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Effect of ZnO seed layer on the catalytic growth of vertically aligned ZnO nanorod arrays

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ABSTRACT

We have grown vertically aligned ZnO nanorods and multipods by a seeded layer assisted vapor–liquid–solid (VLS) growth process using a muffle furnace. The effect of seed layer, substrate temperature and substrate material has been studied systematically for the growth of high quality aligned nanorods. The structural analysis on the aligned nanorods shows *c*-axis oriented aligned growth by homoepitaxy. High crystallinity and highly aligned ZnO nanorods are obtained for growth temperature of 850–900 °C. Depending on the thickness of the ZnO seed layer and local temperature on the substrate, some region of a substrate show ZnO tetrapod, hexapods and multipods, in addition to the vertically aligned nanorods. Raman scattering studies on the aligned nanorods show distinct mode at ~438 cm^{-1}, confirming the hexagonal wurtzite phase of the nanorods. Room temperature photoluminescence studies show strong near band edge emission at ~378 nm for aligned nanorods, while the non-aligned nanorods show only defect-emission band at ~500 nm. ZnO nanorods grown without the seed layer were found to be non-aligned and are of much inferior quality. Possible growth mechanism for the seeded layer grown aligned nanorods is discussed.

1. Introduction

ZnO nanostructures have attracted lots of interest due to its unique features such as wide band-gap (3.37 eV) and large exciton binding energy (60 meV) [1,2] and wide applications in nanosize electronic, optics, sensors and optoelectronic devices [3–6]. ZnO is one of the key materials in nanotechnology and nanosystems. ZnO have the capability to crystallize into many configurations resulting in diverse growth morphologies such as nanocrystalline films, rods, wires, springs, combs, belts, helixes, prisms, tetrapods, etc. [7–15]. Several techniques have been used to grow ZnO nanowires. For example, thermal evaporation and condensation [16], metalorganic chemical vapor deposition (MOCVD) [17] and molecular beam epitaxy (MBE) [18] have been employed. Among them, the vapor–liquid–solid (VLS) deposition method involving the vapor-transfer process and thermal evaporation is the most frequently used method. For the production of high quality ZnO nanowires/nanorods, catalysts, such as Au, Cu and NiO, etc. [19–21] have been most commonly used. The catalysts can improve the controllable growth of ZnO nanostructures. Catalyst free growth of only ZnO tripods [22] or tetrapods [15] has been reported. To our knowledge there was no such report on ZnO seed layer assisted growth of ZnO multipods (tetrapods and hexapods). 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 [23–25]. The crystalline quality of the ZnO seed layer strongly controlled the structural quality of the nanorods. In most of the cases synthesized nanorods were not aligned, hence have limited applications in nanosize electronic and optoelectronic devices. Therefore, it is crucial to have controlled and well aligned growth of ZnO nanorod arrays. Ultra thin layer and uniform distribution of ZnO seed in the ZnO layer are the key factors for well aligned vertical growth of ZnO nanorods. Zhao et al. have reported high temperature growth of vertically aligned ZnO nanorods on Si by with a thin ZnO seed layer [26]. However, effects of growth temperature, substrate material and overall quality of the nanorods have not been studied. Here, we report the effect of pre-depositing ZnO seed layer on the structure, morphology and optical properties of gold catalytic grown vertically aligned ZnO nanorods arrays at different temperatures.

In this work, we have grown vertically aligned ZnO nanorods and multipods by a seeded layer growth techniques, using the VLS process. The effect of ZnO seed layer along with an Au catalyst layer and the growth temperature in the growth of vertically aligned ZnO nanorods are studied using structural and optical tools. Results are compared with the nanorods grown without the ZnO seed layer.

