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Dependence of Al concentration on Al Doped ZnO Films Prepared by Using Atmospheric Pressure Cold Plasma

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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, 38 W) excitation of a mixture of He and O_2 *gases by using a dielectric barrier discharge setup. By feeding Zn-MOPD and Al-MOPD (*$C_{27}H_{45}O_9Al$*) into this plasma with He carrier gas, transparent flat Al-doped ZnO (ZnO:Al) films about 120-240 nm thick were successfully prepared on glass substrates directly under the slit made into the cathode. Deposition rates of the films were about 20-40 nm/min. Concentration of Al was measured by ICP (Inductively Coupled Plasma) atomic emission spectroscopy. Composition ratio of Al to Zn was 7.8 mol% when carrier He gas flow rate of Al-MOPD was 30 ccm. The average transmission of all films was more than 85 % in the wavelength range from 400 to 800 nm. When the composition ratio of Al/Zn is between 1.1 and 7.8 mol%, the optical band gap of the film increases from 3.28 to 3.40 eV. The resistivity of ZnO:Al film was 2.96 Ωcm at 1.3 mol% of Al/Zn. In addition, microstructure of the films was studied by XRD measurement and FE-SEM observation. It was revealed that doped Al is substituted onto the Zn site of the ZnO crystalline structure in ZnO:Al films.*

Keywords: Al doped zinc oxide, Plasma deposition, Atmospheric cold plasma generator, Helium gas, Oxygen gas

1. Introduction

Al doped zinc oxide (ZnO:Al) films have been studied experimentally for application to low-cost transparent electrodes having low resistivity less than 10^{-1} Ωcm and high transmitance above 80 % in solar cells such as amorphous silicon (a-Si), which need. 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 or high voltage pulsed power excitation of flowing Ar, He, O_2 or their mixtures at 1 atm by using a dielectric barrier discharge setup[1,2]. We used it for ZnO thin film preparation[3,4]. In this paper, we report on the use of the atmospheric pressure cold plasma generator to fabricate transparent and conductive 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

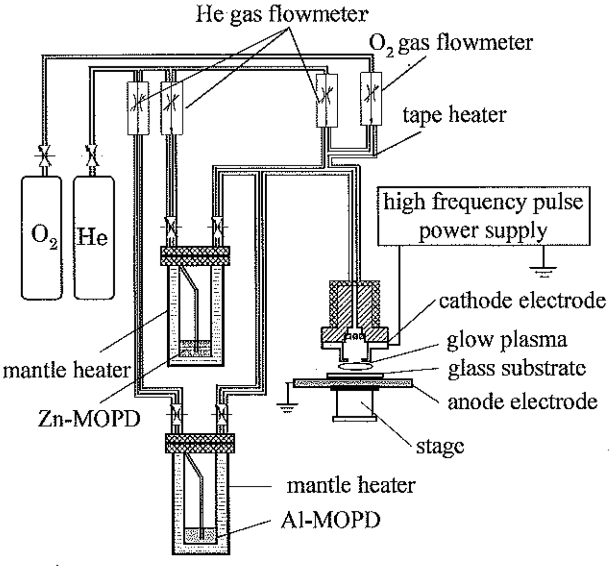


Fig.1 Schematic diagram of the fabrication system.

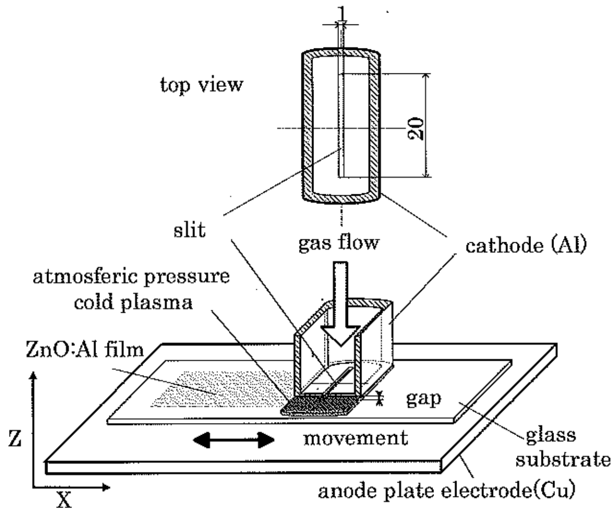


Fig.2 Schematic diagram of movement of the anode plate. The anode moves back and forth during fabrication.

