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Research article

Influence of Al content on microstructure and optical transmittance of sol-gel dip-coated ZnO films

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ABSTRACT

Aluminum-doped zinc oxide thin film (Al:ZnO) was derived by the sol-gel dip-coating technique to analyze the doping effect on the film's crystal structure and optical transparency. The surface structure of the thin film had the particles in the nano-spherical form. Al amount changed surface roughness with the variation of the grain size. The crystal structure of ZnO was wurtzite (in XRD analysis). The surface morphology of the film was also examined with SEM images. The effect of Al doping was investigated to evaluate the necessary amount of Al on the optical properties. The films show high optical transparency (~85%) at specific Al doping amounts (0.8–1.6%).

KEYWORDS

Crystallinity
Sol-gel
Transparency
Optical properties
ZnO

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1. Introduction

The search for alternative energy sources has taken an important place in the scientific world due to the effects of economic conditions and environmental factors. Energy consumption has inevitably increased and the increase in the quality of synthesis techniques depends on the developments in science and technology. Sunlight is the cleanest and most abundant renewable power source that is harnessed with solar cells to convert into thermal or electrical energy. Transparent conductive oxide (TCO) thin films are widely used on the front side of solar cells due to their suitable electro-optical features. Nontoxic TCOs such as ZnO (pure and doped) have received superior attention for adaptable electronic applications. The crystal structure of ZnO exhibits a hexagonal wurtzite structure. It has the tetrahedral configuration displaying sp^3 covalent bonding. ZnO shows characteristic ionic features and it has three different crystal structures such as rock salt, zinc blende, and wurtzite [1–5].

Rock salt phase growth takes place under high pressure. Zinc blende (cubic) is grown on substrates that need the process for being stable. It has high optical transmittance in the visible range (80–90%). Optimum optical loss and electrical conductivity of ZnO have provided rise to the additional benefit of being non-toxic and less expensive.

Even if a small portion of this enormous energy source can be converted into alternative and usable forms of energy related to the synthesis conditions of the semiconductors, it can eliminate concerns about energy requirements. The amount of solar energy reaching the surface of the earth is around 120000 terawatts (TW). The share of solar energy, which has a very important place among renewable energy sources, in electricity production is increasing day by day and scientific studies of the synthesis of the semiconductor layers are gaining importance. Synthesis conditions of the photovoltaic devices, which are used to derive electricity from solar energy, convert the sunlight falling on them into electrical energy. The synthesis conditions allow the use of the ZnO semiconductor layers as a transparent front contact layer in solar cells. The low electrical conductivity of ZnO film limits its capacity for use as an alternative semiconductor to indium tin oxide (ITO) [6–11].

The synthesis parameters of the semiconductor layers affect the structure for the potential applications in photovoltaic devices. The conversion of sunlight into electricity has been working for many years

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related to the science and technology of photovoltaics and the conversion of solar energy into electrical power. The progress in the knowledge of the synthesis parameters of the semiconductor layers has made great strides. Solar energy is an indispensable resource for clean energy. The synthesis and production techniques of photovoltaic cells are increasing day by day and the increase due to the solar cell energy conversion efficiency. There are several techniques such as spray pyrolysis, vapor deposition technique, atomic layer deposition, and sol-gel technique to prepare doped and un-doped ZnO thin films [12–18]. The sol-gel technique is one of the most useful techniques to prepare semiconductor devices due to its simplicity, easily controllable process, and large-area applications [19–23]. Sol-gel coating process provides several advantages in avoiding environmental pollution. It has possible to obtain pure thin films with saving energy and homogeneous films with low production costs at low temperatures [24–30].

In this study the synthesize thin film samples of Al-doped ZnO (AZO) by using a low-cost sol-gel spin coating technique was possible with the optimized conditions for the use of this photovoltaic layer in photocatalytic applications. The effect of Al doping on the ZnO structure was examined considering the optical properties and surface features of pure-ZnO films.

2. Experiments

The optimization of the synthesis process can provide high performance in photovoltaic materials. Hence the synthesized solution samples were optimized by using the sol-gel method in this study. First, zinc acetate dihydrate $Zn(CH_3COO)_2.2H_2O$ (starting chemical ~99.5% purity) powder was added to a solvent (Ethanol) and a stabilizer (diethanolamine: DEA) solution, then the new solution was transferred to a hot plate which was adjusted to 80 °C and stirred for 30 min, consequently, a transparent and homogeneous solution was obtained. As a dopant, aluminum nitrate nonahydrate- $Al(NO_3)_3.9H_2O$ (Al dopant source) was added to the dissolving solution (gel) and stirred for another 2 hours until obtaining a white-colored gel. The gel was aged during the night and used as a stock solution for further dip coating.

