Tuning the doping of epitaxial graphene on a conventional semiconductor via substrate surface reconstruction

Miriam Galbiati, Luca Persichetti, Paola Gori, Olivia Pulci, Marco Bianchi, Luciana Di Gaspare, Jerry Tersoff, Camilla Coletti, Philip Hofmann, Monica De Seta, Luca Camilli

1 Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark
2 Department of Sciences, Roma Tre University, 00146 Rome, Italy
3 Department of Engineering, Roma Tre University, 00146 Rome, Italy
4 Department of Physics, University of Rome “Tor Vergata”, 00133 Rome, Italy
5 Istituto Nazionale di Fisica Nucleare Roma 2, 00133 Rome, Italy
6 Department of Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark
7 IBM Research Division, T.J. Watson Research Center, Yorktown Heights, New York, New York, 10598, USA
8 Center for Nanotechnology Innovation @NEST, Istituto Italiano di Tecnologia, Pisa 56127, Italy
9 Graphene Labs, Istituto Italiano di Tecnologia, Genova 16163, Italy
AUTHOR INFORMATION

Corresponding Author

±: luca.persichetti@uniroma3.it; *: luca.camilli@roma2.infn.it; ‡: paola.gori@uniroma3.it

ABSTRACT

Combining scanning tunneling microscopy and angle-resolved photoemission spectroscopy, we demonstrate how to tune the doping of epitaxial graphene from $p$ to $n$ by exploiting the structural changes that occur spontaneously on the Ge surface upon thermal annealing. Furthermore, using first principle calculations we build a model that successfully reproduces the experimental observations. Since the ability to modify graphene electronic properties is of fundamental importance when it comes to applications, our results provide an important contribution towards the integration of graphene with conventional semiconductors.
Integrating graphene into conventional semiconductor technology is expected to pave the way for the realization of novel device architectures with compelling properties [1-3]. The first experimental demonstrations of such devices include infrared image sensor arrays [4], radio frequency gas sensors [5] and vertical transistors for ultra-high frequency operations [6]. However, unlocking the true potential of these novel architectures is possible only if complete control of the full integration process is achieved. To this end, it is essential to understand the structural and electronic properties of the combined graphene/semiconductor substrate system.

Among conventional semiconductors of technological relevance, germanium (Ge) is unique as a substrate for growth of monolayer graphene [7]. It has sufficient catalytic activity with respect to the precursor gas, without a disruptive chemical affinity for carbon (in contrast to Si). Consequently the graphene/Ge system has recently attracted a great deal of interest both in materials science [8-11] and device physics [12-14]. Previous work has demonstrated that the Ge(001) surface forms high-index facets upon graphene synthesis, making the system unsuitable for further processing [12,15,16]. In contrast, such faceting does not occur for the Ge(110) surface [17,18], which can support growth of single-crystal graphene on wafer scale [7,19].

At present, the understanding of the graphene/Ge(110) interface is largely limited to its morphology, while too little is known of the electronic properties. It has been reported that samples grown via chemical vapor deposition (CVD) feature a hydrogen-passivated Ge surface [20] (from now on, phase α), and that upon annealing in vacuum above 350 °C, this surface reconstructs into a novel (6x2) phase (phase β) after hydrogen desorption [20-22]. It has also been shown that further in-vacuum annealing to temperatures closer to the Ge melting point leads to additional structural modifications of the Ge surface, and possibly to the formation of stronger bonds between graphene and Ge [22] (hereinafter, we refer to this phase obtained by
post-growth high temperature annealing as phase $\gamma$). Yet, despite such morphological studies, nothing is currently known about whether and how these structural changes affect the system’s electronic properties. The reported scanning tunneling spectroscopy (STS) studies have not been conclusive [23], perhaps because that technique provides very local information, and tends to be mostly sensitive to states at low $k$. In order to obtain information on the band structure of the whole system on a larger scale, we preferred to use angle-resolved photoemission spectroscopy (ARPES) which has been previously used to characterize the graphene/Ge(110) interface after annealing of the sample at 800 °C [24]. Yet, there is no information about the electronic properties of phases $\alpha$ and $\beta$. An earlier attempt to perform ARPES after post-growth annealings has been inconclusive because of the absence of a structural characterization of the graphene/Ge interface which is necessary to identify the system’s phase [25]. Moreover, the interpretation of the data in Ref. [25] has been misled by the incorrect hypothesis that hydrogen remains intercalated below graphene up to 900 °C. Moreover, high temperature annealing drives in Ge the formation of defects, such as vacancies, that are known to induce significant electronic modifications in the Ge substrate [26-29]. As a result of the complex behavior and limited information, a compelling theoretical picture has not been developed yet. Earlier attempts to build models able to reproduce the experimental results required the presence of an extraordinary high dopant segregation [24].

