The Influence of x ratio and Annealing Temperatures on Structural and Optical Properties for \( (\text{CuO})_x(\text{ZnO})_{1-x} \) Composite Thin Films Prepared by PLD

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Abstract. Thin films of \( (\text{CuO})_x(\text{ZnO})_{1-x} \) composite were prepared by pulsed laser deposition technique and x ratio of \( 0 \leq x \leq 0.8 \) on clean corning glass substrate at room temperatures (RT) and annealed at 373 and 473K. The X-ray diffraction (XRD) analysis indicated that all prepared films have polycrystalline nature and the phase change from ZnO hexagonal wurtzite to CuO monoclinic structure with increasing x ratio. The deposited films were optically characterized by UV-VIS spectroscopy. The optical measurements showed that \( (\text{CuO})_x(\text{ZnO})_{1-x} \) films have direct energy gap. The energy band gaps of prepared thin films decreased as x ratio increased, while they increased with increasing annealing temperatures. Also the optical constants such as refractive index, extinction coefficient and dielectric constants have been calculated.

Keywords: \( (\text{CuO})_x(\text{ZnO})_{1-x} \) films, Pulsed laser deposition, Annealing temperatures, Structural properties, Optical properties.

1. Introduction

Zinc Oxide (ZnO) is n-type semiconductor with a very useful and important material for multiple applications in both microelectronic and optoelectronic devices. Zinc oxide is a group II-VI wide direct band-gap semiconductor (3.4 ev at room temperature) that has been extremely investigated for many years [1]. Copper oxide (CuO) is p-type semiconductor with band gap energy of about 1.51-1.74 ev [2, 3]. CuO is especially used in solar cell technology and photovoltaic applications [2]. The composite of n-type ZnO and p-type CuO were expected to show the reduced sensitivity, due to their opposite response to gases. Doped CuO was shown to reduce the electrical conductivity of CuO as gases sensors. This was proposed to be responsible to increase sensitivity of CO gas for ZnO-CuO composite by increasing the current...
through p-n function [3]. The conductivity is controlled by ZnO-CuO boundaries [4], due to their superior properties such as high crystalline quality, large aspect ratio, and quantum confinement effects. ZnO nanostructures have attracted great research interest. Different techniques such as molecular beam epitaxy, sputtering, sol-gel processing, vapor deposition, and electrochemical deposition have been employed to fabricate ZnO nanowires and nano rods. These have been widely used in laser devices, gas sensors, ultraviolet–visible light emission devices, and many other applications [5]. CuZnO (CZO) with different forms (e.g., thin films, nano rods and powder which is combined by ZnO and CuO has been extensively studied, owing to its potential applications in many fields, including gas sensors and solar cells [6]. In this study the effects of X ratio and annealing temperatures on the structural and optical properties of thin (CuO)x(ZnO)1-x films prepared by pulsed laser deposition technique have been investigated.

2. Experimental
Zinc oxide and copper oxide powder with 99.999% purity were used as a source materials to prepare (CuO)x(ZnO)1-x thin films by pulsed laser deposition technique with thickness 100nm on glass substrate at room temperature (RT), different x ratios (x= 0, 0.2, 0.4, 0.6, and 0.8) and annealing at 373 and 473K. These materials were mixed in gate mortar for one hour. After that, the mixture was pressed at 5 Ton to form a target with 2.5 cm diameter and 4 cm thickness. Finally, the targets were sintering at 873K temperature to ensure the homogenous of the materials. The target must be as dense and homogenous as possible to ensure perfect quality of the deposit films. The pulsed laser deposition experiment is carried out inside a vacuum chamber generally at (10^-3Torr) vacuum conditions, at low pressure of a background gas for specific cases of oxides and nitrides. Nd:YAG laser focusing on the target surface has been done using a convex spherical quartz lens with focal length 10cm and the lens has been placed inside the vacuum chamber. This laser focusing is necessary in order to exceed the ablation threshold energy density when the laser hit the surface of the target material. The specifications of laser are Nd:YAG laser with pulse energy of 800 mJ and at 6 Hz of frequency and 1064 nm wavelength, and number of shots equals to 600 pulse. Structure properties of (CuO)x(ZnO)1-x thin films were determined by X-ray diffraction using Shimadzu 6000, with Cu-Kα radiations operated at 40kV and 30mA, with scanning angle 2θ o-60o. The optical properties of the deposited films were measured in wavelength range of 190 to 1100 nm using UV-VIS spectrophotometer (Optima-3000).