cold plasma generator is schematically illustrated in **Fig.1**. Our plasma generator is composed of an Al cathode with a thin film coating of dielectric alumina created by a natural oxidation process, and a grounded anode of Cu plate. A dielectric 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 mixture of He and O_2 gases into the gap between cathode and anode. Cathode and anode gap is 0.5 mm. 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 and sweep speed: 1 mm/s). 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. Both of them are easy to handle, because they are liquid in room temperature and stable in air. **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. Thin films are prepared on glass substrates at temperature of 215 ℃. Zn-MOPD and Al-MOPD source materials are heated by mantle heaters at 100 and 90 ℃, respectively. Deposition time is 60 min. Under these conditions, transparent flat films about 120-240 nm thick were successfully prepared on the glass substrate. The films grew only

Table 1 Physical properties of Zn-MOPD.

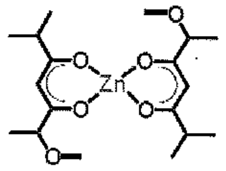
Zn precursor	Zn-MOPD
Structure	
Molecular formula	$C_{18}H_{30}O_6Zn$
Molecular weight	407.8
Melting point	6 ℃
Vapor press	0.2 torr @ 140 ℃
Appearance	Pale yellow viscous liquid
Stability	Stable in air

Table 2 Physical properties of Al-MOPD.

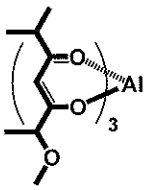
Al precursor	Al-MOPD
Structure	
Molecular formula	$C_{27}H_{45}O_9Al$
Molecular weight	540.6
Melting point	Liquid @ R.T.
Vapor press	0.16 torr @ 130 ℃
Appearance	Pale yellow liquid
Stability	Stable in air & moisture

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
Supply voltage	1.0 kV
Average power	38 W
Sweep distance	10 mm
Sweep speed	1 mm/s
Anode and cathode gap	0.5 mm
Deposition time	60 min

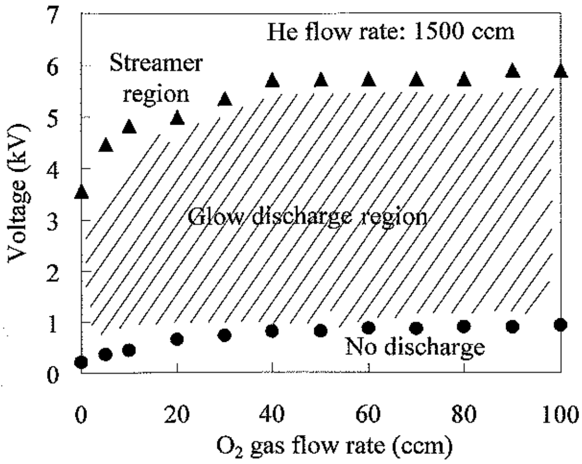


Fig.3 Glow discharge region of the cold plasma generator.

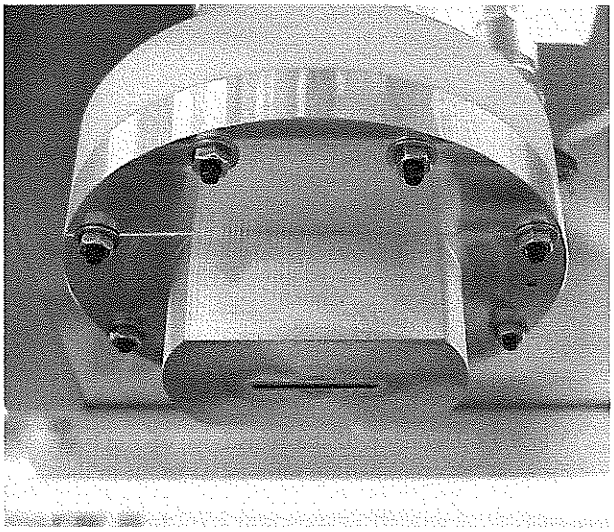


Fig.4 Photo of the cathode (30 mm×50 mm) with the slit (1 mm×20 mm).

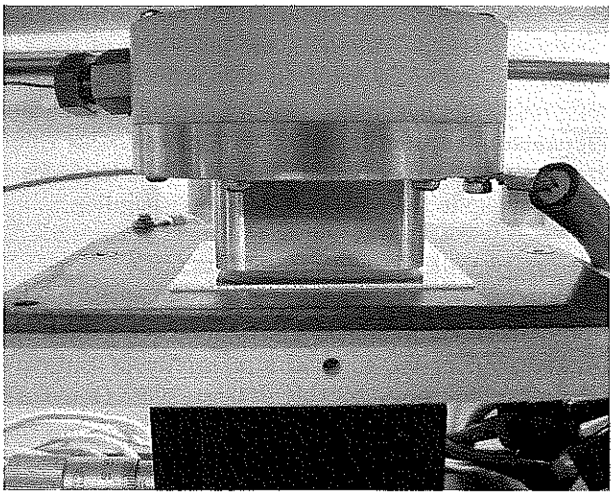


Fig.5 Typical glow discharge. Bright purple light is shown between the aluminum cathode and a glass substrate on the copper anode.

directly under the slit made into the cathode.

