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Optical and Surface Properties of Nanostructured ZnO Semiconductor Thin Films Synthesized by RF Magnetron Sputtering

RF Magnetron Sıçratma ile Sentezlenen Nano Yapılı ZnO Yarıiletken İnce Filmlerin Optik ve Yüzey Özellikleri

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Abstract
In this research, ZnO thin films were deposited on glass microscope slides in three separate experiments with RF input powers of 50 W, 100 W and 125 W by means of RF magnetron sputtering technique. Each deposition process was conducted for 30 minutes. Spectroscopic reflectometer, UV-VIS spectrophotometer and atomic force microscope (AFM) were used to examine the effect of sputtering power on the optical and surface properties of the produced thin films. The level of reflectivity and transparency, refractive index and band gap energy values as well as surface homogeneity and roughness were observed to rely on the RF input power. The optical band gap energy values were about 3.83-3.87 eV. The produced highly transparent ZnO thin films can be used in various optoelectronic devices and future transparent conductive electrode implementations.

Anahtar kelimeler: RF magnetron sputtering, Surface properties, Optical properties, ZnO thin films

Öz
Bu araştırmada, RF magnetron sıçratma tekniği ile 50 W, 100 W ve 125 W RF güçleri ile üç ayrı deneyde ZnO ince filmler cam mikroskop lamlarının üzerine biriktirilmiştir. Her biriktirme işlemi 30 dakika sürdürülmüştür. Spektroskopik reflektometre, UV-VIS spektrofotometre ve atomik kuvvet mikroskobu (AFM), üretilen ince filmlerin optik ve yüzey özellikleri üzerine sıçratma gücünün etkisini incelemek için kullanılmıştır. Yansıtma ve geçirgenlik düzeyi, kırılma indisi ve yasak enerji aralığı değerleri ile yüzey homojenliği ve pürüzlülüğün RF gücüne bağlı olduğu bulunmuştur. Yasak enerji aralığı yaklaşık 3.83-3.87 eV civarındadır. Üretilen son derece şeffaf ZnO ince filmler, çeşitli optoelektronik cihazlar ve gelecekteki şeffaf iletken elektrot uygulamalarında kullanılabilir.

Keywords*: RF magnetron sıçratma, Yüzey özellikleri, Optik özellikler, ZnO ince filmler*

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1. Introduction

Transparent conducting oxides (TCOs) have been an attractive research topic in recent years since they are being used in the production of optoelectronic devices (e.g. touch screens, LCDs, solar cells and LEDs) (Lee et al., 2003; Muchuweni et al., 2016a,b). TCOs are required to show both high electrical conductivity along with high optical transparency in the visible region (Muchuweni et al., 2017). Nowadays, indium tin oxide (ITO) is the most common one among TCO materials (Sathiaraj, 2008; Srivastava and Kumar, 2013). Nevertheless, ITO has a number of drawbacks such as high cost, scarcity and toxicity; thus, there has been an effort to develop alternatives for ITO (Srivastava and Kumar, 2013). Moreover, when exposed to a hydrogen plasma environment, the optical and electrical properties of ITO are negatively affected (Lee et al., 2003). In this respect, it has been revealed that II-VI compound semiconductor zinc oxide (ZnO) may be an alternative material for ITO as it has unique optical and electrical properties, high chemical and mechanical stability, absence of toxicity, abundance in nature of Zn (Bedia et al., 2015; Muchuweni et al., 2016c; Sahal et al., 2008; Zahirullah et al., 2018). ZnO exhibits n-type conductivity. It has a direct wide band gap energy of 3.37 eV and large exciton binding energy of 60 meV at room temperature (Bedia et al., 2015; Panda and Jacob, 2012; Shinde et al., 2012; Zahirullah et al., 2018). As this semiconductor has a direct wide band gap, it is optically transparent for a large wavelength range in the solar spectrum (Bedia et al., 2015; Panda and Jacob, 2012). Depending on the growth conditions, the band gap energy of ZnO can be adjusted. By doing so, ZnO turns into a more usable material for optoelectronic applications (Güney and Ertarğın, 2015). Efficient emission at room temperature can be ensured due to its high exciton binding energy (Zahedi et al., 2014).

