

Highly *c*-axis oriented deposition of zinc oxide on an ITO surface modified by layer-by-layer method

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ARTICLE INFO

Article history:

Received 21 September 2012

Received in revised form 20 February 2013

Accepted 21 February 2013

Available online 4 March 2013

Keywords:

Electrodeposition

Zinc oxide

Nanopillar

Layer-by-layer

Texture coefficient

ABSTRACT

The easy method to construct *c*-axis oriented zinc oxide (ZnO) layer directly attached onto a transparent conducting substrate was studied. On the assumption that anionic organic functional groups serves as a directing group for Zn²⁺ ion, poly(sodium *p*-styrenesulfonate) (PSSNa) was immobilized onto ITO surface by layer-by-layer (LbL) process, and ZnO was electrodeposited onto the modified ITO surface. Nucleation of ZnO crystals was induced by LbL treatment and the nucleated crystals were aligned toward $\langle 001 \rangle$. The ZnO crystals gradually formed a film as the electrolysis progressed maintaining the crystal alignment, resulted in (001)-oriented ZnO continuous film. The obtained ZnO film was more transparent and uniform, and exhibited more intense photoluminescence at UV region than those deposited on a bare ITO. Also, the present method for the orientation selective nucleation of ZnO crystals revealed to be utilized as a seed layer for well aligned ZnO nanopillar array.

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1. Introduction

An *n*-type semiconducting zinc oxide (ZnO) has attracted increasing attentions as components in an ultraviolet-light-emitting diode [1–5], electron-transporting layer in organic thin-film [6,7] and dye-sensitized [8–12] photovoltaic cells, and sensors [13,14]. The pursuit of enhancing the device performance leads to acquire the high quality and to gain the wide range of nanostructures [15–21]. Among those morphologies, (001)-oriented continuous film [15] and pillar array [16,17] are expected to show characteristic properties such as ultraviolet-light-emission and high carrier mobility due to the decrease in the lattice defects including grain boundaries perpendicularly to the film, anisotropic light emission and conductivity of wurtzite ZnO crystal.

Electrochemical deposition is well-established solution based process to obtain ZnO films [22–27], which have some advantages over vapor-phase deposition in terms of low cost, low temperature growth, environmentally friendliness, and ease of morphology control. By electrochemical deposition, the (001)-oriented ZnO film or pillar are usually constructed by heteroepitaxial growth on single-crystalline substrates such as (111) Au [15,22,28] and

(001) GaN [29,30,31], which provide perfectly aligned surface having less lattice mismatch with (001) of ZnO. However, it remained difficult to construct the (001)-oriented ZnO film electrochemically on random polycrystalline surface such as tin-doped indium oxide (ITO) and fluorine-doped tin oxide (FTO), while such transparent conducting electrodes (TCEs) are indispensable component of photovoltaic cells and light-emitting devices. In order to obtain (001)-oriented ZnO film or nanopillar array on TCEs, a seed layer made of textured nanocrystalline is needed, and it often requires high temperature annealing to construct the seed layer [32]. Without the seed layer, the ZnO crystal nucleation generally starts randomly on the surface of TCEs, and it is well known that random-oriented ZnO film tends to align (001) during growth [23], although grain boundaries and lattice defects remain at the junction between ZnO layer and the substrate. Thus, easy method to construct (001)-oriented ZnO layer directly attached onto a transparent conducting substrate is highly required. For that sake, (001)-oriented ZnO nucleation on the substrate should have achieved.

Recently, electrochemical deposition of ZnO on polymer microsphere adsorbed electrode has been reported [33–36]. In the reports, urchin-like ZnO were formed with ZnO pillars aligned perpendicularly to the surface of the polymer microsphere. By the investigation, anionic groups, such as sulfate or acrylic acid groups, on the surface of polymer microsphere were revealed to be indispensable to form ordered ZnO structure [33]. This result clearly suggested that anionic group on the surface of the polymer microsphere favored the nucleation of (001)-oriented ZnO.

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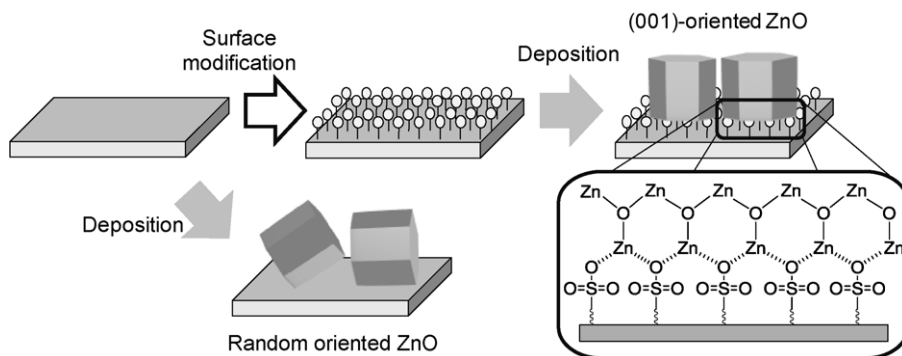


Fig. 1. Schematic view of the construction of highly *c*-axis oriented ZnO film.

