Formation of GeO 2 under Graphene on Ge(001)/Si(001) Substrates by Water Vapor

Pawel Ciepielewski (✉ pawel.ciepielewski@imif.lukasiewicz.gov.pl)
  Lukasiewicz Research Network - Institute of Microelectronics and Photonics

Piotr. A. Caban
  Lukasiewicz Research Network - Institute of Microelectronics and Photonics

Ewa Dumiszewska
  Lukasiewicz Research Network - Institute of Microelectronics and Photonics

Iwona Jozwik
  Lukasiewicz Research Network - Institute of Microelectronics and Photonics

Jacek. M. Baranowski
  Lukasiewicz Research Network - Institute of Microelectronics and Photonics

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Research Article

Abstract

Water vapor penetrates through defects in graphene layers grown on Ge(001)/Si(001) substrates and oxidization of germanium forming GeO_2 is described. The presence of trigonal GeO_2 underneath of graphene has been identified by Raman measurements. It has been found that formation of blisters of GeO_2 under graphene leads to dramatic increase of intensity of graphene Raman spectrum. The increase is the most likely due to screening of graphene by GeO_2 from nano-faced Ge(001) surface.

Introduction

The CVD growth of graphene on Ge(001)/Si(001) substrates has been proposed as a method of obtaining graphene layers on large area substrates [1–7]. Tthe growth of graphene on the Ge(001)/Si(001) substrates [3, 7, 8] seems to be important due to the potential compatibility with the metal oxide semiconductor technology CMOS [7]. The graphene growth on Ge(001)/Si(001) substrates is complicated due to formation of germanium nano-facets underneath of graphene [4, 7]. The hill-and-valley nano structures on the Ge(001) surface are positioned 90° to each other, and run along the < 100 > directions. directions. Graphene nucleation reproduces the Ge(001) nano-faceting and create multidomain graphene formation of polycrystalline character. This was confirmed by LEED measurements, which indicate that two orientations within the graphene layer are preferable [8]. These discontinuities are origin of unintentional oxidation as it was disclosed by Kelvin Probe Force Microscopy (KPFM) and Scanning Tunneling Microscopy/Spectroscopy (STM/STS) studies [9].

Oxidation process of germanium by penetration of water vapor through graphene grown on Ge(001)/Si(001) substrates has been investigated in this work.

Experimental And Experimental Results

Graphene was grown by CVD method on 3 µm Ge(001) thick film grown on Si(001) wafers. During the graphene deposition the pressure of 850 mbar temperature 900°C were sustained. Methane gas was used as a carbon precursor using mixture with Ar in the ratio of 1 : 200. The CVD growth was preceded by the substrate's annealing under a pure hydrogen to reduce native oxides. Scanning Electron Microscope (SEM) (Auriga CrossBeam Workstation, Carl Zeiss) equipped with secondary-electron detector was used to observe the influence of water vapour on graphene morphology. Room temperature Raman measurements have been done using a Renishaw inVia Raman micro-scope system with a 532 nm Nd:YAG laser as an excitation source and with the laser spot diameter of approximately 0.5 µm. The Atomic Force Microscopy (AFM) equipped with Veeco Dimension V SPM with NanoScope V Controller were used. OTESPA Al coated probes with force constant ~ 42 N/m with a typical nominal tip radius 7nm were used for the AFM imaging. The surface AFM images were flattened and plain fitted using Nanoscope analysis software. All measurements were performed in air at room temperature.

After the growth samples were subjected to humid atmosphere at 50^0C for about 3 hours and about 150 hours. After 3 hours of water vapor treatment it was possible to observe in SEM regular spots of the size of a few micrometers on the surface of Gr/Ge/Si(001) sample. The SEM image of such surface is shown in Fig. 1. The spots consist of groups of smaller blisters are located at distances of about 10–20 μm. The AFM image of individual group of blisters is shown in Fig. 2a and the AFM scan through one of blisters is shown in Fig. 2b. It is seen that the area connected with blister is lifted up by about 300nm. It may be expected that the graphene resting on such blister will be tensile strained.

