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Silver telluride nanowires prepared by dc electrodeposition in porous anodic alumina templates

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Silver telluride nanowire arrays were synthesized by cathodic electrolysis into porous anodic alumina membranes from dimethyl sulfoxide (DMSO) solutions containing 0.1 M $NaNO_3$, 5.0 mM $AgNO_3$ and 6.0 mM $TeCl_4$. XRD and SAED patterns of the nanowires were indexed to be a monoclinic structure of Ag_2Te. TEM images show that the nanowires have smooth surfaces with uniform diameters. Near stoichiometric Ag_2Te nanowires were obtained for potentials between −0.55 and −0.65 V *vs.* Ag/AgCl. Furthermore, the composition of the nanowires can be controlled continuously from Ag-rich to Te-rich mainly by changing the concentration of $TeCl_4$ in the solutions.

Introduction

Recently, there has been considerable interest in fabricating nanostructures such as nanotubules, nanowires, and multilayers with interesting optical, electronic, magnetic and giant magnetoresistance properties. These nanostructures have potential applications in nanoscale electronic and optoelectronic devices,[1,2] nanosensors,[3] high-density magnetic memories,[4–6] and field sensing devices[7] *etc.* Among various nanowire fabrication strategies, template synthesis in conjunction with electrochemical deposition (ED) has been widely used to fabricate nanowire arrays in the nanochannels of templates.[4,8–10] In this method, thin fibrils of the desired materials are electrochemically deposited within the pores of the template materials, and the length, structural properties and chemical compositions of the nanowires can be controlled by electrodeposition parameters.

Silver telluride is known as a typical example of mixed ionic–electronic conductivity in solids. Ag_2Te undergoes a structural phase transition at around 145 °C[10] from the low-temperature monoclinic (β) to the high-temperature cubic structure (α).[12] Its low temperature phase is a narrow band-gap semiconductor with high electron mobility and low lattice thermal conductivity. Its band-gap is in the range 0.04–0.17 eV.[13] In its high-temperature phase, Te anions form a face centered cubic (fcc) sublattice through which Ag cations can move easily,[12] thus giving rise to the superionic conductivity.[14] Recently, large positive magnetoresistance (MR) has been observed in both Ag-rich (n-type) and Te-rich (p-type) silver telluride bulk samples[15,16] or thin films.[17] With remarkable magnetoresistance effects at room temperature and its linear field dependence down to 10 Oe,[15,16] n-type $Ag_{2+\delta}Te$ could be a promising material for application in wide range magnetic field sensors. With increasing interest in nanostructured materials and nanodevices, silver telluride nanowires could show potential applications in nanoscale low field sensors.

Metal telluride nanowires such as Bi_2Te_3 and CdTe have been synthesized by the template electrodeposition method. Bi_2Te_3 nanowires were synthesized from acidic aqueous solutions.[18] CdTe nanowire arrays were deposited from an ethylene glycol solution containing $CdCl_2$, $TeCl_4$ and KI at 160 °C.[19] Here, we report the preparation of aligned silver telluride nanowire arrays by dc electrodeposition in anodic alumina (AAO) membranes from dimethyl sulfoxide (DMSO) solution containing $AgNO_3$, $TeCl_4$ and $NaNO_3$. DMSO would be both an electrochemical solvent, which readily dissolves $TeCl_4$ to form $(2DMSO\cdot TeCl_3)^+\cdot Cl^-$, and a weak complexing agent of Ag^+.[20] The resulting Ag_2Te nanowires were characterized by X-ray diffraction, transmission electron microscopy (TEM), high-resolution TEM, and X-ray energy dispersion analysis (EDAX).

Experimental

1 Materials

Tellurium(IV) chloride ($TeCl_4$, 99%, ACROS), silver nitrate ($AgNO_3$, 99.9% A.R.) and DMSO (A.R.) were used without further purification. Sodium nitrate ($NaNO_3$) (A.R.) was recrystallized before use. The porous AAO templates with pore diameters of about 50 and 20 nm and with thicknesses of about 20 and 40 μm were fabricated by anodization of Al plates (99.999%) from 4% oxalic acid and 14% H_2SO_4 respectively as reported previously.[19,21,22] A thin layer of Au (*ca.* 120–140 nm) was evaporated onto one side of the membranes to serve as the cathode in a three-electrode electrochemical system.

