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Effect of different technological approaches on the optical properties of ZnO sol-gel thin films

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Abstract. The work presents a sol-gel approach with two types of solvents for ZnO films deposition in view of varying the films' structural and optical properties. The ZnO films were characterized by X-Ray diffraction (XRD) and found to have a polycrystalline wurtzite phase structure. The grain sizes and the lattice parameters were determined; it was established that the ZnO crystallites' size increases with the annealing temperatures from 25 nm to 36 nm. The ZnO films possess high transmittance in the visible spectral range. Further, the optical band gap values were estimated. The material's vibration properties were analyzed by Fourier Transform Infrared (FTIR) spectroscopy. The two technological sol-gel approaches for deposition of ZnO films, using two different solvents, proved to be successful in producing structures with different structural and optical properties. The thin films fabricated were very smooth and uniform and exhibited a high transparency in the visible spectral range.

1. Introduction

ZnO has been the object of intensive scientific research due to its interesting properties, such as a wide band gap (3.37 eV at room temperature) with large exciton binding energy (60 meV), a high chemical stability, a high refractive index, a high thermal conductivity, as well as binding, antibacterial and UV protection properties [1]. Based on these attractive features, ZnO has found numerous applications as gas sensors, thin-film transistors, surface acoustic wave devices and solar cell windows [2, 3]. Another interesting application is as dilute magnetic semiconductors, which have been lately emerging as materials for spintronic applications [5]. Recently, ZnO films have been prepared by RF magnetron sputtering, chemical vapor deposition, electrochemical deposition, spray pyrolysis [6, 7] etc. The optical properties of ZnO films are of particular interest from both fundamental and technological viewpoints. The advantages of the sol-gel method include excellent control of the stoichiometry, possibilities to modify the composition, etc. Among the variety of factors affecting the quality of the ZnO sol-gel films is the sol concentration, the chelating agent, the pre-heating temperatures, the subsequent annealing treatments, the aging and a dip or spin-coating deposition [8].

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This work describes two sol solutions for spin coating of ZnO films in view of modifying their optical properties. The effect of using two preheating temperatures was also studied. The films' structural and optical properties were investigated by XRD, FTIR and UV-VIS spectrophotometry.

2. Experimental

Two types of sol solutions were developed using zinc acetate dehydrate as a zinc precursor with a concentration of 0,4 M.

Solution 1) The zinc acetate was dissolved in isopropanol. The complexing agent and stabilizer used was trietanolamine (TEA). The molar ratio TEA/Zn was fixed at 1.

Solution 2) the solvent used was absolute ethanol and the corresponding complexing agent was monoethanolamine (MEA). The molar ratio MEA/Zn was fixed at 1.

The films were deposited by spin coating at 4000 rpm on quartz and Si substrates. The preheating temperatures used (the firing between layers) were 250 °C/10 minutes and 300 °C/10 minutes. The films were annealed at temperatures of 500 °C, 600 °C, 700 °C and 800 °C for one hour.

The XRD spectra of the sol-gel films were recorded by means of a Bruker D8XRD diffractometer at a grazing of angle 2° and a step of 0.1° for 8 s per step. The FTIR measurements were performed in the spectral region 350 – 4000 cm⁻¹ on an IR Prestige-21 Shimadzu FTIR Spectrophotometer. The optical measurements were conducted by a Shimadzu 3600 UV-VIS-NIR spectrophotometer.

3. Results and discussions

The film thickness of the ZnO sol-gel films prepared did not differ significantly, which allowed us to compare their structural and optical properties. Depending on the annealing treatment, the ZnO films of solution 1 had thicknesses of 150 – 140 nm in the case of a preheating temperature of 250 °C; the corresponding values for a preheating at 300 °C were in the range 140 – 160 nm. The film thicknesses for the films of solution 2 were 155 – 160 nm (for a preheating at 250 °C) and 160 nm (300 °C).

Figure 1 presents the XRD spectra of the ZnO films of solution 1 treated at the two preheating temperatures and subsequently annealed at high temperatures. The XRD data shows that the films have crystallized in wurtzite ZnO, as the main five reflections correspond to this crystal phase (JCPDS 01-07-8070). The films formed at the lower preheating temperature (250 °C) possess weaker XRD lines compared to the films preheated at 300 °C for all additional annealings from 500 °C to 800 °C. Thus, the preheating temperature influences the crystallization behavior, so that increasing the preheating temperature results in ZnO films of higher crystallinity.