The synthesized semiconductor thin film layers were characterized by

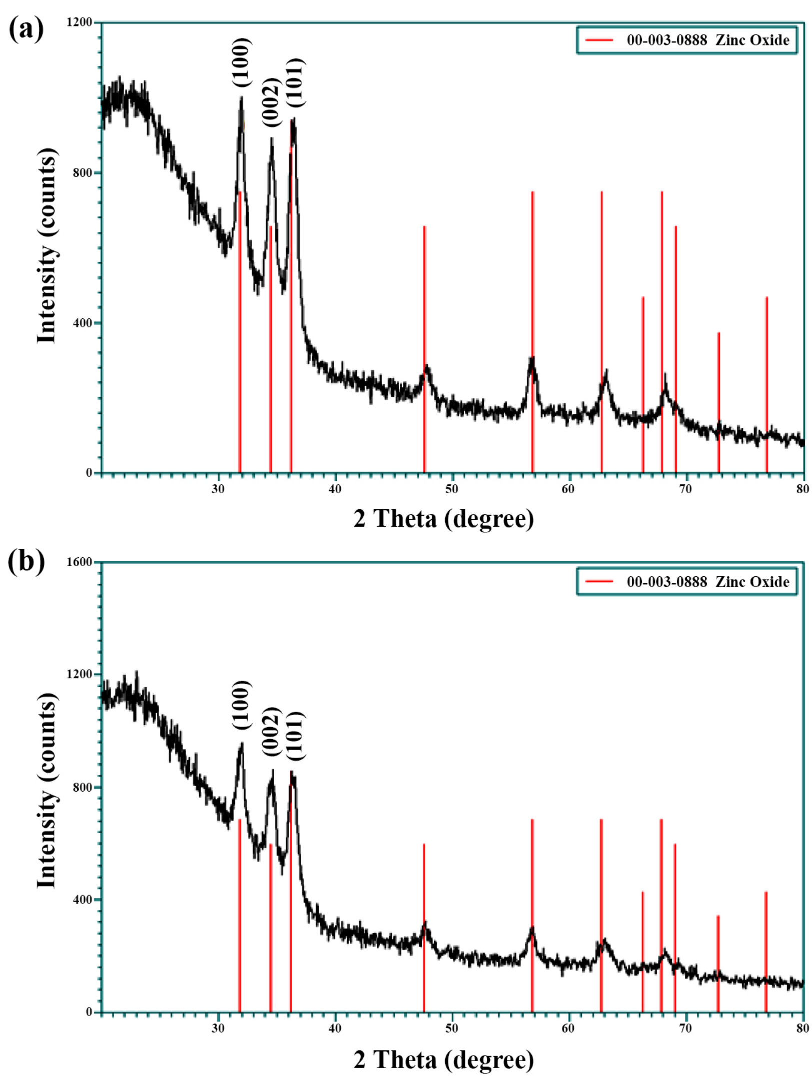

Fig. 1. XRD analysis of Al-doped ZnO thin film samples at a) 0.8 and b) 1.6 wt% Al amounts.

