

Deposition of ZnO thin films by MOCVD using ultrasonic nebulization

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ZnO thin films were deposited on the soda lime glass substrates at the low substrate temperatures of 225~325 °C by the MOCVD using ultrasonic nebulization and their deposition characteristics were investigated. Zinc acetylacetonate, which is not appropriate to the source material in normal CVD because of high melting point, was used as a precursor for Zn source. Deposition rate was controlled by the surface reaction rate up to 275 °C and decreased at the deposition temperatures over 275 °C due to the homogeneous reaction of source gas in the gas phase. All the films deposited were crystalline and (002) preferred orientation of the films increased with the deposition temperature. Resistivity of the films was highly dependent on the deposition temperature and $1.0 \times 10^0 \sim 2.2 \times 10^3 \Omega \cdot \text{cm}$. The average transmittance of films in the visible range was over 90% and the optical band gap of the films was 3.28 regardless of deposition temperature.

Key words: ZnO, Thin films, MOCVD.

Introduction

ZnO, which has hexagonal wurtzite structure, is a piezoelectric material and a wide band gap semiconductor. Thin films of pure or doped ZnO are used in SAW filter, transparent electrode, and transparent transistor [1-6]. Usually, ZnO thin films are made by sputtering [7] and there are some reports on the deposition by ALD [8] or PLD [9]. However, there are few reports on the deposition of ZnO thin films by CVD which has many advantages such as high deposition rate, uniform deposition in large area, high step coverage and so on. This seems to be due to the rarity of zinc compound applicable to CVD source. The required properties for CVD source are proper vapor pressure at the low temperatures, thermal stability at the vaporizing temperature and adequate difference between vaporizing temperature and decomposition temperature and so on. Although Zn alkyl compounds such as dimethylzinc and diethylzinc satisfy these requirements, they are too reactive to treat and very expensive.

In this work, ZnO thin films were deposited on soda lime glass substrates at the low substrate temperatures of 225 ~ 300 °C by MOCVD using ultrasonic nebulization and their deposition characteristics were investigated. As a precursor for Zn source zinc acetylacetonate, which is not appropriate to the source material in the usual CVD, was used.

Experimental

ZnO thin films were fabricated by MOCVD using ultrasonic spraying technique in carrying source materials. Details of this process have been described in our previous paper [10]. Fig. 1 shows a schematic diagram of the MOCVD system used in this research. The reactor was made of quartz glass and takes the T-shape. The substrate was attached to the substrate holder located on the upper side of the reactor in an upside-down posture. The glass substrate was heated by contacting a silicon wafer heated by infrared radiation of halogen lamps and the substrate temperature was controlled by K-type thermocouple located on the substrate surface and a precise control unit. The carrier gas containing the mist of source solution flows upwards to the substrate surface from the glass nozzle of Φ 15 mm inner diameter.

The source solutions were made by dissolving zinc acetylacetonate [$\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$] in the mixture solvent of 70 vol% normal butanol and 30 vol% butyl acetate. 3 cm $\times$ 3 cm soda lime glass (L.C.D TEC) of 0.7 mm thickness was used as the substrates for ZnO thin films after the cleaning by ultrasonic cleaner. All the depositions were carried out at the atmospheric pressure. The deposition conditions are summarized in Table 1.

The crystallographic properties of the films were examined using X-ray diffraction. The instrument used is MPD for thin film and the measurement was carried out by θ -2 θ mode with Cu K α radiation. The morphology of surface and fractured cross section of the films was examined by FE-SEM (Hitachi, S-4800). Electrical resistivity of the films was measured by four point probe method. The optical transmittances were measured using spectrophotometer (Varian Inc, Cary500) in the range of 200-800 nm.

