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# Effects of Annealing on Reflectance of ZnO Grown by PFCVAD

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## Abstract

ZnO thin film was prepared onto microscope glass slide substrate by using pulsed filtered cathodic vacuum arc deposition system. ZnO thin film was thermally annealed for one hour at three different temperatures in air. The film structure was investigated as a function of annealing temperature by x-ray diffraction (XRD). As-deposited film shows amorphous property. The grain size increases with the increase of annealing temperature. The dependence of optical properties on annealing was investigated using UV–Vis-NIR spectrophotometer. When the annealing temperature increased, the diffuse reflection was reduced. When the angle of incidence specular reflectance increased from angle of 30 degrees to angle of 60 degrees, specular reflectance was increased. When annealing temperature increased, specular reflectance was also increased for angle of 30 and 60 degrees. In addition the optical band gap of ZnO film was observed and found to be varying from 3.22 eV to 3.25 eV with the annealing temperature.

**Keywords:** Zinc oxide (ZnO), Annealing temperature, Diffuse and specular reflectance, Optical band gap

# PFCVAD ile Büyütülen ZnO’nun Yansıma Üstüne Tavlamanın Etkileri

## Özet

ZnO ince film atmalı filtreli katodik vakum ark depolama sistemi kullanılarak mikroskop cam alttaş üzerine hazırlandı. ZnO ince film havada üç farklı sıcaklıkta bir saatte ısısal olarak tavlandı. Film yapısı XRD ile tavlama sıcaklığının bir fonksiyonu olarak incelendi. Tavlanmamış film amorf özellik gösterdi. Tavlanan ZnO film (002) düzleminin tercihli yönelimi ile wurtzite yapıda çıktı. Tanecik boyutu tavlama sıcaklığının artması ile arttı. Tavlama üzerine optik özelliklerinin bağlılığı UV-Vis-NIR kullanılarak incelendi. Tavlama sıcaklığı arttığı zaman, dağınık yansıma azaldı. Gelen düzgün yansıma açısı 30 derecelik açıdan 60 derecelik açıya arttığı zaman, düzgün yansıma arttı. Aynı zamanda tavlama sıcaklığı arttığı zaman, düzgün yansıma 30 ve 60 dereceli açılar için arttı. Buna ek olarak ZnO filminin optiksel bant aralığı incelendi ve tavlama sıcaklığı ile 3.22 eV’tan 3.25 eV ‘a değiştiği bulundu.

**Anahtar Kelimeler:** Çinko Oksit (ZnO), Tavlama sıcaklığı, Dağınık ve düzgün yansıma, Optiksel bant aralığı

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# 1.Introduction

Zinc oxide (ZnO) films with a hexagonal wurtzite crystal structure [1] is a wide and direct bandgap of 3.37 eV (300 K) and exciton binding energy up to 60 meV with very interesting properties [2]. Zinc oxide is a promising transparent conductive oxide (TCO) and there is an unceasing interest on its luminescence and electrical properties during the last decades. Transparent conductive oxide (TCO) thin films have used generally for transparent conductive electrodes in flat panel displays and solar cells [3]. Many techniques for the preparation of ZnO films have been used: these include electrochemical deposition [4], cathodic electrodeposition [5], radio-frequency sputtering method [6], pulsed laser deposition [7,8], RF magnetron sputtering [9], metal organic chemical vapor deposition method [10], atomic layer deposition [11], ultrasonic spray pyrolysis [12], filtered vacuum (cathodic) arc deposition (FVAD, FCVD) [13].

Pulsed filtered cathodic vacuum arc deposition (PFCVAD) is a common technique to prepare oxide, where various methods are employed to remove macroparticles inherent to arc evaporation itself. By using this technique, the resultant films can be obtained on a rather low substrate temperature and thermal residual stress in the film could be low compared to other high temperature processes. On the other hand, the films usually adhere well due to the induced ion mixing by the bombardment of energetic particles. ZnO thin films which are deposited using this technique perform high optical transmittance in visible region and low resistivity [14 - 17].

These features make the pulsed cathodic vacuum arc an ideal source for the production of metal oxides and nitrides [18]. Besides that, with the pulsed filtered cathodic vacuum arc deposition (PFCVAD) technique it is possible to control the thickness at the atomic scale and there is no need to cool the system.