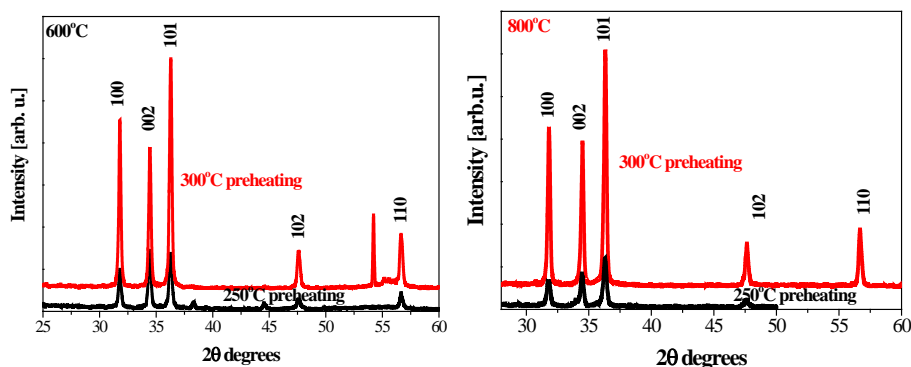


Figure 1. XRD spectra of ZnO sol-gel films prepared from solution 1 as a function of the preheating temperatures (annealing at 600 °C and 800 °C).

The structure of the films deposited from solution 2 was studied for a preheating temperature of 300 °C. Figure 2 shows XRD spectra of films prepared from the two solutions. The degree of crystallization of the films deposited from solution 1 is higher than that of the corresponding samples deposited from solution 2. The films are well crystallized without a preferential orientation.

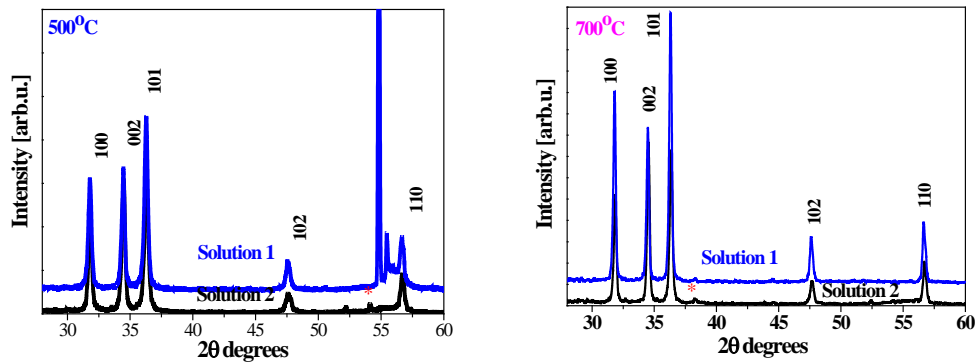


Figure 2. XRD spectra of ZnO films deposited from the two solutions and preheated at 300°C. The asterisk marks cubic ZnO₂.

The average crystallite sizes were estimated from the XRD patterns according to Scherrer's formula; the results are shown in figure 3. In the case of ZnO films of solution 1, the crystallites of the samples preheated at 250 °C are smaller than those of the films preheated at 300 °C. Another interesting feature is that the crystallites' size decreases with the annealing temperatures for the films treated at the lower preheating temperature, while the crystallites grow larger in the ZnO films preheated at 300 °C for for both solutions. When comparing the films of the two solutions, one can see that, for the first set of samples, the crystallites are slightly larger, with the highest value found for the annealing temperature of 700 °C. For the films of solution 2, the rise of the crystallites' size is almost linear when the annealing temperature is raised.

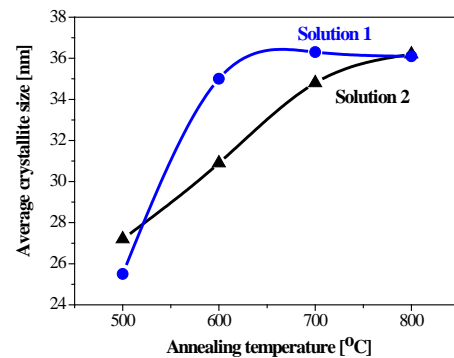


Figure 3. Average crystallites' sizes of the sol-gel ZnO (solution 1 – blue line) and ZnO (solution 2 – black) films, as a function of the annealing temperatures.

Thus, the XRD investigation reveals that both the solvent and the MEA used influence the crystallization behavior of the ZnO films. A difference of 50 °C in the preheating temperature affects the size of the crystallites and the degree of crystallinity.