To bridge this gap, we present here a combined scanning tunneling microscopy (STM) and ARPES study of all three graphene/Ge(110) phases mentioned above. The annealing processes induce structural changes in the interface, and we show that these in turn modify the interaction between graphene and Ge. In particular, these changes affect graphene doping, which is a crucial parameter for device applications. Furthermore, we build a model that, accounting for the
presence of vacancies in Ge, successfully predicts the experimentally measured electronic properties of the system.

**Figure 1.** STM investigation of the graphene/Ge(110) interface for all the different phases. (a, b) STM images of phase α (V = -1.0 V and I= 0.8 nA in (a); V = 0.4 V and I = 1.0 nA in (b)). (c, d) STM images of phase β (V= -1.5 V and I= 0.8 nA in (c) and V= -1.5 V and I= 0.3 nA in (d)). (c) Coexistence of phases α and β. (d) High magnification image of phase β. In black, a and b indicate the unit cell vectors. (e, f) STM images of phase γ (V= -1.2 V and I= 0.8 nA in (e); V = -0.5 V and I = 0.8 nA in (f)). Inset of (f): Atomic-resolution STM image showing the Ge substrate. The black arrow marks the [-110] direction. Inset area is 5 x 5 nm² (V = -1.2 V and I = 0.8 nA).
Figure 1 shows STM images of the three different phases of graphene/Ge(110) interface, phase \( \alpha \), \( \beta \) and \( \gamma \). When the sample is in phase \( \alpha \), it is possible to observe the terraces and monoatomic steps of the Ge substrate (Figure 1a). The graphene film appears to be rippled, but the graphene lattice can be clearly observed (Figure 1b). Upon annealing the sample above 350 \( ^\circ \)C in ultra-high vacuum (UHV), the H-Ge bond is broken and the Ge surface reconstructs into the phase \( \beta \) [21]. The size of the phase \( \beta \) areas depends on the duration of the annealing process. Therefore, phases \( \alpha \) and \( \beta \) can coexist, as shown in the STM image reported in Figure 1c. The occasional protrusions in graphene, indicated by the arrows in Figure 1c, are nanobubbles formed by trapped hydrogen molecules that were formed upon rupture of Ge-H bond [30]. It can be noticed that they are mainly located at the Ge step edges or at the edges between areas of different phases. The atomically-resolved STM image in Figure 1d shows the unit cell of phase \( \beta \) and the corresponding lattice vectors \( (a = 2.06 \text{ nm and } b = 1.30 \text{ nm}) \). Low energy electron diffraction (LEED), Figure S1 in Supplemental Material, confirms the presence of the phase \( \beta \), which gives rise to a moiré pattern around graphene’s primary spots. Finally, Figures 1e and 1f report characteristic STM images of phase \( \gamma \), \textit{i.e.} after annealing the sample above 700 \( ^\circ \)C in UHV conditions. This surface does not show the long-range order characteristic of phase \( \beta \) anymore (Figure 1e). In fact, the Ge terraces appear to be rough, with the atomic steps being hardly recognizable. (In Figure 1e, a step edge is highlighted by a dot-dashed white line just to its right). The graphene lattice is still clearly visible (Figure 1f); however, when the tunneling bias is high enough, graphene becomes transparent and the Ge lattice underneath can be imaged (Inset of Figure 1f and Figure S2 in Supplemental Material). In particular, it is possible to observe that although the Ge atoms are overall aligned along the [-110] direction (marked by black arrow in the inset), many of them appear to be displaced from their lattice site either in the in-plane or
out-of-plane direction. Additionally, the presence of several defects, especially vacancies, can also be noticed.
Figure 2. Photoemission intensity of the graphene/Ge(110) system in (a) phase $\alpha$, (b) phase $\beta$, and (c) phase $\gamma$. The spectra were acquired along the direction orthogonal to the $\Gamma K$ direction ((a–c) upper panels) and along the $\Gamma K$ direction ((a–c) lower panels) in the Brillouin zone, as
schematically shown in the inset in the middle panel in (a). Bottom row: sketch highlighting the graphene doping level in the three phases.