Although there are several studies on ZnO, it still holds its popularity among researchers (Özgür et al., 2019). The results show that thin films of ZnO can be used in varistors (Ezhilvalavan and Kutty, 1997), gas sensors (Xu et al.,2000), solar cell transparent contact fabrication (Bhatt et al., 1997), ultraviolet light-emitting devices (Deng et al., 2013), ultraviolet photodetectors (Soylu and Yakuphanoğlu, 2016), piezoelectric transducers and surface acoustic wave (SAW) devices (Nagayasamy et al., 2013), etc. Regarding its synthesis, ZnO thin films have been produced by several thin film manufacturing techniques including PLD (Sans et al., 2004), RF magnetron sputtering (Yang et al., 2008), CVD (Kashiwaba et al., 2000), spray pyrolysis (Paraguay et al., 1999), electrodeposition (Cembrero et al., 2004), sol-gel process (Kamalasanan and Chandra, 1996), etc. Among these fabrication processes, the RF magnetron sputtering has emerged as a method which is one of the most promising processing routes since it is especially provides economical production of thin, transparent and homogeneous oxide films on various substrates. It enables the adjustment of the refractive index and thickness of the film by changing deposition parameters. In this study, ZnO thin films were manufactured by RF magnetron sputtering method and considered the impact of RF sputtering power on optical and surface properties.

2. Experimental details

In the present study, three ZnO thin films were deposited on 75 mm × 25 mm × 1 mm glass microscope slides in three separate experiments with different RF powers of 50 W, 100 W and 125 W by means of RF magnetron sputtering technique at room temperature. There are many studies in literature where RF input power value is between 50 W and 300 W. The values chosen within them can be arbitrary. In order not to cause high heating of the target and to have more stable conditions during deposition, maximum 125 W RF power was applied to the target in this study A ZnO target was used as source material for all deposition processes. The diameter of the target was 50 mm while its thickness was 3 mm. The target was powered through a RF power supply operating at a frequency of 13.56 MHz. The substrate was directly fixed on a substrate holder positioned at 40 mm away from the target in all cases. For all depositions, sputtering chamber was evacuated down to 1×10^{-2} Torr by using a mechanical pump and then filled with 99.99% purity Ar gas. Chamber pressure was sustained to be 6×10^{-2} Torr during deposition process. Each deposition process was carried out for 30 min. Only top surfaces of the substrates were coated with ZnO. After being deposited, the samples were taken out for characterization. Deposition parameters are summarized in Table 1. The ZNO thin films deposited at the RF powers of 50, 100, and 125 W were labeled as ZNO50, ZNO100 and ZNO125, respectively.

The crystalline structure of the produced ZnO thin films was examined in the 2θ range of 20˚-80˚ by using an X-ray diffractometer (PANalytical Empyrean) with monochromated CuKα radiation (λ=1.54056 Å).

Table 1. Sputtering parameters of ZnO thin films

RF power (W)	Substrate to target distance (mm)	Working pressure (Torr)	Time (min)
50, 100, 125	40	6×10^{-2}	30

The reflectance spectra were obtained in the wavelength range of 400-1000 nm by a spectroscopic reflectometer (Filmetrics F20 Thin Film Analyzer). The film thickness (t) and spectral distribution of refractive index (n) were extracted through the spectral analysis of reflectance. The optical transmittance and absorbance spectra were recorded at normal incidence of light with a double beam UV-VIS spectrophotometer (UNICO 4802). The spectral region observed was 300-1100 nm. The optical energy band gap values were then derived from the absorbance spectra data via Tauc's method. In order to illustrate the surface topography, three-dimensional images were taken over a scale of 4 μm × 4 μm in non-contact mode by using an AFM (Ambios Q-Scope). The root mean square (RMS) roughness (Rq) parameter was acquired over the entire images.

3. Results and discussion

Figure 1 shows the XRD patterns of the produced ZnO thin films. X-ray diffraction study confirms that the synthesized material is ZnO with hexagonal wurtzite crystal structure and the entire diffraction peaks are in agreement with the standard JCPDS data (card No. 36-1451). No other undesired peaks were observed due to secondary phases or impurity phases within the detection limit of the X-ray diffractometer.