Structural, electrical and optical properties of ZnO films are strongly affected not only by the deposition conditions but also by the annealing conditions. Thermal annealing is a method widely used to improve crystal quality and to study structural defects in materials. Annealing is also an important method for changing luminescence character.

In this paper, the structural and optical properties of ZnO thin film prepared by pulsed filtered cathodic vacuum arc deposition technique and the effects of different annealing conditions are studied by x-ray diffraction (XRD) and UV-Vis-NIR spectrophotometer: in particular, the x-ray diffraction, energy band gap, diffuse reflectance and specular reflectance have been measured to observe the effect of the annealing.

# 2. Experimental

## 2.1. Preparation of thin film

ZnO thin film is grown on microscope glass slide substrate by pulsed filtered cathodic vacuum arc deposition using metallic target (Zn) (1 mm in diameter and purity 99.999 %) which was held in an alumina ceramic tube employed as a cathode target. The details of deposition system were published in earlier studies [19]. In this work, the substrate temperature is kept at room temperature, the base pressure of the deposition chamber is around $10^{-8}$ Torr and the working pressure is a least $6.5x10^{-4}$ Torr. High purity (99.999 % pure) oxygen is introduced into the chamber and controlled by multi gas controller. While the film was being deposited, trigger voltage and arc voltage settings were 20 kV and 500 V, respectively. After deposition, the film was annealed at 150, 350 and 500$^{\circ}$C temperature for 1 h in air.

## 2.2. Characterization

In order to investigate the crystalline properties, ZnO film grown on glass substrate is examined by θ-2θ X-ray diffraction (XRD) measurements. For XRD studies, we used Rigaku Smartlab 9 kW rotating anod system with Cu target.

Total and diffuse reflectance of the ZnO was measured over a wavelength range of 200–800 nm, using a double-beam UV–Vis–NIR spectrophotometer (Cary 5000, Varian) with a Cary 5000 Internal Diffuse Reflectance accessory (DRA) consists of a 110 mm diameter integrating sphere and Harrick Scientific's Specular Reflection Accessories (ERA-30G and ERA-60G) for measurement reflectance at 30 and 60 degrees. Baseline was recorded with the polytetrafluoroethylene (PTFE) reference disk covering the reflectance port. The total (diffuse and specular) or the diffuse-only reflectance may be measured by mounting the sample against the sphere port in two different configurations. Data were collected at a scan rate of 600 nm/min with a data interval of 1.0 nm, a signal band width of 2.0 nm, and signal-averaging time of 0.1 s in UV-Vis range. Optical transmission and absorption were measured in the 200–3000 nm wavelength range using the same spectrometer. We have obtained the thickness of the film from the transmission spectra according to the interference theory.

# 3. Results of Discussion

## 3.1. Structural studies

XRD studies used to analyze the growth orientation and the crystallite size of the as-deposited and annealed ZnO thin film at different annealing temperatures. PFCVAD ZnO film was annealed in air at temperatures of 150 and 500$^{\circ}$C with 1 h annealing times. The x-ray diffraction patterns are given in Fig. 1 for as-grown sample and ones annealed at three different annealing temperatures. The bottommost graph belongs to the as-grown ZnO sample and this is followed by that obtained after annealing at 150$^{\circ}$C for 1 h. The third line is obtained for the sample annealed at 350$^{\circ}$C for 1 h. The fourth line is obtained for the sample annealed at 500$^{\circ}$C for 1 h.

The full width at half-maximum, FWHM, decreases with increasing annealing temperatures. That decrease is generally related to an improvement of the crystal quality of the ZnO film and to an enlargement of the grain size. From XRD studies (Fig. 1) it is clear that annealed film exhibits preferential orientation with c-axis perpendicular to the substrate surface, which indicates the ZnO thin film is of hexagonal wurtzite crystal structure. A dominant peak positioned at 34.32$^{\circ}$ corresponding to the (002) hcp direction was observed. As-deposited film showed amorphous property.

