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Systematic Annealing Of Free-Standing Ge Nanoparticles in H_2/Ar (%5/%95) Gas Medium

Ali Karatutlu
Electrical & Electronics Engineering, Bursa Orhangazi University
YILDIRIM, Bursa, Turkey, 16310
ali.karatutlu@bou.edu.tr

Ali Karatutlu, Osman Ersoy, William R. Little, Yuanpeng Zhang, Andrei V. Sapelkin
Centre for Condensed Matter and Materials Physics, School of Physics and Astronomy, Queen Mary, University of London,
London, E1 4NS, UK
a.karatutlu@qmul.ac.uk

Abstract -Free-standing Ge nanoparticles about 3 nm in size were formed using a facile colloidal synthesis method. The effect of systematic annealing in H_2/Ar (%5/%95) gas medium on morphology and structure of the free-standing Ge nanoparticles was investigated using transmission electron microscopy and selective area electron diffraction techniques. We showed that upon annealing in H_2/Ar (%5/%95) gas medium, the size of Ge nanoparticles can be controlled and some exotic phases such as β-Sn II phase and 4H-Ge phase seem to be formed. To our knowledge, free-standing Ge nanoparticles in 4H-Ge phase was demonstrated for the first time.

***Keywords*:** Germanium nanoparticles, annealing, structure, morphology, 4H-Ge phase

1. Introduction

Germanium (Ge) and silicon (Si) are known to be technologically important semiconductors but have a low emission efficiencies due their indirect bandgaps. Optical properties of these semiconductors can be strongly enhanced and made available for imaging applications by reducing their size to nanoscale particularly below their excitonic Bohr radius (Fan & Chu, 2010; Hanada et al., 2013; Liu et al., 2013). As a post-synthesis route, annealing is mostly treated as a physical process which can be operated inside an inert medium and usually at high temperatures to convert amorphous nanoparticles to crystalline (Schrick & Weinert, 2013). Annealing is also used for the reductive thermal processing in H_2 containing medium (Henderson, Seino, Puzzo, & Ozin, 2010). The optimum temperature in annealing process in case of burying of Ge nanoparticles on a substrate also mediates the growth process to be homogeneous (Bosi et al., 2014). Recently, we used a simple benchtop colloidal synthesis method to form free-standing Ge nanoparticles whose structures are best described using thorough characterization techniques by a crystalline core, an intermediate disordered region and a hydrogen-related terminations on the surface (Karatutlu et al., 2015). We also observed possibility of metastable phases upon annealing of the Ge nanoparticles in H_2/Ar (%5/%95) gas medium (Y. Zhang et al., 2015). This study is to fill in the gap and to show the effect of a systematic annealing in H_2/Ar (%5/%95) gas medium on the structure and morphology of the free-standing Ge nanoparticles.

2. Experimental Method

All chemicals were used as purchased from Sigma-Aldrich. Free-standing Ge nanoparticles were synthesized as previously described in our studies (Karatutlu et al., 2015; Y. Zhang et al., 2015). Then, the samples were transferred inside to the split furnace which was heated to 450 ^{o}C from room temperature and treated for 1h, 2 h and 3 h in H_2/Ar (5%/95%) gas flow (100 ccm). The samples were washed upon annealing using hexane and transferred to a Cu coated C grid. The TEM grids were submerged into the Ge nanoparticles dispersed hexane solution. TEM/HR-TEM and SAED measurements were conducted using JEOL 2010 at NanoVision of Queen Mary, University of London. The data for the TEM micrographs and diffraction patterns were analysed using Gatan Digital Micrograph and Diffraction Ring Profiler respectively. The crystalline structures were regenerated using commercial software called CrystalMaker as the structural parameters were obtained using International Chemical Database Service (ICDS) or from the previous relevant studies if not available in ICDS.

3. Results and Discussion

We reported previously that the size of as-prepared Ge nanoparticles using colloidal synthesis method was estimated to be 3.8 ± 0.6 nm using the TEM data (Karatutlu et al., 2015). In Figure 1(a), (b) and (c), TEM micrographs of annealed samples of Ge nanoparticles in H_2/Ar (%5/%95) gas medium are shown for 1 h of annealing, 2 h of annealing and 3 h of annealing respectively. The size of Ge nanoparticles upon 1 h of annealing, 2 h of annealing and 3 h of annealing in H_2/Ar (%5/%95) gas medium were measured to be 4 ± 0.5 nm, 7.7 ± 1.6 nm and 12.9 ± 2.5 nm out of 60 nanoparticles. The size analyses of the TEM data in Figure 1 suggest that the systematic annealing from 1 h to 3 h in H_2/Ar (%5/%95) gas medium shows a firm increase in the size of Ge nanoparticles. The structure of each annealed sample was investigated using selective area electron diffraction technique by analyzing corresponding TEM diffraction pattern. It was shown previously that the structure of annealed Ge nanoparticles in an inert atmosphere would be expected to result in diamond cubic phase (Serincan et al., 2004). However, there are some structures which are known to be metastable and can be observed to be stable upon annealing (Kim et al., 2010). Additionally, applying pressure and then fast or slow pressure release also determine the crystal structure (Nelmes et al., 1993). This brings us to the quest of exploring several structural forms in order to find out the correct form of each sample after the annealing processes.

