

Remote electro-precipitation of transparent ZnO on nano-porous alumina template

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Abstract

Zinc oxide (ZnO) thin film was deposited onto non-conducting alumina template by remote electrochemical and precipitation method. Chronoamperometry (i.e., constant potential mode) of -0.75 V (versus Ag/AgCl) was applied to deposit compact ZnO thin film onto the honeycomb shaped pores of a nano-porous alumina membrane. Analyzing morphological observations by SEM, we observed three distinct regions: (i) conducting platinum substrate; (ii) non-conducting alumina interlayer; (iii) thin film onto alumina template. XRD structural analysis of deposited materials onto alumina template and EDX analysis of alumina layer clearly indicated the formation of ZnO thin film was formed onto non-conducting alumina template not inside of alumina template. This remote-deposited ZnO showed more compact ZnO-hexagonal structure and a little bit higher transmittance than conventionally prepared ZnO onto ITO glass. Experimental observations were further discussed via the understanding of the mechanistic origin of ZnO formation onto alumina template.

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1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor with a bandgap of 3.2 eV and shows transparent and conductive properties. ZnO is a promising material for an application to ultraviolet-emitting diodes, piezoelectric devices, sensors and solar cells [1–4]. ZnO is also based material of high temperature heterogeneous catalyst (Cu/ZnO or CuO/ZnO/Al₂O₃) for methanol reforming into hydrogen and small amount of impurities [5]. We investigated the growth rate of ZnO thin film with and without dissolved oxygen and also studied mechanistic origin of ZnO formation [6]. Izaki et al. [7,8] presented the effect of cathodic current density and the concentration on the ZnO film structure. Gu et al. [9,10]

demonstrated that the growth rate of ZnO film was affected by different substrate materials. Yoshida et al. [11] demonstrated the electrochemical analysis for the process of electrodeposition of ZnO thin films from zinc nitrate baths. Very recently, Cembrero et al. [12] succeeded in the preparation of nano-columnar ZnO films for photovoltaic applications and we prepared ZnO nano-wires on Cu₂O nano-wires deposited into ordered alumina template using zinc chloride solution [13].

Of late, the development of nano-porous alumina template by an easy and low-cost manufacturing process is of great interest in relation to preparation of ordered nano-sized materials in biological, electronic, thermoelectric and photonic devices [14–18]. Most of studies have been forced on the preparation of metal and metal oxide wires inside of alumina nano-pores, whereas Wu et al. [19] only presented that the preparation of Ni nano-dot and nano-wire onto alumina template without conductive interlayer was possible process to date.

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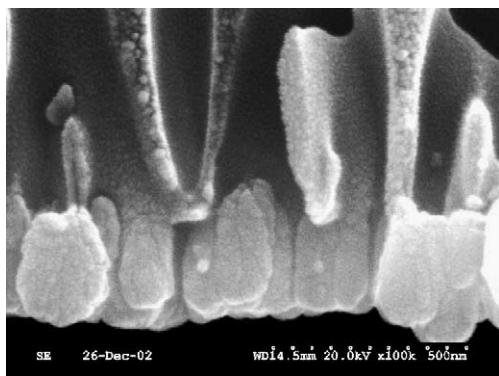


Fig. 1. SEM image of alumina template with deposited Pt.

In this study, we succeeded in the manufacturing of ZnO thin films onto non-conducting alumina interlayer by electrochemical and chemical methods and tried to understand the role of alumina template in the formation of ZnO. New mechanistic origin of ZnO formation was presented by analyzing morphological and structural data.

