Fabrication of ZnO:Al Thin Films by Using an Atmospheric Pressure Cold Plasma Generator

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ABSTRACT

Under 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 ($C_{18}H_{30}O_6Zn$), or Zn-MOPD and Al-MOPD ($C_{27}H_{45}O_9Al$) into this plasma with He carrier gas, transparent flat ZnO or Al-doped ZnO (ZnO:Al) films about 200 nm thick were successfully fabricated on glass substrates directly under the slit made into the cathode. Dependence of Al doping to ZnO films on optical and electrical properties was measured. In addition, microstructure of the films was studied by XRD measurement and FE-SEM observation.

KEYWORDS: Al Doped Zinc Oxide, Plasma Deposition, Atmospheric Cold Plasma Generator, Helium Gas, Oxygen Gas Plasma, Plasma, Plasma

1. INTRODUCTION

Al doped zinc oxide (ZnO:Al) films have been studied experimentally for application to low-cost transparent electrodes in solar cells such as amorphous silicon (a-Si). ZnO:Al 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 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 [1]. In this paper, we report on the use of the atmospheric pressure cold plasma generator to fabricate ZnO:Al films by feeding Zn-MOPD ($C_{18}H_3O_6Zn$) and Al-MOPD ($C_{27}H_{45}O_9Al$) into the plasma, which was generated stably by using a mixture of 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 (1 mm×20 mm) was prepared on the cathode (30 mm×50 mm), in order to let the flow of a

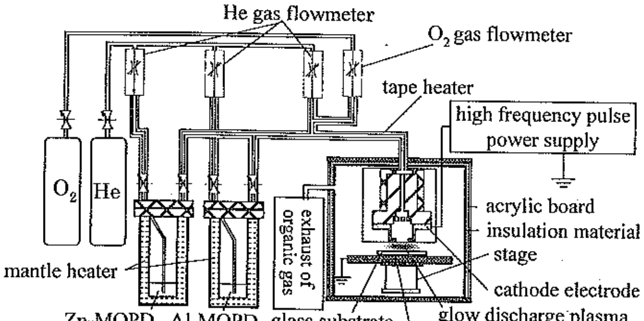


Fig.1 Schematic diagram of the fabrication system.

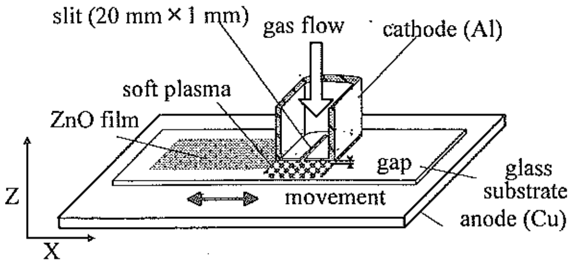


Fig.2 Schematic diagram of movement of the anode plate. The anode moves back and forth during fabrication.

mixture of He and O_2 gases 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 flat films in a large area (sweep distance: 10 mm). A schematic diagram of its movement is shown in **Fig.2**.

Atmospheric pressure cold plasma was generated by using the flowing mixture of 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.). Zn-MOPD and Al-MOPD ($C_{18}H_{30}O_6Zn$ and $C_{27}H_{45}O_9Al$, UBE Industries, Ltd.) were vaporized and carried by the He carrier gas flow into the plasma generated at the gap. **Table 1** and **Table 2** list the physical properties of Zn-MOPD and Al-MOPD, respectively. **Table 3** lists the fabrication conditions for our experiment. Under these conditions, a transparent flat film about 180 nm thick was successfully fabricated on the glass substrate. The film grows only directly under the slit made into the cathode with a deposition rate of about 30 nm/min. In spattering, the deposition rate was found to be 40 nm/min [2]. The deposition rate of our system is almost the same.

Transmittance of the film was measured by a spectrophotometer (UV-3150, Shimadzu Co.). Resistivity of the film was tested by the four-probe method with a multimeter (E2373A, Hewlett Packard Co., Ltd.). The microstructures of the films were studied by a field emission scanning electron microscope (FE-SEM; S-900S, Hitachi, Ltd.) X-ray diffraction (XRD; XRD-6100, Shimadzu Co.)

