Effects of Molarity Variation on The Optical Property and Topography of ZnO Thin Films Deposited Via Spray Pyrolysis

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Abstract. Thin film deposition is very crucial in fabricating ZnO-based electronic devices such as sensors, piezoelectric generators and photovoltaic solar cells. In this study, ZnO thin films were deposited in glass substrates via spray pyrolysis with varying zinc acetate dihydrate concentration. The films exhibited high absorption in the near-UV region (292-400 nm), yet maintaining high transmission over the visible spectra with maximum attenuation of only 33%. The optical bandgap energy of the deposited ZnO films was almost constant at around 3.25 – 3.27 eV. At higher molarity, the optical adsorption is greater especially at near-UV region while the optical transmission is lower at the visible light region. SEM images reveal that the ZnO film is composed of tiny particles. Generally, the film becomes rougher at higher zinc acetate concentration due to the formation of larger ZnO particles.

1. Introduction

ZnO is an important n-type semiconductor due to its wide range of applications in chemical sensing [1-3], piezoelectric generation [4], photocatalysis [5, 6], antibiotics [7], photovoltaics and optoelectronics [8], and transistor fabrication [9], among others. Special attention is given to ZnO due to its interesting electrical properties, good chemical stability, and remarkable thermal properties. Intense researches have been devoted in growing diverse morphologies. ZnO has been synthesized in the forms of nanorods, nanowires, nanopyramids, nanoplatelets, hierarchical structures as well as thin films [10, 11].

Thin film deposition can be done in various ways such as pulsed laser deposition, arc-discharge, physical vapor deposition, hydrothermal method and electrochemical deposition [10, 11]. One of the most widely used method is spray pyrolysis [12-20]. It is a cost-effective and simple way to deposit thin films wherein the precursor-containing solution is basically sprayed over a heated substrate. This process is very suitable for large scale applications. In spray pyrolysis, the morphology of ZnO structures are dependent on a number of parameters including the precursor material, solvent, precursor concentration, substrate, temperature, spray rate, droplet size, nozzle-to-substrate distance, deposition time, etc. [17]. However, there are limited comprehensive studies that investigate the
effects of precursor concentration in the optical property of ZnO film as the trend in current researches is more focused on the deposition of ZnO with unique morphologies. In this work, transparent ZnO films were deposited on glass substrates via spray pyrolysis using zinc acetate dihydrate solution as source. The effects of varying the molarity on the topography and optical property of the film were investigated.

2. Experimental Methods
Microscope glass slides (Sail Brand, clear) having ~1.0 cm² area were used as substrates. These were soaked in hydrochloric acid [HCl, ≈ 30%] for 10 min, washed with soap and rinsed with deionized water. The substrates were then sonicated in ethanol for 10 min and dried in air. The precursor solvent was prepared by mixing isopropyl alcohol [CH₃CHOHCH₃] and de-ionized water in a 1:3 volume ratio. A stoichiometric ratio of zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O, Techno Pharmachem] was mixed with the solvent by magnetic stirring for 10 min at 1000 rpm. To further stabilize the solution, 2.67 mL of glacial acetic acid [CH₃COOH, Macron Fine Chemicals] was added for every mole of zinc acetate (0.13, 0.27, 0.40 and 0.53 mL for 0.05, 0.10, 0.15 and 0.20 M, respectively).

The substrates were pre-heated at 550°C on a hot plate (Corning, PC-420D) maintaining a constant temperature. The precursor solution of desired molarity was sprayed onto the substrates using a commercial atomizer with a nozzle-to-substrate distance of about 20 cm. The solution was sprayed for 40 min at a rate of one spray per 5.0 s. After spraying, the samples were left undisturbed for 10 min at 550°C before reducing the temperature to 450°C, allowing the deposited crystals to settle for 1 h. The samples were cooled to room temperature and sonicated in water for 10 min to remove loose materials and finally dried in air.

The optical absorption and transmission behavior of the deposited ZnO films were investigated using a UV-Vis spectrophotometer (SHIMADZU, UVmini-1240). The morphology and topography of the ZnO films were examined using a scanning electron microscope (JEOL JSM 6010LV).

3. Results and Discussion
3.1. General observations
After 10 min of magnetic stirring, clear solutions were produced for concentrations 0.05, and 0.10 M, suggesting that the zinc salt was dissolved thoroughly. However, for the 0.15 M solution, zinc acetate particles started to precipitate after some time but dissolves back with minimal agitation. When a 0.20 M solution was prepared, some of the zinc acetate crystals remained solid, which indicates that the concentration exceeded the maximum solubility of zinc acetate at room temperature.

After 40 min of continuous spraying, the glass substrates produced rainbow-colored reflections when illuminated with white light – an indication that a thin film has been deposited. However, the rainbow-colored reflections diminished as the precursor concentration was increased.

