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Optical Properties of Al:ZnO Thin Film Deposited by Different Sol-Gel Techniques: Ultrasonic Spray Pyrolysis and Dip-Coating

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Abstract: Undoped and Al-doped ZnO polycrystalline thin films have been fabricated on glass substrates by using a computer-controlled dip coating (DC) and ultrasonic spray pyrolysis (USP) systems. The film deposition parameters of DC process were optimized for the samples. In this technique, the substrate was exposed to temperature gradient using a tube furnace. In the study, the other solvent-based technique was conventional USP. The zinc salt and Al salt concentrations in the solution were kept constant as 0.1 M and 2% of Zn salt's molarity, respectively. The optical properties were compared for the films deposited two different techniques. The optical transmission of Al:ZnO/Glass/Al:ZnO sample dip coated and the optical transmission of Al:ZnO/Glass sample ultrasonically sprayed were determined higher than 80% in the visible and near infrared region. Experimental optical transmittance spectra of the films in the forms of FilmA/Glass/FilmA and FilmA/Glass were used to determine the optical constants. It was observed that the optical band gaps of Al doped ZnO films onto glass substrate were increased with increase of Al content and the absorption edge shifted to the shorter wavelength (blue shift) compared with the undoped ZnO thin film.

Keywords: Sol-gel, dip coating; ultrasonic spray pyrolysis; Al doped zinc oxide; optical constants.

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INTRODUCTION

In 1742, a method of coating iron by dipping it in molten zinc was described by Malouin [1]. Nowadays, this technique has different applications fields such as coating the surface of the materials with protective agents or coloring materials. Materials in almost any geometry can be coated using this technique. In addition to coating of large-scale material, this technique was used to deposit to the metal oxide semiconductors (ZnO, TiO_2, SnO_2 and WO_3). Investigation of compound semiconductor-focused work has gained momentum [2]. It is possible to coat the surface of the material using the liquid phase growth techniques. These techniques are generally divided into three groups such as sol-gel, chemical baths, and electrochemical methods. The sol-gel method is widely used in thin film coating. In the sol-gel process, the precursor solution can be coated on the substrate by dip coating, spray pyrolysis, and spin coating techniques. In recent years, ZnO, prepared by various deposition methods such as reactive evaporation [3], RF sputtering [4], chemical vapor deposition [5], ultrasonic spray pyrolysis [6-8], sol-gel method [9], and dip coating method [10], have found very different application areas for optoelectronics and sensor technology applications. In addition to changes of the optical constants, the change in the band gap may be advantageous in the technological use of the films. While the increase in the band gap can be useful in poly-crystalline solar cells, the decrease in the band gap can be applicable for gas detection such as CO [11]. The number of studies that examined the changes in the optical and electrical properties due to the elements to be incorporated into the ZnO lattice is increasing. The substrate temperature is an important parameter for the formation of the thin film. For example, the substrate temperature is kept at a given temperature in USP technique. However, substrate is kept at room temperature and dip number is increased for the formation of the film for the DC technique. However, during DC process pre-heating or after the deposition-post heating can be done. The samples were exposed to temperature gradient from the room temperature to set temperature then subject to post heating using DC system.

In this study, using the *modified dip coating system (MDC)* pre-heating and post-heating features are added using the tube furnace, which was used in the vertical geometry. Undoped and Al-doped ZnO polycrystalline thin films have been fabricated on glass substrates using dip coating (DC) and ultrasonic spray pyrolysis (USP) systems. In this way, although a small number of dip process to be done the film formation on the substrate becomes more prominent. Substrate temperature was kept at 400 °C for USP system. In order to compare the samples deposited by DC, post heating temperature set at 400 °C. Moreover, the changes in optical transmittance of Al doped ZnO thin films were examined.

MATERIALS and METHODS

Experimental details

The home-made computer-controlled dip coating system was modified by adding the heating facilities after the withdrawing process (Figure 1). In this system, the tube furnace which was used in the vertically was added to the system for pre-heating and post-heating up to 400 °C for the dipping process. The details of the previous dip coating system are given in the reference [10]. The vertical movement distance is also expanded about up to 40 cm using the modified mechanical unit. Stepper motor and threaded spindle is provided with a 5 μm precision movement. Another modification is changing the home-made stepper motors driver unit with a commercial one (Leadshine step motor drive unit M542 model). This unit has a micro-step feature. Thus, a number of steps for one revolution can vary from 400 to 25000 steps. The step control is made by means of the computer's printer port. M542 stepper motor drive unit can be controlled by two data bits such as D1 and D0. Using a suitable computer program such as LabView, dipping time, dwell time, withdrawal rate, and pre-heating time of the substrate can be adjusted to the desired value.

