Film Formation and Characterization of ZnO Thin Film Grown by Mist Chemical Vapor Deposition with Different Temperatures

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Abstract - *This paper shows the experimental results of film formation and characterisation of ZnO thin films on m-plane sapphire substrates by mist-CVD (chemical vapor deposition). The ZnO thin films were deposited at different substrate temperatures. The surface morphologies of ZnO thin films were characterized by using scanning electron microscope (SEM). X-ray diffraction (XRD) was used to analyze the crystallinity of ZnO. The optical properties were measured through photoluminescence (PL) by He-Cd laser. To measure the thickness the stylus profiler was used. There is single peak of m-plane ZnO by XRD measurement at the best condition of the substrate temperature at 600°C. Results of this experiment can be used to improve the growth of ZnO thin films by mist-CVD.*

Keywords: Thin film, Mist-CVD, Characterization, Temperature effect, Surface morphologies

1. INTRODUCTION

Oxide semiconductors are the ideal from the viewpoint of materials safety and environmental friendly since they are free from toxic elements such as arsenic or phosphorus. The existing growth technologies for oxide semiconductor thin films, however, are not always friendly to the environment due to, for example, a large amount of electric power consumption and wastes of hazardous materials [1].

ZnO material, which is with excellent electrical properties, is cheap and non-toxic. ZnO is applied as an n-type semiconductor because of its wide band gap 3.3 eV, large exciton binding energy 60 meV, and high mobility. Its electrical conductivity is mainly due to oxygen vacancies or interstitial zinc. Zinc oxide films exhibit a combination of interesting piezoelectric, electrical, optical and thermal properties, and are applied in the fabrication of a number of devices, including gas sensors, transparent electrodes in solar cells, light-emitting diodes [2], and thin film transistors (TFTs) [3].

In recent years, various techniques have been used to deposit ZnO films, such as pulsed laser deposition, RF magnetron sputtering, chemical vapor deposition, atomic layer deposition and sol–gel processes. Among the preparation techniques of ZnO films, the sol–gel process has become increasingly popular in recent years, because it has advantage of being an inexpensive, non-vacuum, and easy to operate process. Various sol–gel processes involve spin coating and dip coating. The weaknesses of spin coating and dip coating include non-uniformity and wrinkles resulting from spin speed imbalance or the viscosity of the solvent. Among chemical vapor deposition mist CVD method, previously named as mist deposition, is an environmental friendly technology for the deposition of thin oxide films. There are two methods to generate mist particles in mist-CVD system, the one generates from nozzle by pressure and the other by ultrasound. The difference resulting from these methods is the mist particles size where mist particles produced by pressure is larger than that by ultrasound with a factor of 10. As a result mist-CVD has the advantage of good uniformity [4-5].

The mist-CVD process uses solutions of constituent elements without a significant viscosity as the metal sources. The solutions are ultrasonically atomized, and produce mist particles. For the growth of thin films, mist particles are transferred to the reactor by a carrier gas and the mist particles are decomposed on the substrate by thermal energy. Then, the decomposed particles are oxidized to metal oxide. The advantages of this process are that it is inexpensive, a non-vacuum process and easy to operate. Therefore, the mist-CVD process offers the possibility of large-area deposition technique at a low cost [6-8].

We have fabricated, for the above purpose, the mist-CVD system for the deposition of ZnO-based materials and other oxide thin films. In this paper, we show the fundamental properties of ZnO thin films on sapphire substrates grown by the mist-CVD.

2. EXPERIMENTAL PROCEDURE

A mist-CVD process was used to form ZnO thin films. Figure 1 shows the Mist Chemical Vapor Deposition (Mist-CVD) System. Mist-CVD is composed of two zones, the mist making zone and the deposition zone. The first zone consists of the liquid source and ultrasonic vibrator. The generated mist is transferred to the second zone by carrier gas of nitrogen, where mist is pyrolyzed in a reactor.

Fig -1: Mist Chemical Vapor Deposition System

ZnO thin films were deposited using the mist-CVD process on an m-plane sapphire substrate. The zinc source was 0.1mol/L zinc chloride solution and the carrier gas of nitrogen at a flow rate of 8 L/min. The ultrasonic vibrator was operated at 2.4 MHz. The substrate temperature was varied in the range of 550°C - 650°C.

Table -1: Mist CVD conditions for ZnO thin film formation

Mist-CVD system	Lateral flow type
Substrate	Al_2O_3
Solution (zinc source)	$ZnCl_2$
Substrate temperature	550°C, 600°C and 650°C
Carrier gas	N_2
Flow rate of carrier gas	8 L/min
Operation time	30 mins

To analyze the thickness of the ZnO thin films, step profiler (KLA Tencor, Alpha–step D-600) was used. The surface morphologies of the films were examined by field emission scanning electron microscope (FE-SEM) (JEOL, JSM-7600F). The structures of films were analyzed by X-ray diffraction (XRD) (Rigaku). The optical properties of the films were measured using photoluminescence spectroscopy.

