Scientific Research Publishing

World Journal of Engineering and Technology, 2026, 14(4), 992-997
https://www.scirp.org/journal/wjet
ISSN Online: 2331-4249
ISSN Print: 2331-4222

ZnO Films Deposited by MOD Method-Island Behavior Dependent on Thermal Environment during Annealing

Masato Ohmukai, Koichiro Nakamura

Department of Electrical and Computer Engineering, Akashi College of Technology, Akashi, Japan
Email: ohmukai@akashi.ac.jp

How to cite this paper: Ohmukai, M. and Nakamura, K. (2026) ZnO Films Deposited by MOD Method-Island Behavior Dependent on Thermal Environment during Annealing. *World Journal of Engineering and Technology*, **14**, 992-997.
https://doi.org/10.4236/wjet.2026.144059

Received: September 15, 2026
Accepted: October 30, 2026
Published: November 2, 2026

Copyright © 2026 by author(s) and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).
http://creativecommons.org/licenses/by/4.0/

Open Access

Abstract

ZnO nowadays attracts much attention as a transparent conductor, because it does not require rare earth elements. In this study, undoped ZnO films were formed by a metalorganic decomposition (MOD) method; metalorganic liquid is spread over a glass substrate, dried on a hotplate, and then annealed in a furnace. The obtained film was found to have a complicated structure that apparently depends on temperature profiles on the substrate surface. It was concluded that the temperature control over the substrate is critical for obtaining a uniform film.

Keywords

Undoped ZnO, MOD Method, Transparency, Island Behavior, Marangoni Convection

1. Introduction

Indium tin oxide is widely used as a transparent conductor in solar cells, liquid crystal displays and so on. Transparent conductors are an essential technology to realize optoelectronic devices that are vital for the contemporary smart society. Indium is a kind of supply-constrained element, which is a precious and highly valuable element. Nowadays, ZnO has attracted much attention as a substitute for indium tin oxide. The advantage of the material is its low cost and environmentally friendly aspect at the same time. A full description of the properties can be found in the literature [1]. ZnO is basically a semiconductor with a band gap of 3.44 eV; the large band gap results in a transparent property for visible light. It also holds interesting properties such as large exciton binding energy, large piezoelectric constants, and strong non-linear optical coefficients as well. When Al is doped in ZnO, the electric conductivity is drastically enhanced to be a conductor.

Many structures of ZnO have been reported such as nanowall [2], nanoparticles [3] and microrods [4]. Even flower-shaped ZnO nanorods were fabricated with graphene oxide coating [5]. The ZnO:Al is expected to be a candidate for the substitution of indium tin oxide. It is then suitable as a material for window layers for solar cells [6]. The ZnO:Al system has also been widely investigated: heterojunctions with Si [7], homojunction of ZnO [8], and so on.

ZnO films are well deposited by means of sputtering methods that are widely used in semiconductor device fabrication. This method, however, incurs high cost and long lime because it requires a vacuum system. For the purpose of minimizing the cost and time for fabrication, a metalorganic decomposition method was applied in this article. This method is so simple and attractive; the starting liquid is dropped on a substrate, spread out and then annealed under the atmosphere. The method is a proper one for oxide materials such as TiO_2 [9], $LaNiO_3$ [10], $BiVO_4$ [11], $Bi_4Ti_3O_{12}$ [12] and so on. ZnO has not yet been well grown by means of the MOD method. Only a few studies have been reported [13].

The problem is the parameter control such as annealing temperature and time. Another problem is the low reproducibility owing to the use of liquid. So it is a good challenge to reveal the effects of conditions for the ZnO film growth by means of the MOD method.

