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Abstract

Under atmospheric pressure, homogeneous non-equilibrium cold plasma was generated stably by RF power (12.36 MHz) excitation of He gas as well as a mixture of He and O_2 gases. By feeding Zn-MOPD ($C_{18}H_{30}O_6Zn$) into this plasma with He carrier gas, transparent and flat ZnO films about 200-1000 nm thick were successfully fabricated on glass substrates directly under the slit made into the cathode, with a mixture of He and O_2 gases used as plasma gas. An XRD measurement revealed that the ZnO films had a polycrystalline structure oriented c-axis. By increasing the RF power, the grain size of the polycrystalline ZnO increased and its crystallinity was improved.

Keywords: Zinc oxide, Plasma deposition, Atmospheric cold plasma, Helium gas, Oxygen gas

1. Introduction

Transparent electrically conductive zinc oxide (ZnO) films have been studied experimentally to identify possible applications to low-cost transparent electrodes in solar cells such as amorphous silicon (a-Si). ZnO films are usually prepared by methods such as high temperature chemical vapor deposition (CVD), plasma-enhanced chemical vapor deposition (PECVD) and sputtering. Compared to high temperature CVD, PECVD is an attractive process for film growth due to its lower substrate temperature requirement, which is sometimes indispensable for preparing multilayered structures and for fabrication on thermally unstable materials. In conventional PECVD processes, gas pressure is usually regulated in the range of 10^{-1} Pa to 1 kPa. If such a processing plasma can be generated under atmospheric pressure, it is 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 and their mixtures at 1 atm[1-7]. In this paper, we report on the use of an atmospheric pressure cold plasma generator to fabricate ZnO films by feeding Zn-MOPD ($C_{18}H_3O_6Zn$) into the plasma, which was generated stably using He and O_2 gases.

2. Experimental Procedure

The fabrication system in the atmospheric pressure 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 Cu plate. A glass substrate was placed on top of the anode plate. A slit (20 mm×1 mm) was prepared on the cathode (30 mm×50 mm), in order to let He gas flow into the gap between cathode and anode. The anode plate moves with a glass substrate in the direction perpendicular to the slit in order to fabricate flat films in a large area (sweep speed: 0.1 mm/min). A schematic diagram of its movement is shown in **Fig.2.** Atmospheric pressure 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 an RF supply (13.56 MHz). Zn-MOPD ($C_{18}H_{30}O_6Zn$, UBE Industries, Ltd.), then vaporized and carried by the He carrier gas flow into the plasma generated at the gap. **Table 1** lists the fabrication conditions for our experiment. Under these conditions, transparent flat films were successfully

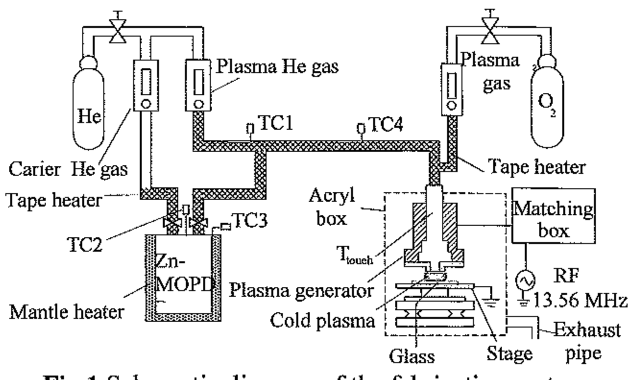


Fig.1 Schematic diagram of the fabrication system.

