# H<sub>2</sub> 효과에 따른 ECR-MOCVD 를 이용하여 poly ethylene terephthalate 위에 제조한 zinc oxide 박막의 특성 분석

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## The effect of H<sub>2</sub> content on characteristics of zinc oxide thin films on a poly ethylene terephthalate substrate prepared by ECR-MOCVD

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#### **1. INTRODUCTION**

ZnO of room temperature deposition has been attracted with much attention due to employment of PET substrate for potential applications for the solar cells, flexible electronic devices and flat panel display [1-4]. Zinc Oxide falls under the classification of transparent conductive oxides. The typical optical transmittance of Zinc Oxide is 90% in the visible wavelength region. The other important property of ZnO which could be used by the optical field is its wide band gap. ZnO has a wide bandgap of 3.2eV - 3.3eV. The additional advantage of being a direct bandgap semiconductor has increased the probability of using ZnO for short wavelength optical applications. ZnO in the form of thin films on a PET substrate replaced by glass gives many advantages due to lighter weight, smaller volume, lower cost and flexibility. We studied chemical vapor deposition at room temperature using organometallic precursors Diethylzinc using ECR (Electron Cyclotron Resonance) plasma. In this work, the relationship between characteristics of zinc oxide film and process parameters such as H<sub>2</sub> gas is investigated.

#### **2. EXPERIMENTS**

The substrates used for the experiments were PET (thickness=0.1 mm) and were cut to  $15 \times 15 \text{ cm}^2$  squares. The PET films were wrapped on a rotating disk with diameter of 200 mm. The electrode stood apart distance of 3cm from the rotating disk. The precursor DEZn (diethylzinc) with purity 99.9% was used as the organometallic source. An ECR plasma system was employed to carry out the experiments. It consists of two separate regions, the plasma zone and the deposition zone. It was

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pumped down to a base pressure of  $1 \times 10^{-6}$  Torr with a turbomolecular pump, backed by a rotary mechanical pump and a roots blower pump. The precursor DEZn was then introduced into the deposition chamber using Ar as a carrier gas. The carrier gas Ar flowed through the by pass line of the DEZn bubbler until the reactor was stabilized; then it flowed through the DEZn bubbler which was maintained at room temperature in order to carry DEZn vapor into the reactor. At the same time, H<sub>2</sub> gas was introduced directly into the reaction chamber. The ECR microwave plasma was generated using a microwave generator (2.45 GHz) coupled with a magnetic field (875 G). The samples were prepared under the following conditions: working pressure of 10 mTorr, 14 sccm of Ar, 3 sccm of O<sub>2</sub>, 0 ~ 6sccm of H<sub>2</sub>, deposition time of 15 min, microwave power of 850 W. So morphology and grain size was determined through micrographs obtained with a field emission - scanning electron microscopy (FE-SEM). The sheet resistance of the films was measured by the four-point probe, with appropriate geometric corrections. Transmittance spectra were obtained from 300nm ~ 900nm in a spectrophotometer UV-VIS. We further demonstrate the photoluminescence (PL) properties of the ZnO films for application to light-emission devices.

#### **3. RESULTS & DISCUSSION**

The higher the effect of H<sub>2</sub>, the more energy will be transferred into DEZn through the inelastic collisions between electrons and DEZn. With greater dissociation, excited DEZn seems to lead the higher deposition rate under high-H<sub>2</sub> gas. However, the deposition rate remains almost constant at H<sub>2</sub> gas range from 0 to 6.0sccm; because the decomposition rate also increased because of enable H<sub>2</sub> gas to decompose. Fig.1 shows scanning electron micrograph of ZnO films on PET film substrate deposited by ECR-MOCVD. The optimized processing conditions were 850 W of microwave power, 160 A of magnetic current power, 0~6.0 sccm of H<sub>2</sub>, 3 sccm of O<sub>2</sub>, 2.2 sccm of DEZn, 5 cm of the distance from magnet to DEZn feeding point, 2 cm of the distance from DEZn feeding point to substrate, 10 mTorr of working pressure, and 15 min of deposition time. Through optimization of the process variables, the ZnO film with very fine grains of 300~400 nm with film thickness of 600 nm were obtained at the optimum condition.



Fig.1. SEM morphology of ZnO films deposited on PET by ECR-MOCVD with  $H_2$  gas (sccm) (a) 0, (b) 1.5, (c) 3.0, (d) 4.5 and (e) 6.0.



Fig. 2. Transmittance of ZnO film prepared by ECR-MOCVD.



Fig. 3. Transmittance and Electrical Resistivity of ZnO film on the PET film measured by UV visible spectrometer and 4 point probe method.



Fig. 4. photoluminescence property for highly oriented ZnO films.

Fig. 2 shows the transmittance of the deposited film on the PET substrate in the visible range of 380-780 nm. The transmittance of the films prepared at optimized processing conditions exhibited the values of 83-98 %. Fig. 3 shows the Transmittance and Electrical Resistivity of ZnO film on the PET film measured by UV visible spectrometer and 4 point probe method. The electrical resistivity of the film which 4.5 sccm H<sub>2</sub> showed  $2.5 \times 10^{-2}$  Ω·cm. The transmittance of ZnO films exhibited their average values of 96 % at range of 380-780 nm. Some holes on the surface of ZnO film was

observed possibly due to the excessive energy exposure. The electrical resistivity decreases with the effect of  $H_2$  at content range. Photoluminescence spectra of ZnO films are obtained at room temperature in photon energy (eV) range from 2.5~3.5 eV using an excitation photon energy (eV) of 3.2~3.3 eV. A strong PL peak centered at 3.2~3.3 eV was observed (fig. 4), corresponding to the near photon energy (eV) edge emission (3.25eV).

### 4. CONCLUSION

Zinc oxide films on PET films are prepared by ECR-MOCVD at room temperature and effects of process parameters on the characteristics of the films were investigated. In our experimental range, increase in H<sub>2</sub> gas brought on formation of ZnO film with low electrical resistivity. Electrical resistivity of the films showed  $2.5 \times 10^{-2} \ \Omega$ ·cm. The films showed ultraviolet lasing action with a photon energy (eV) of about 3.25 eV at room temperature. This novel process to fabricate dense light-emission ZnO thin films can be applied to light-emission devices. The transmittance of the films exhibited their average values of 96 % at wavelength range of 380-780 nm respectively.

#### REFERENCE

- 1. Y. Fujinami, H. Hayashi, A. Ebe, O. Imai, K. Ogata, Mater. Chem. Phys.54 (1998) 102.
- 2. V.W.L. Lim, E.T. Kang, K.G. Neoh, Synth. Met. 123 (2001) 107.
- 3. L.J. Gerenser, J. Vac. Sci. Technol., A, Vac. Surf. Films 8 (1990) 3682.
- 4. H.-J. Kersten, G.K. Wolf, Surf. Coat. Technol. 116-119 (1999) 1183.