Chemically deposited ZnO thin films at relatively high temperatures

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In this study, we used chemical bath deposition to produce thin films of zinc oxide. In an attempt to form a novel approach, ZnO films were obtained at relatively high temperatures such as 80-95 °C. Accordingly, different from the prior literature studies, the bath temperature was increased to 90 and 95 degrees. The absorbance measurement revealed that the film obtained at 95 °C had a relatively low absorbance. Besides, the band gaps of thin films were increased from 3.72 eV to 4.03 eV in response to higher bath temperatures. We used the X-Ray diffraction pattern for analysis and detected that all films were formed in the hexagonal crystal structure. It was understood from the scanning electron microscope images that as the temperature increased, the film became more compact.

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1. Introduction

Zinc oxide (ZnO) is a distinguished material due to its wide band gap and easy production process. It has notable advantages such as low-cost, non-toxicity and richness in availability. Zinc oxide is a II-VI semiconductor which exhibits a hexagonal wurtzite structure[1]. It has large exciton binding energy of 60 meV, a band gap of 3.37 eV, low resistivity and high transparency in the visible range[2]. ZnO has been investigated extensively by virtue of the fact that it is a suitable material for optically transparent electrodes utilized in electronic devices. Conductive and transparent ZnO films have low electrical resistance and high optical transmittance compared to those of indium tin oxide (ITO) films [1]. Currently, ZnO is being considered as a potential material to be used in solar cells, chemical sensors, solid-state emission, piezoelectric transducers, electroluminescent devices, transparent electrodes, photo-catalysts and ultraviolet laser diodes[3].

There are various methods for ZnO production including chemical bath deposition(CBD), sol-gel process, chemical vapor deposition, hydrothermal synthesis, mechano chemical processes, precipitation from micro emulsions[4].Among these methods, the chemical route technique is considered as the simplest one[5]. Chemical bath deposition has been widely used for the deposition of ZnO thin films. In addition to its low cost, it is effective and reproducible; plus, the materials are readily available[6,7].

Previously, various experiments have been made for producing ZnO. Some of these experiments were carried out at room temperature[6,8]and the others were conducted at relatively high temperatures such as 80 and 90 °C[9–11]. However, there was no study on ZnO films regarding the effect of relatively high temperatures such as 95 °C.

In this work, the effect of the relatively high temperatures is being presented in detail. It is seen from the Tauc plots that the band gap of the films increased as the bath temperature increased. Furthermore, the absorbance of the films obtained at 95 °C was nearly at a rate of one third compared to that of the other films. This result is critical because of the fact that low absorbance of n-type films makes them suitable for solar cells. When we examined the literature, we identified that there was no study in terms of producing films at 95 °C. Therefore, the effect of high temperatures on thin films was investigated in this study since the reaction rate increases with temperature in the chemical bath deposition method.

2. Experimental procedure

By using chemical bath deposition, thin films of ZnO were precipitated onto glass substrates. Before the depositions, glass substrates were washed with acetone and were rinsed with deionized water subsequently. In 100 mL deionized water, 65 mM (885 mg) $ZnCl_2$ was used as the Zn source and 5.8 mM (169 mg) ethylenediaminetetraacetic acid (EDTA) were dissolved and the pH of the solutions was adjusted to 10.1 by using 26% ammonia. The final solutions were stirred at 600rpm by using a stirrer and heater. The experiments were carried out at four different temperatures which were 80, 85, 90 and 95 °C. The depositions were completed in 30 minutes. After the depositions, the films were rinsed with deionized water and left to dry in room conditions. All these experimental conditions are tabulated in Table 1 and the experiments were named as T80, T85, T90, and T95 according to the temperatures.

