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Research Article

Investigation of structural and optical properties of ZnO thin films deposited on glass substrates by wet chemical sol-gel technique

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ABSTRACT

Nickel doped ZnO (NZO) and undoped ZnO thin films were deposited by wet chemical sol-gel spin coating method and their optical and structural properties have in detail been investigated by X-ray diffraction and optical absorption measurements to observe the effect of doping with different values of Ni molarity. The NZO and undoped ZnO thin films showed a growing trend along the c-axis perpendicular to the substrate surface. The strong (002) diffraction peaks at 2θ = 35.743°, 35.836°, 35.840° and 36.041° were observed to belong to samples undoped ZnO, NZO (0.25%), NZO (0.50%) and NZO (0.75%) films, respectively. The band gap values have been calculated from the dependencies (α^2 *vs* hν) by extrapolating the straight lines to $\alpha^2 = 0$ and found as 3.2630 eV and 3.2820 eV for 0.75% NZO and undoped ZnO thin films, respectively.

Keywords: Nickel doped ZnO, sol-gel growth, thin film.

Islak kimyasal sol-jel tekniği ile cam alt tabanlar üzerine büyütülen ZnO ince filmlerin yapısal ve optik özelliklerinin incelenmesi

ÖZ

Nikel katkılı ZnO (NZO) ve katkısız ZnO ince filmler ıslak kimyasal sol-jel spin kaplama tekniği ile büyütüldü ve onların optik ve yapısal özellikleri farklı molaritedeki Ni katkılamasının etkisini gözlemlemek için X-ışını kırınımı ve optik soğurma ölçümleri ile ayrıntılı olarak incelendi. NZO ve katkılanmamış ZnO ince filmler, taban malzeme yüzeyine dik olan c-ekseni boyunca bir büyüme eğilimi gösterdi. 2θ = 35.743°, 35.836°, 35.840° ve 36.041° deki baskın (002) kırınım piklerin sırasıyla katkılanmamış ZnO, NZO (%0.25), NZO (%0.50) and NZO (%0.75) filmlerine ait olduğu gözlendi. Yasak enerji aralığı değerleri, (α^2 *vs* hν) grafiğinden $\alpha^2 = 0$ olduğu noktaya ekstrapolasyon yapılarak hesaplandı ve %0.75 NZO ve katkılanmamış ZnO filmler için sırasıyla 3.2630 eV ve 3.2820 eV olarak bulundu.

Anahtar Kelimeler: Nikel katkılı ZnO, sol-jel büyütme, ince film.

1. INTRODUCTION

Zinc oxide (ZnO) and its alloys have managed to capture the attention of many researchers because of their wide applications in optoelectronics and technology. Being a binary transparent conducting oxide and synthesized as thin film, ZnO is most suitable semiconductor for use in optoelectronic devices, and it has gained a great interest due to its usage in basic scientific studies and its potential technological applications such as light emitting diodes,[1] varistors, thin film solar cells[2,3] and transistor,[4-6] surface acoustic-wave devices, touch panels, gas detecting, solar cells, flat panel displays, piezoelectric devices etc. Some of its numerous advantages include the tuning of its physical properties, the low cost, availability in bulk material for homoepitaxial growth (by hydrothermal, melt and Seed Vapor Phase methods), non-toxicity, compatibility with large-scale processes, possibility of wet chemical etching, resistance to radiation damage, high quantum efficiency and its relative easy fabrication. It has a direct energy band gap values (3.3 eV at RT; and 3.43e V at

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2K), large excitation binding energy (60 meV) enabling exciton recombination lasing mode and optical properties which are quite similar to GaN.[7-9]

Since undoped ZnO is an n-type intrinsic semiconductor due to both the presence of oxygen vacancies and the presence of zinc intersititals atoms, it is difficult to control some properties required by many optoelectronic applications. Therefore, in order to improve the quality of grown ZnO, many researchers have carried out experimental studies related to doping of ZnO with fluorine, erbium, tin, indium, nickel, antimony, manganese, iron etc.[10-15] There are much effort on ZnO to study optical and structural properties being associated with Ni doping. Of the elements available for doping, Ni is the most important element of the cation and anion dopants.