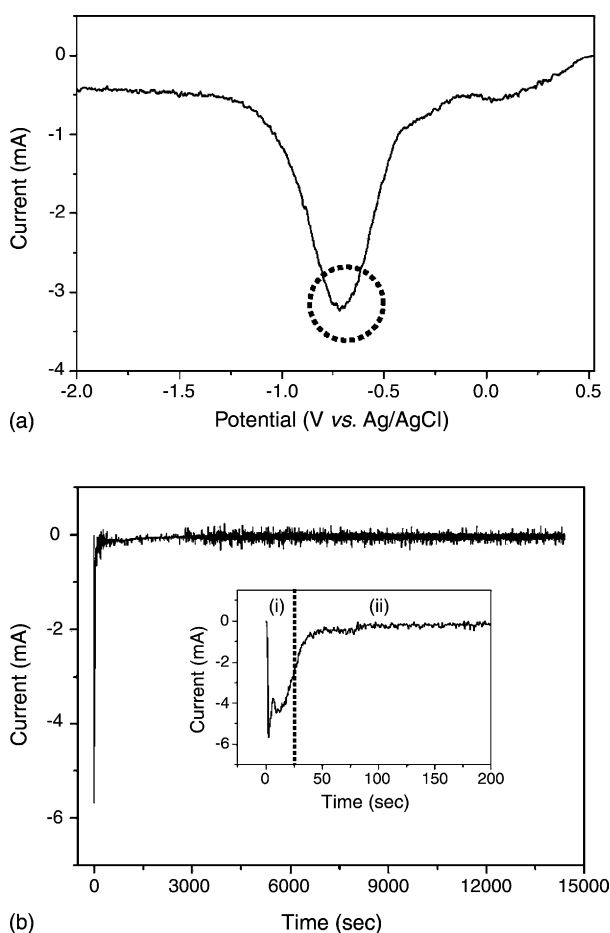


Fig. 2. (a) Linear sweep voltammetry in 0.1 M $\text{Zn}(\text{NO}_3)_2$ on $\text{Al}_2\text{O}_3/\text{Pt}$ cathode with a scan rate of 10 mV/s. (b) Current–time profile of $\text{Al}_2\text{O}_3/\text{Pt}$ electrode when cathodic potential of -0.75 V was applied. Electrolysis time is 4 h and solution temperature is 65°C . Inset presents the blow-up of initial characteristics of current–time curve.

2. Experimental

ZnO thin films were potentiostatically deposited onto porous alumina membrane/Pt and indium tin oxide (ITO) glass using conventional three-electrode system. Applying direct current (DC) sputtering technique (Nuricell Inc.), platinum homogenous islands (see Fig. 1) was deposited on one side of commercial alumina membrane (Whatman, Anodisc 25), which was used as working cathode electrode. Alumina membrane has highly ordered nano-pores at a diameter of 200 nm. Ag/AgCl, saturated KCl and platinum mesh were employed as reference electrode and counter electrode, respectively.

The electrolyte was 0.1 M zinc nitrate (Aldrich, 99.9995%) dissolved in tri-distilled water. Potentiostat and galvanostat (EG&G PAR 273A) was used to apply optimal potential of -0.75 V and the solution temperature of 65°C was constantly maintained during the experiments. In order to avoid reduction effect of dissolved oxygen, high-purity nitrogen gas was bubbled before each experiment.

The surface morphology of ZnO thin film was analyzed by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4300). The crystallinity and quantitative analysis of prepared ZnO thin film was carried out using X-ray diffraction (XRD, Phillips DY616) and energy dispersive X-ray spectroscopy (EDX) coupled with the SEM equipment.

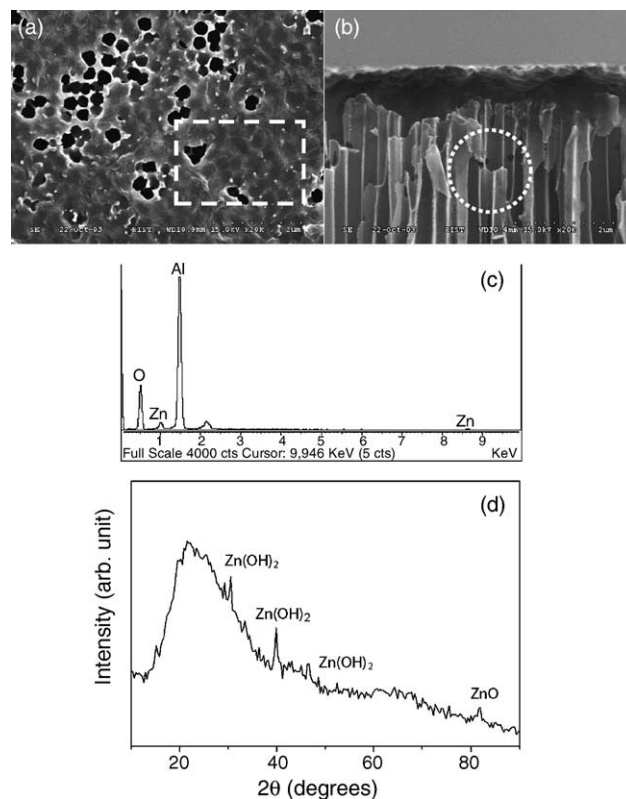


Fig. 3. (a) Top-view and (b) cross-sectional view of $\text{Al}_2\text{O}_3/\text{Pt}$ applying -0.75 V for 30 s. (c) EDX analysis of dashed box in (a) and (d) XRD data presents $\text{Zn}(\text{OH})_2$ formation on $\text{Al}_2\text{O}_3/\text{Pt}$ substrate.

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