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Investigation of Optical and Morphological Properties of Co Doped ZnO Nanomaterials

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Abstract: ZnO is one of the high quality materials for optoelectronic applications due to its wide band gap. ZnO nanostructures must be added to improve the morphological and optical properties of optoelectronic devices for nanotechnology applications. In this study, 1%, 5% and 10% Co elements were added to ZnO nanomaterial and samples were produced by sol gel spin coating method. When the samples were produced, coating process was carried out using a rotation speed of 1500 rpm and a rotation time of 25 seconds. Coating process repeated 5 times. Two-dimensional and three-dimensional images of the films produced using Atomic Force Microscopy (AFM) were analyzed. The surface morphology and surface roughness of the films were examined with the help of these analyzes. The transmittance and absorption spectra of the produced films with UV-VIS spectroscopy were taken and the optical properties were examined by calculating the optical band gap. While the increase in roughness values increased with the addition of co, the decrease in the transmittance values of the optical band gap range increased up to 10% Co contribution and a 10% Co contribution decreased.

Key words: ZnO, Co, Thin Film, Sol Gel Spin Coating.

Co Katkılı ZnO Nanomalzemelerin Optik ve Morfolojik Özelliklerinin Araştırılması

Özet: ZnO, geniş bant aralığı nedeniyle optoelektronik uygulamalar için yüksek kaliteli malzemelerden biridir. Nanoteknoloji uygulamalarda optoelektronik cihazların morfolojik ve optik özelliklerini geliştirmek için ZnO nanoyapılara katkılar eklenmelidir. Bu çalışmada ZnO nanomalzemesine % 1, % 5 ve % 10 Co eklenmiş ve numuneler sol jel spin kaplama yöntemiyle üretilmiştir. Numuneler üretilirken, 1500 rpm'lik bir dönme hızı ve 25 saniyelik bir dönme süresi kullanılarak kaplama işlemi gerçekleştirilmiştir. Kaplama işlemi 5 kez tekrarlanmıştır. Atomik Kuvvet Mikroskobu (AFM) kullanılarak üretilen filmlerin iki boyutlu ve üç boyutlu görüntüleri analiz edilmiştir. Bu analizler yardımıyla filmlerin yüzey morfolojisi ve yüzey pürüzlülüğü incelenmiştir. Üretilen filmlerin UV-VIS spektroskopisi ile geçirgenliği ve absorpsiyon spektrumları alınmış ve optik bant boşluğu hesaplanarak optik özellikler incelenmiştir. Co ilavesinin artması ile pürüzlülük değerlerinde artış meydana gelirken, geçirgenlik değerlerinde azalma meydana gelmiş yasak enerji aralığı değerlerinde ise % 10 Co katkısına kadar artış meydana gelirken % 10 Co katkısında azalma meydana gelmiştir.

Anahtar kelimeler: ZnO, Co, İnce Film, Sol Jel Spin Kaplama.

1. Introduction

In recent years, transition metal-doped semiconductors, photocatalysts [1], piezoelectric devices [2], light-emitting diodes [3], a promising candidate for organic photovoltaic cells [4] and gas sensors [5], [6], [7], [8], [9] and has been the focus of research [10]. Among these semiconductors, ZnO, supplemented with cobalt ions and reinforced with transition metal ions, has been the subject of much research [11]. The metal ion addition with ZnO is preferred to improve electrical, semiconductor, magnetic, anti-bacterial, photo-catalytic, thermal and optical properties [12], [13]. Semiconductor nanomaterials have been needed in the production of small, light, low-cost and high-efficiency optoelectronic devices due to their improved properties. In today's technology 60 meV, 3.37eV [14] wide band gap, zinc oxide (ZnO), which has a relatively large excitation energy and cheap magnetic semiconductors [15], is one of the most useful materials [16], [17], [18], [19]. At the same time, ZnO is wurtzit type. Due to its ability to adjust the magnetic and optical properties of ZnO, numerous studies have been carried out on Co doped ZnO films and nanostructures [17], [18]. Although very good work has been done on co-coated ZnO thin films, there is not much work on optical properties. There are very few studies on the structural, morphological and optical properties of nanostructured ZnO thin films prepared by sol-gel method [20], there is no information about the optical constants of cobalt doped zinc oxide thin films prepared with this technique [21].

