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Influence of Growth Conditions on the Morphology of Zinc Oxide Nanoarrays

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A simple bottom up method for the growth of ZnO nanoarrays using a chemical bath deposition has been widely used due to its promising application in the functional devices, ultraviolet light-emitting, chemical sensors, dye-sensitized solar cells, transparent conductor and piezoelectric materials. The morphology was strongly influenced by experimental conditions including chemical species in the solution, the level of supersaturation, the temperature and the nature of the substrate. Preparation of a ZnO seed template layer was necessary for growth of ZnO nanoarrays film. The effects of different substrates (such as slide glass, Si wafer and F-doped SnO_2 coated glass) and zinc salts which resulted to ZnO seeds on the morphology of ZnO nanoarrays were investigated. Additionally, the influence of the surfactant-like polymer on the crystal morphology was addressed.
Key words: aqueous solution, ZnO nanoarrays, morphology, substrate, zinc source, surfactant-like polymer

1. INTRODUCTION

Wurtzite zinc oxide (ZnO), which is a wide band gap (3.37 eV) semiconductor with a large exciton binding energy (60 meV), possesses unique optical and electronic properties. ZnO is being explored for application as a transparent conductive oxide for gas sensors,[1] varistors,[2] piezoelectric devices,[3] transistors,[4] light-emitting diodes,[5] field emission flat panel displays [6] and photodiodes.[7] Various techniques such as spray pyrolysis,[8] chemical vapor deposition (CVD),[9] sol-gel process,[10-13] sputtering techniques,[14, 15] chemical bath deposition,[16] electrodeposition [17] and pulse laser deposition (PLD),[18] have been used to deposit ZnO. The microstructure and chemical properties of ZnO depend on the synthesis method. The low-temperature chemical bath deposition method, which has advantages such as simplicity, reproducibility, cost effectiveness, and suitability for producing large-area thin films, is attracting considerable attention. Presently, direct deposition techniques in aqueous solutions have been developed for the fabrication of ZnO thin films at low temperature which is based on heterogeneous nucleation and subsequent crystal growth on a specific surface.[19, 20] The deposition of thin films from aqueous solution involves controlled precipitation on a substrate via hydrolysis and/or condensation reactions of metal ions and/or complexes from aqueous solution. The crystal morphology is strongly influenced by experimental conditions including chemical species in the solution (ligand, pH, metal counter-ion, ionic strength are all important), level of supersaturation, temperature, and nature of the substrate.[21] Control of the size, morphology and orientation of ZnO crystallites on the substrates is a prerequisite for high-technology applications such as photovoltaic and optoelectronic devices.[22] The effect of the substrate on the nature of the ZnO films formed was studies using different substrate: gold-coated F-doped SnO_2 coated glass (FTO), ZnO template layers on FTO glass, FTO glass and single crystalline (0001) sapphire. The nucleation of the crystals was promoted by means of underlying thin layers. Well-aligned ZnO films were deposited on both Au-coated and ZnO template FTO substrate [21, 23].

In our previous work,[24, 25] well-aligned ZnO nanowhiskers were deposited on a ZnO coated substrate using an aqueous solution with the addition of polyethylenimine. The ZnO seed layer was derived from the decomposition of zinc acetate after spin-coating of a mixture solution of zinc acetate dehydrate and ethanol. In the present study, we investigated the effects of different substrates (such as slide glass, Si wafer and FTO glass) and zinc salts as a raw material for preparing ZnO seeds on the morphology of ZnO nanoarrays. Additionally, the influence of the surfactant-like polymer on the crystal morphology was addressed.

2. EXPERIMENTAL

The starting materials were zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 99%), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99%), anhydrous ethanol (C_2H_5OH, 99.5%), hexamethylenetetramine (HMT, $C_6H_{12}N_4$, 99%) and polyethylenimine (PEI, $(C_2H_5N)_n$, branched mean molecular weight of 600, 99%). All

chemicals (Wako Pure Chemical Industries, Ltd., Japan) were used as received without further purification. FTO glass, glass slides, Si wafers were used as a substrate.

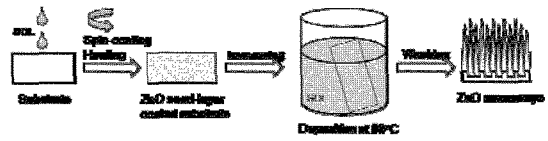

Fig.1 Schematic diagram of experimental processes.

