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Surface modification of carbon fiber by direct growth of zinc oxide nanowalls using a radio-frequency magnetron sputtering technique

Sahendra P. Sharma, C.K. Chang, Jyh-Ming Ting *

Department of Materials Science and Engineering, National Cheng Kung University, Tainan 70101, Taiwan

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ABSTRACT

Zinc oxide nanowalls have been grown uniformly on a carbon fiber substrate at room temperature using a radio-frequency magnetron sputtering technique. The synthesis process involved two steps; application of catalyst using a solution process and subsequent radio-frequency sputter deposition of zinc oxide. The nanowalls were examined by field emission scanning electron microscopy for their microstructure and morphology while their nanostructure was studied by high resolution transmission electron microscopy. Both the X-ray and the electron diffraction techniques were used for crystallographic analysis of the produced nanowalls. Selected area electron diffraction and high resolution lattice image showed highly crystalline structure of the nanowalls. Photoluminescence analysis was carried out for the determination of their optical characteristics which showed a strong ultra violet peak at 393 nm and violet peak centered at 401 nm. The latter is a characteristic peak of zinc oxide which demonstrates oxygen rich composition of nanowalls.

1. Introduction

Zinc oxide (ZnO) is a semiconductor with a wide direct band gap of 3.37 eV and an exciton binding energy of 60 meV. It forms a wide variety of 1-D and 2-D nanostructures such as nanorods [1], nanowires [2,3], nanotubes [4], nanoneedles [5], nanowalls [6,7], nanobelts [8], etc. Over the last few decades these nanostructures have attracted a great deal of interest due to their extraordinary properties and potential applications in diverse fields such as gas sensors [9,10], bio-sensors [11], field effect transistors [12], pressure sensors [13], catalysis [14], optoelectronics and functional materials [15,16]. Most of these applications are very sensitive to the shape and morphology of the ZnO nanostructures determining the performance of the fabricated device. There are several methods used for the synthesis of ZnO nanostructures such as chemical vapor deposition [17], electro-deposition [18], vapor–liquid–solid process [19], sol–gel [20], hydrothermal [21] etc. Both catalyst free and catalyst derived methods can be used to grow these nanostructures on different kinds of substrates such as Si, glass, polyethylene etc. [22,23,24]. Most of these synthesis methods involve high growth temperature which excludes the use of polymeric substrates. It is evident from the literature that over the past few decades' significant progress has been made in identifying and developing methods for the synthesis of ZnO nanostructures.

In particular, the use of non-conventional substrates for the growth of ZnO nanostructures has been reported by a few groups. The growth of carbon nanotubes on carbon fibers leads to excellent field emission [25,26]. Similarly ZnO nanowires grown by thermal vaporization and condensation methods on carbon cloth showed extremely high field enhancement factor due to the combined effect of high aspect ratio and geometry of woven carbon cloth [27]. ZnO nanowires grown on carbon microfibers showed good potential for application as flexible gas sensor [28]. Carbon in the form of CNTs mixed with ZnO has been used to prepare ZnO nanostructures [29]. Au nanoparticles were used to produce crystalline ZnO with good optical properties [30]. Recently, ZnO nanostructures have also been grown directly on graphene for their application as piezoelectric nanogenerator [31]. Yan et al. produced carbon nanotube-zinc oxide hetro-junctions array using a vapor phase transport process which showed low turn-on and threshold fields and stable emission current [32]. However, these growth methods involved a high temperature between 900 and 1000 °C and a long process time. In this study we have used a simple, low cost, low temperature, rapid and scalable method developed previously [33] for the growth of ZnO nanostructures on carbon fibers. The growth process takes place at room temperature and lasts only for 5–10 min. The results from microstructural analysis of the catalyst seed and the grown ZnO nanowalls are discussed along with their X-ray and photoluminescence (PL) characteristics.

2. Material and methods

2.1. Growth of ZnO nanostructures

The synthesis method used in this study involved a two-step process namely, catalyst deposition on the substrate and growth of zinc oxide

* Corresponding author. Tel.: +886 6 2757575x62949; fax: +886 6 2385613.
E-mail address: jting@mail.ncku.edu.tw (J.-M. Ting).

