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Formation of the ST12 phase in nanocrystalline Ge at ambient pressure†

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Amorphous nanophase germanium can crystallize into a high-energy tetragonal phase (Ge-III/ST12) upon thermal annealing, particularly when prepared by the naphthalide-mediated reduction of GeCl₄ and subsequent treatment with t-BuMgCl. The formation of ST12-Ge is typically associated with high pressure, yet the nucleation and coalescence of this phase can be observed by in situ transmission electron microscopy at low pressure and at temperatures well below 200 °C, and can persist at temperatures of up to 500 °C. The low coalescence temperature of nanophase ST12-Ge suggests its compatibility with applications in direct-print electronics.

Introduction

There is considerable interest in creating electronic devices through the use of direct-printing technologies. The reasons for this are manifold, including the potential of improved flexible displays, the creation of inexpensive devices for product identification and tracking, and novel applications in clothing and advertisement. Additionally, printed electronics are compatible with high production rates, easy transfer between low volume and high volume device layouts, low capital cost and environmentally compatible processes and materials.1–5 Of crucial importance to the success of this technology is the development of semiconductor materials that have sufficiently high electron and hole mobilities. Although printable organic field-effect transistors (OFETs) are currently being considered as the next generation of organic integrated circuits, the mobility of the materials is still rather low (of the order of 5–10 cm² V⁻¹ s⁻¹)6 and trends suggest that higher mobilities are unlikely without a major breakthrough in the field.7

An alternative approach to printable electronics involves the deposition of high-mobility semiconductor materials in nanoparticle form, followed by sintering at low temperatures to create a continuous thin film.2,8–10 While the mobilities of granular films may be reduced relative to bulk values due to grain boundary scattering and defect formation, they may still be higher than those of most organic electronic materials. We became interested in the possibility of using nanocrystalline Ge as a printable semiconductor material: Ge has a relatively high mobility and low environmental impact, and when compared with Si for printed electronic applications, brings additional benefits of higher conductivity and a lower melting temperature. Furthermore, nanocrystals are well known to have much lower melting points than bulk-phase materials.11,12 If nanophase Ge can be sintered at temperatures below 150 °C (the thermal stability limit of polyester films), the resulting connectivity should support the production of printable semiconductor patterns with sufficiently high mobilities for device applications.

Nanocrystalline Ge has been prepared by a number of routes, most notably from Ge salts using strongly reducing conditions. This includes the use of alkali metals under reverse-micelle conditions,13 metathesis with Zintl-phase Ge or germanides,14,15 and reduction with sodium naphthalide under homogeneous solution conditions.16–18 The as-formed Ge nanocrystals can also be stabilized against oxidation by treatment with alkyl Grignard reagents such as n-BuMgCl. Several of these syntheses have produced nanocrystalline Ge with a diamond cubic lattice (Ge-I), but often in coexistence with amorphous Ge.11,18,19 The thermally activated transition between crystalline and amorphous Ge phases appears to be variable: Chiu and Kauzlarich have reported that Ge nanocrystals become amorphous at intermediate temperatures (300–500 °C) upon loss of their organic surface layer, but can recrystallize at temperatures above 550 °C with restoration of the diamond cubic phase.19 On the other hand, heating composite films of Ge/organo-Ge polymer at temperatures above 300 °C can result in the growth and coalescence of nanocrystalline Ge with various lattice structures.18

