

Morphological and optical investigation of Sol-Gel ZnO films

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Abstract. This paper presents morphological and optical studies of the properties of spin-coated ZnO films depending on the annealing temperatures. The films microstructure was explored using a scanning nano-hardness measuring device of the NanoScan family, based on the principles of atomic force microscopy, in a constant frequency mode. The surface study revealed that the root-mean-square (RMS) surface roughness of 985.64×985.64 nm ZnO films becomes greater with the increase of the annealing temperature, but the film surface remains uniform and smooth. The results were confirmed by XRD analysis, which demonstrated that the crystallite size grew from 25 to 36 nm with the thermal treatments. The ZnO films possessed high transmittance in the visible spectral range and the optical band gaps in ZnO films varied from 3.25 eV to 3.52 eV. The optical and morphological properties of the ZnO films formed on Si and quartz substrates are very good. The sol-gel approach proposed for deposition of nanostructured ZnO films is promising for applications in optoelectronic devices or solar cells.

1. Introduction

Zinc oxide has been widely studied as one of the binary II–VI semiconductor compounds with a hexagonal wurtzite structure possessing an optical band gap of 3.37 eV and a large exciton energy [1]. Other interesting properties of ZnO include its optical, acoustical and electrical properties, high photosensitivity, high optical transparency in the visible region and stability, which can be applied in the fields of electronics, optoelectronics and sensors [2, 3]. Some potential applications are as piezoelectric transducers, optical waveguides, acousto-optic media, surface acoustic wave devices, conductive gas sensors, transparent conductive electrodes, solar cell windows, and varistors [4].

Currently, many methods are used to prepare ZnO films, such as molecular beam epitaxy (MBE), chemical vapor deposition, electrochemical deposition, pulsed laser deposition (PLD), reactive evaporation, magnetron sputtering, spray pyrolysis and atomic layer deposition [5, 6]. Among these deposition methods, the sol-gel technology has proved to be a low-cost and flexible technique, offering advantages such as simple deposition equipment, easy composition adjustment and incorporation of different dopants, fabrication of uniform films over substrates of large area [7].

In this work, a sol-gel technology was applied to achieve uniform and transparent ZnO thin films. Two types of sol solutions differing in the solvent used were developed. The structural and optical

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properties were compared of ZnO films prepared from the two sol solutions by spin coating. The films morphology was studied by a scanning nano-hardness measuring device depending on the different thermal treatments. Their vibrational and optical properties were also investigated by using FTIR and UV-VIS spectroscopy.

2. Experimental

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

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 to 1.

Solution 2) The solvent used was absolute ethanol and the corresponding complexing agent was trietanolamine (TEA). The molar ratio TEA/Zn was fixed to 1.

The films were deposited by spin coating at 4000 rpm on glass and Si substrates. The films were subjected to annealing at the temperatures of 400, 500 and 600 °C. The thickness of the films obtained from the two solutions was close, which made their properties comparable. The thickness values were in the range of 130 to 100 nm depending on the annealing temperatures.

The films were investigated by a NanoScan scanning nano-hardness measuring device, which is based on the principles of scanning force microscopy. The NanoScan data [8] can yield complex information on the surface roughness, chemical composition and local surface hardness. The FTIR measurements were performed in the spectral region 350-4000 cm^{-1} by an IRPrestige-21 Shimadzu FTIR Spectrophotometer. The optical measurements were conducted by using a UV-VIS-NIR Shimadzu 3600 spectrophotometer.

3. Results and discussions

Previous XRD study [9] have shown that sol-gel ZnO films (Solution 2) start to crystallize at the relatively low temperature of 400 °C. The degree of crystallization increases with the annealing temperature. The XRD diffraction pattern corresponds to the hexagonal wurtzite structure (JCPDS 01-07-8070) with no preferential orientation observed. The crystallite sizes change from 22 nm (400 °C annealing) to 35 nm (600 °C annealing). The XRD study of ZnO films prepared from solution 1 (600 °C) reveals a polycrystalline structure with a wurtzite phase. It exhibits a lower degree of crystallization (lower intensity and broader XRD peaks) compared to the corresponding ZnO films deposited from solution 2. The estimated crystallite size was 31 nm, revealing smaller crystallites compared to ZnO film (solution 2).

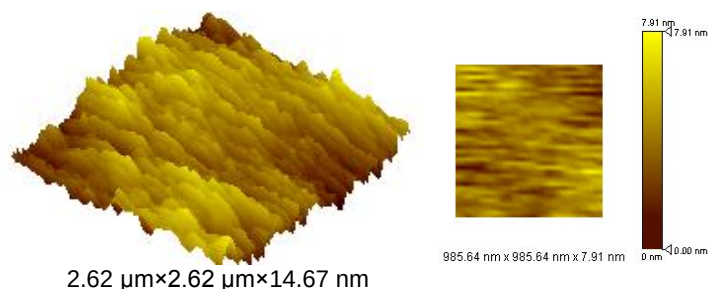


Figure 1. Three-dimensional and plane view images of sol-gel ZnO films obtained from solution 1 and annealed at 600°C.