2 Electrodeposition procedures

The electrodeposition of Ag_2Te nanowire arrays was carried out in a solution containing 0.1 M $NaNO_3$, 5.0 mM $AgNO_3$ and 6.0 mM $TeCl_4$ dissolved in DMSO. The glass cell was immersed in an oil bath with a temperature of 80 ± 1°C. The solution was continuously stirred. The electrodeposition process was performed potentiostatically using a three-electrode system with an Ag/AgCl reference electrode and a platinum plate as the counter electrode. The potentials are expressed *vs.* Ag/AgCl. Silver telluride was then cathodically deposited in the AAO/Au template. After deposition for about 40–50 min, the sample was removed from the electrolyte, first rinsed with hot DMSO followed by ethanol, and then dried in air at room temperature.

3 Characterization

For electron microscopy investigations, the sample was mounted on a Si(100) wafer using epoxy resin, then dipped into 1 M NaOH at 20 °C for about 1 h to dissolve the alumina, and washed several times with deionized water. The nanowires

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were then detached from the Au substrate by ultrasonic dispersion in about 1 ml water. At last, the aqueous suspension was dripped onto copper grids for transmission electron microscope (TEM) and high resolution TEM (HRTEM) observation. TEM and HRTEM observations were carried out on a JEM-2000FX, and a JEM-2011EX (JEOL) operated at 160 kV and 200 kV respectively. The X-ray diffraction (XRD) measurement was performed on a Rigaku D/MAX2000 X-ray diffractometer using Ni-filtered CuKα radiation. The X-ray tube was operated at 70 kV and 100 mA.

Results and discussion

XRD measurement of a bulk sample adhering to an Au substrate was performed after dissolution of the alumina. Fig. 1 shows the XRD pattern of Ag_2Te nanowires with about 50 nm diameter deposited at a potential of -0.60 V *vs.* Ag/AgCl. The diffraction peaks at 28.18, 29.92, 31.04, 38.88, 40.1, 41.3, and 42.28° can be indexed to (111), ($-$211), ($-$210), ($-$113), ($-$303), (310) and (021) of monoclinic Ag_2Te respectively. These peak positions are in good agreement with the standard diffraction data of powder monoclinic Ag_2Te (JCPDS standard 12-695). No obvious preferred orientation in the nanowires was indicated. In addition, no diffraction peaks from elemental Ag or Te were detected. Au(111) and (200) peaks originating from the substrate appeared.

Fig. 2a shows a typical TEM image of Ag_2Te nanowires after dissolution of the template. The nanowires have smooth surfaces with uniform diameters of about 50 nm. A typical diffraction contrast image of an individual nanowire shown in Fig. 2b indicates that the wire is well crystallized and the diameter remains uniform along the whole wire. The selected area electron diffraction (SAED) pattern of this nanowire is illustrated in the inset of Fig. 2b. The diffraction spots with $d = 0.32 \pm 0.01$ and 0.29 ± 0.01 nm have been indexed as (111) and ($-$210) of the monoclinic Ag_2Te respectively. High-resolution TEM was employed to observe the fine structure of the nanowires. Fig. 2c shows an HRTEM image of a nanowire with a diameter of 18 nm. The interplanar spacing, 0.23 ± 0.01 nm, is consistent with the interplanar distance of the ($-$113) planes ($d = 0.231$ nm) of bulk monoclinic Ag_2Te. An X-ray energy dispersion analyzer (EDAX) (9100/6 Philips) attached to the TEM was employed to analyze the chemical composition of the nanowires. The EDAX spectrum shown in Fig. 3 reveals that the nanowires consist of Ag and Te, and quantitative analysis of AgLα and TeLα in the spectrum indicates that the atomic ratio of Ag to Te is very close to 2 : 1.

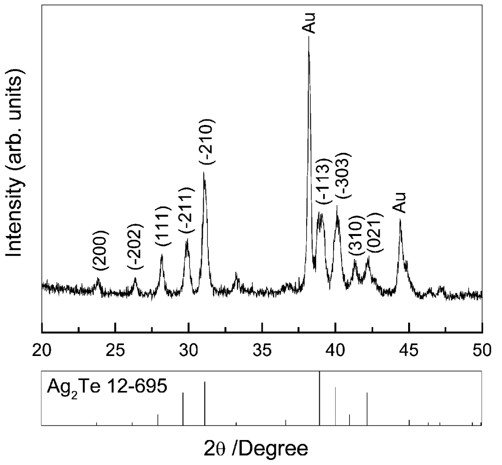

Fig. 1 X-Ray diffractogram of the Ag_2Te nanowires. Below is shown the XRD standard of monoclinic Ag_2Te.