The sol-gel growth technique which is among the many chemical growth methods given in the literature such as chemical bath deposition, spray pyrolysis,[16] electrochemical deposition,[17] successive ionic layer adsorption and reaction[18] and sol-gel,[19-20] is the most preferred method due to its low equipment cost, simplicity, accurate control of stoichiometry, large area coating at low temperatures, high homogeneity, relatively low process, safety and easy control of chemical ingredients.

Undoped ZnO and Ni doped ZnO (NZO) thin films have recently emerged as the leading semiconductors because of their unique properties mentioned above. Kim and co-workers have carried out a study on the structural, electrical and optical properties of ZnO thin films having different Ni doping ratio grown by Sol-gel technique.[21] They have reported that although thin films (002) with dopant ratio of 0.2 mol% and 0.4 mol% had the preferred orientation direction, they have showed non-textured polycrystalline structure with increased Ni content. The smallest resistance and average optical transmittance values for 0.2 mol% Ni-doped ZnO thin film have been obtained as 4.8×10^{-4} Ω cm and 91.2% in the visible range, respecitively.

In another study, Khan and co-workers[22] have characterized the sol-gel grown ZnO thin films using X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, Ultraviolet-visible (UV-vis), Photoluminescence (PL), Scanning electron microscopy (SEM) measurements. In this work, the band gap energy value of the films has been calculated as ~3.24 eV.

On the other hand, the optical and structurel properties of ZnO films grown by Spray Mist-CVD technique have also been study by Derbali and co-workers[23] to observe the effect of depoisiton time by means of XRD, SEM, Atomic force microscopy (AFM), PL spectroscopies. They have reported that the grown films had a hexagonal wurtzite crystal structure with lattice constants a = b = 3.260 Å, c = 5.214 Å and a high degree of crystallinity with [001] preferential orientation from XRD measurements.

In our study, undoped and Ni doped ZnO films (NZO) at variable concentrations (0.25%, 0.50% and 0.75%) were prepared by sol-gel technique and effect of Ni on optical and structural properties of ZnO was investigated by XRD, UV-Vis spectrometry and optical absorption measurements. According to the literature survey, no studies on Ni doped ZnO thin films have been conducted at these doping rates, and therefore this study demonstrates originality.

2. EXPERIMENTAL

Ni doped ZnO (NZO) and undoped ZnO thin films were grown by spin coating sol-gel technique on glass substrates. In order to prepare undoped and Ni doped ZnO: Nickel (II) nitrate-hexahydrate ($Ni(NO_3)_2.6H_2O$), Zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$), monoethanolamine (C_2H_7NO, MEA) and 2-methoxyethanol ($C_3H_8O_2$, 2-MTE) were utilized to be Ni additive source, ZnO precursor source, stabilizer and solvent, respectively. Solution was stirred at 60°C for 2h by magnetic stirrer till uniform and a clear sol was obtained. After cleaning glass substrates in acetone and methanol in the ultrasonic bath, immersing them in diluted 10% hydrofluoric acid for 20 s, rinsing them with de-ionized water and drying gently them with nitrogen gas, the obtained precursor solution was dropped on a substrate and coated at a speed of 3.000 rpm for 25 s. The flowchat for the growth of undoped ZnO and NZO thin films is given in Figure 1.

