
Film Formation and Characterization of Undoped ZnO on M-plane Sapphire by Mist Chemical Vapour Deposition (Mist-CVD) with Different Carrier Gas Flow Rates

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Abstract: ZnO thin films were deposited on sapphire substrate by mist chemical vapor deposition (mist-CVD) with different flow rate of carrier gas. This is a simple and low cost method for large-area deposition system. In this experiment, zinc chloride solution was used as sources, and the crystal growth was achieved at the growth temperature of 600°C and various flow rates of Nitrogen gas. The X-ray diffraction (XRD) spectrum was performed, and the photoluminescence spectra proved near-band-edge emission and strong deep-level emissions. In this work, we obtained the optimum condition for crystal growth of ZnO on m-plane sapphire, where XRD θ -2 θ single peak at m-plane ZnO.

Keywords: Film Formation, Characterization, Mist-CVD, ZnO, LED

1. Introduction

In recent times, II-VI semiconductor materials have been of great interest due to application for luminescence and ultraviolet (UV) optical devices such as light emitting diodes (LEDs) and laser diodes (LDs) [1]. Zinc Oxide (ZnO) has fascinated extensive consideration due to its greater physical properties and potential technological applications. The wide direct-bandgap of ZnO is 3.37eV and it has a large exciton binding energy of 60meV, which errands efficient excitonic emission processes at room temperature and enables devices to purpose at a low threshold voltage. ZnO (as a group-II oxide) proves enormous assure for applications in blue/UV light emitters and photodetectors, over and above transparent electronics, chemical sensors, spintronics, and varistors. Various techniques, such as magnetron sputtering, reactive evaporation, pulse laser deposition (PLD), metaorganic chemical vapor deposition (MOCVD), molecular bean epitaxy (MBE), spray pyrolysis, and sol-gel can be useful for ZnO thin films deposition [2].

We have developed a mist-CVD method as a promising

technique that allows superior controllability in film deposition at low cost with an uncomplicated system and low energy consumption [3]. In this method, a 60ml of zinc chloride (zinc compound) solution is ultrasonically atomized to form mist particles of the solution, and the particles are afterward transferred by a carrier gas of nitrogen onto the heat sapphire substrate, forming ZnO film by pyrolysis and chemical reactions. The fundamental concept may be similar to that of spray pyrolysis, but the main difference is in particle volume and the merits of treating mist particles like nitrogen gas.

In this paper, we report that ZnO layers deposited on m-plane sapphire substrate by mist chemical vapor deposition (mist-CVD) with different flow rate of carrier gas at 600°C experiments. The optical and structural properties of un-doped ZnO layer are characterized by scanning electron microscopy (SEM), photoluminescence (PL), film thickness measurement and X-ray diffraction (XRD). Based on the results, it is confirmed that ZnO films have single orientation of crystal.

2. Experiment

Fig.1 shows the experimental setup of mist-CVD system for crystal growth of undoped ZnO films were grown on m-plane sapphire with different flow rate of carrier gas. Deposition of ZnO thin films was carried at the substrate temperatures of 600°C with various gas flow rates of 6 L/min, 8 L/min and 10 L/min and 60 mL of zinc chloride solution.



Fig. 1. Experimental Setup.

The photoluminescence spectra were verified by using He-Cd Laser which has an excitation wavelength of 325nm. After the thin film was etched by mixed solution of CH₃COOH solution, phosphoric acid and pure water and the film thickness was measured by KLA-Tencor. The surface of film morphology was investigated with JEOL JSM7600F (SEM). The X-ray Diffraction (XRD) scan in the $\theta/2\theta$ mode

was performed to determine the film orientation perpendicular to the film surface.

3. Results and Discussions

The deposition condition for experiment is given in Table I.

Table I. Deposition Conditions for Experiment.

Solution	Zinc Chloride aqueous solution (0.1 mol/L)
Deposition Temperature	600°C
Flow Rate	6 l/min, 8 l/min and 10 l/min
Substrate	m-plane Sapphire
Solution Amount	60ml

Fig.2 shows the photographs of deposited thin films of ZnO at substrate temperature of 600°C with different flow rates for 6 L/min, 8 L/min and 10 L/min of nitrogen gas. The surface morphologies were characterized by SEM. In case of sample grown at 8 L/min and 10 L/min of flow rate, the front side of the sample has almost no grain boundary.

In order to characterize the optical properties of ZnO films deposited on m-plane sapphire, the PL measurements were performed at room temperature and the results are revealed in Fig.3. A weak near-band-edge (NBE) emission peak was observed at 3.26eV, while the deep level emission at 2.48eV which is related to oxygen vacancy [4-10].