Table 1. Experimental conditions for chemically deposited ZnO

Experiments	$ZnCl_2$ (mM)	EDTA (mM)	Temp. (°C)	Ph	Deposition time (min)
T80	65	5.8	80±2	10.1	30
T85	65	5.8	85±2	10.1	30
T90	65	5.8	90±2	10.1	30
T95	65	5.8	95±2	10.1	30

The structural analyses were performed by PANalytical EmpyreanX-Ray diffraction (XRD). Optical and morphological characteristic of the ZnO films was determined by using a JASCO V–530 with double beam UV-vis spectrometer and a Zeiss SUPRA 40VP SEM, respectively.

3. Result and discussion

3.1. Structural analysis of ZnO films

The thicknesses of the films were calculated by using the gravimetric method and it was determined that they were about 800 nm. This value was higher than the thickness of the films mentioned in the literature[10]. It can be said that the formation of a relatively thick film may be resulted from using EDTA and ammonia together and in suitable stoichiometry.

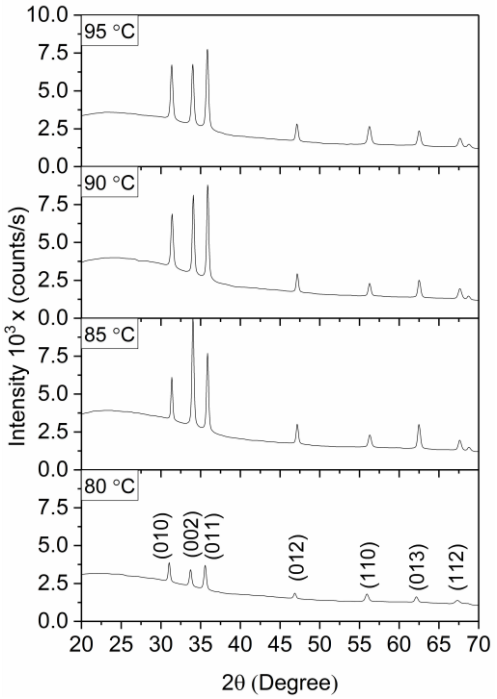

Fig. 1. Diffraction data of XRD for ZnO thin films obtained by various temperatures

Structural features were performed by using XRD patterns and these patterns are given in Fig.1. All films were formed in hexagonal structure and well matched ASTM cart (98-005-7478). The peak intensity of the film obtained at 80 °C was lower than that of the other films. It was determined for the chemical bath deposition that the thickness and crystallization increased as the bath temperature increased[12].When the temperature was increased, the (002) oriented peak was also increased. It may be concluded that the crystallization and preferred orientation were effected by the reaction rate which increases as the temperature increases.

The Texture Coefficients (TC) is a well-known method for determining the preferred orientation. This equation is given below:

$$TC = \frac{I_{(hkl)}/I_{0(hkl)}}{\frac{1}{N}\sum_N\left(\frac{I_{(hkl)}}{I_{0(hkl)}}\right)} \quad (1)$$

Table 2. Calculated Texture Coefficients according to the various planes

hkl	T80	T85	T90	T95
(010)	1.09	0.60	0.77	0.94
(002)	1.14	1.80	1.44	1.28
(011)	0.77	0.59	0.80	0.78

where I_0(hkl) is the standard intensity of the (hkl) plane given in ASTM card, I(hkl) is the measured relative intensity of a (hkl) plane[13]. The Texture Coefficients are given in Table 2 and it is seen in Table 2 that the preferred orientation of the films are predominantly (002) plane. Furthermore, in the film produced at 80°C, there were two texture coefficients above one. As the temperature increased, the preferential orientation was in the 002 direction.

The sizes of the crystallite of the samples were calculated using the Scherrer equation. In this equation, full with half maximum (FWHM) of the peaks was used and given as follows:

$$cs = \frac{0.089*180*\lambda}{314*\beta*\cos\theta_C}\,\text{nm} \quad (2)$$

where β was the full width half maximum, λ is the wavelength of X-ray radiation (1.54056 Å) and 2θC was the peak center [14–19].