3. RESULTS AND DISCUSSION

There are three parts positions on substrate, which are front, center and back in mist flow direction. ZnO thin films grown by the mist-CVD exhibited various crystallographic orientations depending on the growth conditions. A general trend is that at lower temperatures or higher growth rates a ZnO film tended to have random orientation [9-10].

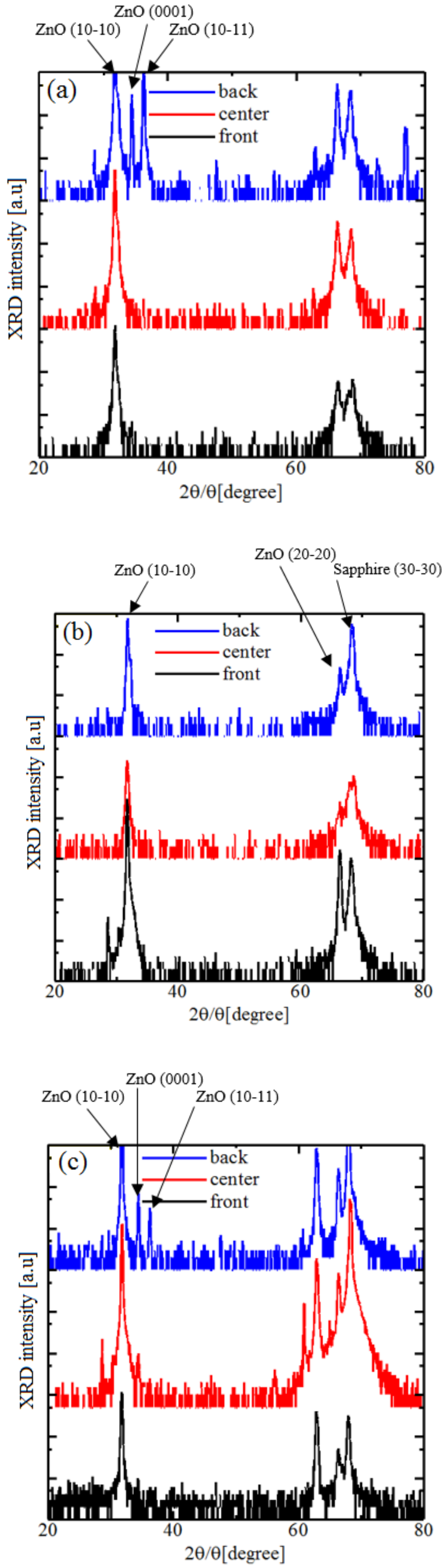

Fig -2: X-ray Diffraction Curves of the ZnO Samples Formed at Various Temperatures (a) at 550°C (b) at 600°C (c) at 650°C

Figure 2 shows results of X-ray θ-2θ curve of the samples grown of the three different substrate temperature at 550°C, 600°C and 650°C. Only m-plane peaks were observed at the position of front and center of 550°C and center and back of 600°C. These results shows that single orientation of m-plane ZnO was formed perpendicular to the substrate. In case of 650°C, not only m-plane but also other planes are observed. Figure 3 shows the SEM surface morphologies of the samples formed at three different temperatures. There are many grain boundaries on the sample grown at 650°C. The front part of the sample formed at 600°C has the smoothest surface comparing to other results.

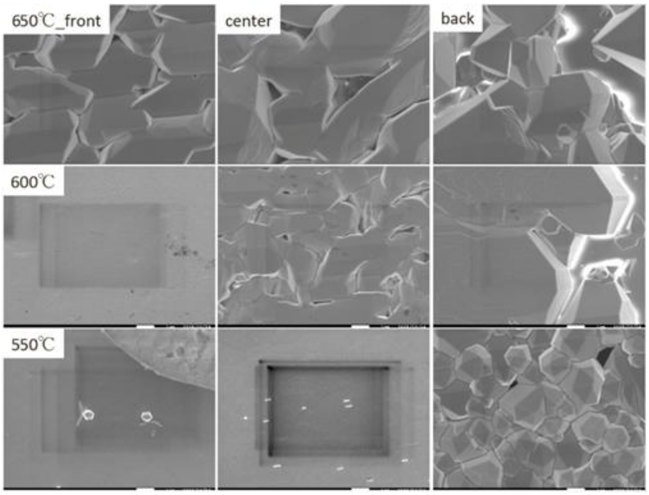

Fig -3: SEM Surface Morphologies of the Samples Formed at the Various Temperatures

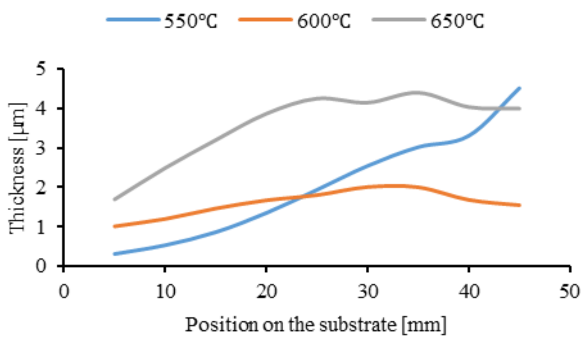

Fig -4: Thickness Distribution of A ZnO Samples Grown By Mist- CVD

The thickness distribution of a ZnO samples grown by the mist-CVD is shown in figure 4. Cold mist from mist making zone comes into the substrate surface, then the temperature of the mist increased with the location on the substrate. Therefore, thickness increases with the location because thermal reaction is enhanced by the mist temperature. Therefore, the film thickness can be controlled by the temperature. When the temperature was increased from 550°C to 650°C, deposition of the mist was increased.