Table 1 shows all possible experimental and theoretical structural configurations for bulk Ge (see also Table 2 for crystalline phases of GeO_2). Using the lattice structural parameters given in Table 1, each structure for Ge was formed using the commercial software called CrystalMaker. Then, the TEM diffraction pattern simulation of each structure was made using the diffraction ring profiler (L. Zhang et al., 2011) and compared with the TEM diffraction pattern of the experimental data given in the insets of Figure 1. The analysis of the TEM diffraction pattern in the inset of Figure 1(a) shows that annealing for 1 h in H_2/Ar (%5/%95) gas medium transforms the very disordered as-prepared sample to a crystal form which was further investigated and suggested to be due to combination of diamond cubic and Beta Sn II phases. We further continued with 2 h annealing of the as-prepared sample in H_2/Ar (%5/%95) gas medium and recorded the corresponding TEM diffraction pattern given in the inset of Figure 1(b). The analysis of the TEM diffraction pattern of 2 h annealed sample shows an exact structural match for a diamond cubic phase. The lattice parameters matched with the experimental TEM diffraction pattern were found to be shrinked (a=5.43 Å, b=5.43 Å, c=5.43 Å, see also Figure 2 for the diffraction pattern intensity profile of the annealed Ge nanoparticles for 2 hours).

Figure 1(c) shows TEM and HR-TEM (bottom inset) micrographs of annealed Ge nanoparticles in H_2/Ar (%5/%95) gas medium for 3 h. The lattice fringes shown in the HR-TEM were measured to be 6.0 Å. SAED technique was additionally used to understand structure of annealed Ge nanoparticles for 3 h in H_2/Ar (%5/%95) gas medium. The analysis of the TEM diffraction pattern shows in the inset of Figure 1(c) that the structure of the annealed sample was found to be close to the simulated TEM diffraction pattern for 4H-Ge phase. There seems to be difference in the lattice structure parameters between bulk 4H-Ge and those in nanoparticles with 4H-Ge phase as in the latter, contraction of lattice might be observed. This is also confirmed by the HR-TEM measurement. Possibility of 4H-Ge phase for Ge nanoparticles is an interesting one owing to its direct band gap as calculated to be E_g=0.81 eV (at 0 K) (Kiefer et al., 2010). This electronic property is essential in direct band gap material applications including imaging applications.

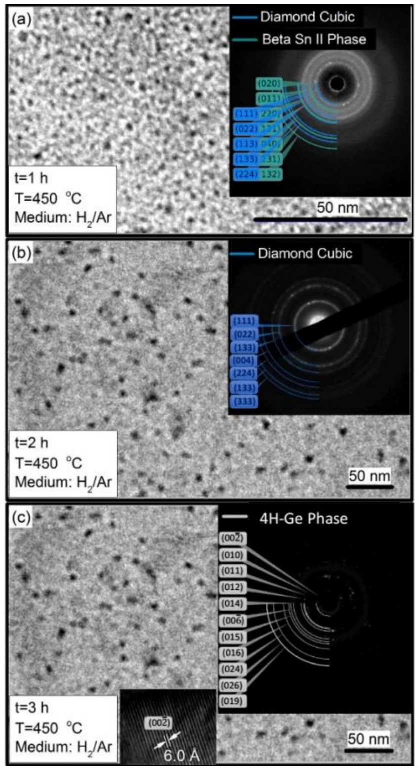

Fig. 1. TEM and diffraction patterns (insets) of annealed Ge nanoparticles in H_2/Ar (%5/95%) gas medium respectively for (a) 1 h, (b) 2 h, (c) 3h. Based on the analyses of the TEM diffraction patterns, highly disordered as-prepared Ge nanoparticles were considered to be transformed to different crystalline phases which were found to be a mixture of diamond cubic phase and Beta Sn II phase at the end of 1 annealing process, a shrinked diamond cubic structure at the end of 2 h of annealing process and 4H-Ge structure at the end of 3 h annealing process.

Table. 1. Possible structural phases of bulk Ge.