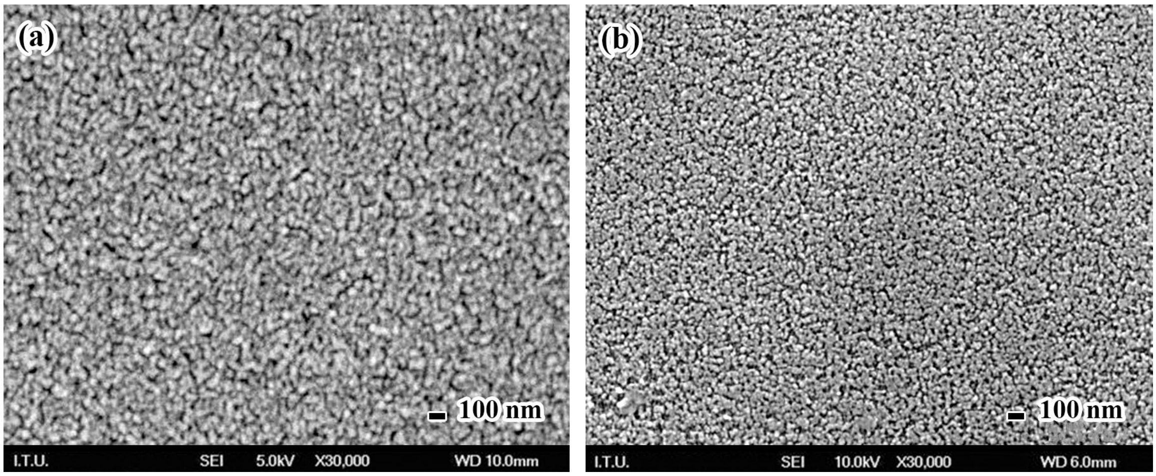

Fig. 2. SEM images of doped ZnO thin films with a) 0.8 and b) 1.6 wt% Al.

several characterization techniques to analyze the physical features of the films as this photovoltaic material (such as the thin film layers) has been a semiconducting material that absorbed light and generates electricity. Structural properties were characterized by an X-ray diffractometer (XRD) which used the C_uK_α radiation (λ=1.54059Å) in the range of 20–60 °. The film's microstructure and surface morphology were examined by Scanning Electron Microscopy (SEM) and the film thickness was calculated by SEM cross-section properties.

The optical properties of the films were analyzed by different methods. First, the transmittance of the films was carried out by a UV-Vis spectrophotometer in the wavelength range between 190–900 nm considering the literature [23].

3. Results and discussion

Fig.1 presents the X-ray diffraction patterns of ZnO thin film doped with Al on a quartz glass substrate. XRD peaks have indicated hexagonal wurtzite crystal structure in the Al-doped ZnO thin film samples. XRD peaks are matched with standard diffraction patterns (such as JCPDS Card No. 80-00075). It was supposed that the intensity of the peaks decreases by increasing Al concentration because of the difference between the atomic radius of aluminum (r_{AL}^{3+} =0.053 nm) and zinc (r_{zn}^{2+} =0.074 nm) ions in the Al-doped ZnO thin film samples.

Additionally, Al doping concentration caused the film structure degeneration and deformation. The film structure has shown the tendency to become amorphs than crystallinity over 1.6% Al concentration in the previous works for the ZnO thin film samples [5, 22–24]. All the thin film samples (at 0.8 to 1.6 wt% Al) have presented the characteristic diffraction peaks at certain diffraction angles. Fig. 1 indicated the X-ray diffraction patterns of ZnO thin films doped with aluminum at 0.8 and 1.6%. All samples have the (100), (002), and (101) diffraction peaks. It was assumed that the thin layer doped with aluminum in the final samples has a crystalline zinc oxide matrix and there were no extra peaks in the XRD patterns in the examined range.

Fig. 2 shows SEM images of the Al-doped ZnO (AZO) thin film samples at different Al concentrations. Increasing the Al amount decreased the average grain size, causing voids and pinholes on the surface up to 1.6%. The particle size was the largest at 0.8%. The grain size decreased slightly over 1.2%. Compared with 1.6%, 0.8% Al-doped film is denser and possesses larger grains.

The thicknesses of the Al-doped ZnO thin film samples were about 250 nm was observed by the SEM cross-section feature. The surface morphology of the films has indicated the grain size and grain boundaries. The surface analysis presented details about pinholes. The impurity (doping) in the film samples is determined by the surface images that result in distortion.

The host atoms in ZnO have a crystalline structure and the doping concentration has an importance on the film. The distortion causes the difference in crystallite size. For diminishing distortion between grains, the result of doping concentration indicates the crucial effect on the ZnO film to obtain valuable performance. The effect of grain boundaries and grain sizes is important to Al concentration. The grain size gradually is grown on the substrate surface. The surface with apparent porosity much rougher is due to the grain size. The high pinholes result in high resistivity. The Al-doped ZnO thin film samples can provide fewer pinholes and low resistivity. It can increase the blocking ability of the hole-electron pairs. It affects the quality of the films as a transparent optoelectronic thin film layer.

The Al amount in the Al-doped ZnO thin film samples was dominant in the morphological features. The grain sizes and grain boundaries are shaped by the amount of Al growth during post-annealing treatment. It was assumed that there are proportional between O vacancies and Zn interstitials during the annealing treatment. It was suggested that the defects were formed during annealing treatment at a lower Al amount while the defects on the film surface behaved like a nucleation center. The generated small size of grains produced the grain and grain boundary in the Al-doped ZnO thin film samples.