The vibrational properties of the ZnO sol-gel films were investigated as a function of the preheating and annealing temperatures. Figure 4 shows FTIR spectra of sol-gel films annealed at 500 °C and 800 °C; the effect of the other annealing temperatures was also analyzed. The FTIR spectra indicate that the solution type and the preheating temperatures (not given here) affect the shapes and

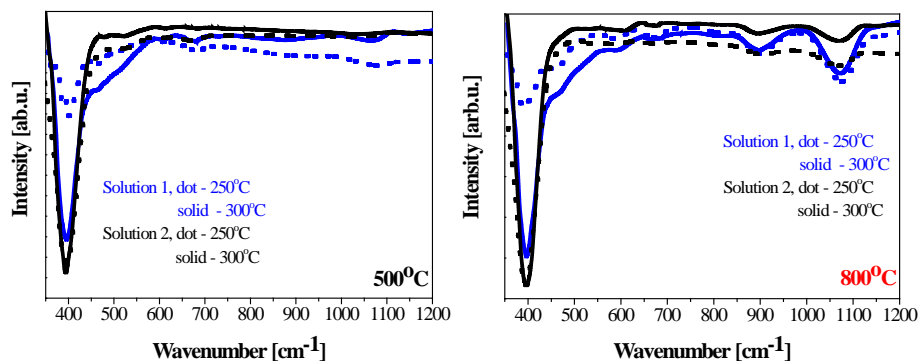


Figure 4. FTIR spectra of sol-gel ZnO films, annealed at 500 and 800°C.

positions of the bands. Intensive absorption bands at $3300 - 3500 \text{ cm}^{-1}$ for the preheated samples due to the stretching vibrations of OH groups [9] can be seen in the spectra of the films of solution 1, while the corresponding bands for the films of solution 2 are weaker. The films of solution 1 (250°C) exhibit a broad band of a lower intensity with two clear maxima at 463.0 cm^{-1} and at 392.1 cm^{-1} . Increasing the preheating temperature to 300°C results in a stronger broad band centered at 433.2 cm^{-1} with two additional peaks at 406.3 cm^{-1} and 386.4 cm^{-1} . The films from solution 2 display stronger absorption bands at 404 cm^{-1} (preheating 250°C) and 390 cm^{-1} (300°C). These absorption bands are typical for ZnO [10]. The high temperature treatments lead to a similar tendency in the spectra. The main absorption band for the samples of solution 1 appears at 402 cm^{-1} with two distinctive peaks at 464 cm^{-1} and 383 cm^{-1} (preheating 250°C) and, respectively, one strong line at 394.5 cm^{-1} (preheating 300°C). In contrast, the films of solution 2 show a strong absorption line at 394 cm^{-1} with a greater intensity for the film preheated at the higher temperature. In all films studied, raising the temperature above 600°C results in a main band at 396 cm^{-1} with slight differences in the position and intensity. In summary, the FTIR analysis reveals that the ZnO films possess different vibrational properties depending on the solution used and the heat treatment.

The optical properties were studied for ZnO films deposited on quartz substrates under similar technological conditions. The differences in the films' properties are presented in figure 5. For the films of solution 1, preheating at 250°C results in more transparent coatings compared with those preheated at 300°C ; it is independent of the heat treatment. For the ZnO films of solution 2, the tendency is reverse, namely, the films preheated at 300°C are always more transparent than those preheated at 250°C . The high-temperature annealing ($500 - 800^\circ\text{C}$) lowers the films' transmittance.

The specific bands observed in the optical spectra below the band gap wavelength are due to the excitonic absorption of ZnO (see table 1). The excitonic feature of bulk ZnO is located near 373 nm . The excitonic absorption of ZnO films from solution 2 for the two preheating temperatures are weaker compared to the other ZnO samples (solution 1).

