Critical effect of reaction pH on the microstructural, optical and electrical behavior of ZnO/CuO hetero-structured nanocomposite films

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Abstract

CuO nanocomposite films and ZnO/CuO nano-heterostructures were synthesized by a series of chemical reactions at different pH values based on the hydrothermal and SILAR (successive ionic layer adsorption and reaction) methods. The ultimate purpose of this work is to explore the impacts of solution pH value and ZnO-based heterostructure on the structural, optical and electrical features of CuO films using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX), transmittance spectrum, current-voltage (I-V) measurements and capacitance-conductance (C-G) measurements in 300–600 K temperature range and 20 Hz–1.5 MHz frequency range. XRD analysis revealed that the crystallite size and strain lattice parameters decrease with the increase in pH value without affecting the crystalline structure of the synthesized films. SEM images revealed the regular growth of ZnO structure without any deterioration in the CuO substrate layer where an increase in the thickness of the formed rods was observed with the increase in reaction pH value. Transmittance dropped greatly with the formation of heterojunction from about 40% (for CuO) to about 1% (for ZnO/CuO) in the visible range followed by a crystallite size-induced change in bandgap from 2.29 eV to 2.32 eV (for CuO) and from 2.03 eV to 2.11 eV (for ZnO/CuO). The increase in pH from 11.0 to 11.2 increased the room-temperature resistance of ZnO/CuO composites from 377 M Ω to 474 M Ω , the ideality factor from 4.41 to 4.68 and the barrier height from 0.74 eV to 0.83 eV. It can be deduced that reaction pH value is an important synthesis parameter that can tune the structural, morphological, optical and electrical properties of ZnO/CuO nanocomposite films for advanced industrial or technological implementations by controlling the nucleation and crystal growth rates during chemical synthesis processes.

1. Introduction

Synthesis of nanoscale materials for wide range applications has been explored by many researches from different areas of expertise. The main motive is to improve their existing features and develop them in accordance to technological or industrial needs. Especially metal oxide materials are very interesting materials in regards to designing new morphologies using different production methods in an aim of putting them effectively into practice. Hexagonal structured ZnO and monoclinic structured CuO are respectively an example of distinctive n-type and p-type functional MOS materials that have distinct promising implementations [1]. The combination of ZnO and CuO nanostructures is yet another distinctive category of hierarchical structures that has been explored in literature studies [2–4] where the formed heterojunction can be n-n, p-p or p-n based on the type of the materials used. ZnO/CuO junctions have small optical bandgaps that can stimulate an acceleration in electron flow leading to enhanced redox characteristics and charge carrier transports.

As important as nanoscale materials, choosing a practical, credible, safe and economical synthesis method is yet another challenge. Many solution-based chemical methods were used for the production of ZnO/CuO heterostructures, such as sol-gel [5], SILAR (successive ionic layer adsorption and reaction) [6], chemical bath deposition [7], co-precipitation [8] and hydrothermal methods [9]. In this study, SILAR and

hydrothermal methods were chosen due to their power in the production of high quality nanocomposite films and their ability of being carried out at room temperature and atmospheric pressure. Moreover, both methods have good reproducibility and are environmentally friendly as they do not involve any reactant in the vapor phase. Hydrothermal synthesis method is based on the reaction between anions and cations, and film deposition occurs through the chemical force between aqueous ions and surface ions [10]. SILAR method is based on the dipping of a substrate in separate anions and cations-containing solutions for a specific number of cycles [11, 12].

Generally, based on literature studies, it was recognized that the same chemical method was exploited in the synthesis of all components of a heterojunction structure [13–15]. In this study, ZnO/CuO heterostructures were produced using a combination of SILAR and hydrothermal methods and it was seen that such heterostructures possess the advanced features of each method. To the best of the authors' knowledge, the crucial effect of pH on the structural, optical and electrical properties of ZnO/CuO heterostructures produced by two different synthesis methods is not reported in literature which makes the present study eligible in filling this gap.

