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One-pot size-controlled growth of graphene-encapsulated germanium nanocrystals

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Abstract

To realize graphene-encapsulated semiconductor nanocrystals (NCs), an additional graphene coating process, which causes shape destruction and chemical contamination, has so far been inevitable. We report herein one-pot growth of uniform graphene-germanium core-shell nanocrystals (Ge@G NCs) in gram scale by the addition of methane as a carbon source during the thermal pyrolysis of germane. The methane plays a critical role in the growth of the graphene shell, as well as in the determination of the nucleation density and diameter of the NCs, similar to a surfactant in the liquid-phase growth of monodisperse NCs. By adjusting the gas ratio of precursors, a mixture of germane and methane, we can control the size of the Ge@G NCs in the range of ~5 nm to ~180 nm. The Ge@G NCs were characterized by various microscopic and spectroscopic tools, which indicated that the Ge core is single crystalline, and is completely covered by the graphene shell. We further investigated the merits of the graphene shell, which can enhance the electrical conductivity of nanocrystalline materials.

Keywords: germanium, graphene, core-shell, nanocrystal, chemical vapor deposition (CVD), thermoelectric

1. Introduction

The incorporation of graphene with a semiconductor have been intensively studied over the past decade, because the superb physical and unique chemical properties of graphene generate synergistic effects in various areas [1-5]. For example, new types of transistors and high-speed optical modulators for next generation electronics have been invented by the integration of graphene with typical Si-based complementary metal oxide semiconductor (CMOS) technology [3, 4]. These convergence systems are particularly required for nanocrystals (NCs) research to surmount the NCs weaknesses, such as their instability, low current density, and poor reliability [6-11]. Wrapping NCs with graphene can be considered an effective route, because the sp^2 -hybridized carbon network improves their physical and

chemical properties. Encapsulation of NCs in a graphene cage is used for anode materials in the lithium-ion battery, to achieve long-life cycles and high capacity [6, 7]. In addition, the graphene shell improved the electrical conductivity, as well as the chemical stability of the NCs for conductive ink [8]. In either case, an additional graphene coating process to realize graphene-covered NCs cannot be avoided. Chemical vapor deposition (CVD) is a widely used method for the direct growth of a graphene shell on the surface of NCs [6-8]. However, after the synthetic process, the shape of the NCs becomes irregular and the size gets poly-disperse, owing to the melting point depression effects at the high graphene growth temperature. Alternatively, solution-based approaches have been reported; however, they also suffer from low crystallinity and chemical contamination issues [12, 13]. Therefore, these approaches are not suitable for electronic devices that require high crystallinity, narrow size distribution, and a clean interface. Recently, Wang *et al.* and Sengar *et al.* introduced one-step growth methods for metal-graphene core shell NCs using organometallic precursor [14, 15]. Although these techniques can satisfy the aforementioned requirements, they are so far only available for metal NCs.

The germanium (Ge) NCs, the group IV semiconductor, have been extensively explored for various types of electronic applications, such as transistor, battery, thermoelectric, and photovoltaics [16-19]. In particular, compared to other semiconductor materials, Ge shows a good catalytic activity for the sp^2 hybridization of carbon atoms [20-22]. In this paper, taking advantage of catalytic behavior of Ge, we demonstrate one-pot growth of graphene-coated uniform Ge NCs (Ge@G NCs) in gram scale *via* the conventional CVD method. The diameter of the Ge@G NCs is controlled by the precursor ratio of methane and germane. Microscopic and spectroscopic analysis confirmed that the Ge core is single crystalline, and is completely covered by the graphene shell. In addition, based on the experimental results,

we describe the growth mechanism of the Ge@G NCs; the role of methane is critical for determination of the density and diameter of the NCs.

