

SELF-ASSEMBLY ZnO NANOSTRUCTURES FOR NANOSCALE DEVICES APPLICATIONS

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Abstract – We demonstrate a synthetic approach to self-assembly ZnO nanostructures on flat, spherical and curved surfaces. Self-assembly of ZnO nanorods was performed in aqueous solution. The effects of electric field, biopolymer assistance, as well as grow parameters, like temperature and molar ratio are studied. The nanostructures were investigated by SEM, XRD, EDX and TEM. All diffraction peaks of the ZnO nanostructures are well indexed to the hexagonal (space group $P6_3mc$) zinc oxide. Self-assembly ZnO nanostructures showed an encouraging characteristic and can be applied in future nanoscale fabrication. The self-assembly, as a tool to manipulate objects at nanoscale, offer possibility to be used in fabrication of electronic and photonic nanodevices applications.

Keywords: *self-assembly, ZnO nanorods, nanoscale devices, nanostructures.*

1. INTRODUCTION

As the limits of photolithography are rapidly approached and continued increases of the density of electronic devices on chip have stimulated the development of novel approaches and changes in the way electronic nanostructures are designed and operated [1]. The controlled fabrication of very small structures at scales beyond the current limit of photolithographic techniques is a technological goal of great practical and fundamental research [2,3]. In this context, self-assembly is a powerful mechanism, a reusable engineering concept which became a control mechanism for the bottom-up manufacture of complex systems. Self-assembly is the basic principle which produces structural organization. Understanding how self-assembly systems are produced in nature will be an enormous step forward in technology of microelectronics. Detailed studies of self-assembly will enable producing faster electronic devices, while current chip manufacturing processes are limited. Advances of systems design that exhibit self-assembly properties have been reported [4]. At the same time, has been observed increasingly research interests for one-dimensional nanostructures such as nanorods and nanowires due to their

importance to understanding fundamental physical phenomenon and to their exciting applied physics as functional nanobuilding units for new generations of nanodevices. Various nanomaterials have been synthesized and studied. Among them, zinc oxide (ZnO) is a semiconductor material with various configuration architectures much richer than of any other known nanomaterial [5,6]. It's properties assures conditions for formation of a richest micro/nanostructure diversity in comparison with other materials [1]. ZnO nanorods with their high carrier mobility serve as direct conduction pathways for excitons. In applications of nanomaterials-based devices, fabrication process represents the most important step in their realization. Thus, it is necessary to be mentioned, that have been developed different methods, techniques for synthesis of nanomaterials. The most developed techniques and detailed described in scientific literature are lithography, mechanochemistry, and more recently self-assembly [7,8], etc. Thus, assemble ZnO nanoscale building blocks into functional nanostructures is an important and very difficult task. In this paper, we report the synthesis and characterization of zinc oxide nanostructures, self-assembly and perpendicular oriented nanorods forming arrays, grown on a silicon wafer by a chemical method. The factors, influences the formation of ZnO arrays, were discussed based on the experimental results.

2. EXPERIMENTAL PART

2.1. Synthesis

Zinc sulfate and sodium hydroxide or ammonia from Fisher Scientific was mixed until complete dissolution. The aqueous complex solution was loaded into a reactor and a piece of cleaned silicon wafer was placed in the aqueous solution. To study the effect of the electric field, of the temperature and growth parameters on nanoarchitectures, the reactor was transferred into respective condition and positioned on

horizontal hot plate. It was heated to a preset temperature (in the range 60 - 100 °C) and held for 15-20 min. After reaction finished, the whole system was allowed to cool down to room temperature. Finally, the substrates were dipped and rinsed in deionized water and then the samples were dried in air at 150 °C for 5 min.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku 'D/B max' diffractometer, CuK α radiation ($\lambda=1.54178 \text{ \AA}$), operating at 40 kV and 30 mA. Samples were studied in a continuous scan mode at 30 - 80 ° (2 θ) with a scanning range of 0.01°/s. Peak positions and relative intensities of synthesized nanomaterials were compared to values from Joint Committee on Powder Diffraction Standards (JCPDS) card for ZnO (JCPDS 036-1451).

