Synthesis of tungsten oxide (WO$_3$) nanorods using carbon nanotubes as templates by hot filament chemical vapor deposition

Nagraj Shankar, Min-Feng Yu, S.P. Vanka, Nick G. Glumac *

Department of Mechanical and Industrial Engineering, University of Illinois at Urbana-Champaign, 1206 West Green St., Urbana, IL 61801, USA

Received 6 May 2005; accepted 3 October 2005
Available online 24 October 2005

Abstract

Synthesis of tungsten oxide (WO$_3$) nanorods using CNTs as templates under typical diamond growing conditions in a hot-filament chemical vapor deposition system is described. Tungsten oxide nanorods were grown on two types of CNT substrates, a Si [100] wafer with dispersed multiwalled CNT and a fresh-grown multiwalled CNT film. The templated growth resulted in an order of magnitude increase in surface area covered by the tungsten oxide compared to a planar Si [100] surface, which when combined with the flexibility of growing CNTs in various forms like pillars and sheets [K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, Science 306 (2004) 1362–1364.], can be effectively utilized in field emission, gas sensing and catalytic applications.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Chemical vapor deposition; Templated growth; Tungsten oxide; Sensors; Catalysts

1. Introduction

The oxides of the transition metal tungsten (WO$_x$, $x=1$–3) have attracted constant research interest for the past few decades due to their wide applicability as gas sensors for SO$_2$ and H$_2$S [1,2], as excellent field emitters (specifically W$_{18}$O$_{49}$) [3] and as photoanodes in photochemical cells [4]. In addition, WO$_x$ thin films have also found unique application in electrochromic devices due to their excellent voltage-modulated optical properties [5]. Small quantities of tungsten oxide have been added to a Pt/Ru catalyst to promote the oxidation of CH$_3$OH in methanol fuel cells [6], and Na doped WO$_3$ has been shown to be superconductive at high temperatures ($T_c \approx 90$ K) [7]. The prospect of functionally modifying surface properties based on templated growth of WO$_x$ is very promising in all of the above mentioned applications, particularly in field emission and catalytic applications. Carbon nanotubes (CNT) have been used as templates to grow a wide variety of one dimensional materials, such as SiC, GaN, WC and TiC [8–10]. CNTs have also been either partially or completely oxidized to form various oxide nanotubes (SiO$_2$ and V$_2$O$_5$) [11,12] and coated with metals like Pt to serve as fuel cell catalysts [13]. The main advantage of using CNTs as templates is the significant increase in surface area of the desired material grown on the CNT compared to a flat surface. Since CNTs can be easily grown on a patterned substrates in various forms, such as vertically aligned tubes, array of pillars and sheets [14], the growth of WO$_x$ on CNT templates may give rise to very interesting functional structures for use as gas sensors, catalysts and electrochromic devices.

In this letter, we describe the growth of WO$_x$ nanorods using CNT films as templates by hot filament chemical vapor deposition (HFCVD). Templated growth of WO$_x$ on two types of CNT substrates, a Si [100] wafer with dispersed multiwalled CNT and a fresh-grown multiwalled CNT film, are presented. The growth of WO$_x$ nanorods was confirmed with detailed energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) analyses.

2. Experimental

Growth of the tungsten oxide nanorods was performed in a typical hot-filament chemical vapor deposition (CVD) system used for growing diamond thin films. The deposition was carried out at a substrate temperature of $\sim 850$ °C and at a
system pressure of 25 Torr in a H₂/CH₄ (1200:3 sccm) environment for 2 h. The leak rate in the chamber was \(\sim 5 \times 10^{-7}\) Torr l/s. A tungsten wire (\(\phi 0.5\) mm, 99.95% metal basis from Alfa Aesar) 100 mm long placed 5 mm above the substrate was used as the filament. The filament temperature was maintained at 2600± 100 K and measured using a two color optical pyrometer. The tungsten filaments were not carburized before performing the experiments.