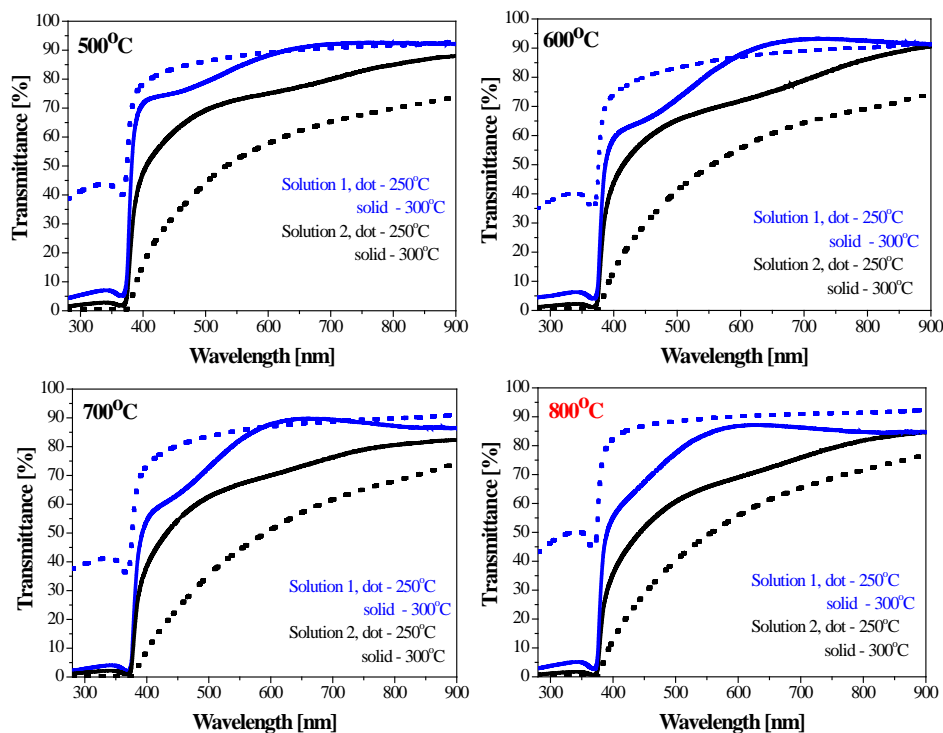


Figure 5. Transmittance spectra of ZnO films depending on the preheating and annealing temperatures.

Table 1. Excitonic absorption and optical band gap energy, estimated from optical data.

Preheating	Annealing	excitonic absorption [nm]		E_g [eV]	
		Solution 1	Solution 2	Solution 1	Solution 2
250 °C	-	301	-	3,52	3,28
	500 °C	335	347	3,33	3,27
	600 °C	339	347	3,31	3,25
	700 °C	341	347	3,31	3,25
	800 °C	344	347	3,30	3,27
300 °C	-	-	331	3,36	3,30
	500 °C	344	337	3,31	3,28
	600 °C	345	337	3,29	3,27
	700 °C	347	343	3,29	3,28
	800 °C	347	347	3,29	3,28

On the other hand, the excitonic absorption in the case of the preheating temperature of 300 °C is better expressed. The values of the optical band gap are close to the reported value (3,37 eV) for bulk ZnO [11] and to those cited in the literature for ZnO films [12]. The films prepared from solution 1 at the preheating temperature of 250 °C have optical band gaps decreasing from 3,33 eV to 3,30 eV depending on the annealing, while the films of the same solution preheated at 300 °C exhibit $E_g = 3.29$ eV regardless of the annealing temperatures with the exception of 500 °C. No clear tendency is seen for the ZnO films of solution 2 with the values ranging from 3,25 eV to 3,28 eV.

4. Conclusions

Nanosized ZnO thin films were prepared by the sol-gel technique using two types of sol solutions. The sols prepared remained stable for more than three months. The ZnO films had the polycrystalline structure of hexagonal wurtzite. The ZnO grain size varied from 25 nm to 37 nm depending on the solution type and the heat treatments. The transmittance in the visible range was 77 – 90 %, while the optical band gaps ranged from 3.25 eV to 3.52 eV. The sol-gel technology was thus proved to be promising for deposition of ZnO films intended for applications in different optoelectronic devices or in solar cells.

References

- [1] Goyal A and Kachhwaha S 2012 *Mater. Let.s* **68** 354–6
- [2] Djuriscic A B, Ng A M C and Chen X Y 2010 *Progress in Quantum Electr.* **34** 191–259
- [3] Lee J H, Ko K H and Park B O 2003 *J. Crystal Growth* **247**/1-2 119–25
- [4] Riaz S, Naseem S and Xu Y B 2011 *J Sol-Gel Sci. Technol.* **59** 584–90
- [5] Hongsingthong A, Yunaz I and Konagai M 2011 *Solar Energy Mater. Solar Cells* **95** 171–4
- [6] Vimalkumar T, Poornima N, Kartha C and Vijayakumar K P 2011 *Appl. Surf. Sci.* **257** 8334–40
- [7] Houg B, Huang Ch-L and Tsai S-Y 2007 *J. Crystal Growth* **307** 328-33
- [8] Caglar Y, Illican S, Yakuphanoglu F, Gao K, Lu P and Xue D 2009 *J. Alloys Comp.* **448** 885-8
- [9] Ning G, Zhao X P, Li Y and Zhang Ch Q 2006 *Optical Mater.* **28**/4 385-90
- [10] Li C P, Jang, B H, Wang X C, Li M J, Su L and Li X W 2011 *Appl. Surf. Sci.* **257** 5998-6003
- [11] Prajapati C S and Sahay P P 2012 *Appl. Surf. Sci.* **258** 2823-8
- [12] Chattopadhyay S, Neogi S K, Pandit P, Dutta S, Rakshit T, Jana D, Chattopadhyay S, Sarkar A and Ray S K 2012 *J. Luminescence* **132** 6-11