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Influence of hydrogen intercalation on graphene/Ge(0 0 1)/Si(0 0 1) interface

Justyna Grzonka [a,*], Iwona Pasternak [a,b], Paweł P. Michałowski [a], Valery Kolkovsky [c,d], Wlodek Strupinski [a,b]

[a] Institute of Electronic Materials Technology, Wólczyńska 133, 01-919 Warsaw, Poland
[b] Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland
[c] Institute of Physics Polish Academy of Sciences, Al. Lotników 32/46, 02-688 Warsaw, Poland
[d] Technische Universitat Dresden, 01062 Dresden, Germany

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ABSTRACT

Hydrogen intercalation is widely used to weaken graphene-substrate interactions and as a result enhancing graphene's electronic properties. This paper presents the study of microstructure of hydrogen intercalated graphene grown on Ge(0 0 1)/Si(0 0 1) substrate using Low-Voltage Scanning Electron Microscopy. The findings reveal a significant change in the surface morphology of germanium substrate: faceting structure disappears almost completely, the germanium surface flattens, and steps/terraces are formed. This leads to degradation of graphene's electronic properties, which shows the negative impact of hydrogen intercalation when graphene is grown on the germanium substrate.

1. Introduction

Graphene as a single layer of carbon atoms attracted worldwide attention due to its remarkable optical, mechanical and electronic transport properties. The implementation of graphene in modern microelectronics imposes its direct synthesis on semiconducting substrates to avoid metal contamination connected with transferred graphene from metal substrates. The direct growth of graphene on silicon results in formation of carbidic phases limiting its application [1]. Recently, germanium has been used as a substrate for graphene growth [2]. To ensure the compatibility of graphene with silicon based technologies it has been grown directly on the Ge(0 0 1)/Si(0 0 1) substrates [3,4]. The electronic properties of graphene grown on Ge(0 0 1)/Si(0 0 1) substrate strongly depend on the surface morphology and it was suggested that they are related to the different strength of germanium-graphene interactions and deteriorated with increasing uniformity of the Ge(0 0 1) surface [5].

Several studies have shown that when graphene is growth on Ge(0 0 1) it results in formation of nanofacets on the germanium substrate [3,6,7] and their pattern exhibits a four-fold symmetry. During growth of graphene the Ge(0 0 1) surface has broken up into hills and valleys structures, which are two families of (107) facets positioned 90° to each other and run along the ⟨1 0 0⟩ direction [6]. According to different papers [3,7] the hill height, in relation to the valley, is in the range of a few nanometers.

The Ge(0 0 1) surface exhibits strong short-range interaction leading to dimerization, as well as a weak long-range interaction connected with various higher-order surface reconstructions [8]. In order to minimize surface energy, the Ge(0 0 1) face forms a wide range of reconstructions. The top two atoms in the base unit cell form a dimer [8]. The relative positions of the remaining surface atoms and the resultant dimers depend on the type of reconstruction [8]. The DFT calculations for graphene interacting with popular buckled b(2 × 1), primitive p(2 × 2) and centered c(4 × 2) germanium surface reconstructions highlight that a moderate affinity between the germanium surface and carbon atoms is always present and responsible for the appearance of additional maxima in the electron density of states superimposed onto the graphene band structure [5]. It is further hypothesized that this effect can be removed by hydrogen intercalation.

The first study of the intercalation of hydrogen under the buffer layer on SiC(0 0 0 1) was reported by Riedl et al. [9] who annealed SiC(0 0 0 1) substrates covered by the buffer layer in an atmosphere of hydrogen at the temperatures from 600 to 1000 °C. The successful decoupling of the buffer layer and conversion into so-called quasi-freestanding graphene (QFMLG) was witnessed by several surface analytical techniques, such as: LEED, ARPES,

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[*] Corresponding author.
E-mail address: justyna_grzonka@o2.pl (J. Grzonka).

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XPS and LEEM. Robinson et al. [10] employed annealing in molecular hydrogen to convert MLEG (multi-layer graphene) to QFBLG (quasi-freestanding graphene bilayer) at H_2 pressure of 800 mbar, temperatures of 600 to 1200 °C, and process length between 30 and 120 min. As-grown monolayer graphene on SiC(0 0 0 1) resides on top of a carbon layer known as buffer layer or zerolayer graphene that exhibits significantly different structural and electronic properties from that of graphene. In this interface, layer carbon atoms are expected to be arranged in a graphene-like honeycomb structure. However, about 30% of these carbon atoms are bound to the Si atoms of the SiC(0 0 0 1) surface. As a consequence of these covalent bonds, the zerolayer is nonmetallic as opposed to graphene which also obstructs π bands development, and in consequence, strongly reduces the mobility of charge carriers. Therefore, hydrogen intercalation is desired to break and saturate covalent bonds at the interface resulting in decoupling of the graphene layer from the SiC substrate [9,11]. Also the growth of graphene on hydrogen-terminated germanium was recently performed on the Ge(1 1 0) substrate having anisotropic twofold in-plane surface symmetry [12]. The authors have observed extremely weak adhesion between graphene and the underlaying substrate, which allowed a facile mechanical exfoliation of graphene. Another group [7] used Ar/H_2 mixture as a carrier gas during graphene growth by CVD on Ge/Si(0 0 1). They attribute the high structural quality of graphene to hydrogen-induced reduction of nucleation probability.