In order to relate the above-mentioned morphological changes to the electronic structure of the graphene/Ge interface, we performed ARPES for the three different phases. The measured dispersion, shown as photoemission intensity as a function of binding energy and $k$, is given in Figure 2a-c, with the upper (lower) panels of the figures showing data collected perpendicular (parallel) to the $\Gamma$-$K$ direction of the graphene Brillouin zone. The crossing point of the linearly dispersing $\pi$-band branches visible in Figure 2a-c defines the position of the Dirac point ($E_D$). By linear extrapolation (see Experimental Methods in Supplemental Material), $E_D$ is found at binding energy of $0.376 \pm 0.018$ eV above the Fermi energy ($E_F$) for phase $\alpha$, indicating that graphene is p-doped. Further information can be extracted from the momentum distribution curve (MDC) line width, which provides insights into the graphene integrity and its interaction with the substrate. The MDC line width (FWHM) orthogonal to the $\Gamma$-$K$ direction and taken at 0.70 eV below the Fermi level is $0.153 \pm 0.002$ Å$^{-1}$. When phase $\alpha$ is annealed in vacuum above 350 °C and turns into phase $\beta$, a reduction in the doping level is observed (Figure 3b). Indeed, $E_D$ is now very close to $E_F$, at a binding energy of $0.045 \pm 0.005$ eV. Thus, graphene is close to an undoped state, indicating little charge transfer with the substrate. Moreover, the MDC line width now measures $0.111$ Å$^{-1}$, a value almost 30% smaller than that of phase $\alpha$, indicating a weaker interaction between substrate and graphene in phase $\beta$. This finding is rather interesting, and highlights the opportunity for controlling the graphene doping and substrate interaction by suitable processing.

An additional modification of the electronic properties is found for phase $\gamma$, i.e. after a high temperature annealing of the sample. In this case graphene is n-doped, with $E_D$ found at $0.478 \pm$
0.007 eV below $E_F$. This experimental finding is similar to others reported ARPES measurements performed on graphene/Ge(110) after the sample was annealed at 800 °C in vacuum [24]. Previously, the best available explanation to the n-type doping was surface segregation of Sb atoms (about 1 monolayer) upon the high temperature annealing. Sb is present as dopant in the bulk of Ge also in our samples and from our STM images we note the bright patches that may appear suggestive of regions of dopant segregations. However, we rule out this interpretation as similar bright patches are seen also in the as-grown sample (compare Figure 1a and Figure 1e). For phase $\gamma$, the MDC line width is $0.148 \pm 0.002 \text{ Å}^{-1}$, similar to that one found for phase $\alpha$ and larger than that of phase $\beta$. Thus, we can conclude that after the high temperature annealing, the graphene/Ge interaction is stronger than in phase $\beta$, but graphene does not degrade because a poorer structural quality would lead to a broadening in the MDC spectral line width with respect to phase $\alpha$. Furthermore, we note the opening of a small band gap in graphene for phase $\gamma$ [Fig. 2(c) and Fig. S5 in Supplementary Information], induced by the stronger interaction with the substrate [22].
Figure 3. Constant binding energy cuts at 0.90 eV below the extrapolated Dirac point for phase α (left), phase β (middle), and phase γ (right). The white arrows in the middle panel point to the position of two out of four replicas.