Possible phases (Ge)	Lattice parameters (Å)	Atomic positions (x/a,y/b,z/c)	Space Group
Diamond Cubic ICDS ID: 636528	a=5.65 b=5.65 c=5.65	(0, 0, 0)	Fd3m
ST12 ICDS ID: 16570	a=5.93 b=5.93 c=6.98	(0.9126, 0.9126, 0) (0.1730, 0.3784, 0.2486)	$P4_32_12$
BC8 (Nelmes et al., 1993)	a=6.932 b=6.932 c=6.932	(0.1004,0.1004, 0.1004)	Ia-3
β-Sn II Phase ICDS ID: 636530	a=4.8000 b=4.8000 c=2.6920	(0, 0, 0)	I 41/a m d
BCT5 (Crain et al., 1995)	a=3.2910 b=3.2910 c=6.2680	(0,0,0.1810)	I 4/m m m
Ge-3H ICDS ID: 245961	a= 9.8138 b= 9.8138 c=5.8439	(0, 0, 0.2825) (0.230(2),-0.0342, 0.2374)	R -3
4H-Ge ICDS ID: 167204	a= 3.99019(4) b= 3.99019(4) c= 13.1070(2)	(0, 0, 0.0941) (0.3333, 0.6667, 0.1552)	P63/mmc

Table. 2. Possible structural phases of GeO_2.

Possible phases (GeO_2)	Lattice parameters	Atomic positions	Space Group
Rutile type (Bolzan et al., 1997)	a=4.4066 b=4.4066 c=2.8619	(0, 0, 0) (0.306, 0.306, 0)	P 42/m n m
α-quartz type (Smith & Isaacs, 1964)	a=4.9870 b=4.9870 c=5.6520	(0.4513, 0, 0) (0.3969, 0.3021, 0.0909)	P3221S

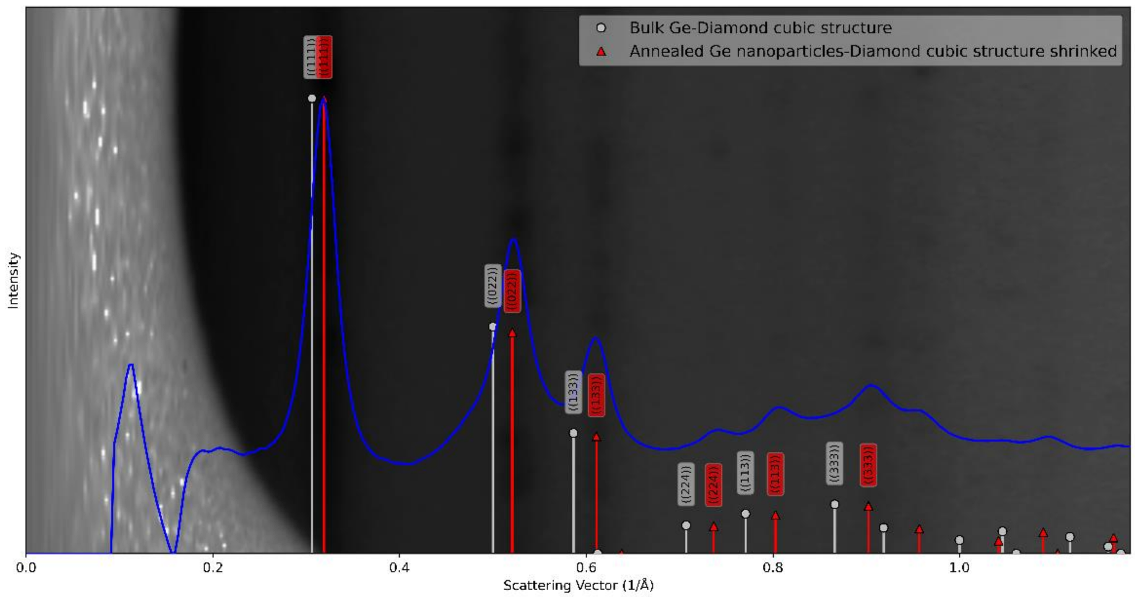

Fig. 2. TEM diffraction pattern intensity profile (blue line) of Ge nanoparticles on top of the corresponding polar pattern. The TEM diffraction pattern of diamond cubic structure for annealed Ge nanoparticles at the end of 2 h in H_2/Ar (%5/95%) gas medium (red triangle) and that (gray sphere) for bulk Ge are simulated for comparison. The simulation shows that the diamond lattice structure matching with the annealed samples for 2 h was found to be shrinked.

4. Conclusion

Free-standing Ge nanoparticles were systematically annealed in H_2/Ar gas medium and shown to be transformed to different crystalline phases depending on the annealing time. The morphology and the size of the annealed Ge nanoparticles were observed to be controlled when changing the annealing time. Based on images given in the TEM micrographs, the morphology of all annealed samples are spherical. The annealing process in H_2/Ar gas medium for 1 h, 2h and 3h results in the size of annealed samples to be 4 ± 0.5 nm, 7.7 ± 1.6 nm and 12.9 ± 2.5 nm respectively. Increasing annealing from 2 h to 3 h were considered to yield structural transformation from diamond cubic phase to 4H-Ge phase.

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