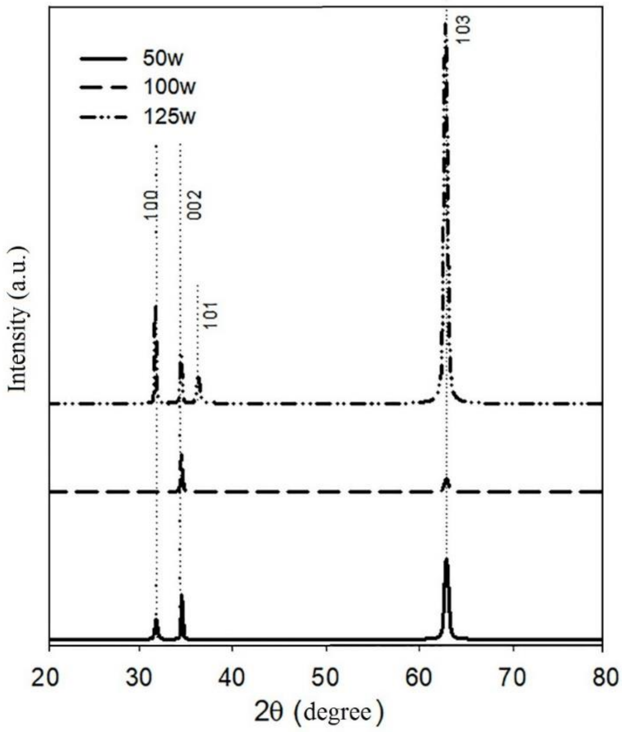

Figure 1. XRD patterns of the produced ZnO thin films

The reflectance spectra of the produced ZnO thin films are presented in Figure 2. The intensity of the reflected light varies with wavelength which depends on the film thickness and the optical constants (n and k) of the film. The experimentally obtained reflectance spectrum is compared with a theoretical reflection spectrum derived from the database of optical constants, and the thickness and optical constants are optimized until the best fit between the curves is achieved. The software gives the value of thickness and spectral distribution of optical constants of the film together with a goodness of fit (GOF) value. The film thickness values obtained from the spectroscopic reflectometry measurements are 30, 39 and 67 nm for the corresponding RF powers 50 W, 100 W and 125 W, respectively. The RF power applied to the target and the obtained film thickness may not be directly proportional (Aznilinda et al, 2012). With the increase in RF power, the kinetic energy of the sputtered particles also increases, which then leads to the increase of the sputtering yield. In other words, at the higher RF power, the bombarding ions have higher kinetic energy due to momentum transfer, so that more atoms will be sputtered (Hwang et al., 2003). The sputtered atoms get higher energy at higher RF power and results the higher ZnO molecules arriving at substrate compare at lower RF power deposition and it contributes to the film growth (Yu et al., 2005). This situation is more prominent here after 100 W. It is also found that produced relatively thicker ZnO films exhibit higher reflectance than thinner ZnO films in the observed wavelength range.

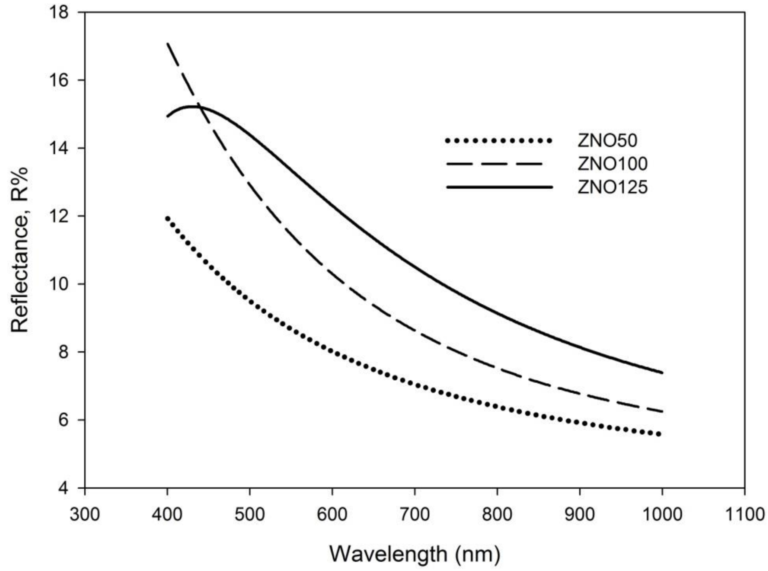

Figure 2. The reflectance spectra of the produced ZnO thin films

The spectral distributions of refractive index of the produced ZnO thin films are presented in Figure 3. The result is in good agreement with relevant literature (Gümüş et al., 2006; Çağlar et al., 2009). Refractive index measurements were realized using Cauchy model. Cauchy equation for the refractive index is given by:

$$n(\lambda)=A_n+B_n/\ \lambda^2+Cn/\ \lambda^4 \text{ and } k(\lambda)=0 \qquad (1)$$

where A_n, B_n and C_n are the fitting parameters used in Cauchy model. As shown in the figure, the refractive index strongly depends on the RF power. The increment of deposition rate with the increasing RF power first levels the refractive index value due to an increase of film packing density. Further rise of RF power brings about a strong decrease of refractive index and density.

