Available online at www.sciencedirect.com
SCIENCE DIRECT
Thin Solid Films 506–507 (2006) 155 – 158
thin solid films
www.elsevier.com/locate/tsf

# Deposition of ZnO film using an open-air cold plasma generator

Yoshifumi Suzaki [a,*], Seiki Ejima [a], Tomokazu Shikama [b], Shunryo Azuma [c], Osamu Tanaka [c], Takahiro Kajitani [c], Hideomi Koinuma [d]

[a] Faculty of Engineering, Kagawa University, 2217-20, Hayashi-cho, Takamatsu, Kagawa 761-0396, Japan
[b] Takamatsu National College of Technology, Takamatsu, Kagawa 761-8058, Japan
[c] Research Laboratory, Okura Industry Co. Ltd., Marugame, Kagawa 763-8508, Japan
[d] Ceramics Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8503, Japan

Available online 8 September 2005

**Abstract**

Under open-air atmosphere, homogeneous non-equilibrium cold plasma was generated stably by high voltage pulsed power (0.8 kV, 20 Hz) excitation of He and $O_2$ gases. By feeding bis(dipivaloylmethanato)zinc ($DPM_2Zn$) into this plasma, transparent flat ZnO films about 200 nm thick were successfully deposited on glass substrates directly under the slit made into the cathode. An XRD measurement revealed that ZnO films had a polycrystalline structure oriented *c*-axis. By increasing the $O_2$ gas flow rate, the grain size of the polycrystalline ZnO became larger and its crystallinity was improved.


*Keywords:* Plasma deposition; Zinc oxide; Atmospheric pressure cold plasma; Helium gas

## 1. Introduction

Transparent electrically conductive zinc oxide (ZnO) films have been studied experimentally for application to low-cost transparent electrodes in solar cells such as amorphous silicon (a-Si) or copper indium diselenide ($CuInSe_2$) [1]. ZnO films are usually prepared by methods such as high temperature chemical vapor deposition (CVD), plasma-enhanced chemical vapor deposition (PECVD) [2,3] and sputtering [4,5]. Compared to high temperature chemical vapor deposition (CVD), plasma-enhanced chemical vapor deposition (PECVD) is an attractive process for film growth due to its lower substrate temperature requirement, which is sometimes indispensable for preparing multi-layered structures and for deposition on thermally unstable materials. In conventional PECVD processes, gas pressure is usually regulated in the range of 1 mTorr to several Torr. If such a processing plasma can be generated under atmospheric pressure, it would become possible not only to simplify the processing system but also to make plasma applicable for wider purposes.

Recently, low temperature plasma (glow discharge) was generated by an RF excitation of flowing Ar, He, $O_2$ or their mixtures at 1 atm [6–8]. In this paper, we will report on the use of the open-air cold plasma generator to deposit ZnO films by feeding bis(dipivaloylmethanato)zinc ($DPM_2Zn$) into the plasma, which was generated stably by using He and $O_2$ gases.

## 2. Experimental details

The deposition system in the open-air cold plasma generator is schematically illustrated in Fig. 1. Our plasma generator is composed of an Al cathode with a thin film coating of alumina created by a natural oxidation process, and a grounded anode of Al plate. A glass substrate was placed on top of the anode plate. A slit (1 mm × 20 mm) was prepared on the cathode (30 mm × 50 mm), in order to let He gas flow into the gap between cathode and anode. Also, the anode plate moves with a glass substrate back and forth in the direction perpendicular to the slit in order to fabricate

* Corresponding author.
*E-mail address:* suzaki@eng.kagawa-u.ac.jp (Y. Suzaki).

0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.08.166

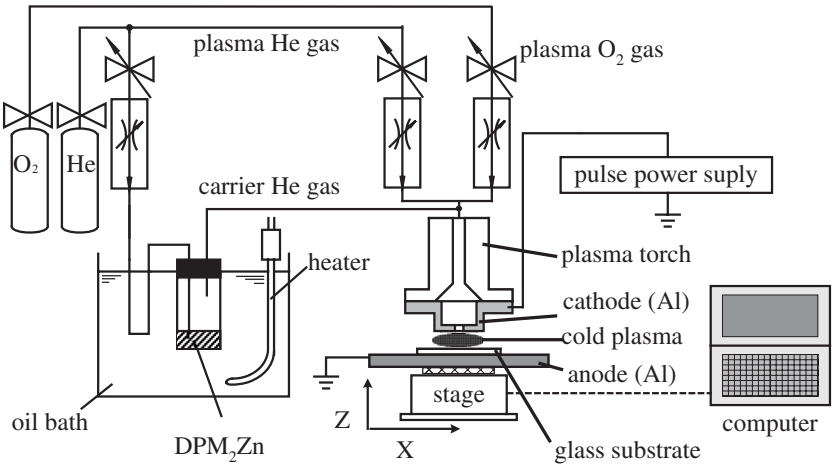



Fig. 1. Schematic diagram of the deposition system with open-air cold plasma.