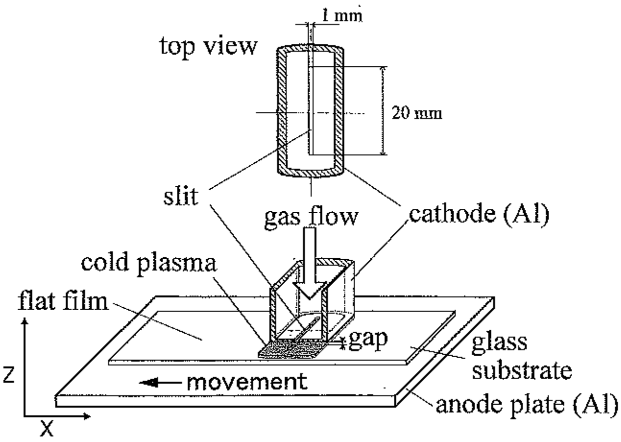
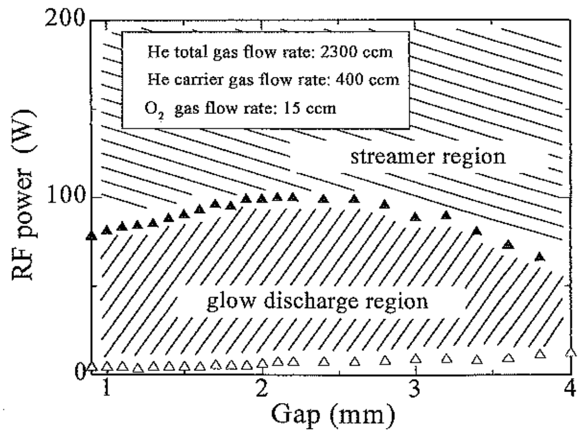


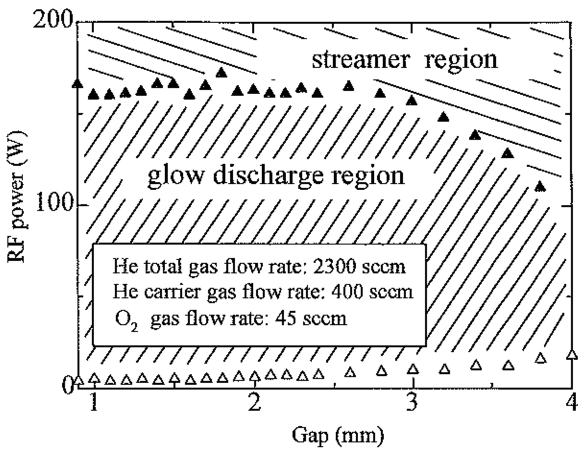
Fig.2 Schematic diagram of the anode plate. The glass substrate moves with the anode plate in the direction perpendicular to the slit of the cathode.

Table 1 Fabrication conditions.

Substrate	#1737 Glass
Substrate temperature	R.T.
Source material	Zn-MOPD ($C_{18}H_{30}O_6Zn$, UBE Industries, Ltd.)
Source material temperature	105 ℃
Temperature at TC2	160 ℃
Temperature at TC4	140 ℃
Carrier He gas flow rate	400 ccm
He gas total flow rate	1900 ccm
O_2 gas flow rate	15, 45, 50 ccm
RF power	70-140 W
Sweep distance	5 mm
Sweep speed	0.1 mm/min
Anode and cathode gap	1.0-4.0 mm
Deposition time	50 min



(a) O_2 gas flow rate: 15 ccm



(b) O_2 gas flow rate: 45 ccm

Fig.3 Glow discharge region of the atmospheric pressure cold plasma generator.

fabricated. The microstructures of the films were examined through X-ray diffraction (XRD) and Atomic Force Microscope (AFM) measurements.

3. Results and Discussion

3.1 Glow discharge range

The ranges of glow discharge with O_2 gas flow rates of (a) 15 ccm and (b) 45 ccm in our experiments are shown in **Fig.3.** The horizontal and vertical axes indicate the gap between anode and cathode and the RF power, respectively. Black triangle (▲) and white triangle (△) data show maximum and minimum values of the glow discharge, respectively. When the O_2 gas flow rate is 15 ccm, as shown in Fig.3 (a), stable glow discharge was observed for RF powers ranging from 4 to 78 W at 1.0 mm of the gap. However, above 78 W, unstable streamer discharge was observed instead. However, at 45 ccm, as shown in Fig.3 (b), stable glow discharge was observed from 4 to 160 W at 1.0 mm of the gap. Since oxygen has a high electronegativity it recombines with electrons in the plasma easily. Therefore, the density of electrons in the plasma is held lower than the limit value for the transition to the streamer discharge. Stable discharge can be obtained at a higher voltage with a higher oxygen flow rate.

