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Abstract

Under open-air atmospheric pressure homogeneous non-equilibrium cold plasma was generated stably by high voltage pulsed power (1 kV, 20 kHz) excitation of a mixture of He and O_2 *gases. By feeding Zn-MOPD* ($C_{18}H_{30}O_6Zn$) *with He carrier gas into this plasma system transparent flat ZnO thin films about 250 nm thick were successfully fabricated on glass substrates. The film was fabricated directly under the slit made into the cathode. Plasma species were observed by optical emission spectroscopy.* N_2 *molecular, He and O atomic species were present in the plasma. In addition, atomic species of O and He increased by increasing the input voltage. The bombardment of the high energy ions at high input voltage may change the growth pattern of ZnO film and its structure.*

Keywords : Plasma deposition, Zinc oxide, Atmospheric pressure cold plasma, He & O_2 gases

1. Introduction

Transparent electrically conductive zinc oxide (ZnO) films have been studied experimentally to determine their application to low-cost transparent electrodes in solar cells such as amorphous silicon (a-Si) and 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) and sputtering3). Compared to high temperature CVD, PECVD is an attractive process for film growth due to its low substrate temperature requirement. It is sometimes indispensable for preparing multilayered 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 plasma can be generated under atmospheric pressure, it becomes 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 atm4~6). In this paper, we describe the effects of discharge condition such as discharge voltage and O_2 gas flow rate on the formation of plasma through optical emission spectroscopy. Using a stable glow discharge, we fabricated ZnO films and observed the microstructure with a Field Emission Scanning Electron Microscope (FE-SEM).

2. Experimental Procedure

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 the plate. A slit (1 mm × 20 mm) was made 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 back and forth in the direction perpendicular to the slit in order to fabricate flat films in a large area (sweep distance : 10 mm). A schematic diagram of its movement is shown in **Fig. 2.** Cold plasma was then generated by flowing He and O_2 gases. He carrier gas was fed through the inner space

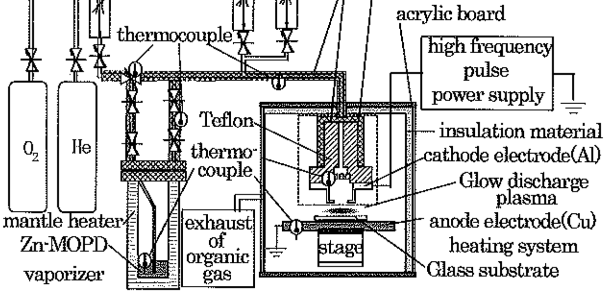

Fig. 1 Schematic diagram of the fabrication system.

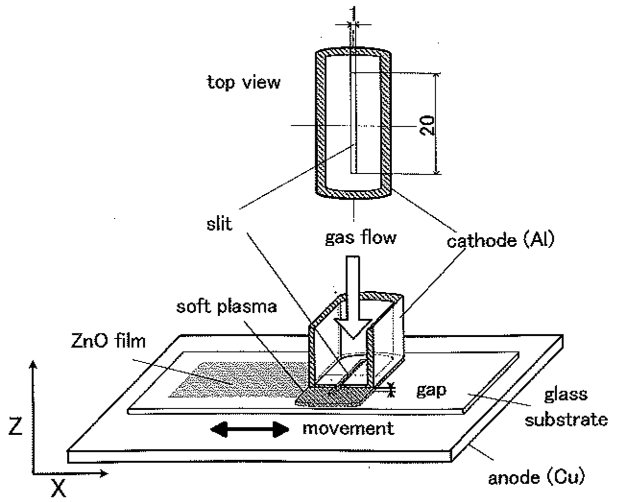

Fig. 2 Schematic diagram of movement of the anode plate. The anode moves back and forth during deposition.

Table 1 Fabrication conditions.

