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Growth of ZnO nanorods on fluorine-doped tin oxide substrate without catalyst by radio-frequency magnetron sputtering

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ABSTRACT

ZnO nanorods were directly grown on fluorine-doped tin oxide (FTO)-coated glass substrate by radio frequency magnetron sputtering without a buffer layer or a catalyst. The deposition time, substrate temperature, and type of substrate were varied to investigate the growth behavior of ZnO nanorods. At an early stage of growth, nano-sized particles were locally formed on the faceted surface of FTO, which were finally grown into the nanorods. The substrate temperature of over 400 °C was required for ZnO nanorod growth. ZnO nanorods were well grown on FTO, SnO_2-coated Si, and SnO_2-coated SiO_2 substrates whereas ZnO thin film was deposited on Cu foil, stainless steel, Au-coated SiO_2, and Pt-coated SiO_2 substrates. Based on the obtained results, a growth mechanism for ZnO nanorods was proposed.

1. Introduction

Zinc oxide (ZnO) is a representative semiconducting material with a large direct band gap (E_g = 3.37 eV), a high exciton binding energy (60 meV), and an excellent chemical and thermal stability. One-dimensional (1-D) ZnO nanostructures have received a great attention due to their application in light-emitting diodes, gas sensors, and dye-sensitized solar cells [1–3]. Various methods [4–14] have been developed for the synthesis of ZnO nanostructures including vapor–liquid–solid (VLS), electro-deposition, hydrothermal, vapor-phase epitaxial growth, chemical bath deposition, and sputtering on single-crystal or non-single-crystal substrates w/o a catalyst or a buffer layer.

Among these techniques, sputter deposition is least employed to fabricate the ZnO nanorods or nanowires although sputtering is well-established, cost-effective, and large scale deposition method and various nanostructures have been synthesized by sputtering at relatively low temperatures [15–17]. It was found that the presence of copper (Cu) or thin ZnO buffer layer is decisive in obtaining ZnO nanorods on non-single-crystal substrates by sputtering [18–21]. For photovoltaic and optoelectronic applications, the growth of ZnO nanorods on the transparent conducting indium tin oxide (ITO)- or fluorine-doped tin oxide (FTO)-coated glass substrate is desirable, but there are a few studies on the synthesis of ZnO nanorods on these substrates by sputtering [22,23] and the growth mechanism is not well established.

In this work, we have demonstrated the direct growth of ZnO nanorods on FTO substrate via radio frequency (rf) magnetron sputtering without a buffer layer or a catalyst. The type of substrate had a profound effect on the growth of ZnO nanorods, and SnO_2 or metallic Sn played a key role. Based on the obtained results, we suggest a mechanism for ZnO nanorod growth.

2. Experimental details

ZnO nanorods were deposited on FTO glass substrate by rf magnetron sputtering (SPS-100, Ultech, Korea) using a ZnO target. The deposition was carried out in an Ar environment with an rf power of 100 W at 0.13 Pa. The substrate temperature during deposition was varied from room temperature to 400 °C, and the deposition time was changed from 1 to 20 min to examine the growth behavior of ZnO nanorods. The surface morphology was observed by field-emission scanning electron microscopy (FE-SEM, SU-70, 15 kV, Hitachi) and transmission electron microscopy (TEM, JSM-3000F, 300 kV, JEOL). The phase was examined by θ–2θ X-ray diffraction (Model D8-Advance, BRUKER MILLER Co.) using Cu Kα radiation (λ = 1.5406 Å). The chemical bonding information was investigated by X-ray photoelectron spectroscopy (XPS, Model AXIS, KRATOS) with a Mg Kα radiation (1253.6 eV). The core level XPS spectra for O1s and Sn3d were measured, and the energy calibration was achieved by setting the hydrocarbon C1s line at 284.6 eV.