The grain sizes of the crystallites were determined from x-ray diffraction data. The crystallite grain size $D$ can be estimated using the Scherrer Formula [20]

$$D = \frac{0.9\,\lambda}{\beta cos\theta}$$

where $\lambda$ is the x-ray wavelength, $\theta$ is the Bragg diffraction angle, $\beta$ is the FWHM in radians. Table 1 shows the variation of grain size with annealing temperature. Grain size increased from 17.33 nm to 20.80 nm as annealing temperature was increased from 150 to 500$^{\circ}$C.

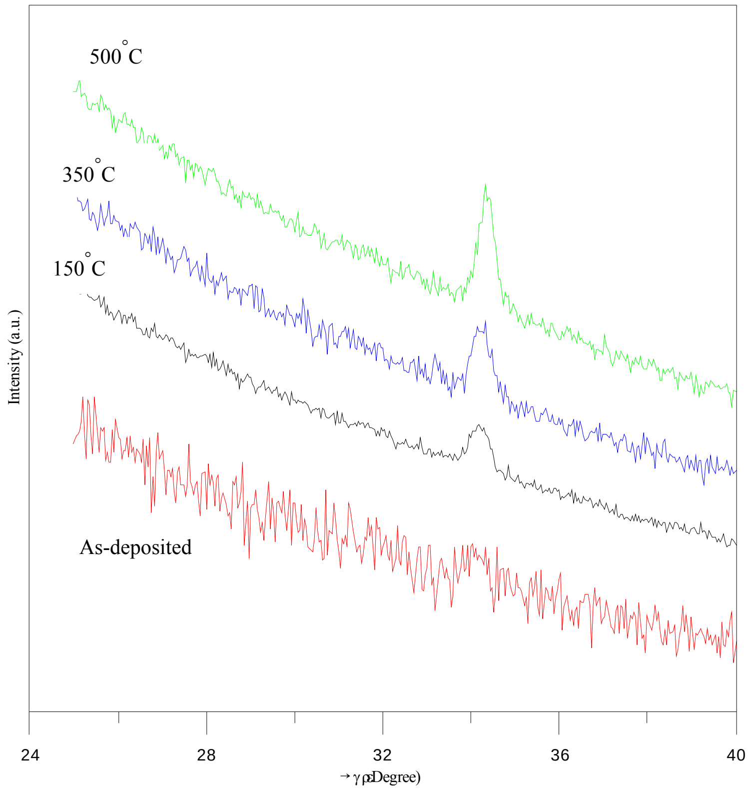


Fig.1. XRD spectrum of as-deposited and annealed ZnO film.

Table 1. The variation of grain size with annealing temperature.

| | Annealing Temperature | | | |
|---|---|---|---|---|
| | As-deposited | 150°C | 350°C | 500°C |
| 2 θ (Degree) | - | 34.32 | 34.32 | 34.32 |
| Grain Size (nm) | - | 17.33 | 18.91 | 20.80 |
| FWHM (Degree) | - | 0.48 | 0.44 | 0.40 |

## 3.2. Optical Result of ZnO thin film on glass substrate

### 3.2.1. UV-Vis total and diffuse reflectance measurement

The optical property of ZnO grown on glass substrate is carried out using a Varian Carry 5000 model UV–Vis–NIR Spectrophotometer with an integrating sphere. We have measured total and diffuse reflectance in a range of 200–800 nm. Fig. 2 shows the total reflectance spectrum of the as-deposited and annealed ZnO thin film at different annealing temperatures. It is observed that the total reflectance for ZnO thin film increases with increasing the annealing temperature. 150°C film show the same optical properties that are similar to as-deposited ZnO. Therefore, optical properties of 150°C film haven't shown in Fig.2.