The \(k\)-dependent photoemission intensity at a constant energy of 0.90 eV below \(E_D\) is shown in Figure 3 for phases α (left), β (middle) and γ (right), respectively. For phase β, four replicas around the K point (we mark two of them by white arrows) can be observed along with the main Dirac cone. These replicas are due to the superperiodic potential imposed by the moiré of graphene and (6x2) Ge surface reconstruction. Accordingly, the pattern from the replicas is consistent with the LEED pattern of the corresponding sample reported in Figure S1 in Supplemental Material. Interestingly, we do not observe any emerging minigaps at the crossing points of the replicas with graphene main cone, in contrast to what is found for the case of, for instance, graphene/Ir(111) [31,32]. In particular, from the analysis of the MDCs taken along \(k_x\) close to the location where the replica crosses the main cone, the intensity of the spectral function does not vanish or decrease as expected in the case of a minigap (see Figure S3 in
Supplemental Material). Furthermore, we notice that the same constant binding energy cut shows no replicas for the other two sample phases.

To gain more insights into the system, we have built a theoretical model based on ab-initio calculations to describe phase $\alpha$ and phase $\gamma$ (see Theoretical Methods in Supplemental Material for more details), which represent the two cases showing opposite doping of graphene. We do not attempt modelling phase $\beta$ because of its large cell and complexity.

Phase $\alpha$ is modelled by a 5-layer Ge(110) 3x5 slab, with both surfaces saturated with H, and a graphene layer on top, with a 4x8 periodicity in the rectangular supercell. The geometry is depicted in Figure 4a. Phase $\gamma$ is modeled by the same supercell, but without H atoms on the top of the Ge(110) substrate (see Figure 4b). A key feature of our models is the presence of a vacancy in the surface layer of the Ge substrate (one vacancy in the 3x5 cell). The location of the vacancy is highlighted by the black circle in Figure 4a,b. As known in the literature [14,26-29], when Ge is brought to high temperature (like the temperature used for graphene growth), a spontaneous formation of vacancies occurs, starting first at the surface and then spreading throughout the bulk. This confers to the Ge wafer a p-doping character regardless of the initial nominal doping. Indeed, by performing Hall measurements on different bare Ge substrates, which are nominally n-doped, we do measure p-type doping after they have been annealed in H$_2$/Ar atmosphere to the same temperature used for graphene growth (Figure S4 in Supplemental Material).
Figure 4. 3D side-view of phase α with all dangling bonds being H-terminated (a) and of phase γ (b). Cyan denotes H atoms, violet Ge atoms and yellow C atoms. The black circles highlight the region where the vacancy has been introduced. (c), (d): Corresponding calculated electronic band structures around K with a total \( k \) range of 0.07 Å\(^{-1}\). Red dots represent graphene-derived states, whereas grey dots represent Ge or H states.

The electronic band structure obtained for phase α shows that the Fermi level lies below the Dirac point, giving rise to p-doping of graphene (Figure 4c). This is qualitatively in agreement with the experiment reported in Figure 2a. To corroborate our hypothesis about the presence of vacancies in the Ge substrate, we have performed additional simulations with (i) no vacancy, and (ii) a Sb atom replacing the vacancy (Sb is the dopant nominally present in our Ge substrate). Both calculations give a Fermi level above the Dirac point, corresponding to n-doped graphene, thus at odds with experiment (see Table S1 in Supplemental Material). Therefore, we believe that
thermally induced vacancies and not Sb segregation play a key role in determining the doping seen in the experiment for phase $\alpha$.

Phase $\gamma$ was simulated by removing the H atoms on the top Ge(110) surface. In this case, we found several local minima in energy after geometrical relaxation, in contrast to the single energy minimum observed for phase $\alpha$. While the most stable structure is an ordered Ge(110) surface, the other minima correspond to slightly disordered Ge surfaces (Figure 4b), with total energy within a few meV/(C atom) from the ordered one. The occurrence of a disordered surface is in fact supported by the STM images displayed in Figure 1e,f and Figure S2 in Supplemental Material. The electronic band structure of this disordered phase is reported in Figure 4d, where we can see that the Fermi level lies below the Dirac point. Hence, graphene is n-doped, in agreement with the ARPES data (Figure 2c). Furthermore, we stress that a similar result – that is, n-doped graphene – is achieved when another disordered configuration of phase $\gamma$ is used, where the surface Ge atoms are intentionally disordered. Instead, when an ordered Ge surface is used to simulate phase $\gamma$, no agreement with the experiment is found (see Supplemental Material, Table S1). Therefore, we believe that disorder in the Ge surface and not Sb segregation play a key role in determining the doping seen in the experiment for phase.

