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Fast synthesis, morphology transformation, structural and optical properties of ZnO nanorods grown by seed-free hydrothermal method

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Abstract

A fast and low cost seed-free hydrothermal synthesis method to synthesize ZnO nanorods with controllable morphology, size and structure has been developed. Ammonia is used to react with water to tailor the ammonium hydroxide concentration, which provides a continuous source of OH^- for hydrolysis and precipitation of the final products. Hence allowing ZnO nanorods to growth on large areas of metal (Au and Ag coated glass), p-type Si and organic flexible (PEDOT:PSS) substrates. Increasing the growth time, the morphology transforms from pencil-like to hexagonal shape rod-like morphology. Within one hour the length of the ZnO nanorods has reached almost 1 μm . The optical characteristics has shown that the grown ZnO nanorods are dominated by two emission peaks, one is in the UV range centered at 381 nm and other one with relatively high intensity appears in the visible range and centered at 630 nm. While the growth duration was increased from 2 hours to 6 hours, the optical band gap was observed to increase from 2.8 eV to 3.24 eV, respectively. This fast and low cost method is suitable for LEDs, UV-photodetector, sensing, photocatalytic, multifunctional devices and other optoelectronic devices, which can be fabricated on any substrates, including flexible and foldable substrates.

Keywords: Seed-free growth ZnO, ZnO nanorods, hydrothermal method, low temperature growth.

1 Introduction Currently, one-dimensional nanostructures materials are attractive due to their excellent physiochemical characteristics. These nanostructures have huge potential for a variety of technological applications. Due to many reasons, zinc oxide (ZnO) is one of the most attractive nanomaterials for nanotechnology. ZnO is a wide band gap (3.37 eV) semiconductor materials having exciton binding energy (60 meV) and having excellent chemical stability, electrical, optical, piezoelectric and pyroelectric properties. Moreover, it is known to be a green material that is suitable for medical and environmental applications [1-4]. Among ZnO nanostructures, ZnO nanorods have been demonstrated to have broad applications in biosensor, photocatalytic, solar cell, light emitting diodes, ultraviolet photodetector, nanogenerators, and nano-piezotronic devices [2-14]. Synthesis of ZnO nanorods via the low temperature hydrothermal growth method is considered a promising technique due to the low cost and ease of fabrication. Moreover the properties and morphology of this nanomaterial can be tuned by controlling the growth conditions, e.g. temperature, precursor types, precursor concentration, pH, growth time, preparation conditions [15-22]. Nevertheless, the surface morphology of nanomaterials has a great influence on their properties and corresponding potential applications [23]. Therefore, to grow nanorods with controlled size, orientation, distribution, and uniformity on any substrates with low cost, fast and easy fabrication is of high interest.

This paper presents a fast synthesis of ZnO nanowires on metal thin films (Au and Ag), p-type Si, and organic flexible substrate (PEDOT: PSS) by seed-free hydrothermal methods. The morphology transformation, structural and optical properties of the grown ZnO nanorods are investigated. The ZnO nanorods growth developed here represents a fast and simpler method compared to the previously adopted approach which utilizes seeded substrate and using hexamethyltetramine (HMT).

2 Experimental procedure The growth procedure is described briefly. First, the 0.075 M precursor solution was prepared by mixing zinc nitrate hexahydrate [$\text{Zn}((\text{NO})_3)_2 \cdot 6\text{H}_2\text{O}$] in deionized water, using magnetic stirring of the mixture in a beaker. Then, ammonia solution was rapidly mixed into the zinc nitrate hexahydrate precursor solution until the solution pH reached 9 under stirring at room temperature for one hour. After that, the pre-cleaned substrates, including gold and silver coated glass, p-type Si, and flexible PEDOT:PSS on plastic were transfer to the growth solution and kept in a preheated oven at 90° C. Finally, the samples grown with different time durations have been collected for further characterization. The morphology of the grown ZnO nanorods were characterized by field emission scanning electron microscope (SEM), and the structure was characterized by x-ray diffraction (XRD) using Philips PW 1729 diffractometer utilizing $\text{Cu}_{k\alpha}$ operated at 40 kV and 40 mA. The optical properties were investigated by cathodoluminescence (CL) and additionally the optical band gap was obtained by UV-VIS-NIR spectrophotometer.

3 Results and discussion In a solution based growth of nano-crystals there are two processes, the nucleation and followed by the diffusion growth of the nanocrystals. The synthesis of nano-crystals should be designed in such a way that the nucleation occurs with the formation of a large number of nuclei in a short period of time [24]. In this experiment, ammonia rapidly reacts with water to produce ammonium hydroxide, which provides a continuous source of OH^- for hydrolysis and aids the precipitation of the final products. The rapidly mixed ammonia into the nutrient solution facilitates the homogeneous nucleation of ZnO on the substrate [25-26]. Therefore, when there is enough ammonia content in the nutrient solution, nuclei of ZnO crystals

were formed on the substrates and dense ZnO nanorods would be produced over a large area. Figure 1 shows the synthesis mechanism of ZnO nanorods via seedless hydrothermal process.

Figure 1 Synthesis mechanism of seedless hydrothermal process of ZnO nanorods.

