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Full Length Article

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

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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 $\langle 1\,0\,0 \rangle$ 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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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

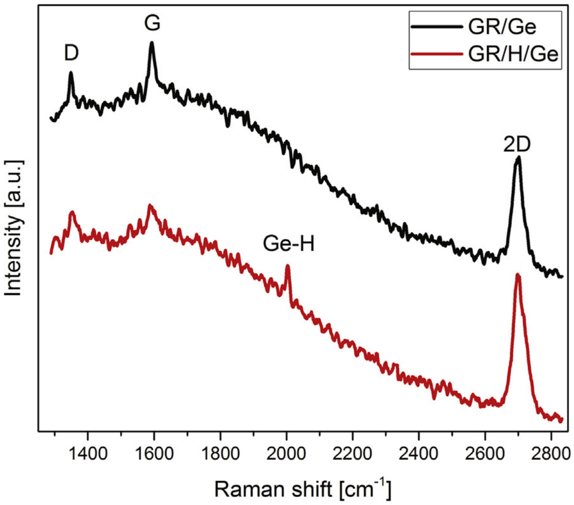

Fig. 1. Raman spectra of graphene on the germanium substrate GR/Ge (black line) and hydrogen intercalated graphene on the germanium substrate GR/H/Ge (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)