These results highlight the richness of the graphene/Ge(110) system and suggest that the experimentally observed behavior reflects not only the role of Ge-H bonds, but also of Ge vacancies and disorder, all of which evolve with increasing temperature.

In conclusion, through a combination of STM and ARPES we have experimentally demonstrated that the electronic properties of the graphene/Ge(110) system are significantly modified by temperature-driven structural changes occurring at the interface. Annealing processing can
indeed be used to tune the doping of graphene via modification of its interaction with the Ge substrate. Notably, graphene is p-doped after CVD growth, nearly intrinsic (undoped) upon annealing above 350 °C when the Ge surface rearranges into the 6x2 reconstruction, and then n-doped if the sample is annealed above 700 °C. Starting from the STM observations we also build a theoretical model that successfully reproduces the ARPES experimental trend. Since a comprehensive understanding of the electronic properties of graphene/semiconductor interface is critical when it comes to applications, our results provide an important contribution towards the integration of graphene with conventional semiconductors.

Supplemental Material

Supplemental Material contains the experimental and theoretical methods; further analysis of the STM and ARPES data; LEED micrographs of phase β; Hall and resistivity measurements of Ge substrates; additional simulations.

ACKNOWLEDGMENT

The authors are grateful to Mads Brandbyge and Fei Gao for the useful discussions. The authors thank Dr. Andrea Notargiacomo for the Hall measurements and Dr. Vaidotas Miseikis for support in growing the samples. This work is supported by the VILLUM FONDEN through the Young Investigator Program (project No. 19130) and the Centre of Excellence for Dirac Materials (Grant No. 11744). L.C. acknowledges support from the Italian Ministry of Education, University and Research (MIUR) via “Programma per Giovani Ricercatori - Rita Levi Montalcini 2017”. O.P. acknowledges funding from the HORIZON2020 EU MSCA-RISE project DiSeTCom (GA 823728). The computing resources and related technical support have been provided by CRESCO/ENEAGRID High Performance Computing infrastructure (ENEA,
the Italian National Agency for New Technologies, Energy and Sustainable Economic Development. C.C. acknowledges the Graphene Flagship Core 3 (contract no. 881603).

REFERENCES

[1] D. Akinwande, C. Huyghebaert, C.-H. Wang, M. I. Serna, S. Goossens, L.-J. Li, H. S. P. Wong, and F. H. L. Koppens, Nature 573, 507 (2019).

[2] D. Neumaier, S. Pindl, and M. C. Lemme, Nat. Mater. 18, 525 (2019).

[3] T. David, J. Phys.: Condens. Matter 27, 133203 (2015).

[4] S. Goossens et al., Nat. Photonics 11, 366 (2017).

[5] S. M. Mortazavi Zanjani, M. Holt, M. M. Sadeghi, S. Rahimi, and D. Akinwande, npj 2D Materials and Applications 1, 36 (2017).

[6] C. Liu, W. Ma, M. Chen, W. Ren, and D. Sun, Nature Communications 10, 4873 (2019).

[7] J.-H. Lee et al., Science 344, 286 (2014).

[8] R. Rojas Delgado, R. M. Jacobberger, S. S. Roy, V. S. Mangu, M. S. Arnold, F. Cavallo, and M. G. Lagally, ACS Applied Materials & Interfaces 9, 17629 (2017).

[9] F. Akhtar, J. Dabrowski, M. Lisker, Y. Yamamoto, A. Mai, C. Wenger, and M. Lukosius, ACS Applied Materials & Interfaces 12, 3188 (2020).

[10] B. Kiraly, R. M. Jacobberger, A. J. Mannix, G. P. Campbell, M. J. Bedzyk, M. S. Arnold, M. C. Hersam, and N. P. Guisinger, Nano Lett. 15, 7414 (2015).

[11] Y. Dedkov and E. Voloshina, Nanoscale 12, 11416 (2020).

[12] R. M. Jacobberger et al., Nature Communications 6, 8006 (2015).
[13] L.-H. Zeng \textit{et al.}, ACS Applied Materials & Interfaces \textbf{5}, 9362 (2013).