The longer water vapor treatment up to 150 hours dramatically change morphology of the graphene surface grown on Ge(001)/Si(001). The SEM image of the surface is shown in Fig. 3. The whole graphene surface is now covered by blisters. The AFM image of one such blister is shown in Fig. 4a. AFM scan through the blister is shown in Fig. 4b. It is seen that the blister consist of smaller ones which are merging together. The height of the blister is about 1 micrometer.

The question arises what is the origin of blisters on the graphene surface obtained on Ge(00!)/Si(001) surface. Raman measurements indicate that in the places of blisters in addition to intense graphene spectrum there is a spectrum characteristic to germanium oxide. The observed lines at 444 cm^{-1}, 166 cm^{-1} and 123 cm^{-1} shown in Fig. 5 are characteristic for trigonal GeO$_2$ [10]. This spectrum is observed only under blister area and does not exist outside of this area.

Intensity of Raman spectra of graphene on blisters are almost two orders of magnitude stronger than outside of them, as it is shown in Fig. 6.

The common feature of both spectra is the D peak connected with defects of a relatively strong intensity. The ratio D/G intensity is about 1.5 for graphene on Ge and 1.4 for graphene on GeO$_2$. That indicates a distance between graphene defects is relatively short [11, 12], and that both kinds of graphene are defected in the same way. The ratio D/D' intensity is about 7, what is characteristic for point defects [13]. The average value of the FWHM of the 2D peak is about 50 cm^{-1}. It is known that FWHM of the 2D peak is highly sensitive to strain inhomogeneity in the length of nanometer scales [13, 14]. Thus, the FWHM of the 2D peak of graphene above of GeO$_2$ area is highly strained. Finally, the intensity ratio of the 2D peak to the G one is close to 2.2 what indicates predominantly a monolayer graphene structure.

Raman intensity of graphene spectrum is closely related with intensity of GeO$_2$ lines. The Raman map of intensity the 444cm^{-1} line connected with GeO$_2$ and the intensity of 2D peak within blister are shown in Fig. 7

It is known that both Raman G and 2D peaks are sensitive to charge fluctuations and to strain due to the difference in the thermal expansion coefficients of graphene and the underlying substrate. The G peak energy is predominantly dependent on charges present on graphene due to the static and non-adiabatic effects [15] and the 2D peak energy is mainly dependent on strain fluctuation.

The contribution from the strain and charge can be deconvoluted using vector decomposition within the position of the 2D peak versus the G peak position [16]. Plots of the position of the 2D peak versus the G peak for graphene/Ge(001) sample before and after treatment with water vapor are shown in Fig. 8.

Figure 8. Plot of position of the 2D peak in relation to position of the G peak. The red points represent plot before treating sample with water vapor. The black points represent results after treatment by water vapor outside the blisters area. Blue points corresponds to results on the blisters. A slope of blue points corresponds to 2.2 and represents the effect of strain on the graphene lattice being on blister.

It is seen that treating graphene being on Ge(001)/So(001) for 3 hours in a humid atmosphere results in a shift group of points on the 2D vs G diagram from the average G peak position $1595 cm^{-1}$ to $1583 cm^{-1}$. This shift has to be connected with decrease of carrier concentration by about one order of magnitude. The points for graphene being on blister behave differently. The spatial spread of the 2D peak position for blue points in Fig. 8 is from $2662 cm^{-1}$ to $2678 cm^{-1}$ which indicates the tensile strain. Data points for blue points are on the line with a slope of 2.2. Such slop coincides with the one observed previously in tensile strained graphene [17]. The G peak position ranges from $1580 cm^{-1}$ to $1586 cm^{-1}$, which agree with the average position of $1583 cm^{-1}$ corresponding to a lower carrier concentration.

Discussion

Formations of GeO_2 blisters on the graphene surface on Ge(001)/Si(001) surface indicate presence of graphene defects through which water vapor goes and oxidize the surface of germanium. Presence of GeO_2 underneath the graphene identified by Raman measurements proves that oxidation of Ge takes place. The oxidation of Ge is a result of the following reaction:

$$Ge + 2H_2O \text{ —— } GeO_2 + 2H_2$$

and indicates that in addition to formation of GeO_2 generation of hydrogen takes place as well. Certain indication of presence of hydrogen may be found in decrease of carrier concentration in the graphene layer subjected by water vapor treatment. This is demonstrated by shift of group of points on the 2D vs G diagram towards lower values of G values shown in Fig. 8. In addition, hydrogen may increased number of structural defects in germanium as it was recently shown [18].

