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Preparation and synthesis of Ag_2Se nanowires produced by template directed synthesis

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We have prepared silver selenide nanowires by a novel synthesis technique. The nanowires were produced through template directed synthesis, in which we used a porous alumina membrane as the template. Silver was deposited on one surface and in the pores close to that surface of the template, followed by electro-deposition of selenium into the pores. Silver selenide nanowires of high quality were produced inside the pores.

Introduction

The movement towards nanostructured materials has driven pure science and applied research over the last few years. Synthesis of nanomaterials becomes more elaborate day by day, and the effort to make these materials in large quantities and at low cost is moving at an even greater pace. In this paper we report a novel technique for producing high quality silver selenide nanowires.

Silver selenide exhibits two distinct crystallographic phases separated by a transition at 406 K. The low temperature phase, β-Ag_2Se, is orthorhombic and is a narrow band gap semiconductor with an energy gap of 70 meV at 0 K. Potentially it has many applications on the nanoscale because of a very low lattice thermal conductivity, high electrical conductivity and high Seebeck coefficient (-150 μV K^{-1}),[1–4] though up until now it has really only been used as a photosensitizer in photographic films or thermochromic materials.[5] The high temperature phase, α-Ag_2Se, is cubic and exhibits super ionic properties.[6]

Experimental method

Electro-deposition of selenium took place in an alumina membrane, which acted as a template in the synthesis of silver selenide nanowires. These membranes, along with colloidal crystalline films, allow the high yield production of nanoscale materials without the imposing cost factors of traditional nanoscale production techniques such as electron beam lithography.[7,8] The alumina template, a Whatman anodisc membrane filter, was 60 μm thick with a pore density of 1×10^9 cm^{-2}. The pores range in diameter from 200 to 350 nm, though the pore wall diameter is not uniform vertically. The pores exhibit a branching at one surface of the membrane where the large cylindrical pore ($\geqslant$ 200 nm) branches to become a capillary with a diameter of 200 nm. The membranes were prepared for deposition by evaporating a 500 nm layer of silver to the bottom side, meaning the side that exhibits branching, to provide electrical contact. Then a 9 μm layer of silver was directly deposited into the pores of the membrane.

The electro-deposition took place at room temperature and at a constant current density of 0.8 mA cm^{-2}. The electrolyte consisted of an aqueous solution of 0.3 *m* SeO_2 and 0.03 *m* H_2SO_4. The current density is understood to be the potentiostat current divided by the effective plating area, which is defined as the number of pores on the membrane multiplied by the average area of a pore at the membrane surface. The alumina membrane was then chemically etched in a 50% HNO_3 solution removing all excess silver, just leaving the silver selenide wires standing in the membrane. Freestanding wires could be produced as well by dissolving the alumina membrane in 1 *m* NaOH. For reference we electro-deposited selenium on glass, coated with 5 nm of chromium and then a 100 nm layer of silver on top, at the same current density. X-Ray diffraction showed only bulk selenium.

Experimental results

The nanowires were characterized by a variety of techniques: SEM, EDACS, energy dispersive X-ray diffraction and EXAFS. Fig. 1a shows an optical micrograph of the cross-section of the template membrane before the removal of residual silver, and Fig. 1b a SEM image of freestanding wires after the removal of residual silver and the dissolution of the template membrane. As can be seen, the wire has a uniform diameter. EDACS, X-ray diffraction and EXAFS confirmed that the wires were predominantly silver selenide. Measurements were carried out on wires within the template and wires after the removal of the template. No differences were observed, and the remainder of the results we report are on nanowires within the alumina template. Rietveld refinement was used to determine the structure and lattice parameters of the nanowires. The X-ray diffraction pattern and resultant fit are shown in Fig. 2. The refinements confirmed that the wires were silver selenide (50%), with F.C.C. silver (50%). The particles had a strong preferred orientation and were primarily aligned along the (2,1,1), (0,3,1), and (0,0,2) crystallographic axes. The lattice parameters from the Rietveld refinement are as follows with the actual values for bulk silver selenide in parentheses: $a = 4.348$ Å (4.333 Å), $b = 7.059$ Å (7.062 Å), and $c = 7.711$ Å (7.764 Å), showing that the values are in good agreement with the bulk sample. The fact that we created silver selenide wires using this technique was quite surprising. Our initial expectation was that

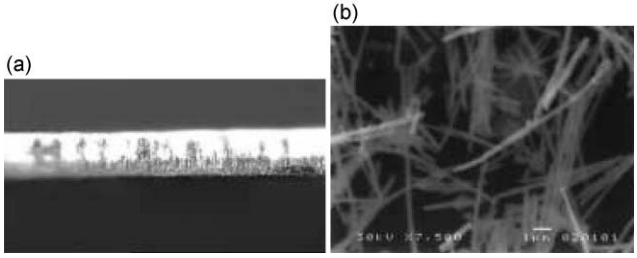

Fig. 1 (a) Optical micrograph of a cross-section of the template membrane showing silver selenide nanowires before the removal of residual silver. (b) SEM image of an Ag_2Se nanowire with an approximately 280 nm diameter.

