The effect of the working pressure on electro-optical properties of aluminium - doped zinc oxide thin film

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Abstract

Zinc oxide films have been actively investigated as transparent electrode materials for display. We report the effect of the working pressures on electro-optical properties of Al-doped ZnO thin films deposited by d.c. magnetron sputtering. The resistivity of the ZnO thin films was depended on atomic bombardment effect by working pressure.

1. Introduction

Transparent conducting oxide (TCO) possesses a wide range of applications in a variety of optoelectronic devices such as flat-panel displays or thin-film solar cells. Although ITO (indium tin oxide) is the most successful TCO, ITO film is high cost and hazardous material to human and environment and It has instable chemical stability property in a reduced ambient. Recently, ZnO (zinc oxide) films have been actively investigated as transparent electrode materials because ZnO is a nontoxic, inexpensive and abundant material. [1,2] In the last decade, ZnO films doped with impurities, such as B, Al, Ga, In and Zr, have been actively studied. [3]

In this study, Al-doped ZnO(ZnO:Al) thin films were deposited on corning glass #1737 substrates by d.c. magnetron sputtering at 150 ℃ using an ZnO-2wt % Al_2O_3 ceramic target. Ar gas was introduced near the substrate. The films were deposited in the working pressure from 1 mTorr to 10 mTorr. The resistivity was varied with working pressure. It was the lowest at the point of 1 mTorr. The most common model explaining effect of the pressure on resistivity property for the sputtering deposition techniques is the “atomic peening model” proposed by D’ Heurle in 1970. [4,5,6,7,8] In the “atomic peening model”, the high energy part of particles contributing to the film growth, is responsible for the compressive stress genesis. The particles with low energy induce a porous and vacancy structure, associated with a tensile stress. [7,8]

2. Experimental

ZnO:Al thin films were deposited on corning glass #1737 substrates by d.c. magnetron sputtering method at 150 ℃ using ZnO-2 wt% Al_2O_3 ceramic target. Argon was introduced near the substrate. The films were deposited in the working pressure from 1 mTorr to 10 mTorr. (**table 1**)

The structural properties of films were observed by x-ray diffractometer (RINT 2000, RIGAKU). The density of the films was estimated by simulating the measured x-ray reflectivity measurement (X'Pert PRO, PANalytical). The surface morphology of the films was investigated using field-emission scanning electron microscopy (JES 6340F, JEOL) and Atomic Force Microscopy (XE-100 system, PSIA).

Table 1. Deposition condition of ZnO:Al film

Sputtering variables	Deposition conditions
Target	2 wt% Al-doped ZnO
Substrate temperature	150 ℃
d.c. power density	0.49 W/cm^2
Target-substrate distance	4 cm
Bass pressure	2×10^{-6} Torr
Working pressure	5×10^{-3} Torr
Substrate rotating	5 rpm
Sputtering gas	Ar gas
Energy gap	3.4 (direct)

The resistivity and Hall coefficient were measured using the Van der Pauw method. The hall coefficient was used for calculating the carrier concentration and mobility.

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[1] If necessary, you may place some address information in a footnote, or in a named section at the end of your paper.

The transmittance of the films was measured with UV-vis-nir spectrometer (UV-3101PC / Kinetics, Shimadzu) in the range of 250–2500 nm. A bare quartz glass plate was used as the reference material. The measured transmittance at 550 nm was higher than 90% for films produced with all the deposition conditions used in this work.

3. Results

3.1 Structural Property

The crystallinity of the samples was characterized by X-ray diffractometry. The surface roughness of thin films was analyzed by AFM and FE-SEM. With increasing working pressure, we observed high roughness property of films.

GIXR(grazing incidence X-ray reflectivity) method was used to investigate the variation of the density. X-ray reflectivity technique is a relatively simple, but powerful method for the determination of thin layer density, thickness and layer interface roughness. [9]

Figure 1 is diffuse reflectivity of ZnO:Al films with various working pressures. Density of films is determined by first peak angle of Yoneda wing. There is film desity list in **table 2**. [10,11]

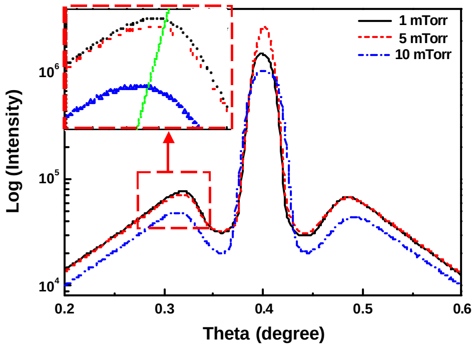

Figure 1. Diffuse reflectivity (Yonede wing) with various working pressures

Table 2. Density and roughness properties of AZO thin film deposited at the working pressure of 1, 5, 10 mTorr

Working Pressure	Density
1 mTorr	5.688 g/cm^3
5 mTorr	5.656 g/cm^3
10 mTorr	5.581 g/cm^3