Difference in the intensity of Raman signal obtained from graphene being on Ge(001) and to the one on GeO_2 is indeed puzzling. The Raman signal from the area of blisters is from one to two orders of magnitude stronger than the one outside of this area. The low Raman signal from graphene/Ge(001) surface has to be connected with a some interaction between graphene and faceted Ge(001) surface. The vibrations of carbon atoms connected with phonon branches near the Γ and K points of Brillouin zone of graphene responsible for G and 2D peaks are in-plane ones. The in-plane vibrations of graphene plane being in direct contact with the hill-and-valley structures on the Ge(001) surface, may suffer higher degree of "friction". One can speculate that this may leads to decrease of intensity of graphene Raman spectra.

On the other hand, oxidation of germanium leads to distraction of hill-and-valleys structures of Ge(001) leading to graphene which is isolated by oxide from germanium. Within the scope of this work we can state that the increase of Raman signal for graphene/GeO_2 seems to be connected with isolation of graphene by the GeO_2 from the nano-faced Ge(001) surface. The 2D vs G diagram shown in Fig. 8 indicate that graphene on GeO_2 is tensile strained, which is in agreement with AFM results shown in Fig. 2b. However, this tensile strain is not uniform and changes from place to place within blister area as in is shown by scattering of blue points in Fig. 8.

The Raman spectrum of graphene outside and inside of blister characterizes by a large D peak. The ratio of intensity of D to G peak being 1.5 is the same for graphene on Ge(001) and on GeO_2. That indicates that formation of GeO_2 underneath of graphene does not introduce new defects. Defects responsible for the D peak have to be connected with growth of graphene on the Ge(001) surface. The most likely they are generated on graphene by hill-and-valley Ge(001) structures which are positioned 90^0 to each other and run along the < 100 > directions. That leads to perpendicular nucleation of the graphene grains on hills of nano-facets. To connect these multi-domains will require formation five- and seven-fold rings on borders of different graphene grains [19]. Such five- and seven-fold rings create defects in the graphene layer. In addition, the ratio of intensity of D to D' peak in Raman spectrum is about 7 what is characteristic for point defects in graphene [13]. Therefore, it should be pointed out that defects responsible for penetration of water vapor through graphene layer may be those connected with presence of D peaks.

Concluding, it has been shown that water vapor penetrates through defects in the graphene being on Ge(001) layer and oxidize underneath germanium forming GeO_2. Formation of GeO_2 under graphene dramatically increase intensity of graphene Raman spectrum. It is believed that the increase is due to screening of graphene by GeO_2 from nano-faced Ge(001) surface.