2. Experimental

2.1. Preparation of CuO and ZnO/CuO structures

ZnO/CuO heterostructures were fabricated on micro-glass substrates by a two-step process: CuO films were first synthesized by SILAR method and were then coated by ZnO films using hydrothermal method. Before the synthesis, all glass substrates were depurated following a proper intensive cleaning technique. All chemical reagents used in the experiment were purchased from Sigma-Aldrich Company with an analytical grade and used directly without further purification. Details of synthesis procedure and synthesis parameters are provided below.

Copper (II) chloride dihydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was used as a cationic precursor in the synthesis of CuO thin films. In order to adjust the pH of the solution at the desired values, ammonium hydroxide NH_4OH was added dropwise and the main pH of the solution was controlled using a pH meter. The solution was left to stir for 10 minutes in a magnetic stirrer with a stirring speed of 40×10 rpm. With the prepared solution, CuO thin films were synthesized using SILAR method. One SILAR deposition cycle lasts for about 2 minutes and consists of the following four steps [16]:

- Immersion of substrates into $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex solution for 20 seconds to allow the adsorption of Cu^{2+} ions on the surface of the substrates and build a thin liquid film.
- Immersion of substrates immediately in hot water (90°C) for 7 seconds to trigger the reaction between OH^- and adsorbed Cu^{2+} ions and obtain a net $\text{Cu}(\text{OH})_2$ layer by withdrawing any residues.
- Holding the substrates in air for 60 seconds for drying purpose.

- Immersion of substrates in distilled water at room temperature for 30 seconds to eliminate any loosely bound $\text{Cu}(\text{OH})_2$ species.

The as-synthesized films were rinsed with distilled water and were allowed to dry at room temperature for one day to enable the demolition of hydroxyl phase and formation of CuO layer. At first, the formed CuO thin film was light brown in color and the color became darker with the increase in the number of growth cycles up to 20 which is the total number of cycles used in the synthesis of CuO thin films in this study.

ZnO structures were grown on the CuO-coated substrates through hydrothermal method. An equimolar ratio 1:1 of zinc nitrate tetrahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (EMSURE) and hexamethylenetetramine $\text{C}_6\text{H}_{12}\text{N}_4$ (MERCK) chemical powders was added into 30 ml deionized water and allowed to shuffle in a magnetic stirrer at room temperature until homogeneity is reached. The obtained solution was then transferred into a hydrothermal autoclave where growth parameters were adjusted based on our previous experience to a temperature of 90°C and a period of 30 minutes [17]. Ultimately, the autoclave was allowed to cool at room temperature after which the samples were rinsed in distilled water and allowed to dry at room temperature.

2.2. Characterization methods

Excluding the electrical measurements, all other analyses were performed at room temperature. The characterization methods employed in the study of the properties of the synthesized films are as follows:

- Structural properties were investigated by X-ray powder diffractometer (Panalytical Empyrean X-ray diffractometer) using $\text{CuK}\alpha$ radiation in 20° to 70° 2θ range.
- Morphological properties were analyzed using field emission scanning electron microscopy (FESEM, HITACHI SU5000) operated at 10 kV.
- Elemental compositions were justified by energy-dispersive X-ray spectrometer (EDX) attached to SEM.
- Optical analysis was performed by absorbance and transmittance measurements (UV-1800 SHIMADZU).
- Energy mode analysis was done through Raman spectrometer with confocal microscope (JASCO NRS4500) using 532 nm laser excitation.
- Electrical analysis was done by DC current as well as AC capacitance and conductance measurements using Keithley 2400 (current-voltage source meter), Keysight E4990A (impedance analyzer) and LakeShore 325 (temperature controller). The measurements were done in 20 Hz–1.5 MHz frequency range and 300–600 K temperature range and controlled by a computer system.