3. RESULTS AND DISCUSSION

3.1 Glow Discharge Region

The glow discharge region of the cold plasma generator 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 circle (●) 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 4.5 kV. But above 4.5 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

Table 1 Physical properties of Zn-MOPD.

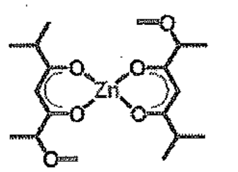
Zn precursor	Zn-MOPD
Structure	
Molecular formula	$C_{18}H_{30}O_6Zn$
Molecular weight	407.8
Melting point	6 ℃
Vapor press	0.2 torr @ 140 ℃
Appearance	Pale yellow viscous liquid
Stability	Stable in air

Table 2 Physical properties of Al-MOPD.

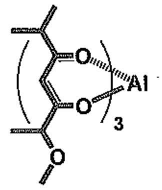
Al precursor	Al-MOPD
Structure	
Molecular formula	$C_{27}H_{45}O_9Al$
Molecular weight	540.6
Melting point	Liquid @ R.T.
Vapor press	0.16 torr @ 130 ℃
Appearance	Pale yellow liquid
Stability	Stable in air & moisture

Table 3 Fabrication conditions.

Substrate	Glass
Substrate temperature	215 ℃
Source materials	Zn-MOPD, Al-MOPD ($C_{18}H_{30}O_6Zn$, $C_{27}H_{45}O_9Al$) (UBE Industries, Ltd.)
Source material temperatures	100 ℃ (Zn-MOPD) 90 ℃ (Al-MOPD)
Carrier He gas flow rates	150 ccm (Zn-MOPD) 0～30 ccm(Al-MOPD)
He gas total flow rate	1550～1580 ccm
O_2 gas flow rate	10 ccm
Voltage	1 kV
Sweep distance	10 mm
Sweep speed	1 mm/s
Anode and cathode gap	0.5 mm
Deposition time	60 min

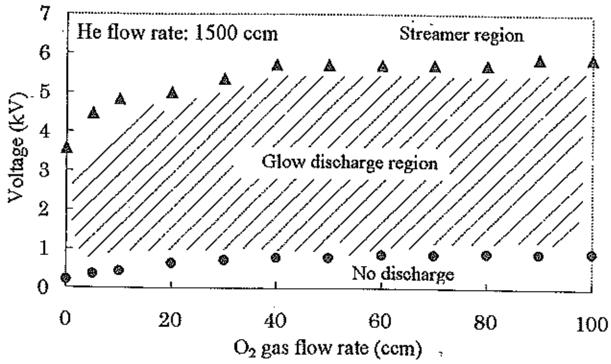


Fig.3 Glow discharge region of the cold plasma generator.

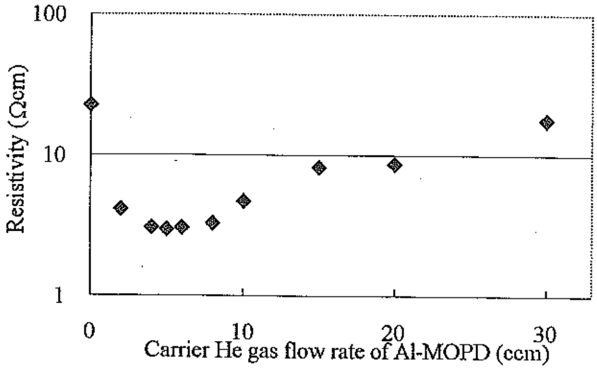


Fig.5 Resistivity of ZnO:Al films.

streamer discharge. Stable discharge can be obtained at a higher voltage with a higher oxygen flow rate.

3.2 Transmittance

Fig.4 shows the typical spectral transmittance of the films for the Al-MOPD carrier He gas flow rates of 0, 5 and 30 ccm. The average transmission of all films was more than 85 % in the wavelength range from 400 to 800 nm. When the Al-MOPD carrier He gas flow rate is 0 ccm (only Zn-MOPD), the band gap calculated from the absorption edge is 3.25 eV, which is close to the value of ZnO (3.26 eV) reported by B.G. Bylander [3]. When the Al-MOPD carrier He gas flow rate is 5 and 30 ccm, the band gap of the film increases to 3.35 and 3.40 eV, respectively. R.J. Hong et al. [4] reported that the band gap of the ZnO:Al films fabricated by spattering was 3.49–3.65 eV. Our values are smaller than their values. However, the tendency of the band gap to increase by Al doping is similar.