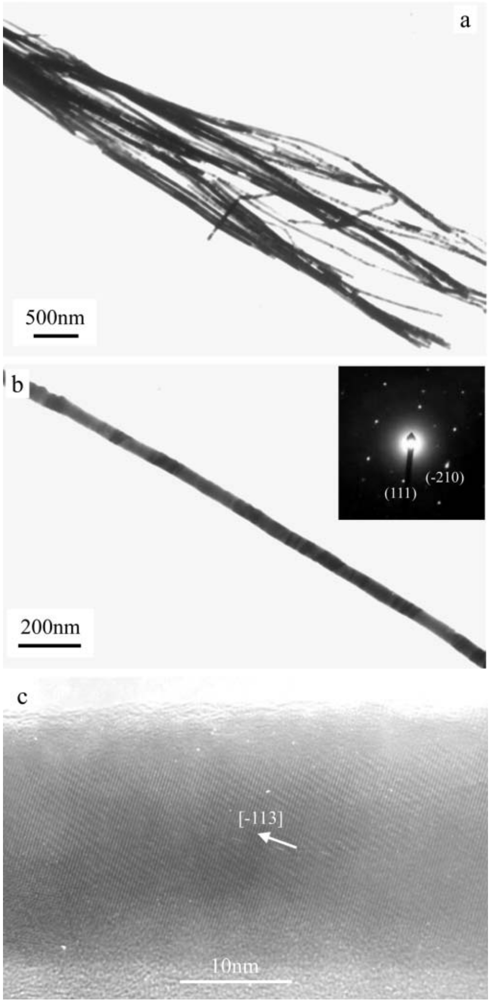

Fig. 2 Typical TEM images of Ag_2Te nanowires. (a) A bundle of 50 nm diameter nanowires. (b) An individual nanowire with a diameter of 50 nm. The inset shows the corresponding selected area electron diffraction (SAED) pattern. (c) High-resolution TEM image of an Ag_2Te nanowire with a diameter of 18 nm.

The technique of cyclic voltammetry was used to study the cathodic deposition process of Ag_2Te. All the cyclic voltammograms were collected in unstirred solutions at the temperature of 80 ± 1 °C using ITO/glass as the working electrodes. Fig. 4(a) shows a scan of a solution containing 5.0 mM $AgNO_3$ and 0.1 M $NaNO_3$. Silver deposition is evident by the appearance of a reduction peak at 0.14 V. Fig. 4(b) presents the cyclic voltammogram of a solution containing 6.0 mM $TeCl_4$ and 0.1 M $NaNO_3$. The reduction of Te^{4+} to Te begins at about -0.13 V and reaches the peak current at -0.54 V. The XRD identification of the deposited film at around -0.3 V confirms the formation of hexagonal Te. The cyclic voltammogram of a

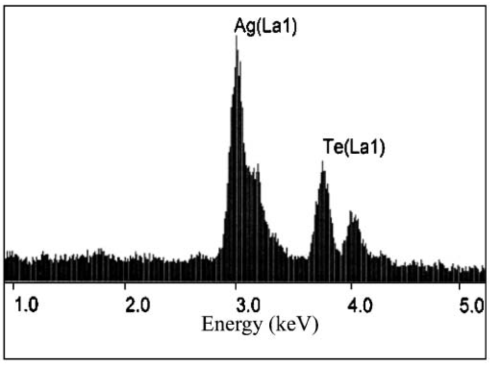

Fig. 3 EDAX spectrum revealing that the nanowires are composed of Ag and Te with the atomic ratio of 2 : 1.

