JOURNAL OF Materials Communication CHEMISTRY

Fabrication and characterization of nanotubular semiconductor oxides In_2O_3 and Ga_2O_3

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Received 8th September 2001, Accepted 15th October 2001
First published as an Advance Article on the web 26th October 2001

Hollow nanotubes comprised of In_2O_3 and Ga_2O_3 have been successfully synthesized for the first time *via* sol–gel chemistry and porous alumina templating thereby providing a new morphology for these important semiconductor oxides. The nanotubes are characterized by SEM, XRD and XPS, and the length (typically tens of microns) and outside and inside diameter (of the order of 100 nm) can be varied by selecting the template dimensions and sol immersion time. This new morphology with a large surface area may be important in applications ranging from gas sensors to optoelectronic nanodevices.

Technological applications in many different areas—catalysis, microelectronic components, high performance ceramics and sensors—are driving the synthesis of nanostructured semiconductor oxides.[1] Catalysts,[2] photocatalysts,[3] solar cells,[4] sensor elements,[5] *etc.* are critically dependent on the semiconductor morphology/surface area, and numerous studies of semiconductor oxides have been designed to effectively and economically prepare two-dimensional thin films and zero-dimensional nanoparticles.[6–8] Stimulated by the novel properties of carbon nanotubes, wire-like and tube-like nanostructures of a variety of semiconductors have been pursued in a number of laboratories.[9–12] For In_2O_3, an n-type semiconductor which exhibits good electrical conductivity and high sensitivity towards some gases,[5] preparation methods including electron-beam deposition,[13] vacuum evaporation[14] and electrodeposition[15] have been described. In the case of Ga_2O_3, a wide band gap material ($E_g = 4.9$ eV) which exhibits both conduction and luminescence properties,[16] synthetic methods including arc discharge[17,18] and physical evaporation[19] have been successful to some degree.

Herein we use the sol–gel porous alumina templating method pioneered by Martin's group[20] to fabricate nanotubes of In_2O_3 and Ga_2O_3 for the first time thereby adding two important semiconductor oxides to the family of known semiconductor oxides having a nanotubular morphology: TiO_2, MnO_2, V_2O_5, Co_3O_4, ZnO, SiO_2 and WO_3.[21,22]

In a typical experiment, In^{3+} and Ga^{3+} sols were prepared in advance as follows: 5 M ammonia was added dropwise at room temperature to an aqueous indium nitrate solution (0.4 M). The final pH of the solution was about 8.5. The hydrated precipitate so formed was separated centrifugally, washed three times with distilled water and peptized with nitric acid (0.25 M) to obtain a translucent, homogeneous and stable sol. The final pH was kept in the range of 2.4–2.5. Similarly, gallium nitrate hydrate was dissolved in ethanol, and concentrated aqueous ammonia diluted in ethanol (50% by vol.) was slowly added dropwise at room temperature until no further precipitate was observed to form. This hydrated precipitate was peptized with nitric acid to get a stable sol.

A porous alumina membrane (pore size of 200 nm) was used as a template by immersing it in a sol of In^{3+} or Ga^{3+} for 5 seconds. The sol-containing membrane was then dried in air for 30 min before annealing in air at elevated temperatures: 973 K for 12 hours (In_2O_3) and 773 K for 12 hours (Ga_2O_3).

Scanning electron microscopic (SEM) images of the template-fabricated oxides were obtained by gluing the oxide-containing membrane to a substrate and polishing the exposed surface (with 13 micron sand paper). The polished membrane was immersed in 6 M aqueous NaOH for 10 min in order to dissolve the alumina template. The resulting substrate and semiconductor oxide was attached to a SEM sample stub with conductive tape, and a very thin layer of Au was sputtered onto its surface. SEM images were obtained using a JEOL JEM-6300 scanning electron microscope.

Fig. 1 shows the SEM images of 200 nm OD ($\sim$100 nm ID) nanotubes of In_2O_3 (a) and Ga_2O_3 (b). The In_2O_3 and Ga_2O_3 nanotubes retain the alignment of the nanochannels in the alumina template because one surface of the template was anchored to the substrate dictating the tube "flux" from that interface. Furthermore, in the SEM images the tubes appear to

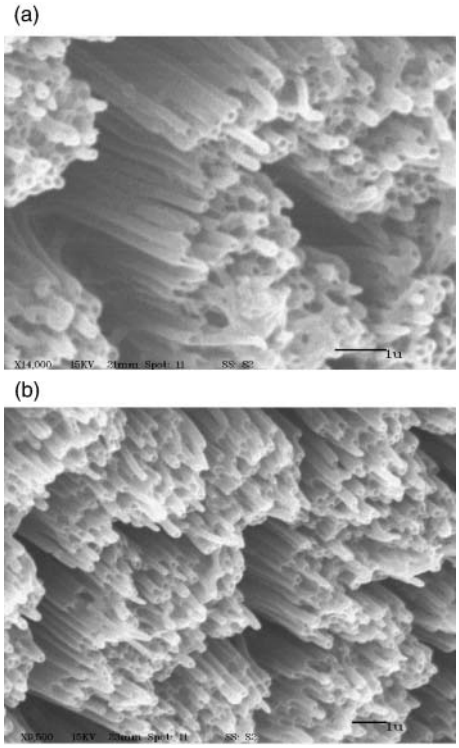

Fig. 1 SEM images of In_2O_3 (a) and Ga_2O_3 (b) nanotubes prepared by the sol–gel template method. The tube parallelism is a remnant of the porous template's morphology; a 1 μm bar is indicated on each plate.

