

The electronic properties of Graphene/Ge(110)

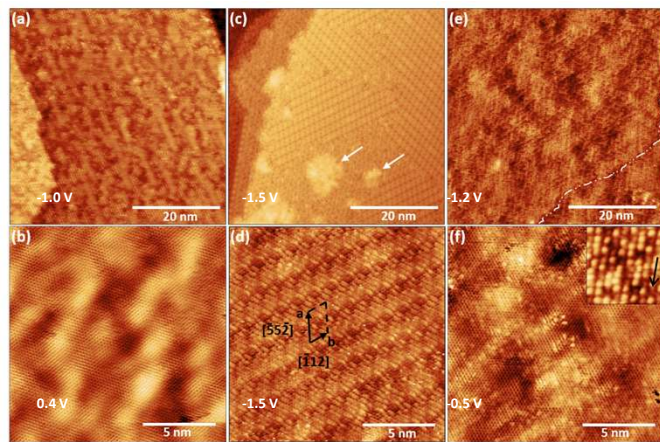
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Abstract

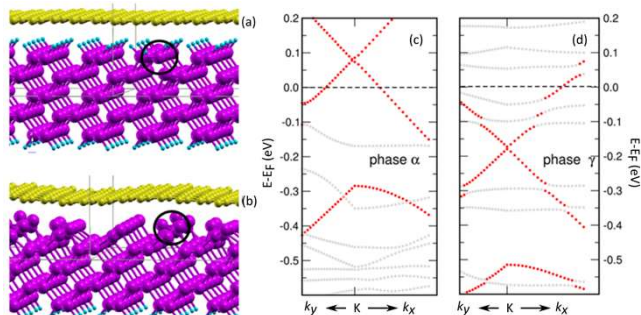
Unveiling the interfacial properties between graphene and conventional semiconductors is crucial to develop novel electronics. Using Graphene/Ge(110) as a model system, we demonstrate how the modifications of the interface structure correspond to modification of its electronic properties as well. Indeed, we use different temperature annealing to gate graphene by changing the interaction with the substrate. Scanning tunnelling microscopy (STM) and angle resolved photoemission spectroscopy (ARPES) are used to characterize the structure and electronic properties of the interface. Moreover, we use density functional theory (DFT) to simulate the cases of as-grown and high-temperature annealed samples. Accounting in our model for the structural modifications of the Ge surface as observed by the STM, our model successfully predicts the ARPES data. Graphene is p-doped after growth via chemical vapor deposition (CVD) and the Ge surface is passivated by hydrogen (**phase α**) [1]. The doping neutrality of Graphene is almost restored upon annealing above 350 °C when the Ge surface reconstructs into the (6x2) phase (**phase β**). Finally, Graphene becomes n-doped when the sample is annealed above 700 °C and local chemical bonds are promoted between Graphene and Ge (**phase γ**) [2]. By providing a path to modulate the interaction and charge transfer between Graphene and Ge, this study represents an example of the flexibility offered by the integration of Graphene with complementary metal-oxide-semiconductor (CMOS) compatible substrates.

STM – Graphene/Ge(110) interface study



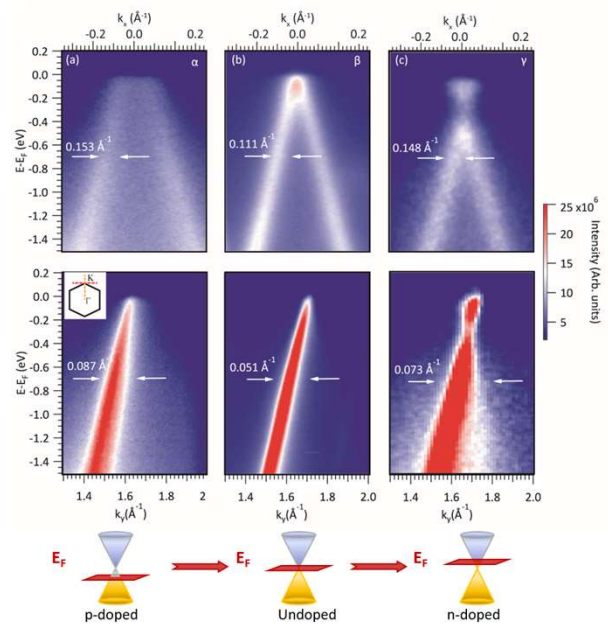
STM investigation of the Graphene/Ge(110) interface in the three different phases. (a, b) STM images of **phase α** ($I = 0.8$ nA in (a) and $I = 1.0$ nA in (b)). (c, d) STM images of **phase β** ($I = 0.8$ nA in (c) and $I = 0.3$ nA in (d)). (c) Coexistence of phases α and β . Bright protrusions, indicated by the arrows, are nanobubbles formed by trapped H_2 that were formed upon rupture of Ge-H bond. (d) High magnification image of phase β . In black, a and b indicate the unit cell vectors of the (6x2) reconstruction. (e, f) STM images of **phase γ** ($I = 0.8$ nA in (e) and $I = 0.8$ nA in (f)). Inset of (f): STM image showing the Ge substrate. The black arrow marks the [-110] direction. Inset area is 5×5 nm² ($V = -1.2$ V and $I = 0.8$ nA).

DFT calculations



3D side-view of the α -phase geometry (a) and of the γ -phase geometry (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 k range of 0.07 \AA^{-1} . Red dots represent graphene-related 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. This is qualitatively in agreement with the ARPES experiments. We found several local minima in energy when simulating phase γ . While the most stable structure is an ordered Ge(110) surface, the other minima correspond to slightly disordered Ge surfaces (as shown in (b)). The occurrence of a disordered surface is supported by the STM images panels (e) and (f).

ARPES – electronic band structure investigation



Photoemission intensity of the Graphene/Ge(110) system in (a) phase α , (b) phase β , and (c) phase γ . The spectra were acquired along the direction orthogonal to the ΓK direction ((a–c) upper panels) and along the ΓK 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. The momentum distribution curve (MDC) line width analysis indicates that in phase β the interaction between graphene and Ge is weaker than in the other phases. The MDC line width value in phase γ is similar to the one found for phase α . Thus, we can conclude that after high temperature annealing, the graphene/Ge interaction is stronger than in phase β , 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 α .

Conclusions

Combining 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. Notably, graphene is p-doped after CVD growth, nearly undoped upon annealing above 350 °C when the Ge surface reconstructs, and then n-doped after annealing above 700 °C. Starting from the STM results we build a model that reproduces the ARPES experimental trend. This study demonstrates the flexibility offered by the integration of graphene with CMOS-compatible platforms [4].

References

- [1] D. Zhou *et al.*, J. Phys. Chem. C **122**, 21874 (2018).
- [2] B. Kiraly *et al.*, Appl. Phys. Lett. **113**, 1 (2018).
- [3] G. P. Campbell *et al.*, Phys. Rev. Mater. **2**, 044004 (2018).
- [4] Galbiati *et al.* Physical Review Letters (under review).