These studies demonstrate that the preparation of the substrate is a very important factor in determining the properties of the graphene layer. In order to achieve a high mobility of charge carriers the interactions between substrate and graphene should be weakened. Based on the success of hydrogen intercalation of graphene grown on SiC(0 0 0 1) a similar procedure has been considered for the germanium substrate. However, as of today there are no experimental results showing the influence of hydrogen intercalation on the substrate's surface morphology and consequently on transport properties of graphene/Ge(0 0 1)/Si(0 0 1) system, which was the main motivation behind this work. Several characterization techniques were applied such as secondary ion mass spectrometry (SIMS), Raman spectroscopy, high resolution scanning electron microscopy (HR SEM) and Hall measurements to realize this.

2. Material and methods

Epitaxial graphene was grown on commercially available Ge(0 0 1)/Si(0 0 1) substrates by chemical vapor deposition technique (CVD), as it was described previously in [3,4]. The thickness of the Ge layer was equal to 3 μm, which prevents silicon diffusion to the surface during annealing and graphene growth. Two types of samples were prepared, namely standard graphene grown on the Ge(0 0 1)/Si(0 0 1) substrate (GR/Ge) and hydrogen intercalated graphene on the Ge(0 0 1)/Si(0 0 1) substrate (GR/H/Ge). The intercalation process was realized by hydrogen atoms diffusion underneath the graphene film from a hydrogen gas flowing through a reactor chamber where graphene was grown. Intercalation started at 600 °C during a cooling procedure under 800 mbar H_2 pressure and continued to the room temperature.

In both cases the presence of the graphene films on the germanium substrates was confirmed by Raman spectroscopy investigations using a Renishaw system with a 532 nm Nd:YAG laser as an excitation source [13,14,15]. Secondary Ion Mass Spectrometry (SIMS) depth profiles were obtained employing the CAMECA SC Ultra instrument using previously established low impact energy measurement procedure preceded by a similar sample preparation (2 nm of chromium was deposited on top of the graphene layer to avoid SIMS artifacts) [16]. The presence of the graphene layer increases the negative ionization probability and thus significantly alters the outcome of the SIMS experiment [17]. To get a realistic distribution of hydrogen in samples, the enhancement effect was reduced, following a similar procedure, as described by Michałowski et al. [18]. The surface morphology of GR/Ge and GR/H/Ge samples was investigated by high-resolution scanning electron microscopy (SEM) Hitachi SU8230 Cold-FEG equipped with a semi-in-lens type objective lens. The observations were performed in low voltage range (from 0.5 to 1 kV) to obtain highly topographical information and simultaneously in deceleration mode to improve resolution of the visualization of fine microstructure details. The magneto-transport measurements were performed on rectangle shape (2 × 7 mm) GR/Ge and GR/H/Ge structures in the magnetic fields up to 9 T at a temperature of 1.6 K to freeze out mobile carriers into the germanium layer. Magnetic field was applied perpendicularly to the graphene surface. Ohmic contacts were prepared by soldering indium in Hall bars geometries.

3. Results and discussion

Fig. 1 shows Raman spectra of as-grown graphene (GR/Ge black line) and graphene intercalated (GR/H/Ge red line) with hydrogen. Raman spectra indicates two prominent and characteristic G and 2D peaks which are the features confirming the presence of predominantly single layer. The disorder-related D peak connected with defects is also present. Moreover, in the case of the hydrogen-treated graphene film, one can notice that the Raman spectrum reveals occurrence of a fourth peak at about 2000 cm^{-1}. This band can be identified as a Ge-H bond, which additionally confirms presence of hydrogen located on the germanium surface [19,20].