3.2. Optical characterization
Figure 1 shows the absorption spectra of the ZnO films with respect to the absorption of the glass slide. As shown, the deposited films selectively absorbed portion of the electromagnetic spectrum at around 300 - 400 nm wavelength, corresponding to the near-ultraviolet region. The sharp fundamental absorption edges of the samples at around 400 nm are consistent with other reports on the deposition of ZnO thin films. [18] The film produced using 0.05M solution has relatively narrower absorption range at around 305 - 400 nm compared to the other three samples which have almost the same absorption in range 292 - 400 nm. This is possibly due to the existence of a fixed maximum range of electromagnetic wave that the ZnO can absorb. An upward trend in the absorption spectra is observed signifying that the absorption is enhanced as the solution concentration is increased. Visible light (380 – 780 nm) and near-infrared regions basically passed through the film with minimal absorbance.

Shown in figure 2 is the transmission spectra of the deposited ZnO films focused in the range 350nm to 900nm. The solution of lowest concentration, 0.05M produced the film with the highest transmittance of about 90.0%, relative to the transmission of the glass substrate in the visible region.
The sample from the 0.20M precursor solution obtained the lowest transmittance, which is approximately 67.0%. It can be observed that the increase in the molarity tends to result in lower transmission. A red-shift in the absorption edge can also be noticed as the concentration increases. These observations are consistent with other studies [12, 13, 15].

Figure 3 shows the corresponding Tauc plots generated from the absorption spectra of the samples. The band gap for each sample was calculated using the absorbance spectra (see Appendix for the computations). The calculated values are almost constant at around 3.25 – 3.27 eV, which is the usual band gap of ZnO, as reported [15], confirming the successful deposition of ZnO films.
Figure 3. Corresponding Tauc plots of the samples produced using zinc acetate solution at concentrations: a) 0.05, b) 0.10, c) 0.15 and d) 0.20M.

3.3. Scanning electronmicroscopy
The SEM images of the ZnO films are shown in figure 4. For the sample that uses 0.05 M zinc acetate solution, the deposited film is characterized with skeleton-like and root-like structures filled with spherical particles. At a higher resolution, it was observed that the film is composed of spherical particles with different sizes. Relatively larger particles, ranging from 0.5-2.0 μm, were randomly scattered but were mostly found near the edge of the glass substrate. When the number of particles is enough to covering the entire surface, they likely cluster and join together forming the film [19]. For the sample sprayed with 0.10M zinc acetate solution, the film appears to be smooth all throughout. Smoothness depends on the size distribution of deposited particles. A smooth surface is a result of deposition of ZnO particles with almost uniform sizes. The roughness of the film was more apparent when the concentration of the zinc acetate solution was further increased. Large particles with an average size of about 1.0 μm were already present in the film deposited using 0.15M solution. For the sample sprayed with 0.20 M zinc acetate solution, large particles with an average size of about 2.0 μm were found embedded on the film. Interestingly, the film appears to be made up of intertwined fibers resulting to a spongy surface appearance.
Figure 4. SEM images of the samples synthesized at different concentrations of the precursor solution: a) 0.05 M, b) 0.10 M, c) 0.15 M and d) 0.20 M
The SEM micrographs show that the film is actually made up of two distinct entities, analogous to the two phases of composite materials. In here, the “matrix” is the base or the plane containing the “inclusions,” which are the relatively larger particles seen on the surface. Though, in this case, the matrix and the inclusions are of the same material. The “matrix” is composed of very minute particles with relatively narrow size distribution that are linked together, forming the flat film. These minute particles are ZnO formed from the reaction of tiny droplets of zinc acetate solution as they approach or reach the surface of the heated substrate. The size of these particles is dependent on two factors: i) size of the droplets and ii) concentration of the solution. For a given concentration, the larger the droplets, the greater the amount of precursor, hence the larger the ZnO particles that will be formed [20]. For the same droplet size, the higher the concentration, the greater the amount of precursor, and thus the bigger the ZnO particles. Particle size generally gets bigger when the concentration is increased as already shown in many literatures [12, 13, 15]. Since the droplets formed during spraying vary in size, the resulting ZnO particles also differ in sizes. This is clearly observed from the SEM image of the sample produced using 0.05M zinc acetate solution. Huge droplets possibly dripped off into the substrate creating gigantic structures (i.e. skeleton- and root-like structures).

The inclusions in samples that use 0.15 and 0.20 M concentrations are possibly ZnO particles that are formed from the transformation of undissolved zinc acetate crystals which precipitated prior to spraying. Thus, it leads to the formation of bigger particles.