Composition ratio of Al to Zn in the mixture of source materials and prepared films were measured by ICP (Inductively Coupled Plasma) atomic emission spectroscopy (ICPS-7510, Shimadzu Co.).

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.) and 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 deposition system is shown in **Fig.3.**The horizontal and vertical axis 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. Average power of the supply was 38 W at 1.0 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 streamer discharge. Stable discharge can be obtained at a higher voltage with a higher oxygen flow rate. We prepared ZnO and ZnO:Al films at 10 ccm of the O_2 gas flow rate.

Photo of the cathode is shown in **Fig.4**. The slit (1 mm×20 mm) was prepared on the cathode (30 mm× 50 mm). Typical glow discharge is shown in **Fig.5**. Bright purple light is shown between the aluminum cathode and the copper anode.

3.2 Composition ratio of Al to Zn

Composition ratio of Al to Zn (Al/Zn) of the film measured by ICP atomic emission spectroscopy is shown in **Fig.6**. ○ with fitted dotted line and ● with fitted solid line indicates the ratio in the source materials and in the films, respectively. The composition ratio of Al to Zn is proportional to the carrier He gas flow rate of Al-MOPD. The ratio in the film is 7.8 mol% when carrier He gas flow rate of Al-MOPD was 30 ccm. The value of Al/Zn in the film is very close to the value in the source material. It reveals that the decomposition rates of Zn-MOPD and Al-MOPD are almost equal.

3.3 Thickness and deposition rate of the film

Fig.7 shows dependence of film thickness on the composition ratio of Al to Zn in the ZnO:Al film. Right axis indicates deposition rate calculated from the

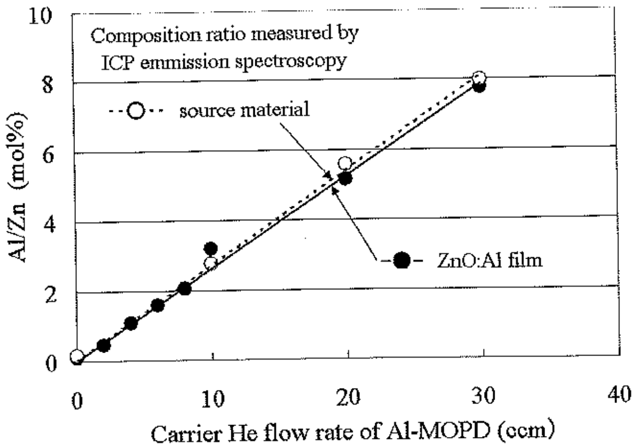


Fig.6 Composition ratio of Al to Zn (Al/Zn) of the film measured by ICP atomic emission spectroscopy. ○ with dotted line and ● with solid line indicates the ratio in the source materials and in the films, respectively.

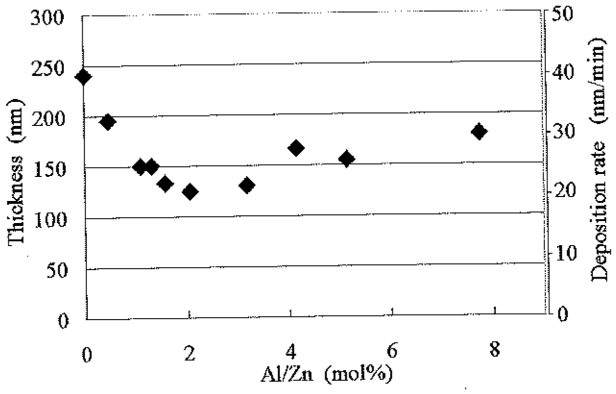


Fig.7 Dependence of film thickness on the composition ratio of Al to Zn in the film. Right axis indicates deposition rate calculated from the thickness and condition of moving stage.