In the first case the substrate was a Si [100] wafer (\(\sim 25\) mm²) that was scratched with a 0.1 \(\mu\)m diamond paste and cleaned in an Acetone-IPA-DI water-IPA bath and then coated with multiwalled CNT (Nanolabs Inc., \(\sim \phi 30–50\) nm and length \(\sim 5–20\) \(\mu\)m). The multiwalled CNT sample was pre-dispersed in lab grade ethanol to 1% by weight (see Fig. 1(b)). After the CVD deposition was completed we observed that the substrate was covered with a dark grayish-blue coating. The coating covers the Si substrate completely.

In another case, the WO₃ nanorods were grown on a Si substrate covered with a freshgrown CNT film. For the growth of CNTs, a Si substrate sputter-coated with stainless steel SS-304 was first heated in a low pressure chemical vapor deposition chamber to 700 °C at 120 Torr in a reducing H₂ (10 sccm) environment. Deposition of the CNTs was then carried out in a N₂ (200 sccm) environment using C₂H₂ (20 sccm) as the carbon source for 30 min. The CNTs loosely covered the whole Si substrate. The CNTs were multiwalled with 20–25 shells, having a mean diameter of \(\phi 30–80\) nm and an average length of \(5–20\) \(\mu\)m (see Fig. 4(b)). WO₃ nanorods were subsequently grown on this CNT film using the same growth conditions described in the first case.

3. Results and discussions

Fig. 1 shows a SEM (Hitachi S4700) micrograph of the nanorod-like coating grown on the surface of Si [100] substrate and CNT. As seen in Fig. 1, the nanorods have an almost uniform diameter of \(\sim \phi 30–80\) nm and a length of \(\sim 200–300\) nm. They grow mostly in a preferred direction perpendicular to the Si surface. Such a vertical growth of tungsten oxide nanorods on a Si surface has been reported in the past [15]. It has been hypothesized that the growth of the tungsten oxide nanorods takes place via the formation of a high density of tungsten oxide nuclei on the surface and the subsequent deposition of tungsten oxide from the gas phase onto the nuclei, which results in the directional growth (i.e. growth along a preferred orientation). If the filament is not carburized, then at the high temperature (2600 K), a significant amount of the filament will be converted to tungsten oxide, which will then deposit onto the CNT surface as nanorods.

Fig. 2. (a) A TEM image showing of the WO₃ nanorods grown on CNT. (b) Close up view of a single nanorod with secondary branching. (c) A high resolution TEM image showing the polycrystalline nature of the nanorod. (d) A nanobeam EDS spectra obtained from the nanorods.
of tungsten vapor evolves from the filament surface. This tungsten vapor reacts with oxygen and water vapor present inside the chamber to produce WO$_3$ in the gas phase, which then deposits on substrate surface. During the synthesis, the hot tungsten filament is constantly bombarded with a flux of CH$_4$ that slowly carburizes the filament to form WC and W$_2$C. This process is known to take about 1–2 h depending on the thickness of the tungsten wire and the flow rate of CH$_4$[16]. We thus ran our experiments for 2 h in order to maximize the templated growth of the WO$_3$ nanorods. It is interesting to note the growth of nanorods on multiwalled CNTs. The morphology of the rods is similar to that seen on the bare Si surface, but they grow out radially from CNT and completely cover the CNT as shown in Fig. 1. The surface density of the nanorods on the CNT is much higher than that on the bare Si surface, implying that CNT may be better nucleators of tungsten oxide than Si. The size distribution of the nanorods is much larger on CNT (∼ 60–120 nm) than on the Si (∼ 60–80 nm) which may be due to the fact that the impinging flux of tungsten oxide vapor is more uniform on the flat Si surface compared to that on the curved CNT surface.