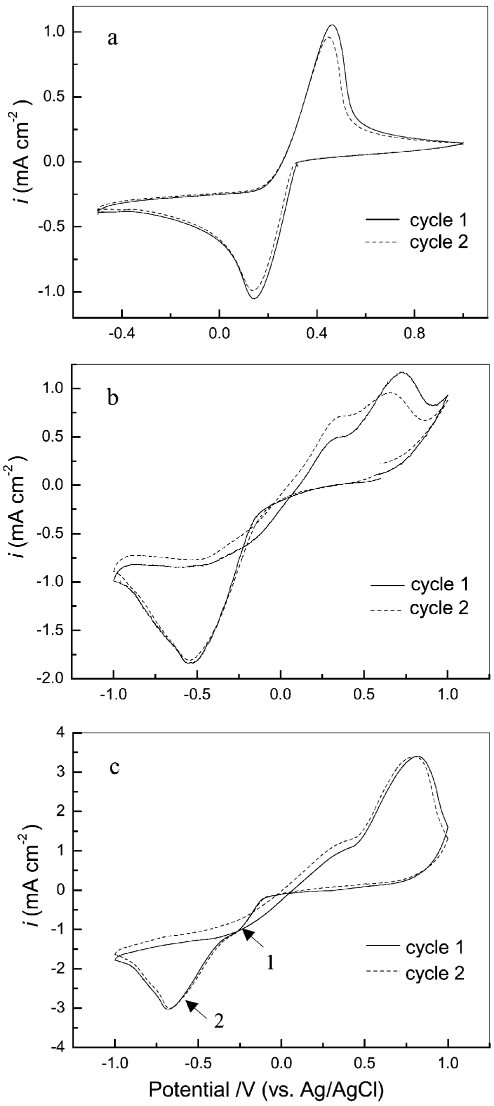

Fig. 4 Cyclic voltammograms for ITO/glass electrode in DMSO solutions containing (a) 0.1 M $NaNO_3$ and 5.0 mM $AgNO_3$, (b) 0.1 M $NaNO_3$ and 6.0 mM $TeCl_4$, and (c) 0.1 M $NaNO_3$, 5.0 mM $AgNO_3$ and 6.0 mM $TeCl_4$, at the temperature of 80 ± 1 °C. Scan rate = 50 mV s^{-1}.

solution containing both $AgNO_3$ and $TeCl_4$ is shown in Fig. 4(c). In this figure, the first reduction wave is mainly caused by the reduction of Ag^+ to Ag. Comparing with Fig. 4(a), the potential of Ag deposition moves to between −0.1 and −0.3 V (peak at about −0.24 V) after $TeCl_4$ is added to the solution. This is caused by the formation of the complex ion $[AgCl_4]^{3-}$, which can move the Nernst potential of Ag^+/Ag by about −0.3 V in theory. When the deposition potential was kept constant between −0.1 and −0.3 V, XRD results demonstrated that the main product was silver, accompanied by the weak diffraction peaks of Ag_2Te, but no diffraction peak of Te was detected. This result implies that the cathodic reduction from Te to Ag_2Te according to eqn. (1) is complete and Ag_2Te began to deposit almost at the potential of Te^{4+} to Te, which was caused by the formation of insoluble Ag_2Te ($\log K_{sp} = -71.7$[23]). With lowering the potential, the formation rate of Te, or Ag_2Te increased. At the same time, the deposition rate of Ag decreased due to the diffusion control of Ag^+. Hence, the excess amount of Ag in the deposit decreases. At potentials around −0.60 V, stoichiometric Ag_2Te was formed. Further, at potentials below −0.60 V, the deposited Te cannot transform to Ag_2Te completely, and excess Te would exist in the product. Another chemical stage of reaction expressed by eqn. (2) can also occur, driven by the strong reactivity of silver and tellurium ($(G_{Ag_2Te})_{298} = -81.66$ kJ mol^{-1}[24]).

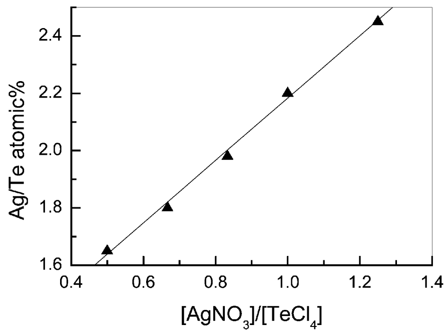

Fig. 5 The Ag/Te atomic ratios for nanowires deposited at a potential of −0.60 V *vs.* Ag/AgCl from solutions containing different concentrations of $TeCl_4$ (4.0, 5.0, 6.0, 7.5 and 10.0 mM). The concentration of $AgNO_3$ was kept constant at 5.0 mM.

$$2Ag^+ + Te + 2e^- \rightarrow Ag_2Te \qquad (1)$$

$$2Ag + Te \rightarrow Ag_2Te \qquad (2)$$

Due to the large magnetoresistence effect shown in both Ag- and Te-rich silver tellurides,[16] the synthesis of silver telluride nanowires with controllable composition by adjusting the electrodeposition parameters could be critical for their applications. From the EDAX quantitative analysis results, the atomic ratios of Ag/Te in the nanowires remain approximately stable at a range of deposition potentials between −0.55 and −0.65 V *vs.* Ag/AgCl from a solution with identical concentration, above −0.55 V, the ratio of Ag increased, and below −0.65 V the ratio of Te increased. On the other hand, the concentration ratio of $AgNO_3$ to $TeCl_4$ in the solution was found to play a significant role in controlling the composition of the nanowires as shown in Fig. 5. When the concentration of $TeCl_4$ increased from 4.0 mM to 10.0 mM, the atomic ratio of Ag/Te in the nanowires could be controlled linearly from $Ag_{2.45}Te$ to $Ag_{1.65}Te$ depending on the concentration ratio of $AgNO_3$ to $TeCl_4$.