3.3 Electrical Resistivity

Fig.5 shows the electrical resistivity of the films. The horizontal axis shows the carrier He gas flow rate of Al-MOPD. The resistivity of ZnO film fabricated by only Zn-MOPD is 22.7 Ωcm. When the carrier He gas flow rate of Al-MOPD is 3 ccm, the resistivity of the film is 2.96 Ωcm. This means that the resistivity decreased because of successful doping of Al into ZnO film. However, at more than 8 ccm, the resistivity increased.

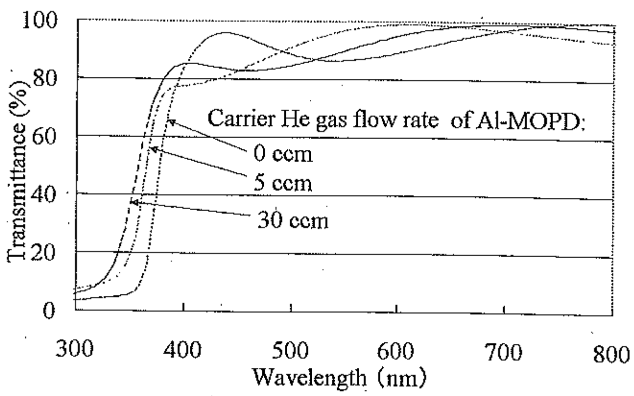


Fig.4 Typical transmittance of ZnO:Al films.

3.3 FE-SEM Observation

Typical FE-SEM observations of the ZnO film for the two flow rates of 5 and 30 ccm are shown in **Fig.6** (a) and (b), respectively. Cross-sectional images of both of the films show a columnar structure. The grain columns were tightly packed and grew through the

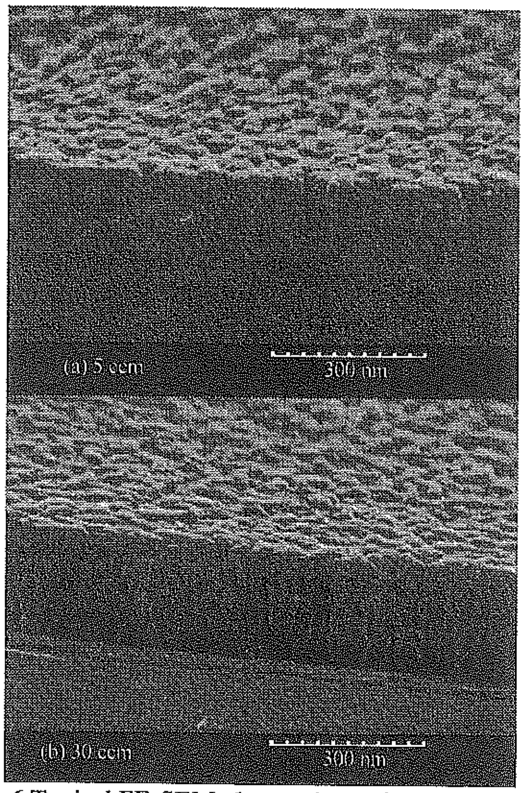


Fig.6 Typical FE-SEM observations of ZnO:Al films for the two carrier He gas flow rates of Al-MOPD of (a) 5 ccm and (b) 30 ccm.