Our morphological study was applied to ZnO films obtained from solution 1 and treated at 600 °C (figure 1), and ZnO films (solution 2) annealed at 400, 500 and 600°C (figure 2). Table 1 presents the roughness parameters determined for the ZnO films. The RMS parameter is the standard deviation of the surface heights values within a given area, where R_a is the average roughness (the arithmetic mean of the absolute values of the height of the surface profile $Z(x)$) and R_z is the arithmetic mean of the highest peaks added to the deepest valleys over the evaluation length measured. The maximum roughness is defined as the distance of the highest to the lowest point within the image. This parameter

is very sensitive to single peaks and valleys in the surface, whereas the R_a value is only slightly affected by a single surface feature. These parameters are derived from the NanoScan software.

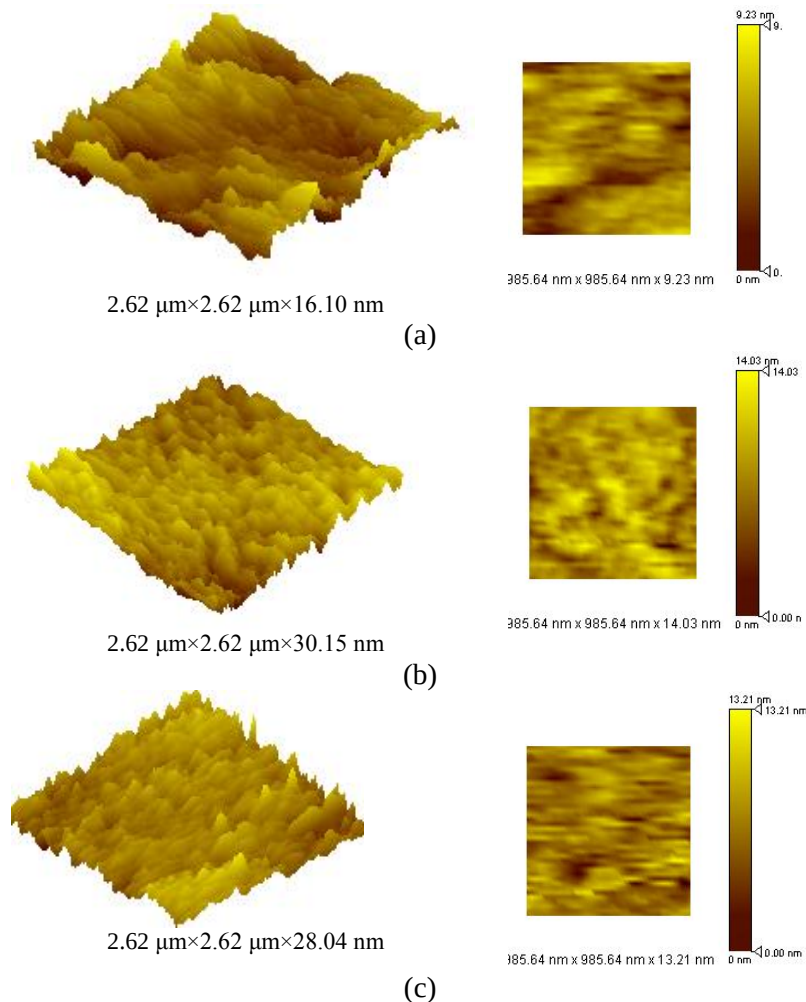


Figure 2. Surface images of ZnO films (solution 2), annealed at 400 (a), 500 (b) and 600°C (c).

The AFM micrographs reveal that the sol-gel ZnO films possess a smooth and uniform surface. The roughness is influenced by the thermal treatment. The RMS values rise with the increase of the annealing temperature. This is in agreement with the XRD results, which indicate that the crystallites grow larger with the annealing. The surface morphology of the films, obtained from the two solutions, is very similar, but the ZnO films obtained from solution 1 show a lower roughness.

Table 1. AFM parameters for sol-gel ZnO films.

