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Novel technique for large scale production of spherical tungsten oxide nanoparticles

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Abstract A simple modification in hot filament chemical vapour deposition has been used to control the growth of tungsten oxide nanoparticles on a large scale where the as-deposited material is mostly amorphous in nature with a few nanoparticles. However, upon annealing in air, almost all the material converts into spherical nanoparticles with a low size dispersion as characterized by TEM. X-ray diffraction, XPS and PL were used for structural, compositional and optical analysis.

Introduction

Nanostructured tungsten oxide is expected to play a crucial role in future technological advances in photocatalyses [1], solar energy devices [2] and color memory devices [3]. Due to phenomenal electro-chromic behavior [4], tungsten oxide has the potential to be used in smart windows and displays. On the other hand, being a non-stoichiometric n-type oxide semiconductor [5], tungsten oxide has extensive applications as a gas sensor [6] for reducing gas pollutants as well as for oxidizing agents. Among the major gas pollutants, NO_x group, H_2S and NH_3 detection are particularly most important and still a challenging goal. Tungsten oxide has proven its capability to sense those gases with better selectivity and sensitivity than the traditional metal oxides [7, 8]. Currently researchers have tried several techniques to grow nanocrystalline tungsten oxide, as the nanostructures offer large surface area and more open and stepped structures which may lead to lower temperature activity during chemical reactions. Different synthetic techniques like solution chemistry [9, 10], solvothermal technique [11], thermal evaporation or sublimation [12], CVD [13] etc. are now being used for nanocrystalline tungsten oxide but all the physical techniques are costly and chemical techniques are not compatible with the microelectronic industry (on chip sensors or micro batteries). Also, the chemical technique has a lack of control over size dispersion.

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Experimental

This paper reports a simple, large-scale preparation technique for tungsten oxide nanoparticles at low cost, which is compatible to microelectronic industry too. We have modified a hot filament chemical vapor deposition (HFCVD) reactor, which can produce tungsten oxide nanoparticles on substrates without decomposing any chemical precursor for tungsten and the technique shows its potential for the synthesis of tungsten oxide nanoparticles of required uniformity and purity. The growth technique is totally free of water and carbon contamination unlike other chemical synthesis techniques. Normally, in hot filament CVD systems the reactant gases come to the chamber and are then pyrolysed by the hot tungsten filament, which is heated by passing current through it. A similar system was utilized for this work. At a low pressure of air or oxygen, the oxidation of the tungsten filament produces tungsten oxide on the substrate. So there is no gaseous or liquid precursor for tungsten. As a result, cost is low for production and the system is simplified. The

tungsten filament itself is the source for tungsten. This technique can also be used for the growth of other transitional metal oxide nanoparticles using the filament of that particular metal and appropriate ambient. The system consists of a steel chamber with an inlet and outlet for gases. The outlet is connected to a rotary pump. A pressure gauge is connected to the chamber to monitor the pressure. The substrate holder is heated and the temperature can be controlled from room temperature to 1200 °C. Therefore, the substrate can be heated during growth and post-deposition annealing may be performed without removing the sample from the chamber. The tungsten filaments can draw up to 100 A. The power to the filament is controlled through an autotransformer and also an ammeter is connected in this path to monitor the current. Production of tungsten oxide can be done on a large scale in the above-mentioned setup where the synthesized material deposits over a circle of diameter 2.8 inches when a single filament was used at a distance of 4.5 inches from the substrate. Using multiple filaments or different architecture one can cover larger areas. The temperature of the filament was determined by a IRCON optical pyrometer through the portholes in the chamber.

The growth has been done under constant current of 42 A for 10 min at a chamber pressure of 380 mTorr of air. The temperature of the filament was 2000 °C and the substrate temperature was kept at 30 °C. The synthesized tungsten oxide was deposited on Si and glass substrate. The thickness was 4.2 μm. Then the sample was annealed at 300 °C in open air for 20 min.

A JEOL JEM-2010 UHR electron microscope with Gatan 622 SC TV camera was used for HRTEM and Philips CM 12 Transmission Electron Microscope was used to record TEM and SAED images. Philips PW 1710 X-ray diffractometer with CuKα source was used for X-Ray diffraction analysis and VG Scientific VG ESCALAB MKII system was used for XPS analysis using MgK_{α} source. PL spectroscopy was done using Perkin Elmer LS 55 system to measure the bandgap and to detect the oxygen deficiency generated defects in the annealed samples with an excitation frequency of 275 nm.