Masjedi-Arani et al., Metals such as Mn, Co, Ni and Cu doped ZnO-Zn2SnO4-SnO2 nanocomposites Green sol-gel synthesis, characterization and photocatalytic activity called various transition metal nanocomposites for the first time using glucose as the green capping agent sol gel method. They examined the optical properties of

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nanocomposites. The best performance of the photocatalytic activity was obtained in the presence of Co additive nanocomposite [15]. Jingjing Xu et al., ZnO microspheres, common production of sponges and superior gas sensing properties for ethanol sensors showed that pure ZnO and Co doped ZnO microspheres (Co / ZnO) were successfully synthesized by a synergistic ultrasonic and microwave radiation. The present work adopted a new strategy for high quality synthesis of a gas sensing material by the transition element of Co, and demonstrated the high performance of the ZnO gas sensor [12]. Prateek Varshney et al., have synthesized Co doped ZnO samples with 2%, 4% and 6% concentration of Co-doped ZnO. XRD and XPS measurements showed that all samples had a hexagonal wurtzit type structure and no second phases and auxiliary clusters were present. Characterization of magnetization showed an increase in Co contribution and increased magnetization. In their study, the evolution of RTFM was due to the infiltration of BMPs [19]. Argha Sarkar et al., Mg-Al Co doped ZnO nanoparticles were synthesized by Sol-gel method. Analysis with SEM and XRD confirmed that nanoparticles were formed [22]. R.Peña Garcia et al., studied the heat dependence of saturation magnetization of Co and Cr doped ZnO nanoparticles by the sol gel method. All samples showed ferrimagnetic behavior saturation magnetization and changes in coercive field with different doped concentrations. [23]. Nantu Karak et al., structural, optical and magnetic properties were investigated in the study of the growth porous alumina-assisted of doped ZnO nanoparticles produced by sol-gel. In the Zn^{2+} lattice region, structural, optical and magnetic properties have been sensitively altered to incorporate Co^{2+} ions [24]. Petronela Pascariu et al., preparation and characterization of Ni, Co doped ZnO nanoparticles for photocatalytic applications in this study; Ni and Co doped ZnO nanoparticles were synthesized by the precipitation method together with advanced photocatalytic activity. Structural, morphological and compositional characterizations have been ensured by the co-precipitation method to successfully produce $Ni_xCo_xZn_{1-2x}O$ nanocrystals. Ni, Co, increased the concentration of the contribution of photocatalytic efficiency has led to a decrease [25]. Muneer M. Ba-Abbad et al., synthesis and characterization of Co^{2+} incorporated ZnO nanoparticles prepared through a sol-gel method in this study, All of the Co^{2+} doped ZnO nanoparticles were spherical without any change in the wurtzit-structure phase of pure ZnO [26].

In this study, Co doped ZnO nanomaterials prepared by sol gel spin coating method. The effect of addition of Co on the morphological and optical properties of Co ZnO nanomaterials was investigated.