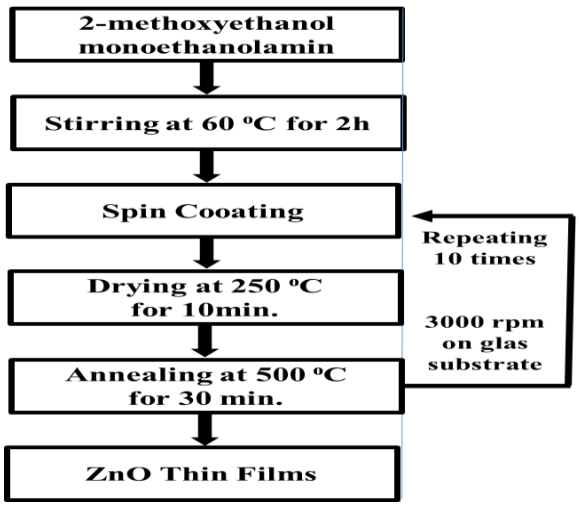

Figure 1. Flowchart for the growth of undoped ZnO and NZO films.

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The coated film was sintered at 250℃ for 10 min to evaporate the remaining solvent. The same process was repeated 10 times to achieve the desired thickness value, and the undoped ZnO and NZO thin films were annealed in air at 500℃ for 30 min.

The optical absorbance of the undoped ZnO and NZO films were recorded in spectral region of 350-600 nm at room temperature (300 K) by a Perkin-Elmer Lambda-35 UV-Vis spectrophotometer working in the range of 200-1100 nm and having a wavelength accuracy of 0.3 nm. The crystalline behaviours of ZnO films were determined by a Rigaku/SmartLab XRD (CuKα radiation, k = 0.154059 nm) operated under 30 mA and 40 kV. The XRD measurements were carried out at room temperature (300K) and the values of 2θ were set between 20° and 80°.

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD images of undoped ZnO and NZO thin films having different Ni concentrations.

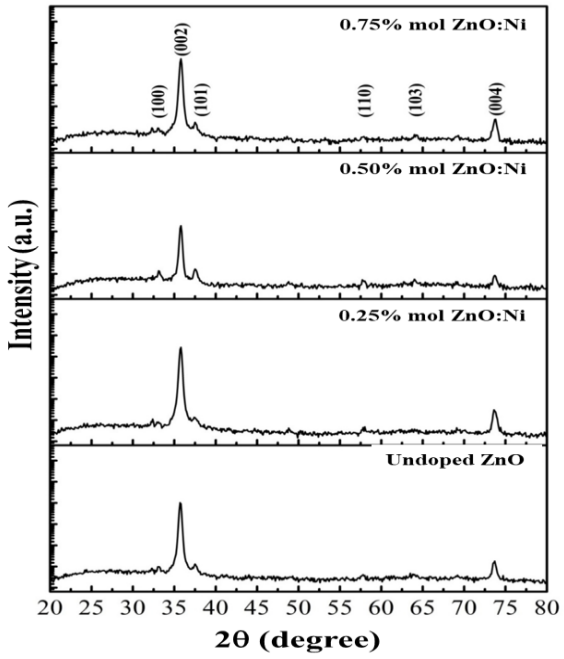

Figure 2. XRD patterns of undoped ZnO and NZO films.

The (002) diffraction peak around the 35.743 degrees shows a preferred growth direction along with the c-axis which is perpendicular to the substrate.[24] While the same dominant (002) diffraction peak have been observed for a dopant ratio of 0.2 mol% and 0.4 mol%, the structure of the film has changed to the non-textured polycrystalline structure with the Ni content exceeding of 0.6 mol%.[21] The strong (002) diffraction peaks observed at 2θ = 35.836°, 35.840° and 36.041° belong to samples NZO (0.25%), NZO (0.50%) and NZO (0.75%), respectively. As can be seen from these values, although the values of 2θ and Full width at half maxium (FWHM) vary slightly with the increase of the Ni ratio, the hexagonal wurtzite crystal structure of the deposited thin films remains unchanged. In addition to (002) dominant diffraction peak, some other peaks having lower intensities such as (004), (103) and (110) were also observed for the films.[25-26] The *a* and *c* lattice constant values of the grown ZnO films can be easily calculated from following equation;[18]

