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Growth and branching of CuO nanowires by thermal oxidation of copper

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Abstract

CuO nanowires have been synthesized by thermal oxidation of copper foils in oxygen atmosphere. Morphology and microstructure of the nanowires was studied as a function of temperature and annealing time using scanning electron microscopy, energy dispersive X-ray analysis, X-ray diffractogram, X-ray photoelectron spectroscopy, transmission electron microscopy and selected area electron diffraction. Nanowires were found to grow preferentially along [0 1 0] direction. Length of nanowires was seen to increase with annealing time and for long times branched structure was observed. A "blue-shift" in comparison to bulk CuO was observed in the band gap as determined from optical absorption spectra. Mechanism of growth of CuO nanowires is discussed.

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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, GaN, ZnO, SnO_2 etc. have been synthesized for different potential applications. Nanowires are 1D nanocrystals with large aspect ratio (length/diameter) and diameter up to 200 nm. Compared to the bulk materials, the ultrafine materials reveal remarkable quantum effects, including electrical, optical and magnetic properties that are in principle tunable by varying size.

CuO is a p-type semiconductor with a narrow band gap that has been a candidate material for photothermal and photoconductive applications [1]. CuO is also used in fabrication of lithium–copper oxide electrochemical cells [2,3]. This material has also attracted much interest in the past as it is the basis of several high-T_c superconductors. CuO nanowires can be potentially applicable in gas sensing [4,5], magnetic storage media [6], in nanodevices for catalysis [7–9] and as field emitters [10]. These 1D nanostructures also provide models for studying the effect of dimensionality and size confinement on electrical, transport and mechanical properties [11]. Nanowires, nanorods, nanowhiskers and nanosheets of CuO can be synthesized by using precursors [12], hydrothermal decomposition

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route [13], self-catalytic growth processes [14] and solvothermal route [15]. A few studies on growth of CuO nanowires by thermal annealing copper foils in oxygen atmosphere [16–18] have also been reported. This technique of nanowire growth is similar to growth of whiskers of several metals reported in earlier studies [19,20]. In comparison to complex chemical methods, thermal annealing of copper foil provides simple, convenient and fast method for synthesizing CuO nanowires. Nanowires synthesized by this method are always found to grow perpendicular to the surface of copper foil. It has been reported that [21] diameter and number density of nanowires are a critical function of oxygen flow rate and annealing temperature. The length of nanowires depend mainly on the annealing time.

Studies on various other metal-oxide nanowires in the literature report the existence of branched structures. In SnO_2 branches are observed in nanowires prepared by using active carbon [22]. Interconnected nanowire networks have also been reported in ZnO synthesized by a high-temperature solid–vapor deposition process [23]. Various kinds of branched structure nanobouquets, nanotrees [24] and nanotetrapods [25] have also been reported for In_2O_3 and ZnO, respectively. However, there is no report on the branching of CuO nanowires. The branching of nanowires is expected to further improve their gas sensing and catalytic properties due to increase in surface-to-volume ratio.

The present work reports the structure and growth of branched CuO nanowires prepared by annealing of Cu foil in the oxygen atmosphere. Cu foils have been annealed for longer duration to maximize the length of CuO nanowires. Branching has been observed for long annealing times (>1.5 h at temperature of 675 °C). Growth mechanism of CuO nanowires has been discussed.

2. Experimental procedure

Synthesis of CuO nanowires was carried out by thermal oxidation of high-purity Cu sheets of 1 mm thickness. Copper sheet of $10 \times 10\,mm^2$ size was first cleaned in dilute nitric acid to remove the native oxide layer and adsorbed impurities. The foil was then throughly rinsed with deionized water followed by ultrasonication in acetone for 5 min. Thermal oxidation of Cu sheet was carried out in a resistively heated furnace at different temperatures (between 400 to 800 °C) and times under flowing oxygen atmosphere. The sample temperature was monitored by placing a thermocouple in vicinity of the sample. In all the experiments, the rate of heating of copper sheet was maintained at 6 °C/min and after oxidation, samples were quenched by removing from furnace. A constant oxygen flow rate was maintained during the complete cycle of heating, oxidation and quenching of the samples. Surface morphology of the samples was studied using a scanning electron microscope (SEM) VEGA MV2300T/40 (TS 5130

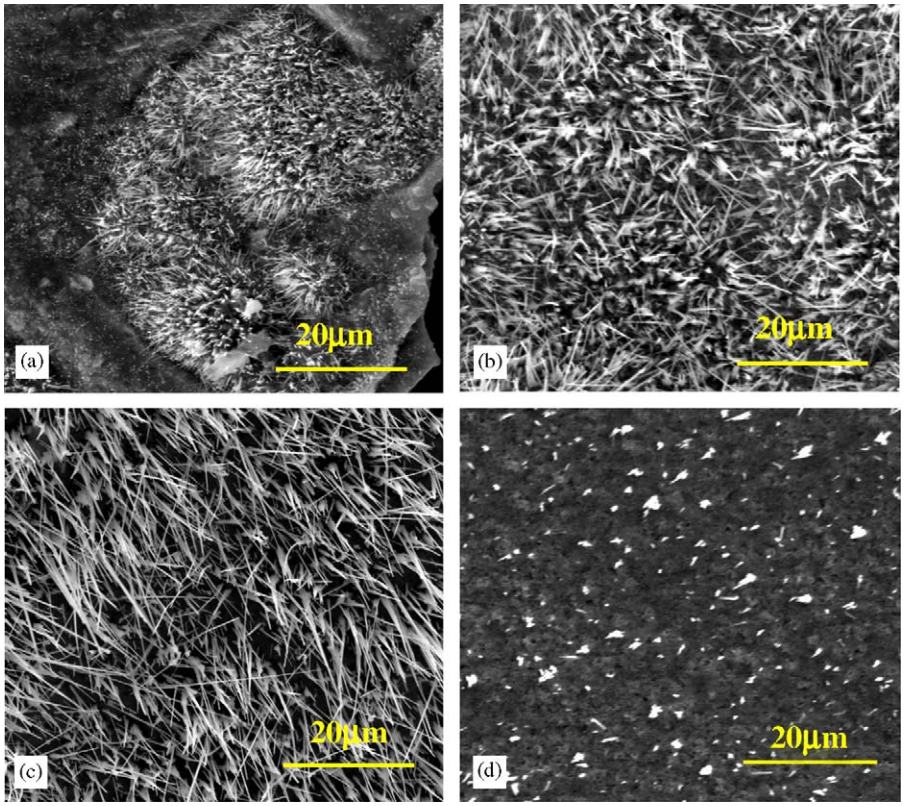

Fig. 1. SEM micrographs of CuO nanowires prepared by annealing copper strips for 4 h under oxygen atmosphere at different temperatures: (a) 500 °C, (b) 600 °C, (c) 700 °C and (d) 800 °C.