Intrigued by the relatively mild conditions reported above, we elected to study the sintering and coalescence behavior of Ge nanocrystals formed via sodium naphthalide reduction of GeCl₄, with subsequent treatment by alkyl Grignard reagents.17,19 In the course of these investigations, we observed that the treatment of freshly reduced Ge with t-BuMgCl resulted in the unexpected dominance of a tetragonal phase known as the Ge-III or ST12 structure (P4ᵥ2,2; a = 5.98 Å, c = 6.98 Å).20–22 It is widely accepted that Ge favors the diamond cubic structure at atmospheric pressure, but can be transformed into the ST12 phase under high pressure. Furthermore, ST12-Ge has been predicted to have a direct band gap of 1.47 eV,23 an optically active transition in the near infrared (NIR) with potential utility for optoelectronics and photovoltaics. Although the ST12 structure has...
been observed previously in Ge nanoparticles at ambient pressure, it is thought to be metastable and should thus convert to the diamond cubic structure upon thermal annealing. Here we report that the ST12 phase is much more stable than previously thought: under the conditions investigated in this work, it is the dominant structure both at room temperature and during thermally induced growth, and can survive annealing temperatures of up to 500 °C. Remarkably, the stability of the ST12 structure is not dependent on size confinement effects. Instead, it persists as the dominant phase during the sintered growth of submicron islands, and can be produced in sufficient quantities for examination of its predicted photoluminescence.

**Materials and methods**

**Synthesis**

All materials were used as received from commercial suppliers unless otherwise noted. The reduction of GeCl₄ was performed by a variation of the sodium naphthalide method described by Chiu and Kauzlarich. Excess sodium metal (0.15 g, 6.5 mmol) was added to naphthalene (0.29 g, 2.3 mmol) in freshly distilled glyme (7 mL) in a Schlenk flask at room temperature, and stirred for 1.5 h under argon. The dark green solution was transferred via cannula to a reaction flask containing GeCl₄ (70 μL, 0.6 mmol) dissolved in anhydrous glyme (30 mL) and stirred for 15 min at room temperature under argon. The reduced Ge mixture was then treated with either n-BuMgCl or t-BuMgCl (2 M in Et₂O, 0.6 mmol) and left to stir for 12 h under argon, prior to fractionation. Batches of Ge nanoparticles treated with these Grignard agents are referred to here as “NB-Ge” and “TB-Ge”, respectively. We note that naphthalide reduction of GeCl₄ without addition of Grignard reagents did not yield stable Ge nanoparticles, and the use of stoichiometric sodium (1 equiv. relative to naphthalene) was not successful in producing significant quantities of Ge nanoparticles.

All batches were subjected to sedimentation using a fixed-angle centrifuge (r = 7 cm) operating at 10 000 rpm (8000 g) for 15 min. The supernatant was concentrated to a dark brown oil, resuspended in hexanes, washed with 1 M HCl and water, then concentrated again and subjected to sublimation to remove excess naphthalene. The resulting solids could be redispersed in hexanes or ethanol. Alternatively, the supernatant was subjected to three rounds of centrifugation (8000 g, 15 min) and redispersed in 25% THF in hexanes with sonication, in order to fractionate Ge-rich materials from inorganic salts.

**Structural characterization**

Transmission electron microscopy (TEM) images were obtained using a Titan 80/300 (FEI, 300 kV) equipped with a Gatan 652 double tilt-heating holder, for in situ characterization of nanoparticle coalescence and phase transformation behavior. TEM samples were prepared by resuspending the sedimented or fractionated products in ethanol, followed by 20 min agitation in an ultrasonic cleaning bath. A drop of the Ge-rich suspension was deposited onto a carbon-coated Cu grid, then dried in air at room temperature overnight (in the case of redispersed sediment) or at 70 °C for 20 min (in the case of redispersed supernatant). Samples were examined in situ before and after thermal annealing; the sample was brought to the target temperature and held constant for 20 min, then cooled to room temperature and reexamined after the sample stage achieved thermal equilibrium. The gun valve of the TEM was closed during heating and cooling, and images were obtained with exposure times of under 10 s to prevent the possibility of electron beam damage. This was confirmed by investigating areas not previously exposed to electron beam irradiation prior to heating. Electron diffraction patterns and high resolution TEM (HRTEM) images were calibrated using colloidal Au particles supported on carbon films or on Si thin film samples at a fixed, optimum objective lens current of the TEM.

