ECR-MOCVD 를 이용한 poly ethylene terephthalate 에 화학적 합성물로 제조된 ZnSnOx 박막의 특성

박지훈 [1,2], 변동진 [2], 이중기 [1,*]
[1] 한국과학기술연구원 이차전지연구센터, [2] 고려대학교 신소재공학과
(leejk@kist.re.kr[*])

Chemical Composite on Characteristics of ZnSnOx Film on Polyethylene Terephalate (PET) Substrate Prepared by Using ECR-MOCVD

J. H Park[1,2], D. J Byun[2] , J. K Lee[1,*]
[1]Secondary Battery Research Center, Korea Institute of Science and Technology,
[2]Department of Material Science & Engineering, Korea University

(leejk@kist.re.kr[*])

Introduction

ZnO and SnO_2 film has been used as an electrode in thin film solar cells, gas sensors, electronic devices and flat panel displays. Various deposition techniques such as spray pyrolysis, reactive thermal evaporation, CVD and sputtering were applied. [1-4]. The ECR-CVD method has attracted much attention for its high electron density of 10^{27}-10^{18} m^{-3} at a gas pressure range of 1×10^{-4}- 5×10^{-3} torr. Enhancement of ionization can be obtained by ECR plasma. The function of ECR is to increase the path of electrons in the plasma by applying a magnetic field normal to the electron trajectory. Resonance is achieved when the frequency at which microwave energy is fed to an electron circulating in a magnetic field is equal to the characteristic frequency at which the electron circulates [4]. In the present work, we investigate the electrical and optical properties of $ZnSnO_x$ films prepared by ECR-MOCVD. Also, characteristics of chemical binding to very important are studied at $ZnSnO_x$ film due to give influence of hall mobility and electrical resistivity.

Experimental

The used ECR-MOCVD system for mixed $ZnSnO_x$ thin film deposition was described in specify in prior work. Microwaves at frequency of 2.45 GHz (magnetic flux density, 875 Gauss) were introduced through a rectangular guide into the plasma chamber to generate plasma. High energy electrons formed in the plasma flow entered into the deposition chamber where they react with volatile organometallic precursors, generated the formation of a solid thin film on the surface of the substrate. The $ZnSnO_x$ films preparation conditions are as follows: 26 sccm of O_2, 5 sccm of H_2, 3 sccm of DEZn and 4 sccm of TMT, 23 sccm of Ar, 10 mTorr of working pressure, 1500 W of microwave power, 180 A of magnetic current power, 8 cm of the distance from magnet to TMT feeding point, 6 cm of the distance from TMT feeding point to substrate, 10 min of deposition time. The feed rate of TMT ($(CH_3)_4Sn$) and DEZn ($(C_2H_5)_2Zn$) were controlled by adjusting bubbler temperature and carrier gas flow rate through reactor. Argon was used as a carrier gas and oxygen, hydrogen gas was fed to the CVD reactor to control the properties of films deposited. Polyethylene Terephthalate (PET) sheets were cut into 17×36 cm^2 pieces and used as substrates for the deposition of film. Substrate of PET film on a home made cylindrical jig is rotated with 7 rpm during the deposition.
To obtain structural information the thin film were characterized by SEM (Scanning Electron Microscopy), AFM (Atomic Force Microscope) measurements. Measurements of electrical resistivity and optical transmittance were performed 4PPM (Four Points Probe Method) and hall mobility (HM), respectively. Chemical composition of films has been examined by X-ray photoelectron spectroscopy (XPS).