[14] M. Pea, M. De Seta, L. Di Gaspare, L. Persichetti, A. M. Scaparro, V. Miseikis, C. Coletti, and A. Notargiacomo, ACS Applied Materials & Interfaces \textbf{11}, 35079 (2019).

[15] A. M. Scaparro, V. Miseikis, C. Coletti, A. Notargiacomo, M. Pea, M. De Seta, and L. Di Gaspare, ACS Applied Materials & Interfaces \textbf{8}, 33083 (2016).

[16] L. Persichetti, L. Di Gaspare, F. Fabbri, A. M. Scaparro, A. Notargiacomo, A. Sgarlata, M. Fanfoni, V. Miseikis, C. Coletti, and M. De Seta, Carbon \textbf{145}, 345 (2019).

[17] P. C. Rogge, M. E. Foster, J. M. Wofford, K. F. McCarty, N. C. Bartelt, and O. D. Dubon, MRS Communications \textbf{5}, 539 (2015).

[18] L. Persichetti \textit{et al.}, Appl. Surf. Sci. \textbf{499}, 143923 (2020).

[19] J. Dai \textit{et al.}, Nano Lett. \textbf{16}, 3160 (2016).

[20] D. Zhou, Z. Niu, and T. Niu, The Journal of Physical Chemistry C \textbf{122}, 21874 (2018).

[21] G. P. Campbell, B. Kiraly, R. M. Jacobberger, A. J. Mannix, M. S. Arnold, M. C. Hersam, N. P. Guisinger, and M. J. Bedzyk, Physical Review Materials \textbf{2}, 044004 (2018).

[22] B. Kiraly, A. J. Mannix, R. M. Jacobberger, B. L. Fisher, M. S. Arnold, M. C. Hersam, and N. P. Guisinger, Appl. Phys. Lett. \textbf{113}, 213103 (2018).

[23] H. W. Kim, W. Ko, W.-J. Joo, Y. Cho, Y. Oh, J. Ku, I. Jeon, S. Park, and S. W. Hwang, The Journal of Physical Chemistry Letters \textbf{9}, 7059 (2018).

[24] J. Tesch \textit{et al.}, Nanoscale \textbf{10}, 6088 (2018).

[25] S. J. Ahn, H. W. Kim, I. B. Khadka, K. B. Rai, J. R. Ahn, J.-H. Lee, S. G. Kang, and D. Whang, Journal of the Korean Physical Society \textbf{73}, 656 (2018).

[26] S. Mayburg, Physical Review \textbf{95}, 38 (1954).
[27] R. A. Logan, Physical Review 101, 1455 (1956).

[28] J. Vanhellemont, J. Lauwaert, A. Witecka, P. Śpiewak, I. Romandic, and P. Clauws, Physica B: Condensed Matter 404, 4529 (2009).

[29] S. H. Segers, J. Lauwaert, P. Clauws, E. Simoen, J. Vanhellemont, F. Callens, and H. Vrielinck, Semicond. Sci. Technol. 29, 125007 (2014).

[30] P. Jia et al., Nature Communications 10, 3127 (2019).

[31] R. Larciprete et al., ACS Nano 6, 9551 (2012).

[32] I. Pletikosić, M. Kralj, P. Pervan, R. Brako, J. Coraux, A. T. N’Diaye, C. Busse, and T. Michely, Phys. Rev. Lett. 102, 056808 (2009).
Supplemental Material for:

Tuning the doping of epitaxial graphene on a conventional semiconductor via substrate surface reconstruction

Miriam Galbiati¹, Luca Persichetti²⁺, Paola Gori³⁺, Olivia Pulci⁴,⁵, Marco Bianchi⁶, Luciana Di Gaspare², Jerry Tersoff⁷, Camilla Coletti⁸,⁹, Philip Hofmann⁶, Monica De Seta², Luca Camilli¹,⁴*  