Photoluminescence (PL) studies were conducted using an Ar ion laser (488 nm, 20 mW) limited by a neutral density filter. The PL emission was dispersed using a single grating monochromator and detected by a liquid nitrogen-cooled charge-coupled device (CCD) camera. Differential scanning calorimetry (DSC, TA Q100, TA instruments) and thermogravimetric analysis (TGA, TA Q500, TA instruments) were used for thermal analysis of the as-synthesized samples under a N₂ atmosphere with a heating and cooling rate of 10 °C min⁻¹. DSC measurements were cycled twice between room temperature and 500 °C; the lack of a measurable change during the second cycle indicated that the observed transitions were thermally irreversible.

**Results and discussion**

The naphthalide-mediated reduction of GeCl₄ at ambient temperatures is known to produce both amorphous and crystalline Ge nanoparticles. These are considered to be capped initially by Cl atoms and amenable to further growth, but their surfaces can be passivated by introducing Grignard reagents. An earlier study by Hope-Weeks demonstrated Ge particle size control as a function of growth time, prior to quenching by n-BuLi. The surface alkylating agents also appear to promote the crystallization of Ge, ostensibly by reducing the surface energy; in most cases, the resulting nanocrystalline domains form the diamond cubic phase. This suggests the possibility of sintering nanophase Ge into crystalline thin films at temperatures compatible with electronic circuitry printing.

Freshly reduced Ge was treated with n-BuMgCl (NB-Ge) in order to produce nanocrystalline domains for subsequent coalescence into thin films. However, attempts to use a stoichiometric ratio of Na and naphthalene often led to the incomplete reduction of GeCl₄, presumably due to the partial generation of Na–naphthalide. Excess Na was found to be more practical for the efficient reduction of naphthalene, and resulted in higher yields of nanocrystalline Ge. The effect of excess Na on the reduction of Ge or its salts has not been fully elucidated: for example, Ge salts can react directly with alkali metals to form germanides or Zintl phases, which can potentially contribute toward the formation of nanocrystalline Ge. However, these reactions are very slow at ambient temperatures whereas naphthalide-mediated reductions proceed rapidly, so the presence of additional sodium is unlikely to have a critical impact on the reaction outcome. On the other hand, the presence of excess inorganic salt and the relatively low conversion of amorphous Ge into crystalline forms (see below) introduced complications for X-ray diffraction analysis, precluding unambiguous assignments...
(Table S1, ESI†). We thus relied on TEM analysis with in situ annealing for structural characterization of nanocrystalline Ge.

As-synthesized NB-Ge was initially fractionated by centrifugation, then redispersed and deposited onto carbon-coated Cu grids for examination by TEM. The sediments comprised mostly inorganic salts, but soluble fractions taken from the NB-Ge supernatant were found to contain Ge nanoparticles with a broad distribution in average particle size (APS = 6 nm, Fig. 1a). The TEM diffraction pattern (inset) supports the coexistence of both amorphous and crystalline Ge particles at room temperature, in accord with earlier reports on NB-Ge.18-19 The diffuse rings and bright spots indicate d-spacings at 3.2 and 2.0 Å, corresponding to the (111) and (220) lattice planes of Ge-I, respectively. The annealing and coalescence behavior of the NB-Ge sample was then monitored by in situ TEM, up to 500 °C. Amorphous Ge (presumed to be in polymer form) began to condense into particles at 300 °C, and further heating produced a bimodal particle size distribution, with the majority population centered around 5 nm (Fig. 1b) and a few particles of the order of 40 nm (Fig. 1c–e).

HRTEM analysis of some larger Ge particles formed after sintering and coalescence supports an ST12 structure (Fig. 1c–e and Table 1). Here it is important to note that surface or interfacial stress can often cause the measured d-spacings of nanocrystalline materials to deviate significantly from those reported for bulk crystals. Despite this, these deviations rarely lead to significant changes in the internal symmetry of the structure, and the relationships between bond lengths, bond angles, and lattice planes all remain the same. In our analysis, we find the d-spacing ratios are well matched with those in the ST12-Ge structure (JCPDS no. 72-1089), even though the measured d-spacings are shorter by 5%. The interplanar angles are also well matched, and are particularly useful for assigning lattices with nearly identical spacings such as the (112) and (120) planes, whose difference is smaller than the relative error for spacing measurements (approximately 1%). Overall, our analysis of the NB-Ge sample is comparable in many respects to that of earlier studies, except for the appearance of cubic Ge at room temperature and the persistence of the ST12 structure at 500 °C.