2. Material and Methods

In this study, thin films were produced by using sol-spin spin coating method at different Co addition rates. $Zn(CH_3COO)$ 2.2H2O (zinc acetate) as source of Zn and $(CH_3COO)_2{\cdot}Co.4H_2O$ (cobalt (II) acetate tetrahydrate) were used as the source of Co and 0.5 M solutions were prepared. The solvent was chemically used as methoxyethanol and the stabilizer was ethanolamine. Then the prepared solutions, 1%, 5% and 10% Co Co-doped ZnO new solutions were prepared. In order to prepare thin films, the quartz substrate material was placed on the spin-coating device in each coating and the rotation speed was set at 1500 rpm and the rotation time was set at 25 sec. The solutions were added dropwise to the quartz substrate and the coating process was carried out. At the end of coating process, pure ZnO (S), 1% Co doped ZnO (S1), 5% Co doped ZnO (S2) and 10% Co doped ZnO (S3) including four film was produced. Coating processes were repeated 5 times in each sample to produce films with more homogeneous surfaces. Finally, the coatings were dried in an oven at 600 ° C for 1 hour. To determine the morphological characteristics of the produced thin films analysis was performed with PARK SYSTEM X-100 model Atomic Force Microscopy (AFM) device. In order to determine the optical properties, transmittance and absorption spectra were taken with SHIMADZU UV3600 UV-VIS-NIR Spectrophotometer and the changes of the reflectance values according to the wavelength were examined by using these spectra. For the calculation of the band gap of the films, the absorption spectra were used and for the n =1/2 for each film, using the Equation 1, graphs of change $(\alpha h\nu)^2$ to hν were drawn for each film separately. Optical band gap of films were determined by using these graphics.

3. Results and Discussion

Sol gel spin coating method is a low cost method. ZnO is particularly suitable for the production of thin films in optoelectronic applications. Figure 1 shows AFM images of the pure ZnO (S), 1% Co doped ZnO (S1), 5% Co doped ZnO (S2) and 10% Co doped ZnO (S3) samples. When the AFM images were examined, it was seen that all the films had a smooth surface. There are inconsistent structures in surface morphology. This discrepancy in surface morphology depends on the different molar composition of the reinforcing solution, growth conditions and growth process. As the Co concentration in the samples increased, wrinkled of the fibrous structures occurred narrowing. The crystal quality of the films decreased as the Co content increased. When transition metal ions were included in the ZnO cage, it was reported that slowing of nucleation and ZnO grains prevent further growth.

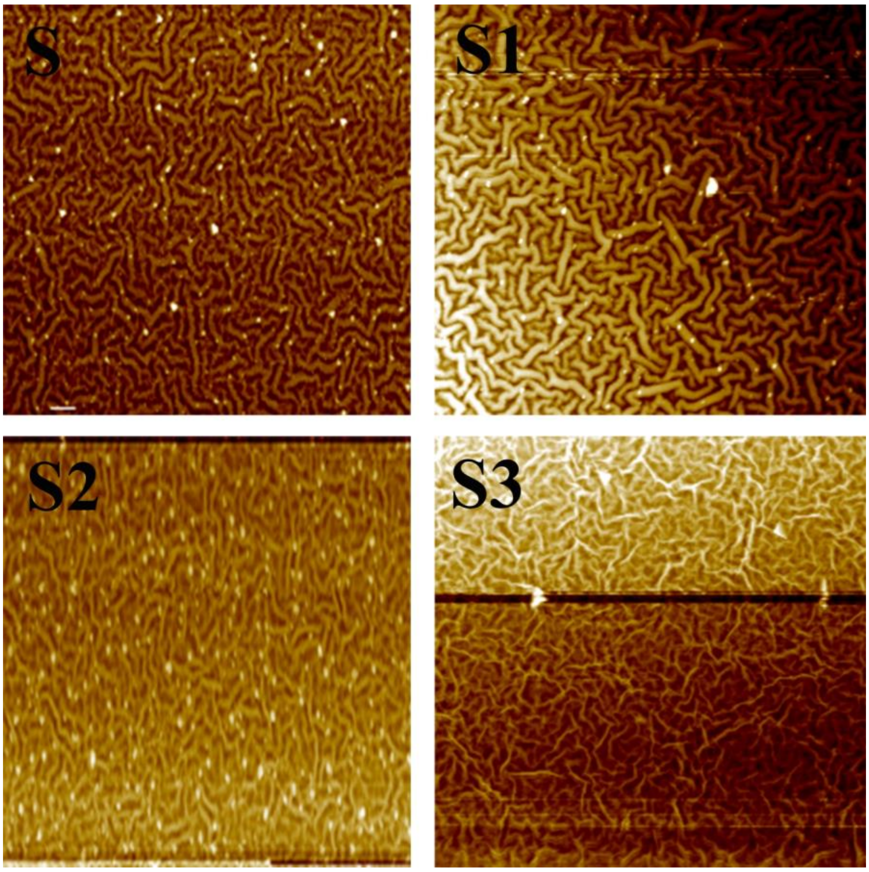

Figure 1. AFM images (40x40) of S, S1, S2 and S3 samples.