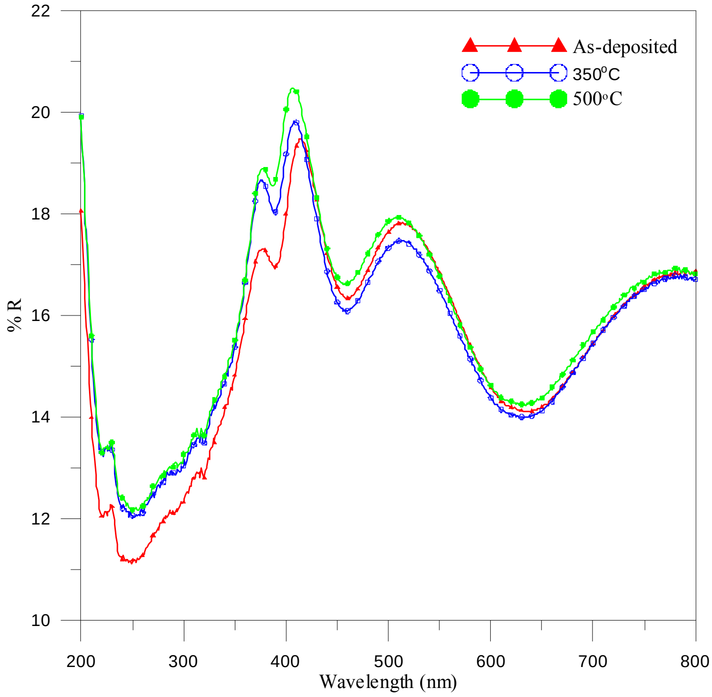


Fig.2. Total reflectance spectra of ZnO film as-deposited and annealed at different temperatures.

Diffuse reflectance spectra of as-deposited and annealed ZnO film is shown in Fig. 3. From the Fig. 3 it is observed that as the annealing temperature increased the diffuse reflectance is reduced.

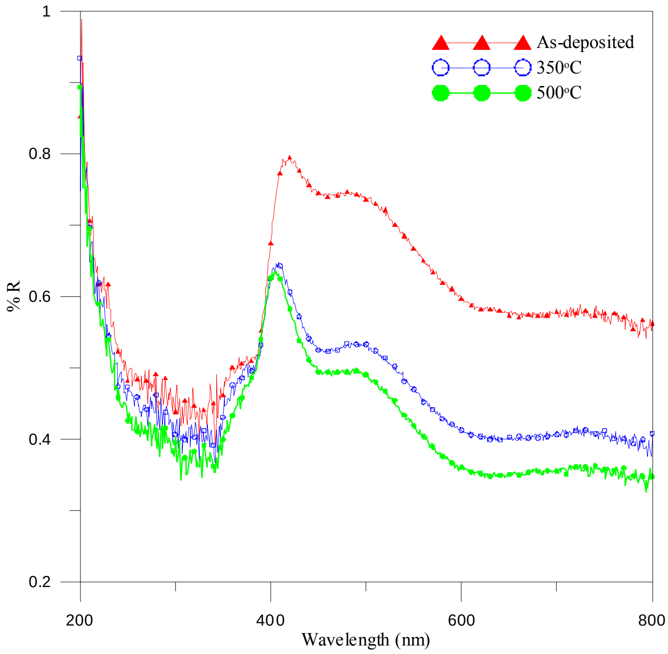


Fig.3. Diffuse reflectance spectra of ZnO film.

The increase of total reflectance and decrease of diffuse reflectance can be related with the increasing crystal quality of the film as the annealing temperature increased. This conclusion is also supported by XRD studies. While the full width at half-maximum decreases with increasing annealing temperatures, total reflectance increases. That is generally related to an improvement of the crystal quality and surface of the ZnO film.

### 3.2.2. Angle of Incident Dependant Specular Reflection measurements

Angle of incident dependant specular reflection spectra of prepared film are measured for 30° and 60° degrees. The variations of the specular reflectance as a function of wavelength for both as-deposited and annealed film of ZnO with different annealing temperatures are shown in Fig. 4 and Fig 5 for 30 and 60 degrees, respectively.