2. Experimental

In this article, only undoped ZnO films were grown as follows. Starting materials were a commercially available MOD liquid for ZnO (SYM-ZN20 by Kojundo Chemical Lboratory Co., Ltd) and a dilution solvent (290353 by Kojundo Chemical Lboratory Co., Ltd); 200 μl each. The solution was mixed well with the help of an ultrasonic cleaner for 5 minutes. The mixed solution of 40 μl was dropped onto a borosilicate glass (S1225 of Matsunami Glass Industry, Ltd.) that was cleansed with an ultrasonic cleaner for 5 minutes in distilled water and then dried by contact with ethanol vapor. Dimension of the glass was 25 × 75 mm. The mixed solution was spread by means of scanning a bar coater on the substrate. The scanning was performed for several seconds at a constant velocity. The nominal value of film thickness was 27 μm. The sample was dried on a hot plated at 120˚C for 5 minutes before annealing at 600˚C in an electric furnace for 40 minutes under the atmosphere environment. There was no ramp region for increasing temperature. During the annealing the sample was installed on a ceramic long bar so that the center part of the glass substrate was only contacted by a bar (sample A). Another sample (sample B) was installed on a ceramic plate where the whole face was contacted to the plate. There exists possibly the difference in the heat conduction to the glass substrate.

It was also performed an experiment how annealing temperature affects film area. The temperature was varied from 200˚C to 600˚C where annealing time was fixed at 50 minutes. All the other conditions were the same as sample B.

Scanning electron microscope (SEM) photos were taken with the microscope of JSM-6510LA (EOL Ltd. Japan). The acceleration voltage was 20 kV.

3. Results and Discussion

Figure 1 shows a photo of sample A, which consisted of two parts: a transparent region in the center and two line-shaped white lines in the upper and lower regions. The sample was transparent before the annealing. The annealing definitely brought a color change. Just after the sample was taken out of the furnace, the white parts looked lightly yellowish and then became white as it was cooled down naturally to room temperature. On the other hand, the transparent part at the center did not change during the cooling.



Figure 1. An optical photo taken from sample A. Two parts were observed: transparent part (center) and white parts (the upper and lower).

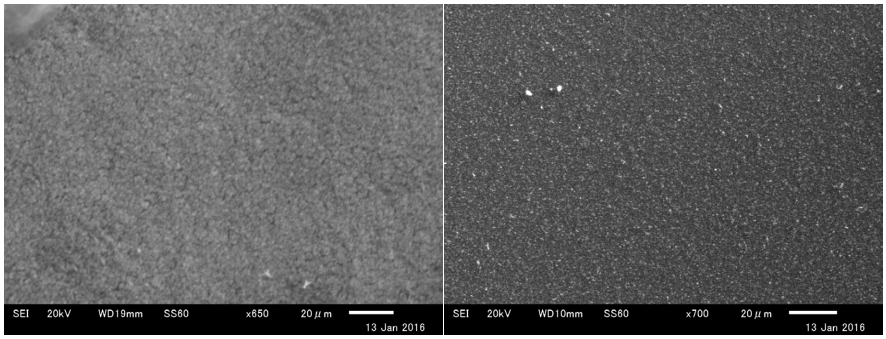


Figure 2. SEM photos from two parts of sample A: the edge part (left) and the center (right).

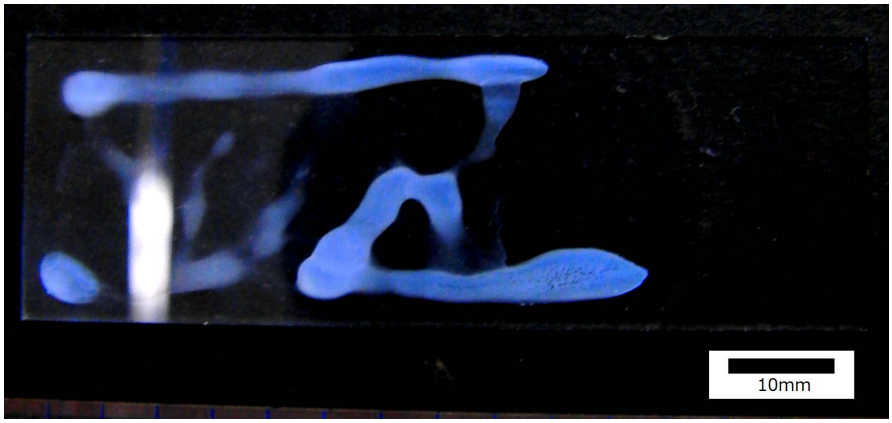


Figure 3. The photo of sample B. white lines exist randomly on the substrate.

