Effect of mixed ZnO/CuO nanoparticles on the structural, morphological, and topographical properties

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Abstract. In the present work, pure and composite ZnO/CuO were effectively deposited by chemical spray pyrolysis. Structural, morphological, and topographical features have been well investigated and explained. XRD analysis showed a polycrystalline structure with hexagonal and monoclinic systems for ZnO and CuO, respectively. The crystal size that calculated from XRD patterns has decreased with the increase of CuO content, while the dislocation density and the micro strain have increased. These results lead to high defects in the structure of the nanocomposite which will be more efficient in a specific application. Moreover, the morphology of the samples was examined by FESEM and it was spherical-like shapes and has elevated points, whereas the EDX confirm the existence of the employed materials without any other undesired materials. The topography of the surface depicted a slightly rough surface which will be suitable for different nanoelectronics devices.

Keywords: CuO, FE-SEM, Spray pyrolysis, AFM, XRD, ZnO.

1. Introduction

Over the ages, attempts were made to look for non-toxic, low cost, efficient new materials for different applications [1]. The preparation of thin films of nanometer size is important due to their potential applications in diverse fields of science and technology including electronics, optics, and space science [2-4]. Mixed metal oxide semiconductors have attracted great attention from researchers from various fields such as physics, chemistry, and material science due to their various practical applications such as photodetectors, gas sensors, microelectronic circuit fabrication, piezoelectric devices, fuel cell, and solar cell [5-9]. Metal oxide semiconductors have many interesting characteristics such as natural p-n features, wide light absorption, fast dynamic response, and better sensitivity of the change in humidity [10]. Zinc oxide (ZnO), is widely receiving greater interest as a UV optoelectronics material due to its direct broad band gap of 3.37 eV at room temperature and its high exciton binding energy of 60 meV. ZnO is identified as one of the most versatile nanostructures producing materials making it an ideal candidate for applications in nanotechnology such as field emission arrays and nano sensors [11]. Literature shows that in comparison to its component (pure ZnO or CuO), and CuO-ZnO nanocomposites exhibit better results.
in various practical fields [12, 13]. For example, Muhammad Sajjad et.al showed the effect of copper mixing on the optical band gap of ZnO nanoparticles and photoluminescence (PL) [14]. D.M. Fernandesas et.al showed ZnO, CuO, and Cu0.05Zn0.95O nanoparticles have been prepared by a sol-gel method using poly (vinyl alcohol) aqueous solutions and metal nitrate precursors [15]. Pradip B. Sable et.al showed the structural, optical and functional group of copper mixed zinc oxide nanoparticles (NPs) synthesized by chemical co-precipitation method [16]. To date and according to our knowledge, most researchers have studied the structural, morphological, and optical properties of ZnO:CuO nanocomposites with lower content of CuO incorporated to ZnO.

In this work, pure and CuO-mixed ZnO nanoparticles with different high concentrations were prepared by using the thermal pyrolysis method. Cu mixing in ZnO is found to modify its structural, photoluminescence, and other morphological properties.

2. Materials and Methods

Pure and ZnO mixed with CuO at different concentrations (75% ZnO:25% CuO and 50% ZnO:50% CuO) thin films were deposited on glass substrates by chemical spray pyrolysis technique as follows:

The Solution of (0.1 M) concentration for copper chloride (CuCl₂·2H₂O), its molecular weight is (170.48 g / mol) with purity (99.999%) supplied by the Indian (Central Drug House) company, which is in the form of a dark green powder. It was prepared by dissolving (1.70452 g) copper chloride in (100 ml) distilled water and by using a magnetic stirrer to ensure complete dissolution of the material for a period of (15 min) at room temperature. Also a solution of concentration (0.1 M) of Zinc chloride (ZnCl₂), its molecular weight is (136.29 g / mol) with purity (99.999%) supplied by the Indian (Central Drug House) company, which is in the form of a white powder. A specific amount of Zinc Chloride (1.3628 g) was dissolved in (100 ml) distilled water, then the solution was carried out to a magnetic stirrer to ensure complete dissolution of the material for a period of (15 min) at room temperature.