In order to characterize the crystallinity of ZnO thin films, XRD analyses were performed and the results are shown in Fig.4. From the XRD spectrum for the sample grown with the flow rate of 6 L/min, c-plane ZnO (002) at 31.7°, r-plane (101), m-plane (002) at 66.3° and sapphire (100) diffraction peaks were shown. But the other two samples grown with flow rates of 8 L/min and 10 L/min possess m-plane (100), m-plane (200) and sapphire.

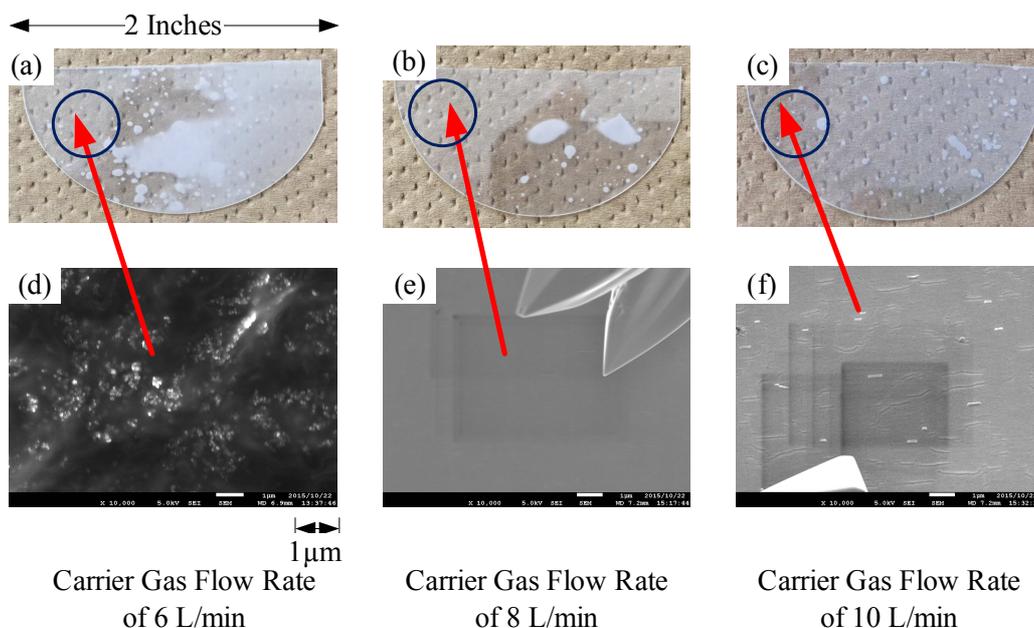


Fig. 2. Photograph and SEM Images are Shown in (a)-(c) and (d)-(f), Respectively.

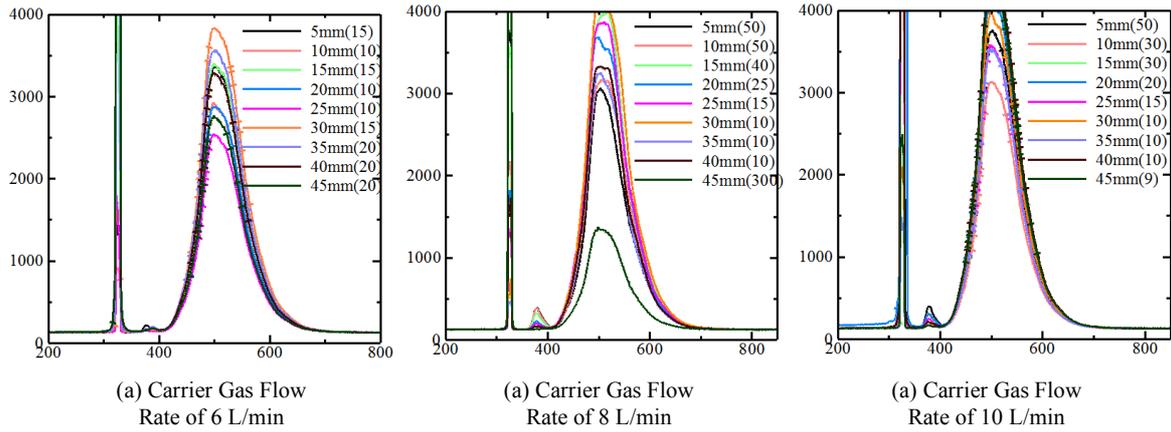


Fig. 3. Photoluminescence Spectra for the Samples Grown with Carrier Gas Flow Rate of (a) 6 L/min, (b) 8 L/min and (c) 10 L/min.

The film thickness results are shown in Fig.5. When the clod mist come into the furnace, then the temperature of the mist increase with the location on the substrate. So, the thickness increases with the location because the thermal reaction is enhanced by the mist temperature. When we increased the flow rate from 8 L/min to 10 L/min, the

decomposition of the mist is decreased because the temperature of the mist is not increased at the high flow rate. According to these responses, the crystal growth condition for the sample grown with the carrier gas flow rate of 8 L/minis was found to be optimal. The summary table for experiment is given in Table II.

