Journal of Alloys and Compounds 455 (2008) 353–357

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

The role of reactants and droplet interfaces on nucleation and growth of ZnO nanorods synthesized by vapor–liquid–solid (VLS) mechanism

S.R. Hejazi [a], H.R. Madaah Hosseini [a,*], M. Sasani Ghamsari [b]

[a] Materials Science and Engineering Department, Sharif University of Technology, P.O. Box 11365-9466, Tehran, Iran
[b] Solid State Laser Division, Laser Research Center, P.O. Box 11365-8486, Tehran, Iran

Received 24 December 2006; received in revised form 17 January 2007; accepted 18 January 2007
Available online 25 January 2007

Abstract

Short ZnO nanorods and long ZnO nanowires have been produced on SiO_2 and Si substrates by VLS and VS mechanisms via a double tube chemical vapor transport and condensation (CVTC) process. The role of reactants and droplet interfaces on the nucleation and growth of ZnO nanorods have been investigated. A conceptual model for nucleation of ZnO nanorods has been proposed by describing the half-oxidation and reduction reactions at the growth front. The importance of Zn vapor in the nucleation phenomena has been studied by changing starting materials. Atomic force microscopy (AFM), scanning electron microscopy (SEM), and EDX analysis have been used to characterize ZnO nanorods and investigate the nucleation model.

Keywords: ZnO nanorods; VLS; Growth mechanism; Oxidation

1. Introduction

Synthesis of one-dimensional nanostructures is an important field of research due to their technological applications in electronics, photonics, biology, and medicine [1–3]. In particular, ZnO nanorods with a wide band gap (3.37 eV) are regarded as promising candidate for using as functional units in nanodevices including UV and laser diodes, optical switches, surface acoustic devices, gas sensors, and solar cells [4–9]. In the past few years, various synthesis mechanism such as vapor–liquid–solid (VLS), vapor–solid (VS) and solution based growth have been developed for fabrication of ZnO nanorods [10–16]. Based on these mechanisms several synthesis techniques including chemical vapor transport and condensation (CVTC), chemical vapor deposition (CVD), thermal evaporation, metalorganic chemical vapor deposition (MOCVD), and physical vapor deposition (PVD) have been employed to synthesize ZnO nanorods [3,17–20].

Recently, the VLS growth mechanism has been widely used for growth of semiconductor nanorods [3,10]. The theory of VLS mechanism was first proposed and established in 1960s for Si whiskers in the presence of Au particles [21]. This theory has subsequently been used for explaining the growth of nanowires. In this growth mechanism, the reactants in the vapor phase are supplied from various sources, a liquid catalyst droplet on a substrate becomes supersaturated and the solid nanorods are formed by precipitation from droplet [1,3,5,10,21]. Unlike the simplicity of understanding the VLS mechanism for single-component wires such as Si, the VLS growth of oxide nanorods such as ZnO is not understood very well due to presence of oxidizing species [3].

The aim of this study is to clarify some complexities of the VLS growth of Au-catalyzed ZnO nanorods synthesized by a double tube CVTC process. These complexities are due to the presence of Zn vapor and CO/CO_2 gases in the CVTC reactor tube.

2. Experimental procedure

SiO_2 substrates (5 mm × 5 mm × 1 mm) were ultrasonically cleaned for 10 min in hydrochloric acid solution and washed in water. P-type (1 0 0) Si substrates with the same dimensions were cleaned using conventional RCA procedure. A thin film of gold was sputter deposited onto substrates under 10^{-2} Torr at 1500 V and 3.5 mA for 20 s in a low vacuum sputtering system (ION SPUTTER JFC, 1100 JEOL). The Au islands were formed on the substrates by heating

* Corresponding author. Tel.: +98 21 66005717; fax: +98 21 66005717.
E-mail address: madaah@sharif.edu (H.R.M. Hosseini).

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2007.01.100

the coated samples in a rapid thermal annealing furnace at 700 °C for 90 min under Ar atmosphere. Equal amounts of ZnO powder (99.99%) and graphite powder (99.99%) were mixed well and placed into a small alumina boat as the source. The boat and Au-coated substrate were placed into a small quartz tube. The substrate was placed about 2–10 cm from the source along the direction of Ar flow. This unit was then loaded into the greater horizontal quartz tube (4 cm diameter and 110 cm length) inside the central hot zone of a tube furnace. The complete unit was heated at 950–1150 °C for 30–90 min under constant flow of argon gas (∼20–80 sccm).

The experiments were repeated by changing source materials to investigate the effects of reactants on the growth of nanorods. In this case, some experiments were performed using pure ZnO powder or pure Zn powder (without graphite addition) as source material to produce ZnO nanorods in absent of CO/CO_2 in growth atmosphere.

Samples were characterized using DS95-50 DME atomic force microscope (AFM) and Philips XLC scanning electron microscope (SEM) equipped with EDX analyzer.

3. Results and discussion

Fig. 1 shows the AFM image of the gold film coated on SiO_2 after annealing. Au islands have been produced by annealing to promote self-assembled growth of ZnO nanorods. Carbothermal reduction of ZnO produces Zn vapor which adsorbs on the Au islands and makes supersaturated Au–Zn droplets. The ZnO nanorods nucleate and grow up at the droplet–substrate interface after supersaturation of Au islands at growth temperature till the Ar flow disrupts or gold tip totally evaporates.