After that, the glass substrate was subjected to the cleaning process by RCA [5], all the materials (pure and mixed) are deposited on the glass substrates at a deposition temperature of (350 °C) with a deposition period of (5) seconds and a stopping period of (90) seconds to avoid the sudden cooling of the substrate, the rest of the conditions were kept constant such as flow rate 5 ml/min, the distance between the nozzle and the substrate was (29±1 cm).

The crystal structures of ZnO and ZnO-CuO films were characterized by XRD diffract meter (Model-XRD-6000 Shimadzu) using CuKα (λ = 0.154056 nm) radiation. Morphological properties after the modification process with pure and CuO mixed ZnO were investigated via using (FE-SEM) along with (EDX) spectroscopy (INSPECT-S50) and (CSP model AA3000 AFM supplied by Angstrom Company).

3. Results and Discussion

The structural properties of ZnO and CuO-ZnO have been well studied by XRD analysis since this radiation can reach the crystal structure of the material without any damage to the surface of the sample. The XRD patterns of pure and incorporated ZnO have demonstrated in Figure 1. For pure ZnO, one could be observed that there are three peaks of planes (002), (101), and (103), which showed a polycrystalline structure within the hexagonal system. After the incorporation of CuO (25 and 50 %) contents within the ZnO, the patterns depicted new peaks related to the CuO nanoparticles which are (002) and (111) planes, it revealed a monoclinic system. The appeared peaks prove the presence of ZnO and CuO nanoparticles without any additional materials. Also, the confirmation of the CuO content increment is noticed by rising the intensity of its peaks. Furthermore, it clarifies the high degree of recrystallization, hence this could be related to the optimized conditions of the preparation. Tables 1 and 2 list the 20 of diffracted peaks, full width at half maximum, crystal size, dislocation
density, and the strain of pure and loaded ZnO. The crystal size (D), dislocation density (δ), and micro strain were calculated by the following formulas [17-19]:

$$D = \frac{0.9 \times \lambda}{\beta \cos \theta} \quad (1)$$

$$\text{Micro strain} = \frac{\beta \cos \theta}{4} \quad (2)$$

$$\delta = \frac{1}{D} \quad (3)$$

Where, λ is the wavelength of the incident radiation, β is the full width at half maximum, 0.9 is the constant of shape factor, and θ is Bragg’s angle.

Figure 1: XRD patterns of pure and mixed ZnO.

Table 1: Characterizations of diffracted peaks.

| Sample          | [2θ] degree | d_{hkl} (Å) | FWHM   | hkl | ZnO   | CuO |
|-----------------|-------------|-------------|--------|-----|-------|-----|
| ZnO (JCPDS)     | 34.35       | 2.60969     | -      | 002 | -     | -   |
|                 | 36.10       | 2.48606     | 101    | -   | -     | -   |
|                 | 62.645      | 1.48175     | 103    | -   | -     | -   |
| ZnO (Pure)      | 34.3614     | 2.60263     | 0.18820| 002 | -     | -   |
|                 | 36.1223     | 2.47663     | 0.23770| 101 | -     | -   |
|                 | 62.6578     | 1.47937     | 0.35390| 103 | -     | -   |
| Zno 75% Cuo 25% | 34.4666     | 2.59932     | 0.19100| 002 | -     | -   |
|                 | 38.767      | 2.30178     | 0.21752| -   | 111   | -   |
The crystal size reduced after the mixing of CuO which indicates an enhancement in a surface area [20]. The reason behind the decrease in crystal size may be linked to the ionic radii of Cu and Zn elements, which are 73 and 74 pm, respectively. The near values of ionic radii or slightly Cu ionic radius lower than that of Zn will lead to two defects process; the first one is that the Cu nanoparticles might take an interstitial position among Zn, the second one is that Cu could detach Zn atom and take its place, the latter process called substitution defects. These processes can play an important role in crystal size variation with the changing of Cu content [21]. The other main factor that is calculated adopted on the resulted peaks is dislocation density. This factor confirms the existence of defects with the increasing of CuO concentration within the ZnO, therefore, this factor leads to more defects which will be good sites for sensing applications. The micro strain also increased with the increment of CuO nanoparticles concentration, leading to high defects and may be cracked within the surface material, therefore, providing a large number of positions for sensing application.