Results and Discussion

The atomic force microscope (AFM) analyses provided measure of surface roughness and surface grain size. A typical AFM reconstructed image of SnO_x; ZnO; SnO_x-ZnO and $ZnSnO_x$ films deposited at dense films on PET kept at room temperature. Fig. 1. (a), (b) shows AFM topographies and RMS of films with the SnO_x; ZnO; SnO_x-ZnO and $ZnSnO_x$ film. The surface roughness was measured on 0.5×0.5 mm^2 regions on the 3D AFM images. The RMS grain size of SnO_x; ZnO; SnO_x-ZnO and $ZnSnO_x$ films deposited on room temperature substrates was 13.4nm, 12.3 nm, 19.7 nm and 10.8 nm, respectively. The average surface grain size obtained with various films for both SnO_x; ZnO; SnO_x-ZnO and $ZnSnO_x$ films, from 30 to 40 nm in the case of SnO_x films, from 160 to 400nm in the case of ZnO, from 145 to 320nm in this case of SnO_x-ZnO, from 28 to 50nm in this case $ZnSnO_x$. The decreased of the $ZnSnO_x$ films surface roughness when deposited on mixed composite film and the increase of grain size in theses films indicates smoother film surface.
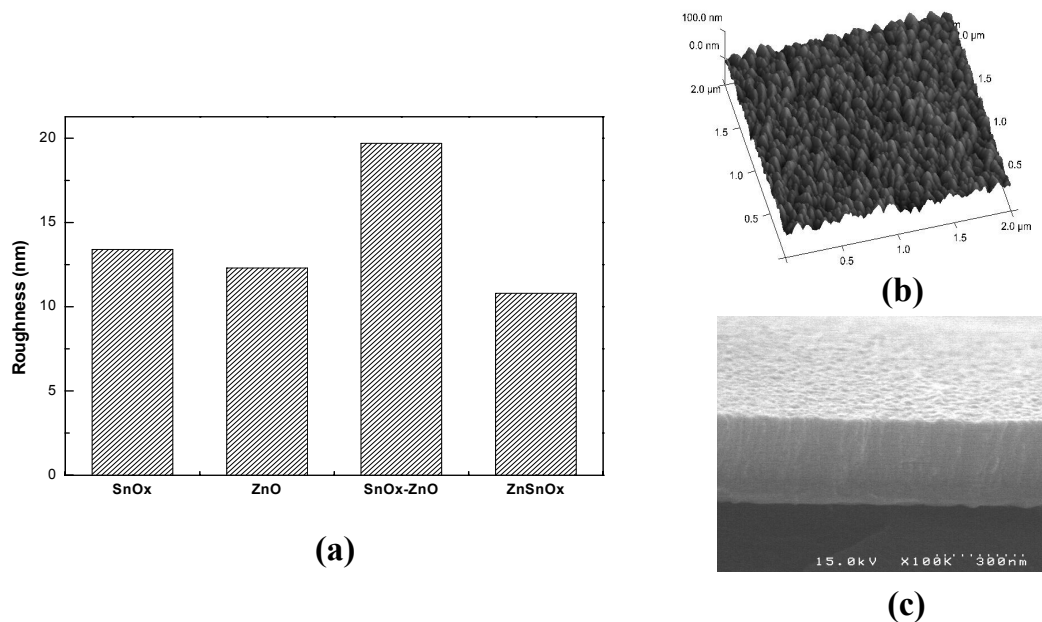

(a)

(b)

(c)

Fig.1. AFM RMS of (a) SnO_x; ZnO; SnO_x-ZnO and $ZnSnO_x$ films deposited on PET by ECR-MOCVD. (b) and (c) are AFM topography and SEM cross-section image of $ZnSnO_x$ film.