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Figures
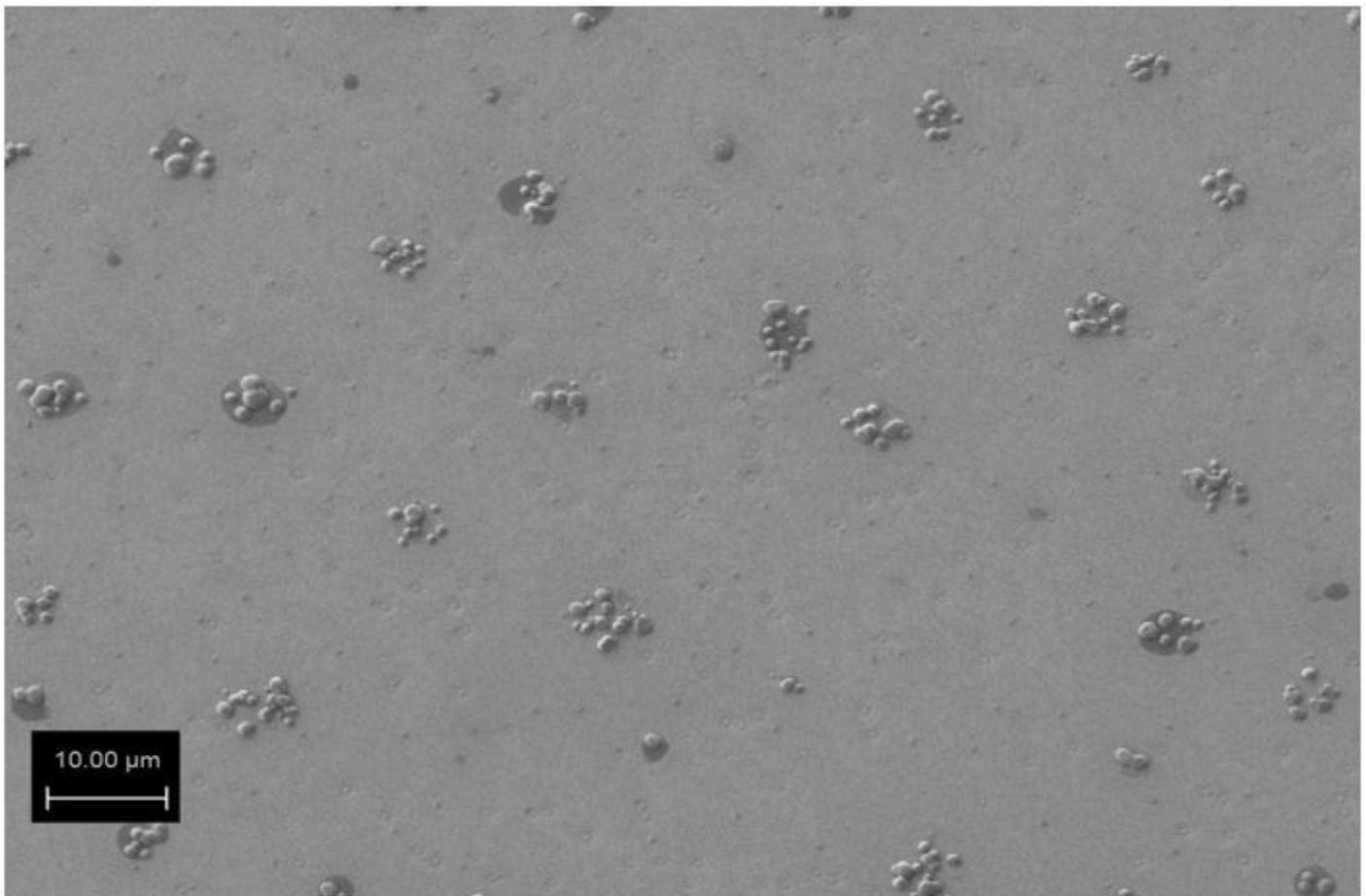
Figure 1

SEM image of the surface Gr/Ge(001)/Si(000) after 3 hours of water vapor treatment
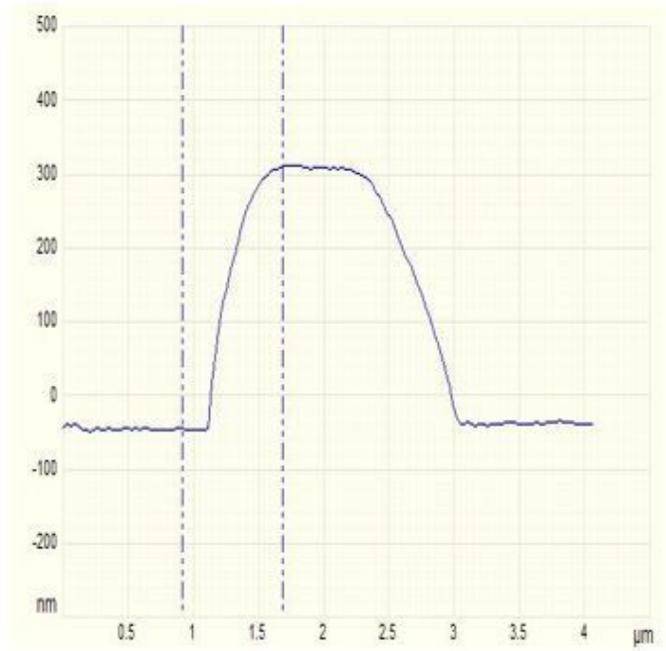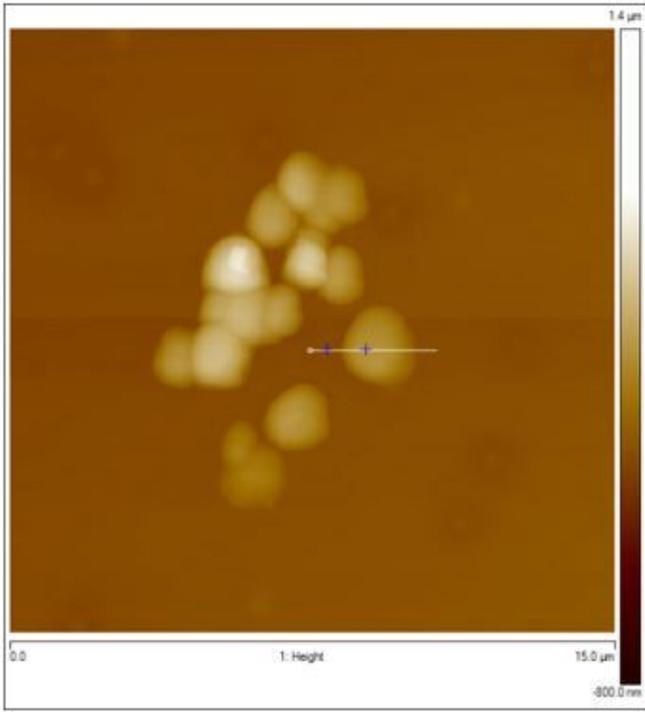
Figure 2

