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ScienceDirect
Ceramics International 40 (2014) 517–521
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Fabrication of single phase CuO nanowires and effect of electric field on their growth and investigation of their photocatalytic properties

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Received 9 February 2013; received in revised form 17 May 2013; accepted 10 June 2013
Available online 24 June 2013

Abstract

Single phase CuO nanowires were grown at a large scale via thermal oxidation of a Cu substrate in air at 500 °C for several times. Usually during the oxidation process, a layer of Cu_2O is grown on the surface of the substrate. Our results showed that by further annealing of the CuO (nanowires)/Cu_2O layer, isolated from the Cu substrate, it is possible to convert the Cu_2O to CuO nanowires. It was found that the Cu ion diffusion through the grain boundaries is the dominant growth mechanism in the thermal oxidation method. Also, effects of applying an electric field on the growth of nanowires have been investigated and it was found that the annealing in the electric field caused an increase in the concentration and uniformity of nanowires diameter. Also the adhesion of the CuO nanowires layer on the Cu substrate was observed. The photocatalytic activities of CuO nanowires were examined by photocatalytic degradation of Methyl Orange and Bromocresol Green dyes. The results showed that the nanowires grown at 500 °C had the best photocatalytic performance on both dyes.

Keywords: A. Sintering; B. Grain boundaries; E. Substrates; CuO nanowires

1. Introduction

In recent years, the one-dimensional nanostructures have been widely studied due to their high aspect ratio and potential applications in different areas. CuO nanowires as p-type semiconductors with narrow gaps and monoclinic structures have promising applications in electronic nanoscale devices [1]. There are many methods for synthesizing CuO nanowires [2–4]. Among them, the direct thermal oxidation of a Cu substrate is the simplest and most suitable for large scale production [5]. A challenge concerning the CuO nanowires is their fabrication in the single phase form. Usually during the oxidation process, a layer of Cu_2O phase grows on the surface of the substrate [6,7] which can alter the CuO nanowires properties. The growth mechanism of CuO nanowires through thermal oxidation is another issue which has been investigated by researchers [6,8] but not all the details are elucidated and need to be studied more. The VLS and VS growth mechanisms are the ones which are believed to be the dominant growth mechanisms of nanowires. Although this is true for most of the nanowires, but the growth mechanism of CuO nanowires seems to be more complicated. Therefore, different mechanisms based on grain boundary diffusion of Cu^{+2} ions and lattice diffusion have been suggested [8]. Another issue related to the CuO nanowires is finding a simple way to align the synthesized nanowires. Although some researchers have used silicon substrate in order to grow aligned nanowires and nanotubes [9,10], it seems applying an external electric field during sintering is another way to control the alignment of one dimensional nanostructures [11,12]. It is worth noting that the photocatalytic performance of CuO nanowires has not been studied enough. CuO nanowires have peculiar properties which make them suitable for photodegradation of some dyes which cannot be degraded by the other photocatalysts. Nowadays, the environmental pollutions have numerous negative effects on the human life. Therefore, decomposition of organic pollutants is one of the main subjects of the new researches. In this regard, the application of photocatalyst semiconductors in the decomposition of hazardous

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http://dx.doi.org/10.1016/j.ceramint.2013.06.032

pollutants has attracted more attention compared to the usual methods [13].

In our previous study, the growth of CuO nanowires by the direct oxidation method at different temperatures was investigated [7]. Here, we will report on the fabrication of single phase CuO nanowires and further studies of the growth mechanism of CuO nanowires. The effect of applying a DC electric field on the aligned growth of nanowires has also been examined. Moreover, the photocatalytic activity of synthesized nanowires is investigated by degradation of Bromocresol Green and Methyl Orange dyes, which are used as pH indicators and tracking dyes.

2. Experimental details

A pellet of Cu as the substrate was cleaned and prepared according to the Ref. [7]. The substrate was then transferred immediately into a furnace and annealed in air at 500 °C for several times ranging from 1 to 38 h. In order to investigate the effect of the electric field on the growth of nanowires, an electric field ranging from 13,000 to 130,000 V/m was applied to the samples during the growth by putting them between two 10×10 cm^2 flat metallic (iron) plates which were 0.3 cm apart and applying various DC voltages of 40, 60, 200, 300 and 400 V across the plates. The experimental setup is schematically shown in Fig. 1.

