COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Macroporous germanium by electrochemical deposition

L. K. van Vugt,[a] A. F. van Driel,[a] R. W. Tjerkstra†,[a] L. Bechger†,[b] W. L. Vos†,[b] D. Vanmaekelbergh[a] and J. J. Kelly*[a]

[a] *Physics and Chemistry of Condensed Matter, Debye Institute, Universiteit Utrecht, P.O. Box 80000, 3508 TA Utrecht, The Netherlands. E-mail: J.J.Kelly@Phys.uu.nl*

[b] *Van der Waals –Zeeman Instituut, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands*

Received (in Cambridge, UK) 16th July 2002, Accepted 5th August 2002
First published as an Advance Article on the web 14th August 2002

Germanium is electrodeposited in a template formed from a dried suspension of silica spheres. The germanium completely fills the pores of the silica matrix. The semiconductor, as deposited, is amorphous but can be crystallized by annealing. Selective dissolution of the silica template gives a macroporous germanium-air sphere matrix, which offers interesting possibilities for photonic applications.

A widely used approach to the fabrication of macroporous systems is to fill the voids of a template, *e.g.* an artificial opal, with the solid of interest and subsequently to remove selectively the template material. Filling methods that have been employed include chemical vapour deposition (CVD), sol–gel chemistry and infiltration using suspensions of nanoparticles.[1–3] Recent work has shown that electrodeposition of a solid in the porous template is a relatively simple and attractive method for producing macroporous systems.[4–6] Electrodeposition has the advantage that the new phase is grown from the plating base; the voids are filled 'from the bottom up', giving volume-templated structures. This enables a higher volume fraction of solid than that generally obtained by other methods in which deposition occurs on the internal surface of the template ("surface templating"). Electrodeposition has been used to make ordered macroporous structures of gold, nickel, CdS and CdSe.[4–6] The resulting materials have interesting optical[4,6] and, in the case of nickel, magnetic properties.[5]

One of the most exciting fields of application of macroporous solids is in photonics. Random porous systems can give strong light scattering and, in the ultimate case, Anderson localization.[7–9] In a photonic bandgap material, the porous matrix must be crystallographically ordered. In both cases solids are required with a refractive index that is large with respect to that of air.

Germanium, with a refractive index of 4 and a bandgap of 0.67 eV, is an interesting candidate for photonic applications in the IR spectral range. Gómez Rivas *et al.* have studied light scattering in a random germanium matrix based on micron-sized particles obtained by pulverizing single crystals.[8] Míguez *et al.*[10] have made networks of air spheres in germanium by a three-step approach involving hydrolysis of tetramethoxygermane in a crystalline silica template, the reduction of the GeO_2 product of this reaction, and the selective removal of the template. Subsequent work by Míguez *et al.*,[11] in which germanium was deposited from digermane by CVD, gave improved results. SEM images show clearly that this is a surface-templated process with the semiconductor being deposited on the silica spheres throughout the layer. Fill factors up to 78% were reported, depending on the deposition temperature. Interesting optical results have been observed.[11]

In this paper we show that germanium can be electrodeposited directly in a porous silica matrix. For this purpose we used a plating bath based on $GeCl_4$ in ethylene or propylene glycol; the bath is an adaptation of one previously reported by Szekely.[12] We also show that it is possible to etch the silica selectively with respect to the plated semiconductor to produce a germanium replica of the template.

As electrode or plating base, cleaned glass slides (1 × 3 cm) were provided with a 50 nm thick gold or copper film by evaporation. Templates were formed by spreading evenly a thin layer of a concentrated suspension of silica particles in ethanol on the gold surface. The particles had an average diameter of 226 nm with a polydispersity of 2%. After drying, the layers were annealed for 3 h at 600 °C under nitrogen to create necks between the particles and make the templates more robust. The thickness of the silica layers was varied between 0.8 and 2 μm. In this work we did not attempt to make well-ordered colloidal crystals.

The solvent used for the plating bath was either anhydrous ethylene glycol (99.8% from Aldrich) or anhydrous propylene glycol (99.8% from Merck). $GeCl_4$ (99.99% from Acros) was added to the solvent to give a 5–10 vol% solution; this was carried out in a nitrogen-flushed glove box to prevent hydrolysis of the $GeCl_4$. The baths also contained KCl and acetic acid (both p.a. quality from Merck) to increase the conductivity and improve the plating properties. Electrodeposition was carried out at 60 °C. Either a two-electrode cell with a large area graphite counter electrode or a three-electrode cell with a Ag/AgCl reference electrode was used for the electrochemical experiments. A nitrogen overpressure was maintained in the cell during operation.