Fig. 3 shows the average visible transmittance in the films in the range of 190–2400 nm. All the films exhibit high transmittance which is around 85%. The film transmittance and reflectance are gradually influenced by Al concentration as shown in Fig. 3.

The transmittance of the synthesized thin films changes depending on the increase in Al concentration. It can be seen that the transmittance in the visible region changes somewhat in the film samples. It was determined that the transmittance was reduced as a result of the doping of the ZnO structure with Al.

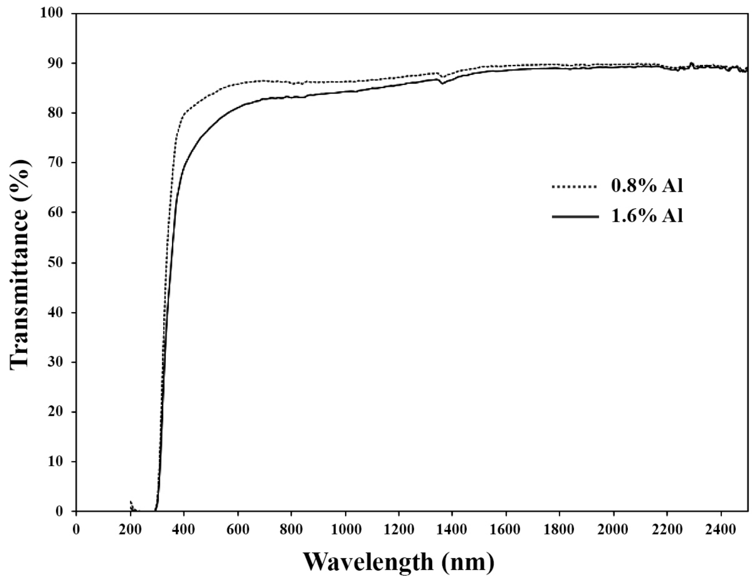

Fig. 3. Transmittance of ZnO:Al thin films with 0.8 and 1.6% Al amount.

Transmittance values of the Al-doped ZnO thin film samples were determined in Fig. 3 as the measured ratio of light at a normal incidence that passed through the soda-lime silicate glass. It was possible to compare clearly the effect of Al doping amount in the ZnO-based thin film in this study.

The thin films have attracted attention because of their good structural and optical properties. The results of this study have indicated that the thin film samples can be used as optoelectronic circuit devices in transparent conductors at solar cell glasses and flat panel displays etc. The thin film samples were derived from an inexpensive n-type semiconductor material. It was determined that the ZnO thin film could be easily controlled by annealing and doping thin films were of interest because of their low-cost, non-toxicity, and easy doping. It was recommended that zinc acetate be preferred in this experimental study as it was a cost-effective and easily obtainable optical substance. ZnO:Al thin films were accepted as economical thin films that could form the basis of optoelectronic device technology in this study. ZnO:Al was accepted as promising optoelectronic material for photoelectronic applications such as in thin-film solar cells and LEDs in this research.

The results in this study have indicated that the development of the synthesis conditions has contributed to the production and generation of ZnO:Al thin film layers as n-type semiconductor layers with optimum transparency properties for the use in photovoltaic solar cells.

4. Conclusions

AZO film layers synthesized in this study have indicated the great importance in optoelectronic applications operating at short wavelengths with this feature. The results of this study have presented that the synthesized conditions of the AZO film layers provide possible to improve optical and structural properties by using suitable additives such as Al.

AZO films were successfully produced by the sol-gel spin coating technique investigated in this study. Increasing Al concentration caused to decrease in the voids and pinholes in opposite directions on the film surface which prohibited the hole-blocking properties of the films. Increasing the Al doping concentration of the film crystallinity prevented high voids and pinholes carried out on the film surface. All the films displayed high transparency in the visible region. Increasing the Al doping concentration of the annealing treatment slightly influenced the film transparency. Especially, in the ultraviolet region, the thin film established high absorption where the interaction of atoms and electromagnetic waves was high, however, in the visible region the films showed low interaction and strong transparency. In conclusion, ZnO thin films doped with Al provided the enhancement at the surface roughness for practical applications as a potential candidate to use in optical devices.

CRediT authorship contribution statement

Mehdi Tonka: Conceptualization, Investigation, Writing – original draft.
Feyza Guzelcimen: Methodology, Validation.
Nilgun Baydogan: Supervision, Writing – review & editing.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

Although the last author of this article is a member of the editorial board of Synthesis and Sintering, her role in the journal did not affect the reviewing process of the article.

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