

A simple and fast technique to grow free-standing germanium nanotubes and core-shell structures from room temperature ionic liquids



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ABSTRACT

A simple and fast technique to grow free standing, open ended germanium nanotubes is demonstrated using template assisted electrodeposition from a room temperature ionic liquid. Germanium nanotubes as long as 2 μm could be grown using this technique. We also show the possibility for the growth of core-shell structures. The technique demonstrated is not limited to the growth of Ge, but can be extended to grow other semiconductor nanotubes and core-shell structures.

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1. Introduction

Nanotubular structures are getting extensive attention due to their unique electronic and optical properties and potential applications in nanoscale sensors, catalysis, biomedicine, solar cells and batteries [1–5]. Metals, semiconductors and metal oxide nanotubes have been grown by vapour-liquid-solid (VLS), vapour-solid (VS), Chemical vapour deposition (CVD), laser ablation and direct anodising techniques [6–8]. Semiconductor nanotubes such as silicon and germanium are of particular interest especially in energy research. Until now semiconductor nanotubes have mainly been grown by vacuum techniques and involve multiple steps. Initially, a nanowire template is grown over which the semiconductor is deposited using CVD. After the deposition step, the inner core nanowire template is removed by selective etching and evaporation [6,9–11]. The nanoscale Kirkendall effect has also been shown to be a promising technique to develop nanotubes, wherein diffusion of one element is faster than the other one, resulting in the formation of nanotubes [12]. Recently, it was shown that germanium nanotubes could be developed using Kirkendall effect for a possible use as a lithium ion battery anode material [13].

Compared to silicon, germanium possesses some advantageous properties: it has a higher intrinsic carrier mobility which is useful in field effect transistors [14]; it also has a larger Bohr exciton radius compared to silicon, yielding a more pronounced quantum confinement effect [15]. Furthermore, it is a potential anode material in lithium ion batteries, as the diffusivity of lithium in Ge is 400 times faster than in silicon at room temperature [13]. As Ge nanowires and nanotubes based on their properties are well suited as an anode in lithium ion batteries [13,16] compared to thin films, a simple route to develop such Ge nanostructures would be of high interest.

In comparison to vacuum techniques, electrodeposition in nanoporous membranes or porous alumina templates is simpler and it has been widely employed to grow nanowires [17–19]. Studies on the growth of metals and alloy nanotubes from aqueous electrolytes by electrodeposition have been demonstrated, most of which required functionalising of the porous alumina template for the preferential growth to take place at the pore walls [20–23]. For example, by modifying a porous alumina template using a triblock-copolymer, nickel nanotubes were grown [21], whereas gold nanotubes were grown in a polycarbonate membrane functionalised with 3-aminopropyltriethoxysilane [20]. A novel technique by using a rotating electric field during electrodeposition was reported which was used to grow copper nanotubes [23]. Group II–VI semiconducting nanotubes such as CdS and CdSe have been synthesised by template assisted

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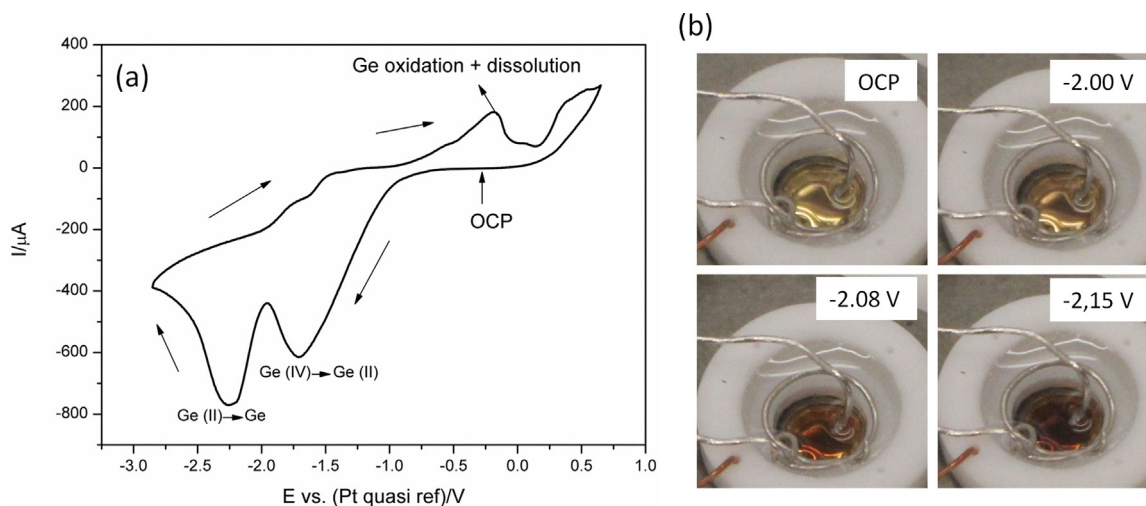