The transmittance and absorbance spectra of the produced ZnO thin films are presented in Fig. 4. Optical transmittance spectrum shows that the films have high transmission in the visible region. This observation is in line with relevant literature (Golovynskyi et al., 2018). The absence of optical interference fringes in the spectrum indicates that the ZnO films are thin (Cruz et al., 2018). High transmittance in the visible region is typical of transparent conductive oxides. However, the transmittance decreased with the increasing film thickness. In relatively thicker films, more states are available for the photons to be absorbed. This observation also confirms relevant literature (Shariffudin et al., 2012). In transparent metal oxides, ratio of metal to oxygen also determines the level of transparency. A metal rich film often shows less transparency (Çağlar et al., 2006). It is found out that the absorbance of the ZnO films is high at short wavelengths (λ<380 nm) and low at longer wavelengths. Hence the films have potential application in fabrication of solar cells (Ezenwa, 2012). As the RF power increases absorption decreases because of inverse relation between transmission and absorption. It can be also seen that the absorption edge moves towards a higher wavelength with the increasing RF power.

The optical band gap energy of the produced ZnO thin films can be obtained from the relationship between the optical absorption coefficient and the absorbance.

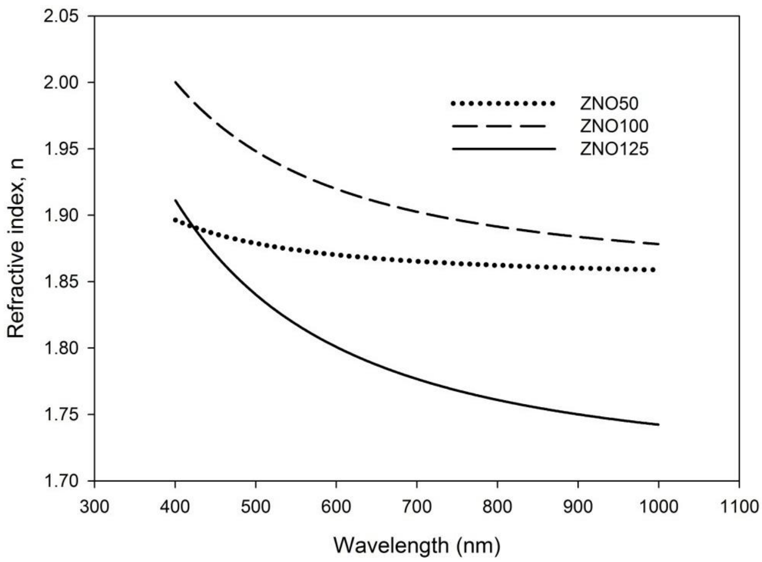

Figure 3. The spectral distributions of refractive index of the produced ZnO thin films

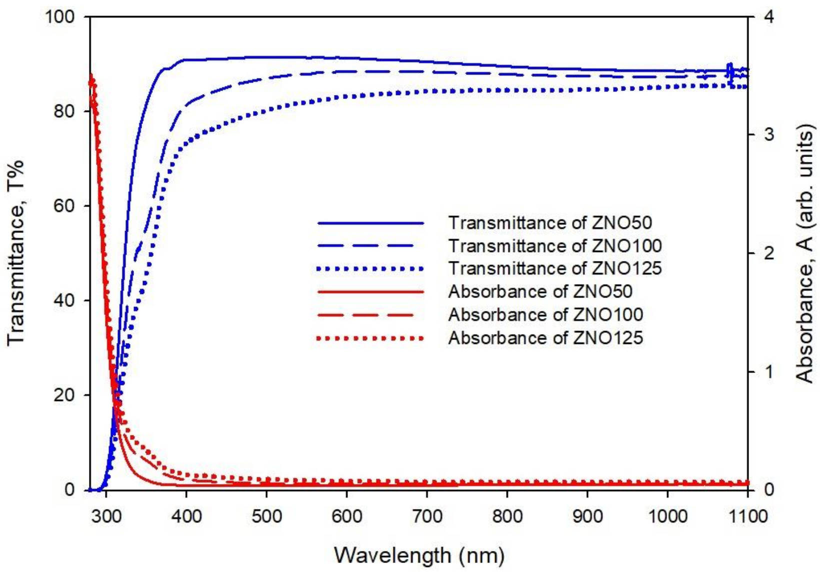

Figure 4. The transmittance and absorbance spectra of the produced ZnO thin films

