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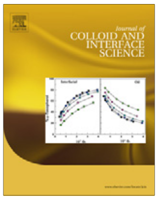

In situ application of polyelectrolytes in zinc oxide nanorod synthesis: Understanding the effects on the structural and optical characteristics

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ABSTRACT

We report a facile and simple means of synthesizing a macroscopic array of ZnO nanorods with high feature densities using a modified hydrothermal approach that involves the in situ introduction of polyelectrolyte. The ZnO nanorod arrays with heights of 1.5 μm and diameters of 350 nm were consistently reproducible and were bestowed with the advantage of in situ process tunability offered by employing polyethylenimine (PEI) as a surface modifying agent. The fabrication combines benefits from the hydrothermal approach in terms of process simplicity and flexibility and from the use polyelectrolyte that offers a better nanorod surface, quenched defect levels and enhancement of the UV band edge emission. Structural and elemental analysis of the PEI-modified and unmodified nanorods emphasize the fact that the intentional introduction of PEI results in a nanorod with better surface quality as evidenced by photoluminescence (PL) spectra. The tunability of the feature dimensions of the nanorods and an analysis of the bulk and surface (surface defect) responses to the PL point to significant promise of high density orthogonal nanorods in a number of optoelectronic applications. While the defects in the ZnO nanorods can point towards the application of ZnO nanorods in charge trap flash memory devices, highly crystalline, size tunable, high aspect ratio nanorods find applications as building components in solid state lighting.

1. Introduction

Nanomaterials conforming to the desired needs of the researchers have always been exploited owing to the advantages offered in terms of material and structural properties, process flexibility and reproducibility ultimately resulting in the commercialization of the products. The ability to fabricate metal oxide structures on a nanoscale has distinct advantages that are widely sought after. Among a variety of materials, ZnO has always been unique and is continuing to be the material of interest owing to its excellent electronic, optical and semiconducting properties along with the flexibility it offers in handling and processing, thereby finding applications in sensing [1], solid state lighting [2,3], electronic devices [4,5] and solar cells [6]. Synthesis of nanorods [7], nanowires [8], nanotubes [9], nanofilms [10,11] using variety of semiconductor materials, and ZnO, in particular, is of crucial importance for engineering devices for specific applications [12]. The functions and capabilities of these devices are very much associated with the morphology of nanostructures and hence they require a good degree of tunability for optimal performance. Although many state-of-the-art techniques for synthesizing ZnO nanostructures with different morphologies such as metal organic chemical vapor deposition (MOCVD) [13], radio frequency sputtering [14], atomic layer deposition (ALD) [15], catalyst assisted vapor–liquid–solid deposition (VLS) [16,17] are employed, they demand either clean room processing conditions with high capital investment or high temperature operations leading to high energy consumption, material wastage and contamination due to catalyst residues.

When a level of control on high feature density over a macroscopic area, as well as the complexity of structures attainable is targeted, hydrothermal synthesis, a simple, cost effective approach is on par with what are achievable utilizing clean room tools [9,18]. Such high density ZnO nanorods on silicon based substrates with tunable geometric characteristics are of prime interest in semiconductor compatible technologies.

In nanomaterials processing, understanding and differentiating the bulk and surface properties becomes vital as they exhibit different optical and structural qualities. This influences and determines the utility of the synthesized nanostructures in many applications. This is best understood when the ZnO nanostructures fabricated using an external surface modifier such as polyelectrolytes is compared for the surface properties with unmodified nanorods. There are reports on the utilization of cationic dispersants like polyethylenimine [19,20] and surfactants like polyvinyl alcohol [21] in the growth of the ZnO nanostructures discussing the protocol to tailor the sizes of the nanostructures. However, sufficient focus has not been placed on the changes that take place

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on material surface due to the introduction of the external agents. In ZnO nanorods, the surface properties differ significantly from those of the bulk counterpart due to the surface related effects; these effects manifest themselves in the emission properties that are studied using photoluminescence spectra [22,23]. In order to demonstrate the distinct variation in the bulk and surface properties of the ZnO features in our investigations, we have developed a cost effective protocol that offers good control over the growth of well aligned ZnO nanorods on a macroscopic scale using high molecular weight polyethylenimine (PEI) whose intentional introduction chemically tailors the size of nanorods in situ and offers a better crystal surface. To probe the influence of PEI on the ZnO surface modification and to study the defects associated with it, a photoluminescence emission map of the nanorods with and without PEI modification revealing information about the nanorod defect levels that act as trap states, helps in differentiating the bulk and surface contributions.

ZnO nanorods were grown on bare Si (1 0 0) substrates using the conventional and cost effective aqueous chemical growth (ACG) technique [7]. The nanorods thus formed had diameters of several hundred nanometers and could be chemically tuned by the introduction of polyelectrolytes in the growth solution which resulted in the formation of rods with controlled diameters and enhanced growth predominantly in the (0 0 2) direction normal to the substrates over macroscopic areas. Optical and structural characterizations were performed to study the nature of the resulting PEI-modified and unmodified nanorods to highlight the role played by PEI in influencing the crystal surface quality.