Results and discussions

TEM observation

Figure 1a shows typical HRTEM image of as-grown tungsten oxide nanoparticles synthesized by modified HFCVD which shows that most of the grown materials is amorphous in nature with few tungsten oxide nanoparticles in it. It is suggested that due to electrical heating of the tungsten filament at very high temperature and at low pressure of air the filament surface changes to tungsten oxide and that tungsten oxide immediately evaporates. The sublimation temperature of tungsten oxide is 850 °C at atmospheric pressure. Then the tungsten oxide vapor condenses on the substrate. The as-grown material shows amorphousness with small percentage of nanocrystals but as the sample is annealed at 300 °C for 20 min in air, mostly spherical nanoparticles are forming which is confirmed from TEM image in Fig. 1b. Annealing of the sample led to low size distribution nanoparticles of WO_3 almost all over the sample and no indication of amorphous matrix. The size distribution over 70 nanoparticles is shown in Fig. 1c. The mean diameter of the nanoparticles is 15 nm and arithmetic standard deviation is 4 nm as calculated from TEM image. Most nanoparticles are spherical in shape and crystallinity was investigated by SAED. Inset of Fig. 1b shows the typical SAED pattern for the nanoparticle cluster at the bottom of the TEM image.

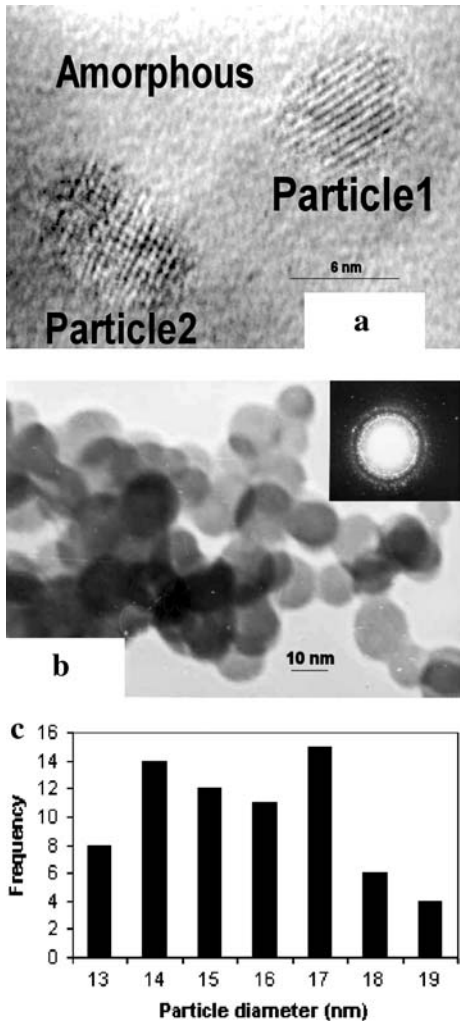

Fig. 1 (**a**), (**b**) TEM images of the as-deposited WO_3 and after annealing it at 300 °C in air, respectively. (**c**) Histogram for the annealed sample

The diffraction pattern (SAED) indicates the polycrystallinity in the sample. The rings identified from the picture from inside to outside are (020), (10$\bar{2}$) and (131) of triclinic WO_3 with lattice values 3.82 Å, 2.66 Å, 2.01 Å and (200) monoclinic phase WO_3 with lattice value of 1.86 Å [14, 15].

X-ray diffraction analysis

Figure 2 shows the typical XRD pattern of the nanocrystalline tungsten oxide by modified HFCVD system after annealing for 20 min. at 300 °C. Peaks identified in X-ray are $2\theta = 24.42°$ (200), 33.81° (202), 34.40° (220) of monoclinic phases and 23.76° (020) of triclinic phase. But the most significant contribution to the XRD pattern came from (020) of triclinic phase and (200) of monoclinic phase. The crystallite size estimated from FWHM of the XRD peak at 23.76° by Scherrer formula is 12 nm, which is smaller than the particle size seen in TEM image. The discrepancies in particle size and crystallite phases are may be due to the fact that TEM data comes from localized area of the sample whereas X-ray analyses larger area of the sample so the data is averaged out over larger no of particles for X-ray analysis.