The germanium layers were characterized by X-ray diffraction (with a Philips PW 1820 diffractometer), by scanning electron microscopy (SEM) and energy dispersive X-ray analysis EDAX (with a Philips XL 305 field emission gun scanning electron microscope). The germanium layer thickness was measured with a Dektak 303 OST auto texture profiler.

Fig. 1 shows a cyclic voltammogram for an experiment with a gold working electrode in an ethylene glycol solution. A scan to negative potentials gives a cathodic peak at about −0.5 V *vs.* Ag/AgCl (range I). If the scan direction is reversed immediately after this peak, an anodic peak (not shown in Fig. 1) is observed. Germanium deposition does not occur in this range; therefore,

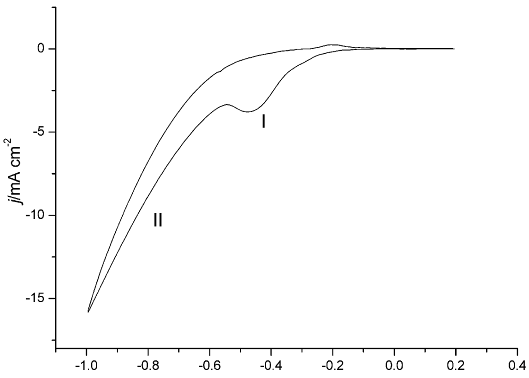

Fig. 1 Cyclic voltammogram of a gold working electrode in a 10 wt% ethylene glycol solution of $GeCl_4$. The bath also contained 1.66 wt% KCl and 1.66 wt% acetic acid.

---

† Current address: Universiteit Twente, P.O.Box 217, 7500 AE, Enschede, The Netherlands.

DOI: 10.1039/b206970a

the peaks are due to the Ge(IV)/Ge(II) couple.[12] At more negative potentials (range II) the cathodic current increases due to deposition of germanium and reduction of protons to hydrogen. The germanium can be stripped anodically at potentials more positive than +0.1 V *vs.* Ag/AgCl. Although the current efficiency is low (~1%) micron-thick germanium layers could be deposited.

The electrochemistry of Ge in silica templates showed results similar to those obtained with the bare gold working electrode. Clearly, the plating solution permeates the porous template and has access to the gold base. The semiconductor could thus be deposited under conditions similar to those for a bare gold electrode.

The silica matrix could be selectively removed in 5% HF solution to expose the plated replica. Fig. 2(a) is a SEM image of an unannealed sample deposited in a two-electrode cell with a cell voltage of 2.3 V, after removal of the silica. An EDAX spectrum confirmed that germanium had indeed been deposited and that the template had been removed. From the absence of peaks in the X-ray diffractogram we must conclude that the as-deposited layer is amorphous. The morphology seen in Fig. 2(a) is typical of the whole sample. Clearly, on removal of the silica a three-dimensional network of air-spheres in germanium is formed. The size of the domains in the silica matrix is rather small (1–2 μm). Germanium is also deposited in vacancies and domain boundaries (not shown); the filling of such large voids provides strong evidence for volume templating, with the germanium growing uniformly from the plating base. Amorphous films are not suitable for photonic applications; consequently we heat-treated the germanium after deposition. The morphology seen in Fig. 2(a) does not change when the sample is annealed for 30 min at 400 °C in a nitrogen atmosphere. From the X-ray diffractogram of Fig. 2(b), however it is clear that the film becomes crystalline during annealing. Peaks in the 2θ diffractogram are observed at 27.28, 45.30 and 53.68° corresponding to the (111), (220) and (311) planes of germanium. Application of the Scherrer equation to the peak widths yields crystallite sizes in the 20–50 nm range. For the electrochemical approach, deposition of an amorphous or a nanocrystalline layer is desirable; formation of larger crystallites with facetted surfaces is clearly unfavourable for perfect filling of the voids.[13]

