Extended Abstracts of the 2019 International Conference on Solid State Devices and Materials, Nagoya, 2019, pp275-276

Synthesis of Ge-based Nanosheet Bundles Using Calcium Germanides as Templates in IP6 Aqueous Solution

Vimal Saxena[1], Yosuke Shimura[2], Hirokazu Tatusoka[1]

[1] Graduate School of Integrated Science and Technology, Shizuoka University,
Johoku, Naka-ku Hamamatsu,
Shizuoka 432-8018, Japan
Phone : +81-906-744-2886 E-mail : vimal.saxena.17@shizuoka.ac.jp
[2] Research Institute of Electronics, Shizuoka University
Johoku, Naka-ku Hamamatsu,
Shizuoka 432-8018, Japan

Abstract

In this work, we attempt to synthesize Ge-based nanosheet bundles from the template $CaGe_2$ via chemical synthesis route using inositol hexakisphosphate (IP6) acid. $CaGe_2$ exhibits a layered Zintl phase compound, enabling deintercalation of Ca-atoms from their lattice sites to result in covalently bonded Ge-nanosheets. A detailed study of the obtained structure is presented in this work.

1. Introduction

The advancements in tunable exfoliation chemistry have invoked production of 2D nanomaterials for intricate applications such as atomic-scale electronic devices, energy storage devices and wide range of applications in surface science. In recently reported work, Ge-based nanosheets have been synthesized using liquid phase exfoliation using chlorides and fluorides [1,2]. It was also reported that Si-based nanosheet bundles from $CaSi_2$ have been synthesized using IP6 acid (Inositol Hexakisphosphate - Phytic acid, $C_6H_{18}O_{24}P_6$) to facilitate exfoliation in much simplistic way [3].

Nanostructures, coexisting as bundles meets the requirement for large volume or large area devices, such as the thermoelectric battery, lithium ion battery electrodes, solar cells, etc [4,5]. Also, Ge-based nanosheet bundles have shown promising results for their potential application in thermoelectric generators and in Li-ion storage, especially in Li-ion batteries. Previously reported silicon nanosheet work shows rapid degradation, which is attributed to interlayer an insulating solid-electrolyte interphase formation, but the GeH system presented here appears to be more robust. Moreover, the rate performance of the GeH-based anodes is much better than that of bulk Ge [5].

This paper describes a simplistic approach to synthesis Ge-based nanosheets using $CaGe_2$ crystals as templates. This work also employs ultrasonication-assisted exfoliation to study the extent of miniaturization of nanosheet bundles obtained via exfoliation [6]. A detailed morphological and phase evolution of the synthesized powders have presented in this work.

2. Experiments

To synthesize $CaGe_2$, Ca and Ge in their stoichiometric ratio were subjected to thermal treatment in a metric lock system. Ca and Ge system were heated at 900 °C for 90 min. and then cooled naturally to room temperature. For exfoliation, both thermally-treated and commercially-available $CaGe_2$ were immersed in 0.43 mol/L of diluted IP6 solution with and without ultrasonication assistance, maintained at 40 °C in a water bath for a reaction time of 5 hours. Post reaction, the samples were washed thoroughly and desiccated before storing.

The morphological and structural properties of the complex structures were characterized by field-emission scanning electron microscopy (FE-SEM) with energy dispersion spectroscopy (EDS), conventional transmission electron microscopy (TEM), high-resolution TEM (HRTEM) with Fast Fourier Transform (FFT), and scanning transmission electron microscopy (STEM) with EDS. For the TEM sample preparation, the products were dispersed in a small amount of ethanol, then transferred onto a lacey-carbon-coated copper grid and dried.

3. Results and Discussion

$CaGe_2$ is a layered Zintl phase compound which inherits a favorable layered morphology to synthesize Ge-based nanosheets. The two dominant XRD peaks of thermally-treated germanides are corresponding to (003) and (006) $CaGe_2$ planes are shown in Fig. 1(a), using tr6-CaG_2 crystallographic notation.

The exfoliated Ge nanosheet bundles showed peak broadening at 16.3° (2θ) (Fig. 1(b)) and the observed plane spacings corroborate the possibility of formation of germanium-based layered structure [1-2,7]. Along with peaks of GeH, several peaks corresponding to elemental Ge can be seen in the XRD plot. The observed lattice constant (a = 5.65 Å) confers the Zinc blend lattice of Ge.

Fourier-transform infrared spectroscopy (FT-IR) for the exfoliated sheets indicated the presence of Ge-H stretching and wagging modes at ~2000 cm^{-1}, 477 cm^{-1}, 510 cm^{-1} and 570 cm^{-1} and weak vibrational modes at ~830 cm^{-1} and 770 cm^{-1} [1,2] (Fig. 2). These spectra details together with XRD peaks indicates that the template $CaGe_2$ has undergone structural evolution with weak signatures of H-bonding.

Morphological study corroborated the formation of

$CaGe_2$, a Zintl phase compound, exhibiting layered morphology in thermally-treated and commercially-available $CaGe_2$ samples. Upon IP6 treatment, morphology of $CaGe_2$ is transformed to thinner bundles of predominantly Ge (Fig 3(a)(d)).

