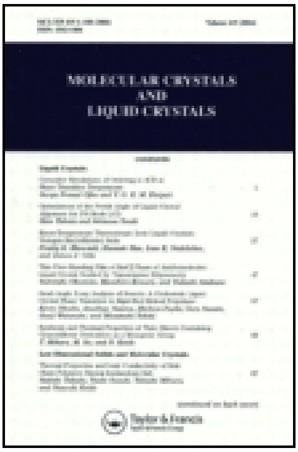

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Effect of Post Annealing in Various Atmospheric Environment Applied to ZnO:Ga Films

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In this study, transparent conductive films (TCO) of ZnO:Ga (GZO) were deposited by facing target sputtering to explore the effect of post-annealing on the structural, electrical and optical properties of the films. As deposited films have been annealed to each different temperature condition in various atmosphere environments (air, N_2, Vacuum N_2). In the result, in air atmosphere condition, ZnO:Ga films have lost their characteristics as TCO films, because rapid oxidation occurred over 300°C. But in other atmosphere condition, contacting with oxygen is reduced more, as rapid rise of resistivity has been prevented.

Keywords ZnO; ZnO: Ga; Solar Cell; OLED; Vacuum Heat treatment; Oxidation

Introduction

Transparent conducting oxide (TCO) thin films which used in substrate materials by their good combination of electrical conductivity at ambient temperature and optical transparency in a visible region have been widely applied for in a variety of optoelectronic devices, such as solar cells, flat panel displays, etc. [1,2] Among the possible materials, zinc oxide (ZnO) is a promising candidate as an alternative material on account of its non-toxicity, low cost, abundance and many applications. The zinc oxide (ZnO) is an n-type wide bandgap (3.3 eV) transparent conducting oxide (TCO). Due to their special properties, ZnO thin films have been extensively studied in the last years. Among other main applications we have; optical devices [3], piezoelectric sensors [4], superficial acoustic waves [5], gas sensors [6], and transparent electrodes [7,8], etc.

Although ZnO in thin film electrode can be expected from a wide variety of application, it is hard to apply practical application because problems occur in some case of manufacturing process. One of them, in a range of temperature (about 300∼800°C), ZnO:Ga had lost their electrical properties by rapid oxidation[9]. Rapid oxidation increase content of oxygen in wurtzite structure and decrease oxygen vacancy. For that reason, it is necessary to watch the change of electrical properties by temperature and various atmospheric environments. A vacuum furnace is used to carry out processes such as brazing, sintering and vacuum

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heat treatment of materials such metals [10], oxides [11] and carbon materials [12], at high temperatures and with high consistency and low contamination. Heating some materials to high temperatures normally causes rapid oxidation, which is undesirable. Vacuum heat treatment removes the oxygen and prevents this from happening.

In this study, transparent conductive films (TCO) of ZnO:Ga (GZO) were deposited by facing target sputtering to explore the effect of post-annealing on the structural, electrical and optical properties of the films. A deposited films have been annealed each different temperature condition and various atmosphere environments (air, N_2, Vacuum N_2).

Experimental

Preparation of ZnO:Ga TCO Films

The ZnO:Ga thin films were prepared on a glass substrate by the facing targets sputtering (FTS) method at room temperature. Figure 1 is an instrument of the FTS method used in the deposition process. The FTS method was designed to array two targets facing each other and to form high density plasma between the targets. The FTS method enable us to reduce the bombardment of the substrate by high-energy particles because the substrate's position was located apart from the plasma. Thus, the FTS system can suppress substrate damage caused by high-energy particles, such as electrons and partial ions [13–16]. The glass substrate was ultrasonically cleaned by using isopropyl alcohol (IPA) and DI-water. Then glass substrate was dried with N_2 gas. The chamber was evacuated to 1.0×10^{-4} Pa before the film deposition began with the pressure maintained at 0.13 Pa throughout the process. Before the deposition, the ZnO:Ga (ZnO:Ga = 97:3 wt.%, 2 inch) targets were pre-sputtered in pure Argon atmosphere for 20 min to remove the natural surface oxide layer of the targets. The thickness of the grown ZnO:Ga films was 300 nm. Deposited film's thermogravimetric Properties have been analyzed by DSC-TGA(Differential Scanning Calorimeter-Thermogravimetric Analyzer).