2. Experimental

2.1. Materials

Acetone and 2-propanol were obtained as anhydrous solvents with purity >99% from Sigma–Aldrich Pte Ltd. and used without further purification. Prime grade silicon wafers were obtained from Silicon Valley Microelectronics (Santa Clara, CA, USA). Zinc acetate dihydrate and hexamethylenetetramine were obtained from Merck. Polyethyleneimine of molecular weight 750,000 g/gmol was purchased from Sigma Aldrich. Point Probe Plus silicon tips for tapping mode imaging measurements with atomic force microscopy were purchased from Nanosensors (Neuchatel, Switzerland).

2.2. Methods

The Si substrates were diced into 2 × 2 cm chips using the Disco automatic dicing and cleaning system. The silicon substrates were cleaned by ultrasonicating in acetone followed by 2-propanol and finally treated with UV/Ozone (SAMCO UV-1, SAMCO Inc., Kyoto, Japan) for 10 min duration. Hydrothermal growth of the ZnO nanorods was carried out using an equimolar quantity (0.001–0.05 M) of zinc acetate dihydrate and hexamethylenetetramine as precursors. To compensate for the lattice mismatch between the silicon substrate and the ZnO nanorods, a seed layer was deposited on the substrate by spin coating a solution of 0.01 M zinc acetate dihydrate in ethanol 4–5 times. After every coating the seeded substrates were heated to 350 °C for 10 min. The substrates were then immersed in the growth solution for 5–8 h at 85 °C. For the PEI modified hydrothermal process, 100 μL of 1 wt.% polyethylenimine (molecular weight of 750,000 g/gmol) was added to the growth solution prior to the immersion of the seeded substrates. The concentrations of the precursors were as high as 200 mM to realize the size tailoring effects of PEI. The seed pattern characteristics were imaged using tapping mode AFM (Nanoscope IV Multimode AFM, Veeco Instruments Inc., NY, USA) and SEM (FESEM 6700F, JEOL, Tokyo, Japan). The EDS (energy dispersive spectroscopy) studies were carried out on a JSM (5600LV) SEM (scanning electron microscopy) instrument. Samples for the transmission electron microscopy (TEM) characterization were obtained by dispersing the nanorods in water and placing a few drops of the solution on a Cu grid. The TEM images were obtained using a Philips CM300 TEM operating at 300 kV. X-ray photoelectron spectroscopy (XPS) measurements were made on a Kratos Analytical AXIS HSi spectrometer with a monochromatized Al Kα X-ray source (1486.71 eV photons) at a constant dwell time of 100 ms and pass energy of 40 eV. In peak analysis, the line width (full width at half-maximum or FWHM) for the Gaussian peaks was maintained constant for all components in a particular spectrum. FTIR spectra for ZnO nanorods were obtained on a Bio-Rad FTIR (model-400 spectrophotometer, PA, USA) with a deuterated triglycine sulfate (DTGS) detector by accumulating 1024 scans at a resolution of 4 cm^{-1} with incidence angle of 75°. A reflectance-mode configuration was employed and a bare silicon wafer was used as the background. The sample compartment was purged with nitrogen for 15 min prior to carrying out the scans. UV–visible absorption spectra were recorded on a Shimadzu UV-3101 PC scanning spectrophotometer. X-ray Diffractometer system (XRD 6000, Shimadzu, Tokyo, Japan) used in the analysis employed Copper as the target with an output voltage of 40 kV and current of 30 mA. The scans were continuous with a scan speed of 3 deg/min and 1° divergence and scatter slit. Photoluminescence spectra were obtained using a luminescence spectrometer (QuantaMaster, Photon Technology International, Inc., Birmingham, NJ, USA) employing a Xenon Flash lamp as the excitation source covering the UV–visible wavelength range. The series of excitation wavelengths was set and the corresponding emission spectra were recorded.

3. Results and discussion

Polyelectrolytes undergo protonization in water to become charged species. The interaction of the protonized molecules with their oppositely charged counterparts can be exploited as an in situ size tailoring agent systematically controlling the local reaction environment during the growth of ZnO nanorods [24]. When a polyelectrolyte such as polyethylenimine protonizes in the nutrient aqueous solution for the growth of ZnO nanorods, a part of the positively charged species wrap themselves around the lateral facets of the nanorods [25]. This offers an opportunity to control the lateral dimensions of the ZnO nanorods in situ. This is further explained in our experiments when we modified the growth solution consisting of equimolar concentrations of zinc acetate dihydrate and hexamethylenetetramine by adding a 100 μL of 1 wt.% PEI. The concentrations of the precursors were as high as 200 mM. It is well established that, as the concentration of the precursor increases, the dimensions of the nanorods formed also increases [26]. Hence, the amount of PEI added is optimized to ensure that the nanorods produced are of the same dimension (~300–320 nm) as the nanorods produced with the growth solution of concentration 0.05 M without PEI to substantiate the tailoring effect of PEI. It is possible to further reduce the size of the rods by adjusting the molar ratio of the precursors and the polyelectrolyte such that there is always the likelihood to produce ZnO nanowires of high aspect ratios [27]. Higher the concentrations of PEI, smaller would be the sizes of the ZnO nanorods and vice versa.

We attribute this feature to the dual role played by PEI [27]. When PEI protonizes at a pH of about ~8.5, it produces the positively charged PEI molecules that aid in the formation of a zinc-amino complex which in turn reduces the supersaturation of zinc