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Araştırma Makalesi - Research Article

Bath Temperature Effect on c-axis Preferred Orientations and Band Gap of Semiconductor ZnO Thin Films

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Abstract- **Semiconductor ZnO thin films were deposited via chemical bath deposition technique (CBD) on glass substrates at varying temperatures (75°C-90°C). Influence of bath temperature on c-axis preferred orientations of ZnO thin films were examined. X-ray diffraction (XRD) results proved that thin films deposited at 80°C and 85°C bath temperature have a preferred orientation towards (011) peak. The preferred orientation changed towards (010) peak when the bath temperature increased to 90°C. Field Emission Scanning Electron Microscope (FESEM) images proved that ZnO thin film structure was formed by flower-like nanorods. In the thin films produced at 80°C and 85°C, the alignment of the nanorods was vertical, while in the films produced at 90°C, the nanorods mostly formed horizontally. These FESEM images also proved that the preferential orientation has changed from (011) to (010). Effects of bath temperature on band gap of semiconductor ZnO thin films were investigated by UV-Visible Spectrophotometer. ZnO thin films band gap value increased to 3.37 eV as the bath temperature increased to 85°C. When the bath temperature increased to 90°C the band gap value strongly decreased to 3.24 eV.**

***Keywords*- Zno Thin Films, Chemical Bath Deposition, Bath Temperature Effect, Preferred Orientations, Band Gap.**

I. INTRODUCTION

Lately, interest in metal oxides such as ZnO, MgO, TiO_2 and CuO has been increasing. Transistors [1], water purification [2], optoelectronic devices [3] are some of the application areas of metal oxides. Owing to its various structures such as nanorods, nanoflowers, nanorings and nanobelts, ZnO is one of the most preferred and investigated materials [4].

ZnO metal semiconductor oxides have a wide direct band gap of about 3.3 eV. ZnO is also low-cost, nontoxic and chemically-inert material. Additionally, ZnO has hexagonal structure [5]. It has been widely utilized in optoelectronic applications such as sensors, LCDs, UV laser diodes, solar cells and plasma displays [6].

There are many publications in literature about ZnO thin film production by using several techniques such as PLD [7], laser ablation [8], sol–gel [9], sputtering [10], MBE [11] and CBD [12].

CBD technique is very low cost. It does not require vacuum and complicated procedures. In addition, the low working temperature and fast thin film deposition times are advantageous over other thin film deposition techniques. [13]. In this work, thin films were prepared via CBD technique. Deposition of ZnO thin film completed only 30 min and no annealing required to crystallize the produced thin film. Effects of bath temperature on c-axis preferred orientations and band gap of semiconductor ZnO films were examined.

II. EXPERIMENTAL STUDY

Thin films were prepared via CBD technique at varying bath temperatures on glass substrates. 100 ml of 0.1M Zinc nitrate hexahydrate solution was prepared. The pH was fixed to 10 by adding ammonia to the solution. Prior to thin film deposition, aceton, methanol and distilled water were used to clean glass substrates. Clean substrates were dipped in the bath solution and it was heated on magnetic stirrer with a temperature-controller. The bath solution was set to 75°C-90°C for A, B, and D series, respectively (Table 1).

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Thin film deposition was performed in 30 minutes for each series. After the deposited thin films were removed from the bath solution, distilled water were used to wash the films. Produced thin films were dried at room temperature. Annealing process was not required to crystallize the thin films.

Table 1. Label of ZnO thin films

Bath temperature	Label
75°C	A
80°C	B
85°C	C
90°C	D

The structural, surface and optical properties of the samples were characterized and the results were examined comparatively.

III. RESULTS AND DISCUSSION

Semiconductor ZnO thin films' crystal structure was determined via XRD measurements. (X-ray diffractometer: Panalytical Empyrean). CuKα radiation was used and the measurement was performed in the 30°-60° 2θ range at the room temperature. In Figure 1, XRD spectra of ZnO semiconductor thin films were shown. All obtained ZnO semiconductor thin films have hexagonal structure. The diffraction patterns were matched with ZnO (hexagonal structure, ICDD:98-003-1052). Also thin films were in polycrystalline nature. In A series, (010) and (011) peaks of hexagonal ZnO structure in poor intensity were started to be observed at 75°C bath temperature. There is no preferred orientation for A series. B and C series deposited at 80°C and 85°C bath temperature have a preferred orientation towards (011) peak. C series have a strong preferred orientation towards (011) peak. When the bath temperature increased to 90°C, the preferred orientation changed towards (010) peak. The increase in bath temperature has changed the preferential orientation.

