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The effect of aging on ZnO thin films for different sol concentrations

I. SORAR, F. Z. TEPEHAN*
Department of Physics, Istanbul Technical University, Maslak 34469, Istanbul, Turkey

Stable optical and structural properties are important for most of the applications of thin films. The effect of time and concentration of the sol on the optical and structural properties of the films have been investigated by evaluating the variation of transmission and reflection over a period of 175 days. Transmittance and reflectance data were obtained from a spectrophotometer and a software program was used to analyze the data and extract optical constants. Structural features were studied by an x-ray diffractometer and an atomic force microscope. Glow discharge optical emission spectroscopic depth analysis was used to look at the composition of the films. Optical and structural properties of the films prepared from the less concentrated solution changed during the aging period of 28 days due to Na diffusion from the substrate.

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Keywords: Zinc oxide, Sol-gel, Aging, Optical properties, Structural properties

1. Introduction

ZnO thin films are important materials for the technology. There have been many applications for their optical and electrical properties such as transparent conductors [1], gas sensors [2], solar cell windows [3], photovoltaic devices [4] and optical waveguides [5].

Many techniques such as thermal evaporation [6, 7], chemical vapor deposition [8-10], spray pyrolysis [11, 12], magnetron sputtering [13, 14], vacuum evaporation [15] and sol-gel deposition [16-19] are available for the preparation of ZnO thin films. Among these, the sol-gel method is of growing interest due to its ability to fabricate thin films of large area with low cost and easy control of the micro-structure of the films.

Stable optical and structural properties of thin films with respect to time are very important for the effective use of the material in industrial applications. Therefore the need for long term stability in thin film substrates is also important. The substrates with higher alkali concentrations cause instability in the optical and electrical properties of thin films [20]. For example Na_2O is immobile up to 4% concentration. In the present work, Corning 2947 glass, which contains 7% Na_2O, was used as substrate. Therefore it is necessary to search for stable conditions for the film concentration.

2. Experimental

In this work two different concentrations of zinc acetate dihydrate (ZnAc) were used. Sols A and B were prepared with 0.2 and 0.4 M of ZnAc, respectively. ZnO thin films were prepared by the sol-gel spin coating method. The solution was prepared by dissolving zinc acetate dehydrate ($Zn(CH_3COO)_2 .2H_2O$, 98%, Aldrich) in 2-propanol (99.5%, Aldrich) and stirred by a magnetic stirrer at 60 ^oC for 10 min. Diethanolamine (DEA, 99%, Aldrich) was added drop by drop to the solution during stirring. The solution was stirred an additional 10 min, during which time distilled water was slowly added to it. Finally, a clear and homogeneous solution was obtained. (DEA:ZnAc=1:1 [mol ratio] and H_2O:ZnAc=2:1 [mol ratio]). The coating solution was still stable after 1 month. Fig.1. shows a flow chart of the preparation of the ZnO thin films.

An amount of ZnO solution was dropped onto Corning 2947 glass substrates on the spin coater, which were rotated at 3000 rpm for 30 s. The films were dried at 250 ^oC for 5 min to evaporate the solvent and remove organic residuals. Finally, the films were heat treated at 500 ^oC for 1 hour.

Transmittance and reflectance of the films were measured in the spectral range of 300-1000 nm using an NKD 7000 (Aquila, UK) spectrophotometer. Refractive index values of the films were determined by the software (Pro-optix Version 4.3) used in the NKD 7000 system. Glow discharge optical emission spectroscopic (GDOES) depth analysis was made using a JY 5000RF instrument. AFM images of the films were obtained using an SPM-9500J3 (Shimadzu, Japan) scanning probe microscope in contact mode. The structures of the films were analyzed by an X-ray diffractometer (GBC-MMA, CuKα radiation).