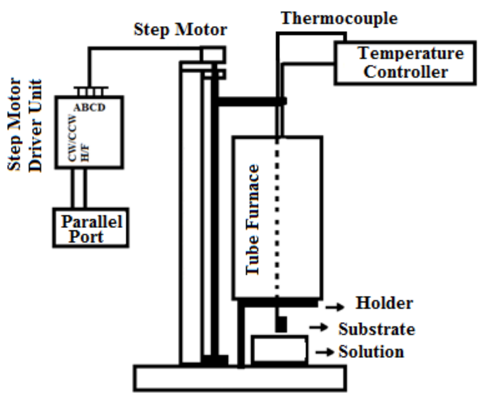

Figure 1. The schematic diagram of modified dip coating (MDC) system.

The salts zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$, 99.9%-Merck) and Al chloride hexahydrate ($AlCl_3.6H_2O$, 99.9%-Merck) as the metal sources were dissolved in methanol. In order to produce a clear and homogeneous solution, monoethanolamine (MEA) was added into the precursor solution which was stirred at 60°C at a moderate speed for 1 h. Al and Zn concentrations were kept at 0.002 M and 0.1 M in the starting solutions, respectively. This precursor solution was used to deposit ZnO and Al:ZnO (AZO) thin films on to ultrasonically cleaned glass substrates using the conventional USP and MDC systems.

The ZnO and AZO thin films (2 layers) were deposited on both sides of the glass substrate, withdrawal speed fixed at 1 cm/min and the deposition time at 30 s. In USP method, the position of substrates was fixed and precursor solution was sprayed over a hot substrate. The substrate temperature was kept at 400°C. The solution flow rate was held constant at 5 mL/min. The nozzle (100 kHz oscillator frequency) used in this study was in a downward vertical configuration. A more detailed description of the USP system was reported in previous papers [8]. X-ray diffraction (XRD) spectra were collected with a D-Max X-ray diffractometer (Rigaku International Corp. Japan) with CuK_{α} (λ=1.5405Å) to obtain the structural information of the films. The optical measurements of the Al:ZnO thin films were carried out at room temperature using T70 Model Spectrophotometer (PG Instrument) in the wavelength range 300–900 nm.

Table 1. Calculated film thickness of the single sided (*t*) and double sided (t_1 *and* t_2) thin films deposited by DC. Calculated refractive index *n* for 700nm wavelength and optical band gap values E_g (eV).

Thin film profile	Dip number	t_1 (nm)	t_2 (nm)	*n* (700nm)	E_g (eV)
ZnO/Glass/ZnO	2	138	120	1.66	3.29
Al:ZnO/Glass/Al:ZnO	2	95	133	1.46	3.33

Table 2. Calculated film thickness of the single sided (*t*) thin films deposited by USP. Calculated refractive index *n* for 700nm wavelength and optical band gap values E_g (eV).

Thin film profile	t_1 (nm)	*n* (700nm)	E_g (eV)
Al:ZnO/Glass	104	1.67	3.32
ZnO/Glass	602	2.00	3.23

RESULTS and DISCUSSION

Structural Characterization

The X-ray patterns for ZnO and Al:ZnO thin films deposited by USP and DC films at room temperature are presented in Figures 2 and 3, respectively. The hexagonal wurtzite structure of ZnO seems to be protected for both samples group. It was observed that the

(002) peak indicating a strong orientation along the *c*-axis for USP type undoped ZnO film. For the USP type Al:ZnO film (200) and (101) as well as (110) and (103) peaks were observed. But the intensities of peaks are decreased when a small amount of Al was inserted into the ZnO lattice structure. There was no impurity and/or unreacted phase of Zn and Al for the DC type ZnO and Al:ZnO thin film. The peaks (100), (200), (101), (102), (110) and (103) were observed. But there are no dominant peaks considering (100), (002) and (101). In addition, detection of (102), (110) and (103) peaks were hard for the DC type Al:ZnO thin film.