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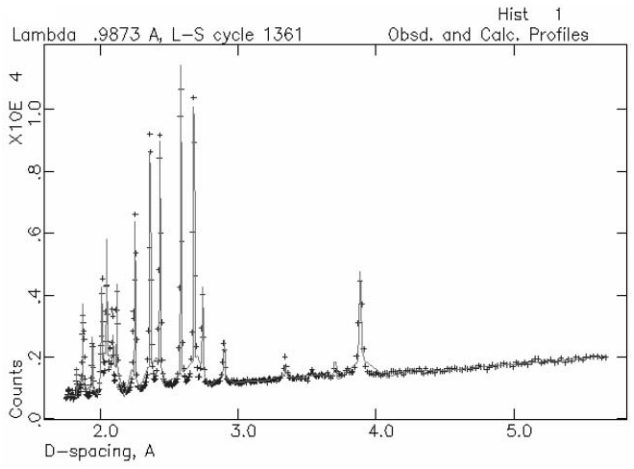

Fig. 2 Rietveld refinement of sample 3 in which selenium was electrodeposited for 12 hours.

selenium nanowires would be formed in the pores, since the glass sample exhibited no evidence of diffusion of silver into the selenium to form silver selenide.

The structure of the nanowires was studied as a function of time elapsing in the electro-depostion process. Selenium was allowed to deposit into the first sample for one hour, sample 2 for five hours and sample 3 for 12 hours. X-Ray diffraction was then used to measure the characteristics of these samples, and then compared to the known pattern for orthorhombic silver selenide. The time dependence of the deposition of selenium is immediately obvious from Fig. 3. On the bottom we have powder diffraction data for bulk silver selenide, directly above is the data for the one hour sample then the five hour sample and finally at the top the data for the 12 hour deposition. It is quite obvious that the production of silver selenide is a time dependent process.

Conclusion

In summary we have found an effective way to produce silver selenide nanowires using template directed synthesis. Deposition of selenium into a template prepared by depositing silver into the pores close to the surface leads to the production of high quality silver selenide wires. The formation of Ag_2Se wires due to the diffusion of silver upon deposition, mediated by the confining geometry of the template is a technique that is quite different from techniques others have used to create Ag_2Se wires. Xia *et al.*,[5] for example used a template directed approach in which single crystalline selenium nanowires were converted to single crystalline Ag_2Se wires through a reaction with aqueous $AgNO_3$.

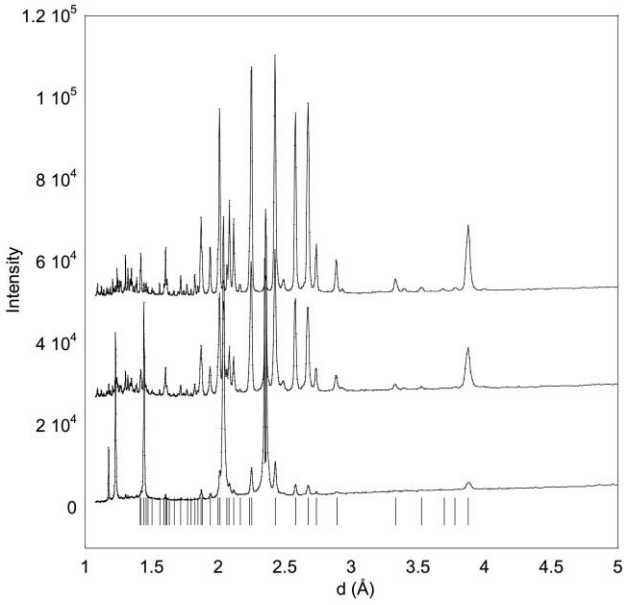

Fig. 3 The dash marks are the known powder diffraction data for silver selenide. Directly above it is the data for the sample in which selenium was deposited for one hour, above that the sample with five hour deposition and then lastly the sample with twelve hour deposition in which it is clear the silver has diffused to form silver selenide.

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References

1 M. Ferhat and J. Nagao, *J. Appl. Phys.*, 2000, **88**, 813.
2 J. B. Conn and R. C. Taylor, *J. Electrochem. Soc.*, 1960, **107**, 977.
3 P. F. Taylor and C. Wood, *J. Appl. Phys.*, 1961, **32**, 1.
4 R. Dalven and R. Gill, *J. Appl. Phys.*, 1967, **38**, 753.
5 B. Gates, Y. Wu, P. Yang and Y. Xia, *J. Am. Chem. Soc.*, 2001, **123**, 11500.
6 R. Simon, R. C. Bourke and E. H. Lougher, *Adv. Energy Convers.*, 1963, **3**, 481.
7 K. Nielsch, F. Müller, A. Li and U. Gösele, *Adv. Mater.*, 2000, **12**, 8.
8 K. M. Kulinowski, P. Jiang, H. Vaswani and V. L. Colvin, *Adv. Mater.*, 2000, **12**, 11.