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Effect of substrate temperature on ZnO thin film fabrication by using an atmospheric pressure cold plasma generator

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Under atmospheric pressure, homogeneous non-equilibrium cold plasma was generated stably by high voltage pulsed power (1 kV, 20 kHz) excitation of He and O_2 gases. By feeding Zn-MOPD ($C_{18}H_{30}O_6Zn$) into this plasma with He carrier gas, transparent flat ZnO films about 240 nm thick were successfully fabricated on glass substrates directly under a slit made into the cathode. Transmittance of the film is about 80 % in the wavelength range from 400 to 600 nm. An XRD measurement revealed that these ZnO films had a c-axis oriented polycrystalline structure. By increasing the substrate temperature from 250 to 400 °C, electrical resistivity of the film decreased from 0.42 Ωm to 9.4×10^{-4} Ωm. A high temperature of the substrate may change the growth pattern of ZnO film and its microstructure.

Photograph of the atmospheric pressure cold plasma

1 Introduction Transparent electrically conductive zinc oxide (ZnO) films have been studied experimentally for their application to low-cost transparent electrodes in solar cells such as amorphous silicon (a-Si). In conventional PECVD (Plasma-enhanced Chemical Vapour Deposition) 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 becomes possible not only to simplify the processing system but also to make plasma applicable for wider purposes.

Recently, cold plasma (glow discharge) was generated by an RF excitation of flowing Ar, He or their mixtures at 1 atm [1-3]. Previously we reported on the use of an atmospheric pressure cold plasma generator to fabricate ZnO and Al doped ZnO films by feeding Zn-MOPD ($C_{18}H_3O_6Zn$) and/or Al-MOPD ($C_{27}H_{45}O_9Al$) into the plasma, which was generated stably using He and O_2 gases [4-7]. In the present study, the effect of substrate temperature on ZnO thin film fabrication was investigated.

2 Experimental procedure The fabrication system of 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, with a heating system. A slit type hole (20 mm × 1 mm) was made into the cathode (30 mm

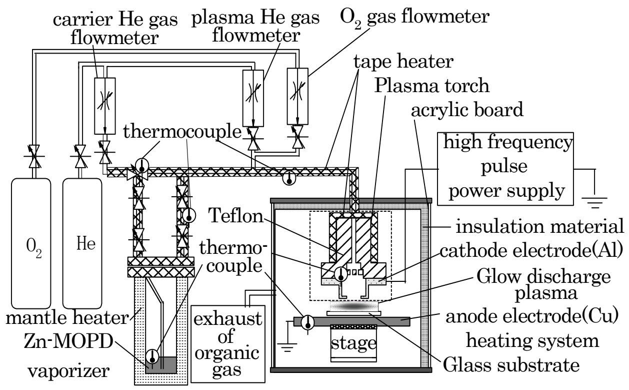

Figure 1 Schematic diagram of the fabrication system.

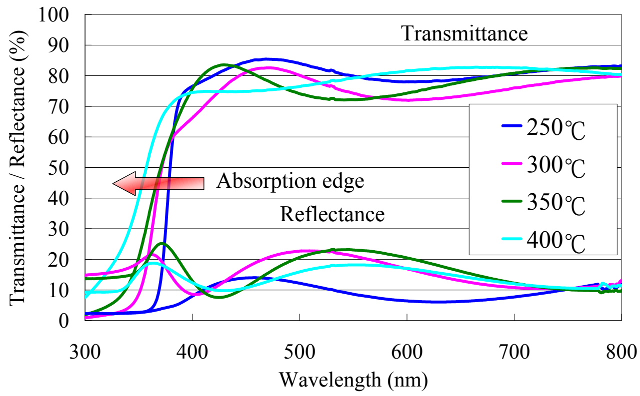

Figure 2 Transmittance and reflectance spectra of the ZnO films.

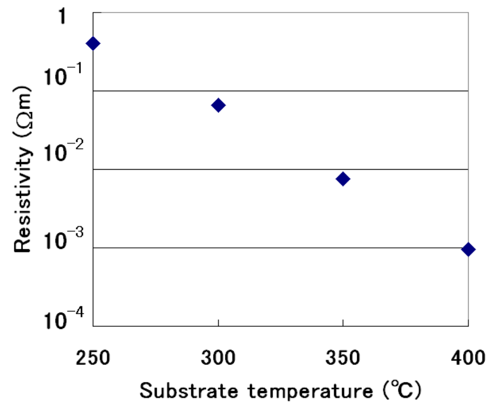

Figure 3 Resistivity of the ZnO films.

× 50 mm), in order to let He gas flow into the gap between cathode and anode. Also, the anode plate moved 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). 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 the high voltage pulse supply (HVP-20K, Haiden Laboratory Co. Ltd., Japan). Zn-MOPD ($C_{18}H_{30}O_6Zn$, UBE Industries, Ltd., Japan) was vaporized and carried by the He carrier gas flow into the plasma generated in the gap. Table 1 lists the fabrication conditions for our experiment.

A film about 240 nm thick grew directly under the slit made into the cathode with a fabrication rate of about 30 nm/min. Spectral transmittance of the film was measured by a spectrophotometer (UV-3150, Shimadzu Co., Japan). The microstructures of the film were examined with a field emission scanning electron microscope (FE-SEM; Hitachi, Ltd., Japan) and X-ray diffraction (XRD; XRD-6100, Shimadzu Co., Japan) measurements. Resistivity of the film was tested by the four-probe method.