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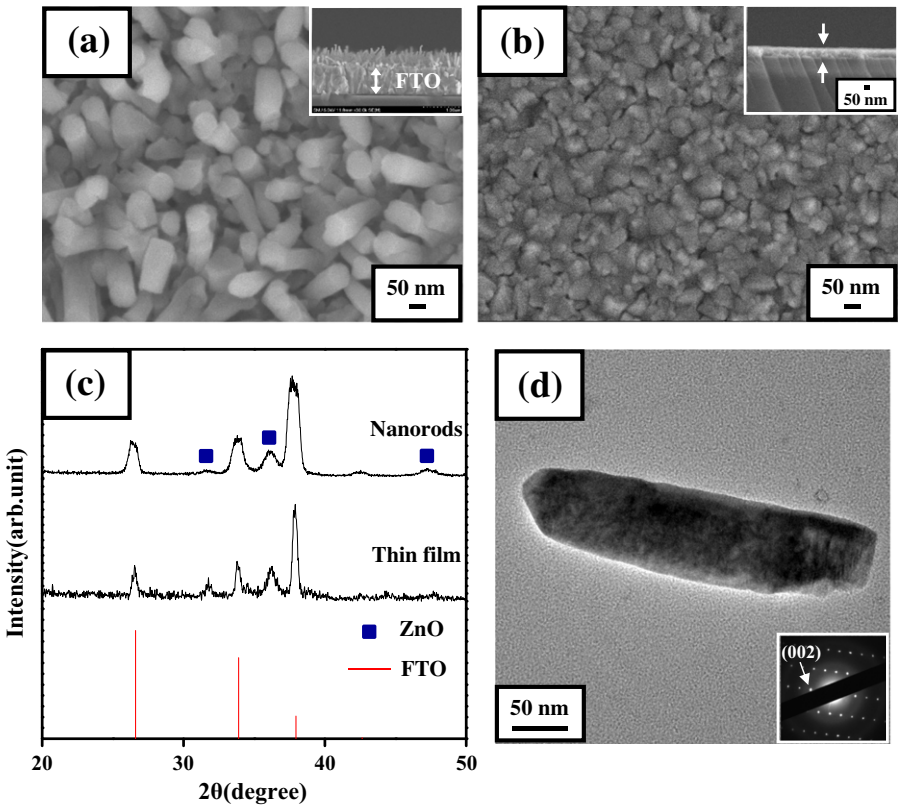

Fig. 1. Surface morphology of (a) ZnO nanorods on FTO and (b) ZnO film on SiO_2 deposited at 400 °C for 15 min (insets are the cross sectional views). (c) XRD pattern and (d) TEM image of ZnO nanorods of (a) (inset is SAED pattern).

3. Results and discussion

The surface morphology of ZnO deposited on FTO substrate at 400 °C for 15 min is shown in Fig. 1(a). As-grown ZnO was the nanorods with round tips. The nanorods were vertically grown without a complete alignment. The diameter of nanorods was 40–50 nm and the length was a few hundred nanometers (inset of Fig. 1(a)). Thus, ZnO nanorods were grown without a buffer layer or a catalyst by rf magnetron sputtering. On the contrary, film-like ZnO was obtained on SiO_2 substrate in the same deposition conditions (Fig. 1(b)),

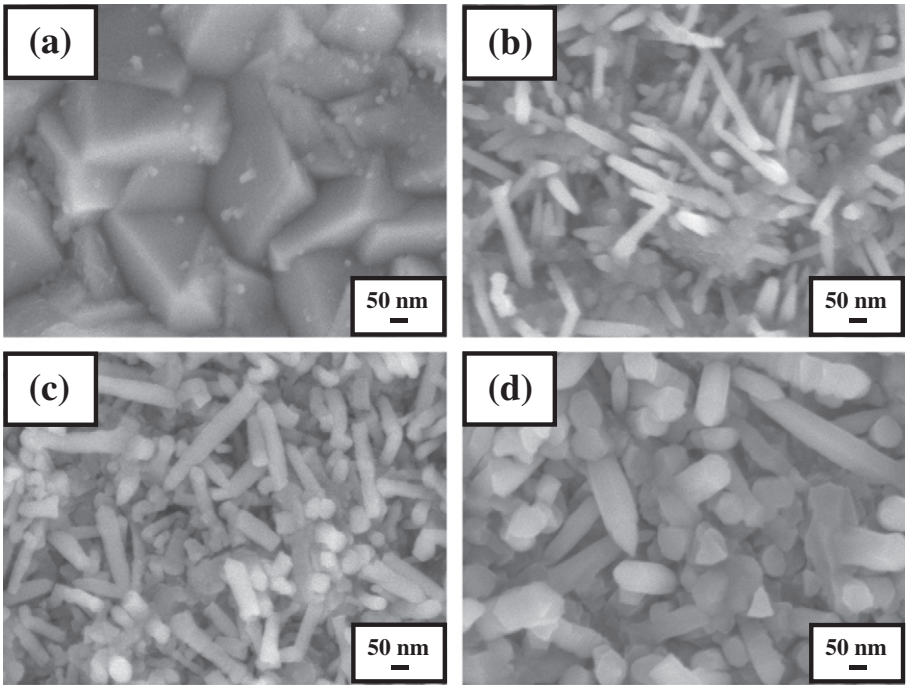

Fig. 2. Morphology change of ZnO nanorods with deposition time coated at 400 °C for (a) 1, (b) 5, (c) 10, and (d) 20 min.