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2. Experimental details

Vertically aligned ZnO nanorods were grown on Si substrates. Si(1 0 0) n-type doped substrate was first cleaned in trichloroethylene, acetone and methanol under ultrasonic bath for 15 min each to remove impurities and organic grease. The native oxide layer was etched out with buffer hydrofluoric acid solution. After each step, the substrate was rinsed with deionized water several times. Finally this was dried with N_2 gas blow. This substrate was used for VLS growth of vertically aligned ZnO nanorods by a three-step process. In the first step, a ZnO seed layer was deposited by RF-magnetron sputtering system. Sputtering was done at incident power of 100 W for 30 min at substrate temperature 300 °C. Argon and oxygen are used as reacting gases. In this process ∼35 μm thick ZnO seed layer was deposited on Si(1 0 0) substrate. In the next step, an ultra thin (∼50 Å) layer of gold was deposited by a mini sputtering system. The thickness of 50 Å for the Au layer was chosen for optimum growth of high quality nanorods. Finally, vertically aligned ZnO nanorod arrays have been grown by VLS process. In this process, a mixture of high purity ZnO powders (Sigma–Aldrich 99.999% purity) and high purity graphite powders (Fluka, 99.99%) at a weight ratio of 1:1 was used as a source. A quartz boat containing powder mixture was loaded in the central hot zone of 1000 °C inside a horizontal quartz tube, which is already placed inside the muffle furnace. The substrates are placed in downstream direction at various temperature zones (700–900 °C). Then furnace is ramped to 1000 °C and deposition was continued for 15 min with Argon gas flow rate 70 sccm (standard cubic centimeter mass). After deposition the entire system was cooled to room temperature and the synthesized product was taken for characterization. For comparison, growth experiment also performed at a substrate temperature of 800 °C on an Au coated Si substrate i.e. without predisposition of ZnO seed layer. To study the effect of substrate materials/orientation, similar experiments were performed on Au coated quartz substrate at 750 °C.

The as-grown ZnO nanorods were characterized with X-ray diffraction (XRD) (Bruker Advance D8, with CuKα radiation), scanning electron microscopy (SEM) (LEO 1430VP). Room temperature photoluminescence (PL) measurements were performed with 325 nm laser excitation from a He–Cd Laser using a commercial fluorimeter with a single monochromator (Edinburg, FS-920P). Raman measurements were performed with a 488 nm Ar ion laser excitation and a monochromator (Jovin-Yvon, Triax 550) in the back-scattering geometry. FTIR measurements were performed in the range 400–4000 cm^{-1} using a standard FTIR spectrometer (PerkinElmer, Spectrum BX).

3. Results and discussion

XRD is an ideal probe to characterize structure and orientation of thin film with respect to the substrate. XRD pattern of the as-grown ZnO seed layer is shown in Fig. 1(a) which reveals (0 0 2) oriented growth of the ZnO film. Fig. 1(b–d) shows the XRD spectra of the ZnO nanorods grown on Au coated ZnO seed layer at 900, 850 and 700 °C, respectively, while Fig. 1(e and f) shows the XRD patterns of ZnO nanorods grown at 800 and 750 °C without the seed layer on Si and quartz substrates, respectively. The nanorods grown with the seed layer show high crystallinity, the strong peak at 34.46° due to the ZnO(0 0 2) plane indicates the growth direction along *c*-axis of ZnO and is normal to the substrate plane. One strong (0 0 2) peak of hexagonal ZnO and small full width at half maximum (FWHM) value from the XRD patterns (Fig. 1(a–c)) indicates the *c*-axis of the single crystalline ZnO nanorods is well aligned and the growth direction is perpendicular to the base surface. Relative intensities of the XRD peaks in Fig. 1(a–f) show that nanorods grown at higher temperature have high value of peak intensity, which confirms higher crystallinity. The as-grown nanorods at 900 °C show small FWHM (0.0305°) and largest XRD peak intensity, which is ∼1.6 times higher than the XRD intensity of nanorods grown at 850 °C. And the nanorods grown at 700 °C (Fig. 1(d)) show large FWHM (0.0987°) and weak (0 0 2) peak intensity, which is ∼46 times smaller than the nanorods grown at 900 °C. XRD results clearly show that no preferential growth takes place for the growth of nanorods at 700 °C. Using Scherrer formula, we have calculated the diameter of the nanorods grown at 900, 850 and 700 °C, which are 273, 315 and 84 nm, respectively. We have found from XRD analysis that Au coating on ZnO seed layer induces a [1 1 1] orientation of the Au clusters at high temperature. The nanorods grown at 700 °C do not show preferential orientation, as evident from Fig. 1(d). Note that nanorods grown without the seed layer does not show any preferred orientation and possess inferior crystallinity as compared to that grown with seed layer. The additional peak of 43.1° in Fig. 1(e) is related to the graphite which is used during the VLS growth as a reducing agent. We have found that a substrate temperature below 800 °C is not favourable for the growth of (0 0 2) oriented nanorods by the VLS method. Note that previous study reported growth of aligned nanorods at 950 °C, which is relatively high [26].