2. Experimental

2.1 Characterization.

The morphology and size of the Ge@G NCs were measured by JEOL JSM-7401F field emission scanning electron microscopy, operating with an accelerating voltage of 10 kV (FE-SEM). The crystallinity and composition of the NCs were characterized by JEOL JEM-2100F field emission transmission electron microscopy (FE-TEM). For TEM measurement, the Ge@G NCs were suspended in ethanol, dispersed onto a Cu grid with a thin lacey carbon support film, and imaged at an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) measurements were performed on a D8 ADVANCE (Bruker) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), and a step size of 0.04° . X-ray photo-electron spectroscopy (XPS) analysis was carried out by ESCA2000 spectrometry using monochromatic Al K α radiation (1,468.6 eV). The peak energies were calibrated to the C 1s peak at 284.6 eV. Raman spectroscopy (Renishaw, RM-1000 Invia) with excitation energy of 2.41 eV (514 nm; Ar ion laser) was used to characterize NCs. For both XPS and Raman measurement, the Ge@G NCs were dispersed on thin gold film (50 nm) deposited Si substrates.

2.2 Plasma Spark Sintering.

The Ge@G NCs were compacted into disk-shaped pellets with a diameter of 10 mm and a thickness of 3 mm using a spark plasma sintering (SPS) technique. Table S1 shows the SPS process conditions. The density (ρ_s) of the synthesized sample was calculated as $5.06 \sim 5.26 \text{ g/cm}^3$, which is more than 95% of the theoretical value of Ge.

2.3 Thermoelectric measurement.

The electrical conductivity (σ) was measured at 300 ~ 860 K using the ULVAC ZEM-3 equipment. The thermal conductivity (κ) was calculated using the equation $\kappa_{tot} = \rho_s C_p \lambda$. The heat capacity (C_p) value used in the equation is the C_p value (0.31 J / gK) of pure Ge at 300 K as the constant value [23]. Thermal diffusivity (λ) values were measured under vacuum by a laser flash method (TC-9000; ULVAC, Japan).

3. Results and Discussion

3.1 Growth and Characterization of the Ge@G NCs

Fig. 1. (a) Schematic of the one-pot growth of the Ge@G NCs. (b) Photograph-, and (c) SEM-image of a large density of the Ge@G NCs on the collecting substrate. The inset in Fig. 1 (c) shows a photograph-image of 80 mg of the Ge@G NCs in a vial.

Fig. 1 (a) shows the schematic of the growth of Ge/graphene core/shell nanocrystals, which was demonstrated by conventional hot-wall chemical vapor deposition (CVD). Firstly, the holder for collecting the Ge@G NCs was loaded into the collection region in the quartz

tube ($\phi=34$ mm), and then the chamber was evacuated to ~ 3 mTorr by rotary pump. Subsequently, the furnace was heated to 900 $^{\circ}\text{C}$ under Ar atmosphere (heating rate was kept at 20 $^{\circ}\text{C}$ per min). When the furnace reached the target temperature, GeH_4 (99.999%, diluted to 10% with H_2) and CH_4 (99.999%) as the Ge and carbon source, respectively, were introduced into the quartz tube, and the total pressure was maintained at 100 Torr for 120 min. All the gases were completely mixed before entering the processing zone. To avoid the aggregation of the Ge@G NCs after the growth process, the cooling block was set at the edge of the furnace, maintaining the temperature of the collecting region lower than 400 $^{\circ}\text{C}$ (see Fig. S1). Figs. 1 (b) and (c) show the photograph and SEM images of the Ge@G NCs at the cooling region during the growth process. Note that we could obtain uniform Ge@G NCs in gram scale at low methane-to-germane gas ratio (inset of Fig. 1 (c)).

Fig. 2. (a)–(c) SEM images of the Ge@G NCs with different methane-to-germane gas ratio (CH_4/GeH_4). Insets show the size distribution of the Ge@G NCs. (d) HR-TEM image of the Ge@G NCs. Inset shows the fast Fourier transform pattern from the Ge core. The average number of graphene layer is around 3-5.

By changing the partial pressure of methane, it is possible to control the diameters of the Ge@G NCs (Figs. 2 (a)–(c)). As the gas ratio of methane and germane increases to 6, the average diameter of the NCs decreases from 177.7 ± 17.3 to 91.4 ± 10.8 nm. As the gas ratio is further increased to 10, NCs as small as 5.7 ± 1.5 nm are obtained (Fig. S2). Fig. S2 shows the low- and high-magnification TEM images of the mono-disperse Ge@G NCs. A detailed growth mechanism is discussed in the later section. The high-resolution TEM image of the as-grown Ge@G NCs indicates that the Ge core is single crystalline, and is completely covered by a multi-layered graphene shell (Fig. 2 (d)).