3.2 Thickness of ZnO films

Figure 4 shows a schematic diagram of a typical sample of the ZnO thin film. Uniform and transparent thin film about 200 to 600 nm thick was fabricated with an area of about 20 mm by 6 mm. Since the slit size and the sweep distance are 20 mm by 1 mm and 5 mm this result means that the film grows only directly under the slit made into the cathode.

Figure 5 shows the dependence of film thickness on RF power when O_2 gas flow rates were 15 and 45 ccm. By increasing RF power, the film thickness decreased from about 600 to about 200 nm. High RF power may thus change the growth pattern of ZnO film and its structure.

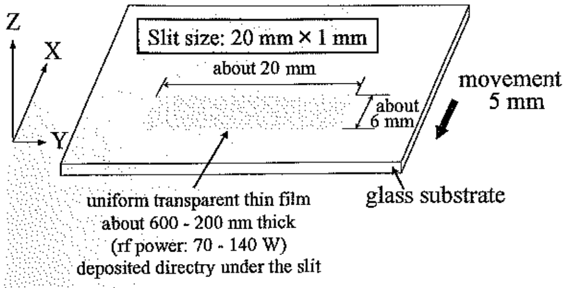


Fig.4 Schematic diagram of the typical sample of the ZnO thin film.

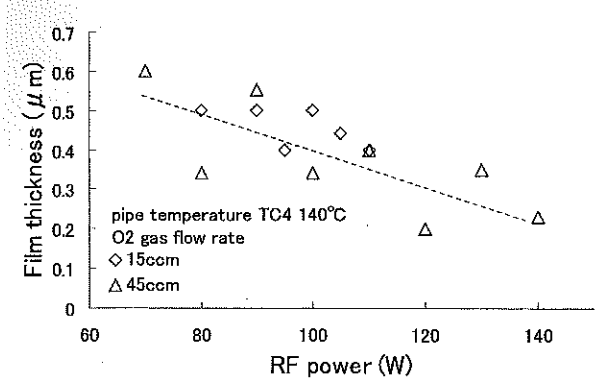


Fig.5 Dependence of film thickness on the RF power.

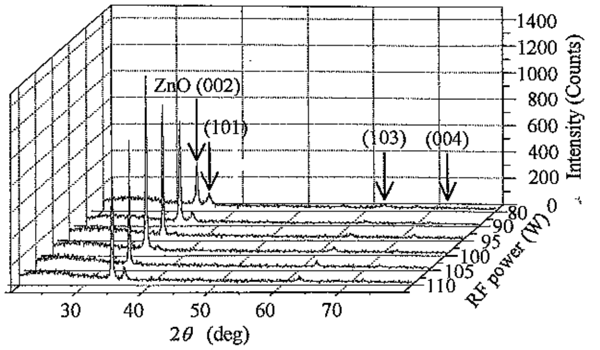


Fig.7 Typical XRD profiles of ZnO films of 80-110 W of RF power. O_2 gas flow rate; 15 ccm.

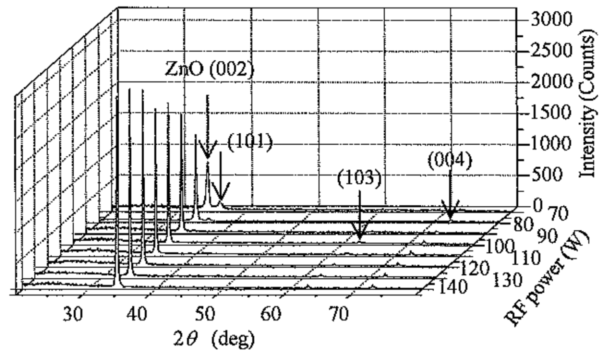


Fig.8 Typical XRD profiles of ZnO films of 70-140 W of RF power. O_2 gas flow rate; 45 ccm.