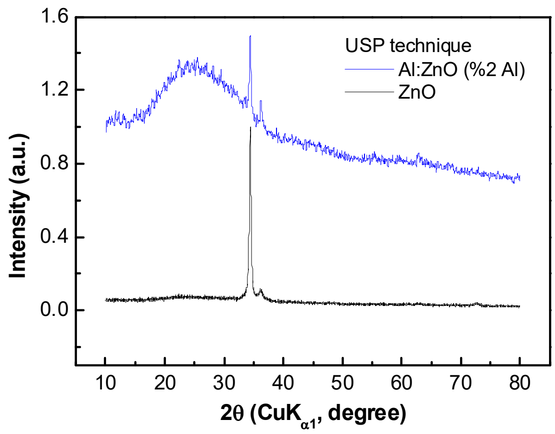

Figure 2. XRD patterns of Al:ZnO and ZnO thin films deposited by USP technique.

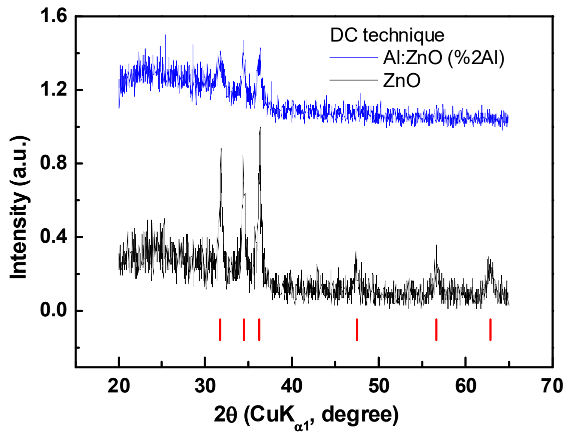

Figure 3. XRD patterns of Al:ZnO and ZnO thin films deposited by DC technique. "|"indicates the reference peaks for ZnO (JCPDS file no. 03-065-3411).

Optical characterization

The optical transmission spectra of undoped ZnO and Al-doped ZnO thin films are shown in Figure 4. The effects of Al doping into the ZnO lattice is clearly observed in the optical transmission spectra. First, optical transmittance increased rapidly due to the incorporation of Al. Because Al incorporation decreases the refractive index that can cause increases for the transmittance. This result is clearly observed in the optical transmission spectrum. Optical band gaps of the thin films can be determined using this wavelength with the relation, $E_g(eV) = 1240.8/\lambda_{inf}$. Where λ_{inf} is the defined as the inflexion wavelength where the second derivative of the transmission curve is zero. The optical band gap (E_g), was estimated from the second derivative of the $T(\lambda)$ (Table 1). The optical band gaps of Al doped ZnO films onto glass substrate are increases with increase of Al content and the absorption edge shifted to a shorter wavelength (blue shift) compared with the undoped ZnO thin film.

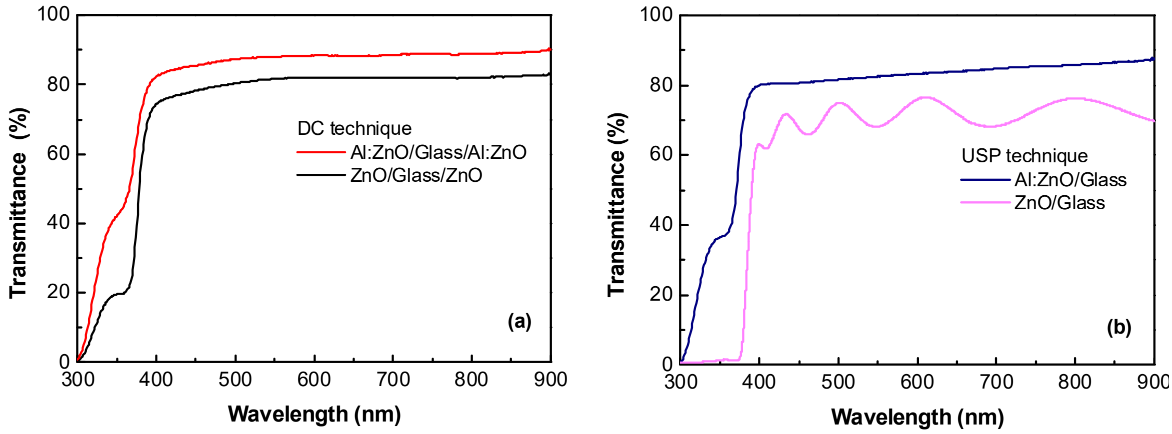

Figure 4. Transmittance spectra of Al:ZnO and ZnO films deposited by **(a)** DC technique and **(b)** USP technique.