The two different parts were separately observed by the SEM. Figure 2 shows the two SEM photos from the two parts. The left one is from the edge part and the right one from the center. By comparison between the two photos, both films have a porous structure and the grain size is bigger at the edge part than that at the center.

The photo of sample B is shown in Figure 3. The photo shows that the white part is not restricted to the edge of the glass substrate but is randomly situated on the plate. The especially bright white vertical line in the left area is the reflection of the fluorescent lamp on the ceiling of our laboratory. The white line was not apparently well controlled.

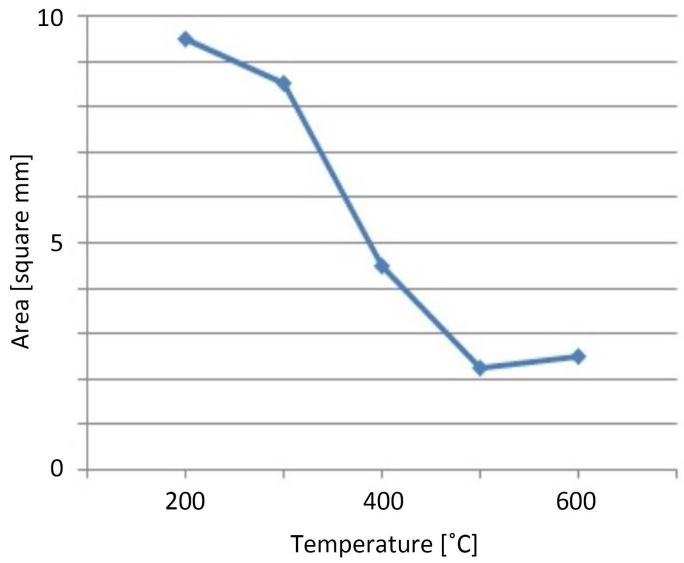


Figure 4. The largest area decreases with the annealing temperature.

The two photos of Figures 1-3 provide interesting differences, though they cannot be estimated quantitatively. It was also confirmed that the Zn was detected more in the white part by the energy dispersive x-ray spectrometry using the SEM. We discuss here the difference between the two cases. As for sample A (Figure 1), the edge part was not in contact with the stage bar. It follows that the temperature at the edge was lower than that at the center because heat flowed directly from the stage bar at the center. This temperature difference caused a Marangoni convection. The film spread on the glass apparently moved from the center to the edge. On the other hand, sample B (Figure 3) provided a random white line that suggests a Bénard-convection-like appearance instead. The Bénard convection usually makes a systematic pattern like a honeycomb. But sample B does not show the one apparently because the film was too viscous to form such a systematic pattern. From these two cases it is expected that the elaborate control of temperature dependent on the site of the glass realizes the better formation of the films although the liquid temperature control cannot be well performed even nowadays.

Next described is the dependence of a film area on annealing temperature. The annealed film often consisted in an island-like form. The area was determined by

measuring the largest one on the glass. The result is shown in Figure 4. The support condition of the substrates was the same as sample B. The area decreases with temperature until 500˚C. As the temperature increases, the convection becomes active. The repellency of the liquid becomes noticeable and then each island shrinks in dimension. Based on the result, the lower temperature is desirable. From the chemical point of view, a high enough temperature is needed for the decomposition of the starting material; this creates a conflict between the two. An idea for surface tension control for hydrophilicity is anticipated. The area slightly increases at 600˚C, but this is considered to be a kind of experimental error.

4. Conclusion

Undoped ZnO films were deposited on glass substrates by means of the MOD method. It was found that the heating condition during annealing greatly affects the film structure. The results are well understood by considering the convection of the starting liquid. The obtained films comprise an archipelago structure. The dimension of the maximum island decreases as the annealing temperature increases till 500˚C. An idea of reducing surface tension for hydrophilic surfaces will be needed to improve the fabrication by this method.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Janotti, A. and Van de Walle, C.G. (2009) Fundamentals of Zinc Oxide as a Semiconductor. *Reports on Progress in Physics*, **72**, Article ID: 126501. https://doi.org/10.1088/0034-4885/72/12/126501

