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Solvent Effect on Zinc Oxide Crystallites Shape using Submerged Photo-Synthesis

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Abstract

Semiconducting nano-materials electrical, optical, and magnetic properties are sensitively dependent on their morphologies. Systematic dopant introduction to altering the crystallites atomic composition provides rational control of crystallites growth. We show specific solvent effect in zinc oxide (ZnO) crystallites shape fabricated on a zinc electrode surface via submerged photo-synthesis process. By submerging and illuminating the electrode inside ultrapure water (H_2O), we found ZnO nanorods and nanoflowers. Then, addition of dopants such as silicon (Si), calcium (Ca), sodium chloride (NaCl), and ethanol (C_2H_6O) resulted in crystallites shape change into spherical, whiskers, microplates, and nanoflakes, respectively. In the case of NaCl, microplates growth indicated dependence in molar ratio. The mechanism of growth is discussed. We demonstrate that this shape modification scheme is environmentally benign approach and can be extended to other solvents systems. Thus, it provides an attractive strategy for fabricating doped crystallites.

1. Introduction

Doping is desirable for most modern semiconductor devices (e.g. photo-detectors, gas sensors, light emitting diodes, and solar cells) [1,2]. In typical, those devices possess metallic electrodes or catalysts as main components. If the electrodes material is carefully processed to contain bi-metal crystallites, their electrical, optical, and magnetic properties can be modified. For this purpose, it is essential to control the crystallites shape, size, and composition, which will foster the route to optimizing the morphology of the electrodes.

In this study, submerged photo-synthesis of crystallites (SPSC) on surfaces technique is introduced in the doping experiments. The technique offers several advantages: (1) simple experimental setup, (2) easy mass production, (3) use of available raw materials for crystallites synthesis. The growth unit/seeds on the material surface are constructed using submerged liquid plasma (surface pretreatment). Then, ultraviolet (UV, λ = 365 nm) light irradiation on the plasma-treated material while being submerged inside different solution will result in crystalline surface of the electrode.

We demonstrate the synthesis of ZnO crystallites due to its well-known tunable properties and has been widely reported [3,4]. Initially, use of ultrapure water in SPSC resulted in ZnO nanorods. Growth is induced by water splitting process, which hydroxyl (OH) radicals production give rise to apical characteristic of nanorods. As if the crystallites seeds interact with other various species (impurities, ions, or molecules) in submerged condition, it significantly altered the growing process as will be discussed later.

The goal is to tune the current SPSC method to fabricate various morphology of ZnO to pursue its realization in environmental and nano devices applications.

2. Method

A potassium carbonate (K_2CO_3) with concentration 0.1 mol/l (300 ml) was prepared as the electrolyte of the submerged liquid plasma experiment. A raw Zn plate with size of 35 x 5 x 1 mm was used as the cathode, and a Pt mesh was used as the anode. A direct current voltage (140 V, 10 min) applied to both electrodes initiated a glow discharge on the cathode. After the plasma treatment, the plasma-treated Zn plate was cut to a length size of 20 mm and immersed in 4 ml of various solution (Table I). Then, the UV irradiation (24 h) for SPSC experiment was conducted in a specified dark chamber.

Solution	Dopant elements	Dimensions (D*L)	Morphology
Tap water	Si	φ500 nm	Spherical shape
Tap water	Ca	1μm in diameter Few μm in length	Microwhiskers
NaCl (0.60 mol/l)	Na, Cl	100 nm*200 nm	Nanorods
NaCl (0.86 mol/l)	Na, Cl	Few μm size	Nanorods & Microplates
NaCl (1.72 mol/l)	Na, Cl	Few μm size	Microplates
Ethanol	C	Few nm size	Nanoflakes

Table I SPSC experimental for plasma-treated Zn in various solution. The SPSC results of the crystallites dimensions and morphologies are included.

3. Results and discussion

For the characterization and analysis, surface morphology was observed using field-emission scanning electron microscopy (FESEM); elemental analysis was conducted using energy dispersive X-ray spectroscopy (EDS). Some of the results are shown as in Figure 1.