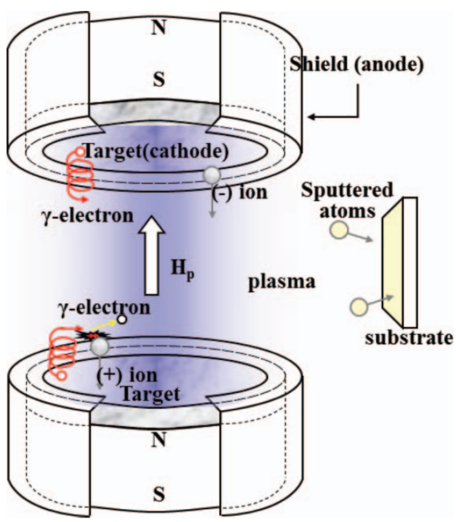

Figure 1. Schematic illustration of the FTS method used in the deposition process.

Table 1. Sputtering conditions of ZnO:Ga thin films

Deposition parameters	Conditions
Targets	ZnO:Ga(Ga_2O_3:3%/ZnO:97%)
Substrate	Glass (Marienfield)
$D_{T\text{-}T}$	50 mm
$D_{T\text{-}S}$	50 mm
Base Pressure	2.0×10^{-6} torr
Working Pressure	1 mtorr
Substrate Temperature	R.T
Input DC Power	65 W
Thickness	300 nm

Post Annealing Progress

Three sets of samples have been deposited and annealed at each different temperature condition and various atmosphere environments (air, N_2, Vacuum N_2) as shown in Tables 1 and 2. Normal atmosphere furnace was normal air atmosphere condition before starting inflow of N_2 gas. Vacuum atmosphere furnace has been evacuated to 1.33 Pa before starting inflow of N_2 gas.

Measurements

The electrical properties of the film were measured by Hall Effect measurement system. The optical and the structural properties were measured by UV-VIS spectrometer, Scanning electron microscope and X-ray diffractometer.

Results and Discussion

Thermogravimetric Properties

Thermal conductivity (κ), a kinetic property determined by the contributions from the vibrational, rotational, and electronic degree of freedom, is an extremely important material property when high-power/high-temperature electronic and optoelectronic devices are considered. For pure crystal, inclusion of lattice distortions and increase of reactivity have been caused by increase of phonon-phonon scattering which is proportional to thermal conductivity. The lattice contribution(phonon scattering) to the thermal conductivity κ is

Table 2. Post Annealing condition

	Normal	N_2	N_2 (Rough vacuum)
Atmosphere	Air	N_2 atmosphere	N_2 atmosphere
Base pressure	101,325 Pa	101,325 Pa	1.33 Pa
N_2 GAS inflow	None	1 slm	0.1 slm
Temperature	150°C, 300°C, 450°C	150°C, 450°C	150°C, 450°C

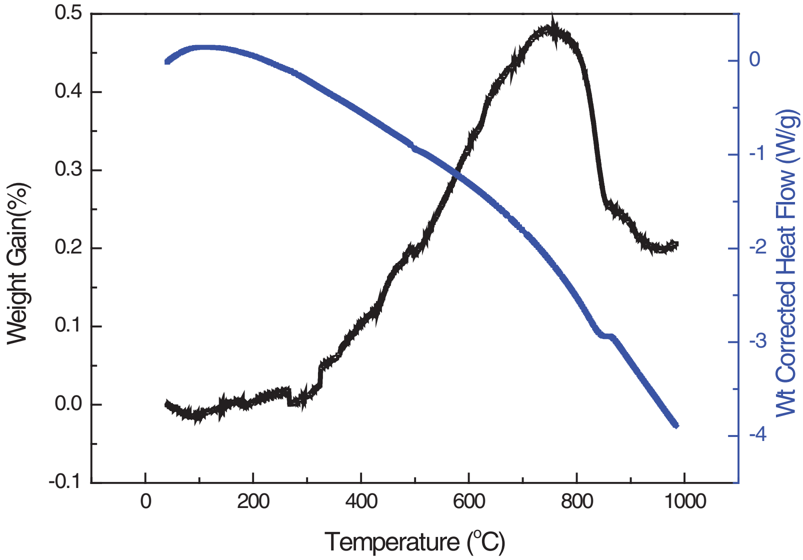

Figure 2. DSC-TGA curves for the mixture of ZnO:Ga.