Freshly reduced Ge was also treated with t-BuMgCl (TB-Ge) and partially fractionated as described above. In contrast to NB-Ge, nanocrystals in the as-synthesized TB-Ge sample were found in both the sediment and the supernatant, with most of these having the ST12 phase (Fig. 2). The TB-Ge sediment yielded Ge nanocrystals (APS = 4 nm, N = 100) embedded in organic or polymeric residue; regions of amorphous Ge without nanoparticles were also observed (to be discussed below). The electron diffraction pattern, lattice parameters, and interplanar angles measured by HRTEM all clearly support the ST12-Ge structure (Table 1).

Nanocrystals taken from the supernatant of TB-Ge appeared to be of two different forms, and were distinguishable by size. Many of the smaller nanoparticles were visibly agglomerated and difficult to characterize as isolated structures, although their diffraction patterns and lattice fringes indicated crystalline features with different orientations relative to the incident beam (Fig. 3a). The d-spacings derived from the electron diffraction rings suggest these agglomerated nanocrystals to be cubic Ge. On the other hand, the larger Ge nanocrystals were determined to have an ST12 phase (Fig. 3b), which was confirmed by simulation of the diffraction pattern (left inset). It is worth mentioning that pentatwinned nanoparticles were infrequently observed in either TB-Ge or NB-Ge (<5% occurrence), at odds with the prediction that icosahedral and decahedral structures should be more stable and prevalent than either cubic Ge or ST12-Ge when the particle size is very small.

Thermal annealing experiments performed on the TB-Ge sample indicated that nanocrystalline Ge with ST12 structure had a low coalescence temperature, and did not undergo a transition to the diamond cubic phase (Fig. 4). In situ TEM analysis performed with incremental temperature changes of 10 °C revealed that particle coalescence was initiated around 170 °C, then proceeded gradually as the temperature was further increased. A number of particles remained intact even at 300 °C but disappeared upon raising the annealing temperature to 400 °C, followed by coarsening and grain growth up to 500 °C. The persistence of the smaller nanoparticles may be attributed to the formation of a carbonaceous shell between 300 and 400 °C which hinders their coalescence, as suggested by earlier in situ TEM heating experiments by Sutter et al.27 Thermal annealing of the Ge nanoparticles to 500 °C without electron beam exposure, followed by TEM analysis at room temperature, established that...
the electron beam was not responsible for the nucleation of crystals shown in Fig. 4. Remarkably, the ST12 phase was maintained throughout the annealing experiment, even as the particles exceeded 100 nm in size. Electron diffraction analysis of these larger crystalline domains revealed \( d \)-spacings of 2.96, 2.70, and 2.67 Å, nearly identical to the \( d \)-spacings for the 102, 112, and 210 planes in bulk ST12-Ge (Table 1). These observations confirm that TB-Ge has a strong tendency to crystallize into ST12-Ge upon thermal annealing, and possibly also at room temperature (cf. Fig. 3b).

The thermal annealing response of the TB-Ge sample was further analyzed by DSC and TGA (Fig. 5). DSC measurements were performed on thin films with solute densities similar to that used in printable inks, and indicated a broad exothermic peak from 150 to 300°C followed by a sharp endothermic peak near 350°C. These phase transitions correlate, respectively, with the sintering and coalescence of Ge nanoparticles (initiated at 170°C) and the spontaneous nucleation and coarsening of crystalline domains within amorphous Ge (see below), both identified by \textit{in situ} TEM analysis. The TGA profile revealed a 65% weight loss between 200 and 400°C, corresponding to the ablation of residual organic materials prior to granulation.