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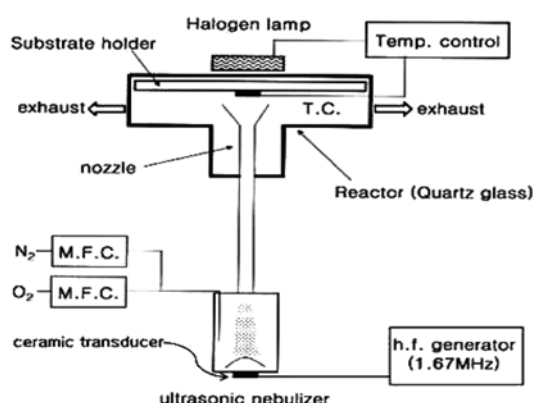


Fig. 1. Schematic diagram of MOCVD apparatus used in this experiment.

Table 1. Deposition conditions of ZnO thin films.

Concentration of source solution	0.6 mol/l
Deposition time	30 ~ 60 minutes
Substrate temperature	225 ~ 325 °C
N ₂ gas flow rate	5 l/min
O ₂ gas flow rate	2 l/min
Carrying rate of misted source solution	0.5 cc/min

Results and discussion

In the MOCVD using ultrasonic nebulization, the mist of source solution was transported to the heated substrate by carrier gas and near the substrate minute particles of source precursor which were formed by evaporation of solvent, and then the vaporized precursor makes the thin film by general CVD process. In this process, various forms of thin films are made depending on the substrate temperature and the thermal properties of source precursor. If the droplets of source solution are directly attached to the heated substrate, uneven and spotted thin film is formed due to the splashing of droplets. And if the precursor does not vaporize, thin films are not formed. If the temperature is too high, the deposition rate is decreased owing to the depletion of source precursor gas by homogeneous reaction in the gas phase. Zinc acetylacetonate, used as the Zn source precursor in this research, has the melting point of 134 °C and sublimate.

Fig. 2 shows the Arrhenius plot of the deposition rate of ZnO thin films. Thin film was not deposited at the substrate temperatures below 225 °C, and in the range of 225 ~ 275 °C the deposition rate increased rapidly with increasing the substrate temperature. On the contrary, the deposition rate decreased at over 275 °C. From this result it is thought that the precipitated particles of zinc acetylacetonate vaporize sufficiently for conventional CVD process at over 225 °C. In a CVD process the deposition rate is controlled by surface reaction rate at

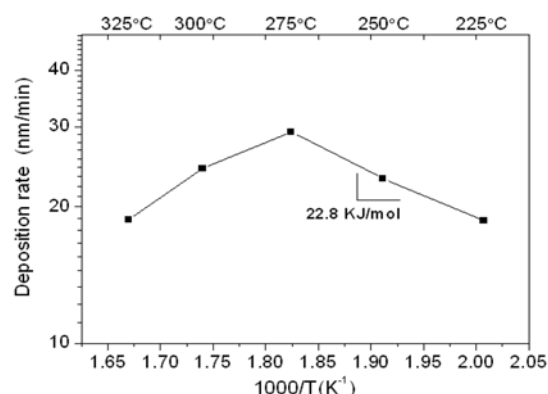


Fig. 2. Deposition rate of ZnO thin films as a function of substrate temperature.

the lower temperature region and controlled by mass transfer rate of reactant gas at the higher temperature region. So the deposition rate of ZnO films was controlled by surface reaction rate at the temperatures of 225 ~ 275 °C and the apparent activation energy of the surface reaction, which is calculated from the slope of plot, is about 22.8 kJ/mol. At over 275 °C the deposition rate was decreased, which seems to be due to the consumption of zinc acetylacetonate gas in the gas flow by the homogeneous reaction in the gas phase.

