Preparation of ZnO thin film by newly designed horizontal-typed MOCVD chamber

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Abstract. ZnO films have been studied as transparent conductive films of displays, organic light-emitting devices and solar cells because they are highly conductive and less expensive than In₂O₃-SnO₂ (ITO). We designed and assembled a horizontal-typed metalorganic chemical vapor deposition (MOCVD) vacuum chamber. ZnO thin film was fabricated on 3 inches substrate of Corning 1737 using bis[dipivaloylmethanato](DPM) complexes of zinc as a precursor by a liquid-delivery method. Smooth surface morphology and c-axis orientation were observed in the film. High homogeneity of ca. 2% in the film thickness was obtained.

1. Introduction

ZnO films have been studied as transparent conductive films of displays, organic light-emitting devices and solar cells because they are highly conductive and less expensive than In₂O₃-SnO₂ (ITO). ZnO films have been prepared by various techniques. Especially, metalorganic chemical vapor deposition (MOCVD) has the advantages as films can be deposited in large area at high growth rates [1][2].

In this report, we designed and assembled a horizontal-typed MOCVD vacuum chamber. ZnO thin film was fabricated by a liquid-delivery method [1][2] on 3 inches substrate of Corning 1737. Characteristics and thickness homogeneity of the film deposited on the 3 inches substrate were studied.

Fig. 1. Gas flow model in horizontal-typed vacuum chamber.
2. Experimentals

2.1. Horizontal-type vacuum chamber
A horizontal-type vacuum chamber was designed and assembled. As shown in Fig. 1, characteristics of the chamber are to disperse precursor gas onto substrate without a shower head and, therefore, to obtain homogeneous film thickness and property on largely sized substrate. Figs. 2 and 3 show schematic illustration and outlook of the horizontal-type vacuum chamber (Takachiho Trading Co., Ltd., TMO-2410-O) for 3 inches substrate, respectively.

2.2. Precursor
Generally used zinc precursors for MOCVD are diethyl zinc (DEZ) [3-5] and bis[acetylacetonato]zinc (Zn(acac)2) [6-8]. Alkyl metals such as DEZ are highly volatile but react violently with air. Zn(acac)2, one of beta-diketonates, is stable against oxygen but both its vaporization and decomposition occur simultaneously in a source vessel because the vaporization temperature is close to the thermal decomposition temperature. Dipivaloylmethanato(DPM) complex (Toshima MFG Co., Ltd.) of zinc was a typical precursor of zinc and used because of its high stability in both air and heat and its higher deposition rate of ZnO film of 3 - 4 nm/min than the evaluated other beta-diketonates. Fig. 4 shows synthesized molecular structure of Zn(DPM)2.

![Diagram of horizontal-typed vacuum chamber](image1)

**Fig. 2.** Schematic illustration of horizontal-typed vacuum chamber.

![Outlook of horizontal-typed vacuum chamber](image2)

**Fig. 3.** Outlook of horizontal-typed vacuum chamber for 3 inches substrate.

![Molecular structure of Zn(DPM)2](image3)

**Fig. 4.** Molecular structure of Zn(DPM)2.
Table 1. Deposition conditions of ZnO thin films.

| Condition                                      | Value         |
|-----------------------------------------------|---------------|
| Substrate temperature                         | 400 - 600°C   |
| Chamber pressure                              | 10 - 50 torr  |
| Carrier gas into vaporizer                    | Ar: 200 ccm   |
| Sub-flow gas                                  | Ar: 320 ccm   |
| Oxygen flow rate                              | O₂: 348 ccm   |
| Precursor concentration                       | Zn(DPM)₂/toluene: 0.02 mol/kg |
| Precursor flow rate into vaporizer            | 0.5 g/min     |
| Rotation rate of substrate                    | 4 - 20rpm     |
| Substrate                                     | Corning 1737, 3 inch-diameter |

2.3. Liquid-delivery method
Deposition conditions of ZnO thin film were shown in Table 1. The precursor solutions were prepared by mixing 0.02 mol/kg toluene solution of the zinc complexes. The flow rates of the precursor solution, argon carrier gas and oxygen were fixed at 0.5 g/min, 520 ccm and 348 ccm, respectively. Temperature of a vaporizer (Lintec Co., Ltd., VU-510) was set at 160°C. The films were deposited on 3” Corning 1737 substrates in the range of 400-600°C at 10 - 50 torr. The substrates were rotated at 4 - 20 rpm.

3. Results and Discussion
Higher conversion efficiency from precursor Zn(DPM)₂ to ZnO film was estimated to ca. 12% using the horizontal typed vacuum chamber, which was estimated by ratio of deposited weight of the thin film determined by inductively coupled plasma spectrometry (ICP) and calculated weight of the precursor in the solution flowed into the chamber.

Fig. 5 shows XRD pattern of ZnO thin film fabricated at the substrate temperature of 550°C. Strong (002) peak at ca. 34° of 2θ and weak (004) peak at ca. 73° were observed in the XRD pattern, which indicates that c-axis oriented (002) ZnO thin film was obtained. Fig. 6 shows that the root mean square of the surface roughness of the film was about 2 nm. The surface roughness of the substrate Corning 1737 was observed about 1 nm.

![Fig. 5. XRD pattern of ZnO thin film obtained at 550°C.](image-url)
Fig. 6. AFM image of ZnO thin film obtained at 550°C.

Table 2: Homogeneity of deposited ZnO thin films.

| Substrate temperature | 600°C | 600°C | 600°C | 600°C |
|-----------------------|-------|-------|-------|-------|
| Chamber pressure      | 10 torr | 10 torr | 30 torr | 50 torr |
| Rotation rate         | 4 rpm | 20 rpm | 20 rpm | 20 rpm |
| Thin film thickness on the substrate (nm) | 64 - 70 nm | 65 - 67 nm | 54 - 57 nm | 44 - 64 nm |
| Thickness homogeneity | ±ca. 5% | ±ca. 2% | ±ca. 3% | ±ca. 19% |

Film thickness homogeneity of the ZnO thin films deposited at 600°C on the 3 inches substrate was estimated in Table 2. Highly homogeneous film was obtained in 10 torr of chamber pressure and substrate rotation rate of 20 rpm.

4. Conclusions
ZnO thin film on 3 inches substrate was fabricated by liquid-delivery MOCVD method using horizontal-typed vacuum chamber which was newly designed and assembled. Higher conversion efficiency from precursor to the film was estimated to ca. 12%, and the higher deposition rate of 3 - 4 nm/min was obtained. The smooth surface morphology and the c-axis orientation were observed. High homogeneity of ca. 2% in the film thickness was obtained.

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