3. Role Of Ph In The Chemical Synthesis Of ZnO/cuo Heterostructures

Hydroxide ions (OH^-) hydrolyzed from NH_4OH , which was used to control the pH of the prepared solutions, adhere strongly to the reactant that generates nanostructures during the chemical synthesis

process. Accordingly, the concentration of OH^- ions in the solution can influence the polymerization degree of the metal-oxygen bonds as well as the dissolution and conglomeration rates of the solution which together play a critical role in the formation of the films and their morphologies. In parallel with elaborations from previous literature studies [15, 18], low pH values result in low OH^- concentration and lead to high nucleation rates and low crystal growth rates which is not enough to create CuO nanoparticles. Contrarily, high pH values result in high OH^- concentration and lead to low nucleation rates and high crystal growth rates which causes a drop in the deposition rate on thin film surface due to rapid dehydration of $\text{Cu}(\text{OH})_2$ species. In both cases a proper formation of films cannot be achieved. In this regard, various literature studies reported different synthesis parameters with respect to pH values in the formation of CuO thin films by SILAR method: Yüksel et al. [19], Daoudi et al. [20] and Mageshwari et al. [21] have adjusted the pH value at about 11.0 while Bayansal et al. [22], Gençyılmaz et al. [23] and Dinc et al. [24] have reported a proper synthesis of CuO films at pH = 10.0, pH = 9.0 and pH = 5.4, respectively. In this work, pH = 10.8, 11.0, 11.2 and 11.4 were attempted in the synthesis of CuO thin films and a proper CuO layer formation was achieved at all attempted pH values. However, the desired hydrothermal growth of ZnO structure over the SILAR-deposited CuO layer was not properly achieved at pH < 11.0 and pH > 11.2 and so only properly formed ZnO/CuO composite structures (at pH = 11.0 and pH = 11.2) were taken into consideration.

4. Results And Discussion

4.1. Structural analysis

X-ray diffraction patterns of CuO and ZnO/CuO nanocomposite films synthesized at different pH values are depicted by Fig. 1. The patterns of CuO nanocomposite films at both pH values revealed the presence of two main diffraction peaks assigned to the monoclinic structure of CuO based on JCPDS card number 01-080-0076 [25]. In ZnO/CuO hetero-structured films, aside from the (111) peak of CuO, the other nine detected diffraction peaks can be indexed to the standard wurtzite hexagonal crystal structure of ZnO based on JCPDS card number 36-1451 [26]. The absence of any secondary phase reveals the high crystallinity nature of the synthesized films and the suitability of hydrothermal and SILAR techniques in the synthesis of high quality heterostructures. The sharp peaks in ZnO/CuO heterostructures suggest their enhanced crystallinity compared to the mere CuO nanocomposite films. The change in pH induced a slight shift in diffraction peaks to the right in CuO samples and to the left in ZnO/CuO samples without affecting crystalline structure nature of the films.

The mean crystallite size (D) of the synthesized structures was estimated based on the detected diffraction peaks using Scherrer equation [27];

$$D = \frac{0.94\lambda}{\beta \cos \theta}$$

where $\lambda = 0.15406$ nm is the incident radiation wavelength, β is the full-width at half-maximum (FWHM) and θ is Bragg diffraction angle. The microstrain (ϵ) in the lattices of the synthesized films was evaluated using Wilson expression [28];

$$\epsilon = \frac{\beta}{4 \tan \theta}$$

2

All estimated parameters are tabulated in Table 1 and are in good agreement with literature [29]. A slight variation in the estimated structural parameters was observed with the small change in solution pH value [30]. The crystallite size of CuO nanocomposite films decreased slightly followed by a slight increase in lattice strain with the increase in pH value. Similar behavior was observed in ZnO/CuO heterostructures where the increase in pH induced a decrease in crystallite size followed by an increase in lattice strain. The pH-induced decrease in crystallite size of ZnO/CuO structures can be due to a decrease in nucleation rates and increase in crystal growth rates which leads to drop in deposition rate on thin film surface due to rapid dehydration of $\text{Cu}(\text{OH})_2$ species.

Table 1
Structural parameters of CuO and ZnO/CuO samples for different pH values.