obtained from the kinetic theory as [17]

$$\kappa_{lattice}(T) = \frac{1}{3}\upsilon_s C_{lattice}(T)L(T)$$

where T is temperature, υ_s is the velocity of sound (almost independent of temperature), $C_{lattice}$*(T)* is the lattices specific heat, and *L(T)* is the phonon mean free path. In almost all materials, κ(T) first increases with temperature, reaches a maximum (κ_{max}) at some characteristic temperature T_{ch}, and then decreases. Figure 2 shows thermo gravimetric Properties of ZnO:Ga film. In a range of temperature (about 300∼800°C), mass of ZnO:Ga and slope of collected heat flow was increased gradually. Therefore, these results mean increase of thermal conductivity of ZnO:Ga films. Generally, inclusive of lattice distortions and increase of reactivity which exposed air condition caused rapid oxidation.

Structural Properties

Figure 3 shows the XRD spectrum for ZnO:Ga films annealed by different atmospheric environment. In terms of its crystalline property, as contacting with oxygen was increased, intensity of crystalline has been improved. This could be attributed to the increase in crystallite size and thus improved crystallinity of the ZnO:Ga films [18,19]. Figure 4 showed the SEM morphologies of the ZnO:Ga films annealed at 450°C with various atmospheric environment. Increase in the surface roughness of ZnO annealed at 450°C with normal air atmospheric environment suggests an enhancement in the grain size. This could be because at higher temperatures the atoms have enough activation energy to occupy the proper sites in the crystal lattice, and grains with lower surface energy become larger [20].

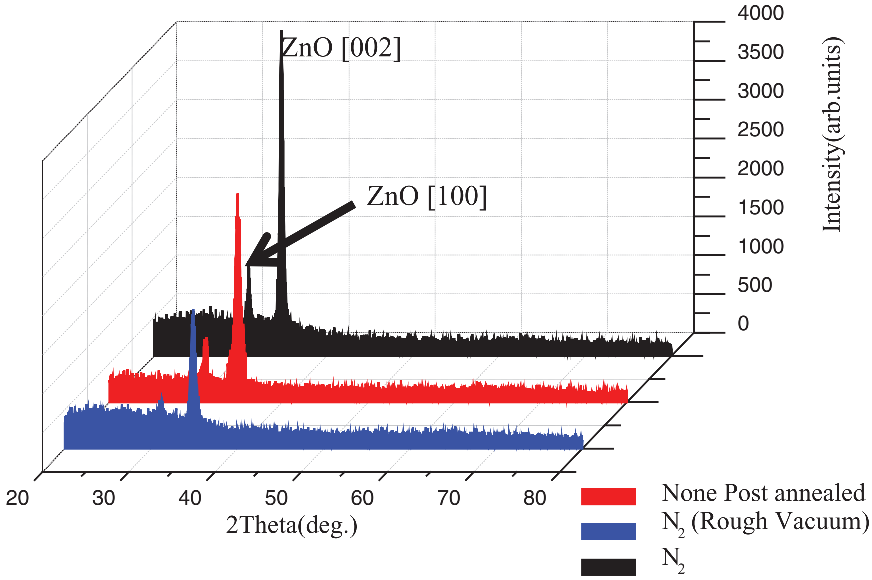

Figure 3. XRD spectrum for ZnO:Ga films annealed by different atmospheric environment.

Electrical Properties

Figures 5, 6 and 7 shows electrical properties of samples. Exposed air condition sample's resistivity was 34.7 MΩ·cm, normal N_2 gas atmosphere condition was 13.64 Ω·cm and vacuum N_2 gas atmosphere condition show lowest resistivitiy 2.9×10^{-3} Ω·cm. And, exposed air condition sample's carrier concentration was 1.142×10^{20} cm^{-3}, normal N_2 gas atmosphere condition was 2.923×10^{20} cm^{-3} and vacuum N_2 gas atmosphere condition show highest carrier concentration 6.231×10^{20} cm^{-3}. Therefore, electrical properties are proportional to exposure on oxygen in annealing process. The absorbed oxygen may have reduced the number of vacancies in the film and thus result in a decrease of free carriers, since the electrical conduction of these oxides depends on oxygen vacancies. Crystallinity of thin film is related to hall mobility. The decrease of hall mobility with higher temperature was due to the decrease of oxygen vacancies with increase crystallinity of ZnO:Ga [21].