DOI: 10.1039/b108167e

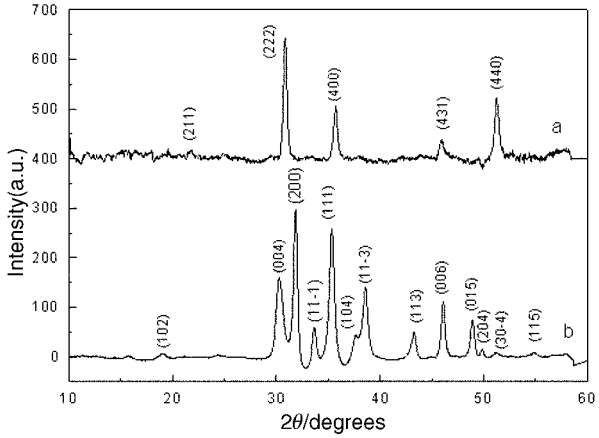

Fig. 2 X-Ray diffraction patterns (intensity *vs.* 2θ) of the nanotubular oxides In_2O_3 (a) and Ga_2O_3 (b).

have been coagulated by the solvent surface tension during the template dissolution step. The length of the tubes is 50 μm, approximately the same as the thickness of the template and its OD is 200 nm, the template pore size.

In order to verify the existence of crystalline In_2O_3 and Ga_2O_3 and characterize the purity of these semiconductor oxide nanotubes, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used. Prior to XRD and XPS measurements, both faces of the composite membrane (the oxide-filled pores of the alumina template) were polished and immersed in 6 M aqueous NaOH for 15 min to completely remove the alumina. The residue, comprised of isolated oxide nanotubes, was collected, washed with distilled water several times, and dried in air.

Fig. 2 shows XRD patterns of nanotubes of In_2O_3 (a) and Ga_2O_3 (b). The XRD patterns were recorded with an Enraf Nonius FR590 X-ray diffractometer with Cu-K_α radiation ($\lambda = 0.154$ nm). The comparison of the In_2O_3 diffraction pattern with the known diffraction pattern (data from JCPDS file 6-416) confirms that the nanotubes consist of the cubic structure of In_2O_3. Five observed peaks with 2θ values of 21.5°, 30.6°, 35.5°, 45.9° and 51.2° correspond to diffraction from the (211), (222), (400), (431) and (440) planes of crystalline In_2O_3, respectively. A similar correlation of diffraction pattern (b) with the JCPDS file 11-370 identifies the gallium oxide nanotubes as β-Ga_2O_3. Thirteen peaks with 2θ values of 19.1°, 30.1°, 31.9°, 33.7°, 35.3°, 37.5°, 38.6°, 43.4°, 46.2°, 48.9°, 49.8°, 51.2°, and 54.9° respectively, correspond to the (102), (004), (200), (11−1), (111), (104), (11−3), (113), (006), (015), (204), (30−4) and (115) planes, respectively, of crystalline β-Ga_2O_3. The XRD results not only reveal that the nanotubes of both In_2O_3 and Ga_2O_3 are crystalline as anticipated from their respective annealing temperatures, but moreover, show no additional impurity diffraction from either semiconductor oxide.

Fig. 3 shows XPS data for the nanotubes of In_2O_3 and Ga_2O_3. The XPS analyses were carried out with a PHI-5400 instrument with an RBD model 147 control interface.

For trace (a), double peaks with binding energy of 446.5 eV and 453 eV correspond to $In3d^{5/2}$ and $In3d^{3/2}$. The peak at 530.3 eV is the O1s of the In_2O_3 nanotubes. For trace (b), double peaks with binding energy of 1117.3 eV and 1139 eV correspond to $Ga2p^{3/2}$ and $Ga2p^{1/2}$. The peak at 530.5 eV is the O1s of the Ga_2O_3 nanotubes. No impurity peaks were observed in the XPS results for both In_2O_3 and Ga_2O_3. This indicates that the alumina template was completely removed by dissolving the composite membrane, resulting in highly pure, tubular In_2O_3 and Ga_2O_3 nanostructures.

The mechanism of formation of nanotubular In_2O_3 and Ga_2O_3 is undoubtedly similar to that for the formation of

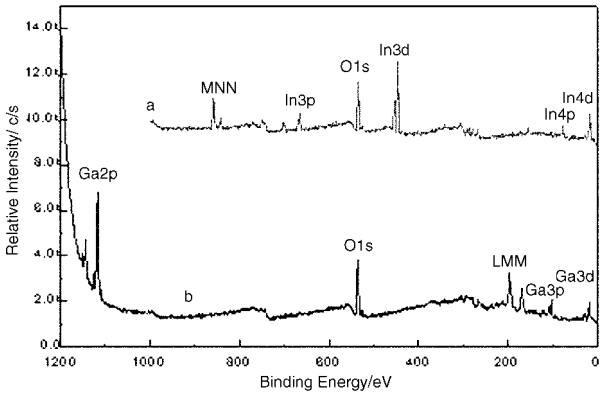

Fig. 3 X-Ray photoelectron spectra of the nanotubular oxides In_2O_3 (a) and Ga_2O_3 (b).

nanotubular TiO_2:[21] the pore walls are negatively charged and the sol particles are positively charged[23] causing the sol to adhere to the pore-cavity walls of the templating membrane. Drying and subsequent oxidation at elevated temperature shrinks the sol–gel causing it to conform to the template pores. This in turn yields a composite, alumina–semiconductor oxide. Removal of the template gives highly pure semiconductor oxides in a high-surface-area tubular morphology.

Acknowledgements

Instrumentation used in this research is supported by the Office of Naval Research MURI Grant N00014-98-1-0597.

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