flat films in a large area (sweep distance: 10 mm). A schematic diagram of its movement is shown in Fig. 2. Cold plasma was generated by flowing He and $O_2$ gases. The He carrier gas was fed through the inner space of the cathode down to the gap, where it was excited by the high voltage pulse supply (HVP-20K, Haiden Laboratory Co. Ltd.). Bis(dipivaloylmethanato)zinc ($DPM_2Zn$, Tri Chemical Laboratories Inc.) was vaporized and carried by the He carrier gas flow into the plasma generated at the gap. Table 1 lists the deposition conditions for our experiment. Under these conditions, a transparent flat film about 200 nm thick was successfully deposited. The film grows only directly under the slit made into the cathode with a deposition rate of about 0.6 nm/s. The transmittance of all films deposited was more than 90% in the wavelength range from 400 nm to 600 nm.

The microstructures of the films were studied by a field emission scanning electron microscope (FE-SEM; Hitachi, Ltd.) and X-ray diffraction (XRD; XRD-6100, Shimadzu Co.) measurement. Resistivity of the film was tested by the four-probe method with a multimeter (E2373A, Hewlett Packard Co., Ltd.).

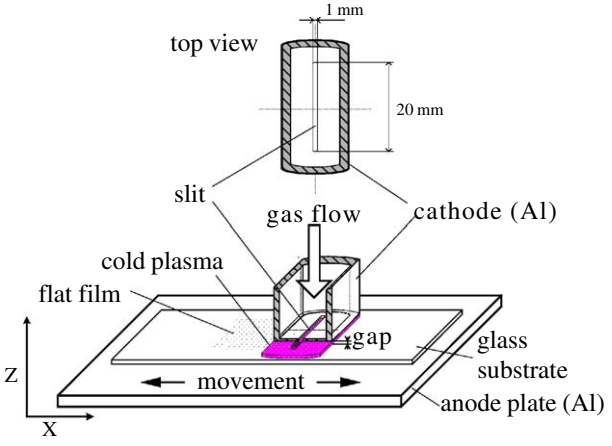



Fig. 2. Schematic diagram of movement of the anode plate. The anode moves back and forth during plasma deposition.

## 3. Results and discussion

### 3.1. Glow discharge range

The range of glow discharge in our experiment is shown in Fig. 3. The horizontal and vertical axes indicate the $O_2$ gas flow rate and the voltage of the pulse supply, respectively. Triangle (▲) and diamond (♦) data show maximum and minimum values of the glow discharge, respectively. When the $O_2$ gas flow rate is 5 ccm, stable glow discharge was observed for voltages ranging from 0.4 to 0.8 kV. But above 0.8 kV, unstable streamer discharge was observed instead. Since oxygen has high electronegativity it recombines with electrons in the plasma easily. So the density of electrons in the plasma is held lower than the limit value for transition to the streamer discharge. Stable discharge can be obtained at a higher voltage with a higher oxygen flow rate.

### 3.2. Analysis of crystal structure using XRD

Typical XRD profiles of films deposited at the $O_2$ flow rates of 5 to 50 ccm are shown in Fig. 4. The profile shows a

Table 1
Deposition conditions

| Substrate | Glass |
|---|---|
| Substrate temperature | 140 °C |
| Source material | Bis(dipivaloylmethanato)zinc ($DPM_2Zn$) |
| Source material temperature | 110 °C |
| He gas total flow rate | 2300 ccm |
| He carrier gas flow rate | 300 ccm |
| $O_2$ gas flow rate | 5~50 ccm |
| Voltage | 0.8 kV |
| Sweep distance | 10 mm |
| Sweep speed | 1 mm/s |
| Anode and cathode gap | 0.5 mm |
| Deposition time | 60 min |

