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Improved Synthesis and Air Stability of Two-Dimensional Material GeH

Na Shao[1], Renrong Liang[1], Chuanchuan Sun[1], Lei Xiao[1], Jing Wang[1,*], and Jun Xu[1]

[1] Tsinghua National Laboratory for Information Science and Technology, Institute of Microelectronics, Tsinghua University, Beijing 100084, People's Republic of China
Phone: +86-010-6278-9152 E-mail: wang_j@mail.tsinghua.edu.cn

Abstract

GeH flakes with millimeter scale size was synthesized at -18 ℃ without agitation, which is simpler than the reported process. The synthesis process and properties of the fabricated GeH were characterized in detail. The measured results showed that we successfully synthesized high purity GeH using simplified process flow.

1. Introduction

Two-dimensional materials have been regarded as promising candidates used in nano-technologies, such as optical devices, chemical sensors and hybrid materials, due to their extraordinary properties [1]. GeH is a novel two-dimensional material [2]. To synthesize GeH, $CaGe_2$ crystals were stirred in concentrated HCl aqueous for 5-10 days at -40 to -20 ℃ [2]. However, stirring at such temperature increases the complexity of preparation process. And the reported GeH flakes suffer from small size at about 0.2-0.3 cm in diameter. In this work, large GeH flakes were synthesized by mixing $CaGe_2$ and concentrated HCl aqueous at -18 ℃ without agitation, the average size of flakes is about 0.5×0.5 cm^2. The properties of the $CaGe_2$ and GeH flakes are characterized in detail.

2. Experiment

To prepare high quality $CaGe_2$ crystals, Ca and Ge elements with a ratio of Ca:Ge=1:2 are sealed in a quartz tube under vacuum. The following temperature profiles were employed: (1) heating to 1273 K at a rate of 600 K/h; (2) sufficient reaction at 1273 K for 20 h; (3) slow cooling to 1118 K at a rate of 3 K/h; (4) slow decreasing to 873 K/h at a rate of 24.5 K/h; (5) naturally cooled to room temperature. To synthesize GeH flakes, the as-prepared $CaGe_2$ crystals were mixed with concentrated HCl aqueous at 255 K (-18 ℃) for one or two weeks. Then the GeH product was washed by isopropanol, alcohol and deionized H_2O for three times, respectively. The purified GeH samples were naturally dried at room temperature. The properties of the fabricated $CaGe_2$ and GeH samples were investigated by powder X-ray diffraction (XRD), scanning electron microscope (SEM), Raman spectroscopy, Fourier Transform infrared spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS) and atomic force microscopy (AFM).

3. Results and Discussion

The optical images of as-prepared $CaGe_2$ and GeH are shown in Fig. 1(a) and (b), respectively. Compared with standard pattern of $CaGe_2$, it is confirmed by XRD measurement (Fig. 2) that $CaGe_2$ is almost free of any impurities [3]. Fig. 3 shows a SEM image of the cross-sectional morphology of GeH. The XRD pattern of the fabricated GeH flakes shown in Fig. 4(a) have a number of disorders along the c-axis, which is commonly observed in layered materials. The theoretical calculations also suggest the presence of two Raman modes (223 cm^{-1} and 289 cm^{-1}), in accordance with the experimental results shown in Fig. 4(b) [4] [5]. Fig. 5 shows the FTIR spectra of the as-prepared GeH, a strong Ge-H stretching vibration, and wagging vibrations are observed. A faint Ge-H_2 vibration also appears at ~823 cm^{-1}. Fig. 6 indicates that compared with the surface sample, 50 nm-etched sample shows a decrease in the O 1s peak after exposure to air for 11 days. Fig. 7 verifies that after exposure to air for 2 months, Ge^{2+} only exists at the surface. Ge^{1+} dominates when ~0.5-1 nm-thick of the surface is etched, which is the state of GeH. The disappearance of Ge^{2+} also proves the antioxidant capacity and anti-fouling performance of GeH. The exfoliated multi-atom-thick GeH layers on 110nm thick SiO_2/Si substrate were observed using microscope and AFM (Fig. 8). The measured height difference of the multi layers is about 0.6 to 1 nm, which is consistent with the single layer thickness [2], confirming the existence of single GeH layer in the exfoliated sample.

4. Conclusion

An improved method is presented to synthesize GeH flakes. The reaction condition is improved and large pieces of GeH flakes are obtained. Measurement results show that the GeH flakes exhibit high purity and good air stability.

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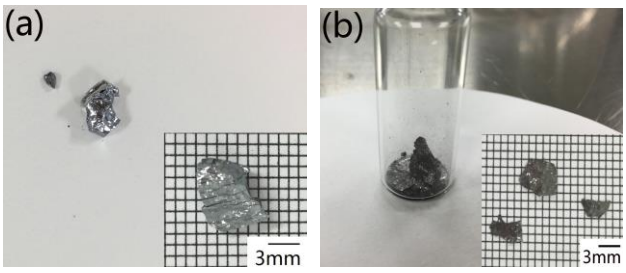

Fig. 1 Optical images of (a) $CaGe_2$ crystals and (b) GeH flakes with a 1mm grid, which are fabricated by the developed synthesis method. The average size of flakes is about 0.5 x 0.5 cm^2.