3.3 Optical band gap of ZnO films

The transmittance of all films fabricated was more than 90 % in the wavelength range from 400 to 600 nm. **Figure 6** shows dependence of the optical band gap on the RF power. The optical band gap of the film was 3.25-3.27 eV. This value is close to the value of bulk ZnO (3.30 eV)[8]. This result indicates that ZnO films were successfully fabricated.

3.4 Analysis of crystal structure using XRD

Typical XRD profiles of films fabricated at RF powers of 80 to 110 W are shown in **Fig.7**. The O_2 flow rate was 15 ccm. The profile shows a large peak for the (002) plane of ZnO. This result reveals that ZnO films have a polycrystalline structure oriented c-axis. By increasing the RF power, the (002) peak becomes larger and more distinct. However, above 100 W, intensity of the (002) peak decreases as RF power is increased. Fig.3 (a) shows that unstable streamer discharge was observed above 100 W. This result reveals that uniform glow discharge is necessary to fabricate ZnO film possessing a good polycrystalline structure. Typical XRD profiles of films fabricated at RF powers of 70 to 140 W are shown in **Fig.8**. The O_2 flow rate was 45 ccm. The profile shows a large peak for the (002) plane of ZnO. This result reveals that ZnO films have a polycrystalline structure oriented c-axis. By increasing the RF power, the (002) peak becomes larger and more distinct. Crystal grain size was calculated from FWHM of (002) peaks in the X-ray profiles, as is shown in **Fig.9**. The grain size of the polycrystalline ZnO increases and its crystallinity is improved by increasing the RF power.

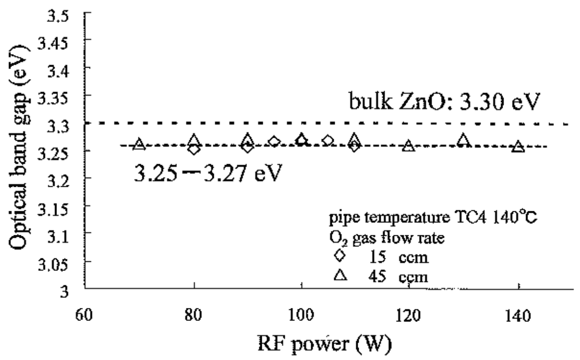


Fig.6 Dependence of optical band gap on the RF power.

3.5 AFM observationss

Figure 10 shows AFM observations of the surface of ZnO films for (a) 70 and (b) 100 W of RF power at 45 ccm of O_2 flow rate. In Fig.10 (a), the film has a rough surface and many voids and sub-grains can be observed. On the other hand, as Fig.10 (b) shows, the film has a flat surface with fewer voids and larger