Fig. 2(a–c) shows typical SEM morphology of ZnO nanorods grown on Au/ZnO/Si substrate at various growth temperatures. The nanorods grew in vertically on the substrate at 900 °C, as seen from Fig. 2(a). The inset in each case shows the magnified view of the aligned nanorods. The sizes of the nanorods are in the range of few

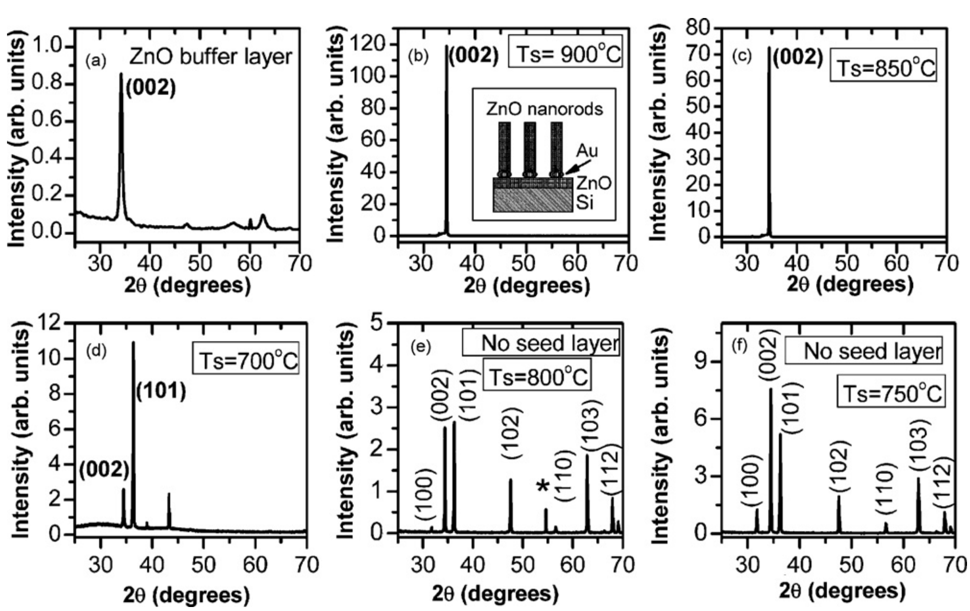

Fig. 1. XRD spectra of ZnO seed layer and nanorods array. (a) Sputter deposited ZnO seed layer on Si substrate. (b–d) Vertically aligned ZnO nanorods grown at substrate temperature (T_s) 900, 850 and 700 °C, respectively. Inset in (b) shows schematic diagram of various layers grown along with the ZnO nanorods. (e) Non-aligned ZnO nanorods grown at T_s = 800 °C without any ZnO seed layer, (f) ZnO nanostructure grown on quartz substrate at 750 °C. Seeded layer grown nanorods show only *c*-axis oriented structures, while the nanorods grown without the seed layer show no preferred orientation.