Table 3. Lists of crystallite sizes and band gaps of the ZnO films

Experiments	cs (nm) (010)	cs (nm) (002)	cs (nm) (011)	cs Average	Band Gap (eV)
T80	46	37	37	40	3.72
T85	30	37	37	35	3.83
T90	36	30	30	32	3.92
T95	24	30	30	28	4.03

In the experiments, when the temperature was increased, the average crystallite size was decreased from 40 nm to 28 nm (as seen in Table 3) depending on the temperature. In a previous study [20], it was found that the crystallite size increased depending on bath temperature, however, after a certain temperature, crystallite size decreased although the bath temperature was increased.

3.2. Optical properties of the ZnO films

The values of absorbance versus wavelength were recorded by using a UV-vis spectrophotometer. The plots of the samples are given in Fig. 2.

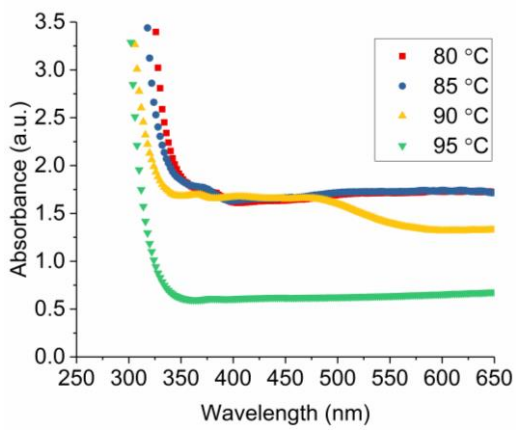

Fig. 2. Measurements of absorbance versus wavelengths between 300 and 650 nm (color online)

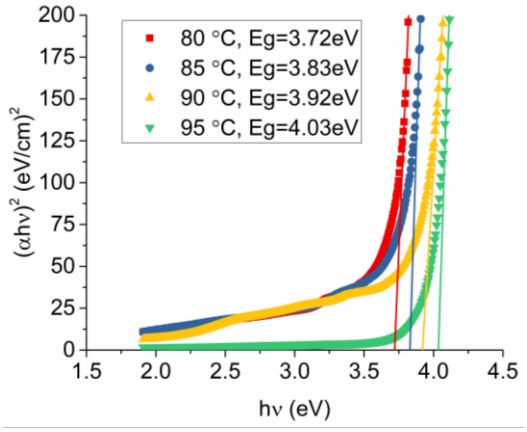

Fig. 3. Energy band gaps and Tauc plots for ZnO films (color online

When Fig. 2 is investigated, it is seen that the absorbance of the film obtained at 95 °C is nearly three times lower than that of the other films. There might be two reasons for this result. One of them might be that the film thickness being relatively lower, however, it was determined that all films had nearly the same thicknesses. The other reason might be that the surface roughnesses being relatively lower than that of the other films. This is significant due to the fact that low absorbance makes the film suitable for a solar cell. This low absorbance was observed only in the film obtained at 95 °C. As seen in Fig. 2, it was observed that the absorbance values did not vary much at the temperatures 80, 85 and 90 °C.

The Tauc plots were employed to estimate the band gaps of the ZnO samples. The absorption coefficient can be pointed out as a function of the energy of the photon, as is given in equation 3 for the direct allowed transition:

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g)^n \quad (3)$$

where; Eg is the optical band gap energy, n=1/2 for directly allowed transitions, hν is the photon energy, and A is a constant. The band gap energy is obtained by extrapolating the straight line portion of the plot to a zero absorption coefficient [21–24] and these plots were given in Fig. 3.

The band gaps of the ZnO samples were varied from 3.72 to 4.03 eV depending on the increasing bath temperatures. These values were higher than that of the bulk ZnO. It can be seen from Table 3 that the temperature increase causes the crystallite size to decrease, thus, causing the Energy band gap to increase with temperature. In this study, EDTA and ammonia were used together. Thus, crystallite sizes were lower than that of the films produced by the conventional production procedure.