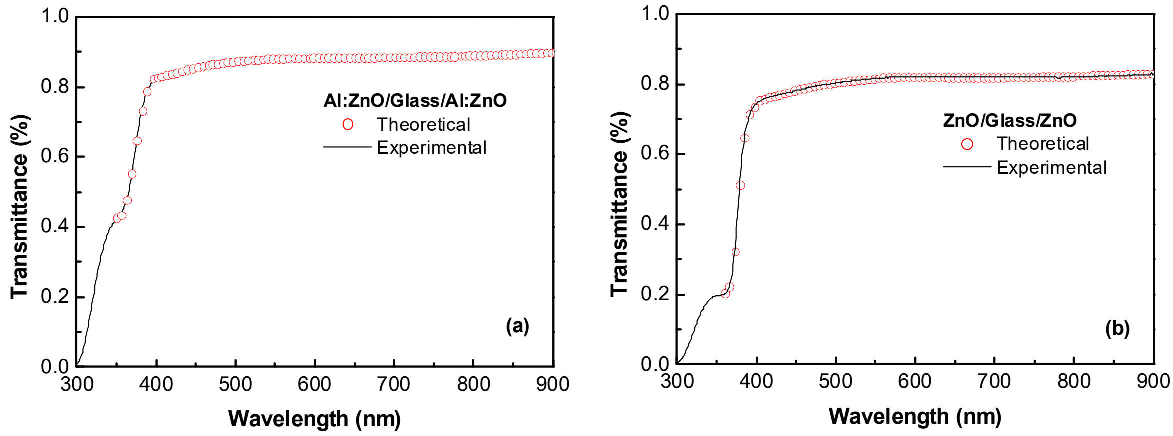

Figure 5. Experimental and calculated optical transmittance spectra of **(a)** double sided Al:ZnO and **(b)** double sided ZnO films deposited by dip coated technique.

The estimated thicknesses of thin films were obtained using the optical transmittance spectra in the range 300-900 nm. The optical constants such as thickness and refractive indexes of thin films in the form of Film A/Glass/Film A or Film A/Glass can be obtained using a method called *Pointwise Unconstrained Minimization Algorithm (PUMA)* developed by Birgin [12]. The main advantage of this method is that it does not need the interference fringes in the optical transmission spectrum. There is excellent agreement between the experimental spectra and theoretical spectra for all the Al:ZnO/Glass/Al:ZnO, ZnO/Glass/ZnO and Al:ZnO/Glass and ZnO/Glass samples. Two of the experimental and computed optical transmission spectra for the Al:ZnO/Glass/Al:ZnO and ZnO/Glass/ZnO thin films are shown in Figure 5. Calculated film thickness and refractive index for 700 nm are given in Tables 1 and 2. Decreasing the refractive index that is indicates the band gap shift and increase in transmittance.

CONCLUSION

We have demonstrated an effective dip-coating method for synthesis of undoped ZnO and Al:ZnO thin films. In this method, although a small number of dip process to be done, the film formation on the substrate becomes more prominent. It is because the samples were exposed to temperature gradient between the dipping periods. As a result, considerable changes were observed in the optical transmission spectra of the films. Optical transmittance spectra of the films in the form of Film A/Glass/Film A were used to determine the film thickness and optical band gaps. The optical transmission of Al:ZnO/Glass/Al:ZnO samples was higher than 80% in the visible and near infrared region. The optical band gaps of Al doped ZnO films onto glass substrate are increases with increase of Al content and the absorption edge shifted to a shorter wavelength (blue shift) compared with the undoped ZnO thin film. According to the results an increases of the band gap for AZO films prepared by both DC and USP techniques. The hexagonal wurtzite structure of ZnO seems to be protected for Al:ZnO thin film. However, there is no preferential orientation such as (002). In addition, the peaks intensities are decreased when a small amount of Al was inserted into the ZnO lattice structure.

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REFERENCES

[1] http://en.wikipedia.org/wiki/Hot-dip_galvanizing

[2] Ignjatovic N, Brankovic Z, Dramicanin M, Nedeljkovic J. M, and Uskokovic D. P, Preperation of TiO2 and ZnO Thin Films by Dip-Coating Method. Materials Sciences Forum. 1998; 282-283:147-152. DOI:10.4028/www.scientific.net/MSF.282-283.147.

[3] Jin M, Ying L. S, Preperation of ZnO films by reactive evaporation. Thin Solid Films. 1994; 237: 16-18. DOI:10.1016/0040-6090(94)90230-5.