The absorption coefficient α near the absorption edge is given by $\alpha = 2.303A/t$ where t is film thickness. For a semiconductor with a direct band gap, the optical band gap can be expressed by the Tauc method (Tauc et al., 1966):

$$(\alpha h\gamma)^2 = A(h\gamma - E_g) \quad (2)$$

where A is a proportional constant, hγ is the photon energy of the incident photon, and E_g is the optical band gap energy. The optical band gap energy is obtained by extrapolating the tangential line to the photon energy axis in the plot of $(\alpha h\gamma)^2$ versus hγ, as shown in Figure 5. The optical band gap values obtained via the Tauc method are 3.87, 3.84 and 3.83 eV for the corresponding RF powers 50 W, 100 W and 125 W, respectively. These values are in parallel with related literature (Mursal et al., 2018).

The 3D AFM images of the produced ZnO thin films are presented in Figure 6. The produced ZnO film surfaces show mount-like structures. ZNO50 has the most homogenous surface without pores and the smallest grains. When RF power increases from 50 W to 100 W, grains become larger in both lateral and vertical directions. ZNO125 has a more homogenous surface than ZNO100. The grain size of ZNO125 is lower than that of ZNO100. The RMS (Rq) values obtained from the AFM measurements are 1.08, 9.04 and 4.11 nm for the corresponding RF powers 50 W, 100 W and 125 W, respectively.

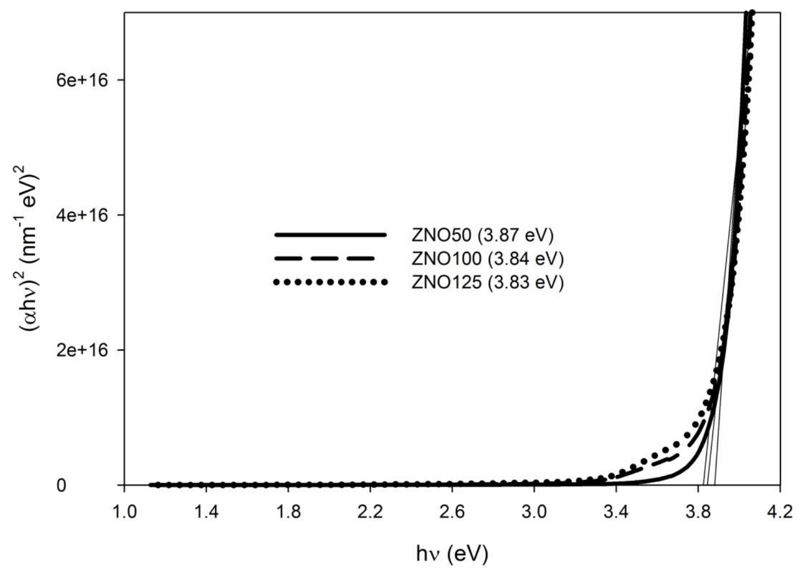

Figure 5. Plots of $(\alpha h\nu)^2$ vs. hν to estimate the Eg values of the produced ZnO thin films

The surface roughness can affect optical properties of thin films and depends not only on grain size but also on the number, shape and orientation of grains. As a result, the RMS roughness of the produced thin films increases with the decreasing surface homogeneity due to a textured surface formation with larger pyramidal structures. This result is partly similar to the observation reported in the relevant literature (Silva et al., 2014).