3. Results and Discussion
The structure of the prepared (CuO)x(ZnO)1-x films has been investigated by using XRD to ensure the stoichiometry of material. Figure 1 and 2 show the XRD patterns of the deposited (CuO)x(ZnO)1-x films on glass substrate with different x ratio (0, 0.2, 0.4, 0.6 and 0.8) and annealed at (373 and 473) K. These figures show polycrystalline structure of all the prepared samples, also from these figures, the phase change from ZnO hexagonal to CuO monoclinic with increasing x ratio from 0 to 0.8. Tables 1 and 2 give the interplaner distance (d), intensity (I/Io) and crystallite size (D) for the prepared samples in comparison with the standard value as in JCPDS card. The values of d and 2θ are nearly similar to that in the JCPDS cards (96-900-4180 for ZnO and 96-410-5686 for CuO) as listed in these Tables. Similar result has been emphasized by Buchholz et al [7]. Figure 1 shows the X-ray diffraction patterns for (CuO)x(ZnO)1-x films at different x ratio where annealed at 373K. This figure illustrates that all peaks in the first and second patterns which correspond to x = 0 and 0.2 are identically with the (CuO)x(ZnO)1-x standard peaks. There are four peaks for polycrystalline hexagonal ZnO phase for x = 0 and 0.2 located at 2θ equal to 31.8°, 34.5°, 36. 25° and 56.6° with hkl (100), (002), (101) and (110) respectively. Also there are four peaks for polycrystalline hexagonal ZnO and monoclinic CuO for x = 0.4 located at 2θ equal to 35.6°, 36.45°, 38. 9° and 56.85° with hkl (11-1), (101),(111) and (110) respectively, while at x=0.6 the peak for (110) plane
disappear compared with ZnO and another peak appears at \(2\theta\) equal to 48.70 for (20-2) for monoclinic CuO. Finally, at x=0.8, it is observed that the peak for (101) plane was disappeared compared with ZnO at x=0.6 as shown in Figure 1 and Table 1. The figure shows that all peaks in the first and second patterns which correspond to x=0 and 0.2 are identically with the \((\text{CuO})_x(\text{ZnO})_{1-x}\) standard peaks. It is observing four peaks for polycrystalline hexagonal ZnO phase for x= 0 and 0.2 located at \(2\theta\) equal to 31.65°, 34.5°, 36.25° and 56.65° with (100), (002), (101) and (110) planes respectively. Also five peaks for polycrystalline hexagonal ZnO and monoclinic CuO appeared for x= 0.4 was located at \(2\theta\) equal to 35.6°, 36.45°, 38.85°, 48.65° and 56.9°.

Figure 1: X-ray diffraction pattern for \((\text{CuO})_x(\text{ZnO})_{1-x}\) with different x ratio and annealed at 373K.

Table 1: Structural parameters: \(2\theta\), \(d_{\text{hkl}}\), (hkl), FWHM and D of \((\text{CuO})_x(\text{ZnO})_{1-x}\) films with different x ratio and annealed at 373K.
with hkl (11-1), (101), (111), (20-2) and (110) respectively, whereas at x=0.6 the peak for (110) plane disappeared compared for ZnO at x=0.4. Finally at x=0.8 the peak for (101) plane disappear compared for ZnO at x=0.6 as shown in figure 2 and Table 2.