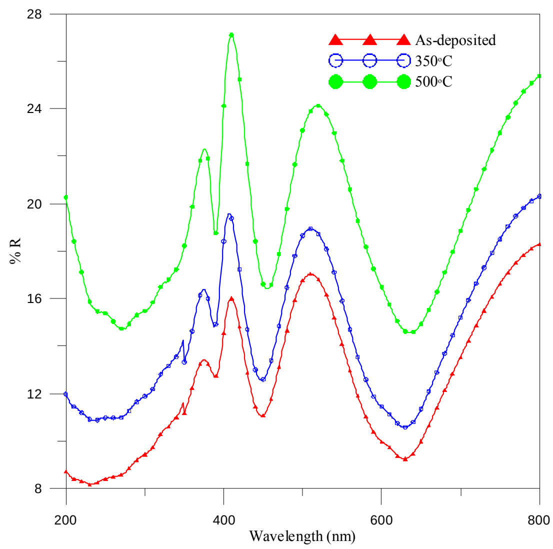


Fig.4. The variations of the specular reflectance (for 30 degrees) as a function of wavelength for as-deposited and annealed films of ZnO with different annealing temperatures.

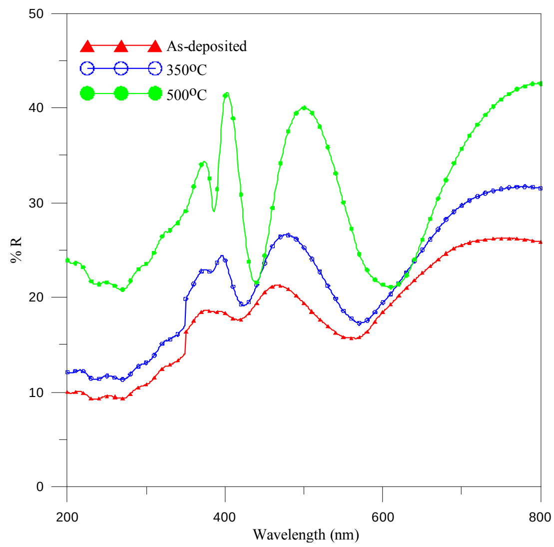


Fig.5. The variations of the specular reflectance (for 60 degrees) as a function of wavelength for as-deposited and annealed films of ZnO with different annealing temperatures.

In Fig 4, it has been observed that the value of specular reflectance for 30 degrees increases with the increase in wavelength. A similar behavior is encountered in Fig. 5 which shows the angle of incident specular reflection spectra for 60 degrees of the as-deposited and annealed ZnO thin film recorded in the range 200–800 nm. However, for higher angle of incident higher reflectance intensities are observed.

As a result, we conclude that the incident specular reflectance increases for both the increase in annealing temperature and the angle of incidence which clearly displays that as the annealing temperature increases from 350 to 500°C the optical quality of the sample is enhanced [21].

### 3.2.3. UV-Vis-NIR Absorbance Measurements

Optical properties of as-deposited and annealed ZnO thin film are studied in the wavelength ranging from 175 to 3000 nm. In Fig. 6, the absorption spectra of as-deposited and annealed ZnO thin film for 350°C and 500°C are shown. Sharp changes in the spectra at 350 and 800 nm are caused by experimental artifacts for switching sources.

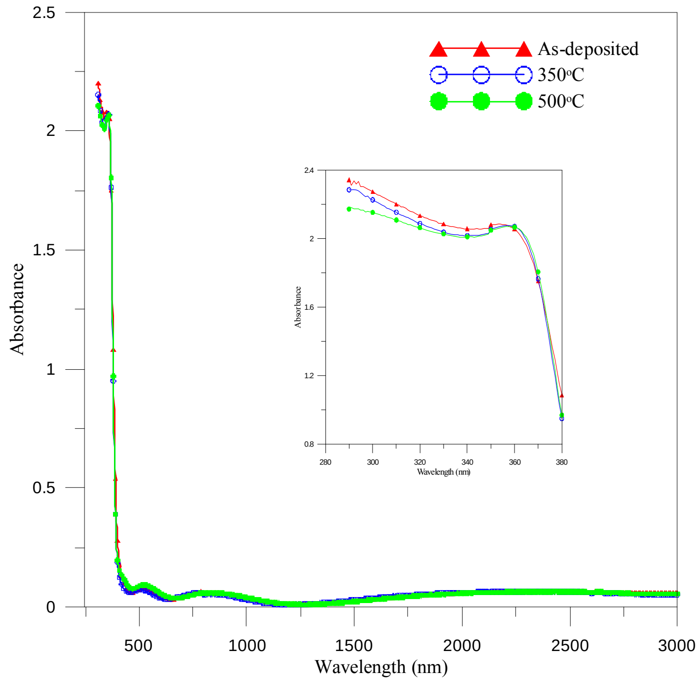


Fig.6. The absorption spectra of as-deposited and annealed ZnO thin film.