Fig. 3. (a) Raman spectra of the Ge@G NCs. (b) Powder XRD pattern of the Ge@G NCs. The red star indicates the peak from the graphene shell. (c) and (d) XPS spectra of the Ge@G NCs for the core level of C 1s and the Ge 3d region.

Various spectroscopic measurements were performed to verify the crystal structure and chemical properties of the Ge@G NCs. The Raman spectra in Fig. 3 (a) provides information about the crystallinity of both the Ge core and graphene shell [24, 25]. The strong and narrow peak at around 300 cm^{-1} , corresponding to the first order Raman signaling of Ge, indicates

the high crystallinity of the Ge core [24]. Other obvious three peaks located at 1,350, 1,580, and 2,700 cm^{-1} are consistent with the representative Raman spectra of graphene, which are assigned to D band, G band, and 2D band, respectively [25]. The D band, implying the disorder of the sp^2 carbon network, might be caused by the step edges of the several-layered graphene shell or the finite particle-size effect [8, 14, 25, 26]. Size of graphene domain is obtained from the integrated intensity ratio of D band and G band, indicating it is approximately 11.31 nm (Fig. S3) [27]. The crystal structure of the Ge@G NCs was investigated by XRD. The (111), (220), (311), and (331) planes of the diamond cubic Ge (JCPDS 4-0545), corresponding to 2 theta values of 27°, 45°, 55°, and 72°, respectively, are labeled in Fig. 3 (b) [16]. In particular, the peak at around 24° represents the graphite (002) plane (JCPDS 1-0646), supporting the existence of a multi-layered graphene shell [10].

The chemical states of the Ge@G NCs were characterized by XPS. Figs. 3 (c) and (d) show the core level peaks of C 1s and Ge 3d in the XPS spectrum. The area under the peak at 284.6 eV corresponding to the C–C component is 94.1%, whereas that of the peak at 288.8 eV corresponding to C=C carbon is 5.1%, confirming that the graphene shell is predominantly composed of a sp^2 -hybridized carbon network [28]. However, although graphene covered the surface of the Ge core, a small portion of Ge-O peaks located at around 33 eV is also observed [29]. These oxidation states of the Ge core can be explained by the existence of defects in the outer graphene shell [8, 30, 31]. In either case, there are no peaks related to the Ge–C alloy, because the carbon solid solubility in Ge is negligible at the growth temperature used [20, 29, 32].

3.2 Growth mechanism of the Ge@G NCs

Fig. 4. Schematic of the growth mechanism of the Ge@G NCs.

On the basis of the experimental results, we are able to propose a possible growth mechanism of the Ge@G NCs, as shown in Fig. 4. The overall process follows three growth stages: (1) Thermal decomposition of germane and methane; (2) nucleation of the Ge core and graphene shell; and (3) agglomeration of the Ge core and the growth of the graphene shell. In particular, we believe that methane plays a critical role in the growth of the graphene shell, as well as in the determination of the nucleation density and diameter of the Ge@G NCs, similar to a surfactant in the liquid-phase growth of the NCs [33, 34].

At the initial stage of the Ge@G NCs growth, methane can affect the nucleation density. When the growth temperature is higher than 800 °C, the gaseous mixture of methane and germane is completely decomposed and produces labile Ge-C molecules. As Ge-C is thermodynamically unstable at the growth temperature [35, 36], they begin to agglomerate with each other, and then produce Ge clusters as a seed for the Ge core. If the growth temperature is decreased lower than 800 °C, which is the critical decomposition temperature of methane, the density of the Ge@G NCs is also significantly reduced (see Fig. S4) [37].

In typical pyrolysis reactions, the size of the NCs is controlled by the residence time of the precursors under the same pressure and growth temperature [16, 38]. Here, in contrast, the average diameter of the NCs is determined by the partial pressure of methane, which is related to the growth rate of the graphene shell, as shown in Fig. 2 and Fig. S2. Because Ge

shows a good catalytic behavior for sp^2 -hybridization, both the Ge core and graphene shell are synthesized simultaneously through the entire growth process. Further, although the sample is still passing through the hot-region of the quartz tube, the growth of the Ge@G NCs can be stopped when the graphene shell completely covers the surface of the NCs, because the graphene shell effectively prohibits further growth of the Ge core [39]. If the flow rate of methane is decreased to as small as 1 standard cubic centimeter per minute, larger, irregularly shaped NCs are formed with a partially covered graphene shell, as shown in Fig. S5.