Figure 2: X-ray diffraction pattern for (CuO)x(ZnO)1-x with different x ratio and annealed at 473K.

Table 2: Structural parameters: 2θ, dhkl, FWHM and D of (CuO)x(ZnO)1-x films at different x ratio and annealed at 473K.

| x ratio | 2θ (Deg.) | FWHM (Deg.) | Int. (Arb. Unit.) | dhkl Exp. (Å) | dhkl Std. (Å) | D (nm) | hkl | Phase |
|---------|-----------|--------------|-------------------|---------------|---------------|-------|-----|-------|
| pure    | 31.65     | 0.4778       | 14                | 2.8196        | 2.817         | 17.2807 | (100) | ZnO   |
|         | 34.5      | 0.2555       | 9                 | 2.6093        | 2.603         | 27.8379 | (002) | ZnO   |
|         | 36.25     | 0.2585       | 19                | 2.4801        | 2.478         | 27.9812 | (110) | ZnO   |
| 0.2     | 36.65     | 0.4181       | 10                | 1.6274        | 1.626         | 21.5669 | (110) | ZnO   |
| 0.4     | 31.73     | 0.3184       | 11                | 2.8248        | 2.817         | 25.0376 | (002) | ZnO   |
|         | 34.5      | 0.2559       | 6                 | 2.6085        | 2.603         | 34.7973 | (002) | ZnO   |
|         | 36.3      | 0.2585       | 15                | 2.4841        | 2.478         | 27.9764 | (110) | ZnO   |
|         | 36.45     | 0.5376       | 9                 | 1.6243        | 1.626         | 16.7817 | (110) | ZnO   |
| 0.6     | 32.6      | 0.3844       | 16                | 2.5204        | 2.521         | 22.2783 | (111) | CuO   |
|         | 36.45     | 0.2585       | 20                | 2.4602        | 2.478         | 28.0012 | (110) | ZnO   |
|         | 38.85     | 0.2585       | 20                | 3.3146        | 2.315         | 28.2001 | (111) | CuO   |
|         | 48.65     | 0.7165       | 7                 | 1.8713        | 1.857         | 12.1062 | (202) | CuO   |
|         | 56.9      | 0.4181       | 10                | 1.6164        | 1.626         | 21.6094 | (110) | ZnO   |
| 0.8     | 35.55     | 0.2589       | 10                | 2.5286        | 2.521         | 34.9059 | (111) | CuO   |
|         | 36.55     | 0.2589       | 19                | 2.4644        | 2.478         | 28.0003 | (110) | ZnO   |
|         | 38.85     | 0.2585       | 25                | 2.3180        | 2.315         | 28.2000 | (111) | CuO   |
|         | 48.75     | 0.5176       | 11                | 1.8670        | 1.867         | 16.2213 | (202) | CuO   |
|         | 58.9      | 0.4186       | 25                | 2.3180        | 2.315         | 20.1428 | (111) | CuO   |
|         | 48.75     | 0.4673       | 10                | 1.8664        | 1.897         | 18.642  | (202) | CuO   |

The crystallite size (grain diameter D) of the (CuO)x(ZnO)1-x films has been calculated by using the Scherrer's formula [8]:

$$D = \frac{K\lambda}{\beta \cos\theta}$$  \hspace{1cm} (1)
where $D$ is the crystallite size, $\lambda$ the X-ray wavelength used, $\beta$ the angular line width of half maximum intensity, $\theta$ the Bragg's diffraction angle and $K$ some constant with a value of 0.9, which can be deduced from the lower full width at half maximum (FWHM) of diffraction peaks associated these processes as shown in Tables 1 and 2. It is observed that the crystallite size in general increases with increasing of annealing temperatures and decreases with increasing $X$ ratio.

In addition, it is observed from these Tables a decreasing in $d_{hkl}$ with increasing $X$ ratio. This is nearly in agreement with Chowa et al [6]. The intense and sharp peak in X-ray diffraction pattern reveal the good crystallinity of the films.

