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Crystallinity Formation and Characterization Analysis of Zinc Oxide Thin Film Grown by Mist Chemical Vapor Deposition

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***Abstract*—**This paper shows the experimental results of the crystallinity of zinc oxide (ZnO) thin films on m-plane sapphire substrates by mist Chemical Vapor Deposition (mist-CVD). The ZnO thin films were deposited at different substrate temperatures with various flow rate of carrier gas. 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. There is single peak of m-plane ZnO by XRD measurement at the best condition of the substrate temperature at 600°C with the flow rate of carrier gas at 8 L/min. Results of this experiment can be used to improve the growth of ZnO thin films by mist-CVD and it will be very useful to the application of lighting emitting diodes and solar cells.

Keywords*—Characterization; Flow rate effect; Mist-CVD; Single peak; Surface morphologies; Temperature effect; Thin film formation.*

I. INTRODUCTION

Several materials are used in light emitting diodes (LEDs) for visible light. For example, white LEDs of gallium nitride/indium gallium nitride (GaN/InGaN) are widely used in backlight of display screens. However, Indium is very expansive and it is a rare earth material. LEDs fabrication will be more expansive year by years. Therefore, alternative low-cost materials should be developed. On the other hand, 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], [7], [8].

The mist-CVD system had been fabricated, for the above purpose, 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.

In the previous experiment, SEM surface morphologies of the samples which were formed at three different temperatures with the constant flow rate of carrier gas (8L/min) were observed. 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.

The results of X-ray θ-2θ curve of the samples which were grown of the three different substrate temperature at 550°C, 600°C and 650°C were discussed in previous work. 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 the case of 650°C, not only m-plane but also other planes are observed.

Although the optimum condition depended on temperature was observed in previous work, the various flow rate of carrier gas of nitrogen (N2) have to be observed.

II. EXPERIMENTAL PROCEDURE

A mist-CVD process was used to form ZnO thin films. Fig. 1 shows a schematic of the 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.

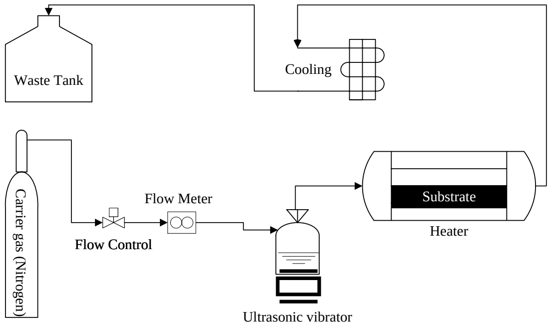


Fig. 1. Schematic Diagram of the Mist CVD System

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 was varied in the range of 6-10 L/min. The ultrasonic vibrator was operated at 2.4 MHz. The substrate temperature was varied in the range of 550°C - 650°C.

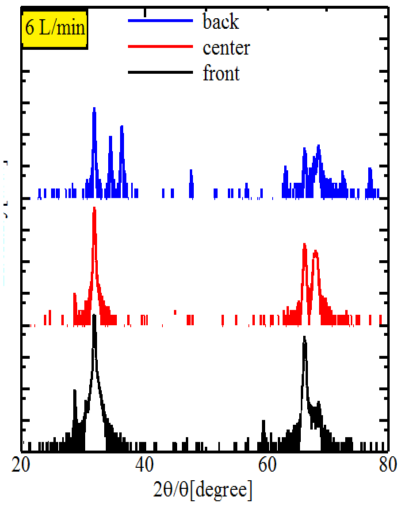
Table 1: Mist CVD Conditions For Zno Thin Film Formation

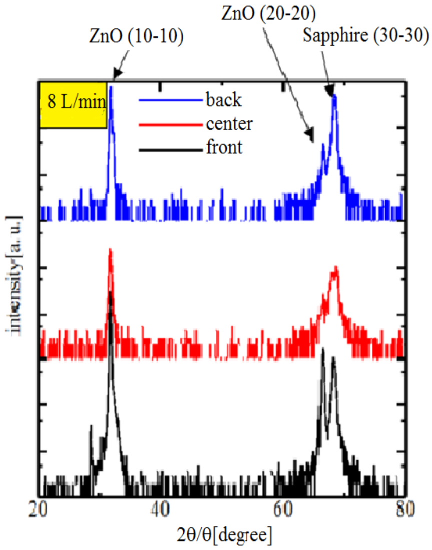
Mist-CVD system	Lateral flow type
Substrate	Al_2O_3
Solution (zinc source)	$ZnCl_2$
Substrate temperature	550°C, **600°C** and 650°C
Carrier gas	N_2
Flow rate of carrier gas	6L/min, **8L/min**, 10L/min
Operation time	30 mins