Figure 2 shows three-dimensional (3D) surface photographs of S, S1, S2 and S3 samples taken with AFM. The surface roughness values of these samples were ZnO (S) 42 nm, ZnO (S1) 63 nm with 1% Co, ZnO (S2) 91 nm with 5% Co and ZnO (S3) with 10% Co added to 135 nm. The surface roughness values of the films increased with the increase in Co concentration. An increase in co-concentration resulted in an increase in the number of nucleation centers, which led to an increase in surface roughness. At the same time, due to the increase of defect intensities in the structure of ZnO films with Co contribution, it was thought that there was an increase in surface roughness due to crystal structure and deterioration in surface distribution.

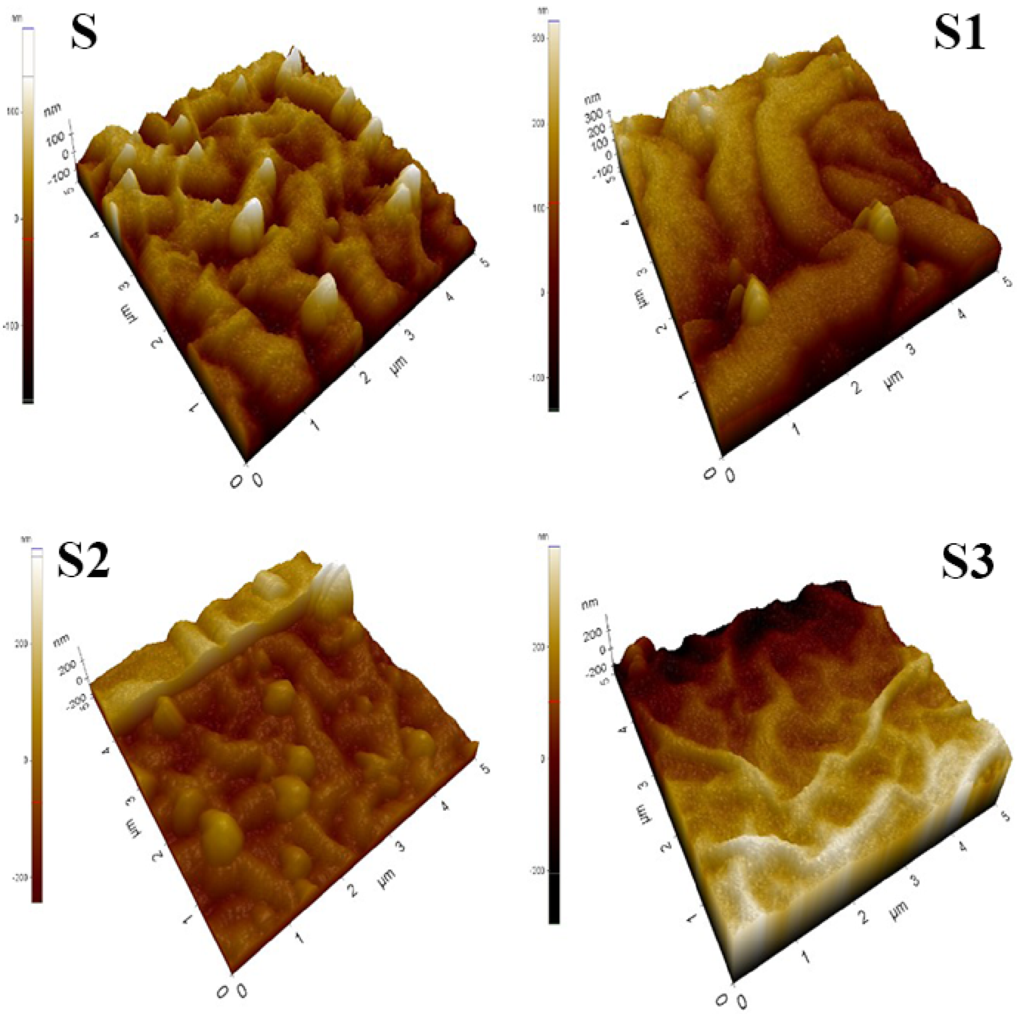

Figure 2. 3D -AFM images of S, S1, S2 and S3 samples.