Substrate	Glass
Substrate temperature	150 □
Source material	Zn-MOPD ($C_{18}H_{30}O_6Zn$, UBE Industries, Ltd.)
Source material temperature	100 □
He gas total flow rate	1500 ccm
O_2 gas flow rate	0 – 90 ccm
Voltage	1 kV
Sweep distance	10 mm
Sweep speed	1 mm/s
Anode and cathode gap	0.5 mm
Deposition time	60 min

of the cathode down to the gap, where it was excited by the high voltage pulse supply (HVP-20K, Haiden Laboratory Co. Ltd.). Zn-MOPD ($C_{18}H_3O_6Zn$, UBE industries, Ltd.), vaporized, and then carried by the He carrier gas flow into the plasma generated at the gap.

Table 1 shows the fabrication conditions of our experiments. Under these conditions, a transparent flat film about 250 nm thick was successfully fabricated on the glass substrate. The film grew only directly under the silt made into the cathode. The deposition rate was about 40 nm/min. The microstructure of the films were examined using an FE-SEM (Hitachi, Ltd.).

3. Results and Discussion

3. 1 Glow discharge region

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.

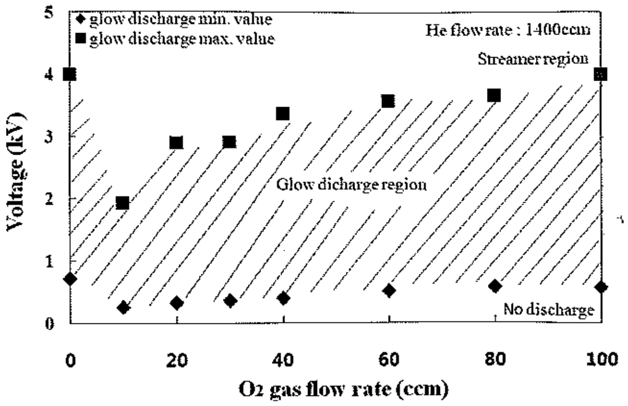

Fig. 3 Glow discharge region of the cold plasma.

Squares (■) and diamonds (♦) represent maximum and minimum values of the glow discharge, respectively. When the O_2 gas flow rate is 10 ccm, stable glow discharge was observed in the voltage range from 0.25 to 1.9 kV. However above 1.9 kV, unstable streamer discharge was observed instead. Stable discharge can be obtained at a higher voltage with a higher O_2 gas flow rate. Since oxygen has a high electronegativity, it recombines with electrons in the plasma easily. Thus, the density of electrons in the plasma was held lower than the limit value for transition to the streamer discharge.

3. 2 Optical emission spectra from plasma

To investigate the degree of ionization and dissociation with the glow discharge, the optical emission spectrum was measured, and the intensities of the molecular, ionic, and atomic species in the plasmas were also measured. Typical optical emission spectrum measured from 200 to 800 nm for the mixture of He and O_2 (10 ccm) gases at 1 kV of input voltage, as shown in **Fig. 4.** In the mixture of He and O_2 gases, peaks were observed in N_2 (300~500 nm), O (778.08 nm) and He (668.49, 707.17 nm)[7]. These N_2 peaks appeared to be caused by the air and H_2O in the atmosphere.

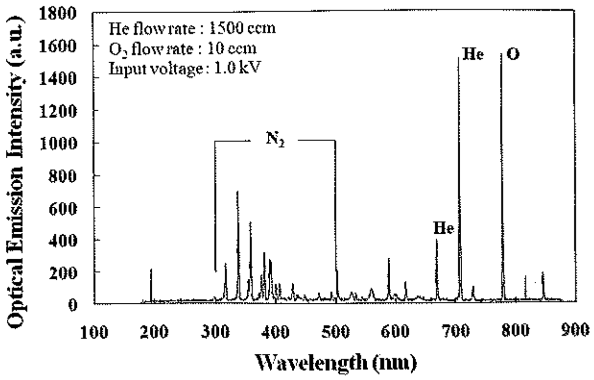

Fig. 4 Optical Emission spectrum of the plasma.