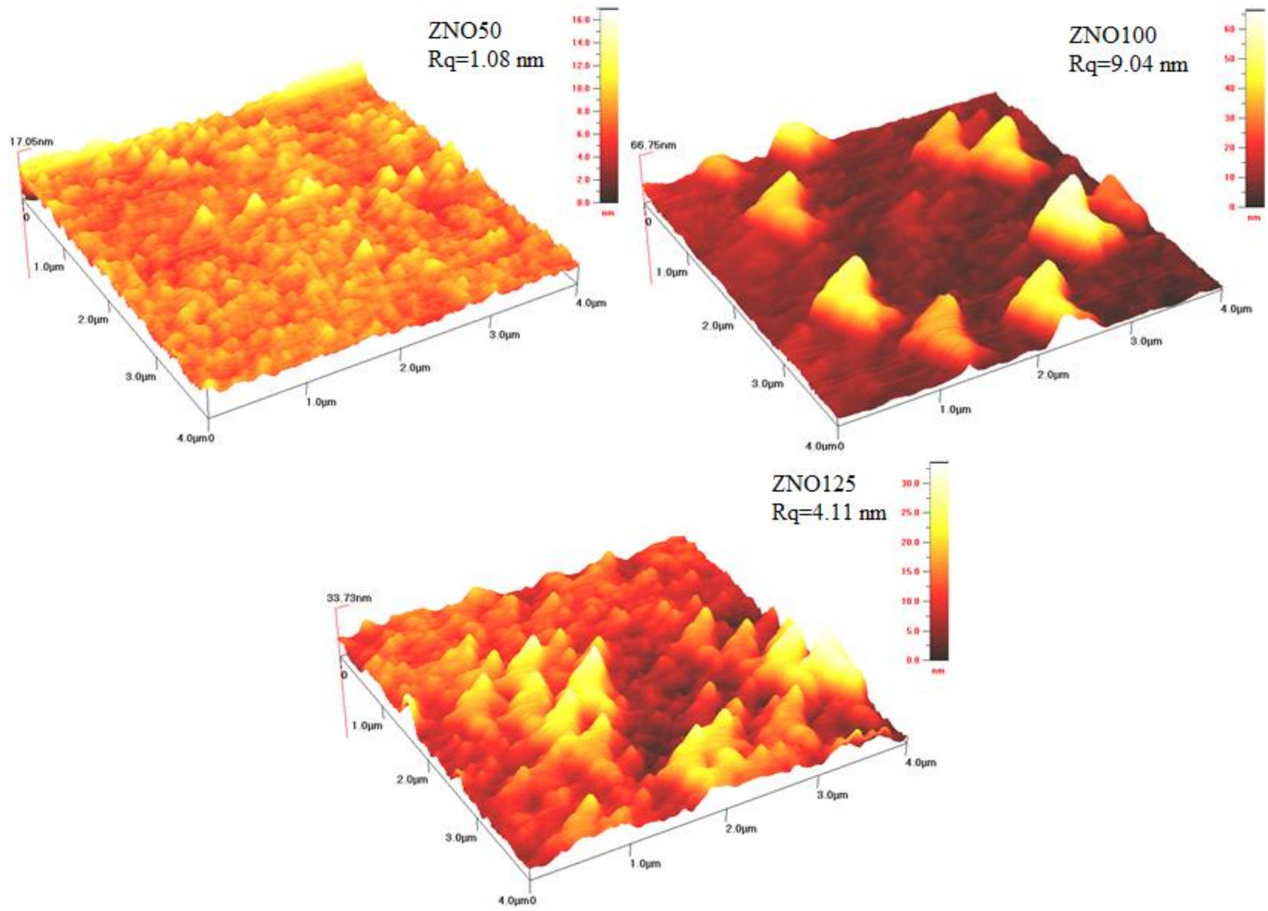

Figure 6. 3D AFM images of the produced ZnO thin films.

4. Conclusion

In conclusion, ZnO thin films having different thickness values were produced on glass substrates in three separate experiments with RF powers of 50 W, 100 W and 125 W by means of RF magnetron sputtering technique. The produced ZnO thin films were investigated by several instrumentation techniques. According to the current results, deposition rate increases with the increasing RF power. The produced films are highly transparent in the visible region. Relatively thicker ZnO films exhibit higher absorption and reflection. The high UV absorption of ZnO can be used in various areas such as cosmetics, paints, and varnishes. The refractive index values show normal dispersion and decrease with the increasing wavelength. It is observed that the refractive index value of ZnO films can be tuned by changing RF power. The optical band gap energy values are about 3.83-3.87 eV. A ZnO thin film having a smooth and homogenous surface can be obtained with a relatively low RF power such as 50 W.

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