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Supplementary material for this article is available [online](#)

Abstract

We report a facile one-pot solution phase synthesis of one-dimensional $\text{Ge}_{1-x}\text{Sn}_x$ nanowires. These nanowires were synthesized *in situ* via a solution-liquid-solid (SLS) approach in which triphenylchlorogermane was reduced by sodium borohydride in the presence of tin nanoparticle seeds. Straight $\text{Ge}_{1-x}\text{Sn}_x$ nanowires were obtained with an average diameter of 60 ± 20 nm and an approximate aspect ratio of 100. Energy-dispersive x-ray spectroscopy (EDX) and powder x-ray diffraction (PXRD) analysis revealed that tin was homogeneously incorporated within the germanium lattices at levels up to 10 at%, resulting in a measured lattice constant of 0.5742 nm. The crystal structure and growth orientation of the nanowires were investigated using high-resolution transmission electron microscopy (HRTEM). The nanowires adopted a face-centred-cubic structure with individual wires exhibiting growth along either the $\langle 111 \rangle$, $\langle 110 \rangle$ or $\langle 112 \rangle$ directions, in common with other group IV nanowires. Growth in the $\langle 112 \rangle$ direction was found to be accompanied by longitudinal planar twin defects.

1. Introduction

$\text{Ge}_{1-x}\text{Sn}_x$ has attracted much research interest as an exciting material with potential applications in next-generation rechargeable lithium-ion battery anodes and optoelectronic devices, due to their high carrier mobilities [1–3] and a direct band gap which can be tuned by varying the tin concentration [4–12]. Additionally, cubic $\text{Ge}_{1-x}\text{Sn}_x$ allows the lattice dimensions to be tuned over a wide range, which is beneficial when used as a buffer layer to reduce strain arising from lattice mismatch between III–V or II–VI compounds with silicon or germanium substrates [13–15].

The synthesis of $\text{Ge}_{1-x}\text{Sn}_x$ is challenging due to the low solubility of tin in germanium (<1%) [16], large lattice mismatch (~14%) and a tendency of metallic tin to segregate from germanium [17, 18]. $\text{Ge}_{1-x}\text{Sn}_x$ alloys are commonly fabricated using ion implantation, laser melting [4, 5, 19], molecular beam epitaxy (MBE) [7], and chemical-vapor deposition (CVD) approaches [6, 20–22]. Apart from these thin film based preparations, there are limited reports of the synthesis of anisotropic $\text{Ge}_{1-x}\text{Sn}_x$ nanostructures by top-down and bottom-up approaches [12, 23–28].

The most established synthetic approaches, for group IV nanowires (such as Ge and $\text{Ge}_{1-x}\text{Sn}_x$), involve the use of metal growth-promoters in bottom-up processes such as: vapour-liquid-solid (VLS), vapor-solid-solid (VSS), In-plane-solid-liquid-solid (IP-SLS), supercritical fluid-liquid-solid (SFLS) and solution-liquid-solid (SLS) mechanisms. [12, 18, 23, 26, 27, 29]. Amongst these, the SLS approach offers benefits such as low equipment cost, high scalability, mild-reaction conditions, easy control, and access to non-flammable germanium precursors (such as triphenylchlorogermane) [30]. To date, only a few studies have been conducted

on the growth of $\text{Ge}_{1-x}\text{Sn}_x$ nanowires via the SLS mechanism [28]. $\text{Ge}_{1-x}\text{Sn}_x$ nanowires produced from microwave-assisted decomposition of $\text{Sn}(\text{N}(\text{Si}(\text{CH}_3)_3)_2)_2$ and $\text{Ge}(\text{N}(\text{Si}(\text{CH}_3)_3)_2)_2$ precursors have been reported, but the presence of defects such as bending and twisting coupled to a low aspect ratio demand further improvements [28]. Geaney *et al* and Mullane *et al* have reported the synthesis of germanium nanowires using tin catalyst seeds at a decomposition temperature of more than 350 °C, but no $\text{Ge}_{1-x}\text{Sn}_x$ was formed in these processes [30, 31]. In order to fabricate $\text{Ge}_{1-x}\text{Sn}_x$ nanowires incorporating high tin content, non-equilibrium introduction of tin into the germanium lattice has been proposed and demonstrated by several groups. These used either a VLS mechanism from liquid-injection CVD upon Au [18] or AuAg catalysts [12, 26], or IPSLS approach [23, 27]. However, reports focused on self-seeded SLS growth of high quality $\text{Ge}_{1-x}\text{Sn}_x$ nanowires from tin catalyst are rare.