XPS analysis

Figure 3 shows the X-ray photoelectron spectrum for the annealed sample. A well-resolved double peak due to the $4f_{7/2}$ and $4f_{5/2}$ components (spin orbit splitting of 2.1 eV) clearly denotes the presence of stoichiometric tungsten oxide (WO_3) [15, 16]. The largest component of the binding energy is at 35.8 eV, which is assigned to the W^{6+} of the stoichiometric WO_3. Besides the stoichiometric WO_3 peaks, there is also a small shoulder at 34 eV that is a clear indication of the presence of reduced W of the sub-stoichiometric WO_{3-X} [16, 17] in the sample even after annealing in atmosphere.

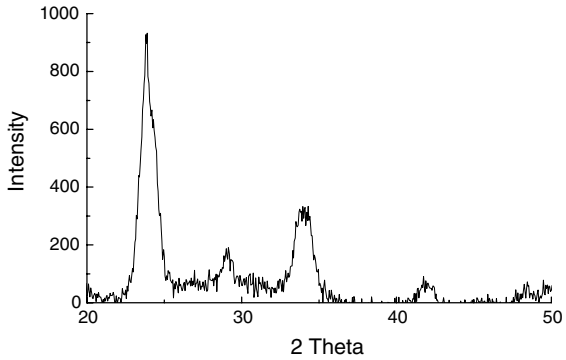

Fig. 2 XRD pattern for the tungsten oxide nanoparticles

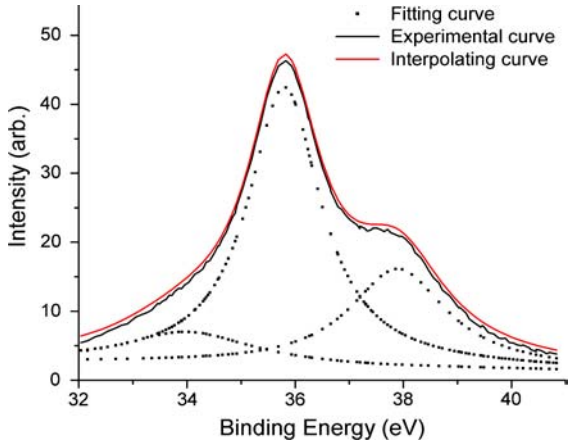

Fig. 3 XPS analysis of tungsten oxide nanoparticles

Photoluminescence study

Room temperature photoluminescence spectrum in the wavelength range of 280–600 nm for the annealed sample is shown in Fig. 4. The strongest peak is around 442 nm and a small intensity peak is in the region of 356 nm (3.48 eV). This 3.48 eV peak is well matched to estimated optical bandgaps for WO_3 in the reported value [18]. This 356-nm peak is due to band-to-band transitions where as the band to impurity transitions due to defects (mostly oxygen vacancy), produces the 442-nm peak [19]. The appearance of the as-grown film was blue whereas after annealing it became whitish in color.

Summary

We report the first large-scale, low cost, liquid or gaseous precursor less growth of nanocrystalline tungsten oxide by a simple modification of hot filament chemical vapor deposition technique. This simple mass scale production

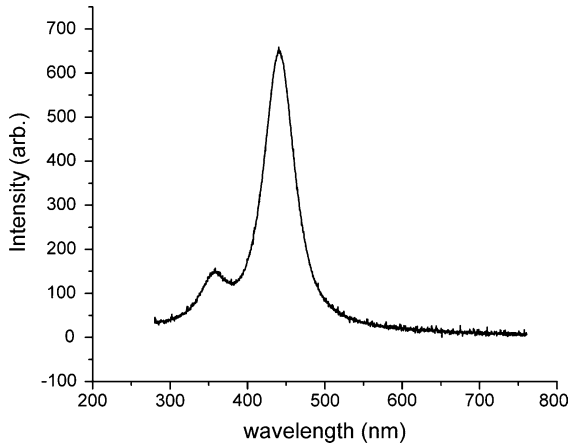

Fig. 4 PL spectrum of the tungsten oxide nanoparticles

technique for transitional metal oxide nanoparticles would be very useful for smart windows, gas sensors and other industrial and household applications. The technique is also promising for the synthesis of other transition metal oxide nanoparticles like molybdenum, nickel, copper or ferrous oxide.

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