SIMS depth profiling of samples as thin as graphene are always challenging. Primarily, the challenge relates to: (i) non-stationary conditions at the beginning of the experiment which render a near-surface part of the depth profile unreliable, (ii) presence of organic contamination on the surface of a sample usually results in a strong peak of hydrogen, and carbon related signals at the beginning of the depth profile which may complicate the analysis of hydrogen-intercalated graphene. To prevent both problems it

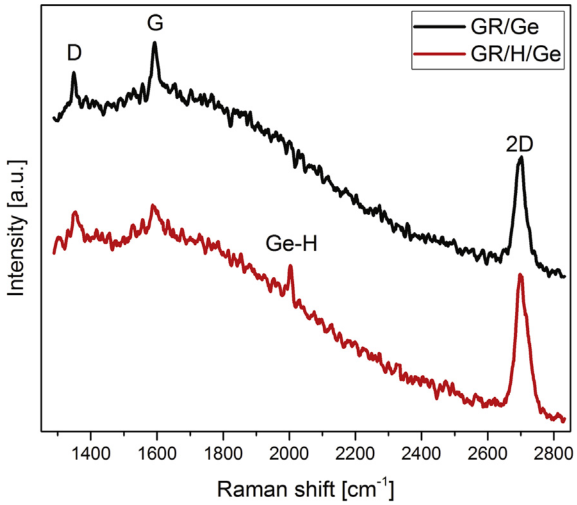

Fig. 1. Raman spectra of graphene on the germanium substrate GR/Ge (black line) and hydrogen intercalated graphene on the germanium substrate GR/H/Ge (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

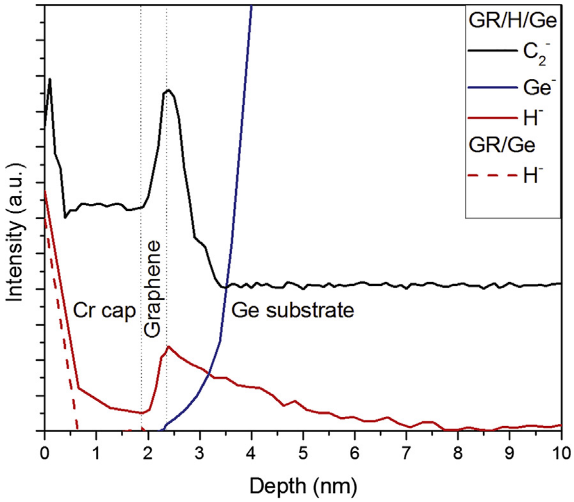

Fig. 2. SIMS depth profiles of hydrogen in GR/H/Ge (red line) and GR/Ge samples (red dotted line). A very strong peak of the H^- signal can be observed at the interface between graphene and the Ge substrate for the intercalated sample only. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

was necessary to cover graphene with a 2 nm thick Cr cap, so that the graphene layer would be adequately characterized. Fig. 2 compares SIMS depth profiles of GR/H/Ge with GR/Ge samples. As expected, a strong peak of H^- and C_2^- signals at the surface is coming from residual contamination. Some contamination can still be detected in Cr cap region and thus carbon related signals do not disappear completely but reach a constant value. In our previous work, [16] we established a reliable procedure of distinguishing graphene from any residual contamination: graphene is a very strong material and is not easily fragmented during the SIMS experiments and thus polyatomic signals (like C_2^-) should be used to precisely localize the graphene layer in the depth profile – the interface between the Cr cap and the graphene layer is defined at the point where C_2^- signal starts to increase rapidly. The second interface, between the graphene layer and the germanium substrate, is less problematic and can be defined at the point where germanium signal appears. Using these definitions, it is possible to compare the as-grown and the hydrogen intercalated samples. Most signals were identical for both samples and thus were presented only once. The only notable exception was the H^- signal. For the GR/Ge sample no hydrogen was detected in depth of the sample, whereas for the GR/H/Ge sample a clear agglomeration of hydrogen at the interface between graphene and the Ge substrate can be observed. The decay length of this signal is long because at such low impact energy (150 eV) sputtering of light elements is not efficient and they are easily pushed deeper into a sample (mixing effect). It is regarded that this minor measurement artifact does not diminish a clear difference between these two samples.

The SEM images (Fig. 3a) showing the topography contrast reveal the presence of characteristic nanofaceted structure on the entire surface which is covered by graphene for GR/Ge sample (presented picture is representative for the entire sample surface). The hills and valleys are positioned 90° to each other and run along ⟨100⟩ direction surrounding flat areas of 300 nm in diameter. During the graphene growth the Ge(0 0 1)/Si(0 0 1) substrate became morphologically unstable and underwent nanoscale faceting when covered by the graphene layer. Faceting is directly related to the graphene growth. The Ge(0 0 1)/Si(0 0 1) surface remain flat and there are no facets until graphene is grown in it. According to Madey et al. [21] faceting is a form of a self-assembly at the nanometer scale on adsorbate-covered single-crystal surfaces, which lead to minimization of a total surface energy by developing facets.