Here we report a facile one-pot solution phase synthesis of uniform, straight $\text{Ge}_{1-x}\text{Sn}_x$ nanowires with high aspect ratio (~ 100) in high yield. Tin was homogeneously incorporated within the germanium matrix at up to 10 at%, with no tin segregation observed on either the surface or along the length of the nanowires. These nanowires were grown via the SLS mechanism through sequential reduction of SnI_4 and $\text{Ge}(\text{Ph})_3\text{Cl}$ with NaBH_4 . This synthesis is simple and time-efficient due to the use of commercially available precursors and conventional laboratory glassware.

2. Materials and methods

2.1. Materials

Tin iodide (SnI_4 , anhydrous, 98%) and sodium borohydride (NaBH_4 , 2.0 M in triethylene glycol dimethyl ether) were purchased from Sigma-Aldrich. Trioctylamine (TOA) and toluene were obtained from Acros Organics. Triphenylchlorogermane ($\text{Ge}(\text{Ph})_3\text{Cl}$) was purchased from ABCR.

2.2. Preparation of $\text{Ge}_{1-x}\text{Sn}_x$ nanowires

$\text{Ge}_{1-x}\text{Sn}_x$ nanowires were fabricated via a one-pot two-step synthesis. Tin nanoparticles were first formed by reducing SnI_4 with NaBH_4 at 300 °C in TOA in a three-neck round bottom flask, followed by the swift loading $\text{Ge}(\text{Ph})_3\text{Cl}$ and NaBH_4 consecutively, and then maintaining the temperature at 300 °C for a few hours. The optimal molar ratio of SnI_4 to $\text{Ge}(\text{Ph})_3\text{Cl}$ used was 1:30. This produced a black precipitate which was repeatedly washed in toluene and methanol prior to characterisation. All reactions were carried out under N_2 gas using Schlenk techniques to eliminate air and moisture.

2.3. Characterization

The washed and dried $\text{Ge}_{1-x}\text{Sn}_x$ nanowires were studied using scanning electron microscopy (SEM) (JEOL-6500F, equipped with an energy dispersive spectrometer EDS), transmission electron microscopy (TEM) (JEOL 2010 equipped with a field emission gun operated at 200 keV), and x-ray diffraction analysis (XRD Philips PW3710 diffractometer). XRD samples were prepared as drop-cast films of nanowires deposited on single crystal silicon substrate. The silicon substrate also served as an internal calibration standard since peaks due to silicon do not overlap those from cubic $\text{Ge}_{1-x}\text{Sn}_x$ in the range of 2θ from 20 to 60 degrees. The incorporation of Sn into the Ge lattice was determined by both x-ray diffraction (XRD) using Vegard's law, and energy dispersive x-ray (EDX) spot analysis.

3. Results and discussion

SEM images in figures 1(a) and S1 is available online at stacks.iop.org/MRX/7/064004/mmedia (in supporting information) reveal that the synthesized material contained a high yield of $\text{Ge}_{1-x}\text{Sn}_x$ nanowires. The nanowires were largely straight with smooth surface morphology. Measurement of more than one hundred individual nanowires showed that the average nanowire diameter was 60 ± 20 nm (measured at the half length of the nanowires, see figure 1(b)) whilst the average nanowire length was 5.5 ± 2.0 μm , with more than 15% of the nanowires reaching a length of at least 10 μm .

Figure 1(b) shows that the as-synthesized $\text{Ge}_{1-x}\text{Sn}_x$ nanowires have slightly tapered ends which point away from the seed nanoparticle, indicating that the taper is formed during the early stages of nanowire growth. The tapered ends have diameters of 30–40 nm, similar to the initial diameter of the Sn nanoparticle seeds (figure S2). At high temperature, molten metal nanoparticles such as Sn are prone to quick aggregation even in the presence of surfactant, as nanoparticles are thermodynamically unstable. The initial diameter of the Sn seeds used in this synthesis were around 30–40 nm, but as the reaction proceeded at 300 °C, these seeds grew bigger over time, leading to a progressive enlargement of the nanowire diameter. It is well-documented that during metal catalyzed VLS, VSS and SLS growth, the size of the metal catalyst determines the diameter of the nanowire

Figure 1. (a) A low-magnification scanning electron microscopy (SEM) image of as synthesized $\text{Ge}_{1-x}\text{Sn}_x$ nanowires (b) A SEM image of a single $\text{Ge}_{1-x}\text{Sn}_x$ nanowire image showing the smooth surface morphology, a spherical seed and thin tapered end.