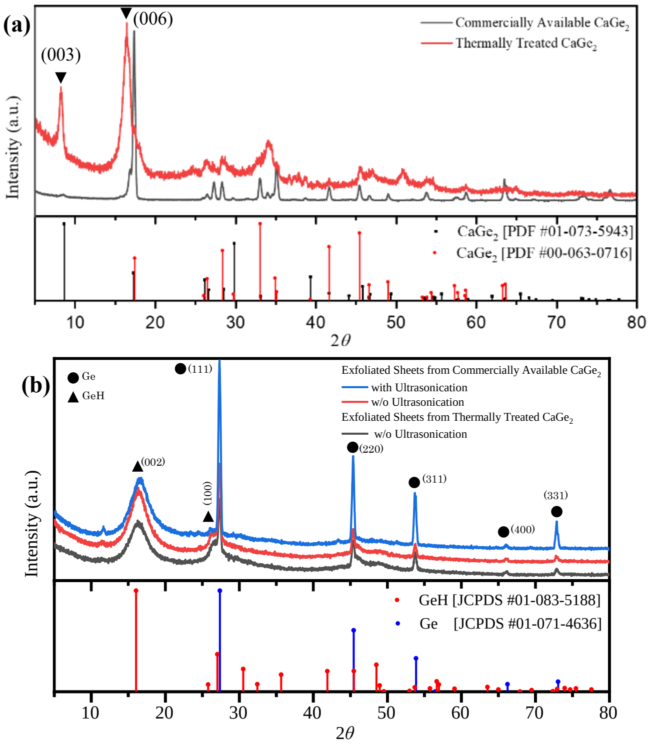

Fig. 1(a) XRD pattern for thermally-treated and commercially-available $CaGe_2$ (b) XRD pattern for exfoliated Ge-based nanosheets.

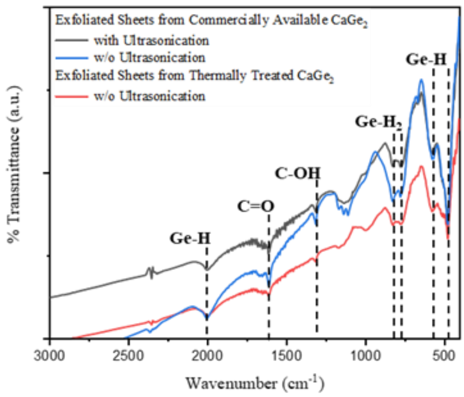

Fig. 2 FT-IR spectra of exfoliated Ge-based nanosheets with Ge-H stretching and wagging, weak vibrational modes of Ge-H_2.

Fig 4(a) show plan-view TEM, HRTEM and corresponding FFT pattern for the exfoliated nanosheet from the thermally-treated $CaGe_2$. Observed fringes with plane spacing 0.32 nm are observed with FFT pattern corresponding to 1/3 {422} spots [8]. Fig 4(b) shows the TEM, HRTEM images of cross-sectional Ge sheets intertwined with each other which can be clearly observed in the corresponding FFT pattern. The ultrasonication-assisted exfoliated sheets were thinner than the sheets obtained via without ultrasonication. The Ge-based nanosheet bundles obtained via liquid phase exfoliation are held together by weak Van-der-Waal force, which can be dissociated from each other very easily (Fig. 3(g)(h)). This layered morphology promotes its application in the large volume or large area devices with superior material properties.

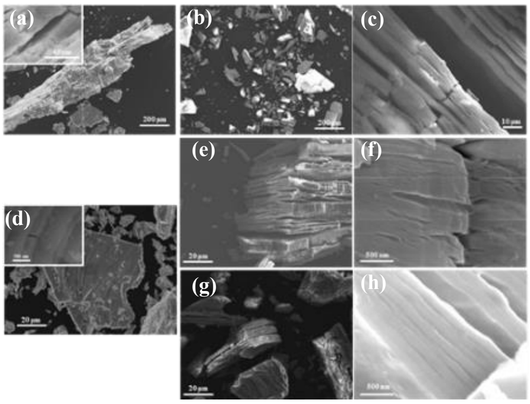

Fig. 3(a) FE-SEM images of thermally treated $CaGe_2$ (b)(c) exfoliated Ge-nanosheets w/o ultrasonication (d) commercially-available $CaGe_2$ and exfoliated Ge-nanosheets (e) (f) w/o ultrasonication (g)(h) with ultrasonication

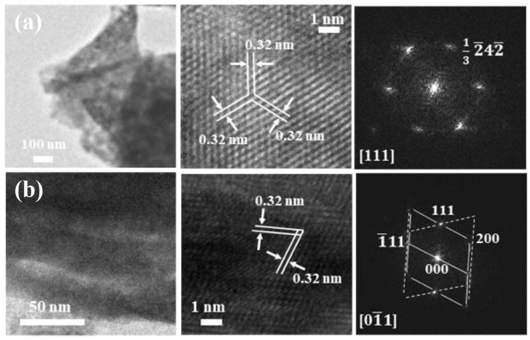

Fig. 4(a) TEM, HRTEM, and FFT pattern of exfoliated nanosheets (plan view), (b) cross-sectional view.

3. Conclusion

This study investigates the morphological and phase evolution of Zintl phase compound $CaGe_2$ in synthesizing Ge-based nanosheet bundles using IP6 acid. This synthesis method puts forward a new and simplistic approach to obtain Ge-based nanosheets.

References

[1] E. Bianco et al., ACS Nano 7 **(2013)** 4414.
[2] R. Yaokawa et al., Chem Select 1 **(2016)** 5579 – 5583
[3] X. Meng et al., Jpn. J. Appl. Phys. 56 **(2017)** 2002.
[4] H. Tatsuoka et al., ECS Trans. 50 **(2012)** 3.
[5] A. C. Serino et al., ACS Nano 11 **(2017)** 7995−8001.
[6] Valeria Nicolosi et al., Science 340 **(2013)** 1226419.
[7] Nicholas D. Cultrara et al., Chem. Mater. 30 **(2018)** 1335−1343
[8] E. Meng et al., Applied Surface Science 378 **(2016)** 460–466

Acknowledgements

Part of this work was supported by KAKENHI Grant Number 17K06347.