

Structural and chemical stabilization of the epitaxial silicene

A. Molle¹, D. Chiappe¹, E. Cinquanta¹,
C. Grazianetti^{1,2}, M. Fanciulli^{1,2}, E. Scalise³,
B. van den Broek³, M. Houssa³

¹ Laboratorio MDM, IMM-CNR, via C. Olivetti 2, I-20864 Agrate Brianza (MB), Italy, Email: alessandro.molle@mdm.imm.cnr.it, Website: www.mdm.imm.cnr.it

² Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, via R. Cozzi 53, I-20126, Milano (MI), Italy

³ Semiconductor Physics Laboratory, Department of Physics and Astronomy, University of Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium.

The silicon counterpart of graphene, the so called “silicene” [1,2], has been so far a fascinating theoretical hypothesis but its synthesis constituted a formidable challenge because, unlike carbon, silicon atoms naturally hybridize sp^3 , thus preventing the spontaneous formation a 2D graphene-like crystal. Nonetheless, recent efforts have moved up this fascinating hypothesis to a concrete evidence [3][4] thus triggering a tremendous interest in silicene for electronic application and fundamental investigations. Indeed, in addition to graphene, silicene is expected to provide an intimate affinity with the Si-based technology which may pave the way to an easier integration. On the other hand, unlike graphene, non-trivial atomic arrangements of the silicene nanosheets are shown to occur which are dictated by a delicate balance between planar and buckled bonding in a quasi-2D Si layer. Indeed, due to the large ionic radius of silicon, silicene is naturally prone to occur with a variety slightly-buckled configurations which are driven by the silicene/substrate local interactions and by self-assembling of Si adatoms [1]. This structural complexity discriminates the experimentally observed silicene from its carbon counterpart, the graphene, and it is expected to bring absolutely peculiar and unexplored physical properties such as topological phase transitions, quantum spin Hall effect, or band gap opening [5]. Here we report on experimental evidences of the formation of 2D silicene epitaxially grown on Ag(111) substrates based on in situ scanning tunnelling microscopy-spectroscopy investigations [4]. Moreover, it is shown how the vertical buckling, an intimate parameter which confer a mixed sp_2 - sp_3 hybridized character to the silicene bonding, can dictate the details of various silicene superstructures, and how this multi-phase character can be used to tune the electronic state of the silicene (from a semi-metal state to a semiconducting one and a metal one) by making use of Raman spectroscopy and self-consistent density functionals based interpretation. Accessing Raman spectroscopy of silicene as well as other ex situ diagnostic tool is not a straightforward task because, despite the structural flexibility,

silicene is technologically limited by its intimate chemical instability. Indeed, silicene undergoes oxidation when exposed to dry air. Therefore, interfacing silicene with a gate dielectric material is essential for any feasible voltage bias application but also to barely save it from possibly destructive reactivity in ambient conditions. While disentangling silicene from metallic templates is still an open challenge, on-top interface engineering of silicene is here addressed with the goal to develop an unreactive encapsulation process. This effort enabled us to fabricate a chemically stable Al_2O_3 /silicene/Ag heterostructure through a carefully tailored co-deposition of Al and O_2 [6]. Raman spectroscopy is here proposed as a powerful ex-situ characterization with the aim of demonstrating the structural stability of the encapsulated silicene and the true chemical nature of the silicene bonding.

Finally, new perspectives of the growth of silicene nanosheets on *ad hoc* 2D templates such the 2D-layered chalcogenide MoS_2 , will be discussed aiming at the silicene “portability” for a device-oriented exploitation.

These outcomes disclose exceptionally novel issues in the physics of the emerging silicene and promote a renewed interest in nanoscaled silicon as active material for electronic devices.

References

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