[4] Aktaruzzaman A. F, Sharma G. L, Malhotra L.K, Electrical and Optical Properties of Germanium-Doped Zinc Oxide Thin Films. Thin Solid Films. 1991; 198: 67-74. DOI:10.1016/0040-6090(91)90325-R.

[5] Chen Z, Shum K, Salagai T, Zhang W, Strobl K, ZnO thin films synthesized by chemical vapor deposition. Applications and Technology Conference (LISAT), 7 May 2010; 1-6. DOI: 10.1109/LISAT.2010.5478331.

[6] Erarslan N, Güngör T, The determination of the thickness and optical constants of the ZnO crystalline thin film by using pointwise unconstrained minimization algorithm. Journal of Graduate School of Natural and Applied Sciences of Mehmet Akif Ersoy University. 2010; 2: 181-193.

[7] Gungor E, Gungor T, Effect of the substrate movement on the optical properties of ZnO thin films deposited by ultrasonic spray pyrolysis, Advances in Materials Science and Engineering. 2012;1-7 Article ID 594971. DOI: 10.1155/2012/594971.

[8] E. Gungor, T. Gungor, D. Caliskan, A, Ceylan, and E. Ozbay, Applied Surface Science, 2014; 318; 309–313. DOI:10.1016/j.apsusc.2014.06.132.

[9] Lee J. H, Park B. O, Transparent conducting ZnO:Al, In and Sn thin films deposited by the sol–gel method. Thin Solid Films. 2002; 426: 94-99. DOI: 10.1016/0040-6090(91)90325-R.

[10] Gungor T, Gungor E, Computer Controlled Dip Coating System Design. Journal of Graduate School of Natural and Applied Sciences of Mehmet Akif Ersoy University. 2012; 3:1-4.

[11] Hadipour N. L, Peyghan A. A, and Soleymanabadi H, Theoretical Study on the Al-Doped ZnO Nanoclusters for CO Chemical Sensors. The journal of Physical Chemistry C. 2015; 119; 6398-6904. DOI:10.1021/jp5130192.

[12] Birgin E. G, Chambouleyron I, and Martinez J. M, Estimation of optical constants of thin films using unconstrained optimization. Journal of Computational Physics. 1999; 151: 862-888.

Türkçe Öz ve Anahtar Kelimeler

Farklı Son-Gel Teknikleri ile Biriktirilmiş Al:ZnO İnce Filmlerinin Optik Özellikleri: Ultrasonik Sprey Pirolizi ve Daldırmalı Kaplama

Ebru Gungor* and Tayyar Gungor

Öz: Aşılanmamış ve Al ile aşılanmış çok kristalli ince filmler cam substratlar üzerinde bilgisayarla kumanda edilen daldırmalı kaplama (DC) ve ultrasonik püskürtmeli piroliz (USP) sistemleriyle üretilmiştir. DC sürecinin film biriktirme parametreleri örnekler için en uygun hale getirilmiştir. Bu teknikte, substrat bir tüp fırını kullanılarak sıcaklık gradyanına maruz bırakılmıştır. Çalışmada, diğer çözücü esaslı teknik ise geleneksel USP'dir. Çözeltide çinko tuzunun ve alüminyum tuzunun derişimleri sırasıyla 0,1 M ve çinko tuzunun molaritesinin %2'si olarak sabit tutulmuştur. Optik özellikler iki farklı teknikle biriktirilen filmler için karşılaştırılmıştır. Daldırmayla kaplanmış Al:ZnO/Cam/Al:ZnO örneğinin ve ultrasonik yöntemle püskürtülmüş Al:ZnO/Cam örneğinin optik geçirgenliği görünür alanda ve yakın kızılötesi alanda %80 daha yüksek bulunmuştur. Optik sabitleri belirlemek için FilmA/Cam/FilmA ve FilmA/Cam biçimlerinde filmlerin deneysel optik geçirgenlik spektrumları kullanılmıştır. Cam üstüne Al ile aşılanmış ZnO filmlerinin kaplandığı örneklerde optik band aralıkları Al içeriğinin artması ile yükselmiştir ve aşılanmamış ZnO ince filmleriyle karşılaştırıldığı zaman soğurma eşiği daha düşük dalgaboyuna (maviye) kaymıştır.

Anahtar kelimeler: Sol-jel, daldırmalı kaplama, ultrasonik püskürtmeli piroliz, Al aşılı çinko oksit, optik sabitler.

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