# Synthesis of ZnO nanostructures using homo-seed layers by aqueous method

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ZnO nanostructures are grown on Si(100) substrate by two-step approach, including the synthesis of homo-seed layer and growth of ZnO nanostructures in aqueous solutions at low temperature. The effects of the seed layer concentration on the orientation, morphology and wettablility of ZnO nanostructures are investigated. The possible growth mechanism of ZnO nanostructures assisted with the seed layer is also discussed. The results show the seed concentration plays crucial role in determining the performance of ZnO nanostructures grown on Si(100) by aqueous solution. Different nanostructures can be obtained by controlling the seed concentration which will promote significantly the practical applications of ZnO materials.

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## 1. Introduction

ZnO is a promising material with unique properties of UV emission, optical transparency, electric conductivity, and piezoelectricity due to a wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature [1-3]. Various ZnO nanostructures, such as nanobelts, nanoribbons, nanotubes, and nanorods, have been fabricated by vapor phase techniques, such as metalorganic vapor phase epitaxy (MOVPE) [4], metalorganic chemical vapor deposition (MOCVD) [5], molecular beam epitaxy (MBE) [6] and pulsed laser deposition (PLD) [7], and by solution phase processes [8-9] such as solvothermal process and impregnation method [10]. However, the preparation methods cited above involve complex procedures, sophisticated equipment. Recently various low-temperature chemical methods have been developed to grow 1D ZnO nanostructures. Consequently, an exploration of ZnO nanostructures in highly oriented, aligned and ordered arrays is of great significance for the progress of novel devices. Many present efforts have been devoted to synthesize well-aligned ZnO low dimension nanostructures using ZnO seed layer [11-12]. Different groups have reported effect of ZnO seed layer for catalyst free growth of ZnO nanorods and its morphology, crystallinity and diameter by different methods [13-15]. For example, Vayssiers et al. have reported that the seeds had a weak effect on the morphology of ZnO nanostructures by using aqueous method [16].

In this work, we reported synthesizing morphology-controlled ZnO nanostructures by adjusting the seed layer concentrations. The effects of the seed layer concentrations on the orientation, morphology and wettablility of ZnO nanostructures were investigated. The possible growth mechanism of ZnO films assisted with the seed layer was also discussed. The results show the seed layer concentrations play crucial roles in determining the performance of ZnO nanostructures grown on Si(100). Different morphology and wettablility can be obtained by controlling the seed concentration. It will promote significantly the practical applications of ZnO materials.

## 2. Experimental

ZnO nanostructures were synthesized on Si(100) substrate through two-step growth, including the synthesis of homo-seed layer and the growth of ZnO nanorods in aqueous solution. The Si(100) substrate was seeded via spin-coating by various zinc acetate (Zn $(CH_3COO)_2 \cdot 2H_2O$) concentration solution. Three different seed concentration 5 mM, 10 mM, 50 mM were adopted to prepare ZnO seed layer, then annealing at 200°C to achieve a good adhesion. In a typical experiment an equimolar (0.05M) aqueous solution of zinc acetate $[Zn(C_2H_3O_2)_2]$ and hexamethyltetramine($C_6H_{12}N_4$) was prepared. All chemical reagents in the experiments were of analytical grade (AR) and used without further purification. The seeded substrates were putted into the above solution of 90°C for 5h. After deposition, the samples were cleaned with deionized water and then dried in an air atmosphere. Structural characteristics of as-grown ZnO nanostructures were investigated using X-ray diffraction (XRD). Field emission scanning electron microscopy (FE-SEM Hitachi S-4800) was used to investigate the morphology. The wettability of water on the ZnO nanostructures was measured using a SEO(Phoenix 300A, Surface Electro Optics Co. Ltd.) contact angle analyzer.