[2] Zhou, L., Bai, J., Liu, Y., Liu, F., Wang, H., Zhang, Y., *et al.* (2020) Highly Sensitive C2H2 Gas Sensor Based on Ag Modified ZnO Nanorods. *Ceramics International*, **46**, 15764-15771. https://doi.org/10.1016/j.ceramint.2020.03.120

[3] Kumar, P., Kumar, A., Rizvi, M.A., Moosvi, S.K., Krishnan, V., Duvenhage, M.M., *et al.* (2020) Surface, Optical and Photocatalytic Properties of Rb Doped ZnO Nanoparticles. *Applied Surface Science*, **514**, Article ID: 145930. https://doi.org/10.1016/j.apsusc.2020.145930

[4] Lee, H., Jung, H.K., Kim, Y.E., Beom, K., Mun, J.H., Hong, A., *et al.* (2020) Facile Synthesis of ZnO Microrod Photodetectors by Solid-State Reaction. *Journal of Alloys and Compounds*, **825**, Article ID: 154110. https://doi.org/10.1016/j.jallcom.2020.154110

[5] Boukhoubza, I., Khenfouch, M., Achehboune, M., Leontie, L., Carlescu, A., Doroftei, C., *et al.* (2020) Graphene Oxide Coated Flower-Shaped ZnO Nanorods: Optioelectronic Properties. *Journal of Alloys and Compounds*, **831**, Article ID: 154874.

[6] Zhu, H., Niu, X., Wan, M. and Mai, Y. (2019) A Study of ZnO:Al Thin Films Reactively Sputtered under the Control of Target Voltage for Application in Cu(In,Ga)Se_2 Thin Film Solar Cells. *Vacuum*, **161**, 297-305. https://doi.org/10.1016/j.vacuum.2018.12.053

[7] Urper, O., Karacasu, O., Cimenoglu, H. and Baydogan, N. (2019) Annealing Ambient

Effect on Electrical Properties of ZnO:Al/p-Si Heterojunctions. *Superlattices and Microstructures*, **125**, 81-87. https://doi.org/10.1016/j.spmi.2018.10.027

[8] Kampylafka, V., Kostopoulos, A., Modreanu, M., Schmidt, M., Gagaoudakis, E., Tsagaraki, K., *et al.* (2019) Long-Term Stability of Transparent n/p ZnO Homojunctions Grown by Rf-Sputtering at Room-Temperature. *Journal of Materiomics*, **5**, 428-435. https://doi.org/10.1016/j.jmat.2019.02.006

[9] Padmanabhan, K., Harvey, N.E., Kurel, P., Talagala, P., Naik, R., Auner, G.W., *et al.* (2006) Structural Studies of Titanium Oxide Films Deposited with Metalorganic Decomposition. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **249**, 540-543. https://doi.org/10.1016/j.nimb.2006.03.048

[10] Li, A., Wu, D., Liu, Z., Ge, C., Liu, X., Chen, G., *et al.* (1998) TEM and AFM Study of Perovskite Conductive LaNiO3 Films Prepared by Metalorganic Decomposition. *Thin Solid Films*, **336**, 386-390. https://doi.org/10.1016/s0040-6090(98)01289-9

[11] Galembeck, A. and Alves, O.L. (2000) $BiVO_4$ Thin Film Preparation by Metalorganic Decomposition. *Thin Solid Films*, **365**, 90-93. https://doi.org/10.1016/s0040-6090(99)01079-2

[12] Liu, W.L., Xia, H.R., Han, H. and Wang, X.Q. (2004) Structural and Dielectrical Properties of Bismuth Titanate Nanoparticles Prepared by Metalorganic Decomposition Method. *Journal of Crystal Growth*, **269**, 499-504. https://doi.org/10.1016/j.jcrysgro.2004.05.089

[13] Zou, Y., Wang, Y., Zhang, H., Chen, Z., Wang, J. and Li, Y. (2007) Thermochemical Process in Preparation of ZnO Film by TFA-MOD Method. *Applied Surface Science*, **253**, 4356-4360. https://doi.org/10.1016/j.apsusc.2006.09.044