A simple two-step approach by the solution deposition technique was used for fabricating ZnO nanoarrays as shown in Fig.1. First, the substrate cleaned by ultraviolet irradiation (SUV110GS-36, SEN Light Corporation) was spin-coated with 0.01 M zinc salts-anhydrous ethanol solution. Spin coating process was carried out by two-step of 500 rpm for 5 seconds and 3000 rpm for 30 seconds. Zinc acetate dihydrate- and zinc nitrate hexahydrate-derived ethanol solution were used as spin coating solution, respectively. And the droplet coating method was performed in order to investigate the effect of seeds size on morphology of ZnO nanoarrays. After repeating the coating process four times, the resultant layer was subsequently heated at 350 °C for 20 min in air in order to obtain ZnO seeds from the decomposition of zinc salts. Separately, the pre-treated substrate was immersed in a 200-ml aqueous solution of zinc nitrate, HMT and PEI with molar ratio of 5:5:1 which was kept at 88 °C in a thermostatically regulated oil bath for fabricating ZnO nanoarrays. Subsequently, the fabricated substrates were washed repeatedly with deionized water and ethanol, and then dried in air at room temperature for characterization.

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 a 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 samples were observed directly without Pt or carbon coating.

3. RESULTS AND DISCUSSION

All the X-ray diffraction peaks of as-prepared ZnO nanoarrays are in good agreement with the JCPDS card No.36–1451 for the typical wurtzite-type ZnO crystal (hexagonal, $P6_3mc$). The significantly higher intensity of the 0002 diffraction peak indicated that ZnO nanoarrays were preferentially orientated along the *c*-axis direction (grown along the (0001) crystallographic face direction). It clarified that the underlying ZnO thin layers promoted the heterogeneous nucleation and growth of ZnO nanoarrays in the case of chemical bath deposition. The degree of seed dispersion on the surface of substrate affected the morphology of ZnO nanoarrays.

3.1 The effect of substrate

Fig.2 showed the FE-SEM images of ZnO arrays formed on the different substrates. The micrographs on the smooth and rough surfaces of Si wafer were shown in Figs.2-a1and 2-a2 and Figs. 2-b1 and 2-b2, respectively. There are remarkable differences in average diameter of the crystallites and distribution on both surfaces. On the rough surface, relatively dense ZnO nanoarrays with smaller size in diameter developed. Figs.2-c1 and 2-c2 showed many independent and circle-shaped ZnO nanoarrays were randomly deposited on the slide glass. While uniform and dense ZnO nanoarrays were deposited on the whole surface of FTO substrate as shown in Figs.2-d1 and 2-d2. These results clarified the morphologies of ZnO nanoarrays were affected by the degree of seed dispersion on the substrate.

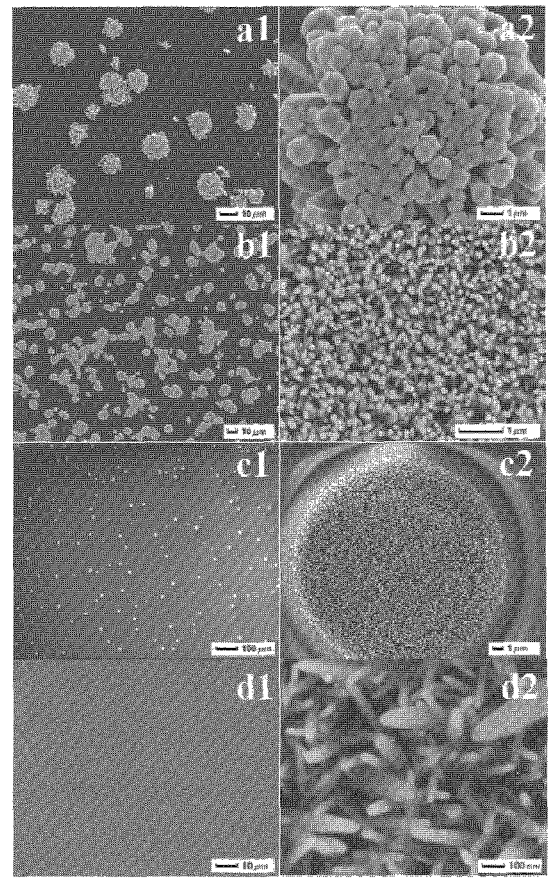

Fig.2 FE-SEM images of ZnO nanoarrays deposited on different substrate. (a1, a2) and (b1, b2) are for smooth and rough surface on Si wafer in 0.1 M solution for 30 min, respectively; (c1, c2) : slide glass in 0.025 M solution for 2 h; (d1, d2): FTO substrate in 0.025 M solution for 2 h. all of ZnO seeds derived from zinc acetate dihydrate.