The morphology of the products was investigated using a scanning electron microscope (SEM, JEOL and a Hitachi S800) and high resolution transmission electron microscopy (TEM) (FEI Tecnai F30 TEM). The cathodoluminescence (CL) spectroscopy measurements with high spatial resolution were carried out at room temperature using a Gatan MonoCL3 cathodoluminescence system integrated with a Philips XL 30 SEM. The emitted radiation was analyzed using a single grating (1200 lines/mm, blazed at 500 nm) and a Hamamatsu photomultiplier tube. An electron beam accelerating voltage of 10 kV was used, corresponding to an electron penetration depth of about 0.5 μm . The CL measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

XRD measurements were used to probe the crystal structure, the phase composition and phase purity of ZnO nanorods. Typical patterns are depicted in Fig. 1(a). All diffraction peaks of the products are well indexed to a hexagonal wurtzite structured zinc oxide (space group $P6_3mc(186)$; $a = 0.32498 \text{ nm}$, $c = 0.52066 \text{ nm}$, JCPDS card #036-1451). From Fig. 1(a) for ZnO nanorods-based structures, only diffractive peaks in the pattern which belong to ZnO wurtzite structure were observed. From the Fig. 1a can be observed that the sample has a good crystalline phase, and dominated by the (002) plane and that all intensities indicate the good crystalline ZnO material. The EDXs (Figure 1b) further confirm that the nanorods are composed of zinc and oxygen with an atomic ratio 1:1.

Fabricating macroscopic objects as self-assembly is applicable but in scale of micro or nano it is a problem under worldwide research. That's why our research on self-assembly of special components as a strategy for producing ordered matters is strong. But, for designing

and fabricating these components, particularly those are on micro or nano-scale, there is no exact pathway to fabricate them. Next steps in report are presents the effects of temperature, biopolymers assistance, and electric field on the self-assembly process.

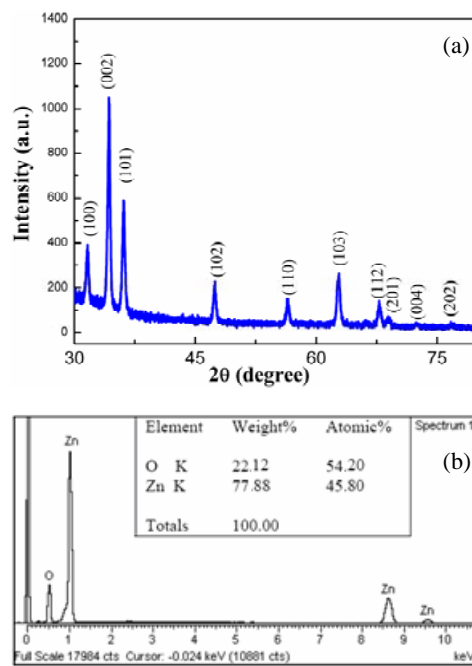
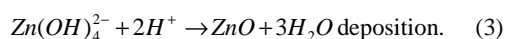
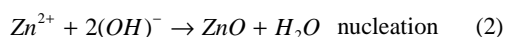


Figure 1: XRD pattern (a) and EDX spectrum of the ZnO nanorods-based nanoarchitectures.

The preferred crystallization can be explained by considering that ZnO wurtzite crystals have different growth rates for different planes: $V_{(0001)} > V_{(10\bar{1}0)}$. Because of these different growth rates, the controlled synthesis of preferred nanoarchitecture for specific applications can be realized. Due to the fact that the nucleation takes place at a low level of supersaturation of the complex solution, we can grow different ZnO nanoarchitectures (figure 2) by controlling the molar ratio, and process temperature. According to our experimental observation the growth of ZnO nanorods in aqueous solution can be explained as follows: As the temperature increases the following reactions occur [9]:



When the concentration of Zn^{2+} and OH^- exceed supersaturation, ZnO nuclei are formed. With

increasing temperature these complexes become dehydrated and heterogeneous nucleation of ZnO crystals takes place at the interface between substrate and solution. After that, the crystals will grow into nanorods. The $Zn(OH)_4^{2-}$ ions decompose to produce ZnO molecular species [10], which form seeds and grow to form hexagonal nucleus and finally individual nanorods and branched nanorod and three-dimensional nanoarchitectures.

Scanning Electron Microscopy image in Figure 2 shows the effect of temperature regimes on the self-assembly ZnO nanorods in sphere structure.

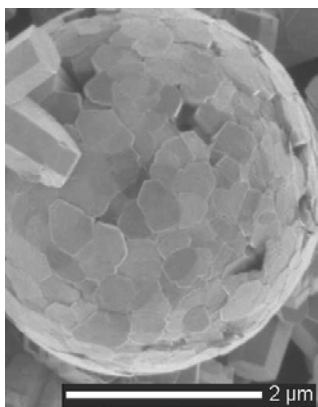


Figure 2: SEM images of ZnO nanorods self-assembled in spheres prepared by hydrothermal technique at 85°C for 20 min.

At the same time we observed an effect of the complex solution temperature on the one-dimensional growth. The higher is temperature the greater the Zn, ZnO mobility and 1-D nanorod growth.

Typical SEM micrographs of the ZnO architectures obtained by biopolymer-assisted self-assembly method is shown in Figure 3. Under the right circumstances, described in previous work [6], it is possible to grow ZnO nanorod-based microspheres using biopolymer concentration in the range 0.02 – 0.005 M of SA and reaction duration from 10 to 30 min at 100 °C. The morphology of the same sizes ZnO sphere presented indicates the 3D architectures consisted of ZnO nanorods with an average diameter of 100 nm. From Figure 3 we can see that the ZnO nanorods are arranged in a perfect spherical structure. The radius of ZnO nanorods-based spheres are around 5 μm. We investigate the possibility to control self-assembly process of 1D ZnO nanorods in 3D superstructures by different concentrations of organic biopolymer along with growth parameters.