Nanocrystals also nucleated within the amorphous Ge residue at higher temperatures, albeit with greater variability in lattice structure than that observed during the coalescence of preformed nanoclusters. Thermolysis of the amorphous residue from the sediment of the TB-Ge sample at 300°C yielded nanoparticles with a relatively low size dispersity (APS = 5.4 nm) (Fig. 6a). Raising the temperature to 500°C resulted in further growth of these nanocrystals (APS = 7 nm), which were characterized as

<table>
<thead>
<tr>
<th>( hkl )</th>
<th>ST12 (^a)</th>
<th>Ratio (^b)</th>
<th>NB-Ge (^c)</th>
<th>Ratio (^b)</th>
<th>TB-Ge (^d)</th>
<th>Ratio (^b)</th>
<th>Interplanar angles/deg</th>
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<tr>
<td>111</td>
<td>3.59</td>
<td>1.19</td>
<td>—</td>
<td>—</td>
<td>3.4</td>
<td>1.13</td>
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<tr>
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<td>—</td>
<td>2.86</td>
<td>—</td>
<td>3.0</td>
<td>—</td>
<td>102/112 64.3</td>
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<td>0.89</td>
<td>2.52</td>
<td>0.88</td>
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<td>0.88</td>
<td>2.51</td>
<td>0.88</td>
<td>—</td>
<td>—</td>
<td>120/112 52.6</td>
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<tr>
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<td>2.48</td>
<td>0.82</td>
<td>—</td>
<td>—</td>
<td>2.4</td>
<td>0.80</td>
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<tr>
<td>202</td>
<td>2.26</td>
<td>0.75</td>
<td>—</td>
<td>—</td>
<td>2.3</td>
<td>0.77</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) From JCPDS no. 72-1089. \(^b\) Ratios relative to \( d \)-spacing for (102). \(^c\) From HRTEM analysis in Fig. 1c, with precision of ±0.02 Å. \(^d\) From HRTEM analyses in Fig. 2, with precision of ±0.1 Å. \(^e\) \( d \)-Spacing assignment to (102) favored over (200) (2.97 Å), based on interplanar angle measurements.
Ge-I based on \( d \)-spacings of 1.8 and 2.1 Å (Fig. 6b). On the other hand, thermolysis of the amorphous Ge residue from the supernatant of the TB-Ge sample resulted in the formation of ST12-Ge nanocrystals upon heating to 300 °C, followed by coalescence and coarsening to grain sizes of the order of 30 nm after annealing at 500 °C (Fig. 7 and S1, ESI†).

The lattice structures were again established by HRTEM image analysis and electron diffraction, which revealed a different set of ST12-Ge lattice planes (Table 2). The quality of the diffraction patterns, \( d \)-spacings, and interplanar angles is comparable to those described earlier (Fig. 1c–e). The capriciousness of the Ge nanocrystal phase reveals that the cubic and ST12 structures have comparable lattice energies, and that their nucleation is likely dependent on local environmental factors.

Our studies indicate that the ST12-Ge structure is kinetically more stable and accessible than previously believed. The ST12 structure has most often been reported in bulk Ge samples subjected to high pressures: Menoni et al. performed diamond anvil experiments to demonstrate the transition of the semiconducting Ge-I phase to the metallic Ge-II (\( \beta \)-Sn) phase under a hydrostatic load of 10.6 GPa, whereas a reduction in pressure to 7.6 GPa induced a second transition from Ge-II to Ge-III (ST12). Additional transformations have been reported from nanoindentation experiments. Additionally, the observation of the ST12 phase in small Ge nanocrystals at atmospheric pressure is not entirely unexpected, and has been reported previously by others. Kauzlarich and co-workers have postulated that the additional surface tension generated by removal of the organic coating at 300 °C may contribute toward the crystallization of Ge nanoparticles into the observed tetragonal structure. This is a reasonable argument: Bottomley et al. have estimated the surface energy of a 4 nm particle to be of the
order of 1 J m$^{-2}$, which translates into an internal pressure of 1 GPa. Furthermore, Pizzagalli et al. predicted that while Ge-I is more stable than ST12-Ge irrespective of particle size, the formation of metastable tetragonal clusters is possible by trapping amorphous nanoparticles with unsaturated and reconstructed surfaces at low temperatures. Surface tension may also contribute toward the persistence of the ST12 phase in larger Ge nanostructures such as those featured in Fig. 4, although the influence of surface strain on lattice structure decreases with particle size.