## 3. Results and discussion

Fig. 1(a–c) show the typical XRD patterns of ZnO nanostructures grown on Si(100) with different seed layers at, 50 mM, 10 mM and 5 mM, respectively. All the XRD patterns show the high degree of crystallinity, and the peaks match well with the standard wurtzite structure. In comparison with spectra Fig. 1 (b) and Fig. 1 (c), Fig. 1 (a) shows the strong sharp reflection of (002) with other diffraction peaks, indicating the multi-orientation character of ZnO nanostructures. With increasing the seed concentration, the other diffraction peaks decrease. For the nanostructures using 50mM seed concentration, it shows only (002) diffraction peak. In this study, the contribution of the diffraction peak intensity of the seed layer to can be reasonably neglected because of the small thickness of the seed layer, therefore the X-ray diffraction pattern can be directly referred to the following ZnO nanostructures. These results demonstrate the seed layer with different concentration can effectively induce the growth of the oriented ZnO nanostructures. As a result, the higher concentration of the ZnO seed layer, the better orientation of the following nanostructures becomes.

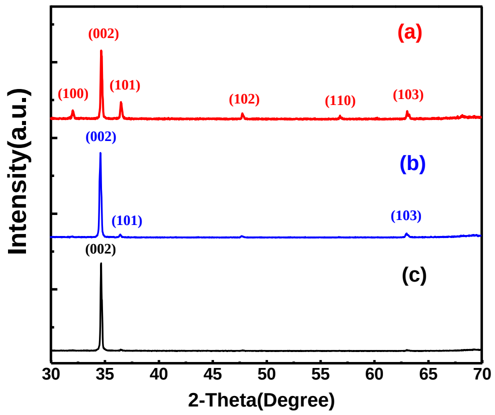


*Fig. 1. X-ray diffraction profiles of ZnO nanostructures grown with different seed concentrations: (a) 5 mM; (b)10 mM; (c)50 mM.*

Fig. 2 is the plan-view SEM images of the samples grown under different seeding concentrations. The SEM images reveal that morphologies of the nanostructures synthesized by various seeding concentrations are apparently different. Fig. 2(a-b) shows the ZnO nanostructures grown with 5 mM seed concentrations. These images reveal that flower-like bunches exist. Every bunch is composed of closely packed nanorods forms radiating structures. High magnification image shows that flower-shaped structures are composed of hexagonal ZnO nanorods. All the nanorods are observed apparently originated from a single center exhibiting flower-like morphologies. The typical diameters of these individual nanorods are in the range of 100–200 nm. Fig. 2(c-d) display the ZnO nanostructures grown with 10mM seed concentration. As it can be observed, the substrate was covered with quite dense and uniform ZnO nanorod arrays. Well-aligned hexagonal ZnO nanorods were grown vertically onto the surface of the ZnO-coated Si(100), which was also confirmed by the XRD analysis. The ZnO nanocrystals with obvious edges and corners can be observed in the high magnification. Fig. 2(e-f) represent the as-synthesized sample grown with 50 mM seed concentrations under different magnification. It can be seen film-like structure is obtained. It is composed of fully coalesced hexagonal rods which form continuous film with smooth surface morphology.

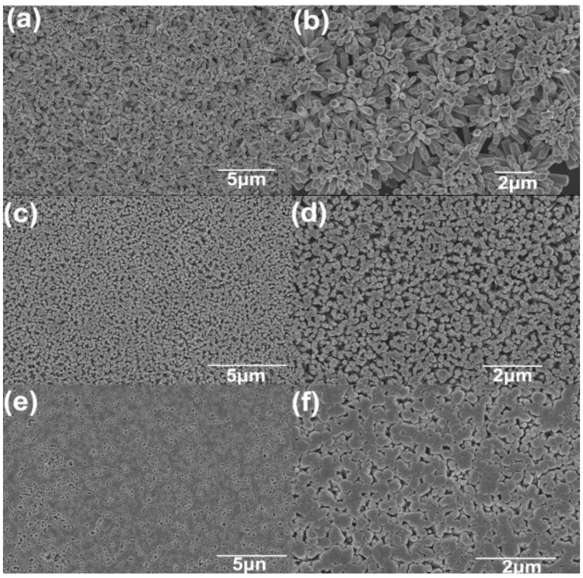


*Fig. 2. Low(a,c,e) and high(b,d,f) magnification SEM image of ZnO nanostructures grown with different seed concentrations. (a-b) 5 mM, (c-d) 10 mM, and (e-f) 50 mM.*