Figure 2. A XRD pattern of the nanowire synthesized at an optimal reaction condition (Cu radiation). The expected positions and intensities for peaks corresponding to cubic Sn (ICDD 00-005-039), cubic Ge (ICDD 00-004-0545) and tetragonal Sn (ICDD 00-004-0673) are marked by lines labelled with '●', '▼', '■', respectively. (*single crystal Si subtract was used as an internal standard).

produced [32, 33], and similar observations of tapered nanowires have also been reported by others [12, 28]. Another possible contribution reason for the tapered profile could be that at the start of the synthesis the concentration of germanium in the tin nanoparticles was low, which resulted in an initially exsolved nanowire being thinner than the seed particles. However, as the reaction progressed, more germanium dissolved in the tin seed and therefore the diameter of $\text{Ge}_{1-x}\text{Sn}_x$ nanowires increased.

The average diameter of the interface between the tin nanoparticle seed and the $\text{Ge}_{1-x}\text{Sn}_x$ nanowire was around 80 nm, with sizes ranging from 50 nm to 140 nm. For example, the diameter of the interface of the nanowire shown in figure 1(b) is about 110 nm, whilst the diameter of the interface region of the nanowire in figure 3(a) is about 75 nm (The corresponding magnified images are shown in figure S3.) The interface between the seed particle and nanowire is typically smaller than the diameter at half-length because of the growth mechanism involved in this type of nanowire synthesis [28, 34–37].

A typical XRD pattern of the $\text{Ge}_{1-x}\text{Sn}_x$ nanowire is shown in figure 2. Three diffraction peaks were indexed and labelled as (111), (220) and (311) of the crystalline diamond structure of $\text{Ge}_{1-x}\text{Sn}_x$. The scattering angle 2θ of each peak is shifted to low scattering angles, relative to those of pure germanium (space group $\text{Fd}\bar{3}\text{m}$, $\alpha = 5.658 \text{ Å}$). The corresponding d values were determined by employing Bragg's law, using the {111} diffraction from the silicon substrate to provide a highly accurate internal calibration standard (space group $\text{Fd}\bar{3}\text{m}$, $\alpha = 5.4309 \text{ Å}$).

To determine of the molar fraction of Sn present in the nanowires, we derived x from the XRD peak shift by assuming the validity of Vegard's law based on the previous theoretical and experimental studies of Ge-Sn system published [14, 38, 39]. The lattice parameter α of Ge was calculated from the d values for the Ge (111),

Figure 3. (a) A SEM image of a single $\text{Ge}_{1-x}\text{Sn}_x$ nanowire with a Sn seed; (b) the corresponding EDX-line scanning analysis; and (c), (d) EDX elemental maps of the nanowire.

(220) and (311) peaks, which established an average lattice constant of $5.742 \pm 0.003 \text{ \AA}$ (inset of figure 2). According to work by Denton *et al* [39], this implies that about 10 at% Sn was incorporated into the Ge lattice.

Several peaks corresponding to the tetragonal phase of Sn are also observed in the diffraction pattern. These are also shifted slightly toward higher scattering angle, indicating a slight distortion of the tetragonal cell of β -Sn. No detectable XRD peaks corresponding to cubic phase α -Sn were observed.

The local elemental composition of several individual nanowires was investigated by EDX elemental mapping during SEM studies. Figure 3 shows a tin-rich nanoparticle at the tip of a $\text{Ge}_{1-x}\text{Sn}_x$ nanowire, once again confirming the SLS growth mechanism. EDX line scanning and mapping revealed homogeneously distributed tin throughout the nanowire with no evidence of tin segregation or a tin-rich shell has been observed in other work [18]. EDS spot analysis was performed on more than twenty individual $\text{Ge}_{1-x}\text{Sn}_x$ nanowires at the seed (A), growing zone (B), middle (C) and tip (D) sections. This showed that the tin composition decreased from about 80% at the seed to about 10% at the middle and taper sections of each nanowire (figure S4 in the supporting information). The $x = 10\%$ obtained by EDX-spot analysis of the nanowire is consistent with the XRD analysis result, supporting the validity of this value.