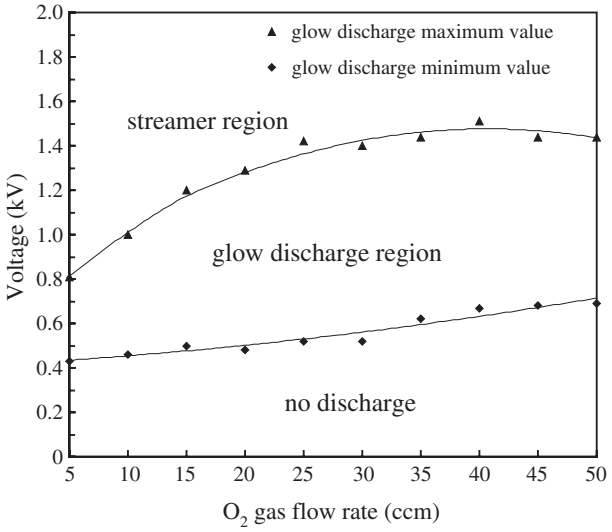
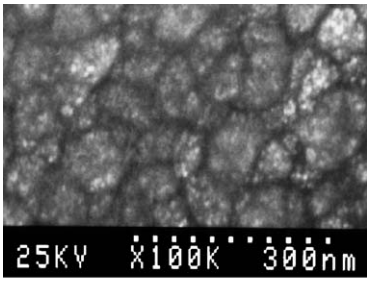



Fig. 3. Glow discharge region of the open-air cold plasma generator.

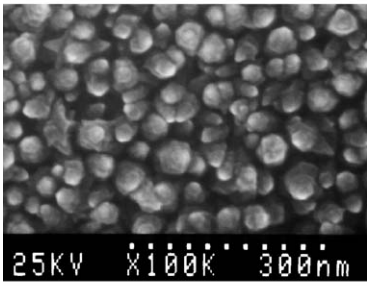
peak only for the (002) plane of ZnO. This result reveals that ZnO films have a polycrystalline structure oriented *c*-axis. By increasing the $O_2$ gas flow rate, the peak becomes larger and sharper, which means that the grain size of the polycrystalline ZnO becomes larger and its crystallinity is improved.

### 3.3. FE-SEM observations

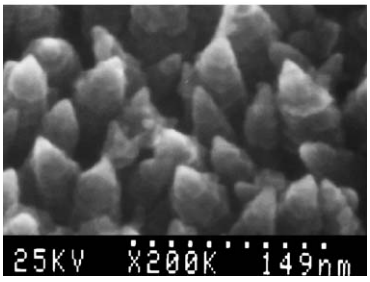
Typical FE-SEM observations of the ZnO film for the $O_2$ flow rate of 10 ccm and for 30 ccm are shown in Fig. 5(a) and (b), respectively, whereas panel (c) shows the same sample as panel (b) viewed from a 30° angle. Fig. 5(a) shows fine sub-grains of about 10 nm, but panel (b) shows crystal grains of about 50 nm with wide grain boundaries. Fig. 6(c) reveals that the ZnO crystal grain has a conic shape which looks like a bamboo shoot grown on the glass substrate. A high flow rate of $O_2$ gas may change the growth pattern of ZnO film and its microstructure into one of columnar crystallites.




(a) $O_2$ gas flow rate: 10 ccm




(b) $O_2$ gas flow rate: 30 ccm




(c) $O_2$ gas flow rate: 30 ccm (sample inclined 30°)

Fig. 5. Typical FE-SEM observation. (a) $O_2$ gas flow rate: 10 ccm. (b) $O_2$ gas flow rate: 30 ccm. (c) $O_2$ gas flow rate: 30 ccm (sample inclined 30°).

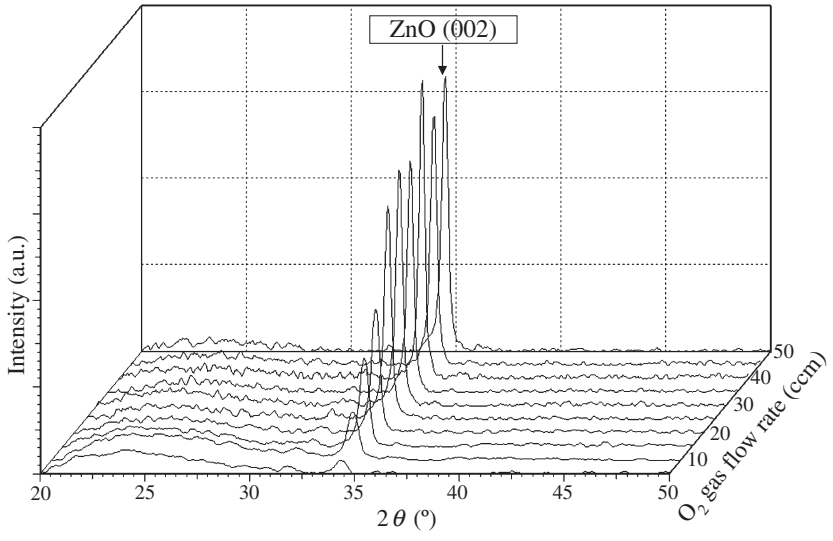



Fig. 4. Typical XRD profiles of the films.