Significant structure changes in the germanium substrate have been observed for GR/H/Ge sample (Fig. 3b). The intercalation process results in almost complete disappearance of hill and valley structures, flattening of the germanium surface and formation of steps/terraces. It seems to be opposite to the process of creating

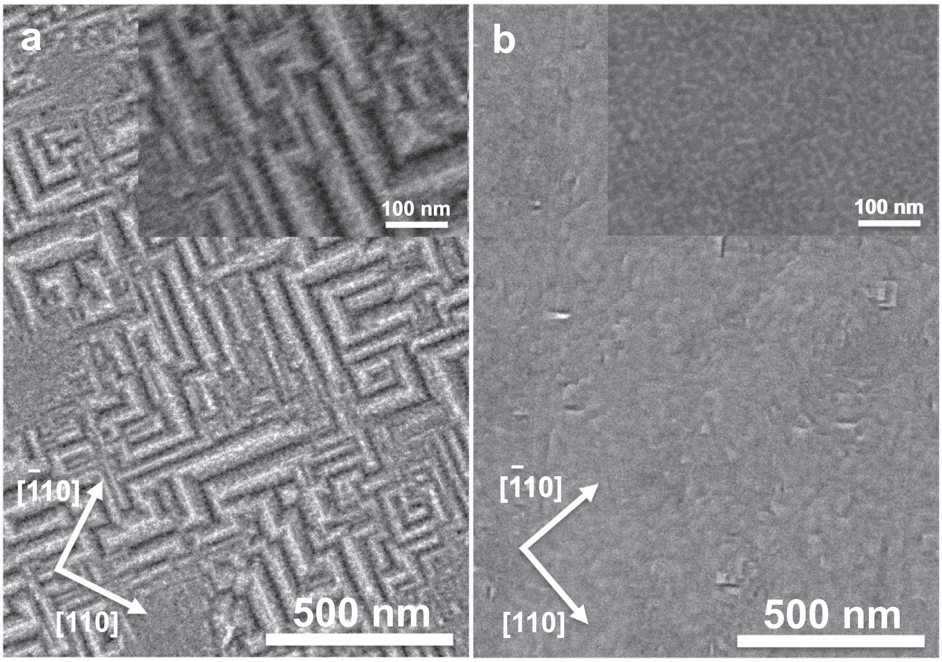

Fig. 3. SEM images showing the topography contrast of (a) GR/Ge and (b) GR/H/Ge samples. A significant change in surface morphology of the germanium substrate is observed after hydrogen intercalation. Nanofacet structure undergoes substantial flattening. Insets present nanometer size wrinkles of graphene, which are more pronounced for GR/H/Ge sample.

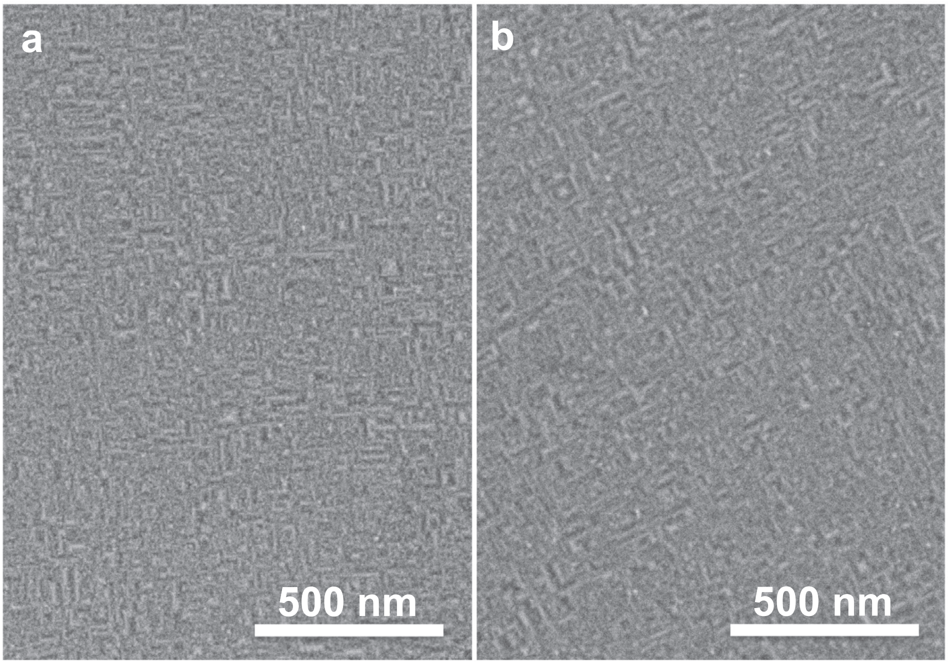

Fig. 4. SEM images showing the topography contrast of graphene/Ge(0 0 1)/Si(0 0 1) samples after annealing at 850 °C in (a) Ar and (b) in vacuum at 10 mbar.