a) AFM image of group of spots on the surface of Gr/Ge(001)/Si(0001) sample. b) AFM scan through one of blister showing that graphene is lifted up in respect of Ge(001) level.
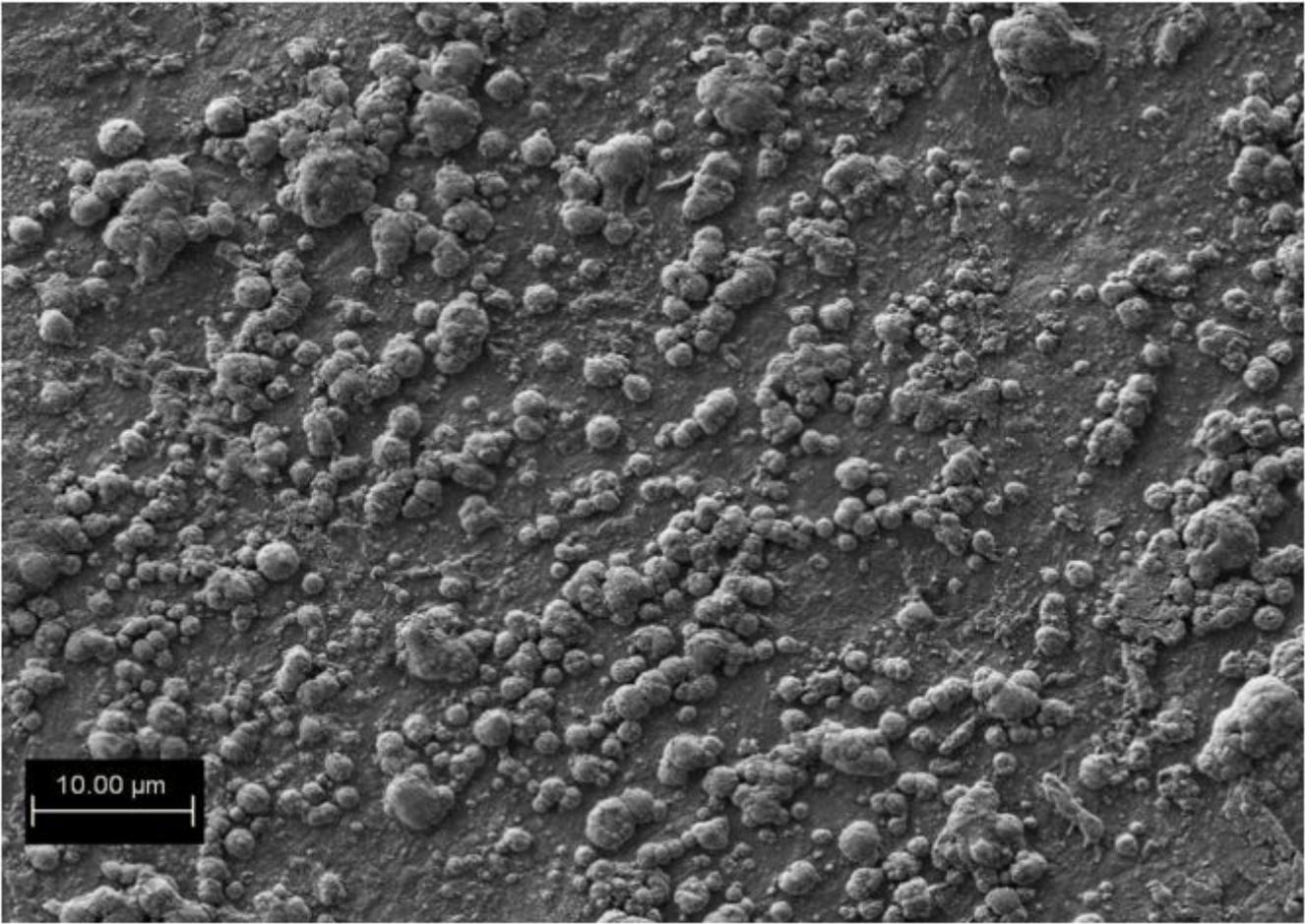
Figure 3