SEM images of ZnO nanorods grown on Au/SiO_2 and Au/Si substrates are shown in Fig. 2a–d. The range of nanorods diameter are 40–120 nm with aspect ratio 2–3 for SiO_2 substrate (Fig. 2a and b) and 40–60 nm with several microns in length for Si substrate (Fig. 2c and d).

Fig. 3a and b show EDX spectra of the tip and the body of ZnO nanorods, respectively. The results indicate that Au–Zn alloyed droplets are present at the tips of nanorods. This could

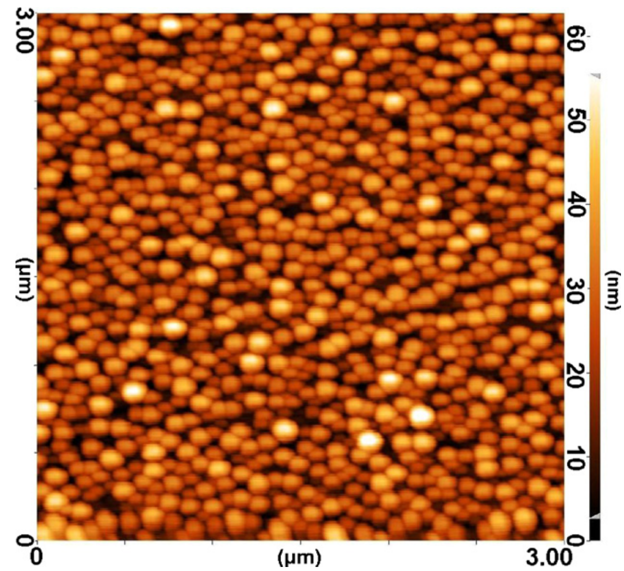

Fig. 1. AFM images of 40 s Au sputtered sample after 180 min thermal annealing at 700 °C.

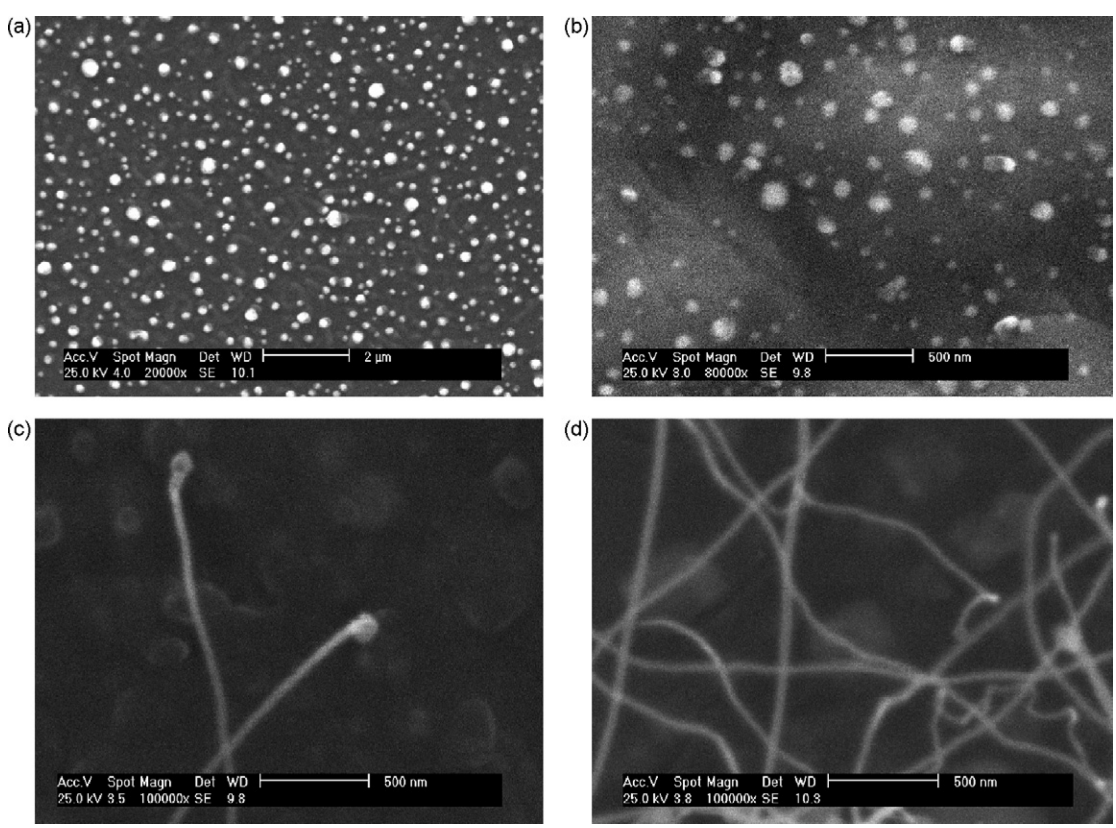

Fig. 2. SEM images of ZnO nanorods (a) top view of short nanorods with diameter 60–100 nm and aspect ratio 2–3 on SiO_2 substrate (scale bar is 2 μm), (b) 30° oblique view of ZnO nanorods grown on SiO_2 substrate (scale bar is 500 nm), (c) and (d) ZnO nanorods with diameter 40–60 nm on Si substrate and length of several microns (scale bar is 500 nm), Au droplet in tip of each nanorods is observed.