The typical morphology of the ZnO nanorods prepared by hydrothermal synthesis under electric field after the growth time of 20 min is shown in Figure 4.

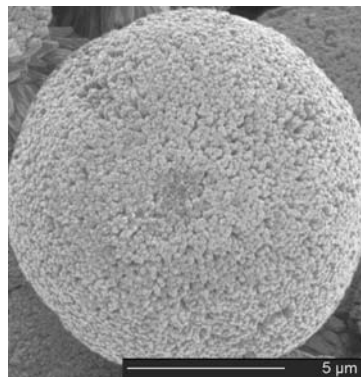


Figure 3: SEM images of ZnO nanorods prepared by biopolymer-assisted self-assembly route in the presence of 0.5M SA at 85 °C.

A SEM view in the Figure 4 illustrates ZnO with hexagonal symmetry nanorods on Si grown under electric field ($\sim 5 \cdot 10^2$ V/m) assistance. The radius of nanorods is 50 nm and the length is about 1 μm.

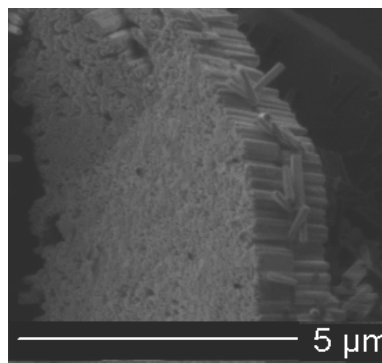


Figure 4: SEM images of self-assembly ZnO nanorods as bilayers grown under electric field assisted-assembly.

The impact of electric field on the assembly of nanorod arrays can be explained by the following mechanism. At the weaker electric field there is a larger distortion of electric field around the nanorod tips. This distorted electric field will conduct to attraction of more positively charged species Zn^+ , Zn^{2+} to the nanorod tip. But at the stronger electric field, the larger is the field enhancement and the distortion, which will contribute to a higher growth rate for the rods.

According to the TEM analysis can be mentioned that the entire as-grown ZnO nanorod is single-crystalline ZnO with a wurtzite structure grown along the [001] direction, which is consistent with the XRD results.

Figure 5 reveals an intensive UV emission at around 389 nm, which should correspond to the near band edge emission of the wide band gap of ZnO due to the

annihilation of excitons. Cathodeluminescence spectrum of the ZnO nanorods-based radial spherical structures exhibits an intensive UV emission at 389 nm at room temperature, which suggests a new candidate for fabricating optoelectronic nanodevices.

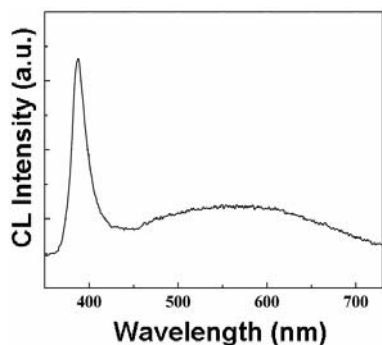


Figure 5: Cathodeluminescence spectrum of the ZnO nanorods-based nanostructures.

The method is simple, and may be extended to synthesize other inorganic materials with complex structures.

4. CONCLUSIONS

ZnO microspheres and nano-structures were synthesized through a temperature or biopolymer-assisted self-assembly route without template. The architectures are constructed of high-quality ZnO nanorods of 100-500 nm in diameter and 2-5 μm in length. Localized growth and alignment of ZnO nanorods on Si substrates was realized by a assisted-assembled system. This technique allows to ZnO nanorods synthesis and alignment using a DC electric-field. Enhanced control over ZnO nanorod alignment and organization is evident at higher field strengths. This process with its improved control yields a simple and reproducible fabrication method, which could be used in fabrication of nanodevices.

X-ray diffraction, energy dispersion X-ray spectroscopy, scanning electron microscopy, cathodeluminescence measurements have been used to characterize the samples. These characterizations reveal that the ZnO architectures assembled from hexagonal faced nanorods are found to have good crystal quality with *c*-axis orientation.

The benefits of this method are that it is possible to control the thickness in nano order and to construct heterostructures. Applications of nano-architected materials may overrun different industries including energy, electronics, medicine, display, and others. From the standpoint of such a versatile design, further investigations are underway.

Further work on the optimization of pure and doped ZnO nanorod -based 3-D architectures may lead to an extension of the proposed cost-effective and efficient self-assembly technique for fabrication of nano-scale devices and nano-system applications are in progress.

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