Fig.3 showed the surface micrographs of bare and ZnO seed layer coated rough surface of Si wafer and FTO substrate, respectively. The surface of FTO substrate

was rougher than that of Si wafer. Zinc acetate-derived ZnO seeds were kept on the rough surface of Si wafer as aggregates of ZnO nanocrystals (Fig.3-a2), while ZnO seeds were homogeneously dispersed on the FTO whole surface so that they are hard to be observed even though using high magnifications FE-SEM (Fig.3-b2).

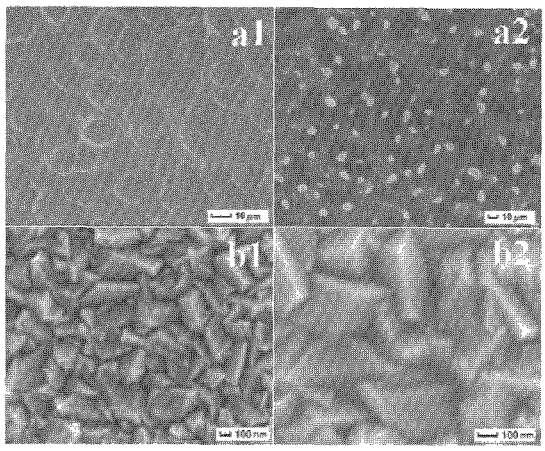

Fig.3 FE-SEM images of bare and ZnO seed-coated substrate surface. a1, a2: bare and ZnO seed-coated rough surface of Si wafer, respectively; b1, b2: bare and ZnO seed-coated FTO substrate, respectively. ZnO seeds derived from zinc acetate dihydrate.

3.2 The effect of ZnO seeds derived from different zinc salts

Instead of zinc acetate dihydrate, zinc nitrate hexahydrate was used as a raw material for preparing ZnO seeds by spin coating and thermal decomposition. The FE-SEM images of the ZnO seeds derived from the zinc nitrate hexahydrate were shown in Fig.4-a1. The white and random shaped compounds are ZnO particles. The magnified images shown in Fig.4-a2 revealed that ZnO particles were aggregates of ZnO nanosheet. This may be explained by the physical and chemical properties of zinc nitrate hexahydrate as the raw material. Zinc nitrate hexahydrate has low melting point of 36.4 °C and low boiling point of 131 °C. During the process of heating treatment in air, it underwent melting, dehydration, formation of intermediate phases and decomposition.[26] Figs.4-b1, 4-b2, and 4-b3 showed the as-deposited ZnO nanoarrays. High crystalline ZnO nanowhiskers with perfect hexagonal symmetry were only selectively deposited onto the active sites of pre-coated ZnO seeds. Therefore semi-circular shaped ZnO nanowhisker assemblies were deposited. In the case of zinc acetate dihydrate, uniformly ZnO nanoarrays were deposited on the whole surface FTO substrate (Figs.2-d1 and 2-d2). The XRD patterns (Fig.4-c) clarified the as-deposited ZnO nanowhisker assemblies are good agreement with the JCPDS card No.36-1451 for the typical wurtzite-type crystal. The significantly higher intensity of the 0002 diffraction peak indicated that ZnO nanowhiskers were preferentially orientated along the *c*-axis direction.