3.2 Electrical Property

The resistivity was varied with working pressures. It was the lowest at the point of 1 mTorr. Electrical properties were measured by four-point probe (CMT-SR1000N, Changmin-Tech) and Hall measurement. With an increasing deposition pressure, we observed a large decrease in the carrier mobility. And we calculated mean free path of electrons in the films [12,13]

Table 3. Electrical properties of ZnO:Al films deposited at various working pressures

Working Pressure	Resistivity (Ωcm)	Measuring Equipment	Hall Mobility (cm^{2}V^{-1}s^{-1})	Carrier Density (cm^{-3})	Mean Free Path
1 mTorr	2.22×10^{-3} 1.97×10^{-3}	Hall measurement 4-point probe	13.4	2.10×10^{20}	0.0162 nm
5 mTorr	3.27×10^{-3} 2.37×10^{-3}	Hall measurement 4-point probe	9.56	2.00×10^{20}	0.0114 nm
10 mTorr	6.34×10^{-3} 5.92×10^{-3}	Hall measurement 4-point probe	6.01	1.64×10^{20}	0.0067 nm

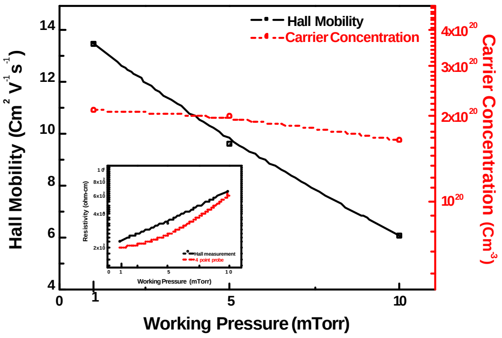

Figure 2. Electrical properties of ZnO:Al films varied with working pressures: Hall mobility and carrier concentration and resistivity

3.3 Optical Property

Optical properties were measured by UV-vis-nir spectrometer. Transmittance of 100 nm-AZO films is over 90 %. And optical bandgap calculated using transmittance is showed in **figure 3** and **table 4**. [14,15]

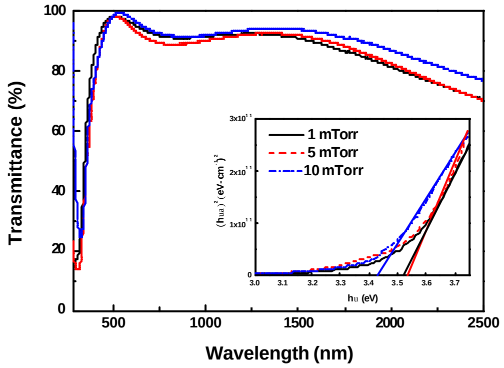

Figure 3. Transmittance spectra and optical bandgap of ZnO:Al films deposited at different working pressures

Table 4. Optical bandgap of ZnO:Al films deposited at different working pressures

Working Pressure	Band Gap
1 mTorr	3.53 eV
5 mTorr	3.53 eV
10 mTorr	3.43 eV

4. Discussion

The film density was varied with working pressures and it was the highest at the pressure of 1 mTorr. It was explained by atomic bombardment effect.

At high pressure the particle scattering increases oblique angle and low energy component of film bombardment so that atomic peening is minimized. Thus, the appearance of shadowing effects leading to intergranular voids within the growing layer and films deposited at high pressures are tensile. At low pressure the mean free paths of the particles are longer, and under these conditions it is likely Ar contribute to film bombardment. Due to few collisions occurring within the plasma, incident angles tend to be close to normal and bombarding energy tends to be high. And the deposited films have a high adatom mobility and density properties. Thus the film has high orientation property and compressive film stress. [4,5]

The resistivity was the lowest at the point of 1 mTorr. Hall effect measurement analysis was done to understand the variation of the resistivity. It was found that carrier mobility is a dominant factor for controlling the resistivity more than the carrier concentration.

It was found experimentally that an ZnO:Al film having both maximum conductivity and carrier mobility has highest density of various films. ZnO:Al films with lowest density, the mean free paths were smallest. It is suggested that electron scattering at pores and voids within the grain is the major obstacle for electron conduction in the ZnO:Al films having a lower density.

5. Conclusions

Working pressure was found to have a major influence on the electo-optical and structural properties of the ZnO:Al films. We found that working pressure affects to film density and the film density is related with electo-optical properties.

The film density was varied with working pressures and it was the highest at the pressure of 1 mTorr. It was explained by atomic bombardment effect. X-ray reflectivity method was used to investigate the variation of the density. The resistivity was the lowest at the point of 1 mTorr. Hall effect measurement analysis was done to understand the variation of the resistivity. It was found that carrier mobility is a dominant factor for controlling the resistivity more than the carrier concentration.

6. Acknowledgements

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