:

$$\alpha = \frac{\ln(T)-1}{t} \quad (3)$$

where $t$ is the film thickness and $T$ is the transmittance [11]. The equation is simplified by Tauc’s Equation 4:

$$\alpha h\nu = A(h\nu-E_g)^{n/2} \quad (4)$$

where $\alpha$ is the absorption coefficient, $A$ is a constant, $n$ is the exponential integer depending upon the quantum selection rules for the particular material and $h\nu$ is the photon energy obtained from Equation (5):

$$E = h\nu = \frac{hc}{\lambda} \quad (5)$$

where $h$ is Plank’s constant, $c$ is the speed of light, $\nu$ is the frequency of light and $\lambda$ is the wavelength.

The band gap energy can be determined by measuring the absorption of light the semiconductor as a function of the photon energy, $h\nu$. The light is strongly absorbed only when $h\nu$ is larger than $E_g$. The absorbed photon energy is consumed to create an electron-hole pair while as $h\nu$ is reduced below $E_g$, the specimen becomes transparent to the light.

![Figure 4. Tauc’s plot of the specimens.](image)

Figure 4 shows the band gap results by Tauc’s plotting for each sample at temperature 300C, 400C, 500C and baseline measured from blank specimen. The band gap energy was obtained from the $(\alpha h\nu)^2$ versus $h\nu$ curve. The highest value of the band gap energy is recorded by at temperature 400C at 3.9 eV at while the bandgap narrowing is observed on 500C specimen with 3.7 eV which is same with base line energy, 3.7eV. Kamarulzaman et al. [7] reported that the coexistence of transitional metal Cu in the composite system causes bandgap narrowing and this is said to mainly due to a downward shift of conduction band [8].

3.4. XRD analysis
To confirm the crystalline structure of the element in the sample, X-ray diffraction analysis (XRD) was carried out give out the information about on the crystalline components present in the sample. 500C specimen was selected and the information about the crystalline components and its orientation
is shown in Figure 5. Crystal regrowth of CuO and ZnO were confirmed, with CuO lattice presence is monoclinic and lattice of ZnO is hexagonal. The result is compared with blank substrate as reference. The element that exist at the sample is CuO with the orientation of the element are (0 0 4) and (2 0 6) and ZnO with the orientation of the element are (0 0 2), (1 0 1). All the element was selected from the highest peak of the graph and from the information that were obtain from XRD analysis. The highest peak reflects that the composite exhibits high crystallinity. According to Izaki et al. [12], single orientation of formed crystal promotes uniform growth of crystalline structure. Clean single oriented crystal can be achieved by controlling the synthesizing parameters. Single crystal orientation peak (1 1 1) is reported achieved by electrodeposition technique [12,14]. While promoting a uniform growth of crystals, the advantage of single orientation is formation of voids and space between molecules and grain boundaries can be minimized.

![Figure 5. XRD pattern of sample and reference FTO.](image)

4. Conclusion

The sol-gel synthesized CuO/ZnO composite thin film has been established. The initial mechanical centrifugation HEBM has aided the process for homogenizing the composite and boost the heterointerface between the semiconductors by mechanochemical effects such as phase transformations and solid-state reactions. EDS analysis reported that 500C annealed specimen giving the lowest percentage of ratio gap than others temperature and the heterocontact surface between molecules of material also increased. Uv-Vis analysis also agrees with EDS, showing the specimen having highest absorbance spectra. However, bandgap narrowing occurred in the specimen, as resulted by the coexistence of transitional metal Cu in the composite system. XRD analysis shows a near single oriented crystal growth which promotes clean growth of crystal structure and hypothetically reduce the presence of unwanted voids and large boundaries.

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