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Synthesis of vertical arrays of ultra long ZnO nanowires on noncrystalline substrates

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ABSTRACT

Vertically aligned arrays of ultralong ZnO nanowires were synthesized on SiO_2 substrates with carbothermal vapor phase transport method with Au seeding layer. High density of vertically aligned ZnO nanowires with lengths from a few to ~300 μm could be grown by controlling growth conditions. Supply of high concentration of Zn vapor and control of the ratio between Zn vapor and oxygen are found to have the most significant effects on the growth of long ZnO nanowires in the vapor–solid growth mechanism. The nanowires are of high crystalline quality as confirmed by various structural, compositional, and luminescent measurements. Luminescent and electrical properties of ZnO nanowires with different growth conditions were also investigated.

1. Introduction

There have been a plethora of studies on ZnO and its nanostructures in the last decade [1–3]. As a wide-bandgap II–V compound semiconductor with the bandgap of ~3.6 eV, ZnO has attracted interests for its possible applications in optoelectronic and electronic devices [1]. In the last decade, it has been shown that various kinds of ZnO-based nanostructures such as nanorod/nanowire [4], nanobelt [5], and more complicated branched structures such as tetrapod [6] and nanoflowers [7] can be synthesized relatively easily and have attracted renewed interests with their unique optical, electrical, and piezoelectric properties. In addition to the applications in optoelectronic devices such as light emitting diode, various new applications especially with nanostructures have been proposed and demonstrated. For example, it was demonstrated that ZnO, both as a semiconducting and piezoelectric material, can be used to generate electricity with mechanical excitations [8,9]. ZnO nanowires can also be used in photovoltaic devices as transparent n-type conductors or efficient carrier paths [10,11]. For many applications based on ZnO nanostructures, synthesis of ZnO nanostructures on specific substrates suitable for each application is required. For example, vertically or horizontally aligned array of long ZnO nanowires on both conducting and nonconducting substrate can be useful for piezoelectronic or photovoltaic applications. Also growth on cheap noncrystalline substrates can be more useful for commercial applications.

Various methods have been employed to synthesize ZnO nanostructures, especially quasi-one-dimensional (1D) structures such as nanowires and nanorods. ZnO nanowires or nanorods have been successfully grown by various ways such as molecular beam epitaxy [12], metalorganic chemical vapor deposition [13], carbothermal chemical vapor phase transport [4], electrochemical deposition [14], and hydrothermal [15] method with or without catalyst. In most cases, the synthesized ZnO nanowires are crystalline with wurtzite structures and grow along [0 0 0 1] direction. Chemical vapor phase transport method is one of the most widely employed methods to grow ZnO nanowires for its ease of use and high growth rate. In this method, either vapor–liquid–solid (VLS) or vapor–solid (VS) mechanism seems to work depending on the growth condition such as temperature, catalyst, and vapor pressure of reactive gas even in the presence of catalyst (usually Au) [16,17]. Despite many efforts to optimize or control the growths of ZnO nanowires, reports of vertically aligned ZnO nanowires on various substrates longer than tens of μm are rare [18,19] and process variables affecting growth morphologies are still not well known. Also growths of arrays of ZnO nanowires on nonconducting and noncrystalline substrates such as SiO_2 are relatively less studied [20,21] than on crystalline substrates such as Si and Sapphire.

In this work, we investigated various growth conditions to synthesize vertically aligned ultra-long ZnO nanowires on Si/SiO_2

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substrate by vapor phase transport method using Au seed layer. We tried to identify growth conditions allowing fast growth of vertically aligned long ZnO nanowire arrays. By optimizing vapor ratio between Zn and oxygen, we could grow vertically aligned ZnO nanowires on SiO_2 substrates as long as 300 μm. We also investigated structural, compositional, optical, and electrical properties of ZnO nanowires grown this way.

2. Material and methods

ZnO nanowires are synthesized using vapor phase transport method with carbothermal reduction process in a dual tube low pressure chemical vapor deposition (LPCVD) system as schematically shown in Fig. 1 [22,23]. The dual tube CVD system consists of an outer horizontal quartz tube (750 mm in diameter) and inner quartz tube (800 mm in length and 20 mm in diameter). Temperature at the center region (~15 cm) of the furnace at the reaction temperature range (850–1000 °C) is stable within 5 °C. The inner tube has only one end open. A mixture of pure ZnO (0.5 g, Aldrich, 99.99%) and graphite powder (0.5 g, Sigma Aldrich, particle size ≤20 μm) is used as a source material and loaded into the inner tube. By employing the dual tube geometry, we could maintain high concentration of Zn vapor around the substrates without contaminating the rest of the outer tube. As shown in Fig. 1, the open end of the inner tube is directed to downstream of the gas flow. In this way, reactive gas molecules diffuse into the reaction area and have more dwell time around the substrates in more static environment. We tried both Si(100) and Si(100)/SiO_2(200 nm-thick) as substrates for the growth with similar results. Only the results on Si(100)/SiO_2 substrates are presented in this paper. Substrates are cleaned using a standard wafer cleaning procedure and then coated with a thin Au layer (<5 nm as measured with a quartz crystal thickness monitor) by e-beam evaporation. The Au coated substrates are located at the downstream of the small tube, 30 mm away from the source. Before heating, the furnace is purged with high purity nitrogen gas and pumped down to ~1 kPa in order to remove residual oxygen in the furnace. For the growth, both the source and the substrate is heated to the reaction temperature (850–1000 °C) under high purity nitrogen (carrier gas, 140 sccm) and oxygen gas flow (5–110 sccm). The system is kept for 40 min for the growth. After evaporation and deposition, the inner quartz tube is drawn out of the furnace when it has cooled down to about 60 °C. This procedure produced a white layer of ZnO nanowires on the substrates.