Sample		(hkl)	2 θ (°)	β (°)	D (nm)		$\times 10^{-3}$ (line ⁻² m ⁻⁴)	
					Scherrer	W-H	Scherrer	W-H
pH = 11.0	CuO	(-111)	35.34	0.729	11	–	11.27	–
		(111)	38.41	0.900				
	ZnO/CuO	(100)	31.71	0.226	32	30	3.14	9.75
		(002)	34.38	0.195				
		(101)	36.20	0.228				
		(111)	38.46	0.626				
		(102)	47.50	0.271				
		(110)	56.56	0.309				
		(103)	62.83	0.304				
		(200)	66.37	0.335				
		(112)	67.92	0.360				
		(201)	69.06	0.366				
pH = 11.2	CuO	(-111)	35.37	1.191	8	–	11.59	–
		(111)	38.48	0.927				
	ZnO/CuO	(100)	31.69	0.235	31	28	3.22	4.28
		(002)	34.37	0.203				
		(101)	36.19	0.239				
		(111)	38.43	0.633				
		(102)	47.49	0.278				
		(110)	56.55	0.326				
		(103)	62.82	0.323				
		(200)	66.33	0.345				
		(112)	67.90	0.364				
		(201)	69.04	0.359				

However, it is not logical to predict a 1 nm reduction of crystallite size in ZnO/CuO structures merely from the Scherrer equation due to the fact that it does not consider instrumental and strain broadening effects

on the FWHM values of diffraction peaks. Accordingly, to consider all the sources of peak broadening based on which FWHM is calculated, the crystallite sizes and microstrains of ZnO/CuO structures were re-estimated based on Williamson-Hall (W-H) model given by Eq. (3) [31];

$$\beta_T = \frac{0.94\lambda}{D\cos\theta} + 4\epsilon\tan\theta$$

3

where β_T is the total broadening. Based on the linear fitting plots presented by Fig. 2, crystallite sizes and microstrains were estimated respectively through the obtained ordinate intercept and slope values and are included into Table 1. With the increase in pH, a clear reduction in crystallite size of ZnO/CuO structures was further confirmed followed by a decrease in strain opposed to Scherrer model. Indeed, the slight increase in strain obtained by Scherrer model with the increase in pH seems to be misleading because the model does not consider instrumental or strain broadening effects. Therefore, it can be safely said that the increase in pH induced a decrease in crystallite size followed by a decrease in strain in both samples as was demonstrated by W-H model.

4.2. Morphological and elemental analyses

Top-view surface images of the synthesized samples at three different magnifications are given by Fig. 3. A careful examination of Fig. 3a tells that although sheet-like CuO structure appears, it is made up of thin wires elongated in different directions forming flower-like structures, and the increase in pH value resulted in particle accumulation giving rise to thicker agglomerative flower-like structures as shown by Fig. 3b. No deterioration in film quality was observed with the change in pH [32]. Aside from that, from Fig. 3c and 3d, it is clearly seen that the formation of ZnO structure on CuO layer did not lead to any deterioration in the substrate layer in both composites where the thicknesses (t) of the formed rods increased from about 269 nm for pH:11.0 to about 456 nm for pH:11.2 as predicted by the Gaussian distribution in Figs. 3 (e) and (f). This implies that particle agglomeration happened in the CuO substrate layer with the increase in pH has a direct effect on the thicknesses of the formed ZnO rods.

EDX analysis was performed to verify the existence of the desired elements in the synthesized samples and investigate the feasible effect of pH on the ratios of the available elements. EDX spectra of all the synthesized samples and their elemental compositions are provided by Fig. 4. At first, it is important to note that all expected elements (Cu and O in CuO samples as well as Cu, Zn and O in ZnO/CuO samples) were detected with significant amounts along with some negligible amount of other impurities (Si, Na, C and Ca). With the increase in pH, the amount of Cu decreased while the amount of O increased in the CuO samples as was reported earlier in Ref. [33]. In ZnO/CuO composites, the amount of O remained nearly the same while the amount of Zn increased and the amount of Cu decreased with the increase in pH. This signifies the fact that SILAR and hydrothermal methods when combined have a promising power in the production of highly pure samples as was also verified by the former XRD analysis.