High-resolution TEM images and selected area diffraction patterns (SAED) of two individual nanowires are shown in figure 4. These confirm that the $\text{Ge}_{1-x}\text{Sn}_x$ nanowire adopted a face-centred cubic crystal structure, as found in the XRD analysis. The SAED pattern (shown as insets) indicate that the growth of the $\text{Ge}_{1-x}\text{Sn}_x$ nanowires was along the $\langle 111 \rangle$ (figure 4(a)) and $\langle 110 \rangle$ (figure 4(b)) directions respectively. In figure 5, an individual $\text{Ge}_{1-x}\text{Sn}_x$ nanowire with twin defects along the $[112]$ axis was identified. The SAED pattern (inset, figure 5) clearly shows twin diffraction reflections, indicating the formation of longitudinal $\{111\}$ twins. The twin boundary extends parallel to the growth direction.

Of the twenty $\text{Ge}_{1-x}\text{Sn}_x$ nanowires examined under high-resolution TEM, about 70 to 80% of the nanowires exhibited single crystal growth along the $\langle 110 \rangle$ or $\langle 111 \rangle$ directions (figure 4). The remaining 20%–30% of the nanowires exhibited growth along the $\langle 112 \rangle$ direction with accompanying twin defects.

The surfactant assisted tin-seeded growth of $\text{Ge}_{1-x}\text{Sn}_x$ nanowires can be divided into four stages based on the SLS growth mechanism (figure 6). Firstly, SnI_4 was reduced by NaBH_4 at 300°C to form nanoscale molten spherical tin droplets. Then $\text{Ge}(\text{Ph})_3\text{Cl}$ was reduced to form Ge^0 . Ge^0 attached on the surface of tin droplets where it could either diffuse around the outer surface of the droplet or penetrate and dissolve within it. In the third stage, a nucleation event occurred and the $\text{Ge}_{1-x}\text{Sn}_x$ nanowire started to grow. In the final stage, a high concentration of Ge^0 was maintained in the tin seed resulting in the steady growth of long $\text{Ge}_{1-x}\text{Sn}_x$ nanowires.

The high Sn content of the nanowires is attributed to non-equilibrium ‘solute-trapping’ phenomenon [40] which occurs at the nanowire-seed interface during the steady growth phase.

For practical applications in optoelectronic and electric devices, the thermal stability of $\text{Ge}_{1-x}\text{Sn}_x$ material is a crucial property which has been widely studied and reported [17, 23, 24, 41–45]. Zaumseil *et al* showed that the tin segregation temperature of $\text{Ge}_{1-x}\text{Sn}_x$ alloys increases with decreasing Sn content, and that $\text{Ge}_{0.91}\text{Sn}_{0.09}$ was stable at temperatures up to 400 °C [17]. This is consistent with the growth temperature of 300 °C used in this work, and hence the $\text{Ge}_{0.9}\text{Sn}_{0.1}$ nanowires produced here are expected to remain thermally stable at temperatures suitable for optoelectronic applications.

4. Conclusion

In summary, we have demonstrated a facile one-pot two-step synthesis of high aspect ratio $\text{Ge}_{1-x}\text{Sn}_x$ nanowires with an average diameter of 60 ± 20 nm and average length of 5.5 ± 2.0 μm . The nanowires were produced via self-catalyzed SLS growth in a process using low-cost commercially available precursors, namely $\text{Ge}(\text{Ph})_3\text{Cl}$, SnI_4 and NaBH_4 . Elemental analysis revealed highly homogeneous incorporation of Sn in the Ge matrix at up to 10 at%, as evidenced by results from both XRD and EDX spot analysis. SAED studies of individual nanowires indicated that the $\text{Ge}_{1-x}\text{Sn}_x$ nanowires adopted a face-centred cubic structure, with growth directions oriented in either the $\langle 111 \rangle$, $\langle 110 \rangle$ or $\langle 112 \rangle$ direction. Future studies will examine the formation mechanism of the twin defects and the optical properties of the synthesized $\text{Ge}_{1-x}\text{Sn}_x$ nanowires.

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