Bulk ZnO nanorod assemblies fabricated by spin coating of organo-precursor gels on CuO nanowires

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Bulk ZnO nanorod assemblies have been successfully fabricated on CuO nanowires through spin coating of organo-precursor gels. A thin film of CuO nanowires was first generated by direct heating of a metallic Cu-foil at 500 °C in an air atmosphere. A stable colloidal organo-precursor sol synthesized by dissolving equimolar zinc acetate dihydrate and monoethanolamine in 2-methoxyethanol was subsequently repeatedly deposited onto the CuO nanowires by spin coating. The formation of ZnO nanorod assemblies was controlled by varying the number of coatings. The average diameter of the ZnO rods was determined to be ~ 600 nm.

Keywords: ZnO; CuO; sol-gel; Raman spectrum; SEM
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1. Introduction

Nanostructured materials have attracted much scientific attention due to their interesting size-dependent chemical and physical properties and potential technological applications. Nanowires and nanorods of various semiconducting materials, including Si, Ge, CuO, GaN, ZnO, SnO2, etc. have been synthesized for different potential applications. Compared to the bulk materials, the ultrafine materials reveal remarkable quantum effects, including electrical, optical and magnetic properties that can be in principle tailored by varying the size. Zinc oxide (ZnO) is a fascinating, n-type II – VI semiconductor with a wide energy band gap (3.3 eV) and high exciton binding energy (60 meV). It also exhibits high carrier mobility and high transparency at room temperature. Due to its almost indefinite stability and environmentally friendly properties, ZnO is recognized as a potential source for the fabrication of dye-sensitized solar cells and LEDs [1, 2]. Among the various ZnO nanostructures, ZnO nanorods and nanowires are extremely important for the development of solar cells because they offer an increased interfacial area and a direct path for the photo-generated electron transport. However, an increased efficiency is possible only when well-oriented ZnO nanorods are fabricated. Therefore, active research is underway to synthesize the oriented semiconducting ZnO nanostructures. One-dimensional ZnO nanostructures, including nanowires, nanobelts and nanotubes have been fabricated by vapor phase evaporation [3], chemical vapor deposition [4], sol-gel [5], template method [6], laser ablation [7], and solution [8] processes. Most of these techniques are found to be successful for achieving bulk nanostructures with randomly oriented nanowires and rods.

Copper oxide (CuO) has been extensively studied due to its suitability for the application in high Tc superconductors and as a heterogeneous catalyst. Recently, CuO structures have found a variety of applications in gas sensing [9], field emis-
Cupric oxide is a p-type semiconductor with the band gap energy between 1.96 and 2.38 eV. A solar cell assembly with high open-circuit voltage can be fabricated if a suitable n-type semiconductor is combined with CuO. Since the 1950s, there has been significant research into the growth of copper oxide whiskers and nanowires. Solution-techniques, template assisted growth, and thermal oxidation of Cu metal and Cu$_2$S are a few of the known techniques reported for this purpose. The thermal oxidation process is remarkably simple, because in this technique the growth of CuO whiskers/nanowires (100 – 200 nm) is accomplished by the conventional heating of thick copper sheets or foils at temperatures from 400 to 700 °C in an ambient air environment. The thick copper substrates effectively provide a large excess of copper during oxidative growth. In this work we have attempted to fabricate bulk ZnO nanorod assemblies on CuO nanowires. Here we report on a simple method for the fabrication of ZnO–CuO nanorods on Cu substrates by heating them in an air atmosphere. This is followed by the deposition of ZnO layers by the sol-gel spin coating method. SEM and Raman spectroscopy are employed to investigate the nanorod formation and the optical properties of the nanorods. The advantage of this technique is that it is simple and relatively inexpensive to implement.

2. Experimental procedure

Metallic copper foils, procured from Nilaco Metals and Chemicals, Japan (1 cm × 1 cm, with thickness of 0.1 mm), were used as substrates for growing the CuO nanowires. The copper foil was heated in an electrical coiled furnace at 500 °C in air for 4 hours. Upon heating, the shiny copper surface turned black. A coating precursor solution was prepared by dissolving zinc acetate di-hydrate (Zn(CH$_3$COO)$_2$·2H$_2$O), Nacalai Tesque Chemical Co. Ltd., 99.5 %) and equivalent molar quantity of monoethanolamine (MEA, Nacalai Tesque Chemical Co. Ltd., 99.5 %) in 2-methoxyethanol (Nacalai Tesque Chemical Co. Ltd). The precursor solution was homogenously mixed by simple stirring for 3 hours at room temperature and then at 60 °C for 2 hours. The precursor sol was deposited onto the preheated copper foils by spin coating at 2000 rpm for 20 seconds and then at 3000 rpm for another 20 seconds at room temperature. Immediately after the coating, the precursor films were subjected to curing at 300 °C for 10 min to remove the excess solvents and residual moisture. The coating process was repeated 2, 5 and 10 times. Finally, the coated substrates were annealed at 600 °C for 2 h in air atmosphere. Coatings were also prepared on the glass and silicon substrates under identical conditions for the purpose of comparison. The as-prepared products were observed and characterized by scanning electron microscopy (SEM, S-3000H Hitachi), X-ray diffraction (X-ray diffractometer – JEOL) and Raman spectrometer (NRS 1500W Raman Spectrometer – JASCO).

3. Results and discussion

3.1. XRD analysis

The X-ray diffraction analysis of the as received Cu-foil, the Cu-foil thermally heated to 500 °C and the ZnO precursor layers heated at 600 °C on Cu foil are presented in Fig. 1 (a – e). The as received Cu-foil shows two sharp crystalline peaks at 2θ = 43.46° and 50.6° that confirms that the foils are phase-pure cubic-metallic Cu as shown in Fig. 1(a). The diffraction peaks of thermally heated Cu-foil in Fig. 1(b) represent the fully crystalline monoclinic CuO phase (JCPDS 48-1548) [18]. In this case, when copper is oxidized in air, Cu$_2$O is initially formed and then it transforms into CuO through secondary oxidation. The Cu$_2$O actually serves as a precursor for obtaining CuO nanowires. The high vapor pressure of the bulk Cu-metal reactants serves to accelerate the growth of the CuO nanowires [19]. We assume that the oxidation of copper to Cu$_2$O and then to CuO provides the energy required to form additional surfaces for the nanowires. Oxidation leads to stress in the foil due to volume and structural changes. Sufficiently high rates of oxidation coupled with the low mobility of atoms in the solid lead to relaxation of stress by the formation of small crystallites of CuO from which