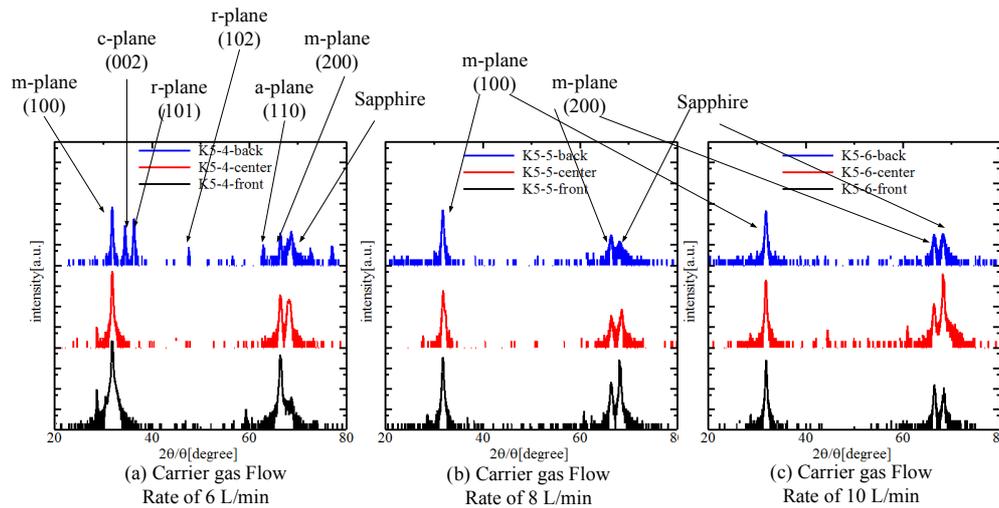


Fig. 4. XRD Spectra for the Samples Grown at Various Flow Rates.

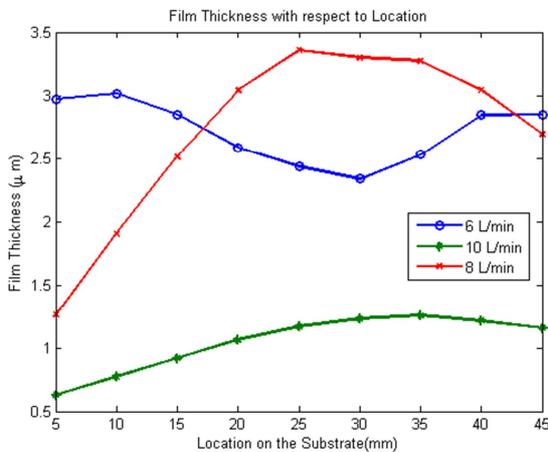


Fig. 5. Film Thickness Measurement for 550°C, 600°C and 650°C.

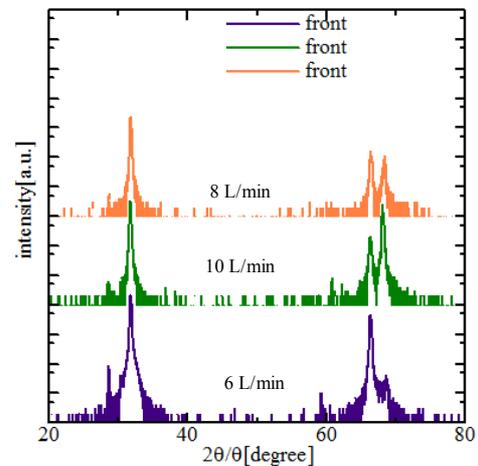


Fig. 6. PL Measurement for Front Side of the Sample on 550°C, 600°C and 650°C.

Table II. Summary for Experiment.

	Film Thickness	PL	SEM	XRD
6 l/min	Large	Weak	Rough	Multi-peak
8 l/min	Large	Strong	Flat	Multi-peak
10 l/min	Small	Weak	Flat	Only m-plane

4. Conclusion

In this paper, undoped ZnO grown on sapphire by mist-CVD technique has been characterized. The undoped ZnO on m-plane sapphire was growth with different flow rate of carrier gas at 600°C. From the PL measurement, weak near-band-edge (NBE) emission peak was observed at 3.26eV while the deep level emissions were very strong. Film thickness decreased with the flow rate. According to this experiment, the optimum values for mist CVD techniques of undoped ZnO with m-plane sapphire are substrate temperature of 600 °C and the carrier gas flow rate of 8 L/min. In this work, we found the optimum condition for crystal growth of ZnO on m-plane sapphire and single orientation of m-plane ZnO was observed by XRD θ -2 θ scanning mode.

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