The optical absorption of thin $(\text{CuO})_x(\text{ZnO})_{1-x}$ films was studied in the wavelength ($\lambda$) range from 200 nm to 1100 nm. Figure 3 shows the transmittance for $(\text{CuO})_x(\text{ZnO})_{1-x}$ films deposited on glass at different $X$ ratios at RT(293K) and both annealing temperatures (373 and 473)K. In general, It can be observed from this figure that the transmittance decreases with increasing of $X$ ratio which means increase in the reflection and absorption. The onset of absorption edge for films became less sharp which is due to the fact that bigger crystalline sizes are deposited, and because in the case of more atoms are present in the film so more states will be available for the photons to be absorbed. The shifts of transmittance spectrum to longer wavelengths (lower energies) indicating decreasing of $E_g$ with increasing $X$ ratio [9,10]. Also it can be seen from figure 3 that the transmittance increases with increasing of annealing temperatures. The shifts of transmittance spectrum to shorter wavelengths (higher energies) with the increase of $T_a$ may be attributed to the crystallization of film structure by increasing the crystallite size. This result in agreement with Chih Hung Hsu et al [11].

![Figure 3: Transmittance spectrum as a function of wavelength for $(\text{CuO})_x(\text{ZnO})_{1-x}$ films at different $X$ ratio and annealing temperatures.](image)

The absorbance spectrum for $(\text{CuO})_x(\text{ZnO})_{1-x}$ films with different $X$ ratio and annealing temperatures was recorded in the wavelength range 190-1100nm. Figure 4 shows that the absorption spectrum within the visible wavelength region in range (400-500) nm for $(\text{CuO})_x(\text{ZnO})_{1-x}$ thin film spectrum. It is obvious that the absorbance spectrum decreases with increasing of annealing temperature. This may be due to improve the crystallite size and increasing the transmittance which is led to increase in the energy gap. Also it can be observed from Fig.4 that the absorbance increased with increasing of $x$ ratio. This is due to create the localized states in the energy gap lead to decrease in the transmission and then decrease in the energy gap.
Figure 4: Absorbance spectrum as a function of wavelength for (CuO)\textsubscript{x}(ZnO)\textsubscript{1-x} films at different x and T\textsubscript{a}.

The absorption coefficient (\(\alpha\)) was measured from the region of high absorption at the fundamental absorption edge of the film from equation [10]:

\[
\alpha = 2.303 \frac{A}{t}
\]

where A is the absorbance and t is the thickness. Figure 5 shows the variation of the absorption coefficient versus the wavelength at both annealing temperatures (T\textsubscript{a}) and x ratio of (CuO)\textsubscript{x}(ZnO)\textsubscript{1-x} films. It can be noticed that \(\alpha\) decreases with increasing of T\textsubscript{a} for all x ratio as listed in Table 1 and figure 5. This is due to increase in energy gap with T\textsubscript{a} due to improvement in crystal structure with increasing annealing temperatures and decreasing the absorption [11]. Also, the value of \(\alpha\) increases with increasing x ratio for all samples due to create of localized states in the gap (as mentioned previously). In the shorter wavelength the absorption coefficient exhibits high values of \(\alpha\) (\(\alpha > 10^4\)) which means that there is a large probability of the allowed direct transition. The values of the absorption coefficient are nearly in agreement with values reported by other researchers [10-12].

Figure 5: Absorption coefficient as a function of wavelength for (CuO)\textsubscript{x}(ZnO)\textsubscript{1-x} films at different x and T\textsubcript{a}.