Figure 5 shows the relationship between input voltage and optical emission intensities of O (778.08 nm), He (707.17 nm) and N_2 (390.31 nm) for the two O_2 gas flow rates of (a) 10 ccm and (b) 60 ccm. When the O_2 gas flow rate is 10 ccm (Fig. 5 (a)), the optical emission intensity of O and He have similar values at 0.5 kV, which increased as the input voltage was increased. Also, the optical emission intensity of N_2 increased. However, when the O_2 gas flow rate is 60 ccm (Fig. 5 (b)), optical emission intensities of O and He at 0.5 kV are smaller than the values at the same input voltage in Fig. 5 (a). By increasing the input voltage, the intensities increased. However, the increase of optical emission intensities stopped between 2.5 kV to 3.0 kV of input power and then increased above 3.0 kV. This is because the plasma may change in this region, even if glow discharge was observed. These results reveal that atomic species of O and He increase by increasing the input voltage.

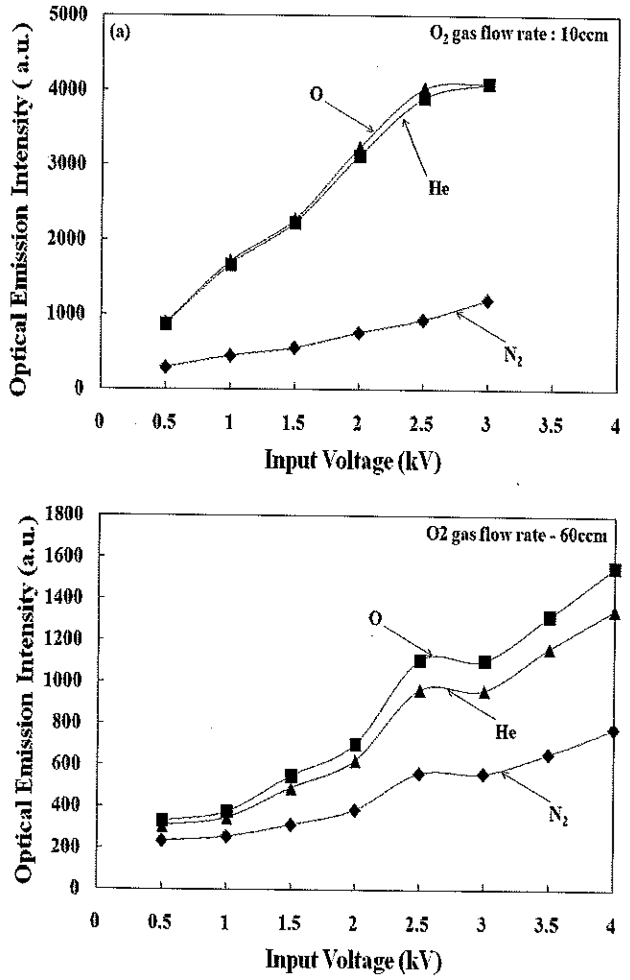

Fig. 5 The relationship between input voltage and optical emission intensity of O (778.08 nm), He (707.17 nm) and N_2 (390.31 nm) for the two O_2 gas flow rate (a) 10 and (b) 60 ccm.

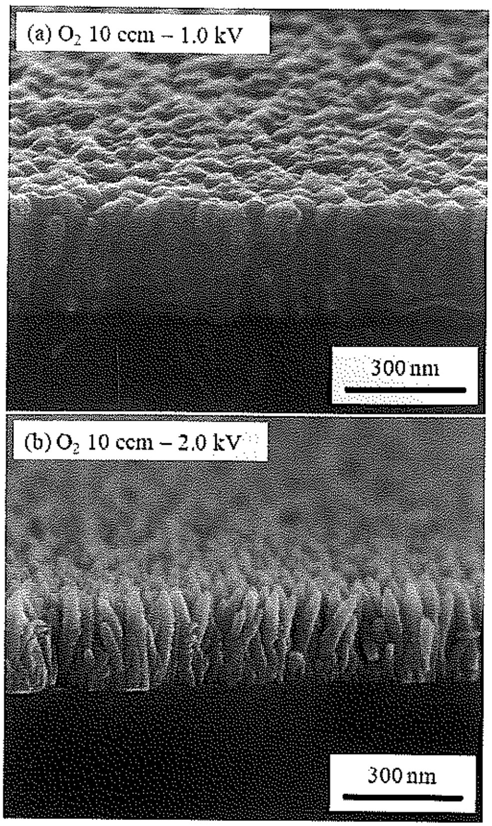

Fig. 6 Typical FE-SEM observations of the ZnO film for O_2 flow rate of 10 ccm at (a) 1.0 and (b) 2.0 kV.