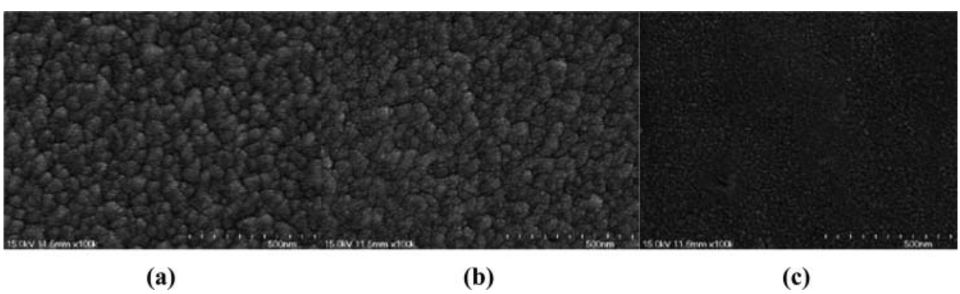

Figure 4. SEM morphologies of the ZnO:Ga films annealed at 450°C with various atmospheric environment. (a) Air, (b) None post-annealed, (c) N_2 (Rough Vacuum).

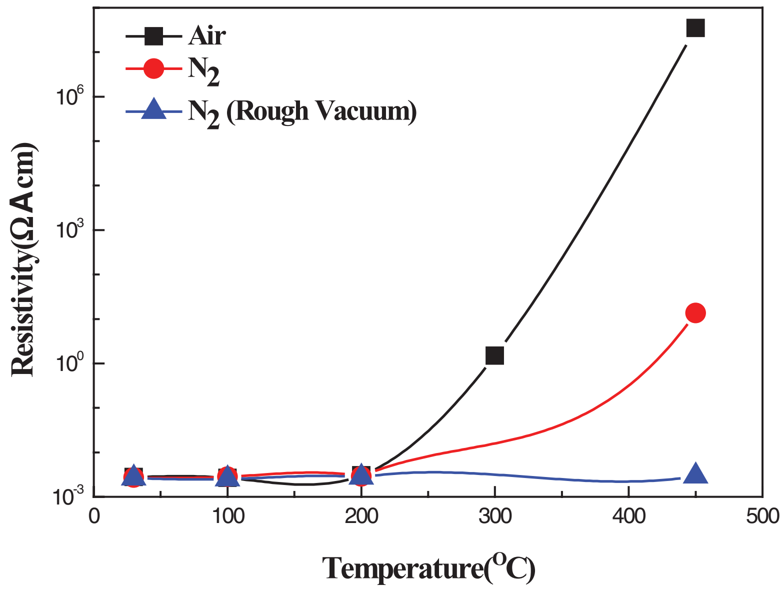

Figure 5. Resistivity of post-annealed ZnO:Ga films in various atmosphere and temperature.

Optical Properties

Figure 8 shows the transmittance as a function of wavelength in the visible range annealed by different atmospheric environment. Average transmittance of these samples in the range 350–800 nm was over 80%. When exposure to oxygen was increased, transmittance curve

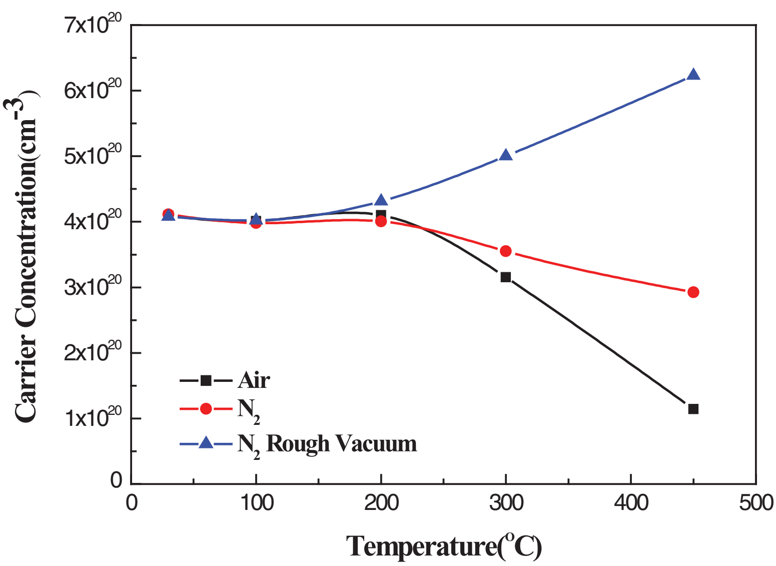

Figure 6. Carrier concentration of post-annealed ZnO:Ga films in various atmosphere and temperature.

