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Time dependent size and shape control of germanium nanocrystals†

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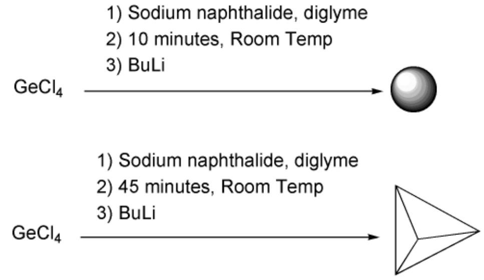
The use of elemental silicon in the computer industry has prompted research on nanocrystalline silicon owing to its novel size dependent optical and electronic properties.[1,2] Of the group IV semiconductors, there has been extensive work carried out on the synthesis and characterization of both porous silicon,[3] and silicon nanocrystals.[4] Recently, octanol and *n*-butyl capped silicon nanocrystals have been synthesized by $SiCl_4$ reduction with sodium naphthalide.[5,6] However, there are few reports on the synthesis and characterization of porous germanium,[7] and nanocrystalline germanium.[8–11]

Reports of procedures that result in the single crystals of nanometer size germanium crystals often indicate that both high pressure and high temperature is required to induce crystallization.[8,9] However, there are also reports of low temperature synthesis.[10,11] For example, metathesis reactions using Zintl salt (KGe) precursors result in large size distributions (1–10 nm). This is a consequence of the poor solubility of the Zintl salt in all common organic solvents, which in turn results in a long nucleation period and therefore the large size distribution.[10] The use of inverse micelles to control crystal size has limited success because nucleation is not restricted to the hydrophilic interior of the micelle as a consequence of the high solubility of $GeCl_4$ in the hydrophobic region.[11] While these low temperature methods give rise to germanium nanocrystals, most work in this area performed at high temperature and high pressure, or by other extreme measures such as laser annealing of amorphous material.[9]

Here, the time dependent growth of halide capped germanium nanocrystals to give narrow size distributions using a room temperature reduction of $GeCl_4$ with sodium naphthalide in 1,2-dimethoxyethane is reported‡. Following the addition of reducing agent, the halide capped nanocrystals were terminated with BuLi after a specific time period to passivate the surface and prevent further growth. By varying the growth time period, it is possible to control sizes of nanocrystals formed (Scheme 1). Growth times of 10 minutes produced nanocrystals of 3–7 nm. A longer growth time of 45 minutes resulted in nanocrystals with a size distribution of 30–49 nm. In each case the nanocrystals formed were a pale orange, slightly oily solid which were soluble in dichloromethane. Solution ^{1}H NMR spectra of the nanocrystals in $CDCl_3$ are consistent with the presence of *n*-butyl groups on the surface of the nanocrystals. This is supported by the IR spectra, in which bands corresponding to C–H stretching of the alkyl groups were observed at ~ 3000 cm^{-1}. In both cases, a band corresponding to the Ge–O stretch at ~ 890 cm^{-1}, was not present in the spectra, indicating that the surface is fully passivated.



Scheme 1 Reduction of $GeCl_4$ with sodium naphthalide and surface passivation with BuLi.

The bright field TEM image of *n*-butyl capped germanium nanocrystals with a growth time of 45 minutes on an ultra thin carbon grid is shown in Fig. 1. To prepare the TEM grids, a sample of the nanocrystals was diluted in dichloromethane and sonicated to solubilize the nanocrystals. The 2 nm ultra thin carbon grid was dipped into the solution and dried in an oven at 100 °C for 1.5 hours. The size distribution was determined by measuring 52 nanocrystals from different areas on the grid. This gave edge lengths of 30–49 nm with 57% of the crystals falling in the 40–46 nm range. The HRTEM image (insert in Fig. 1) shows the lattice fringes from one nanocrystal. The measured *d* spacings were ~ 3.27 Å for $<111>$ plane which are consistent with the diamond cubic lattice of germanium. Dichloromethane solutions of these nanocrystals showed no evidence of photoluminescence that could be attributed to quantum confinement, which is consistent with their large size.