3.3. FTIR of the ZnO films

Fourier Transform Infrared (FTIR) is a technique used to analyze the chemical composition. The FTIR transmission spectra of nano composite thin films was used to spectrometer in the range of 500–4000 cm^{-1} [25]. The FTIR plots versus wavenumber were recorded by using Fourier transform infrared photometer (FTIR) and these plots are given in Fig. 4. Infrared studies were carried out in order to investigate the purity and nature of the metal nano particles. Metal oxides generally show absorption bands below 1000 cm^{-1}arising from inter-atomic vibrations[26].

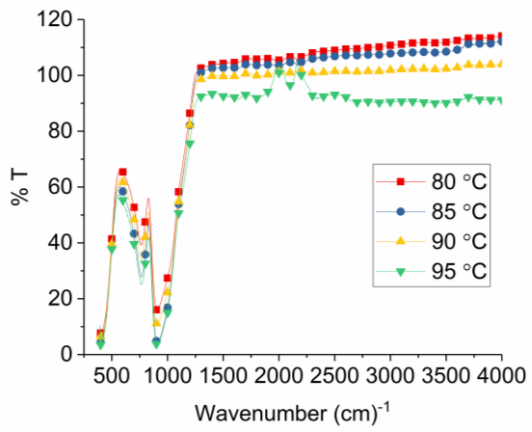

Fig. 4. FTIR spectrums versus wavenumber for ZnO films (color online)

ZnO absorption stretching was observed at around 901 cm^{-1} and 770 cm^{-1}. Latter was the stretching mode of ZnO[20].

3.4. SEM analysis of the ZnO films

Both 100 times magnified and 20,000 times magnified scanning electron microscope (SEM) images are given in Fig. 5 and Fig. 6, respectively. When Fig. 5 is examined, the clusters are seen on the surface of the films obtained at 80 °C and 85 °C.

These temperatures were already used in the literature. Different from literature, for the films obtained at 90 and 95 °C, the surfaces appeared very compact and homogeneous. Besides, there were no clusters on the surface of these films. When the surface of the films obtained at 80, 85 and 90 °C (as seen in Fig. 6) were analyzed, it was seen that all the surface was covered with nanoflower densely. Besides, it is seen from the Fig. 6 that the number of nanoflowers is decreased on the surface of the film obtained at 95 °C. This situation explains the reason why the absorbance is relatively lower for this sample.