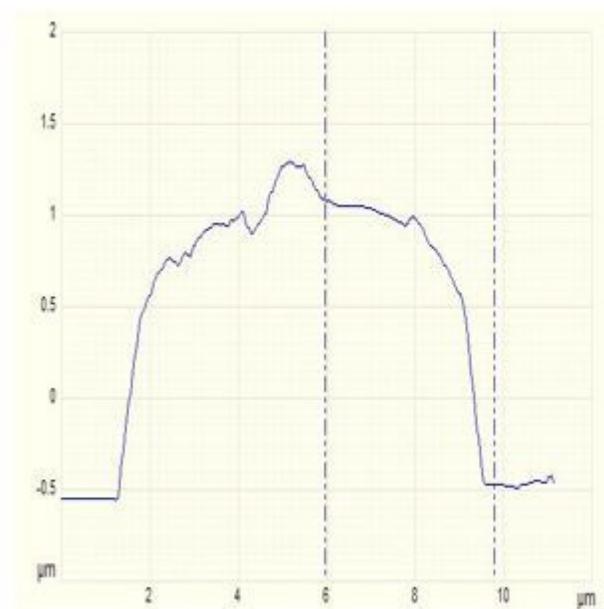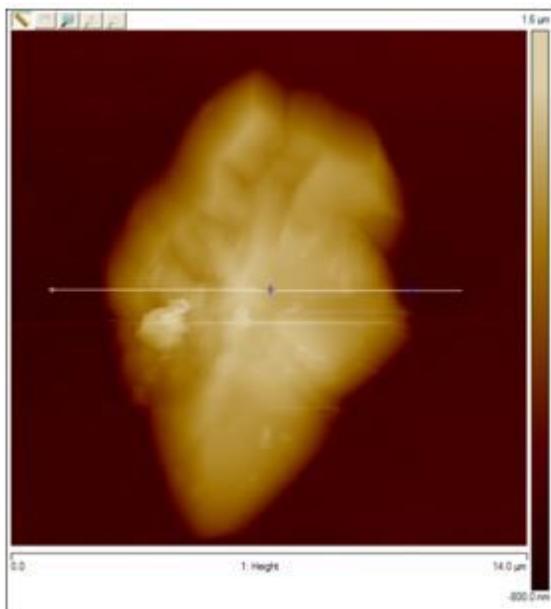SEM image of Gr/Ge/Si(001) surface after 150 hours of water vapor treatment