Solution	Thermal treatment	RMS [nm]	R_a [nm]	R_z [nm]	Max h [nm]
1	600°C	3.48	2.77	14.78	33.12
2	400°C	4.56	3.52	17.80	37.75
2	500°C	6.32	4.96	20.95	44.27
2	600°C	4.58	3.38	19.83	43.00

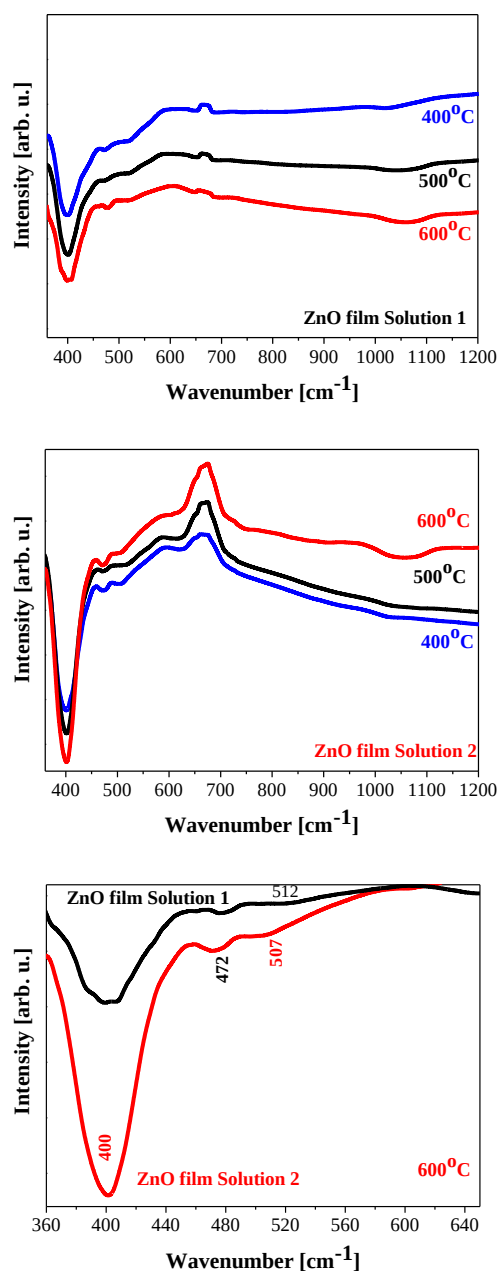


Figure 3. FTIR spectra of the sol-gel ZnO films annealed at different temperatures and a comparison of ZnO films prepared from the two solutions and annealed at 600°C.

the wavelength of 550 nm, while the films annealed at 500 and 600 °C reveal transmittance values of 86 and 80% ($\lambda = 550$ nm), respectively. This reduction of the transmittance in the visible range can be explained by the increase in the film crystallinity and bigger crystallites, causing scattering of the incident light. The same tendency of film transmittance decrease with the annealing temperature has been reported by other authors [13]. The comparison of the ZnO films prepared using the two solutions (figure 5a) shows that the transparency of ZnO (solution 1) is considerably higher, which is in agreement with the AFM investigation that reveal a smoother surface and lower RMS (table 1).

The vibrational properties of the ZnO films were studied by FTIR spectroscopy in the spectral range 350-4000 cm^{-1} . The absorption bands positions, shape and number depend on the films' chemical composition, crystalline structure and morphology [10]. The FTIR spectra of the films are given in figure 3. The spectra are narrower in the spectral region of 350-1200 cm^{-1} , where metal – oxygen vibrations are expected. The weak broad bands around 1058 cm^{-1} can be assigned to Si-O-Si bonds originating from the Si substrate. The absorption bands observed for the films obtained from the two solutions are at close positions; they differ only in the intensity of the main strong line.

The absorption band of ZnO films (Solution 2) is considerably more intense compared to the other ZnO films. This agrees with the XRD study showing that the ZnO films from solution 1 present a lower crystallinity. The weak broad peaks at 510 cm^{-1} (ZnO, Solution 1) and near 502 cm^{-1} (solution 2) are related to crystalline wurtzite ZnO. The strong main bands of ZnO around 404 cm^{-1} are attributed to Zn-O bonding in wurtzite ZnO. The IR active modes (408 and 513 cm^{-1}) are theoretically confirmed for the wurtzite phase [11]. The weaker bands at 425, 470 cm^{-1} are assigned to Zn-O stretching vibrations [12]; they appear in the FTIR spectra of ZnO (solution 2). The FTIR analysis reveals that the ZnO films possess different vibrational characteristics depending on the sol solution indicating that the solvent influences considerably the vibrational properties of the resulting sol-gel ZnO films.

The optical properties of the ZnO films were determined by spectrophotometric measurements (see figure 4). The transmittance spectra reveal very different optical behavior depending on the sol solution used. The ZnO films (solution 1) show an almost negligible change in the optical transparency, which reaches 91 % at 550 nm. On the other hand, the ZnO films deposited from solution 2 reveal a clear tendency of decreasing transmittance with the increase of the annealing temperature. The ZnO film treated at 400 °C shows a transparency of 91 % at

The small shoulders below the absorption edge indicate excitonic absorption. They differ for the two sets of sol-gel ZnO films. The ZnO films (solution 1) exhibit excitonic peaks at 345-350 nm, while the peaks of the ZnO films from solution 2 are located at 345 nm. However, these shoulders show a substantial blue shift relative to bulk ZnO (~ 373 nm), which could be due to the confinement effects in films [14]. The presence of excitonic absorption is an indication that the sol-gel ZnO films possess a high optical quality.