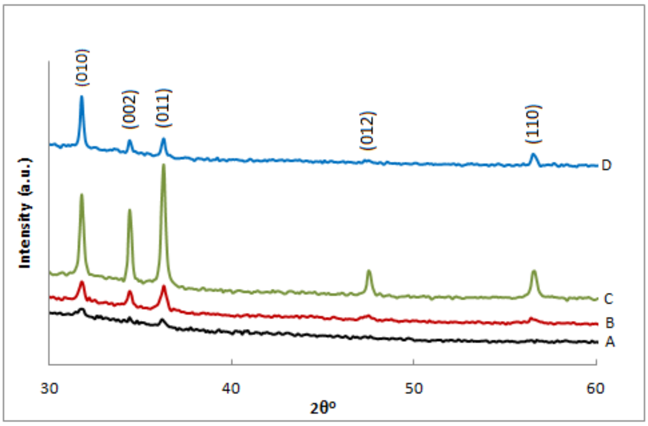


Figure 1. XRD spectra of ZnO semiconductor thin films.

The crystallite sizes of all samples were calculated by Scherrer's equation [14];

$$D = \frac{0,9\lambda}{\beta cos\theta} \tag{1}$$

Where λ; the wavelength of X-rays, β; the full width at half maximum value and θ is the angle of diffraction. The crystallite size values were given in Table 2. As seen from the table, the crystallite size values increase as the bath temperature increases.

Table 2. The crystallite size values of ZnO thin films

Series	D (nm)
A	30
B	38
C	47
D	62

The morphological properties of ZnO semiconductor thin films were determined by Zeiss Supra 40 VP FESEM. FESEM images showed that ZnO thin film structure was occured by flower-like nanorods. FESEM images of ZnO semiconductor thin films were shown in Figure 2. As it seen in the series A, the flower-like nanorod structure was not fully developed. In the thin films deposited at 80°C and 85°C (B and C series), the alignment of the nanorods was usually vertical, while in the films deposited at 90°C (D series), the nanorods mostly formed horizontally. These FESEM images also proved that the preferential orientation has changed from (011) to (010). FESEM images are in agreement with XRD results.

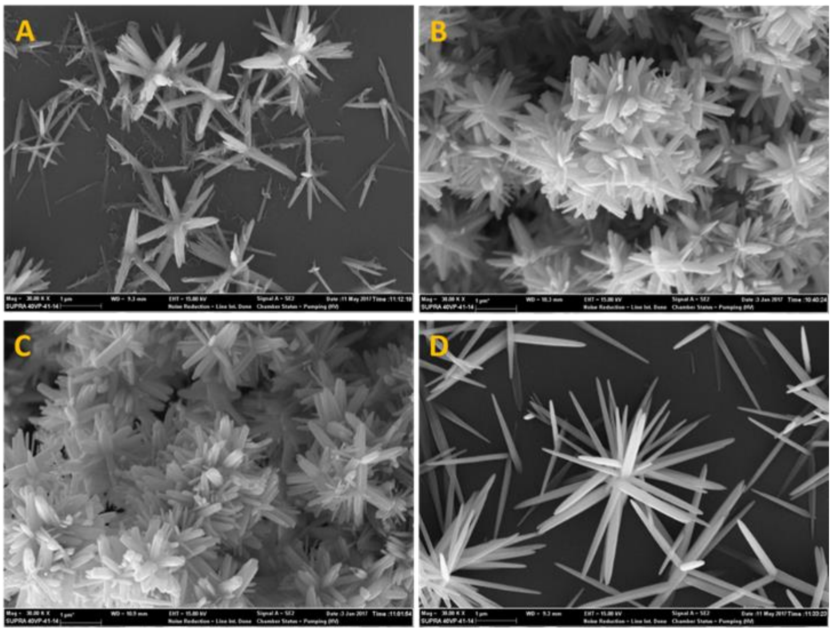


Figure 2. FESEM images of ZnO semiconductor thin films.

