Control of Crystal Growth of ZnO Nanowiskers in Aqueous Solution and Synthesis of Transparent Nanoarrays

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SYNOPSIS

Transparent and porous ZnO nanowisker arrays were prepared in 0.025 M zinc nitrate-hexamethylenetetramine aqueous solutions with the addition of polyethylenimine (PEI) at a low temperature. The effect of free zinc ion concentration was controlled by changing the immersing temperatures at which the pre-treated FTO substrates were got into the mixing solution such as 25 °C, 75 °C and 85 °C. The free Zn ion concentration is a main factor for control of the transmittance. It was found that high Zn ion concentrations resulted in relative thick white and low transparent ZnO film, while the low concentrations gave high transparencency in the nanoarray. A transmittance of about 85% for porous ZnO films with thickness of 800 nm in the visible range was achieved.

KEY WORDS

aqueous solution, ZnO nanowisker arrays, transmittance, immersing temperature, concentration

1 Introduction

Transparent conductive oxides (TCOs, such as ZnO, CdO, In₂O₃, SnO₂) are an indispensable materials as transparent electrodes applied to optoelectronic devices²,³ such as dye-sensitized solar cells and gas sensors. Since zinc oxide (ZnO), which is a wide band gap (3.37 eV) semiconductor and a large binding energy (60 meV) possessing unique optical and electronic properties, is a realistic candidate for the host material of TCO due to low cost of material and fabrication. ZnO is being explored for application as a transparent conductive oxide for gas sensors⁴, varistors⁵, piezoelectric devices⁶, transistors⁷, light-emitting diodes⁸ and photodiodes⁹. Recently, photovoltaic devices based on bare and dye-sensitized thin films have shown the high potential of ZnO for photoanodes, short-wavelength lasing, and cathodoluminescence due to its broad emission band in the yellow-green region. Porous films with very large internal surface area offer a number of intriguing features that are advantageous in the design of optoelectronic devices¹⁰. However, nanostructured ZnO electrodes based on interconnected spherical particles have shown low photocurrent efficiency due to charge-carrier recombination losses at grain boundaries between nanoparticles in the film. Additionally, the performance

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aqueous solutions at about 88 °C. The effects of free Zn ion concentration in the solution on the transparency of ZnO nanowhisker arrays were discussed.

2 Experimental

The starting materials utilized are zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, 99%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 99%), hexamethylenetetramine (HMT, C₆H₁₂N₄, 99%) and polyethyleneimine (PEI, (C₂H₄N₆), branched mean molecular weight of 600, 99%). All chemicals from Wako Pure Chemical industries, Ltd., in Japan were used as received without further purification. F–doped SnO₂ conductive glass (FTO, Sheet resistivity: 9.5 Ω/□, Asahi Glass) was used as substrate.

A simple two-step approach by the solution deposition technique was used for growing well-aligned ZnO nanowhiskers. First, a textured ZnO–seed layer was prepared on the FTO substrate. The FTO substrate cleaned by ultraviolet irradiation (SU110GS-36, SEN Light Corporation) was spin-coated with 0.01 M zinc acetate-ethanol solution. The as deposited thin layer was dried in an oven at 60 °C for 10 min in air. After repeating the spin-coating process four times, the resultant layer was subsequently heated at 350 °C for 20 min in air in order to get ZnO–seed layer from decomposition of zinc acetate dihydrate. Separately, a 200-ml solution was prepared by mixing 0.025 M equivolamolar of zinc nitrate hexahydrate and hexamethylenetetramine (HMT), and 0.005 M polyethyleneimine (PEI) in deionized water for growth of ZnO nanowhiskers. The pre-treated FTO substrate was immersed in the mixing solution at different temperatures such as at 25 °C, 75 °C and 85 °C, and then kept at about 88 °C for ZnO film growth for 2 h.

The crystalline phase and orientation of products were identified using X-ray diffraction (XRD; RINT-2100V, Rigaku) with CuKα radiation (40 kV, 30 mA) and scan rate of 2°/min. The morphology and microstructure were observed using a field emission scanning electron microscope (FE-SEM; JSM-6335FM, JEOL Ltd.) with accelerating voltage of 5 kV and emission current of 12 μA. The optical properties were investigated in the wavelength range from 300 to 850 nm, using a Model U-4100 UV-Visible-NIR Spectrophotometer.