The surface texture of the film seems to follow a specific trend. At 0.05M, the film contains a gigantic structure that makes its surface uneven, although the rest of the film is somewhat flat. The film obtained its smoothest state at 0.10M. The surface becomes rougher upon further increase in the concentration of the zinc acetate solution.

The observations agree well with the results of the optical transmission and absorption studies. An increase in the concentration of zinc acetate solution resulted to the formation of larger particles, increasing the surface roughness, thus leading to the lowering of the optical transmittance of the deposited ZnO film.

4. Conclusions
ZnO thin films were successfully deposited in glass substrate by means of spray pyrolysis using zinc acetate dihydrate in aqueous solution as source. The films generally absorb near-UV radiation, around 292 – 400 nm and transmit visible light with maximum attenuation of 33%. The optical band gap was calculated to be around 3.25 - 3.27 eV, with no significant variation among the samples confirming the successful deposition of ZnO. The optical absorbance of the film increases as the zinc acetate solution concentration increases. Subsequently, the optical transmittance decreases as the concentration rises. The results might have been affected by the morphology of the particles and the surface topography of the deposited film. Generally, ZnO particles become coarser at higher concentrations leading to poorer transmittance of visible light.

5. Appendix
The band gaps of the four samples are estimated using Tauc’s empirical formula [21]:

\[(a\nu)^{1/n} = c(\nu - E_g)\]

Here, \(a\) is the absorption coefficient, \(h\) is the Planck’s constant, \(\nu\) is the frequency of the incident light, \(c\) is a proportionality constant, \(E_g\) is the optical band gap energy, and \(n\) is a constant which is dependent on the nature of the sample transition (\(n = 1/2\) for direct allowed transition, \(n = 3/2\) for direct forbidden transition, \(n = 2\) for indirect allowed transition, and \(n = 3\) for indirect forbidden transition). For this study, the exponent is 1/2 since ZnO has a direct band gap.

The values of \((a\nu)^{2}\) are plotted against \(\nu\). Linear extrapolation towards the x-axis is done along the steep portion of the resulting curve. The intercept of the regression line at \((a\nu)^{2} = 0\) gives the value of the band gap energy \(E_g\).

The absorption coefficient \(a\) is taken to be
where \( t \) is the film thickness and \( A \) is the absorption value at the corresponding electromagnetic wavelength. Equation 1 becomes

\[
(Ah\nu)^2 = \frac{e^2}{(2303)^2} c(h\nu - E_g)
\]

The film thickness is presumed to be uniform for a given sample. Thus, it is already sufficient to obtain the band gap by plotting \((Ah\nu)^2\) against \( h\nu \), even without the knowledge of the film thickness.

References

[1] Shinde S, Patil G, Kajale D, Gaikwad V and Jain G 2012 J. Alloy. Compd. 528 109
[2] Mani G, Bosco J and Rayappan B 2014 Sensor Actuator B 198 125
[3] Charpe S, Raghuwanshi F, Lamdhade G and Kalymwar V 2015 IJEE 3 (2) 12
[4] Kumar B and Kim S 2012 Nano Energy 1 342
[5] Hsiao K, Liao S and Chen Y Mater. Sci. Eng. A 447 71
[6] Bizarro M, Sanchez-Arzate A, Garduno-Wilches I, Alonso J and Ortiz 2011 Catal. Today 166 129
[7] Cuevas A, Balangcod K, Balangcod T and Jasmin A 2013 Procedia Engineer. 68 537
[8] Djurisic A, Ng A and Chen X 2010 Prog. Quant. Electro. 34 191
[9] Goldberger J, Sirbuly D, Law M and Yang P 2005 J. Phys Chem B 109 (1) 9
[10] Yi G, Wang C and Park W 2005 Semicond. Sci. Tech. 20 (4) S22
[11] Wang Z 2004 J.Phys. Condens. Matter 16 R829
[12] Ali A 2014 IJSER 5 (1) 2250
[13] Habubi N, Abood Z and Algamel A 2015 World Sci. News 22 91
[14] Sakthivelu A, Saravanan V and Anusuya M 2011 J. Ovonic Res. 7 (1) 1
[15] Tarwal N and Patil P 2010 Appl. Surf. Sci. 256 (24), 7451
[16] Benramache S, Belahseen O, Guettfa A and Arif A 2014 J. Semiconductors 35 4
[17] Perednis D and Gauckler L 2005 J. Electroceram. 14 103
[18] Rameshkumar C and Subalakshmi R 2015 JCHPS 7 (1) 459
[19] Nehru L, Umadevi M and Sanjeeviraja 2012 IJME 2 (1) 12
[20] Ghaffarian H, Saiedi M and Sayyadnejad M 2011 IJCCE 30 1
[21] Tauc J, Grigorovici R and Vancu A 1966 Phys. Stat. Sol. B 15 (2) 627