Table 2: XRD parameters of pure and mixed ZnO.

| Sample | ZnO pure | CuO 75%: CuO 25% | CuO 50%: CuO 50% |
|--------|----------|------------------|------------------|
| $\beta$(FWHM) rad | 0.003285 | 0.003334 | 0.003643 |
| $\theta$(rad) | 0.29986 | 0.300778 | 0.300795 |
| $d$(nm) | 44.2 | 43.5 | 39.8 |
| $\delta$(cm$^{-2}$) $\times 10^{-11}$ | 5.1 | 5.2 | 6.3 |
| Micro strain $\times 10^{-4}$ | 7.8 | 7.9 | 8.7 |

The surface morphology of the samples has been well investigated by FESEM analysis. This test is significant to get the surface morphology in a high-resolution image, and hence it is essential analysis to show the shape, grain size, and distribution of grains along the surface. Figure 2 manifests the nano-size morphology of ZnO and ZnO-CuO nanoparticles. Un-mixed ZnO depicted nanoparticle shapes and the average grain size was 55 nm. Whereas the mixed ZnO with 25 % CuO, shows finer grains and a smooth surface, and an average grain size of around 48 nm. When the content of CuO has increased to 50 %, the average grain size decreased to 41 nm. The last mixture demonstrated the finest grains, nevertheless, all of the samples are spherical-like structures. The reduction in grain size with the augmentation of CuO content could be related to small grains of CuO that inhibited within the nanocomposite. This trend is compatible with what obtained from XRD analysis.
To investigate the chemical elements and to confirm the presence of the used materials in this work, EDX analysis has been employed for this purpose. **Figure 3** reveals the chemical element peaks of pure and CuO mixed ZnO nanoparticles. The appeared elements are Zn, Cu, O, C, and Cl, hence these elements confirm that there are no other elements or impurities within the tested samples. The presence of carbon (C) element is linked to the deposited carbon layer over the sample before the test since it is necessary for decreasing the resistivity of the materials and to obtain a fine image. While chloride (Cl) element is related to the fact that the deposition temperature did not lead to evaporate all the chloride amount. Nevertheless, these samples showed a perfect distribution and the expected increment in Cu element has been observed. Furthermore, there is another notice related to the oxygen (O) element, which clarifies the decreasing in (O) element with the incorporation of Cu nanoparticles. The explanation for the decrease in (O) element is concerned to the number of oxygen vacancies, consequently, the reduction of (O) element, the increment of oxygen vacancies [22].
Figure 3: EDX of (a) pure ZnO, (b) 75% ZnO:25% CuO, and (c) 50% ZnO:50% CuO.

The topography of the sample’s surface was examined by atomic force microscope (AFM) which determine the roughness and particle size of the surface. Figure 4 evident 3D images of pure ZnO, 75% ZnO-25% CuO, and 50% ZnO-50% CuO. The topography of pure ZnO showed a smooth surface with an average particle size of around 31.26 nm and the average roughness is 4.14 nm, while for the sample that mixed with 25 % of CuO recorded 27.66 nm for average particle size and 6.08 nm average roughness, and for the sample mixed with 50 % CuO depicted 14.19 nm average particle size and 8.48 nm average roughness. The decrement in average particle size with the increase of CuO concentration is compatible with the obtained crystal size behavior in XRD and FE-SEM analyses. The increase in roughness could be attributed to the coalescence of particles within the nanocomposite making the surface has high regions, which resulted in elevated points that the cantilever of the instruments interact with by Van der Waals force.
Figure 4: 3D images taken by AFM instruments for pure and CuO mixed ZnO.

Conclusion

The chemical spray pyrolysis technique was successfully utilized for the creation of pure and CuO mixed ZnO thin films under optimized conditions. A polycrystalline structure with sharp peaks has been obtained and the related factors have been well inspected. The decrement in crystal size and the augmentation of defects with the addition of CuO nanoparticles were the most significant findings. Furthermore, the morphology and topography of the films showed relatively rough spherical structures with some elevated positions. The obtained outcomes lead to the benefits of these films for sensing applications and electronic devices.
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