Independent of the annealing temperature the film is displayed high transparency in visible wavelength, infrared and far infrared regions. However in the beginning of the UV region, there is a relatively sharp absorption band for 360-400 nm and right on the left shoulder of this absorption band, the exciton absorption peak maxima at 354, 358 and 361 nm can be observed for as-deposited, annealed at 350°C and 500°C, respectively as shown in inset of Fig. 6. From these values it is clear that the exciton absorption peaks are shifted towards the longer wavelengths as increasing annealing temperatures [22, 23].

As a direct band gap semiconductor, ZnO film has an absorption coefficient (α) obeying the following relation for high photon energies ($h\nu$)

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2} \tag{1}$$

where $E_g$ is the optical band gap of thin film, and A is a constant [24,25]. Near the absorption edge, can be expressed as

$$\alpha = -\mathrm{Ln}(T)/d \tag{2}$$

where $d$ is the film thickness [26].

In the present case, the Tauc plot of $(\alpha h\nu)^2$ versus $(h\nu)$ (Fig.7) indicates the direct band gap nature of the film.

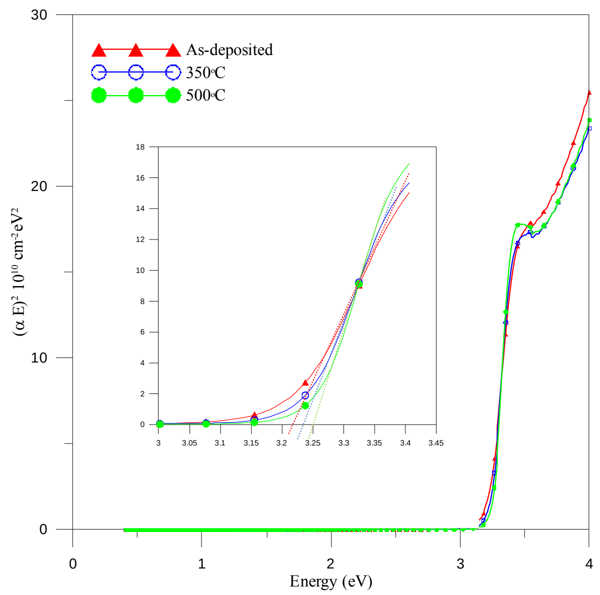


Fig. 7. $(\alpha E)^2$ against photon energy ($E$) in ZnO: as-deposited and annealed film for 1h.

Extrapolating the linear portion of the curve onto the x-axis gives the energy band gap of the film [24,25]. The band gap increased from 3.22 eV to 3.25 eV for film annealed at 350°C and 500°C. Here the band gap increased with increase in annealing temperature [27,28]. Several factors can be effective for the energy band gap dependence to annealing temperature some of these effects are the $O_2$ absorption of the film [28] and Burstein-Moss (BM) effect as discussed in details in Ref [29-31].

# Conclusion

401 nm thick ZnO thin film, deposited on glass substrate by filtered cathodic vacuum arc deposition system, are studied by using optical and XRD characterization methods. Our measurement show that the structural and optical properties of the ZnO thin film is enriched as the annealing temperatures increased in the range of room temperature - 500°C. From XRD studies, we see no crystallinity for as-deposited samples but annealing caused an enhancement in crystallinity. All the annealed film show (002) wurtzite crystal structure which is the preferred orientation of ZnO since it is the lowest surface energy of that plane. The grain sizes are 17.33, 18.91 and 20.80 nm for annealed ZnO thin film at 150, 350 and 500°C, respectively.

Complementary to XRD findings, we have found that the total reflectance for ZnO thin film increases with increasing annealing temperatures and diffuse reflectance decreases as annealing temperature increases. Finally, the optical energy bandgap of ZnO film is found to increase with increasing annealing temperatures. As a result, it is demonstrated that good quality ZnO thin film can be deposited by using the pulsed filtered cathodic vacuum arc deposition (PFCVAD) technique.

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