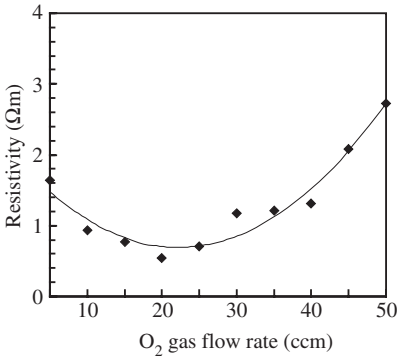



Fig. 6. Resistivity of the ZnO films.

### 3.4. Electrical resistivity

Fig. 6 shows the resistivity of the ZnO films deposited at $O_2$ flow rates of 5 to 50 ccm. By increasing the $O_2$ flow rate, resistivity of the film first decreased and reached a minimum value of 0.273 Ω m at an $O_2$ flow rate of 20 ccm, and then the resistivity increased. Decrease of the resistivity for the rates below 20 ccm is due to the progress of ZnO crystallinity as revealed by the XRD measurements. However, when the $O_2$ flow rate increases above 20 ccm, the grain boundary becomes wider, as shown in Fig. 5. This could be attributed to increasing resistivity of the film. This research suggests the need for further experiments in order to produce higher quality ZnO films.

## 4. Conclusion

Our open-air plasma generator successfully generated stable glow discharge by high voltage pulsed power (0.8 kV, 20 Hz) excitation of He and $O_2$ gases. Using this generator, we deposited ZnO films on the glass substrates, and the results are summarized as follows.

1) By feeding bis(dipivaloylmethanato)zinc ($DPM_2Zn$) into the plasma, transparent flat films about 200 nm thick were successfully deposited directly under the slit made into the cathode. The typical input power was 30 W.
2) The transmittance of the films was more than 90% in the range from 400 nm to 600 nm.
3) XRD measurement revealed that ZnO films had a polycrystalline structure oriented *c*-axis. By increasing the $O_2$ gas flow rate, the grain size of the polycrystalline ZnO became larger and its crystallinity was improved.
4) By increasing the $O_2$ gas flow rate, the surface of the ZnO film developed a somewhat rough structure.

ZnO film has a rough structure and its resistivity appears to be high. Further studies and experiments on the effects of the gas flow rate in the gap or other conditions are in progress to enable ZnO of better quality and resistivity to be prepared in the near future. Our goal is to develop a simple depositing system by using low cost materials such as $N_2$ gas or air at 1 atm.

## Acknowledgement

We thank Mr. Ian Willey for his careful correction of our manuscript. This work was funded by the Kagawa Techno Foundation.

## References

[1] A. Ennaoui, M. Weber, R. Scheer, H.J. Lewerenz, Sol. Energy Mater. Sol. Cells 54 (1998) 277.
[2] T. Minami, H. Sonohara, S. Tanaka, H. Sato, Jpn. J. Appl. Phys. 33 (1994) L743.
[3] S.J. Baik, J.H. Jang, C.H. Lee, W.Y. Cho, K.S. Lim, Appl. Phys. Lett. 70 (1997) 3516.
[4] R. Wendt, K. Ellmer, Surf. Coat. Technol. 93 (1997) 27.
[5] K. Tominaga, H. Manabe, N. Umezu, I. Mori, T. Ushiro, I. Nakabayashi, J. Vac. Sci. Technol., A 15 (1997) 1074.
[6] H. Ha, K. Inomata, H. Koinuma, J. Electrochem. Soc. 142 (1995) 2726.
[7] H.G. Teong, Y. Suzaki, T. Shikama, O. Tanaka, T. Kajitani, H. Koinuma, Proceedings of the 9th International Conference on Production Engineering, Osaka, Japan, JSPE Publication Series, vol. 3, 1999, p. 596.
[8] Y. Suzaki, S. Ejima, T. Shikama, O. Tanaka, T. Kajitani, H. Koinuma, Abstract of the MRS 2002 Spring Meeting, San Francisco, USA, 2002, p. 157.