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Figure 3 shows the absorbance graph of the samples, Figure 4 shows the transmittance graph and Figure 5 shows the reflectance graph. When these graphs are examined; the optical transmission spectra of the samples in the visible region are between the wavelengths of 350 and 800 nm. The permeability of the ZnO thin film is above 80%. However, a decrease in permeability has occurred with the addition of Co. This is due to the fact that Co accumulates in the grain boundaries, causing high density and increasing the scattering of light. At the same time, the increase in grains with increasing Co concentration also reduces permeability. The permeability of ZnO thin films depends on three factors. these factors; surface roughness, film thickness and grain boundary density [27]. Pure ZnO is white color because it does not absorb visible light. With the addition of Co, Zn^{2+} ions and Co^{2+} ions are replaced and the ions in the ZnO cage absorb the light and the films become dark green. It was observed that pure ZnO and Co doped ZnO thin films had low absorption after wavelength of 400 nm and sharp increase in absorbance values in all films was between 380-430 nm. When the absorption margins of all films in the 350-450 nm wavelength range were examined, it was determined that the absorption edge of ZnO films shifted to more wavelengths as Co contribution increased. When the changes of optical reflection values according to the wavelength were examined for all films, the reflection on shorter wavelengths increased as the amount of Co increased. As the wavelength of the incoming light increases, its energy will increase and thus the material will be more refractory for high energy light. The reflectivity of the material will be increased at high refractivity.

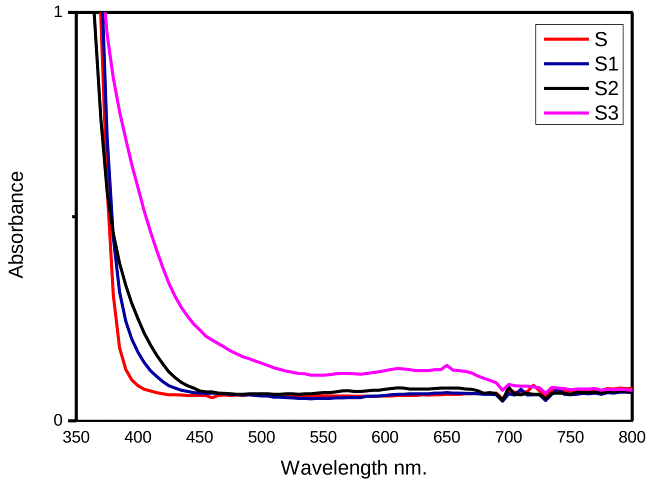

Figure 3. Absorbance spectra of S-S1-S2 and S3.

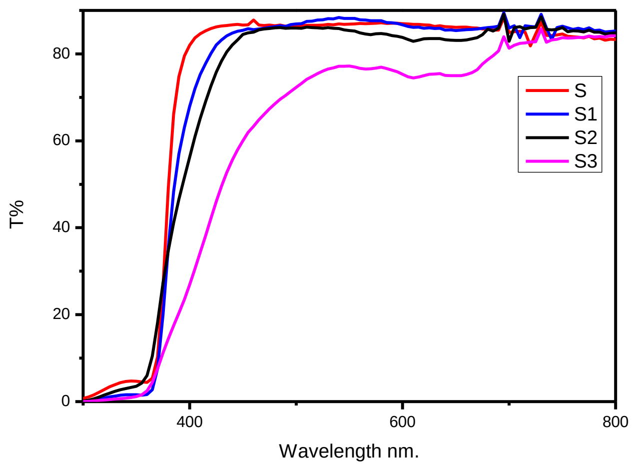

Figure 4. Transmittance spectra of S-S1-S2 and S3.