4.3. Optical analysis

Figure 5 displays the optical transmittance spectra of CuO and ZnO/CuO composites for different pH values in 300–900 nm wavelength range. CuO nanocomposite films revealed high transmittance of about 40% compared to ZnO/CuO heterostructures which showed poor transmittance of about 1% in the visible range. This can be ascribed to the good absorption capacity of CuO films due to their shallow energy bandgaps [34, 35].

Using the transmittance plots, Tauc plots of $(\alpha h\nu)^2$ versus photon energy were extracted as presented by Fig. 6. The optical direct bandgaps of the synthesized films were estimated by extrapolating the linear region of Tauc plots to $\alpha h\nu = 0$ using Tauc relation [36];

$$(\alpha h\nu)^2 = A (h\nu - E_g)$$

4

where A is a proportionality constant, α is the absorption coefficient, h is Planck's constant, ν is the incident photon frequency and E_g is the optical bandgap energy. With a proper linear fit of the optical edge, the estimated bandgap values are as follows: 2.29 eV (at pH:11.0) and 2.32 eV (at pH:11.2) for CuO nanocomposites as well as 2.03 eV (at pH:11.0) and 2.11 eV (at pH:11.2) for ZnO/CuO heterojunctions. The shift in optical bandgap of both samples with the change in pH is a crystallite size-induced phenomenon [32]. That is, the decrease in crystallite size of CuO samples induced a 1% increase in optical bandgap and the decrease in crystallite size of ZnO/CuO samples induced a 4% increase in optical bandgap with the increase in pH. This is based on the fact that the decrease in crystallite size results in a decrease in overlapped energy states which causes a narrowing of the bands and an increase in bandgap [37]. Different ammonia concentration could limit the generation of Cu^{2+} ions in the solution which affects the overall concentration of ions and thus the rate of growth, crystallite size and consequently bandgap of the synthesized samples.

4.4. Energy mode analysis

Raman spectra of CuO composites and ZnO/CuO heterostructures are given by Fig. 7 in an aim to analyze the energy modes and crystallographic orientation of the synthesized samples. Referring to Fig. 7a, three main Raman peaks were detected at a wavenumber of 283, 336 and 618 cm^{-1} (for CuO at pH:11.0) and 279, 334 and 616 cm^{-1} (for CuO at pH:11.2) with a pH-induced decrease in intensity followed by little shift to lower wavenumbers. The detected bands can be assigned respectively to the standard A_g , B_g^1 and B_g^2 modes of CuO nanostructures with zone-center mode of $A_g + 2B_g + 4A_u + 5B_u$ and are in good agreement with previously published literature results [38–42]. The presence of these three active Raman modes emphasizes the proper formation of a single pure CuO phase under the discussed experimental terms as was also seen from the XRD patterns in Fig. 1. Referring to Fig. 7b, four main Raman peaks were detected at a wavenumber of about 331, 379, 438 and 578 cm^{-1} . The most prominent peak (at 438 cm^{-1}) is consistent with the $E_{2(\text{High})}$ mode of a classic wurtzite ZnO phase. The wide peak at 331 cm^{-1} corresponds to the multi-phonon scattering processes represented by the $E_{2(\text{High})} - E_{2(\text{Low})}$ mode

while the small peak at 379 cm^{-1} corresponds to phonons with A_1 symmetry represented by the transverse optical frequency $A_{1(\text{Transverse})}$ mode. The broad and small peak at 578 cm^{-1} is correlated with the $E_{1(\text{Longitudinal})}$ polar mode of optical phonons that may have emerged due to ZnO lattice defects like oxygen vacancies and zinc interstitial sites.