3 Results and discussion

3.1 Transmittance and reflectance Figure 2 shows the typical spectral transmittance and reflectance of the films for the substrate temperature of 250, 300, 350 and 400 °C. The average transmittance of the films was about 80 %, in the wavelength range from 400 to 800 nm. These spectra have absorption edges. When substrate temperature increased, the absorption edge shifts to a short wavelength. When the substrate temperature is 250 °C, the optical 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 [8]. When the substrate is between 250 to 400 °C, the band gap of the film increases from 3.25 to 3. 35 eV.

Table 1 Fabrication conditions.

Substrate	Glass
Substrate temperature	250–400 °C
Source material	Zn-MOPD (UBE Industries, Ltd., Japan)
Source material temperature	100 °C
Carrier He gas flow rate	150 ccm
He gas total flow rate	1550 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

3.2 Electrical resistivity Figure 3 shows the electrical resistivity of the ZnO films. The resistivity of the film is 0.40 Ωm at a substrate temperature of 250 °C. By increasing the substrate temperature, resistivity of the film decreased to 9.4×10^{-4} Ωm at a substrate temperature of 400 °C. This finding suggests the need for further experiments in order to produce lower resistivity of the ZnO films.

3.3 Analysis of the film structure Typical XRD profiles of the films fabricated at substrate temperatures of 250 and 400 °C are shown in Fig. 4. The profile shows a peak only for the (002) plane of ZnO. This result reveals that ZnO films have a c-axis oriented polycrystalline

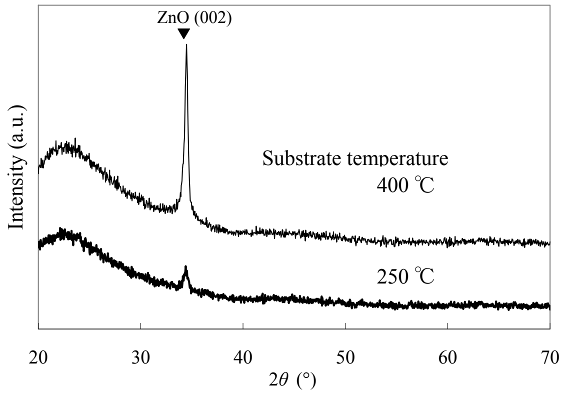

Figure 4 Typical XRD profiles of the ZnO films.

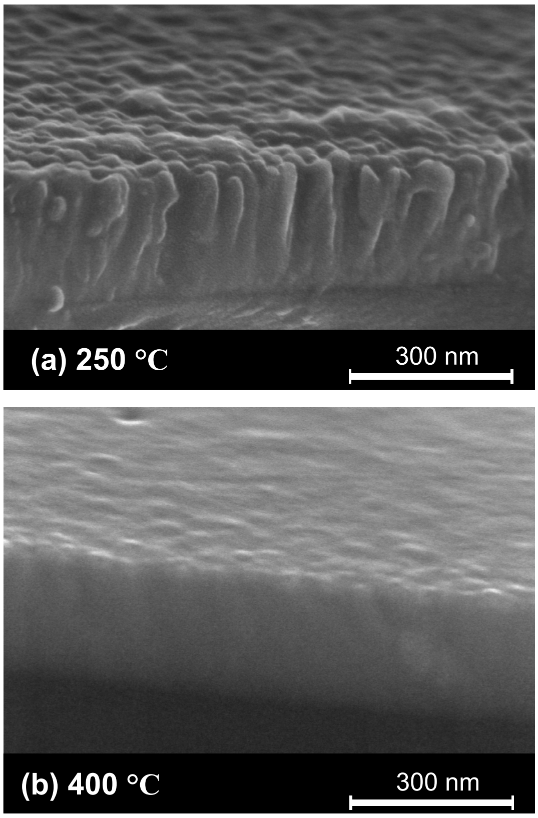

Figure 5 Typical FE-SEM observations of the ZnO film for the substrate temperature of (a) 250 and (b) 400 °C.

structure. By increasing the substrate temperature, the peak becomes larger and sharper, which means that the grain size of the polycrystalline ZnO becomes larger and its crystallinity is improved.

Typical FE-SEM observations of the ZnO film at substrate temperatures of 250 and 400 °C are shown in Fig. 5 (a) and (b), respectively. Flat and continuous films were obtained. The cross-sectional image in Fig. 5(a) shows a columnar structure. The grain columns were tightly packed and grew through the entire film. However, the cross-sectional image in Fig. 5(b) shows a uniform and smooth structure. A high substrate temperature may cause the growth pattern of ZnO film and its microstructure to become smooth

4 Conclusions Atmospheric pressure cold plasma was generated stably by high voltage pulsed power (1 kV, 20 kHz) excitation of a mixture of He and O_2 gases. We fabricated ZnO films on glass substrates by feeding Zn-MOPD into the plasma. Results are summarized as follows.

(1) Transparent flat films about 240 nm thick are successfully fabricated directly under the slit made into the cathode. The deposition rate of the film is 30 nm/min.

(2) The average transmittance is about 80 % in the range from 400 to 800 nm. The optical band gap calculated from the absorption edge is 3.35 eV at a substrate temperature of 400 °C.

(3) ZnO films have a c-axis oriented polycrystalline structure. When the substrate temperature is 400 °C, the microstructure of the ZnO film becomes smooth and its crystallinity is improved.

(4) Electrical resistivity of the ZnO film is 9.4×10^{-4} Ωm at a substrate temperature of 400 °C.

Further studies and experiments on the effects of the gas flow rate in the gap and 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 using low cost materials such as N_2 gas or air at 1 atm.

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