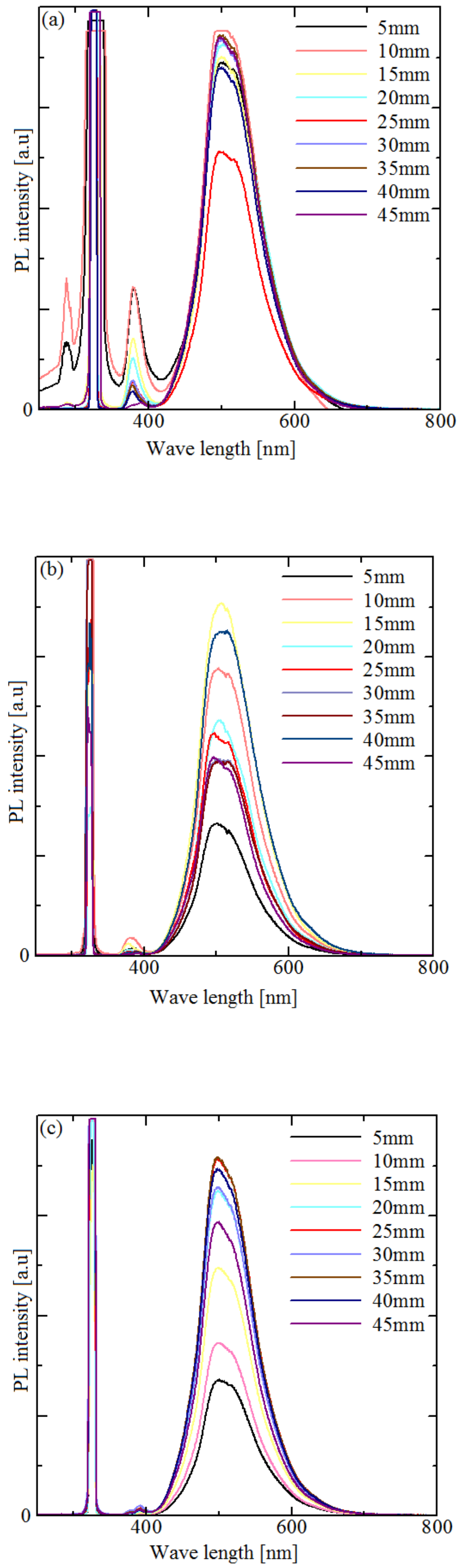

Fig -5: Measurements of Photoluminescence Spectroscopy
(a) at 550°C (b) at 600°C (c) at 650°C

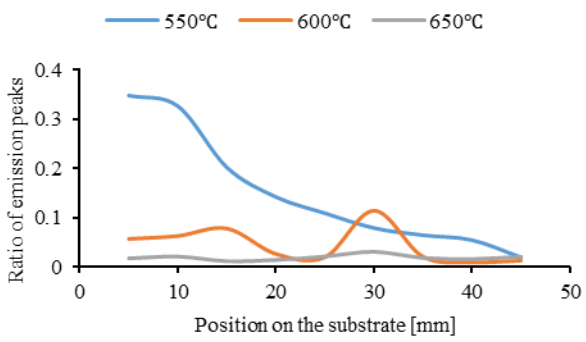

Fig -6: The Ratio of Emission Peaks of the Band Edges and the Defects

According to the measurements of the photo-luminescence spectroscopy, emissions at about 500 nm are strong in all samples, which is probably related to oxygen vacancy defect. By contrast the ratios of the band edge emission peaks (380 nm) and the defect emission peaks are the best at the substrate temperature 550°C as shown in figure 6. It was found that the more increasing in temperature, the less ratio of band edge emission peaks and defect emission peaks.

4. CONCLUSION

This paper discussed film formation and characterization of ZnO thin film formed by mist-CVD with the different temperatures. The experimental results of the substrate temperature at 600°C is better in crystallinity of ZnO thin film because the single peak of m-plane ZnO was found in XRD results. In addition, the surface morphology at this condition is smooth as discussed above. Thus, ZnO thin films were successfully deposited by fine-channel mist chemical vapor deposition at substrate temperature of 600°C with the flow rate of the nitrogen carrier gas of 8 L/min. The crystallinity of ZnO significantly depends on the temperature of mist-CVD system. In these experimental results, the defect emissions of all conditions are still strong and it will be the next problem of this research.

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