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nanostructures using a radio-frequency (RF) magnetron sputter deposition technique. An aqueous solution was prepared by dissolving 0.5 g tin chloride ($SnCl_2.2H_2O$) salt in 50 ml reverse osmosis (RO) water and ultrasonicated for 10 min to obtain a uniform solution. The as prepared solution was acidic in nature which has a pH value 1.6. K-321 carbon fiber (from Mitsubishi Kasei Co.) consisting of 2K filaments was first acid cleaned with nitric acid for a fixed time of 5 min to remove the sizing. The fibers were cut into pieces of length 30 mm and stacked onto the glass support. The fiber pieces were adhered with vacuum tape to keep them intact during processing. The etched fiber was rinsed in deionized water for a couple of times, dried at 80 °C in a hot air oven and then immersed into the aqueous solution of tin chloride for a dwell time (τ_d) ranging from 3 to 30 min to deposit a catalyst seed on them. Subsequently, the fiber was dried by a controlled nitrogen shower. The fiber was mounted on the specimen stage and placed in the deposition chamber evacuated to 1.33×10^{-4} Pa. Ar gas was introduced into the chamber and a pressure of 6.67 Pa was achieved by adjusting the vacuum pump valve. An RF power of 200 W was applied resulting in the formation of plasma which can be observed through the glass window. A pre-deposition cleaning of ZnO target was carried out for 5 min to eliminate any contamination. The fiber substrate was shielded with a shutter during this pre-deposition step. The power was reduced to a desired value in the range of 50–150 W and the shutter was removed for the growth of ZnO nanostructures on the catalyst coated fiber substrate. Different deposition time (τ_g) ranging from 1 to 10 min was used for growing ZnO nanostructures. No external heating was done to heat the substrate; however, the temperature of the substrate may rise slightly higher than the room temperature due to bombardment of high energy particles from the plasma. A silicon wafer used in this study was first cut into pieces of dimension 10 mm × 10 mm, cleaned ultrasonically in deionized water and subsequently in ethanol. The small pieces of silicon wafer were used for the catalyst deposition and subsequent ZnO nanowall growth following exactly the same way as described for carbon fibers.

2.2. Characterization of nanostructures

A standard pH meter PHM 210 from *Mater* Lab was used for carrying out pH measurements of the catalyst solution. Control of catalyst chemistry played a key role in determining the morphology of the grown ZnO nanostructures. The morphology of ZnO nanostructures was examined using JSM-6701F field emission scanning electron microscope (FEG-SEM) from *Jeol* with a cold emission gun operated at different accelerated voltage (10 to 20 kV) while the elemental analysis of the deposited catalyst and the grown ZnO nanowalls was carried out using *Quanta* 400 environmental scanning electron microscope (ESEM) from FEI. The structural examination of ZnO nanostructures at nano level was carried out using a JEM 2010 high resolution transmission electron microscope (HRTEM) from *Jeol* equipped with LaB_6 filament operated at 200 kV, capable of providing a point to point resolution of 0.1 nm. X-ray diffraction study was carried out by D/MAX250 X-ray diffractometer from *Rigaku*, with Cu anode operated at 40 kV tension and 30 mA current providing a radiation wavelength of 1.54056 Å. The scanning range was 20° to 80°, the step size 0.01° and the integration time 5 s. Photoluminescence (PL) study was performed by *Jobin Yvon*, Horiba spectrometer using a laser source at room temperature with an excitation wavelength of 325 nm and a back scatter filter was also used. A power of 10 mW was used and the resolution of the instrument was 1 cm^{-1}.