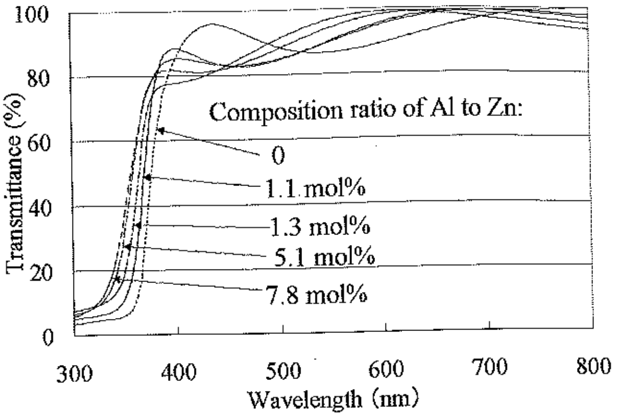


Fig.8 Typical transmittance of ZnO:Al films.

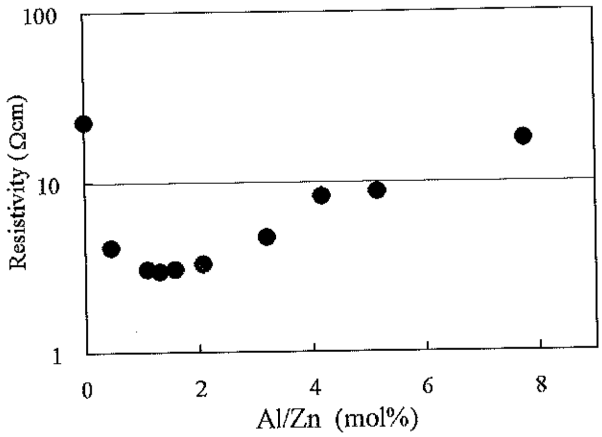


Fig.9 Dependence of the resistivity of ZnO:Al film on the composition ratio of Al to Zn in the film.

thickness and condition of the moving stage (Sweep distance; 10 mm). The deposition rate of ZnO film fabricated by only Zn-MOPD is 40 nm/min. The deposition rate of ZnO:Al film decreases by increasing the ratio of Al/Zn. However, above 2.0 mol% of Al/Zn, the thickness increases instead. Spattering at low pressure, the deposition rate was found to be 40 nm/min[5]. The deposition rate of ZnO:Al film in our system is lower than in sputtering.

3.4 Transmittance

Fig.8 shows the typical spectral transmittance of the films for the composition ratio of Al to Zn of 0, 1.1, 1.3, 5.1 and 7.8 mol%. 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 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[6]. When the composition ratio of Al/Zn is between 1.1 and 7.8 mol%, the band gap of the film increases from 3.28 to 3.40 eV. R.J. Hong et al.[7] 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.

3.5 Electrical Resistivity

Fig.9 shows the electrical resistivity of the ZnO:Al films. The horizontal axis shows the composition ratio of Al to Zn in the film. The resistivity of ZnO film fabricated by only Zn-MOPD is 22.7 Ωcm. The resistivity of the film is 2.96 Ωcm at 1.3 mol% of the composition ratio of Al/Zn. This means that the resistivity decreased because of successful doping of Al into ZnO film. However, at more than 1.3 mol %, the resistivity increased.