nanofacets. Due to the lack of interaction between graphene and germanium surface connected with the hydrogen incorporation, flattening of germanium surface occurred for minimization of total surface energy. Similar effect of nanofacet reduction and surface flattening has been observed for graphene grown on Ge(0 0 1)/Si(0 0 1) after annealing without hydrogen in 850 °C during 10 min, but the result was not as strong as in the case of hydrogen intercalation [5]. Annealing causes little surface flattening in some regions where smaller faceting scale and flat terraces are observed. Additionally, the nanometer size wrinkles of graphene have appeared in our samples, which were observed under higher magnification (insets in Fig. 3), which are more prominent for GR/H/Ge sample, whereas for GR/Ge sample the graphene layer seems to be stretched on germanium facet hills. The observed nano-wrinkles could originate from a thermal stress release and can cause scattering of charge carriers in graphene, resulting in degradation of electronic properties.

It has been expected that the growth of temperature will have significant influence on the graphene/germanium interface structure. We put special attention to understand the effect of heating during the intercalation process. We annealed the graphene/Ge(0 0 1)/Si(0 0 1) samples in different conditions. First sample was annealed just after the graphene growth in Ar at 850 °C during 1 h. The second one - in the same conditions but in vacuum of 10 mbar. Fig. 4 depicts the SEM images of the samples' surfaces after annealing processes. The nanofaceting structure can still be observed. Based on the above, it can be concluded that the heating process is not contributing much to the flattening the surface during hydrogen intercalation process. It becomes clear that the main factor responsible for this process is hydrogen.

Simultaneously, the electrical measurements of GR/Ge and GR/H/Ge structures have been conducted. The examined graphene layers demonstrated homogeneous properties on the whole investigated area, both before and after the intercalation process. The mobility of electrons varied in the range 950–1050 cm^2/Vs for GR/Ge samples and possess decreasing tendency to 470–520 cm^2/Vs for GR/H/Ge samples, whereas the concentration changed from $6.8 \times 10^{12}\ cm^{-2}$ to $9.2 \times 10^{12}\ cm^{-2}$ for GR/Ge and GR/H/Ge samples, respectively. It should be also noted that the influence of germanium substrate on magneto-transport measurements of graphene layers was insignificant due to the freezing of mobile carriers into the germanium layer at the temperature of 1.6 K. Similar effect was observed for graphene/Ge(0 0 1)/Si(0 0 1) samples after annealing in hydrogen atmosphere at 850 °C [5], where the LC-AFM electrical conductivity measurements revealed much lower conductivity, compared to the samples before heat treatment. Dabrowski et al. [5] has shown that graphene grown on hills of nanofacets presented higher conductivity than graphene positioned in valleys which was connected to stronger graphene-germanium interactions at valleys regions. They have shown, based on the density of states (DOS) and partial density of states (PDOS) calculations, that for buckled, primitive and centered surfaces reconstructions the Ge substrate affect the graphene electronic properties. They have also suggested that weakening of graphene-germanium interactions on high-index germanium surfaces could be obtained by way of hydrogen intercalation. Our studies have shown that the hydrogen intercalation contrariwise results in a deterioration of the electronic properties. We have consistently observed that hydrogen intercalation flattens Ge surface after nanofacets generation during graphene growth. As a consequence, graphene layer adheres to the substrate surface which increases the interaction between graphene and germanium substrate resulting in stronger scattering of carriers.

4. Conclusions

In summary, we have demonstrated a significant impact of graphene hydrogen intercalation on Ge(0 0 1)/Si(0 0 1) surface morphology. The Ge(0 0 1)/Si(0 0 1) surface structure, converted into nanofacets during graphene growth, undergoes flattening and uniformization, which in turn degrades graphene's electronic properties, as opposed to graphene/SiC(0 0 0 1). Carriers mobility is lowered by a factor of 2 owing to the larger charge of scattered carriers. This could be explained by higher Ge-graphene interaction as a consequence of the substrate flattening and smaller distance between graphene layer and Ge. Additionally, due to the lack of hills and valleys graphene tends to adhere to the entire substrate surface creating nano-wrinkles, which further reduces charge carriers' mobility.

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