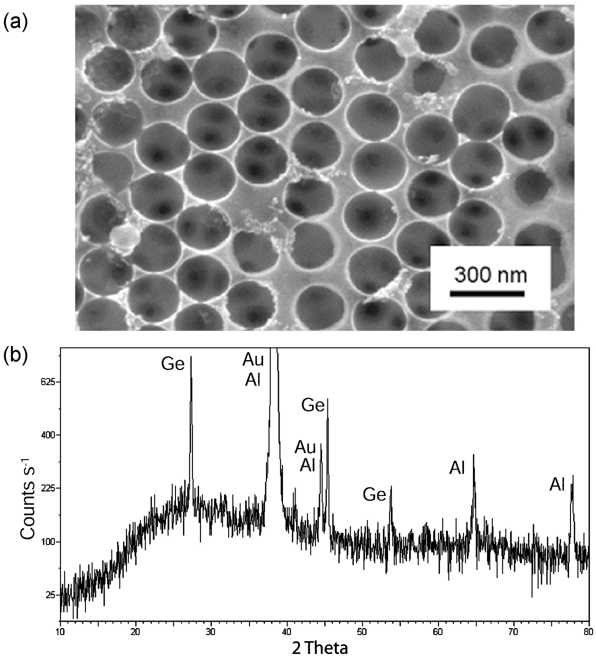

Fig. 2 (a) SEM image of a macroporous amorphous germanium layer electrodeposited from a propylene glycol solution after removal of the template (b). The X-ray diffractogram indicates that after annealing for 30 min at 400 °C under nitrogen crystalline germanium is formed. The gold and aluminium peaks are due to the substrate and sample holder. The large background is due to the glass substrate.

This electrochemical method provides an interesting alternative to the CVD approach of Míguez *et al.*[11] High fill factors are obtained. Two requirements have to be met in order to produce a photonic bandgap in germanium: (i) a thicker template crystal with long-range order is needed; (ii) because the bandgap of germanium corresponds to the IR spectral range, the silica spheres forming the artificial opal must have a diameter larger than those used in the present work. In principle, it is quite possible to meet both of these requirements.

Our results show that electrodeposition in silica templates provides an interesting route to the formation of both random and ordered networks of air spheres in germanium. Such networks can act as a high scattering medium for IR light[8] or as a photonic bandgap material.

We would like to thank Dr Ralf Wehrspohn of the Max Planck Institute, Halle for suggesting germanium electrodeposition. The work of L. B. and W. L. V. is part of the research programme of the ‘Stichting voor Fundamenteel Onderzoek der Materie (FOM)’, which is financially supported by the ‘Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)’. The work of A. F. v. D. and R. W. T. was financed by NWO-CW.

Notes and references

1 A. Stein, *Microporous Mesoporous Mater.*, 2001, **44–45**, 227–239.
2 Y. A. Vlasov, X.-Z. Bo, J. C. Sturm and D. J. Norris, *Nature*, 2001, **414**, 289.
3 J. E. G. J. Wijnhoven and W. L. Vos, *Science*, 1998, **281**, 802.
4 J. E. G. J. Wijnhoven, S. J. M. Zevenhuizen, M. A. Hendriks, D. Vanmaekelbergh, J. J. Kelly and W. L. Vos, *Adv. Mater.*, 2000, **12**, 888.
5 L. Xu, W. L. Zhow, C. Frommen, R. H. Baughman, A. A. Zakhidov, L. Malkinski, J.-Q. Wang and J. B. Wiley, *Chem. Commun.*, 2000, 997.
6 P. V. Braun and P. Wiltzius, *Adv. Mater.*, 2001, **13**, 482.
7 F. J. P. Schuurmans, M. Megens, D. Vanmaekelbergh and A. Lagendijk, *Phys. Rev. Lett.*, 1999, **83**, 2183.
8 J. Gómez Rivas, R. Sprik, A. Lagendijk, L. D. Noordam and C. W. Rella, *Phys. Rev. E*, 2000, **62**, 4540R.
9 F. J. P. Schuurmans, D. Vanmaekelbergh, J. van de Lagemaat and A. Lagendijk, *Science*, 1999, **284**, 141.
10 H. Míguez, F. Meseguer, C. López, M. Holgado, G. Andreasen, A. Mifsud and V. Fornés, *Langmuir*, 2000, **16**, 4405.
11 H. Míguez, E. Chomski, F. García-Santamaría, M. Ibisate, S. John, C. López, F. Meseguer, J. P. Mondia, G. A. Ozin, O. Toader and H. M. van Driel, *Adv. Mater.*, 2001, **13**, 1634.
12 G. Szekely, *J. Electrochem. Soc.*, 1951, **98**, 318.
13 P. E. de Jongh, D. Vanmaekelbergh and J. J. Kelly, *Chem. Mater.*, 1999, **11**, 3512–3517.