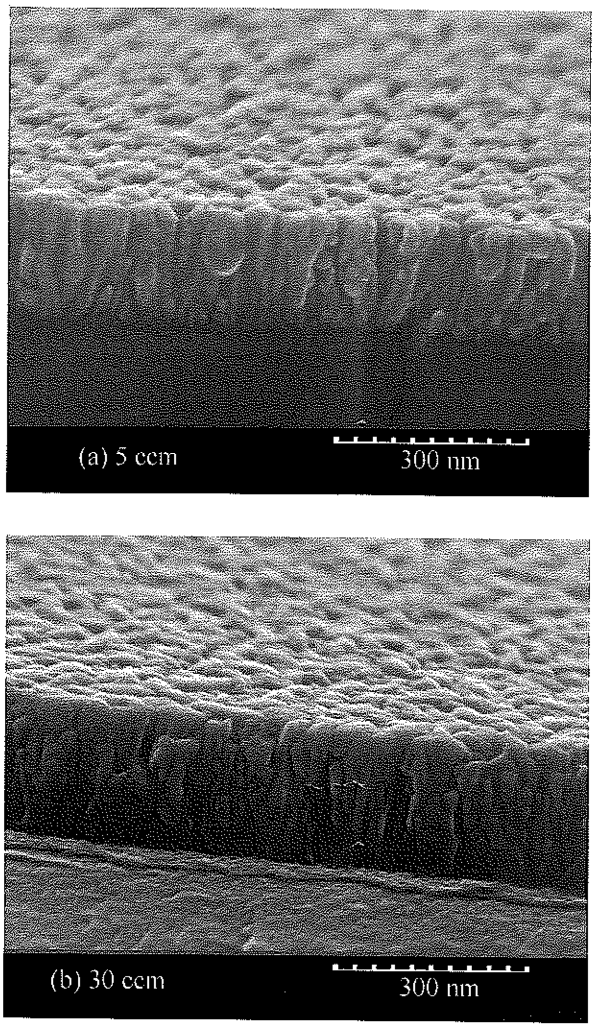


Fig.10 Typical FE-SEM observations of ZnO:Al films for the two carrier He gas flow rates of Al-MOPD of (a) 5 ccm and (c) 30 ccm.

3.6 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.10** (a) and (b), respectively. Flat and continuous films are obtained. Cross-sectional images of both of the films show a columnar structure. The grain columns were tightly packed and grew through the entire film. These structures are almost identical.

3.7 Analysis of crystal structure using XRD

Typical XRD profiles of ZnO and ZnO:Al films of 1.3, 2.1 and 7.8 mol% of the composition ratio of Al/Zn are shown in **Fig.11**. The profile of the ZnO film (Al/Zn: 0) shows a large peak for the (002) plane of hexagonal ZnO crystal. This result reveals that the ZnO film has 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 1.3, 2.1 and 7.8 mol% of Al/Zn. 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 γ-Al_2O_3 crystalline are shown in the profiles of 2.1 and 7.8 mol%. This reveals that a part of Al is not substituted onto the Zn site of the Zn crystalline and becomes Al_2O_3.

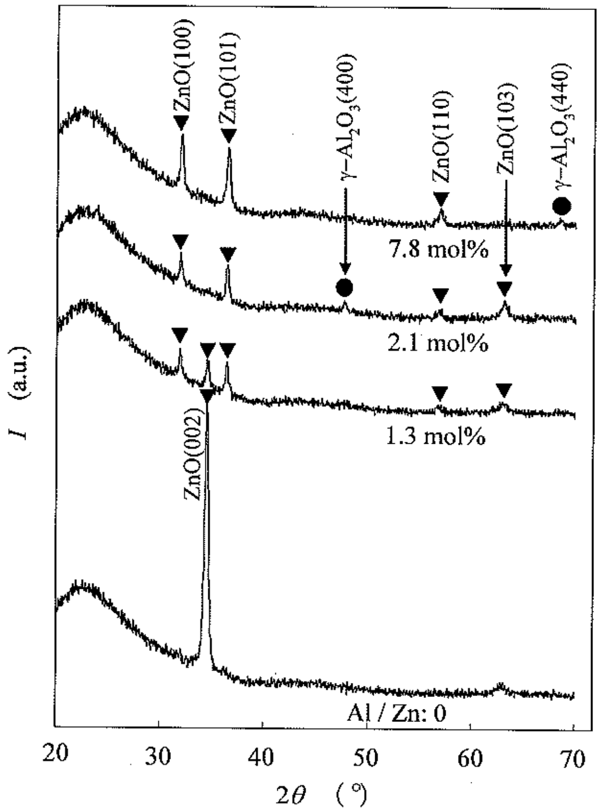


Fig.11 Typical XRD profiles of ZnO and ZnO:Al films of 1.3, 2.1 and 7.8 mol% of Al/Zn composition ratio.

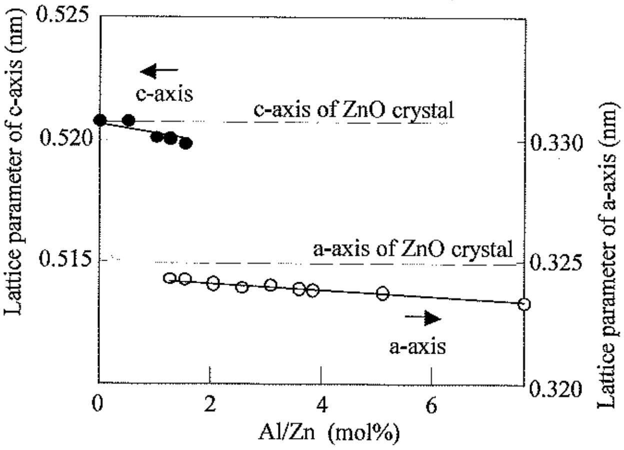


Fig.12 Lattice parameters of a and c of ZnO or ZnO:Al crystalline structure calculated from positions of the peaks of ZnO or ZnO:Al in Fig.11.

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