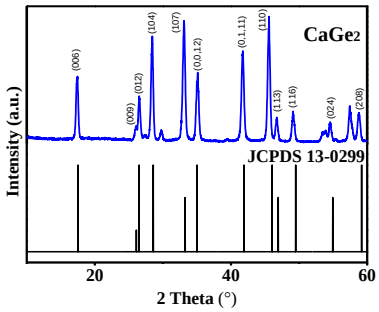

Fig. 2 Powder XRD patterns of the as-prepared $CaGe_2$ crystals and of standard $CaGe_2$ pattern taken from JCPDS file (no. 13-0299).

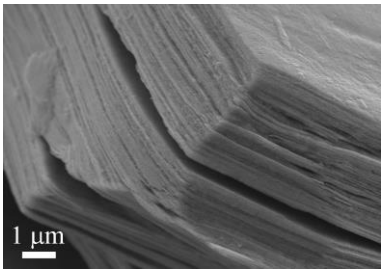

Fig. 3 Typical SEM image of the cross-sectional morphology of GeH flakes, which shows a graphite-like structure stacked by layers.

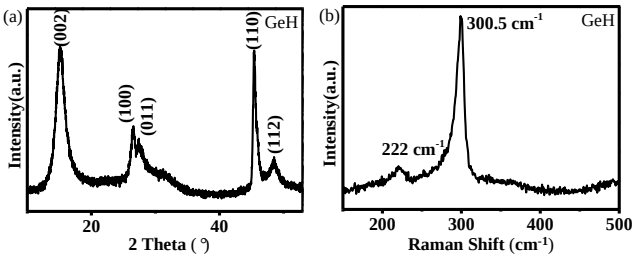

Fig. 4 (a) Powder XRD pattern, (b) Raman spectroscopy of the as-prepared GeH flakes. The structure can be fitted to a 2H unit. The main Ge-Ge stretching vibration in GeH appears at 300.5 cm^{-1}. The other vibrational peak appears at 222 cm^{-1}.

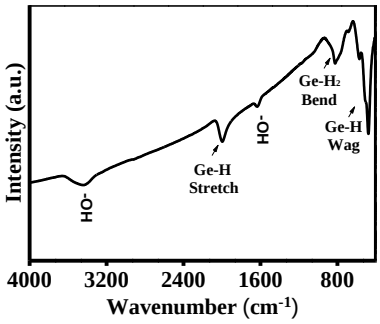

Fig. 5 Transmission-mode FTIR of the as-prepared GeH showed a strong Ge-H stretching vibration occurring at about 2000 cm^{-1}, and a number of wagging vibrations at about 572, 503 and 477 cm^{-1}. Moreover, faint vibration also appeared at about 823 cm^{-1}.

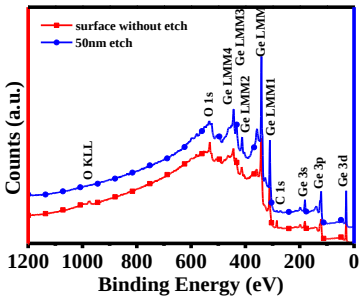

Fig. 6 XPS spectra of the GeH sample which is exposed to air for 11 days before (red) and after surface etching (blue). An Ar ion gun was used at 1.0 keV for 5 nm/min and about 50 nm of the surface was etched.

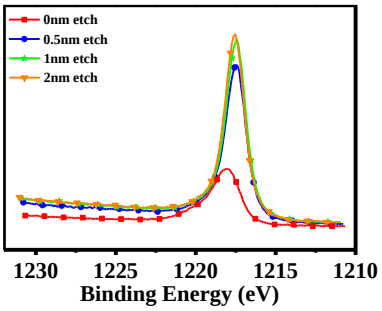

Fig. 7 Depth profile XPS spectra of the Ge 2p peak for GeH sample, which is exposed to air for 2 months before (red) and after a 0.5 nm (blue), 1 nm (green) and 2 nm (orange) etch of the GeH surface, respectively.

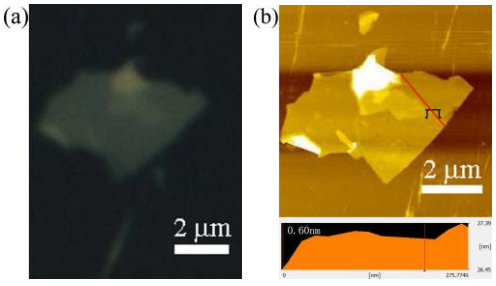

Fig. 8 (a) optical image of multilayer GeH flakes. (b) AFM image of multilayer GeH (top), height profile (bottom).