Conclusions

We describe a method for synthesizing crystalline Ag_2Te nanowire arrays by dc electrodeposition in AAO templates from DMSO solutions. Near-stoichiometric Ag_2Te nanowires were obtained at potentials between −0.55 and −0.65 V *vs.* Ag/AgCl from solutions containing appropriate concentrations of Ag and Te sources. The obtained nanowires are well-crystallized monoclinic Ag_2Te. In addition, the chemical compositions of the silver telluride nanowires could be controlled continuously by mainly adjusting the concentration of $TeCl_4$ in the solutions. This provides a simple and mild route for the preparation of Ag-rich and Te-rich nanowires. The method of using DMSO as a solvent and $TeCl_4$ as a Te source could be extended to the synthesis of other metal tellurides by electrodeposition.

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References

1 D. H. Cobden, *Nature*, 2001, **409**, 32.
2 Y. Cui and C. M. Lieber, *Science*, 2001, **291**, 851.

3 Y. Cui, Q. Q. Wei, H. K. Park and C. M. Lieber, *Science*, 2001, **293**, 1289.

4 T. M. Whitney, J. S. Jiang, P. C. Searson and C. L. Chien, *Science*, 1993, **261**, 1316.

5 F. Li, R. M. Metzger and W. D. Doyle, *IEEE Trans. Magn.*, 1997, **33**, 3715.

6 G. A. Prinz, *Science*, 1998, **282**, 1660.

7 K. Liu, C. L. Chien, P. C. Searson and Y. Z. Kui, *Appl. Phys. Lett.*, 1998, **73**, 1436.

8 D. Routkevitch, A. A. Tader, J. Haruyama, D. Almawlawi, M. Mokovits and J. M. Xu, *IEEE Trans. Electron Devices*, 1996, **43**, 1646.

9 J. C. Hulteen and C. R. Martin, *J. Mater. Chem.*, 1997, **7**, 1075.

10 C. R. Martin, *Science*, 1994, **266**, 1961.

11 V. Damodara Das and D. Karunakaran, *J. Appl. Phys.*, 1989, **66**, 1822.

12 J. Schneider and H. Schulz, *Z. Kristallogr.*, 1993, **203**, 1.

13 W. Gorbachev, *Semiconductor compounds* $A^{I}{}_{2}B^{VI}$, Metallurgy, Moscow, 1980.

14 M. Kobayashi, K. Ishikawa, F. Tachibana and H. Okazaki, *Phys. Rev. B*, 1988, **38**, 3050.

15 R. Xu, A. Husmann, T. F. Rosenbaum and M. L. Saboungi, *Nature*, 1997, **390**, 57.

16 H. S. Schnyders, M. L. Saboungi and T. F. Rosenbaum, *Appl. Phys. Lett.*, 2000, **76**, 1710.

17 I. S. Chuprakov and K. H. Dahmen, *Appl. Phys. Lett.*, 1998, **72**, 2165.

18 S. A. Sapp, B. B. Lakshmi and C. R. Martin, *Adv. Mater.*, 1999, **11**, 402.

19 D. S. Xu, D. P. Chen, Y. J. Xu, X. S. Shi, G. L. Guo, L. L. Gui and Y. Q. Tang, *Pure Appl. Chem.*, 2000, **72**, 127.

20 D. W. A. Sharp, *Inorganic Chemistry Series two, vol. 5, Transition Metals—Part 1*, Butterworths, London, 1974.

21 D. S. Xu, Y. J. Xu, D. P. Chen, G. L. Guo, L. L. Gui and Y. Q. Tang, *Adv. Mater.*, 2000, **12**, 520.

22 D. S. Xu, X. S. Shi, G. L. Guo, L. L. Gui and Y. Q. Tang, *J. Phys. Chem. B*, 2000, **104**, 5061.

23 E. A. Buketov, M. Z. Ugorets and A. S. Pashinkin, *Russ. J. Inorg. Chem.*, 1964, **9**, 292.

24 K. C. Mills, *Thermodynamic Data for Inorganic Sulfides, Selenides and Tellurides*, Butterworth, London, 1974.