3 Results and Discussion

The clear aqueous solution gradually became white opaque at about 70 °C. It took for 1 h at 87 °C, the solution changed to bright light yellow coloration and transparent little by little. These phenomena clarified ZnO deposits began to form in the solution by homogenous nucleation and growth via the decomposition of HMT at about 70 °C. In order to clarify the zinc ion concentration change, the changes of pH value and temperature were investigated in situ for 5 h in the solution. Fig. 1 showed the changes in pH value and temperature with reaction time in the 0.025 M solution. Temperature rapidly raised and then maintained at the desired value. The pH quickly decreased to the lowest value of 5.85 at 84 °C in 30 min, and maintained it for 10 min, and then increased slowly to a constant value of 6.45 after about 4.5 h. These results indicate that zinc ion concentration decreased with the formation of ZnO deposits by the reaction of zinc ion and OH anion supplied by the decomposition of HMT in the solution. Changes in pH value in 0.1 and 0.05 M aqueous solutions with reaction time at 88 °C were also investigated, and showed similar tendencies to the 0.025 M solution. However, the lowest pH values differed as 5.72 and 5.63 for 0.05 and 0.1 M, respectively. After a long time, a higher-concentration solution always maintained a relatively lower pH value. In order to investigate the effect of zinc ion on the growth of ZnO whiskers film on the pre-treated FTO substrate, we controlled temperature when the pre-treated FTO substrate was immersed in the solution. The immersing temperatures were selected as 25 °C, 75 °C and 85 °C in 0.025 M solution.

The XRD patterns of prepared ZnO nanowhiskers film were shown in Fig. 2. Peaks originating from the FTO substrate were evident. All the diffraction peaks of as-prepared ZnO films are in good agreement with the JCPDS card No. 36-1451 for the typical wurtzite-type ZnO crystal (hexagonal, P6₃mc). While the relative peaks intensities are clearly different, 0002 diffraction peak is the strongest and also 10 11, 10 12 and 10 13 diffraction peaks were detected. The significantly higher intensity obtained from
the 0002 diffraction peak indicated that ZnO nanowhiskers were preferentially orientated along the c-axis direction (grown along the [0001] crystallographic face direction).

Fig. 3 showed the FE-SEM images of ZnO nanowhiskers film grown at different immersing temperature. These top-view images showed the diameter of whiskers decreased with increasing of the immersing temperature. That is, the growth of ZnO nanowhisker was affected by the free Zn ion concentration in the solution. When the ZnO–coated substrate was immersed to the solution at 25 °C, the zinc ion concentration is higher. The heterogeneous nucleation and growth proceeded when the decomposition of HMT occurred. And then it resulted in lower aspect ratio as shown in Fig. 3a1 and a2. While in case of high temperature such as 85 °C, because the zinc ion concentration decreased with the formation of ZnO deposits in the solution, the lowered zinc ion concentration resulted in thin and uniform ZnO nanowhiskers with higher aspect ratio as shown in Fig. 3c1 and c2. ZnO nanowhiskers are well oriented and growing with c-axis perpendicular to substrate surface.

Fig. 4 showed the optical transmittance spectra with wavelengths from 300 to 850 nm of pre-treated FTO substrate and as-prepared ZnO nanowhiskers film at various immersing temperatures. Both pre-treated and bare FTO substrates showed almost the same transmittances.
independent of the existence of textured ZnO-seed layer. While ZnO film grown from ambient temperature (25 °C) showed higher absorption in the visible range of 390–530 nm. And also the film showed a sharp absorption edge at the wavelengths range of 368–393 nm, which is very close to the intrinsic band gap of ZnO (3.30 eV). The UV was almost completely absorbed by the ZnO film. While the film with the thickness of about 800 nm, which was formed with the higher immersing temperatures such as 75 °C and 85 °C, showed higher transmittances more than that of the FTO substrate in the visible range. This result was considered to be due to the existence of well-aligned ZnO film increasing the in-line transmittance and decreasing of the diffuse transmittance. And a sharp absorption edge at wavelength of 368 – 393 nm was also observed. The results indicated a good structural quality of films. In UV range, it showed difference absorption. A lower immersing temperature resulted in a higher absorption. This should be assigned to the diameters and disperse of ZnO nanowhiskers.

4 Conclusions
Transparent and well-aligned ZnO nanowhiskers were produced in 0.025 M zinc nitrate-hexamethylenetetramine aqueous solutions with the addition of polyethylenimine (PEI) by controlling the immersing temperatures of the pre-treated FTO substrate. The free Zn ion concentration in the solution is the main factor for control of transmittance of film. Higher Zn ion concentrations resulted in relative thick white and low transparent ZnO arrays, while the low concentrations gave high transparencies in the nanowire. A transmittance of about 85% for porous ZnO films with thickness of 800 nm in the visible range was achieved. Such highly transparent ZnO films will have potential application in dye-sensitized solar cells and dye-sensitized sensor.

References