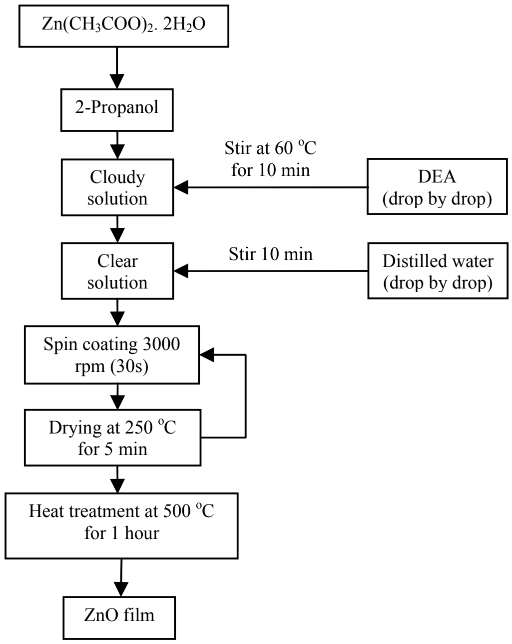

Fig. 1. The flow chart of the spin coating preparation of ZnO thin films.

3. Results and discussion

3.1 Optical properties

Optical transmittance, reflectance and refractive index values of the ZnO films between wavelengths of 300 - 1000 nm, as they vary with time and sol concentration, are shown in Fig. 2., Fig. 3. and Fig. 4. The aging was investigated for a period of 175 days. The transmittance of the films is about 80-87% in the visible range. Transmittance (at 550 nm) decreased by 4% and reflectance increased by 2% after 28 days of aging for the films prepared using Sol A. The refractive index increased from 1.6 to 1.7 at 550 nm during this period of aging. There was no significant change in the optical parameters between 28 and 175 days. On the other hand, the transmittance and reflectance of the films prepared using Sol B remained almost stable during 175 days of aging.

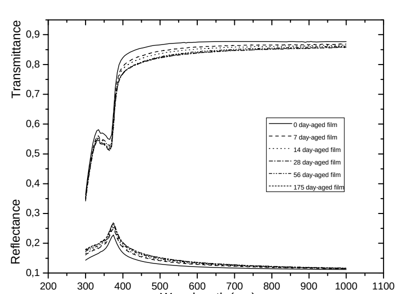

Fig. 2. The effect of time on the optical transmittance and reflectance spectra of the ZnO films prepared using Sol A.

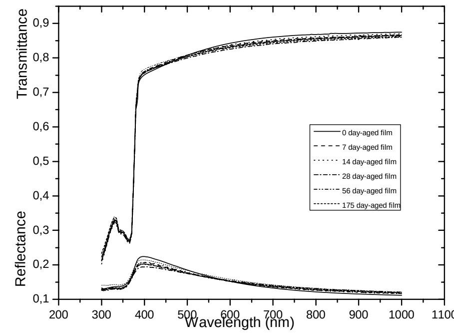

Fig. 3. The effect of time on the optical transmittance and reflectance spectra of the ZnO films prepared using Sol B.

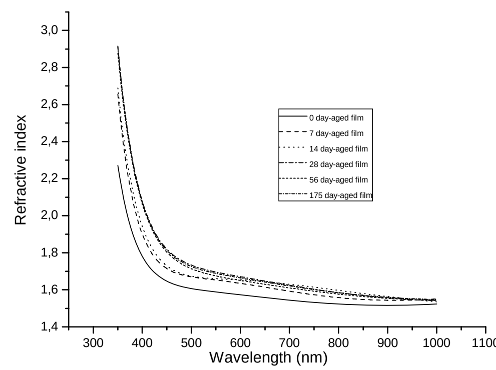

Fig. 4. The effect of time on the refractive index of the ZnO films prepared using Sol A.

3.2 Glow discharge optical emission spectroscopy (GDOES) analysis

Depth profile analysis was carried out by a GDOES system to look at the composition of the films prepared using Sols A and B. The depth profile of the ZnO film prepared using Sol A is shown in Fig. 5. The surface layer of the prepared film contains Zn, O, Na and C. The carbon originates from the organic compounds used in sol preparation. Fig. 5(b) show that Zn, C and Na concentrations near the surface increase with aging time. Na in the substrate starts to move through the film during the time period of 28 days. Since films produced from Sol A have a more porous structure, Na diffuses easily through the film and fills this porous structure. Fig. 6. shows that Na content in the film gradually increases in 28 days of aging.

Fig. 7 compares Zn and Na content of films aged 28 days made from Sols A and B, respectively. The depth analysis for Sol B shows no Na accumulation on the surface during the aging period. Zinc inside the film shows a regular distribution. The dense structure of ZnO at this concentration prevented the diffusion of Na through the film.