Fig. 2(a) shows a low magnification TEM image of the nanorods growing on the CNT. The nanorods have similar diameters in the range of 60–100 nm. The existence of isolated clean CNTs is also shown along with the WO$_3$ nanorods, which could be the result of the catalytic growth of CNTs with tungsten [17]. Fig. 2(b) shows that there is no particular growth direction for the nanorods, but they tend to grow outward from the CNT surface. Some secondary branches growing from the nanorods are also clearly visible. Fig. 2(c) shows that the nanorods are polycrystalline with no particular crystal orientation. The nanobeam EDS acquired from individual nanorods inside TEM, as shown in Fig. 2(d), indicates that tungsten and oxygen are the only major elements present in the nanorods. The Cu signal shown in the spectrum is from the copper TEM grid.

The elemental analysis of the samples was further performed using glancing angle XRD (Rigaku DMAX) with a Cu-Ka source at 45 kV and 20 mA using 1° inlet and 0.3° outlet slits and with a scanning rate of 0.02°/min. The spectrum was taken from a limited amount of nanorod/CNT sample collected from the Si substrate to avoid the spectrum interference from Si. As seen in Fig. 3 the XRD data indicates that the dominant growth phases are WO$_3$ and WC (according to the Joint Committee on Powder Diffraction Standards card nos. 85-2460 and 72-0097, respectively) with traces of WO$_2$.9. A rough estimate of the percentage of WO$_3$/WC in the sample is 77:23. The WC signal is most probably from the nanorod/CNT interface, as there is no evidence of carbon in the nanobeam EDS spectrum shown previously in Fig. 2(d) taken from isolated individual nanorods.

Fig. 4 shows the WO$_3$ nanorods synthesized on the fresh-grown CNTs. The nanorods grow radially outward from the CNTs. On closer observation (see the inset in Fig. 4) these nanorods have a diameter of ∼ 100–150 nm and have an average length of ∼ 400–500 nm. Further TEM analyses showed that the nanorods are polycrystalline and do not follow any particular crystal orientation during growth. A TEM nanobeam EDS study on individual nanorods revealed that tungsten and oxygen are the only dominant species present in the nanorods. Overall, the growth and the characteristics of the nanorods on this fresh-grown CNT film are very similar to that in the first case.

As the density of the CNT in the second case is orders of magnitude larger than the first case, the surface coverage of WO$_3$ nanorods is also noticeably higher. Furthermore, the WO$_3$ nanorods grow ubiquitously on every individual CNT and form dense radially branched structures. The quality of the CNT and its effect on the nucleation of WO$_3$ on CNT is an interesting issue which needs to be further addressed but is beyond the scope of this work. The growth density of WO$_3$ nanorods on the surface of CNT in the two separate cases is much larger than on the planar Si [100] surface. A simple estimate of the surface area of WO$_3$ nanorods on CNT compared to that on the flat Si surface revealed an order of magnitude increase. This increase in surface area of WO$_3$ due to templated growth on CNT can be effectively harnessed in gas sensing, field emission and catalytic applications. Furthermore, with demonstrated flexibility of patterning CNTs in various structures [14], novel photonic nanostructures taking advantage of the voltage modulated optical properties of WO$_3$ could also be envisioned.

4. Conclusions

We have demonstrated the templated growth of polycrystalline WO$_3$ (x = 2.9–3) nanorods on CNTs in a hot-filament CVD reactor with uncarburized tungsten filaments under typical diamond growing conditions. The density of the WO$_3$ nanorods on CNTs is shown to be much larger than that on planar Si [100] surfaces, suggesting that CNTs are able to nucleate WO$_3$ more effectively than a Si surface. The templated growth on the CNT provides an order of magnitude increase in the surface area...
covered by tungsten oxide. The relatively simple growth process indicates the potential for scaling up for large scale production.

Acknowledgments

The work is supported by NSF grant CTS-0304132. The materials characterizations were performed in the Center for Microanalysis of Materials, University of Illinois, which is partially supported by the U.S. Department of Energy under grant DEFG02-91-ER45439. We would also like to acknowledge the help of Dr. J. Wen for the CNT growth, Dr. R. Tweseten and Dr. M. Sardela for TEM and XRD analyses.

References