Using the data of the transmittance measurements one can estimate the optical band gap considering a direct gap semiconductor or to determine it by the second derivative of the transmittance spectrum [15, 16]. As can be seen from figure 5b, the optical band gaps of the ZnO films derived from solution 1 are larger and increase slightly with the annealing temperature. On the other hand, the optical band gap of ZnO films (solution 2) tends to decrease after a high temperature annealing. Other authors [17] have observed a similar reduction of the optical band gap as the annealing temperature is increased, which they assigned to the improved crystallinity of the films and the lower number of defects in them. It is known that the energy band gap of the ZnO film could be affected by the residual strain defects and grain size confinement [18]. The values are smaller than the optical band gap 3.37 eV of bulk ZnO.

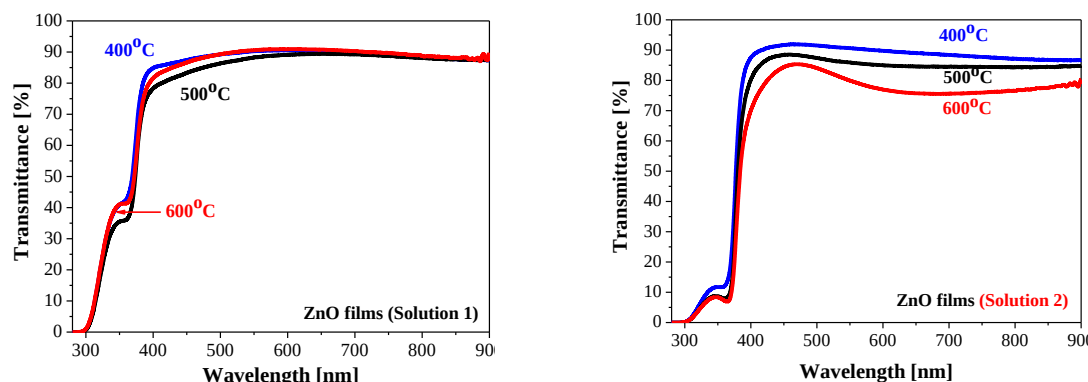


Figure 4. UV-VIS transmittance spectra of ZnO films annealed at different temperatures.

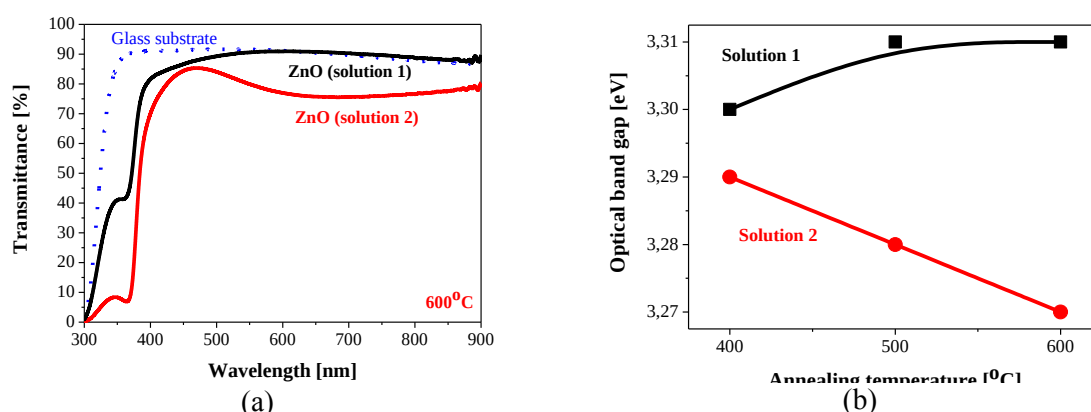


Figure 5. Comparison of ZnO films obtained from the two solutions and annealed at 600°C (a). The spectrum of bare glass is also given. Optical band gaps of the sol-gel ZnO films (b).

4. Conclusions

This work presents an easy to perform sol-gel process for depositing ZnO films, which proved to be a very flexible approach to modifying the structural, vibrational and optical properties by only changing the solvent used in the sol solution. The surface morphologies of ZnO films are very smooth with a

tendency to become rougher with increasing the annealing temperatures up to 600°C. The FTIR investigation shows the appearance of absorption features indicative of hexagonal wurtzite ZnO. The optical study reveals that the sol-gel ZnO films are very transparent (up to 90 %) in the visible spectral range with an optical band gap ranging from 3.27 to 3.31 eV, characteristic for ZnO.

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