Ionic interaction between anionic groups and Zn^{2+} ion would form Zn atom rich layer on the surface, leading (001) face directly grown from the surface. Also, specific affinity between acrylic acid enriched polymer microsphere surface and Zn-terminated surface of ZnO crystal was directly observed by Golovko et al. [37], which agreed with the assumption. Similar selective electrodepositions onto polymer microsphere adsorbed electrodes have been reported for CeO_2 [38] and TiO_2 [39]. Therefore, if there is a flat and smooth surface, on which anionic functional groups are immobilized in high concentration, it would be expected that the anionic groups would serve as a directing group for Zn^{2+} ion and the (001)-oriented ZnO film can be electrodeposited. In this paper, we demonstrate a novel strategy that enables to construct the (001)-oriented ZnO film by the electrodeposition onto anionic groups immobilized electrode (Fig. 1).

In order to immobilize an anionic functional group on surface of a substrate, layer-by-layer (LbL) method [40,41] was chosen as a surface modification process. Although there are a lot of surface modification methods available, including self-assembled monolayer, surface initiated atom transfer radical polymerization and so on, LbL method seems simple way to mimic the environment of the polymer microsphere surface on a substrate. LbL method is a process of surface modification just by immersing the substrate into aqueous solutions of cationic and anionic polymer-electrolyte alternately, resulting in the formation of insoluble thin layer of polymer-electrolytes due to their multipoint ionic interaction between each other. The anionic functional group of the adsorbed polymer chain on the substrate may serve as a similar function as an anionic group on the surface of polymer microsphere, and interact with Zn^{2+} ion, leading to the construction of (001)-oriented ZnO film. Thus, the electrodeposition onto the LbL modified transparent conducting substrate was investigated.

2. Experimental

LbL modification of ITO: The surface of ITO glass (Geomatec, 9–10 Ω /square) was cleaned by UV-ozone cleaner (UV/Ozone ProCleaner, BioForce Nanosciences) prior to use. The ITO glass was immersed into a 5 w/v% solution of poly(diallyldimethylammonium chloride) (PDDA, Aldrich, MW 200,000–350,000, Fig. 2) in deionized water for 5 min, and washed by deionized water. Then, the ITO glass was immersed into a 5 w/v% solution of poly(sodium *p*-styrenesulfonate) (PSSNa, Scientific Polymer Products Inc., MW 500,000, Fig. 2) in deionized water for 5 min, and washed by deionized water. This immersion cycle was repeated for several times, and then the modified ITO glass was dried by clean air blow. The samples were abbreviated as LbL_x/ITO, where *x* stands for the immersion cycle times. To characterize the modified ITO surface, atomic force microscope

(AFM) analysis was conducted using Shimadzu SPM-9600 on tapping mode equipped with Si cantilever.

Electrochemical deposition of ZnO: Electrodeposition of ZnO was carried out under galvanostatic condition using conventional three electrode cell equipped with the modified or bare ITO-glass working electrode, Pt-sheet counter electrode, and Ag/AgCl reference electrode. Electrolysis was applied in aq. 80 mM $\text{Zn}(\text{NO}_3)_2$ (Nacalai) with current density of -0.25 mA/cm^2 for an electric charge of 100–500 mC/cm^2 at 60 °C without stirring.

Formation of ZnO nanopillar: ZnO nanopillars were fabricated by two-step electrolysis method. In the first step, ZnO seed layer was formed by the same condition described above with an electric charge of 50 mC/cm^2 . And then the second-step electrolysis was applied in aq. 1 mM $\text{Zn}(\text{NO}_3)_2$ at 60 °C with current density of -0.5 mA/cm^2 for an electric charge of 5.0 C/cm^2 .

Characterization of ZnO crystals: X-ray diffraction (XRD) measurements were performed using a Rigaku RINT 2500 system with monochromated $\text{Cu K}\alpha$ radiation generated at 40 kV and 200 mA. A field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F) was used for the observation of structural morphologies. UV-vis and photoluminescence spectra of the obtained ZnO films were measured on JASCO V-560 spectrophotometer and JASCO FP-6500 spectrofluorometer equipped with 100 mm-size integrating sphere unit, respectively. The texture coefficient, which represents the texture of the particular plane, deviation of which from 1 implies the preferred growth, was calculated according to the following formula [42,43]:

$$TC(hkl) = \frac{(I(hkl)/I_0(hkl))/1}{1 / (n \sum_n (I(hkl)/I_0(hkl)))}$$

where $I(hkl)$ is the measured intensity of a diffraction peak corresponding to plane (*hkl*), $I_0(hkl)$ is the standard intensity of the plane (*hkl*) taken from the JCPDS data (no. 36-1451), *n* is the number of diffraction peaks. In this case, XRD peaks corresponding to

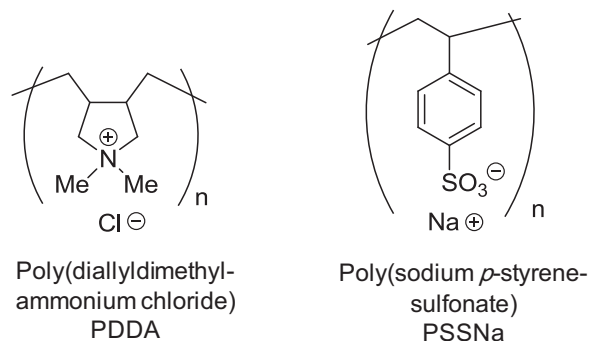


Fig. 2. Chemical structures of PDDA and PSSNa.

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