Fig. 3 shows the XRD patterns of ZnO thin films deposited at various substrate temperatures. Even at the low deposition temperature of 225 °C the films were crystallized. In the case of the films deposited at the low temperatures the relative peak intensity of each crystal plane was similar to that of ZnO powder, which means that each crystallite constructing the film grew with random orientation. However the relative intensity of (002) peak increased largely with increasing the deposition temperature. This means that the relative quantity of crystallite which grew with the [001] preferred orientation perpendicular to the substrate surface increased as the deposition temperature increased. In ZnO crystal which has the hexagonal wurtzite structure, (002) plane is the densest-packed plane and has the lowest surface energy. So the Zn, O or ZnO molecule created by surface reaction stick to (002) plane preferentially. If the surface mobility of adatoms is low owing to the

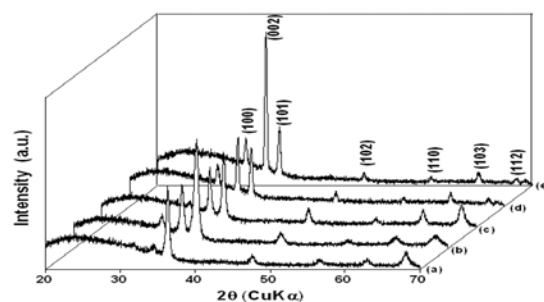


Fig. 3. X-ray diffraction patterns of the ZnO thin films deposited at (a) 225 °C, (b) 250 °C, (c) 275 °C, (d) 300 °C, and (e) 325 °C.

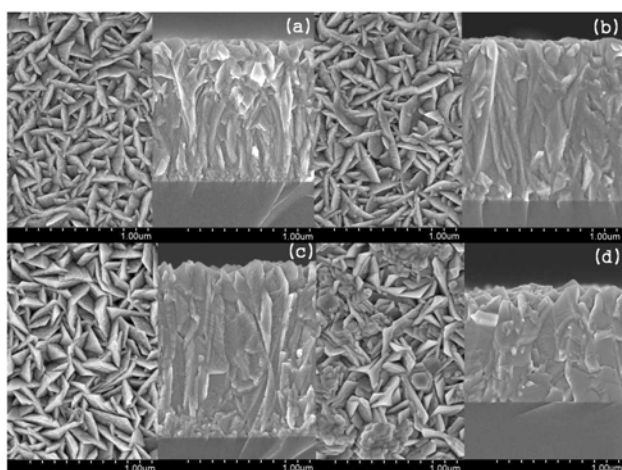


Fig. 4. FE-SEM micrographs of the surface and fractured cross-section of the ZnO thin films deposited at (a) 225 °C, (b) 250 °C, (c) 275 °C, and (d) 300 °C.

low substrate temperature, the adatoms stick to the plane adsorbed. However, if the surface mobility is high, the adatoms move and stick to (002) plane. So the growth rate of the crystallites which have [001] direction normal to the substrate surface is faster than that of the other crystallites. As a result only the crystallites in which [001] orientation coincides with the normal to the substrate surface survive and the others are hidden underneath the former.

Fig. 4 shows the FE-SEM micrographs of the surface and fractured cross section of the ZnO thin films deposited at various temperatures. In all the films, the interface between film and substrate is sharp and clear, which means that there was no reaction between ZnO film and glass substrate during the deposition at the deposition temperature used in this experiment. The surface of films is faceted and rough. The size of facets increased with increasing the deposition temperature and the films became more porous and rough at the higher temperatures.

Fig. 5 shows the variation of resistivity of ZnO films with deposition temperature. The film deposited at 225 °C has a high resistivity of $2.2 \times 10^3 \Omega \cdot \text{cm}$ and at the deposition temperature of 250 °C the resistivity of film decreased abruptly to $1 \Omega \cdot \text{cm}$ and then the resistivity increased gradually with increasing the deposition temperature. The resistivity of single crystals of ZnO without any addition is $7\text{--}30 \Omega \cdot \text{cm}$ at room temperature. Pure ZnO is an n-type semiconductor and the donor centers are supplied by the interstitial zinc atoms. ZnO has the nonstoichiometry of Zn excess in normal environment and the amount of excess Zn increases with the temperature at a constant oxygen partial pressure. So the density of charge carrier (free electron) increases with increasing the deposition temperature. In polycrystalline thin films, the mobility of charge carrier is largely dependent on the microstructure of films such as grain