With respect to the predominance of the ST12 phase in the TB-Ge sample, we suggest that the addition of $t$-BuMgCl promotes the nucleation of this structure by imparting surface strain onto nascent amorphous Ge nanoclusters. Sterically hindered organometallic reagents such as $t$-BuMgCl are strong bases but relatively poor nucleophiles, and are well known to induce eliminations via proton abstraction or metal–halogen exchange. Here $t$-BuMgCl reacts with amorphous Ge particles, whose surfaces are passivated with Cl atoms and are more likely to favor elimination over direct substitution, resulting in a metastable surface with a high degree of unsaturation (Scheme 1). In contrast, $n$-BuMgCl is a much better alkylating agent than $t$-BuMgCl, so treatment of amorphous Ge with $n$-BuMgCl is more likely to proceed with substitution. The fact that the larger Ge domains are able to sustain the ST12 structure after coalescence during in situ annealing attests to its kinetic stability, despite earlier references to its higher lattice energy.

Finally, the nanocrystalline grains of ST12-Ge were examined by photoluminescence (PL) in order to identify the predicted direct band gap at 1.47 eV ($\lambda = 843$ nm). However, none of the samples exhibited a resonant absorption or demonstrated a measurable PL response in this spectral region, either at room temperature or at 77 K (Fig. S2, ESI†). The lack of PL response is not completely unexpected: prior studies by Sato et al. involving granular thin films comprising ST12-Ge nanoparticles (10–40 nm) also failed to yield a detectable PL response in the NIR. Only oxidized films exhibited a PL response in the visible region at 2.8 eV, as previously noted. The direct band gap for ST12-Ge thus remains unconfirmed.

### Conclusions

Ge nanocrystals with ST12 structure can be produced from amorphous Ge under highly activated conditions, particularly by introducing $t$-BuMgCl following the naphthalide reduction of GeCl$_4$. In situ TEM analysis revealed that the ST12-Ge structure remains the dominant phase during particle coalescence and coarsening under thermal annealing conditions up to 500 °C. The apparent stability of the ST12 phase at standard pressures is independent of particle size, and can exist in structures with

**Table 2** Selected $d$-spacings and interplanar angles from nanocrystalline grains nucleated from amorphous Ge, compared with JCPDS data for ST12-Ge

<table>
<thead>
<tr>
<th>$d$-spacings/Å</th>
<th>( hkl )</th>
<th>ST12$^a$</th>
<th>Ratio$^b$</th>
<th>TB-Ge$^c$</th>
<th>Ratio$^b$</th>
<th>Interplanar angles/deg</th>
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<td>122</td>
<td>2.11</td>
<td>1.00</td>
<td>2.12</td>
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<td>122/131 67.2</td>
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<tr>
<td></td>
<td>131</td>
<td>1.81</td>
<td>0.86</td>
<td>1.82</td>
<td>0.86</td>
<td>213/131 49.8</td>
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<tr>
<td></td>
<td>213</td>
<td>1.75</td>
<td>0.83</td>
<td>1.78</td>
<td>0.84</td>
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</tr>
</tbody>
</table>

$^a$ From JCPDS no. 72-1089. $^b$ Ratios relative to $d$-spacing for (122). $^c$ From HRTEM analysis in Fig. 7, with precision of $\pm 0.01$ Å.
lateral dimensions in excess of 100 nm. The onset of coalescence at temperatures well below 200 °C merits further investigation in the application of Ge nanoparticles for printed electronics.

Acknowledgements

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