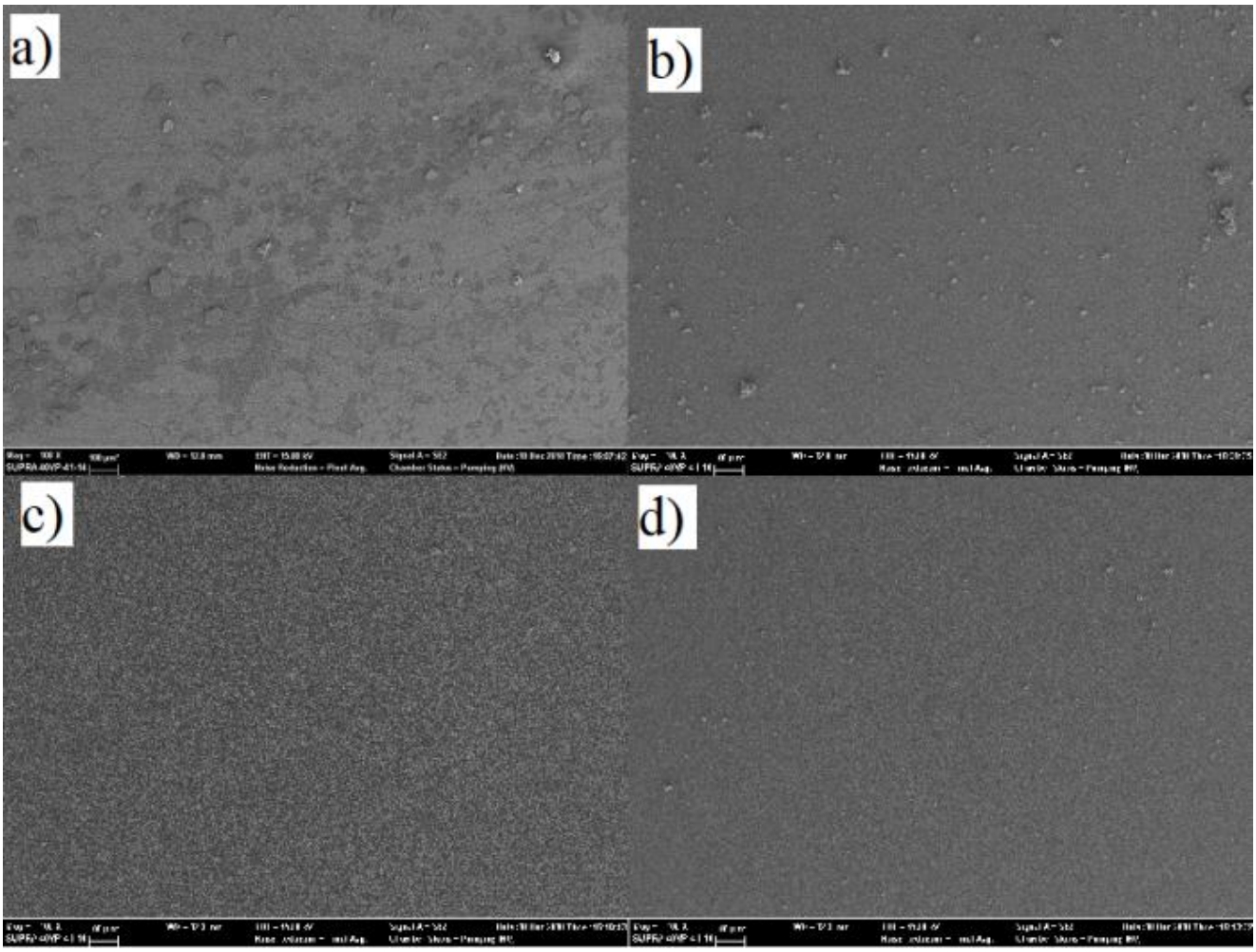

Fig. 5. 100 times magnified SEM images of the ZnO films obtained at a) 80 °C, b) 85 °C c) 90 °C, and d) 95 °C