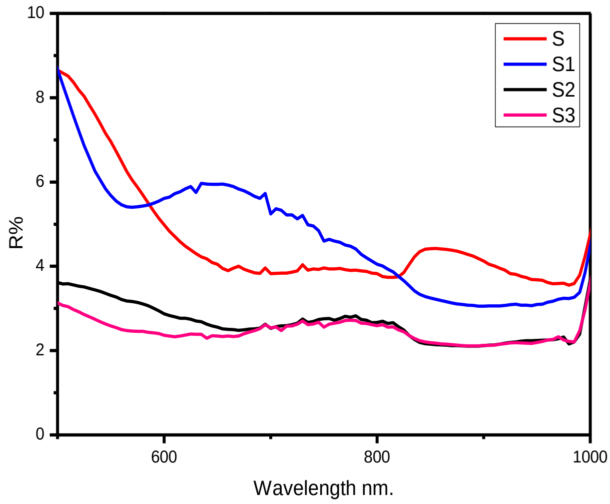

Figure 5. Reflectance spectra of S-S1-S2 and S3.

The optical band gaps of the samples were found to be based on the basic absorption, which conducts the transmission band from the valence band to the transmission band [28].

In semiconductor materials optical transitions are provided indirectly or directly. The absorption coefficient for direct passages is expressed by Equation 1 [29]:

$$\alpha h\nu = B(h\nu - Eg)^n \quad (1)$$

where, B is taken as constant, α is the absorption coefficient, h is the Planck's constant, Eg is the optical band gap, ν is the frequency of the incident photon and the exponent n describes the transition type [30].

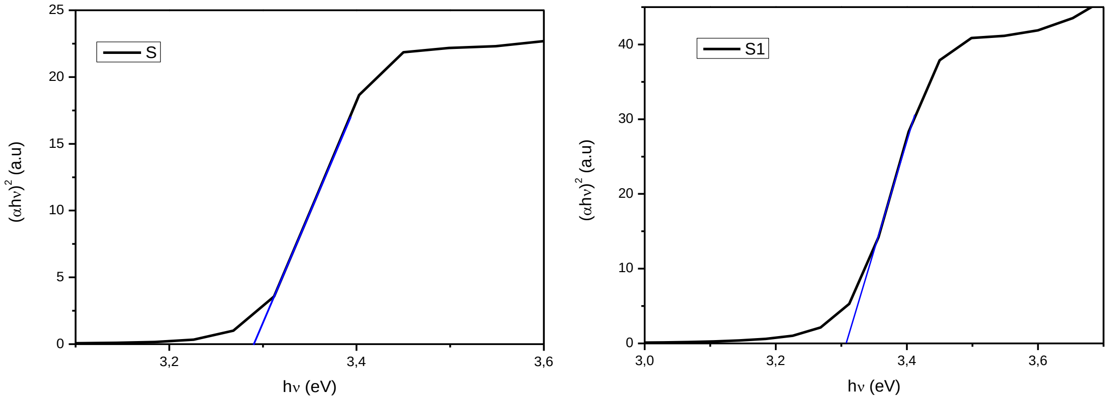

Figure 6. Optical band gap of S and S1.