In order to investigate the photocatalytic performance of CuO nanowires, the degradation of Bromocresol Green and Methyl Orange was examined. The dye solutions were prepared by dissolving the dye powders in de-ionized water with the concentration of 20 mg/l. For each experiment, after adding 0.1 g CuO nanowires to about 100 ml of dye solution, the sample was placed in a home-made photoreactor and stirred in darkness for 30 min. The mixture was then illuminated under a UV source while being stirred and the sampling was carried out in 30 min intervals. After separating the CuO nanowires from the dye solutions using a 3000 rpm centrifuge, the UV–visible absorption spectra of the clear solutions were taken.

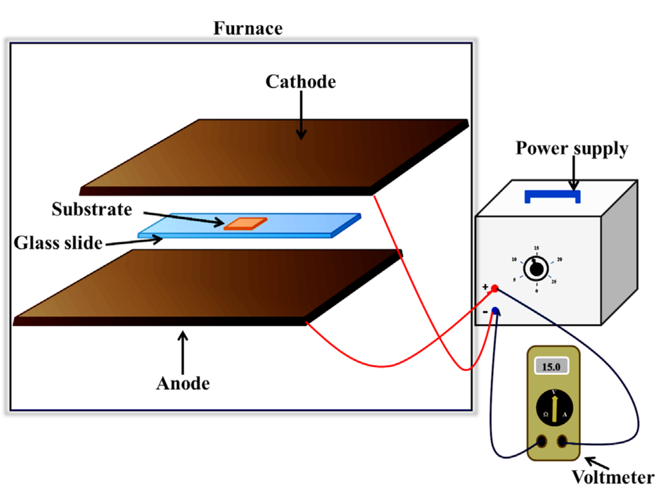

Fig. 1. Schematic drawing of the samples in the electric field.

The characterization of nanowires was performed by taking SEM images using a 1455 VP scanning electron microscope and XRD using a PW-1840 Philips diffractometer and UV–vis absorption measurement by use of a GBC, Cintra 100 spectrophotometer.

3. Results and discussion

In our previous study [7] we found that the annealing of a Cu substrate at 500 °C for 4 h was the best condition to synthesize CuO nanowires. Based on different studies, the growth of CuO nanowires is accompanied by the growth of a Cu_2O layer on the surface of the Cu substrate [6,7]. The growth of CuO nanowires occurs according to the following oxidation reactions:

$$4Cu + O_2 \rightarrow 2Cu_2O$$

$$2Cu_2O + O_2 \rightarrow 4CuO$$

It seems that the growth of a Cu_2O layer during the oxidation process is inevitable. Since the second reaction is a very slow one, we decided to examine a longer growing time to investigate whether is it possible to change the phase fraction of the two copper oxide phases in order to produce pure CuO nanowires or not. Fig. 2a, b, and c shows the XRD patterns of nanowires which were grown at 500 °C for 4, 24 and 36 h respectively. One can observe that by increasing the annealing time up to 24 h, the intensity of CuO peaks increases and that for Cu_2O phase decrease, but by further annealing, once again the Cu_2O phase fraction starts to increase (see Table 1) and cannot be removed. The pattern in Fig. 2d belongs to a black and fragile CuO/Cu_2O layer grown at 500 °C for 24 h (sample b), peeled off from the substrate and annealed again for another 14 h. All peaks except some very small Cu_2O peaks belong to the CuO phase. This means that as long as the Cu substrate exists, the Cu_2O phase continues to

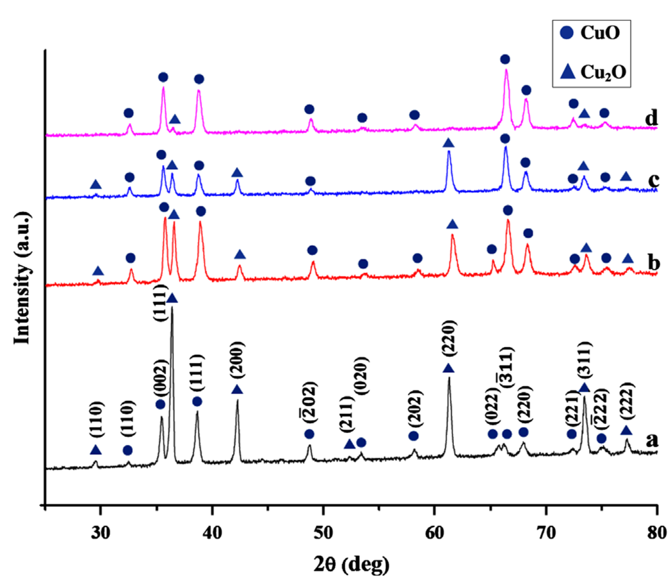

Fig. 2. XRD pattern of samples grown at 500 °C for (a) 4 h, (b) 24 h, (c) 36 h and (d) the sample b, peeled off from substrate and annealed for another 14 h.