¹ Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark  
² Department of Sciences, Roma Tre University, 00146 Rome, Italy  
³ Department of Engineering, Roma Tre University, 00146 Rome, Italy  
⁴ Department of Physics, University of Rome “Tor Vergata”, 00133 Rome, Italy  
⁵ Istituto Nazionale di Fisica Nucleare Roma 2, 00133 Rome, Italy  
⁶ Department of Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark  
⁷ IBM Research Division, T.J. Watson Research Center, Yorktown Heights, New York, New York, 10598, USA
Experimental Methods

The graphene was grown on Ge(110) substrates (n-type, Sb-doped, n=10\(^{16}\) cm\(^{-3}\)) using a commercially available CVD reactor (Aixtron BM). Ge substrates were cleaned ex-situ by several rinsing and drying steps using isopropyl alcohol and de-ionized water followed by in-situ annealing to 930 °C in H\(_2\)/Ar atmosphere (200/800 sccm) without methane. Graphene was then grown after adding 2 sccm of methane to the gas mixture, at a total pressure of 100 mbar. The samples were cooled down to room temperature in a protective H\(_2\) and Ar atmosphere.

Ex-situ STM measurements were performed with etched-W tips at temperature of 9-10 K in UHV (base pressure < 2x10\(^{-10}\) mbar) using a Sigma Surface Science Infinity system. After loading them into the STM chamber, the samples were degassed at around 180 °C until the pressure in the chamber would drop back to the initial base pressure value.

The ARPES measurements were carried out at the SGM-3 beamline of the synchrotron radiation source ASTRID-2 (Aarhus, Denmark) with the sample temperature kept at 66 K\(^1\). The photon energy used was 47 eV for phases \(\alpha\) and \(\beta\), and 100 eV for phase \(\gamma\) with a combined energy and \(k\) resolution better than 34 meV and 0.01 Å\(^{-1}\), respectively. Before performing ARPES measurements on phase \(\alpha\), the sample was annealed in vacuum at a temperature below 300 °C for 2 h. To prepare phases \(\beta\), phase \(\alpha\) was annealed in-situ in the ARPES chamber. In-situ STM measurements and LEED patterns were collected before performing ARPES on each phase.
LEED spot size was up to 1 mm. To estimate the Dirac point binding energy, the MDCs corresponding to the branches of the $\pi$-band are fitted with a Lorentzian function and two peaks positions are used for linearly extrapolate the Dirac point considering a range of binding energies from 0.3 to 0.6 eV below the Fermi level.

**Theoretical Methods**

DFT-LDA calculations for the geometries and the electronic band structures of the alpha and gamma phases were performed using the Quantum Espresso package\(^2\).

The Ge(110) surface was simulated by a 5-layer slab in a 3x5 rectangular geometry (150 Ge atoms). The bottom of the slab was passivated by hydrogen atoms. The graphene layer was simulated using a 4x8 rectangular cell (128 C atoms). An angle of 30° between the [-110] direction of Ge(110) and the armchair direction of graphene allows for a commensurate matching with a strain less than 2%. A vacuum layer of about 15 Å was used to decouple periodic images of the slabs along the direction perpendicular to the surface.

We employed norm-conserving pseudopotentials, and a kinetic energy cutoff of 45 Ry. Tests with ultrasoft pseudopotentials explicitly containing the semicore d states of Germanium were performed, leading to no significant differences. Dipole corrections were added. Van der Waals interactions were introduced following the schemes described in Refs. [3] and [4].

Equilibrium geometries were obtained by relaxing the atoms till the forces were below $10^{-3}$ a.u. and the total energy changed less than $10^{-5}$ a.u. A mesh of 4x4x1 k-points in the Brillouin zone was used.
Figure S1. LEED pattern acquired on a sample with phase β with primary electron energy of 97 eV. A moiré pattern can be observed around the six graphene diffraction spots. The ratio between the two edges of the moiré pattern is consistent with the ratio between the lattice vectors of the β phase as measured in STM.

Figure S2. STM image of phase γ showing the atomic-resolution of the Ge substrate. The scanned area is 15 x 15 nm² (V = -1.2 V and I = 0.8 nA).
**Figure S3.** Absence of minigaps at the crossing of graphene main Dirac cone with its replica for phase $\beta$. a) ARPES intensity map. b) Intensity of Dirac cone dispersion extracted by MDCs analysis. The main Dirac cone and replica (dashed red lines) dispersion bands cross at $\sim 1.2$ eV. The intensity of the band does not vanish or decrease at the crossing point, as one would expect in the case of a minigap openings.