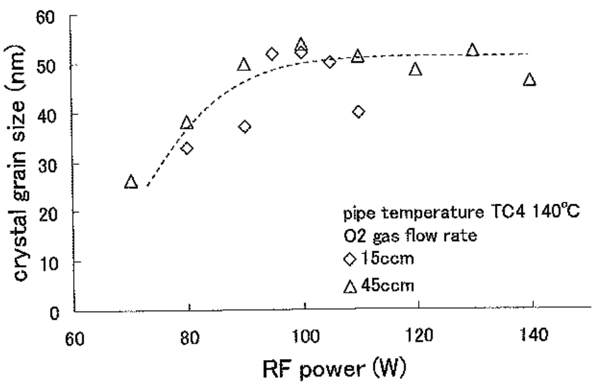


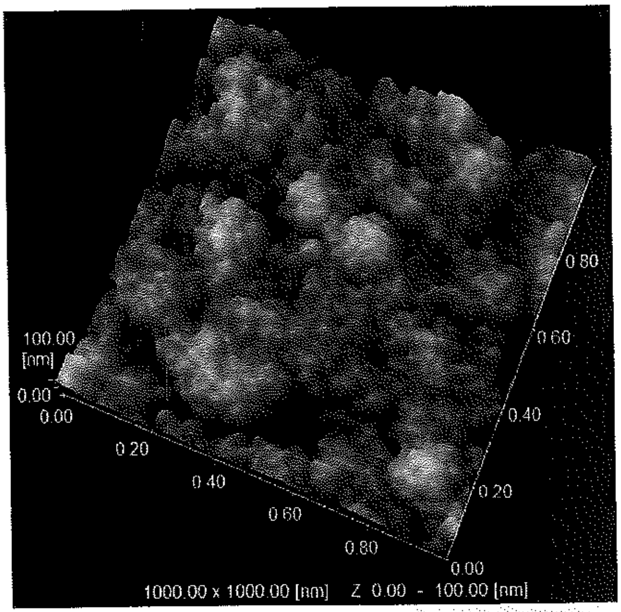
Fig.9 Dependence of the crystal grain size on the RF power.

grains. The thickness of the film decreased by increasing RF power, as shown in Fig.5. It seems that the rough surface increases film thickness. In addition, as shown in Fig.9, the crystal grain size increased by increasing the RF power, which shows the same tendency as found in the AFM observations. Finally, flat and high density ZnO film with fewer voids and larger grains could be fabricated at 100 W of RF power and an O_2 flow rate of 45 ccm .

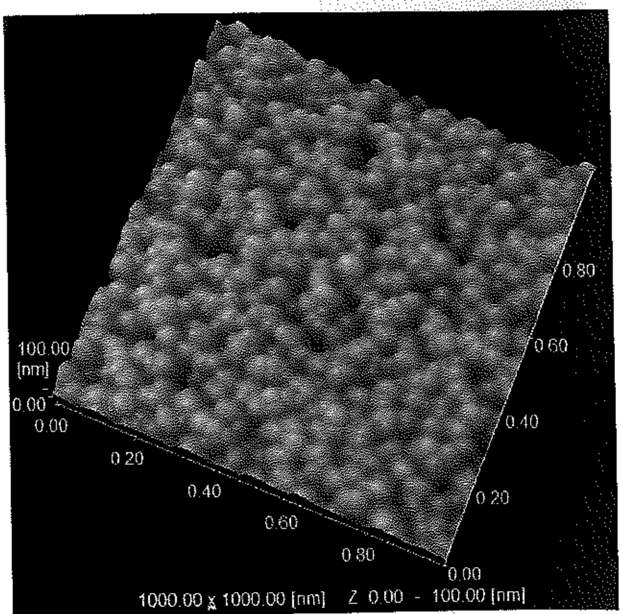
4. Conclusions

Using our open-air atmospheric pressure cold plasma generator, we fabricated ZnO films on glass substrates by feeding Zn-MOPD into the plasma. The results are summarized as follows.

(1) When the O_2 gas flow rate is 15 and 45 ccm, stable glow discharge was observed for RF power ranging from 4 to 78 W and from 4 to 160 W at 1.0 mm of the gap, respectively.
(2) By feeding Zn-MOPD into the plasma using a mixture of He and O_2 gases, transparent flat films about 200-600 nm thick were successfully fabricated directly under the slit made into the cathode.
(3) The transmittance of ZnO films was more than 90 % in the wavelength range from 400 to 600 nm. Optical band gap of the ZnO films were 3.25-3.27 eV.
(4) ZnO films have a polycrystalline structure oriented c-axis. By increasing the RF power, the (002) peak in the XRD profile became larger and more distinct. The grain size of the polycrystalline ZnO increased and its crystallinity was improved by increasing RF Power.
(5) Uniform glow discharge was found to be necessary to fabricate ZnO film with a good polycrystalline structure.
(6) Flat and high density ZnO film with fewer voids on the surface and larger grains could be fabricated at 100 W of RF power and an O_2 flow rate of 45 ccm.



(a) 70 W



(b) 100 W

Fig.10 AFM observations for (a) 70 W and (b) 100 W of RF power at 45 ccm of O_2 flow rate.

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