The shapes, structures, and composition of the samples are examined using a field emission scanning electron microscope (HITACHI, S4800 FESEM) and a field emission transmission microscope (JEOL, JEM-2100F Cs-corrected TEM), both equipped with energy dispersive X-ray spectrometers (EDS). The X-ray diffraction (XRD) patterns are acquired by a Rigaku system using graphite monochromated CuKα (λ = 0.1541 nm) radiation. Room temperature Raman scattering spectra were measured using a McPherson 207 spectrometer equipped with a nitrogen-cooled-charge-coupled device (CCD) array detector. The samples were excited with 1.5 mW of 488 nm line of a diode laser focused to ~1 μm using a microscope objective. Luminescence properties of nanowires are investigated both by photoluminescence (PL) and cathodluminescence (CL) measurements. PL spectra of the samples are acquired at room temperature with an excitation wavelength of 325 nm (Hitachi, F-7000). CL spectra are obtained at room temperature with a Gatan MonoCL3+ system equipped with a high-sensitivity photo multiplier tube (PMT) attached to an SEM (HITACHI, S-4300SE). Acceleration voltage of 10 kV is used for all the CL measurements presented in this paper. For the electrical measurements, as-grown ZnO nanowires are transferred to highly doped Si substrates (n-type, <0.005 Ω cm) with a 200 nm-thick SiO_2 layer by mechanical rubbing of the as-grown samples (contacting a substrate with as-grown vertical ZnO nanowires on a clean target substrate and sliding sideways while exerting pressure) and or after dispersing in ethanol solution with ultrasonic agitation. Electrode patterns with gap sizes of 2–6 μm are defined by photolithography and metal electrodes consisting of Ti (100 nm)/Au (20 nm) are formed by e-beam evaporation and lift-off processes. I–V characteristics are obtained with a probe station in the ambient environment with a semiconductor parameter analyzer (Keithley, 4200-SCS).

3. Results and discussion

Representative results of the ZnO nanowires grown on Si/SiO_2 substrates are shown in Fig. 2, although differences exist depending on the growth conditions. Fig. 2a shows a side view SEM image of ZnO nanowires grown at 920 °C with 40 sccm of O_2 flow. Fig. 2a shows that ZnO nanowires are vertically well aligned with length of ~35 μm while diameters are 100–150 nm. Fig. 2b shows a top view image of ZnO nanowires grown with the same condition. Fig. 2a and b show all the general features of ZnO nanowires synthesized as explained in Section 2; (1) Vertically well aligned and mostly longer than 10 μm. (2) No catalyst particles are found at the end of the nanowires. (3) Nanowires show hexagonal cross-sections. (4) There is a thick underlayer (up to several μm) between the substrates and nanowires. Atomic resolution TEM image and SAED pattern in Fig. 2c, and XRD spectrum in Fig. 2d also demonstrate high crystallinity of the ZnO nanowires with the wurtzite structure and dominant growth direction along *c* axis with a lattice spacing of 0.52 nm. Raman spectrum in the inset of Fig. 2d shows transverse optical (TO) and longitudinal optical (LO) components of the A_1 and E_1 branches, along with strong E_2 branch as expected for ZnO with the wurtzite structure [24]. EDS spectra taken together with TEM along an individual nanowire show only Zn and O signals without a trace of Au within instrumental resolution as shown in Fig. 3. SEM EDS spectra taken at the underlayer also shows only Zn and O signals as shown in Fig. 4 (Si signal is from the substrate). These observations unequivocally suggest VS mechanism for ZnO nanowires synthesized in this study [16,25–28]. The thin Au layer in the starting substrate aggregates to small Au dots at higher temperature and these dots only act as initial nucleation centers for Zn or ZnO_x adsorption [28]. After formation of Zn or ZnO_x droplets around Au dots, further deposition of Zn leads to the formation of films and inhomogeneous nucleation results in favorable anisotropic growth of long ZnO nanowires. No formation of ZnO film or droplets on Si/SiO_2 substrate was observed without Au layer as demonstrated from the patterned growth of ZnO nanowires as shown in Fig. 5. In VS growth of nanowires, both energetics and kinetics of adsorption, diffusion, and evaporation of reactant atoms are believed to be involved [16,25,26]. Because of the minimization of the surface energy, the surface of high energy becomes the growth front surrounded by surfaces of low energies [29]. Nucleation and growth only at the growth front cannot account for the high growth rate of the nanowires typically found in the experiments. Kinetics of nucleation of reactant atoms on the surface of nanowires followed by diffusion to the growing tip which acts as a sink for atoms or re-evaporation to the environment are important in determining growth morphologies of nanowires [16,25,26]. Two-dimensional (2D) nucleation probability of atoms on the surface, P_n is given by [26]

$$P_n = A \exp\left(-\frac{\pi\sigma^2}{k^2T^2 \ln\alpha}\right) \quad (1)$$

In this equation, σ is the surface free energy of the surface on the nanowire, k is the Boltzmann constant, T is the temperature, and α is the supersaturation ratio as defined by $\alpha = p/p_0$, where p is the actual vapor pressure and p_0 is the equilibrium vapor pressure of