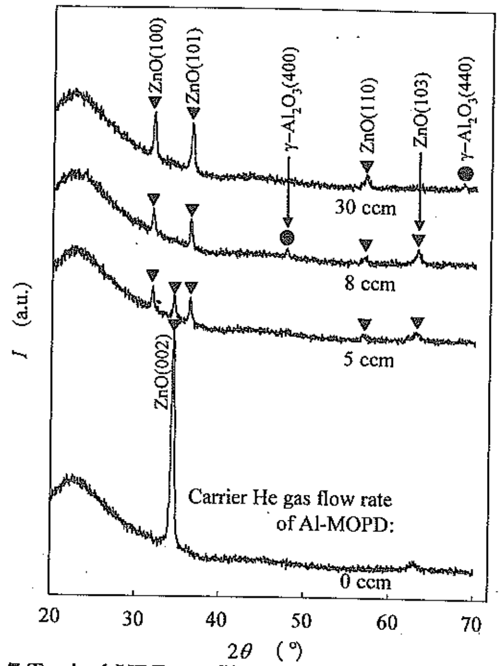


Fig.7 Typical XRD profiles of ZnO or ZnO:Al films.

entire film. These structures are almost identical.

3.4 Analysis of Crystal Structure Using XRD

Typical XRD profiles of films fabricated at the carrier He gas flow rates of Al-MOPD of 0, 5, 8 and 30 ccm are shown in **Fig.7**. The profile of the film at 0 ccm (fabricated only by using Zn-MOPD) shows a large peak for the (002) plane of hexagonal ZnO crystal. This result reveals that ZnO films have a polycrystalline structure oriented c-axis. On the other hand, by feeding Al-MOPD, peaks of ZnO crystal can be seen in the profiles of 5, 8 and 30 ccm. This result reveals that doped Al is substituted onto the Zn site of the ZnO crystalline structure. Therefore, ZnO:Al films are successfully obtained. However, the orientational structure has not appeared. The peaks of g-Al_2O_3 crystalline are shown in the profiles of 8 and 30 ccm. This reveals that a part of Al is not substituted onto the Zn site of the Zn crystalline and becomes Al_2O_3.

Fig.8 shows lattice parameters of a and c of ZnO or ZnO:Al crystalline structure calculated from positions of the peaks of ZnO or ZnO:Al in Fig.7. Both a and c are decreased by increasing the carrier He gas flow rate of Al-MOPD. Because the ionic radius of Al^{3+} is smaller than Zn^{2+}, the lattice parameters, a and c, decrease by substitution of Al onto the Zn site of the ZnO crystalline structure.

4. CONCLUSIONS

Our Atmospheric Pressure Cold Plasma generator successfully generated stable glow discharge by high voltage pulsed power (1 kV, 20 kHz) excitation of a

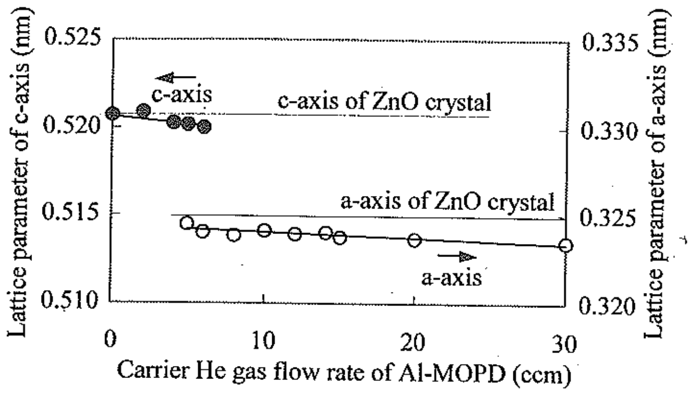


Fig.8 lattice parameters of a and c of ZnO or ZnO:Al crystalline structure calculated from positions of the peaks of ZnO or ZnO:Al in Fig.7.

mixture of He and O_2 gases. Using this generator, we fabricated ZnO:Al films on the glass substrates by feeding Zn-MOPD and Al-MOPD into the plasma. The results are summarized as follows.

(1) When the He and O_2 gas flow rate are 1500 and 10 ccm, respectively, stable glow discharge was observed for voltages ranging from 0.4 to 4.8 kV. However, above 4.8 kV, unstable streamer discharge was observed instead.

(2) Transparent flat films about 180 nm thick were successfully fabricated directly under the slit made into the cathode. The average transmittance of the film is more than 85 % in the range from 400 to 800 nm. The band gap calculated from the absorption edge is 3.25–3.40 eV.

(3) XRD measurement revealed that ZnO:Al films have a hexagonal polycrystalline structure.

(4) Electrical resistivity is 2.96 Ωcm when the composition ratio of Al to Zn is 1.29 mol%.

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