Superlattices and Microstructures 75 (2014) 358–370

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Synthesis of zinc oxide nanowires on seeded and unseeded gold substrates: Role of seed nucleation and precursor concentration

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ARTICLE INFO

Article history:
Received 3 July 2014
Received in revised form 8 July 2014
Accepted 15 July 2014
Available online 7 August 2014

Keywords:
ZnO nanowires
Hydrothermal growth
Nanoparticle seeds
Nucleation process

ABSTRACT

ZnO nanowires were synthesized on gold-coated glass substrates using the hydrothermal method. The effects of precursor concentration, substrate annealing and seeding on the morphology, dimension, and distribution of resultant nanowires were investigated. We found that the density of nanowires on substrates pre-seeded with ZnO nanoparticles is about two orders of magnitude greater than unseeded ones, while the dimension of ZnO nanowires for pre-seeded samples is much smaller than unseeded samples. In addition, we found that the fraction of substrate area covered by nanowires for unseeded samples is proportional to the precursor concentration, and proposed a simple nucleation model to explain this behavior. For pre-seeded substrates, ZnO nanowire density first increases with concentration and decreases as concentration exceeds 20 mM. We attribute this behavior to the competition for ions among the dense wires of varying length as well as the fusion of neighboring wires into larger ones.

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http://dx.doi.org/10.1016/j.spmi.2014.07.030
0749-6036/

1. Introduction

In recent years, zinc oxide (ZnO) nanomaterials have attracted the interest of many researchers due to their thermal and mechanical toughness, high luminescence efficiency, chemical stability, lowered lasing threshold, and transparency to visible light [1,2]. These properties make them ideal for a variety of applications such as light-emitting diodes [3,4], gas sensors [5–7], photosensors [8], field effect transistors [9], solar cells [10,11], anti-bacteria and UV-blocking coating on fabrics [12,13], room-temperature polariton lasers [14] and nanowire lasers [15–17], high efficiency quantum well structures [18], and efficient optical nanowaveguides [19,20].

ZnO nanowires can be synthesized using different methods: gas phase synthesis, sol–gel based synthesis, and solution phase synthesis [2,21]. Several processes have been used regularly to synthesize ZnO nanowire structures, but the hydrothermal growth method is especially attractive due to its simplicity and moderate growth conditions [22,23]. Vertically aligned ZnO nanowires have been grown using this process on a variety of substrates [24–26]. However, there have been few studies providing a systematic, quantitative comparison of the resultant nanowires synthesized on substrates with different pre-growth treatment and varying precursor concentrations. In this study, we report the synthesis of ZnO nanowires on gold-coated glass substrates using the hydrothermal method and investigate how the morphology, distribution, and dimension of nanowires are affected by the precursor concentrations and the annealing and pre-seeding of the gold substrates with ZnO nanoparticles.

2. Materials and methods

2.1. Preparation of substrates

ZnO nanowires were synthesized using a hydrothermal growth process on glass cover slips pre-coated with a 10-nm-thick gold film (Phasis, Geneva). Two different methods of substrate preparation were explored. In the first approach, the unseeded method, the substrate is prepared by sonicating in acetone, methanol, isopropyl alcohol, and deionized water consecutively for 10 min each, and then baking in air at 350 °C for 30 min. For this unseeded method, substrate pre-heating at temperatures ranging from 150 °C to 350 °C is conducted to study its effect on subsequent nanowire synthesis.

In the second approach, the pre-seeded method, we adapted the procedure established by Greene et al. [23,24]. The substrates are wetted with one 5 μL droplet of 1 mM zinc acetate dihydrate (99.999%, Sigma Aldrich) in ethanol after the same cleaning and pre-baking procedures are carried out as explained in the unseeded approach. Upon the drying of the seeding solution droplet, the sample is immediately rinsed with an ample amount of ethanol and blown dry with nitrogen gas. The sample is then baked in an air oven at 350 °C for 30 min to thermally decompose zinc acetate into ZnO nanoparticle seeds [24]. The morphology and size of the ZnO nanoparticle seeds are examined using high resolution transmission electron microscopy (TEM).

2.2. Hydrothermal synthesis of ZnO nanowires

Zinc oxide nanowires are then synthesized in a hydrothermal growth environment [22,23]. The growth solution used is a 400-mL equimolar aqueous solution of zinc nitrate hydrate (99.999%, Sigma Aldrich) and hexamethylenetetramine (HMTA) (99.5%, Sigma Aldrich) at various concentrations. The samples are placed to float on the solution surface with the gold coating side facing down in a sealed PYREX wide mouth media storage bottle inside a Yamato DKN-402C oven maintained at 95 °C. The growth time is set to be 3 h. Upon completion of the growth process, the samples are taken out, rinsed in deionized water and blown dry with nitrogen gas, and are examined using scanning electron microscopy (SEM), TEM, and x-ray diffraction (XRD) analysis.