Figure 4

a) AFM image of 10 m blister on surface of Gr/Ge/Si(001) after 150 hours of treatments in water vapor,
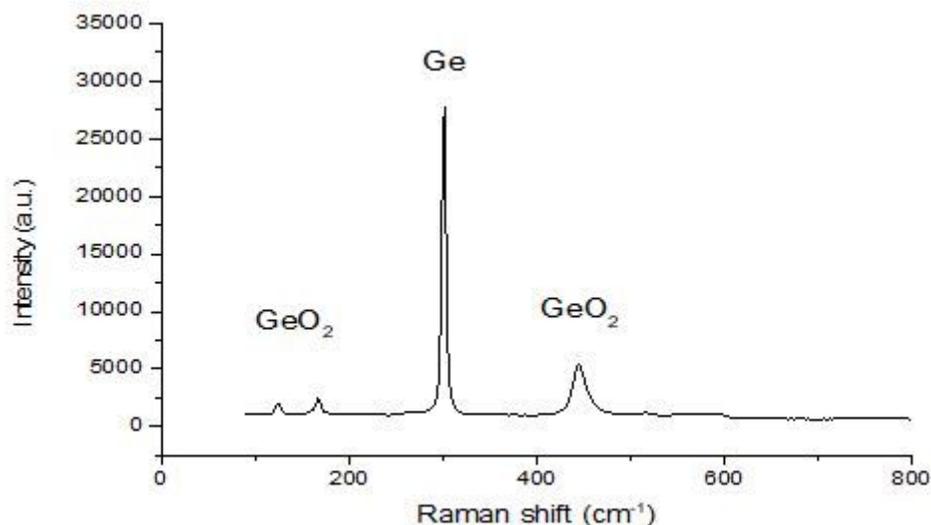b) AFM scan through the blister

Figure 5

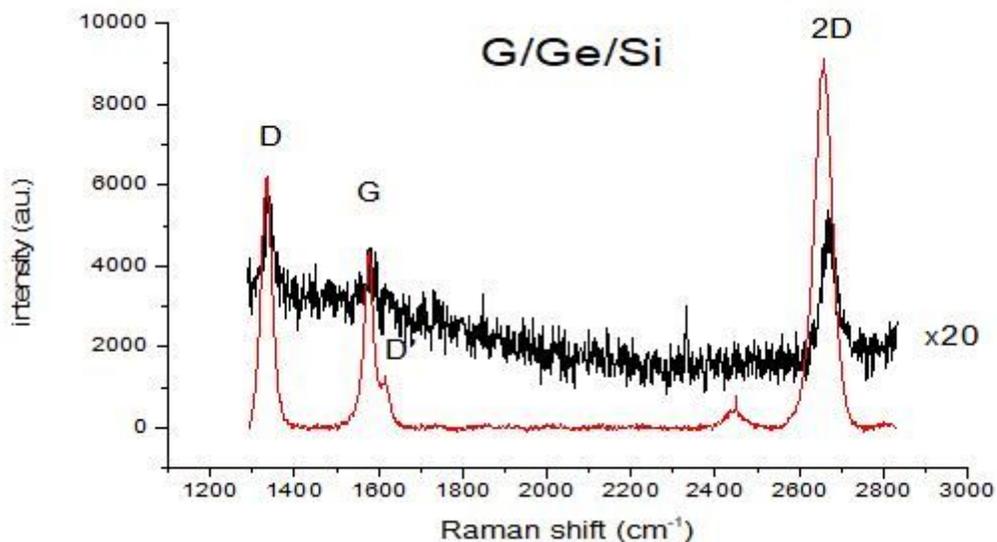Raman spectrum of germanium oxide observed on the blister on the surface of graphene on Ge(001)/Si(001).