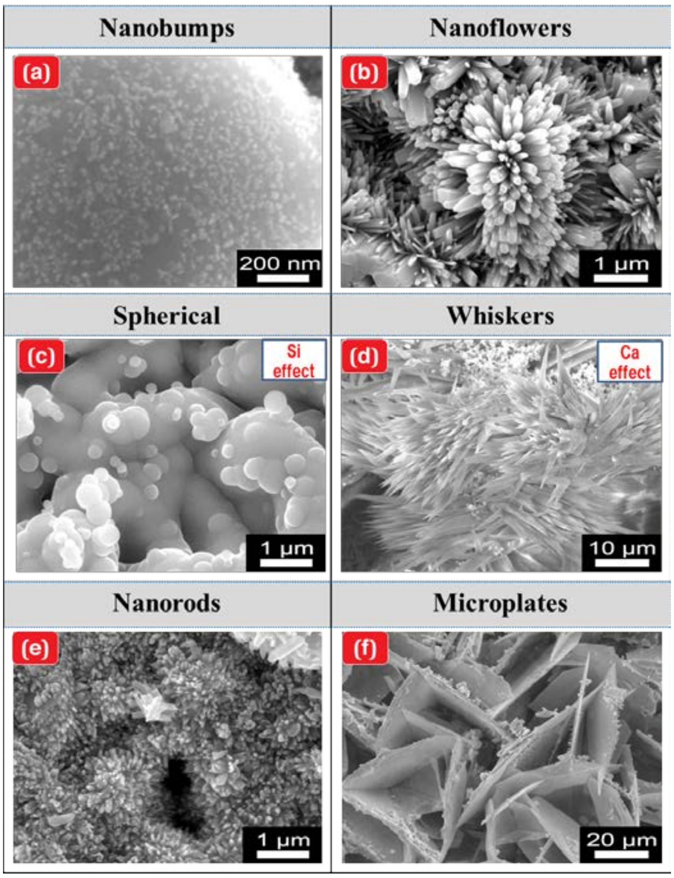

Fig. 1 Several FESEM images of morphology on Zn electrode. a, Plasma$_{(140\text{ V, }10\text{ min})}$. b, UV_{24h} in ultrapure water. (c-d), UV_{24h} in tap water. e, UV_{24h} in NaCl (0.60 M). f, UV_{24h} in NaCl (1.72M).

ZnO nanobumps (Fig.1a) is the growth seeds (ZnO nanoparticles) of the crystallites (Fig. 1(b-f)). It has a protruded characteristic when viewed from a direction that is perpendicular to the Zn base. The surface protrusion assumed to affect the ease of photo-induced water splitting process occurrence. Then, aggregation and recrystallization of ZnO nanoparticles resulted in the nanocrystallites growth at the apex of the protruded surface. This give rise to apical characteristic of the nanorods (some bunch of nanorods formed to be nanoflowers). The principles of the growth process can be explained by equations below:

$$ZnO + h\nu \rightarrow ZnO(e^-_{CB} + h^+_{VB}) \quad (1)$$

$$H_2O + h^+_{VB} \rightarrow OH + H^+ \quad (2)$$

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_{2\,(g)} \quad (3)$$

$$Zn^{2+} + OH + e^-_{CB} \rightarrow ZnO + H^+ \quad (4)$$

Net reaction:

$$Zn + H_2O + h\nu \rightarrow ZnO + H_{2\,(g)}$$

For the growth mechanism of solvents effect on crystallites (Fig. 1(c-f)) shape, it is proposed that the various species of ions and molecules constituting the growth medium affected the thermodynamics and kinetics of the crystallites growth at the protruded surface of nanobumps. In this aspect, the growth rate is shifted in an anisotropic fashion, to result in modification shape from nanorods to final shapes as in Fig. 1(c-f).

Fig. 1(e-f) exhibited the dependence of denser microplates formation on the increased molar ratio of NaCl. This result supports that addition of impurity is the key factor of the growth rate/phase change. It also remarks the necessity in tuning the other shapes by means changing the concentration.

4. Conclusion

We have demonstrated a working shape modification of ZnO crystallites by using SPSC technique. Nanobumps is essential as the initial growth unit and to allow photo-induced water splitting. In the case of changing the solutions, we propose that the growth rate of crystal is shifted at the protruded surface of nanobumps, which resulted in different shapes of crystallites. There is also dependence of molar ratio toward the formation of microplates. This highlights the key role of impurities for the modification of crystallites shapes.

5. Future work

Our future work is set to determine the chemical composition of the crystallites using X-ray diffraction analysis (XRD). Then, carry out concentration dependence experiments for the optimization of crystallites morphology, study their detail structures using transmission electron microscopy (TEM), and finally, to initiate opto-functional investigation towards the products.

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