The optical energy gap values (E\textsubscript{g}) for (CuO)\textsubscript{x}(ZnO)\textsubscript{1-x} films with different x ratio (x= 0, 0.2, 0.4, 0.6 and 0.8) and both annealing temperatures (373 and 473)K have been determined by using Tauc equation[13]:

\[
\alpha(h\nu) = B (h\nu - E_g)^{r}
\]

where B is inversely proportional to amorphosity, r is a constant depending on the nature of type optical transition, by plotting the relations of \((h\nu)^2\) versus photon energy (h\nu) and selecting the optimum linear part, as shown in Figure 6. It is shown that the values of E\textsubscript{g} have direct transitions, and it is increased with
increasing $T_a$ for all prepared samples. This is due to the growth of grain size and the decrease in defect states near the bands and these in turn increase the value of $E_g$ [14]. Also the optical energy gap decreases with increasing $x$ ratio as given in Table 3, $E_g$ decreases about half value from 3.0 to 1.3 eV and from 3.2 to 1.4 eV and from 3.3 to 1.5 eV for samples prepared at RT, 373 and 473K respectively, when $x$ ratio increases from 0 to 0.8. This may be attributed to the fact the addition of CuO to the ZnO made the material more opaque (more absorbance). The decrease of $E_g$ when $x$ ratio is added to the ZnO is in agreement with Chowa et al [6] and Thakur et al[14].

Figure 6: $(\alpha h\nu)^2$ as a function of $h\nu$ for $(\text{CuO})_x(\text{ZnO})_{1-x}$ films at different $x$ and $T_a$.

The variation of the refractive index as a function of the wavelength in the range 190-1100 nm for different $x$ ratio and annealing temperatures is shown in Figure 7. The refractive index for $(\text{CuO})_x(\text{ZnO})_{1-x}$ films has been calculated from the equation [15]:

$$n = \left( \frac{4R}{(R-1)^2} - k^2 \right)^{1/2} - \left( \frac{R+1}{(R-1)} \right)$$

where $R$ is the reflectance and $n$ is refractive index. It can be observed from these figures and Table 3 that the refractive index decreases with increasing of $T_a$ which means decreasing of the reflection because the increase in energy gap is due to the expansion of the lattice and growth of the grain size. Whereas the value of refractive index increases with increasing of $x$ ratio, from 2.336 to 2.613, 2.25 to 2.612 and 2.02 to 2.61 for samples annealed at 293, 373 and 473 K respectively, when $x$ ratio increases from 0 to 0.8. This attitude may be due to the change in the bond length due to the decrease in the defect density which means decreasing of the reflection where the refractive index depends on it. This result is close to this obtained by Cheng et al [16].

Figure 7: The refractive index as a function of wavelength for $(\text{CuO})_x(\text{ZnO})_{1-x}$ films at different $x$ and $T_a$. 
Figure 8 shows the variation of extinction coefficient (k) as a function of wavelength at different x ratio and annealing temperatures. The values of extinction coefficient are determined by using equation [15]:

\[ k = \frac{\alpha \lambda}{4\pi} \]  

(5)

The extinction coefficient decreases from 0.2 to 0.14 with increasing annealing temperature from RT to 473K due to decrease the absorption coefficient as shown in Table 3, whereas it increases (0.2-1.07, 0.19-0.67, 0.14-0.67) with increasing of x ratio at RT, 373 and 473K respectively due to more grain boundaries with addition of CuO to ZnO and decreased the energy gap as a result to increasing the absorption with increasing x ratio, that was shown by Austin and Mott [17].

Figure 8: Extinction coefficient as a function of wavelength of (CuO)x(ZnO)1-x films at different x and Ta.

The plots of real and imaginary (\(\varepsilon_r\) and \(\varepsilon_i\)) parts of the dielectric constant with wavelength in the range of 190–1100nm for (CuO)x(ZnO)1-x thin films deposited at different x ratio and annealing temperatures are shown in Figures 9 and 10. Real and imaginary dielectric constants were calculated using equations [12,13]:

\[ \varepsilon_r = n^2 - k^2 \]  

(6)

\[ \varepsilon_i = 2nk \]  

(7)

The behavior of \(\varepsilon_r\) is similar to that of refractive index because smaller value of \(k^2\) compared with \(n^2\) and \(\varepsilon_i\) mainly depends on the k values. It is observed that \(\varepsilon_r\) and \(\varepsilon_i\) increased with increasing of x ratio, while \(\varepsilon_r\) and \(\varepsilon_i\) decrease with increasing of annealing temperatures as shown in Table 3. This behavior is in agreement with Bahsi and Oral results [18].