Fig. 1. (a) CV of 0.1 M GeCl_4 on 30 nm Au sputtered polycarbonate membrane (200 nm pore size) in $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$ at room temperature. The scan rate was 10 mV sec^{-1} . (b) A series of photos showing the evolution of red colour during the CV scan.

electrodeposition from aqueous solutions [24,25]. However, electrodeposition of semiconductors such as silicon and germanium from aqueous solutions is not feasible due to the hydrogen evolution in the cathodic regime. In comparison, ionic liquids provide wide electrochemical windows of up to $\pm 3 \text{ V}$ vs NHE for the electrodeposition of reactive semiconductors like silicon and germanium. The growth of semiconductor nanowires of silicon and germanium with variable lengths and diameters has hitherto only been successful using template-assisted electrodeposition in ionic liquids [26,27]. Recently, it was also shown that silicon nanotubes can be grown using this technique [28]. In order to use nanostructures directly in devices like e.g. lithium ion batteries, free-standing nanowires or nanotubes are of potential interest.

In this paper, we show for the first time the growth of open ended free-standing germanium nanotubes by template-assisted electrodeposition from room temperature ionic liquids. We have also attempted to develop core-shell structures. We have characterised the deposit using scanning electron microscopy, energy dispersive X-ray and Raman spectroscopy.

2. Experimental

1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ($[\text{Py}_{1,4}]\text{Tf}_2\text{N}$) was purchased in the highest available quality from Io-Li-Tec (Germany) and was used after drying under vacuum at 100°C to remove the water content to below 2 ppm. GeCl_4 (99.999%) was purchased from Alfa Aesar. The working electrode was a 30 nm sputtered film of gold on a nuclear track-etched polycarbonate membrane (Ion Track Technology for Innovative Products, IT41P, Belgium) with a pore diameter of 200 nm. The pore density of the membrane is 5×10^8 pores/ cm^2 and the thickness of the membrane was $21 \mu\text{m}$. The gold sputtered membrane is shown in the supporting information (supporting information, Figure S1). Platinum wires were used as a counter and a quasi reference electrode which gave good stability in the ionic liquid throughout the experiments. The electrochemical cell was made of Teflon and clamped over a Teflon-covered Viton O-ring onto the substrate. Prior to the experiments, the Teflon cell and the O-ring were cleaned in a mixture of 50:50 vol% of concentrated H_2SO_4 and H_2O_2 (35%) followed by refluxing in distilled water.

The electrochemical measurements were performed in an argon-filled glove box with water and oxygen contents of below 2 ppm (OMNI-LAB from Vacuum Atmospheres) by using a VersaStat II (Princeton Applied Research) potentiostat/galvanostat controlled

by powerCV software. The entire scan rate during cyclic voltammetry was 10 mV sec^{-1} .

After the deposition of Ge on the gold sputtered membrane, Au was further electrodeposited from a commercially available electrolyte (Enthone, gold electrolyte) to support the layer and obtain free standing nanotubes. The deposit was then washed in isopropanol and the membrane was dissolved in dichloromethane. The deposits obtained by constant potential deposition were characterised using scanning electron microscopy (SEM, Carl Zeiss DSM 982 Gemini) and energy dispersive X-ray spectroscopy (EDX). Raman spectra were recorded by a Bruker Senterra Raman microscope using 50X objective with a laser excitation of 532 nm.

3. Results and Discussion

Fig. 1 shows the cyclic voltammogram (CV) of 0.1 M GeCl_4 in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ($[\text{Py}_{1,4}]\text{Tf}_2\text{N}$) on a Au sputtered polycarbonate membrane, but for a technologically cheaper process, a Cu sputtered membrane can be used as well.

The first reduction peak at -1.7 V is the reduction of Ge (IV) to Ge (II) species and the second reduction peak at -2.2 V corresponds to the reduction of Ge (II) species to Ge. In the anodic regime, an increase in current is observed above -0.2 V which corresponds to the partial oxidation and dissolution of the deposited Ge. Fig. 1b shows a series of photos taken during the CV of 0.1 M GeCl_4 in $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$. At open circuit potential (OCP), only the Au sputtered membrane is seen. On reaching a potential of -2.0 V which corresponds to the start of the second reduction peak in Fig. 1a, a slightly reddish deposit is observed.

On further decrease in potential, the intensity of the red deposit increases as seen at -2.08 V (Fig. 1b). At about -2.15 V , a black deposit starts to form and a black deposit is rapidly obtained at -2.2 V . The formation of the red deposit might be due to small nanoparticles of Ge over the Au sputtered membrane showing a quantum confinement effect. The red colour is also a hint for Ge^{1+} species, but none of our analyses supports this assumption. Henderson et al. [29] also reported on the formation of red Ge colloidal particles. A similar reddish deposit was obtained on a Cu sputtered membrane which confirms that the red colour is not due to a reaction of Ge with Au. It can also happen that during the initial few seconds of electrodeposition at constant potential, the red deposit quickly changes to a black one.

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