**Figure S4.** Examples of Hall and resistivity measurements performed at room temperature on different Ge substrates after annealing in atmosphere to 930 °C in H$_2$/Ar atmosphere during simulated growth experiments. The measurements have been carried out with Van der Pauw
configuration. Magnetic field: 0.7 T. For all the samples investigated, we always observed a p-type Hall behavior with sheet carrier density in the range 0.8–7.0 x 10^{14} cm^{-2}.

|                  | E_D-E_F (eV) |
|------------------|--------------|
|                  | Pristine     | Vacancy    | Sb          | Experiment |
| Phase α          | -0.22        | +0.08      | -0.49       | +0.376     |
| Phase γ (ordered)| +0.08        | +0.05      | +0.02       | ----        |
| Phase γ (disordered) | -0.13      | -0.18      | -0.23       | -0.478     |

Table S1. Comparison between the experimental (Experiment) and DFT calculated position of the Dirac point with respect to the Fermi level (E_D-E_F), for the phase α, ordered phase γ and disordered phase γ. The following notation is used: Pristine refers to the intrinsic, undoped Ge substrate; Vacancy refers to the Ge substrate with 1 vacancy in the 3x5 cell; Sb refers to the Ge substrate with 1 Sb atom segregated at the surface.

Figure S5. Opening of small band gap in phase γ. The MDCs analysis, taken along k_x close to the Dirac point in the range 0.04 – 0.56 eV, reveals the opening of a band gap of ≈120 meV (grey area).
Figure S6. Bias-dependent STM imaging. After a short annealing in vacuum at approximately 300 C, the sample has transformed in phase β (that is, hydrogen has deintercalated and the Ge surface has reconstructed into 6x2) everywhere but in same small areas where phase α (that is, hydrogen still intercalated between graphene and Ge) is still present. See for example the area below the hydrogen bubble at the center of the image, and the triangular area at its right. At low bias voltages (±0.2 V), the graphene lattice is easily imaged, while the Ge surface is not clearly visible. At higher bias voltages (±0.6 V), both the graphene lattice and the Ge surface are observable. At even higher bias voltages (±1.0 V), graphene becomes transparent to the tunneling electrons. It is also interesting to point out how the Ge surface changes appearance depending on the applied bias voltage, regardless if it is reconstructed or not. Notably, for the case of unreconstructed surface (phase α), the surface looks disordered at positive voltages (0.6 V and 1.0 V), while it appears ordered (we can see the atomic chains running along the [-110]
direction) at negative voltages (-0.6 V and -1.0 V). This is an important piece of information to bear in mind and could explain why the same unreconstructed surface is considered to be disordered in some earlier publications and ordered in others. In all images the tunneling current is 0.1 nA.

REFERENCES

(1) Hoffmann, S. V.; Søndergaard, C.; Schultz, C.; Li, Z.; Hofmann, P. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 2004, 523, (3), 441-453.

(2) Giannozzi, P.; Stefano, B.; Nicola, B.; Matteo, C.; Roberto, C.; Carlo, C.; Davide, C.; Guido, L. C.; Matteo, C.; Ismaila, D.; Andrea Dal, C.; Stefano de, G.; Stefano, F.; Guido, F.; Ralph, G.; Uwe, G.; Christos, G.; Anton, K.; Michele, L.; Layla, M.-S.; Nicola, M.; Francesco, M.; Riccardo, M.; Stefano, P.; Alfredo, P.; Lorenzo, P.; Carlo, S.; Sandro, S.; Gabriele, S.; Ari, P. S.; Alexander, S.; Paolo, U.; Renata, M. W. J. Phys.: Condens. Matter 2009, 21, (39), 395502.

(3) Dion, M.; Rydberg, H.; Schröder, E.; Langreth, D. C.; Lundqvist, B. I. Phys. Rev. Lett. 2004, 92, (24), 246401.

(4) Tkatchenko, A.; Scheffler, M. Phys. Rev. Lett. 2009, 102, (7), 073005.