To analyze the surface morphologies of the films, field emission scanning electron microscope (FE-SEM) (JEOL, JSM-7600F) was used. The structures of films were analyzed by X-ray diffraction (XRD) (Rigaku). According to the results of XRD and SEM, the crystallinity of ZnO samples are discussed in details.

III. RESULTS AND DISCUSSIONS

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].





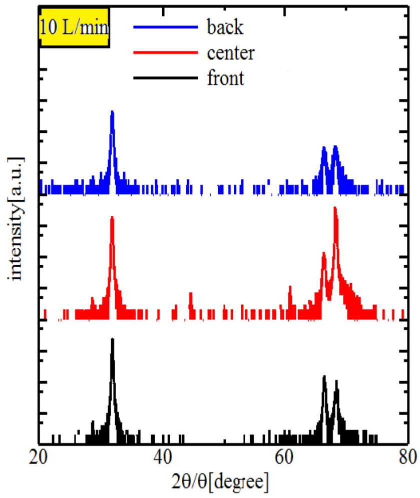


Fig. 2. X-ray diffraction curves of the ZnO samples formed at constant substrate temperature with various flow rates of carrier gas

Fig. 2 shows results of X-ray θ-2θ curve of the samples grown of the three different flow rates of carrier gas at 6L/min, 8L/min and 10L/min. Only m-plane peaks were observed at the position of front and back of 10 L/min and center and back of 8L/min. For the sample grown at the flow rate of carrier gas of 6L/min, not only m-plane but also other planes are observed.

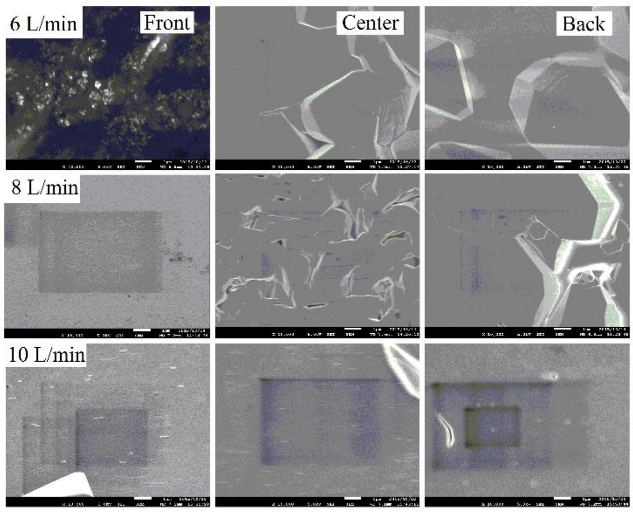


Fig. 3. SEM surface morphologies of the samples formed at the various flow rates of carrier gas with the constant temperature

Fig. 3 shows the SEM surface morphologies of the samples formed at three different flow rate of carrier gas with the constant temperature (600°C). There are many grain boundaries on the center and back parts of the sample grown at the flow rate of 6L/min and un-succeeded zinc oxide crystal on the front part of this sample. There are also many defects on all parts of the sample grown at the flow rate of 10L/min. The front part of the sample formed at 8L/min flow rate of nitrogen gas has the smoothest surface comparing to other results. Although there are many grain boundaries on the center and back parts of this sample, they are connected each other.

CONCLUSION

This paper discussed characterization of ZnO thin film formed by mist-CVD with the different substrate temperatures and various flow rate of carrier gas. The experimental results of the substrate temperature at 600°C and 8L/min 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 lateral flow type 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. Therefore, we can conclude that ZnO thin film is successfully formed by mist chemical vapor deposition method at atmospheric pressure.

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