The expected chemical reactions are given below [26-27]:

In addition, ammonia will lead to form zinc ionic complexes, which are absorbed on the side planes of the ZnO nanorods. This would lead to suppress the growth velocity of the side surface [27-28]. The generation of zinc ionic complex is given as:

To understand the morphology transformation during growth, the samples grown on p-type thin film substrates have been collected after 1 hour, 2hours, 4hours and 6 hours of growth durations. Figure 2 (a-c) show the SEM surface morphology images of ZnO nanorods grown at 1, 4 and 6 hours have transformed the morphology from pencil-like, truncated pencil-like, and rod-like morphologies, respectively. These results revealed that the growth duration plays an important role for decorating the morphology of the ZnO nanorods. It also noted that within one hour the nanorods with diameter vary from 150 to 360 nm reached almost $1\mu m$ length. This is an advantage compared to the much longer growth durations when HMT is used [29]. In addition, ZnO nanorods grown on metal thin films (Au and Ag) and organic flexible substrate (PEDOT: PSS) at 6 hours are shown in Figure 2 (d-f), respectively. It is clear that hexagonal shaped ZnO nanorods are possible to obtain using the present growth without HMT and without seed-layer on any type of substrates.

Figure 2 SEM images of seed-free grown ZnO nanorods on (a) Si wafer after 1 hour, (b) Si wafer for 4 hours, (c) Si wafer for 6 hours, (d) Au coated glass, (e) Ag coated glass and (f) flexible PEDOT: PSS substrate.

Figure 3 represents the XRD patterns of the ZnO nanorods samples grown on p-type Si wafer for 2, 4 and 6 hours. All the diffraction peaks located at 2θ values between $30^\circ - 65^\circ$ degrees are well consistent with the hexagonal phase of pure ZnO diffraction peaks (JCPDS #800075). Silicon peak appearing at 68° is not shown here. The x-ray diffraction spectra of ZnO nanorods show that the diffraction peak corresponding to the (002) planes is increasing as the growth duration has increased. This indicates that as the growth duration is increased, the ZnO nanorods are growing with a higher orientation along the c-axis. The increased intensity of the (002) peak

indicates that the aspect ratio of the ZnO nanostructures are also increasing [27], which is in good agreement with morphology transformation seen from the SEM (Figure 2). Therefore, in this method, the morphology and orientation of the ZnO crystals can be controlled to grow c-axis oriented nanorods by the growth duration used.

Figure 3 XRD pattern of ZnO crystal grown at 2, 4 and 6 hours.

Figure 4 shows a comparison of the room-temperature cathodoluminescence (CL) spectra of pure ZnO nanorods achieved for growth durations of 2, 4 and 6 hours, respectively. As can be seen, the CL spectra of the ZnO nanorods are dominated by two typical emissions; one is in the UV range centered at 381 nm, which is attributed to the near-band-edge emission, resulting from excitonic transitions between electrons in the conduction bands and holes in the valence band. The other peak is in the visible range and is centered at 630 nm. This peak is correlated to the electron–hole recombination due to deep levels within the band gap due to intrinsic point defects and surface defects, e.g., oxygen vacancies, zinc interstitials etc.. [2, 6, 8, 17 and 30]. This mission is very useful for visible LEDs and photo catalysis applications.

Figure 4 Room temperature cathodoluminescence spectra of nanorods at 2, 4 and 6 hours.

Figure 5 (a) shows the absorption spectra of the ZnO nanorods grown at different durations. The optical band gap of the grown ZnO nanorods was estimated using the following equation [31]:

$$\alpha = \left(\frac{k}{hv} \right) (hv - E_g)^\beta \quad (5)$$

Where α is the absorption coefficient, $\beta = \frac{1}{2}$ for direct band gap semiconductors and $k = \frac{\alpha\lambda}{4\pi}$ is the extinction coefficient, h is Planck's constant and hv is the incident photon energy.

$$\alpha = \left(\frac{k}{hv} \right) (hv - E_g)^{1/2} \quad (6)$$

$$(\alpha hv)^2 = C(hv - E_g) \quad (7)$$

The optical energy gap of the samples was obtained from the intercept of the linear portion with the x -axis of $(\alpha hv)^2$ vs hv curve of each sample. In our experiment, the optical energy gap of the grown ZnO nanorods using 2, 4, and 6 hours of growth duration are estimated to be 2.8 eV, 3.1 eV and 3.24 eV as shown in Figure 5 (b), respectively. These results indicated that then the growth time was increased the optical band gap of the samples were increased closer to the band gap of the crystal quality of ZnO (3.37 eV). Therefore, the growth time dependent the crystal quality of ZnO nanorods can improve by increase of growth time [32]. The result is in good agreement with our XRD analysis.

Figure 5 (a) UV-VIS spectrum of ZnO nanowires growth at 2, 4 and 6 hours, (b) optical band gap of ZnO nanorods growth at 2, 4 and 6 hours.

4 Conclusion In summary, we have demonstrated a fast and low cost synthesis procedure for growing ZnO nanorods with controllable morphology, size and structure by a seed-free hydrothermal method on large areas of metal thin films (Au and Ag coated glass), p-type Si, and PEDOT: PSS substrates. By increasing the growth duration, the morphology transforms from pencil-like to rod-like and within one hour the nanorods can reach almost 1 μm of length. All the grown ZnO nanorods were dominated by two emission peaks, one is in the UV range centered at 381 nm and other one appearing with high intensity is in the visible range and centered at 630 nm. The optical band gap of the grown ZnO is increased from 2.8 eV to 3.24 eV, when the growth duration was increased from 2 to 6 hours, respectively. Therefore, this rapid method is suitable for some important applications such as LEDs, UV photo detectors, sensing, photo catalysis, and for other optoelectronic devices.

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