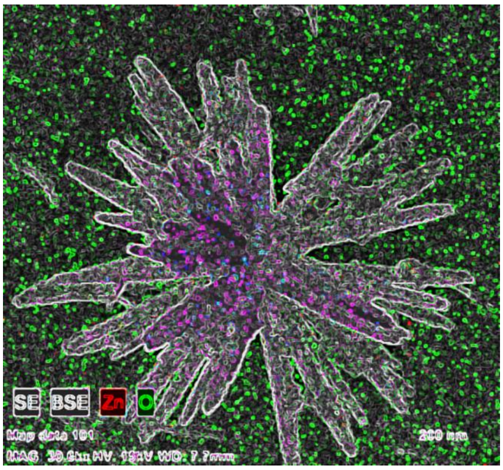
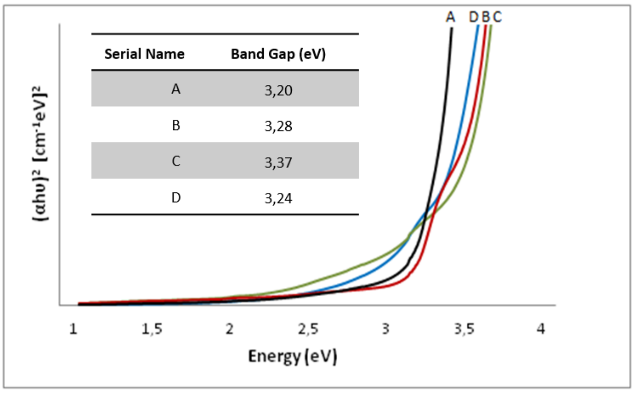


Figure 3. Elemental mapping image of ZnO nanoflower.

Elemental mapping results of ZnO nanoflower taken by the EDX detector was given in Figure 3. The green dots show the oxygen (O) atoms, and the red dots show the zinc (Zn) atoms. This image indicates that the nanoflower is zinc oxide (ZnO).

The band gap values of ZnO semiconductor thin films was specified by absorption spectra which were measured by Perkin Elmer Lambda 25 UV-Vis. Spectrophotometer (Wavelength: 300-1100 nm). Tauc method [15] was used to find out the band gap values. Due to Tauc method, the band gap energy value of the material is the point at which the linear part of the graph cuts the energy axis. In Figure 4, the of plots of (αhυ)2 versus energy and band gap values of ZnO semiconductor thin films were presented. The band gap values of ZnO films determined between 3.20 to 3.37 eV. The band gap value of ZnO thin films increased to 3.37 eV as the bath temperature increased to 85°C. When the bath temperature increased to 90°C the band gap value strongly decreased to 3.24 eV. The decrease in the band gap value is due to the dramatic increase in the crystallite size value at 90°C of bath temperature and the change in preferential orientation. This results showed that the band gap values of ZnO semiconductor thin films depend on the bath temperature.



Serial Name	Band Gap (eV)
A	3,20
B	3,28
C	3,37
D	3,24

Figure 4. The plots of $(\alpha h\upsilon)^2$ vs. energy and band gap values of ZnO semiconductor thin films.

IV. CONCLUSION

ZnO semiconductor thin films were produced via CBD technique at varying bath temperatures to investigate effects of varying temperature on c-axis preferred orientations and band gap values. In this technique, deposition of ZnO thin film completed only 30 min and no annealing required to crystallize the produced thin film. All obtained ZnO semiconductor thin films have hexagonal structure and polycrystalline nature. Although hexagonal ZnO structure in a very small intensity were started to be observed at 75°C bath temperature, there is no preferred orientation in A series. B and C series deposited at 80°C and 85°C bath temperature have a preferred orientation towards (011) peak. When the bath temperature increased to 90°C, the preferred orientation changed towards (010) peak. It was showed that the increase in bath temperature has changed the preferential orientation. It was seen from FESEM images that that ZnO structure was formed by flower-like nanorods. In the series A, the structure was not fully formed. In B and C series, the alignment of the nanorods was usually vertical, while in the films deposited at 90°C (D series), the nanorods mostly formed horizontally. These FESEM images also proved that the preferential orientation has changed from (011) to (010). These structural and morphological characterizations indicated that preferred orientation of ZnO thin films can be easily changed by increasing the bath temperature in chemical bath deposition technique. The band gap values of ZnO thin films varied from 3.20 to 3.37 eV. The band gap value of ZnO thin films increased to 3.37 eV as the bath temperature increased to 85°C. When the bath temperature increased to 90°C the band gap value strongly decreased to 3.24 eV. This results showed that the band gap values of ZnO semiconductor thin films depend on the bath temperature. In ZnO semiconductor thin film applications that require lower band gap, the band gap value can be reduced by increasing the bath temperature in chemical bath deposition technique.

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