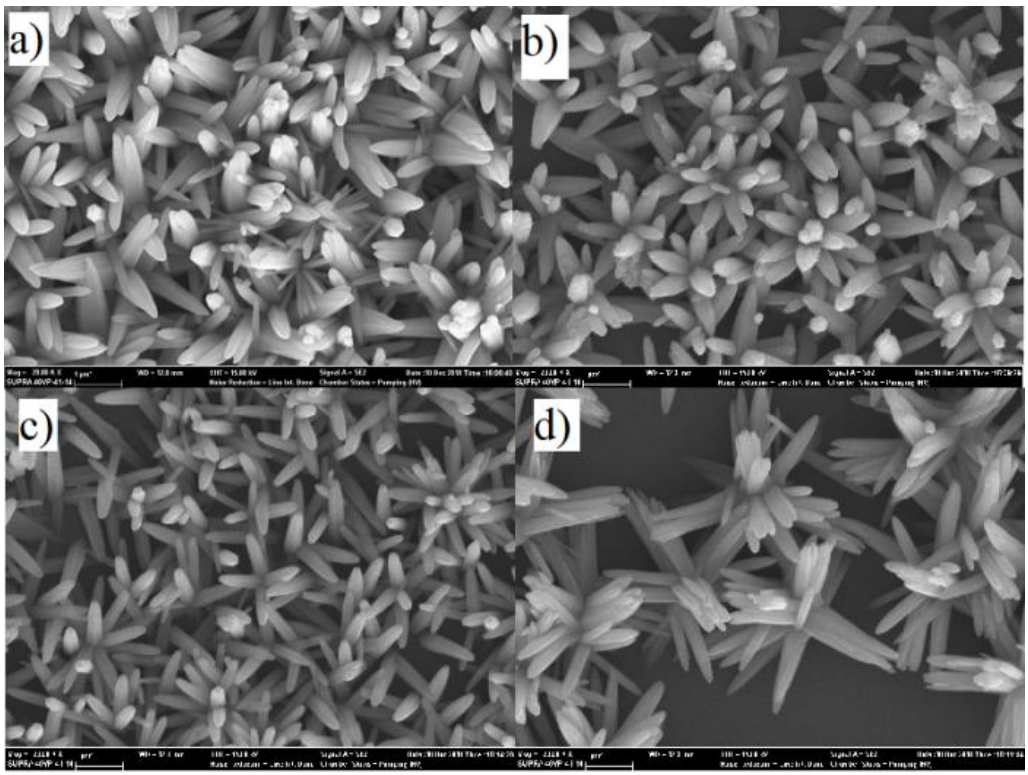

Fig. 6. 20,000 times magnified SEM images of the ZnO films nanoflowers obtained at a) 80 °Cb) 85 °C c) 90 °C, and d) 95 °C

3.5. Visual analysis of the ZnO films

The photos of the ZnO samples were taken and they are given in Fig. 7. When Fig. 7 is investigated, it is seen that the ZnO nanoparticles adhered surface of the glass substrates very well. All the films are compact and homogenous. Especially, the surface of the film obtained at 95 °C is seen more homogeneous than that of the surface of other films. Besides, this study revealed that the ZnO films can adhere to the surface effectively without any other processes such as annealing.

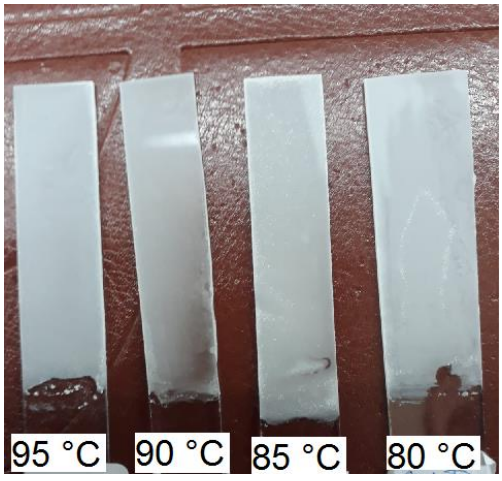

Fig. 7. Photograph of the produced ZnO samples (color online)

4. Conclusions

In this study, we presented that depositing ZnO thin films by using chemical bath deposition is a low cost, quick and simple process. Also, four different bath temperatures which are 80, 85, 90 and 95°C were carried out for ZnO precipitation. In this study, all samples were produced in a solution at a pH of 10.1.The gravimetric method was used to calculate the thicknesses of the films and it was understood the thickness average was 800 nm. For thin films, this value is considerably thick. All films were produced in hexagonal structures and crystallite sizes of the films were varied from 40 to 28 nm according to the increasing bath temperatures. It was seen from the absorbance measurement that the absorbance of the film obtained at 95 °C was almost three times lower than that of the other films. This is a critical finding because of the fact that low absorbance properties of the films area desirable situation for thin film solar cells. The band gap of the ZnO films varied between 3.72 and 4.03 eV. These values were higher than that of the previously recorded band gap of the ZnO films. It was concluded that this situation might result due to mixing EDTA and NH3 in the bath container. The surface morphology of the films was investigated by SEM. The SEM images showed that there were no clusters on the surface of the films obtained at 90 and 95 °C. Besides, it was realized that the surface of the film produced at 95 °C had relatively fewer nanoflowers. It was understood from the surface photos of the films that all films adhered very well onto the surface of the substrates.

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