# Experimental Investigation of ZnO Thin Film Formed by Use of Negative Oxygen Ion Plasmas and DEZn II

酸素負イオンプラズマとDEZnを用いたZnO薄膜生成実験Ⅱ - プラズマパラメーター依存性-

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ZnO thin films are deposited by a method of PE-MOCVD containing lots of negative oxygen ions to investigate a possibility of a new low-temperature plasma process. Negative oxygen ions are generated by a pulsed-ICP discharge. Data are taken with changing the substrage bias voltage  $V_b$  from -80 to +80 V. Preliminary data show that all absorption spectra of the produced ZnO thin films indicate the absorption edge at 3.4 eV clearly. On the other hand, spectrum shapes of XRD change slightly, by changing  $V_b$ .

## 1. Introduction

There are various deposition processes of ZnO films such as the RF magnetron sputtering [1], the pulsed laser deposition [2], the atomic layer deposition [3], and the chemical vapor deposition (CVD) [4-6]. Among these, CVD is superior to ordinary PVD processes because of its high deposition rate, good step coverage, and facility of large area on a substrate. These advantages will be suitable for developing a fabrication process of nanoscale semiconductor devices with 3-D structure. On the other hand, one of disadvantages of CVD is that the method needs to heat the substrate, which limits the choice of substrate material.



Fig.1 A schematic drawing of the prototype PE-MOCVD machine. M.B. represents an RF automatic matching box (T161-6013HA, THAMWAY Co., Ltd.). The helical antenna is used for the RF launching.

For the purpose of developing a new CVD working under lower temperature, we have started an experiment on PE-MOCVD containing lots of negative oxygen ions O<sup>-</sup>. As mentioned in companion papers [7,8], it is actually well known that O<sup>-</sup> has high reactivity in low temperature. However, the effect of O<sup>-</sup> on PE-MOCVD has not been reported yet. To investigate it, we have examined dependences of ZnO film properties on the substrate bias voltage  $V_b$  in this paper.

## 2. Experimental Setup

Figure 1 shows a schematic drawing of the prototype machine. Here, O is generated through the dissociative electron attachment process to oxygen. As for the plasma source, we have employed a pulsed inductively coupled plasma discharge [9]. Regarding the zinc precursor, we have used diethyl zinc (DEZn). The produced ZnO is deposited on a glass substrate (Eagle XG, Corning Inc.). Vacuum pressure is variable, but during this experiment, fixed to be 20 Pa. Other parameters are listed in Table I.

Table I. Nominal parameters for ZnO depositions.

O <sub>2</sub> flow (sccm)	7
DEZ flow (sccm)	3.16
Deposition pressure (Pa)	20
Deposition time (min.)	3
Substrate temperature A(°C)	300
RF power (W)	200
RF on/off time (ms)	50/350
Substrate DC bias $V_b$ (V)	-80 to +80



Fig.2. Absorption spectra of the produced ZnO films. Those films are produced by changing  $V_b$ .

#### 3. Results and Discussion

As the first series of experiments, we perform ZnO depositions with the substrate temperature T > 250 °C, where the thermal decomposition of DEZn can occur in gas phase [10]. Figure 2 displays typical absorption spectra of the produced ZnO films. For all spectra, rapid absorption edges at 3.4 eV are observed clearly. These results mean that ZnO films are produced on the glass substrate successfully, despite the change in  $V_b$  between -80 and 80 V.

Figure 3 shows the set of XRD patterns of those ZnO films. As recognized, all data have clear peaks at 34°. This value means that the ZnO crystal grows to (002) direction. However, spectral intensities at 34° are not constant, suggesting some dependence of the crystal orientation on  $V_b$ . Further data are required, which must be obtained with precisely controlling the plasma space potential and the O<sup>-</sup> density in experiments.

#### 4. Summary

For the purpose of developing a new CVD process at lower temperature, we have started experiments using O<sup>-</sup>. In this paper, we have examined the dependence of ZnO film properties on  $V_b$ . Preliminary data suggest some dependence of the crystal orientation on  $V_b$ .

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Fig.3. XRD patterns of the produced ZnO films. Those films are produced by changing  $V_b$ .

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