3.3 Thermal and electrical conductivity of the Ge@G NCs

Fig. 5. (a) Thermal and (b) electric conductivity of the Ge@G NCs pellet as a function of temperature. Inset of (b) shows a photograph of the Ge@G NCs pellet.

To further investigate the merits of the graphene shell for device applications, temperature dependence of the thermal and electric conductivity measurements was evaluated. Two sintered pellets of the Ge@G NCs were prepared by a spark plasma sintering method (Inset of Fig. 5 (b)). Although the value of thermal conductivity of the Ge@G NCs pellets can be expected to be increased due to the high thermal conductivity of graphene, both pellets show significant decrease in thermal conductivity compared to the theoretical and measured conductivity values of un-doped single crystal Ge substrate. (Fig. 5 (a)) [40-42]. There are various factors that can reduce the overall thermal conductivity of the Ge@G NC pellet. In general, the lattice thermal conductivity is directly related to the mean free path of phonon, and large density of grain boundaries generates phonon-grain boundary scattering [43-47]. Therefore, the thermal conductivity decreases sharply when the size of grain is close to the nanometer scale (<100 nm). Based on the theoretical studies, we can predict the thermal conductivity of individual nanocrystalline graphene shell. Since the estimated domain size of the graphene is approximately 11.31 nm, the calculated thermal conductivity is close to the 25 W/mK, two orders of magnitude smaller than that of the freestanding graphene [44, 48]. The phonon scattering also occurs at the interface between Ge and graphene because of strong flexural phonon scattering (ZA mode or out-of-plane transverse acoustic mode), causing dramatic reduction of the thermal conductivity [43, 48]. Above all, as the heat moves in the form of the flux, the thermal conductivity of the Ge@G NCs cannot be calculated by simply combining the thermal conductivity of Ge and graphene [49, 50]. It should be calculated considering the cross-sectional area (A) portion of each other. From the HR-TEM image of Ge@G NCs in Fig. 2(d), A_{shell} is less than 3% of the total cross-sectional area.

In contrast, it was found that the electrical conductivity of the graphene incorporated pellets (pellets #1 and #2) are comparable to that of lightly-doped single crystalline Ge wafer (Ga doped, 5.7×10^{16}), while being higher than that of a laser-sintered un-doped Ge NCs film [40, 51].

Fig. 6 (a) and (b) SEM images of bubble-wrap structure of graphene after wet-chemical etching process. The Ge@G NCs film is prepared by annealing of the Ge@G NCs at 500°C for 1h. And then we dipped it into a mixed solution containing $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ (6:1) for 30 min.

These results can be elucidated by the interconnected 3D network of graphene in the Ge@G NCs pellets (Fig. 6). Although un-doped Ge shows a low intrinsic charge carrier density at the lower temperature region, the conductive bubble-wrap structure of graphene helps to increase the overall electronic conductivity of the sintered pellets (See Table S2) [11, 50, 52-56]. Moreover, when the temperature is higher than 600 K, it can work as a charge

collector for the thermally activated excess charge carriers. Thus, the results confirm that the presence of the graphene shell is useful for satisfying the conditions that improve the performance of a thermoelectric device based on nanomaterials, which should be lowered thermal conductivity, without any reduction of electric conductivity. We expect that adding various elements into the Ge core will further enhance the thermoelectric performance [40, 51, 57].

4. Conclusion

In conclusion, we introduced a facile, one-pot, and scalable process for the growth of graphene-coated Ge NCs using a conventional CVD method. Unlike other typical gas-phase growth methods, we could control the diameter of the Ge@G NCs in the range of ~5 nm to ~180 nm by tuning the gas ratio of methane and germane. Spectroscopic and microscopic analysis confirms that the Ge core of the NC is single crystalline, and is completely covered by a multi-layered graphene shell. We believe that this growth approach will provide a facile route for the scalable growth of uniform semiconductor NCs, such as Si and SiGe alloys.

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Appendix A: Supplementary data

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/~>

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