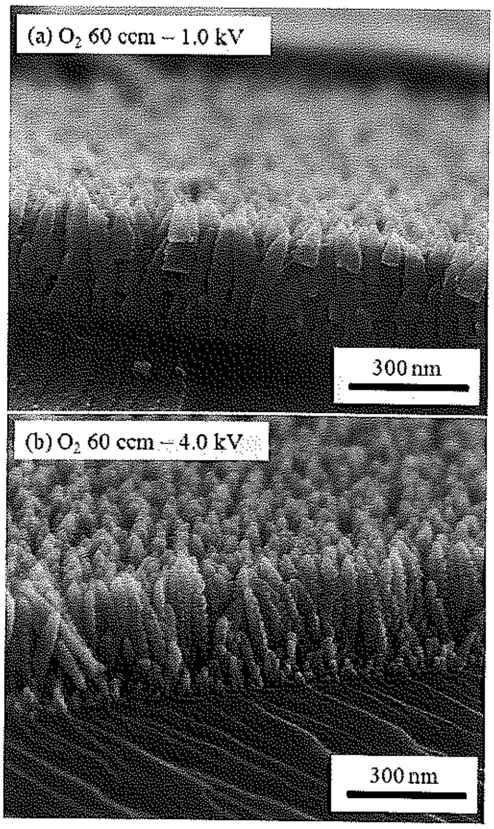

Fig. 7 Typical FE-SEM observations of the ZnO film for O_2 flow rate of 60 ccm at (a) 1.0 and (b) 4.0 kV.

3. 3 FE-SEM observations of ZnO films

By feeding Zn-MOPD into the plasma using a mixture of He and O_2 gases, transparent flat films about 250 nm thick were successfully fabricated directly under the slit made into the cathode. Typical FE-SEM of ZnO films for the O_2 flow rate of 10 ccm at (a) 1.0 and (b) 2.0 kV is shown in **Fig. 6.** Figure 6 (a) shows columnar structures on a cross section of continuous thin film, which has a rough surface. There are fine sub-grain of about 10 nm in diameter in the columnar structure. On the other hand, Figure 6 (b) shows rod shapes with spaces between them instead. **Figure** 7 shows the typical FE-SEM observations of the ZnO film for O_2 flow rate of 60 ccm at (a) 1.0 and (b) 4.0 kV. Figure 7 (a) shows pile up conic shapes with space between them. On the other hand, in Fig. 7 (b), ZnO grain looks like a bamboo shoot grown on the glass substrate. Also, the space between them is wider than the space in Fig. 7 (a). The bombardment of the high energy ions at high input voltage may change the growth pattern of ZnO film and its structure[8]. 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 to be prepared in the near future. Our goal is to develop a simple fabricating system by using low cost materials such as N_2 gas or air at 1 atm.

4. Conclusions

Our atmospheric cold plasma generator successfully generated stable glow discharge by high voltage pulse power (1 kV, 20 kHz) excitation of a mixture of He and O_2 gases. Using this generator, we fabricated ZnO films on the glass substrate, and the results are summarized as follows.

(1) When the O_2 gas flow rate is 10 ccm, stable glow discharge was observed for voltages ranging from 0.25 to 1.9 kV. However, above 1.9 kV, unstable streamer discharge was observed instead.

(2) By feeding Zn-MOPD into the plasma using a mixture of He and O_2 gases, transparent flat films about 250 nm thick were successfully fabricated directly under the slit made into the cathode.

(3) Optical emission spectra revealed that N_2 molecular, He and O atomic species existed in the plasma. In addition, atomic species of O and He increase by increasing the input voltage.

(4) The bombardment of the high energy ions at high input voltage may change the growth pattern of ZnO film and its structure.

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