4.5. Electrical analysis

The current-voltage measurements of ZnO/CuO heterostructures were carried out in the voltage range of -10 V to +10 V under dark conditions at room temperature as shown by Fig. 8a. DC resistivity was estimated using Ohm's law $R = V/I$, where R is the resistance (in ohms), V is the applied voltage (in volts) and I is the measured current (in amperes). The obtained resistances are $377\text{ M}\Omega$ and $474\text{ M}\Omega$ for ZnO/CuO heterostructures synthesized at pH:11.0 and pH:11.2, respectively. The pH-induced increase in resistance is a direct result of the increase in bandgap of ZnO/CuO structures with the increase in pH (Fig. 6b). The logarithmic plots of current versus voltage (Fig. 8b) demonstrate a clear rectification behavior which is a good evidence of the appropriate establishment of the junction in n-ZnO/p-CuO hetero-structured films. Hence, the synthesized hetero-structured films can behave as diodes due to the rectification behavior and the proper formation of potential barrier at the interface between ZnO and CuO. By thermionic emission model [43], the ideality factor (n) and barrier height (Φ_B) were estimated respectively as 4.41 and 0.74 eV (at pH:11.0) as well as 4.68 and 0.83 eV (at pH:11.2). Both diodes exhibited high ideality factor which can be attributed to several factors, like discrepancy between work functions of the layers, image force effect, formation of native oxide layer, rapid recombination of charge carriers at the depletion zone, non-uniform distribution of interface states, inhomogeneous barrier height distribution, tunneling current, high series resistance, impurity of the substrate crystal bulk or the amorphous nature of interlayer [44–46]. Moreover, with the increase in pH, the barrier height increased which can be justified by the widening of the bandgap illustrated in Fig. 6b. Compared to the barrier height of ZnO/CuO structures synthesized at pH:11.0, that of ZnO/CuO structures synthesized at pH:11.2 is higher which is a good indicator of the ability of the latter diode to obstruct or reduce tunneling currents more efficiently than the former diode.

In addition to DC electrical analysis, AC analysis was carried out by capacitance (C) and conductance (G) measurements through dielectric spectroscopy represented by the complex dielectric function ϵ^* as;

$$\epsilon^*(\omega) = \epsilon'(\omega) + j\epsilon''(\omega)$$

5

where ϵ' and ϵ'' are respectively known as the dielectric constant and the dielectric loss and can be expressed in terms of the thickness (d) and cross-sectional area (A) of the capacitor by the following equations [43];

$$\epsilon' = \frac{C}{C_0} = \frac{Cd}{\epsilon_0 A}$$

$$\epsilon'' = \frac{G}{\omega C_0} = \frac{Gd}{\omega \epsilon_0 A}$$

The dielectric parameters of ZnO/CuO heterostructures produced at pH:11.0 and pH:11.2 are given respectively by Figs. 9 and 10 as a function of frequency at different temperatures. In general, a similar dielectric behavior was observed in both diodes under the effect of frequency and temperature. The increase in frequency induced a decrease in both dielectric parameters due to capacitive discharge effect; that is, the struggling of electrical dipoles in following the applied electric field and the resulting decrease in polarization effect. At very high frequencies, dipoles become totally incapable of following the AC signal and oscillations stop which is manifested by the constant dielectric plateau behavior at 10^5 Hz and above. Nevertheless, the increase in temperature induced a monotonic increase in the dielectric parameters and can be explained by the boosted mobility of the electrical dipoles within the dielectric medium [43]. Although the solution pH value had no effect on the behavior of dielectric parameters with frequency and temperature, it remarkably affected their magnitude where dielectric constant increased but dielectric loss decreased with the increase in solution pH value [47]. The pH-induced increase in dielectric constant can be interpreted as an increase in capacitance of the films with the increase in pH value, and the latter can be due to the increase in interaction with hydroxyl ions which shows the role of functional groups as active centers of charge adsorption.