3. Results

Fig. 1 presents the FEG-SEM images of carbon fiber used as substrate in this study. Fig. 1(a) shows the as received carbon fiber before undergoing any surface treatment while Fig. 1(b) shows carbon fiber after acid cleaning. The micro pits formed by etching at the fiber surface

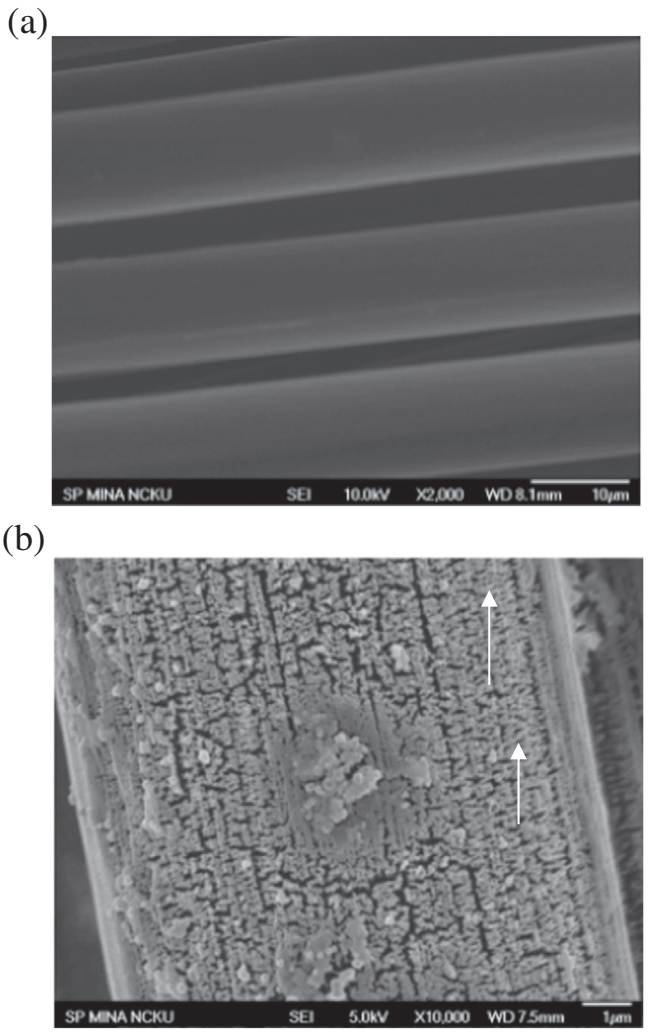

Fig. 1. FEG-SEM image of the as carbon fiber (a) before acid cleaning (b) after acid cleaning.

can be evidently observed. Fig. 2 presents the FEG-SEM images of $SnCl_2$ catalyst seed deposited on Si substrate for different immersion (dwell) times (τ_d). Fig. 2(a), (b), and (c) shows the catalyst seed deposited for 3, 5, and 30 min, respectively. Fig. 3 shows the ZnO nanowalls grown on the catalyst seed deposited for different dwell times on Si substrate using the same growth time (τ_g) 5 min. Fig. 3(a), (b), and (c) shows the ZnO nanowalls grown on the catalyst seed with dwell time 3, 5, and 10 min, respectively.

The morphology of the ZnO nanowalls grown on carbon fiber is shown in Fig. 4. Fig. 4(a) presents a low magnification image illustrating uniform coverage of several fibers with the grown nanowalls. Fig. 4(b) is a very high magnification image ZnO nanowalls grown on a single fiber. The nanowalls are densely (high number density) grown on the carbon fibers which have an average length of 550 nm and an average thickness of 30 nm (as calculated from several high magnification images) thus possessing a high aspect ratio (l/t) of ~18. High magnification image covers only a few nanowalls; therefore, a relatively low magnification image covering a large number of nanowalls was used to compute their average length and thickness. Fig. 4(c) is an image of nanowalls grown on a planar Si substrate. The nanowalls grown in clusters are observed in this case. The number density computed from the high magnification SEM image was found to be 12/μm^2.

Fig. 5 shows TEM images taken on the catalyst precursor prepared from $SnCl_2.2H_2O_{(aq.)}$ for a short immersion time of 1 min. Fig. 5(a), (b) shows a bright field image and its corresponding selected area