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + k^2 + hk}{a^2}\right) + \left(\frac{l^2}{c^2}\right)$$

Where (*hkl*) and *d* indicate the miller indicies and interplaner distance, respectively. The mean values of the *a* and *b* latis parameters given in Table 1 were calculated to be *a* = *b* = 3.125 Å and c = 5.009 Å. The calculated *a* and *c* values match the ones given in JPCDS card no: 36-1451 and are almost agree with the findings of Derbali and co-workers.[23]

Table 1. The calculated lattice constant values of the films

Sample	2θ	FWHM	a (Å)	c (Å)
Undoped ZnO	35.743	0.33	3.131	5.019
NZO (0.25%)	35.836	0.38	3.126	5.012
NZO (0.50%)	35.840	0.41	3.122	5.005
NZO (0.75%)	36.041	0.43	3.119	5.000

Optical absorption spectra of undoped ZnO and NZO thin films were obtained in the wavelength range 350-600 nm (see Figure 3). The band gap values were calculated using the relation given below;[27]

$$(\alpha h\nu) = A(h\nu - E_g)^n$$

Where *A* is the absorbance, *α* is the absorption coefficient in cm^{-1}, *n* is a constant indicating the type of optical transition, and the *n* = 2 and *n* = 1/2 values are used for the allowed indirect and direct transitions, respectively. As could be seen in Figure 3, the band gap values were calculated from the dependencies (α^2 *vs* hν) by extrapolation to α^2 = 0 and found as 3.2820 eV and 3.2630 eV for undoped ZnO and NZO (0.75%), respectively. The optical band gap values obtained are in agreement with those of Khan and co-workers.[22]

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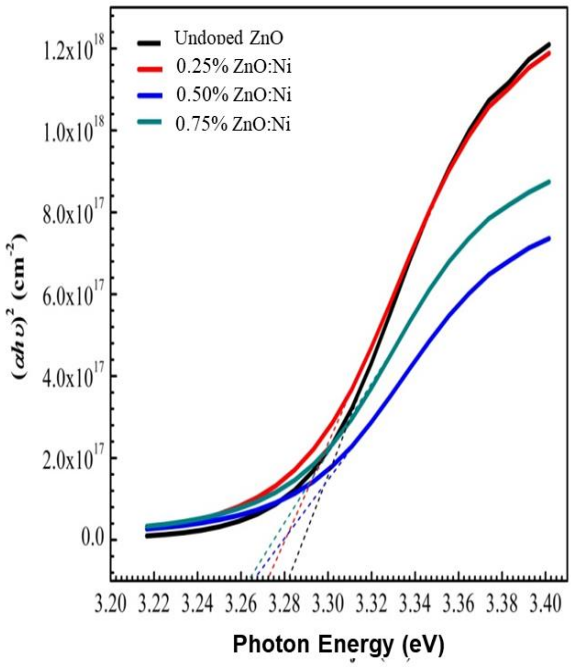

Figure 3. Optical absorption spectra of undoped ZnO and NZO films.

4. CONCLUSIONS

In this work, nickel doped ZnO (NZO) and undoped ZnO thin films were grown by wet chemical sol-gel spin coating method. The NZO and undoped ZnO thin films had a (002) diffraction peak around the 35.85 degrees which is an indication of high quality ZnO thin film growth. The strong (002) diffraction peaks at 2θ = 35.836°, 35.840° and 36.041° were observed for NZO (0.25%), NZO (0.50%) and NZO (0.75%), respectively. The band gap values calculated from the dependencies (α^2 vs hν) by extrapolation of the straight lines to $\alpha^2 = 0$ and were found as 3.2630 eV and 3.2820 eV for NZO (0.75%) and undoped ZnO thin films, respectively. As a conclusion, ZnO thin films can be considered a promising material for solar cell applications by adding nickel into them at different doping ratios due to their transparent properties.

Conflict of interests

I declares that there is no a conflict of interest with any person, institute, company, etc.

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