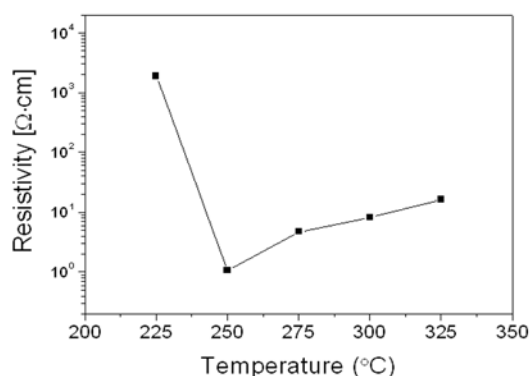


Fig. 5. Variation of resistivity of the ZnO thin films with the deposition temperature.

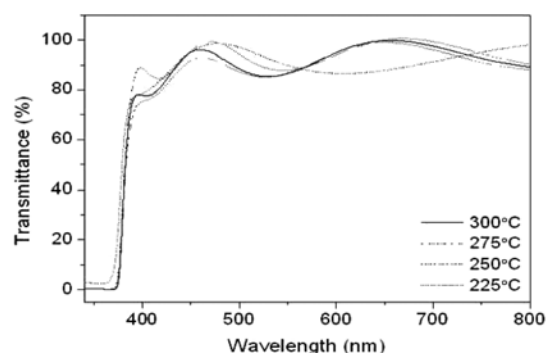


Fig. 6. Optical transmittance of the ZnO thin films deposited at various substrate temperature.

size, porosity and surface roughness. As shown in Fig. 4, as the deposition temperature was increased, the film became more porous and rough. So the mobility of charge carrier will be decreased as the deposition temperature is increased. It is thought that the abrupt decrease of resistivity at 250 °C is due to the increase of charge carrier density and the gradual increase at over 250 °C is caused by the decrease of mobility.

Fig. 6 shows the optical transmittance spectra in the wavelength range of 300 ~ 800 nm of the ZnO films deposited at various temperatures. All the films were highly transparent in the visible range with sharp band

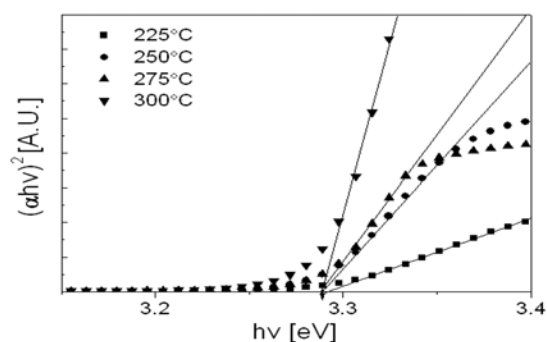


Fig. 7. Optical absorption plots of the ZnO thin films deposited at various substrate temperature.

edge absorption at the wavelength of 375 nm. The average transmittance of films in the visible range was over 90% in all the films. Optical band gap of the ZnO films was calculated using the Tauc's plot shown in Fig. 6. The band gap of ZnO films was 3.28 eV regardless of the deposition temperature. And whereas the absorption edge of the ZnO film deposited at 300 °C was sharp and clear, that of ZnO films deposited at the lower temperatures was broadened more and more as the deposition temperature is lowered. This seems to be due the lack of crystallinity of the films deposited at the lower temperatures.

Conclusion

ZnO thin films could be deposited on soda lime glass substrates at the low substrate temperatures of 225~300 °C by MOCVD using ultrasonic nebulization, using zinc acetylacetonate as the Zn source precursor. Deposition rate was controlled by the surface reaction rate up to 275 °C and decreased at the deposition temperatures over 275 °C due to the homogeneous reaction of source gas in the gas phase. All the films deposited were crystalline and (002) preferred orientation of the films increased with the deposition temperature. Resistivity of the films

was highly dependent on the deposition temperature and $1.0 \times 10 \sim 2.2 \times 10^3 \Omega \cdot \text{cm}$. The average transmittance of films in the visible range was over 90% in all the films and the optical band gap of the films was 3.28.

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