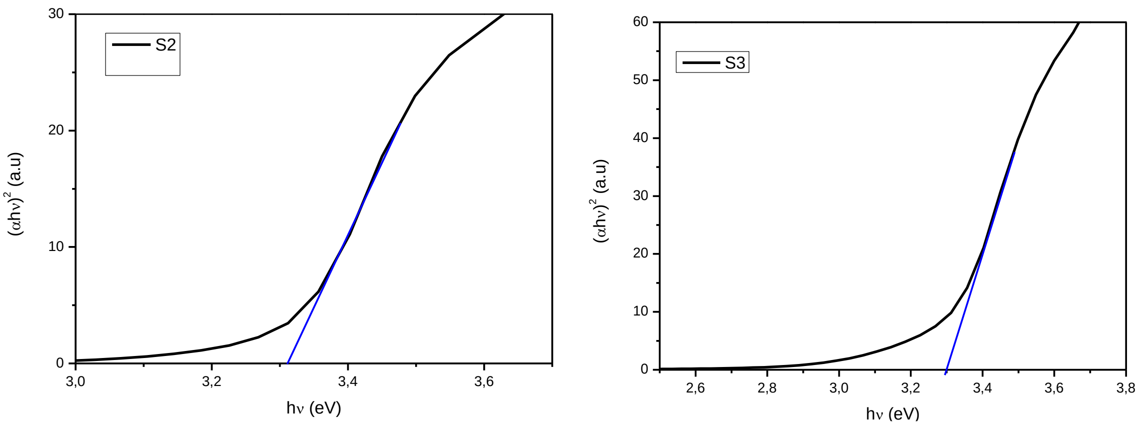

Figure 7. Optical band gap of S2 and S3

Figure 6 shows the optical band gap of the samples with pure ZnO and 1% Co-doped, Figure 7 shows the optical band gap of the samples 5% and 10% Co-doped. Eg value of the pure Zno (S) sample 3.29 Ev, Eg value of 1% Co doped ZnO (S1) sample 3.34 Ev, Eg value of 5% Co doped Zno (S2) sample 3.36 Ev and Eg value of 10% Co doped ZnO (S3)sample is 3.30 Ev. When these graphs were examined, Eg values increased in 1% and 5% Co doping and Eg value decrease was observed with 10% Co doping. Poongodi et al. ın their study, they stated that the band gap energy decreased from 3.32 Ev to 3.05 Ev with the addition of Co in ZnO [31]. Ping Li et al. of the pure ZnO's band gap energy at 3.27 Ev, while % 8 mole Co addition of Co: ZnO indicated that the band Gap energy fell to 2,87 Ev and there was no change in the addition of more Co [11]. Dhruvashi et al. considered that the reduction in band gap was due to the formation of the ZnCo2O4 spinel phase at high Co concentration [18]. In contrast to these results, Baghdad et al. reported that the band gap increased with increasing concentration of Co and 5% Co concentration decrease. They stated that the increase in cobalt concentration was red-shift in the band gap [14]. Prateek et al. ın their study, they stated that band gap value is 3.304 Ev with 2% Co doping and 3,387 Ev with 6% Co doping. They reported that the sp-d exchange between the ZnO band eletrons and the resident d electrons associated with the doped Co+2 cations would cause such a change in the band structure [19]. Baghdad et al. reported that this interaction led to corrections in the energy bands. They stated that the conduction band was reduced and the valence band increased so that the band gap narrowed [14]. At the same time, Peng et al. found red-shift in band gap of ZnO main material and blue-shift band ends [32]. Dhruvashi et al. they stated that as the concentration of co increases, the Eg value is increased from 3,26 Ev to 3,31 Ev. Correlated this increase in band gap with the strong sp-d exchange between the band electrons and the settled "d element electrons. At the same time, $Zn_xCo_{3-x}O_4$ (for x = 0) for the 1.4- 1.6 Ev (low energy side) and 2.0-2.1 Ev (high energy side) have stated that there are two optical band gap. With the increase in x value, the band gap value on the high energy side increases [18].

4. Conclusion

In this study, 1%, 5% and 10% Co were added to ZnO nanomaterial which is very important for optoelectronic applications and it was aimed to produce a new material by sol gel spin coating method and to improve the morphological and optical properties.

Co doped ZnO thin films were examined with AFM and the surface homogeneity of the films were found to be homogenous. When the surface roughness values of the films were examined, it was seen that the roughness values increased with the increase in Co concentration. The effects of reflectance values on wavelength were investigated by using the transmittance and absorption spectra of ZnO films with Co doped. As the amount of Co increases, the reflectance shorter wavelengths have increased. Again, the decrease in transmittance has occurred with the increase of Co amount. Optical band gap values of samples increased up to 10% Co addition while 10% Co addition decreased.

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