Figure 9: Real and imaginary parts of the dielectric constant of (CuO)x(ZnO)1-x films at different x and Ta.
Figure 9: Real part of dielectric constant as a function of wavelength for \((\text{CuO})_x(\text{ZnO})_{1-x}\) films at different \(x\) and \(T_a\).

Figure 10: Imaginary part of dielectric constant as a function of wavelength for \((\text{CuO})_x(\text{ZnO})_{1-x}\) films at different \(x\) and \(T_a\).

Table 3: Optical parameters of \((\text{CuO})_x(\text{ZnO})_{1-x}\) films at different \(x\) ratio and \(T_a\).

| \(T_a\) (K) | \(x\) ratio | \(E_g\) (eV) | \(10^4\sigma (\text{cm}^2)\) | \(n\) | \(k\) | \(\varepsilon\) | \(\varepsilon\) |
|-------------|--------------|---------------|----------------|-------------|-------------|---------------|-------------|
| pure        | 3.0          | 3.13          | 2.15           | 0.150       | 4.600       | 0.646         |
| RT          | 0.2          | 2.3            | 3.85           | 2.28        | 0.183       | 5.164         | 0.837       |
|             | 0.4          | 1.7            | 8.16           | 2.64        | 0.389       | 6.834         | 2.059       |
|             | 0.6          | 1.5            | 11.26          | 2.32        | 0.557       | 6.067         | 2.711       |
|             | 0.8          | 1.3            | 14.88          | 2.11        | 0.710       | 3.666         | 3.004       |
| pure        | 3.2          | 2.78           | 2.07           | 0.123       | 4.281       | 0.551         |
| 373         | 0.2          | 2.4            | 3.85           | 2.28        | 0.184       | 5.164         | 0.837       |
|             | 0.4          | 1.9            | 6.54           | 2.59        | 0.312       | 6.604         | 1.616       |
|             | 0.6          | 1.6            | 9.16           | 2.64        | 0.389       | 6.834         | 2.059       |
|             | 0.8          | 1.4            | 9.18           | 2.63        | 0.438       | 6.739         | 2.308       |
| pure        | 3.3          | 1.86           | 1.81           | 0.089       | 3.409       | 0.327         |
| 475         | 0.2          | 2.7            | 3.13           | 2.13        | 0.150       | 4.600         | 0.646       |
|             | 0.4          | 2.4            | 4.26           | 2.35        | 0.203       | 5.463         | 0.954       |
|             | 0.6          | 1.7            | 7.50           | 2.63        | 0.349       | 6.773         | 1.831       |
|             | 0.8          | 1.5            | 9.20           | 2.65        | 0.438       | 6.739         | 2.308       |
4. Conclusions
A polycrystalline structure for the \((\text{CuO})_x(\text{ZnO})_{1-x}\) films prepared successfully by pulsed laser deposition at different x ratio \((x = 0, 0.2, 0.4, 0.6 \text{ and } 0.8)\) and annealing temperatures \((373 \text{ and } 473) \text{ K}\). The phase change from hexagonal ZnO to monoclinic CuO with increasing x ratio. Also the prepared films have better crystalline with annealing temperatures. The optical transitions in \((\text{CuO})_x(\text{ZnO})_{1-x}\) film is direct transition and the value of optical energy gap increases with increasing of annealing temperatures, and decreases with increasing x ratio. The optical constants increase with increasing of x ratio, while they decrease with increasing annealing temperatures. Thus the characteristic of \((\text{CuO})_x(\text{ZnO})_{1-x}\) thin films prepared by pulsed laser deposition depend strongly on the prepared condition like annealing temperatures and x ratio.

5. References
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