Fig. 2 shows the bright field HRTEM images of butyl capped germanium nanocrystals with a growth time of 10 minutes. The size distribution was again determined by measuring 156 nanocrystals from different areas on the grid. The nanocrystals measured showed a size distribution of 3–7 nm with 87% of the nanocrystals falling in the 3–5 nm range. This is consistent of a mean diameter of 4.64 nm. This distribution is far narrower than those achieved *via* inverse micelle (1–10 nm) or metathesis reactions (1–10 nm). The HRTEM image shows a single nanocrystal of 4 nm where the lattice fringe spacing ~ 3.27 Å is consistent with $<111>$ plane of germanium. A hexane solution of the nanocrystals, exhibits photoluminescence in a relatively narrow region of 360 to 460 nm with a maximum intensity from 380 nm for an excitation at 320 nm, which is comparable to reported studies.[10] This is consistent with the quantum confinement model however contribution from the non-uniform size distribution, the possibility solvent nanocrystal interactions, defects and participation of the surface terminating groups have not been determined.

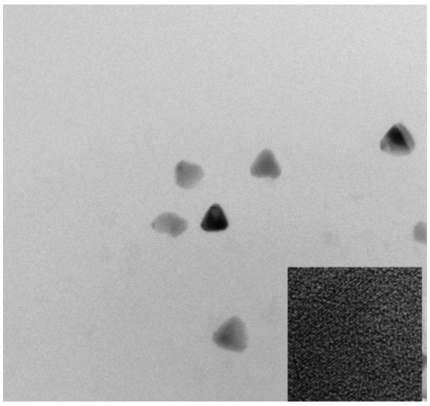


Fig. 1 Bright field TEM images of *n*-butyl germanium nanocrystals (45 min growth period) on an ultra thin carbon grid. Inset: HRTEM image of the lattice fringes for one of the germanium nanocrystals.

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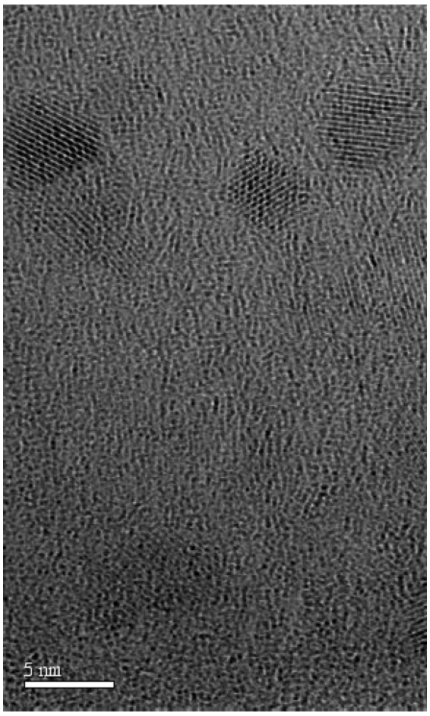

Fig. 2 Bright field HRTEM images of *n*-butyl capped germanium nanocrystals (10 min growth period) on an ultra thin carbon grid.

In conclusion, different growth times can be used to synthesize germanium nanocrystals in solution in two discrete sizes, each with narrower size distributions than previously published procedures. Future work will optimize these conditions, such as initial $GeCl_4$ concentration in solution to further control the size distribution of the nanocrystals.

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Notes and references

‡ Sodium naphthalide was freshly prepared: [sodium (1.2 g, 52 mmol) and naphthalene (5 g, 39 mmol) was stirred in 150 ml of degassed diglyme]. $GeCl_4$ (2.3 g, 10.4 mmol) was added rapidly *via* syringe to the solution with vigorous stirring at room temperature. An orange suspension was immediately obtained with the formation of NaCl precipitate. The reaction was stirred for 10 minutes or 45 minutes after which an excess of BuLi (15 cm^3, 1.6 M in hexane) was added. A pale orange solution with a colorless precipitate was immediately obtained. The precipitate was removed *via* gravity filtration. The solvent and excess naphthalene were removed *via* Kugelrohr distillation. The orange solid was dissolved in hexane and washed with slightly acidic water to remove residual salts. The organic layer was collected and removed *in vacuo* to give an orange oily solid (0.65 g).

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