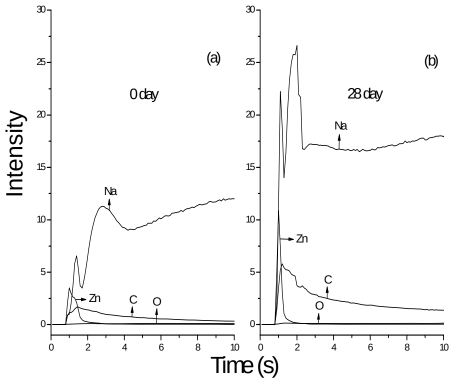

Fig. 5. GDOES graph of (a) 0 and (b) 28 day aged ZnO films prepared using Sol A.

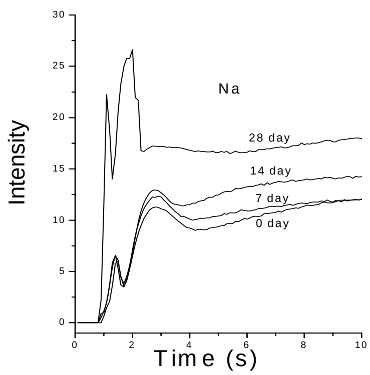

Fig. 6. GDOES graph of ZnO films prepared using Sol A showing that Na content gradually increases with time.

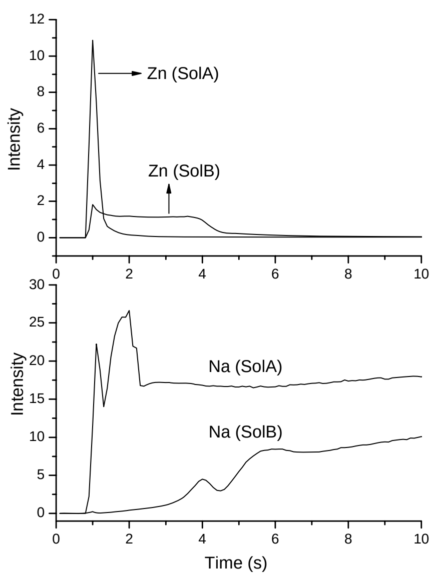

Fig. 7. GDOES graph of Zn and Na content for 28 day aged films prepared using Sol A and Sol B.

3.3 Structural properties

The XRD patterns of the films heat treated at 500 ^{o}C for different concentrations are shown in Fig. 8. The relative intensities of the peaks increase with sol concentration, as shown in the figure. The XRD diffraction peaks belonging to the (100), (002) and (101) planes were seen in both of the ZnO films which were heat treated at 500 ^{o}C for 1 hour. The relative intensities of the peaks coincide exactly with the JCPDS data of ZnO which crystallizes in the hexagonal wurtzite structure.

The AFM images of the films prepared using Sol A and B, and heat treated at 500 ^{o}C for 1 hour are shown in Fig. 9. The surface morphology varies slightly with sol concentration. Root mean square (Rms) surface roughness increased with an increase in sol concentration. The Rms roughness values of the films are 3.9 and 6.3 nm for Sol A and B, respectively. Grains are tightly packed and the average grain diameter is about 40 nm for Sol A and 60 nm for Sol B. No cracks were observed in any of the samples.

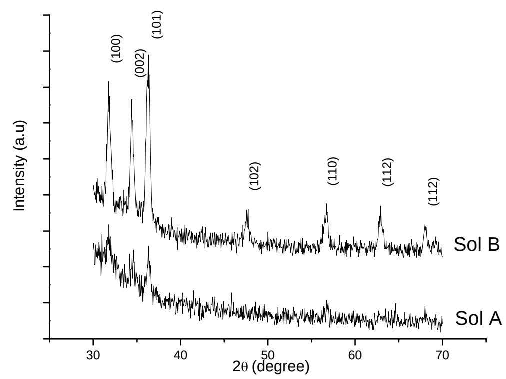

Fig. 8. The XRD patterns of the films prepared using Sol A and Sol B, and heat treated at 500 ^{o}C for 1 hour.