Figure 6

Raman spectra of graphene on the Ge(001)/Si(001) (black spectrum) multiplied by factor 20, and the one on the blister (red spectrum).
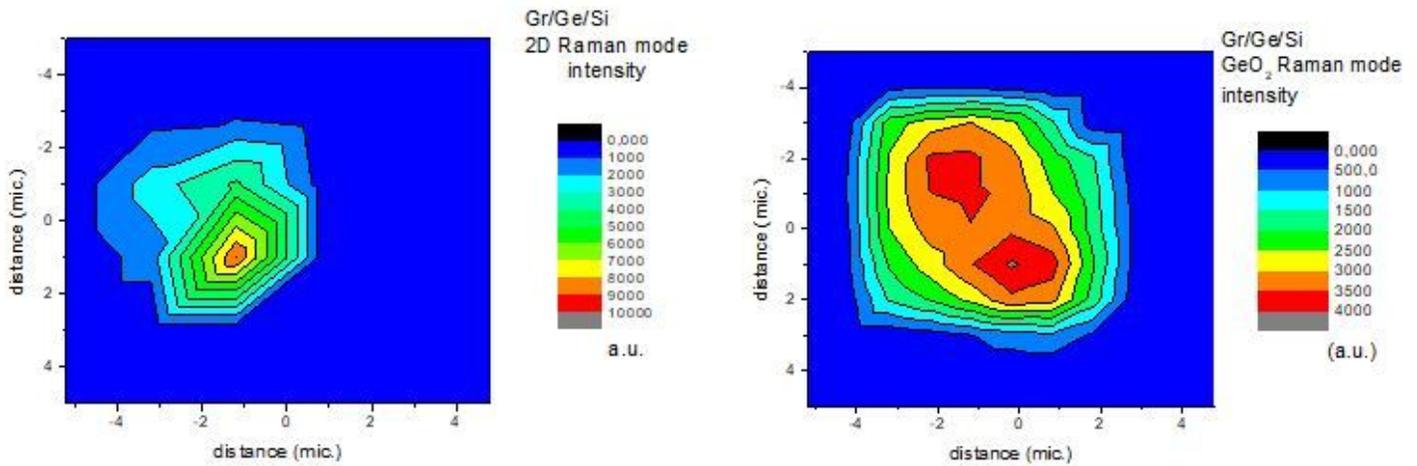
Figure 7

The map of Raman intensity of the 444cm-1 line due to GeO2 (right map) and the corresponding map of the 2D peak intensity (left map) measured on one of the blister.
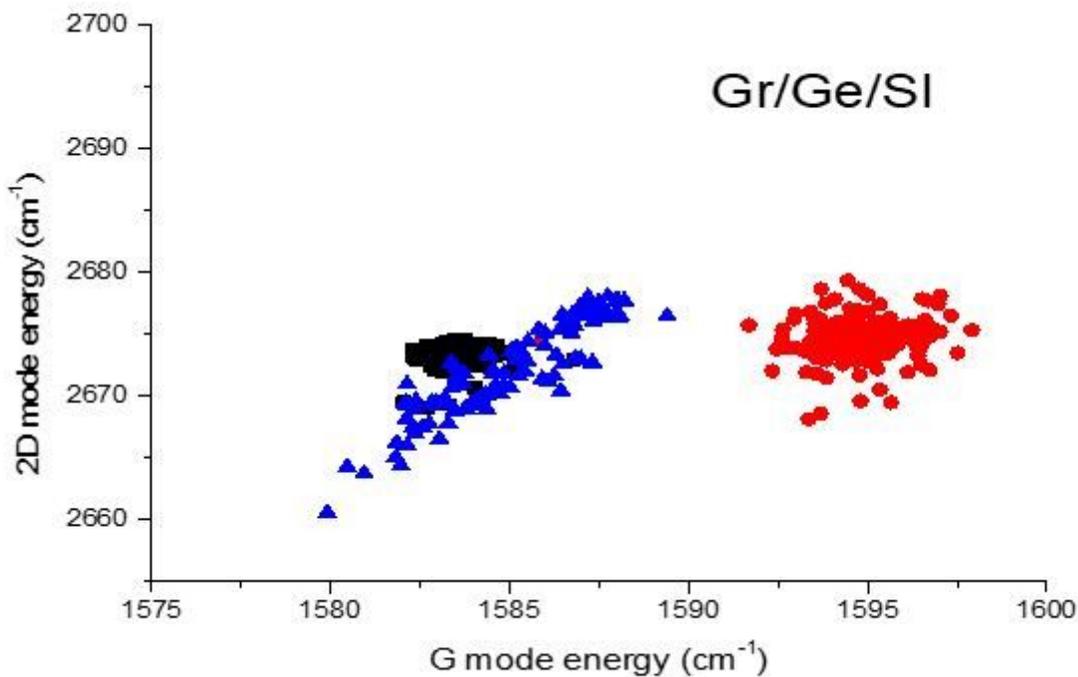

Figure 8

Plot of position of the 2D peak in relation to position of the G peak. The red points represent plot before treating sample with water vapor. The black points represent results after treatment by water vapor outside the blisters area. Blue points corresponds to results on the blisters. A slope of blue points corresponds to 2.2 and represents the effect of strain on the graphene lattice being on blister.