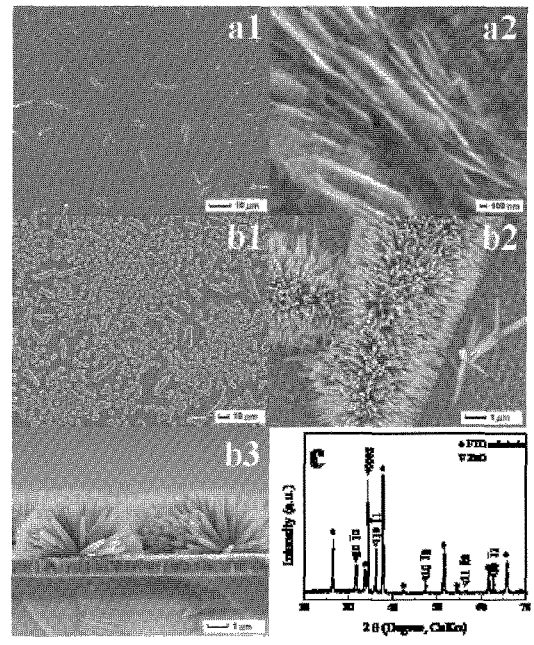

Fig.4 FE-SEM images of ZnO seeds (a1, a2) prepared from the decomposition of zinc nitrate hexahydrate and as-deposited ZnO nanoarrays (b1, b2, b3), and XRD patterns of as-deposited ZnO nanoarrays (c) in 0.1 M solution for 30 min. FTO was used as substrate.

3.3 The effect of coating method

As shown in the former, zinc acetate dihydrate derived ZnO seeds were well dispersed on the whole surface of FTO substrate. Fig.5 showed the FE-SEM image of ZnO seeds prepared on the FTO substrate by droplet coating method and as-prepared ZnO nanoarrays, respectively. There are remarkable differences compared to the morphology of nanoarrays on the seeds prepared by spin coating method. In the case of droplet coating, the surface became rough and ZnO seeds were clearly observed. While there seems to be no difference in the surface of seeds compared to bare FTO in the case of spin coating (Fig.3-b2), ZnO seeds were hard to be observed. The smaller and almost uniform ZnO nanoarrays were deposited easily in the case of spin coating method; while larger and non-uniform diameter ZnO nanoarrays were deposited in the case of droplet coating method. It was concluded that the growth of ZnO was affected apparently by the seed size, and large one resulted in large nanowhiskers in diameter.

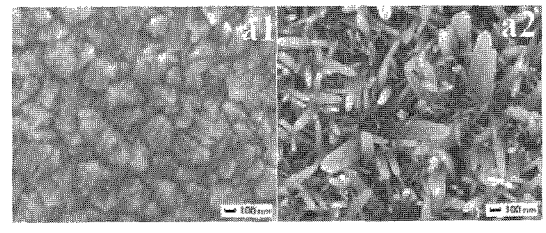

Fig.5 FE-SEM image of ZnO seeds (a1) and nanoarrays (a2) prepare in 0.025 M solution for 2 h by droplet coating method. ZnO seeds derived from zinc acetate dihydrate.

3.4 The effect of surfactant-like polymer PEI

Fig.6 showed the FE-SEM images of ZnO nanoarrays deposited with or without PEI. ZnO nanorods with a clearly hexagon at the top were deposited without the addition of PEI. While ZnO nanowhiskers with a pointed tip were deposited with the surfactant-like polymer PEI. It was considered that surfactant-like PEI was adsorbed on the nonpolar planes to inhibit the growth in diameter and improve the growth in length along the *c*-axis. These results clarified the addition of surfactant-like PEI resulted in formation of the ZnO whiskers with smaller diameter.

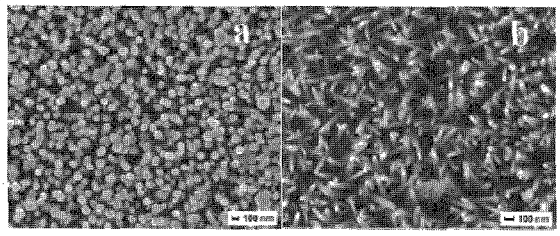

Fig.6 FE-SEM images of ZnO nanoarrays deposited in 0.025 M solution. a, without surfactant-like PEI; b, with surfactant-like PEI.

4. CONCLUSIONS

The underlying ZnO seeds improved the crystallographic properties of ZnO nanoarrays by proceeding heterogeneous nucleation and growth. The morphology of ZnO nanoarrays were affected by the nature of substrate, coating method, raw materials for preparing ZnO seeds and surfactant-like polymer in the solution. Well-dispersed seeds were easily prepared by zinc acetate dihydrate. Relatively flat surface of substrate resulted in low density ZnO nanoarrays. Circle-shaped ZnO nanoarrays were formed on the slide glass by spin coating method. Uniform and high dense ZnO nanoarrays were formed on the spin-coated seeds pre-deposited on the FTO substrate. The aggregates of ZnO nanosheets were formed as seeds from zinc nitrate hexahydrate and semi-circular shaped ZnO nanowhisker assembles were deposited on the FTO substrate. The addition of surfactant-like PEI resulted in changes of the morphology of ZnO crystals to show the crystal habit during the deposition.

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