Electrical conductivity of ZnO/CuO heterojunction was estimated using [48];

$$\sigma_{ac} = 2\pi f \epsilon' \epsilon_0 \tan \theta$$

and plotted versus frequency at different temperatures in Fig. 11. Up to about 10^5 Hz, conductivity of both composites exhibited a plateau behavior at all temperatures referred to a DC behavior. At high enough frequency, conductivity increased almost linearly due to localized conduction known as the AC conduction that occurs by the hopping or tunneling relaxation mechanisms of charge carriers at equilibrium sites [49]. With temperature, conductivity can be thermally activated where the conductivity of ZnO/CuO synthesized at pH = 11.0 recorded a decrease in 300–375 K temperature range and an increase in 375–600 K temperature range while the conductivity of ZnO/CuO synthesized at pH = 11.2 showed a continuous increase with temperature. That is, the former sample showed a confused semiconductor-conductor behavior while the latest sample showed a mere semiconductor behavior. Excluding low temperatures, conductivity of the latest sample (few hundreds of nS/m) is highly improved compared to that of the former sample (few tens of nS/m).

5. Conclusions

In conclusion, ZnO/CuO hetero-structured nanocomposite films were produced at different pH values using SILAR and hydrothermal routes. XRD patterns showed the proper formation of hexagonal ZnO and monoclinic CuO crystal structure and suggested a slight decrease in crystallite size and strain with the increase in the solution pH value without any deterioration in the structure of the produced crystalline system. SEM images manifested the successful formation of ZnO layer on CuO film without any deformation in the CuO substrate layer, and was also seen that a small change in pH (from 11.0 to 11.2) led to the formation of thicker ZnO rods on the produced CuO films. Such a small change in pH also recorded remarkable effects on optical bandgap (from 2.03 eV to 2.11 eV), room-temperature resistance (from 377 MΩ to 474 MΩ), ideality factor (from 4.41 to 4.68), barrier height (from 0.74 eV to 0.83 eV) and dielectric parameters of ZnO/CuO diodes. These results demonstrate the remarkable effect of reaction pH value in controlling nucleation and crystal growth rates during chemical synthesis processes which sequentially affects grown crystallite sizes, allowed bandgap transitions and electrical resistance of the material. Additionally, hydroxyl functional groups seem to act as active centers for charge adsorption which in turn alters dielectric properties of the material dependent on the density of existing hydroxyl ions. Eventually, it was deduced that although a small change in pH could not deform the crystalline nature of the produced CuO/ZnO heterostructures, it could change the morphology and remarkably tune the optical bandgap, electrical resistance as well as capacitance and dielectric properties for the purpose of designing desired materials for specific usages.

Declarations

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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Figures

Figure 1

X-ray diffraction patterns of CuO and ZnO/CuO hierarchical structures at (a) pH:11.0 and (b) pH:11.2.

Figure 2

Williamson-Hall plots of ZnO/CuO structures at (a) pH:11.0 and (b) pH:11.2.

Figure 3

SEM images of CuO ((a) pH:11.0 and (b) pH:11.2) and ZnO/CuO ((c) pH:11.0 and (d) pH:11.2). Rod thickness distribution of ZnO/CuO at (e) pH:11.0 and (f) pH:11.2.

Figure 4

EDX analysis of CuO ((a) pH:11.0 and (b) pH:11.2) and ZnO/CuO ((c) pH:11.0 and (d) pH:11.2).

Figure 5

Transmittance spectra of (a) CuO and (b) ZnO/CuO composites at different pH values.

Figure 6

Tauc plots of (a) CuO and (b) ZnO/CuO samples for different pH values.

Figure 7

Raman spectra of (a) CuO and (b) ZnO/CuO composites at different pH values.

Figure 8

(a) I-V and (b) $\ln I$ -V response of n-ZnO/p-CuO heterostructures at different pH values.

Figure 9

Frequency and temperature dependence of (a) ϵ' and (b) ϵ'' of n-ZnO/p-CuO heterostructures synthesized at pH:11.0.

Figure 10

Frequency and temperature dependence of (a) ϵ' and (b) ϵ'' of n-ZnO/p-CuO heterostructures synthesized at pH:11.2.

Figure 11

Conductivity of ZnO/CuO nanocomposites synthesized at (a) pH:11.0 and (b) pH:11.2 versus frequency at different temperatures.