Fig.1. (c) shows scanning electron micrograph of $ZnSnO_x$ films on PET film substrate deposited by ECR- MOCVD. The cross-sectional image of SEM analysis shows that the $ZnSnO_x$ films have columnar structure with the different grain size from 30 up to 40 nm with 280 nm thickness.
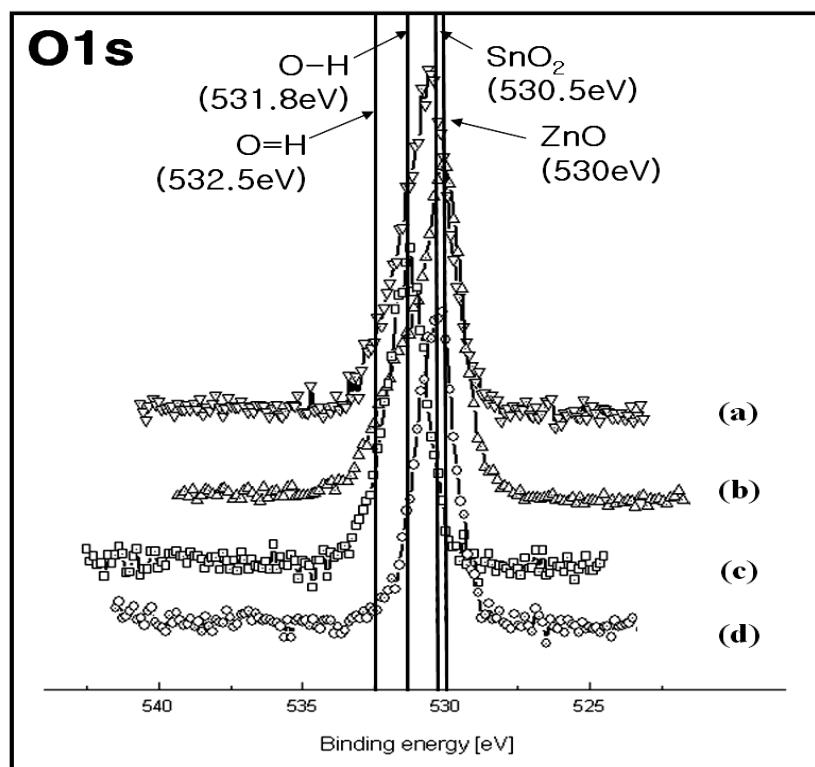
Fig.2. XPS depth profile of O1s peaks: (a) SnO_x; (b) ZnO; (c) SnO_x-ZnO and (d) $ZnSnO_x$ films deposited on PET by using ECR-MOCVD.

　Fig. 2 showed the spectra among obtained spectra of O1s and the chemical state of the film surface prepared ECR-CVD was analyzed by XPS. The component of tin precursor, $(CH_3)_4Sn$ and $(C_2H_5)_2Zn$, was incorporated into the surface structure of the films. Fig. 2. (a) showed the O1s spectrum for the SnO_x deposited film by ECR-MOCVD consisted of two distinct peaks: SnO_2 (530.5 eV), O-H (531.8 eV). Fig. 2. (b) showed the O1s spectrum for the ZnO deposited film consisted of two distinct peak: ZnO (530 eV), O-H (531.8 eV). Fig. 2. (c) showed the O1s spectrum for the SnO_x-ZnO deposited film consisted of three distinct peak: SnO_2 (530.5 eV), ZnO (530.4 eV), O=H (532.5 eV). Fig. 2. (d) showed the O1s spectrum for the $ZnSnO_x$ deposited film consisted of three distinct peak: SnO_2 (530.5 eV), ZnO (530 eV), O-H (531.8 eV). Those results indicated that the chemical binding energy of O1s deposits with SnO_x; ZnO; SnO_x-ZnO and $ZnSnO_x$ films. The double binding oxygen can possibly reacts with hydrogen fragments and formed gas phase hydrogen-oxygen. Therefore, the chemical composite film was concluded at double binding oxygen and hydrogen of high acid in mixture of tin oxide and zinc oxide.

Conclusions

ZnSnO$_x$ films could be synthesized from tetra-methyl tin (TMT) and diethylzinc (DEZn), interactions of ZnO and SnO$_x$ on PET substrate at room temperature by ECR-MOCVD. Scanning electron micrograph indicated that its grain size ranged from 30 to 40 nm with 280 nm thickness. The influence of chemical mixture composite film on electrical resistivity and roughness could be explained by the double binding oxygen and hydrogen of high acid etching in combination of tin oxide and zinc oxide. The mixture composite film increases to some extent with mixed ZnSnO$_x$ films and then the surface roughness ought to have decreased. The other side, high surface roughness was also observed at high hydrogen of high acid etching. This means that composition rate of oxygen fragments from decomposition TMT and DEZn could be increase because double binding oxygen can possibly reacts with hydrogen fragments and formed gas phase hydrogen-oxygen. It can be concluded that effect of mixture composite film on electrical resistivity and surface roughness is due to combination of tin oxide and tin oxide. The observed low electrical resistivity of 7.0×10^{-3} ohm ·cm and surface roughness of from 28 to 50nm at ZnSnO$_x$ films is the result of an optimum stability of these two layers. The electrical properties of ZnSnO$_x$ film increases at mixed tin oxide and zinc oxide due to partial oxidation of film by combination compound.

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