Fig. 3 shows the schematic growth diagram of ZnO nanostructures with different ZnO seed concentrations. The formation of nanostructures from aqueous solution involves two steps, nucleation and growth. Controlling the seed concentration during spin coating process has a strong effect on controlling the density of nucleation. In the case of using 5 mM seed concentration, the nucleation center will randomly distribute due to the lower concentration. During the process of growth, several ZnO nanorods are formed from the same nucleation site, resulting in the single center arranging shape of ZnO flower-like nanostructure. With higher seed concentration, such as 10 mM, the uniformly distributed ZnO seed layer will grow high alignment nanorods arrays. For using the 50 mM seed concentration, the two or more adjacent nanorods will coalesce by self-growth due to high nucleation densities. The lateral growth is promoted resulting in larger-diameter rods and film-like structure is obtained.

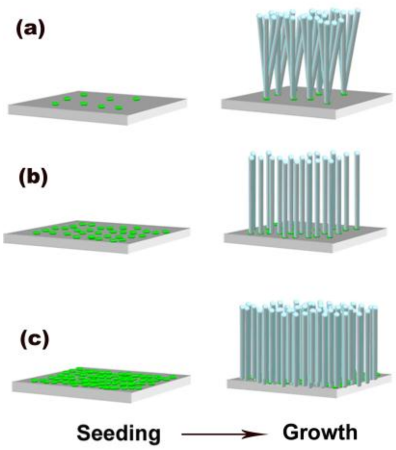


*Fig. 3. Schematic images presenting the ZnO nanostructures formation as a function of ZnO seed density.*

Fig. 4 shows the typical shape of water droplet on ZnO nanostructures grown by different seed layers. The wettability measurement of ZnO nanostructures on Si substrate with different seed concentrations shows that the water contact angle of 5 mM, 10 mM, and 50 mM is 122, 115, 94. The water contact angles of the ZnO nanostructures decrease with increasing the seed concentrations. As the single crystalline ZnO surface is relatively hydrophilic [17], water can easily wet the nanorods and fill the troughs in ZnO nanostructures. In this circumstance, the water contact angle on ZnO nanostructures can be described by Wenzel's model. According to the Wenzel's model, the surface roughness enhances not only hydrophobic but also hydrophilic properties. That is the contact angles less than 90° are decreased by roughness, while those greater than 90° are increased by roughness. In our case, the morphologies from nanorod arrays to film-like structures with the increase of seed concentrations. Thus, the nanostructures with different wettability can be achieved.

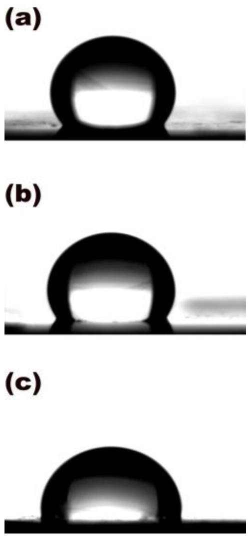


*Fig. 4. Photographs of water droplet shape on ZnO nanostructures grown with different seed concentrations: (a) 5 mM, (b) 10 mM, and (c) 50 mM.*

## 4. Conclusions

In summary, morphologies-controlled ZnO nanostructures were grown on Si(100) using different seed concentrations by aqueous method. The orientation, morphology and wettability of ZnO nanostructures grown on the different seed layers were studied. The results show the seed concentrations play crucial roles in determining the performance of ZnO nanostructures. The physical mechanism for the effect of the different seed layers on the nucleation and growth mode of ZnO nanostructures was also discussed. This study has a great significance in improving the performance of ZnO nanostructures grown on Si(100) materials, which will promote significantly the practical applications of ZnO materials.

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