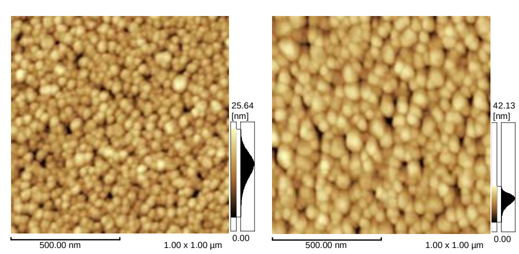

Fig. 9. The AFM images of the ZnO films prepared using (a) Sol A and (b) Sol B, and heat treated at 500 ^{o}C for 1 hour.

4. Conclusions

The results showed that optical properties of the films prepared using the diluted solution changed, while the films prepared using the concentrated solution showed no change. GDOES analysis revealed diffusion of Na from the substrate through the film structure when the less concentrated solution is used. The concentration of 7% N_2O in the Corning 2947 glass caused instability in the less concentrated ZnO films. On the other hand, concentrated solutions showed no instability on the optical properties of the film.

The AFM pictures showed that grain size and Rms values of the films increased with sol concentration. The films prepared using Sol A and Sol B are crystalline with hexagonal wurtzite structure. This study showed that sol concentration has a considerable effect on the evolution of the optical and structural properties of ZnO thin films with aging.

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References

[1] T. Minami, H. Nanto, S. Takata, Thin Solid Films **124**, 43 (1985).
[2] V. Musat, E. Fortunato, F. B. Fernandes, R. J. C. Silva, J. Optoelectron. Adv. M. **9**, 1395 (2007).
[3] Z. W. Li, W. Gao, R. J. Reeves, Surf. Coat. Technol. **198**, 319 (2005).
[4] T. Pauporte, D. Lincot, Electrochim. Acta **45**, 3345 (2000).
[5] W. S. Hu, Z. G. Liu, J. Sun, X. L. Guo, Z. J. Yang, L. J. Shi, D. Feng, Mater. Sci. Eng. B **40**, 165 (1996).
[6] Y. M. Hu, C. W. Lin, J. C. A. Huang, Thin Solid Films **497**, 130 (2006).
[7] R. Maity, S. Kundoo, K. K. Chattopadhyay, Sol. Energy Mater. Sol. Cells **86**, 217 (2005).
[8] P. K. Shishodia, H. J. Kim, A. Wakahara, A. Yoshida, G. Shishodia, R. M. Mehra, J. Non-Cryst. Solids **352**, 2343 (2006).
[9] H. Deng, J. J. Russell, R. N. Lamb, B. Jiang, Y. Li, X. Y. Zhou, Thin Solid Films **458**, 43 (2004).
[10] S. Fay, L. Feitknecht, R. Schluchter, U. Kroll, E. Vallat-Sauvain, A. Shah, Sol. Energy Mater. Sol. Cells **90**, 2960 (2006).
[11] M. Miki-Yoshida, F. Paraguay-Delgado, W. Estrada-Lopez, E. Andrade, Thin Solid Films **376**, 99 (2000).
[12] B. J. Lokhande, P. S. Patil, M. D. Uplane, Mater. Lett. **57**, 573 (2002).
[13] D. Dimova-Malinovska, O. Angelov, H. Nichev, M. Kamenova, J. C. Pivin, J. Optoelectron. Adv. M. **9**, 2512 (2007).
[14] D. Song, P. Widenborg, W. Chin, A. G. Aberle, Sol. Energy Mater. Sol. Cells **73**, 1 (2002).
[15] P. Prepelita, C. Baban, F. Iacomi, J. Optoelectron. Adv. Mater. **9**, 2166 (2007).
[16] M. Wang, J. Wang, W. Chen, Y. Cui, L. Wang, Mater. Chem. Phys. **97**, 219 (2006).
[17] D. Bao, H. Gu, A. Kuang, Thin Solid Films **312**, 37 (1998).
[18] Y. Natsume, H. Sakata, Thin Solid Films **372**, 30 (2000).
[19] V. Musat, B. Teixeira, E. Fortunato, R. C. C. Monteiro, P. Vilarinho, Surf. Coat. Technol. **180**, 659 (2004).
[20] L. Eckertova, Physics of Thin Films, Plenum Press, New York, 1986.

*Corresponding author: tepehanf@itu.edu.tr