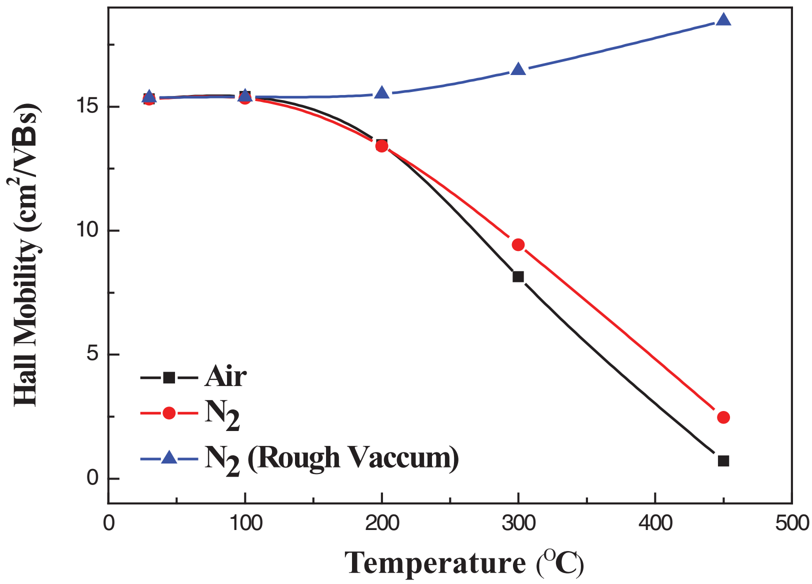

Figure 7. Hall mobility of post-annealed ZnO:Ga films in various atmosphere and temperature.

shift which is due to the carrier concentration effect (Moss-Burstein Effect) has been occurred. It is known that ZnO:Ga film with larger electron carrier concentration above 10^{20} cm^{-3} is degenerated and the Fermi energy penetrates into the conduction band with the increase of carrier concentration [21, 22].

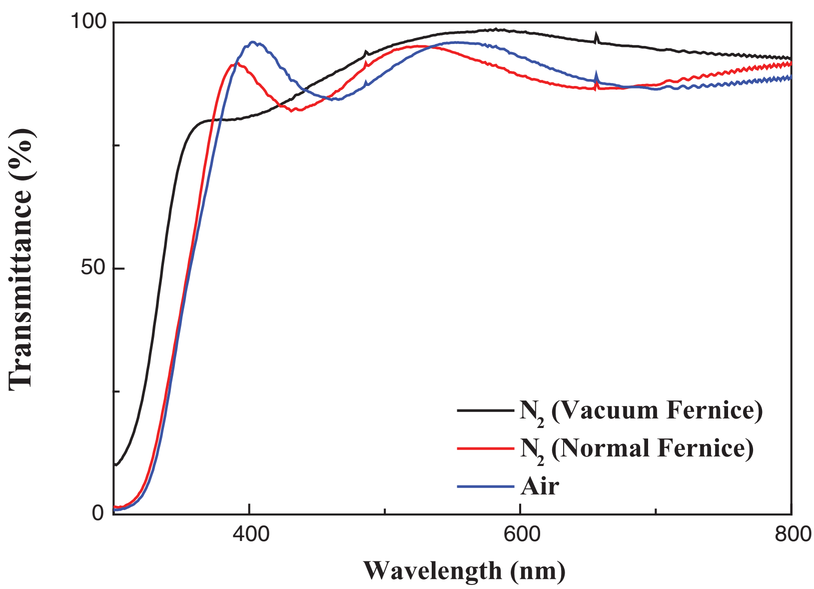

Figure 8. Dependence of the transmittance of ZnO:Ga thin films annealed at different atmosphere enviroments.

Conclusions

In a range of temperature (about 300∼800°C), increased ZnO:Ga films thermal conductivity caused rapid oxidation in exposed environment by oxygen. As deposited films have been annealed each different temperature condition and various atmosphere environments to observe the transition of ZnO:Ga films properties and increase of resistivity was proportional to exposure on oxygen in annealing process. Thus, Vacuum heat treatment using inert gases atmosphere removes the oxygen and prevents from depletion of electronic properties in high temperature.

Acknowledgment

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