First steps of silicene growth on Ag(111)

Mohamed Rachid Tchalala¹, Hanna Enriquez¹, Andrew J. Mayne¹, Abdelkader Kara², Gérald Dujardin¹, and Hamid Oughaddou¹,3,*

¹ Institut des Sciences Moléculaires d’Orsay, ISMO-CNRS, Bât. 210, Université Paris-Sud, F-91405 Orsay, France
² Department of Physics, University of Central Florida, Orlando, FL 32816, USA
³ Département de Physique, Université de Cergy-Pontoise, F-95031 Cergy-Pontoise Cedex, France

*e-mail : Hamid.Oughaddou@u-psud.fr

Abstract. In this paper we report on the first steps of silicene growth on Ag(111) using scanning tunneling microscopy. We show that the topmost atomic layer is composed of both silicon and silver. The STM observations are consistent with an exchange process between the silicon and silver atoms preferentially taking place at the step edges of the Ag substrate. In addition, silicon stripes are observed as precursors of the formation of the silicene sheet.

1. Introduction

Two-dimensional (2D) materials hold great promise for future electronic devices [1]. Indeed, even though graphene is now used in a number of applications, its semi-metal character and the absence of a band gap [2] have posed significant limitations to its widespread use. Nevertheless, the discovery of graphene has spurred research into similar new 2D materials. Silicene and germanene are two of these emerging materials. Early theoretical studies predicted that their structures would show similar electronic properties to graphene, such as a Dirac cone at the high symmetry k-point of the Brillouin zone, large charge carrier mobility, and the quantum spin Hall effect [3-5]. However, both silicene and germanene differ from graphene in that they have better opto-magnetic properties [6-8].

The major challenge has been to grow these new 2D materials, since the theoretical models indicated that freestanding germanene and silicene layers had buckled structures that were unstable compared to graphene. So far, single 2D layers of germanium and silicon have been grown on metal surfaces. In the case of germanene, the initial studies were performed on Ag(111) [9-12] and more recently on Al(111) [13-16], Au(111) [17-18] and Pt(111) surfaces [19], where several models for the structure of the germanene layer have been proposed. Following early theoretical calculations proposing the existence of silicene [4-5], the growth of silicene was investigated on Ag(111), where a 2D sheet of silicene was observed by STM measurements for the first time [20]. Subsequent studies have shown that several silicene structures can be grown on the Ag(111) surface, and they can co-exist under certain growth conditions [21-30]. At the same time, experiments were performed on the Ag(110) surface [31-35]. On the Ag(110) substrate, self-assembled silicene nano-ribbons (NRs) 1.6 nm wide were obtained [34], which were found to be weakly reactive towards oxidation [33]. Silicene has also been grown on several other metallic surfaces including Ir(111) [36], ZrB2(0001) [37], Pt(111) [38], and recently on Au(110) [39] and Au(111) [40-41]. A more in-depth description of these studies is given in two recent review articles [42-43].

In this paper we report on the complexity of the first stages of silicene growth on Ag(111). We show that there is a strong interaction with the substrate and that growth proceeds via the expulsion of Ag atoms from the top layer of the terraces. In the STM images, atomic structures are observed that are consistent with the formation of a mixed Si-Ag top layer.

2. Experiment
The STM experiments were performed at room temperature (RT) in an UHV chamber equipped with low energy electron diffraction (LEED), and a commercial Omicron STM. The sample was prepared in an ultrahigh-vacuum system with a base pressure of ~ 1x10^{-10} mbar. After repeated cycles of Ar⁺ sputtering (600 eV and P = 5 x 10^{-5} mbar) and annealing at 450°C for a few minutes, the Ag(111) surface showed a sharp (1x1) LEED pattern. Silicon was evaporated under UHV conditions by direct current heating of a 12x5 mm Si wafer at about 1250°C. The temperature of the substrate can be controlled during the silicon deposition.

3. Results and Discussions

Figure 1a displays a 60x60 nm² STM topography recorded after a sub-monolayer coverage of silicon on the Ag(111) surface, held at 250°C during the deposition. The STM image shows three different domains corresponding to different silicene superstructures. The first one, identified as domain A, exhibits a periodic 4x4 structure with respect to the substrate. The second domain (B) has a (2√3x2√3)R30° structure. These two well-known superstructures correspond to a silicene sheet oriented by 0° and 30° with respect to the principle lattice directions of Ag(111). In Figure 1a, a new structure composed of silicon stripes is observed (domain C) that has not been reported in the literature. Figure 1b shows a zoom of this domain. The line scan measured along the line L gives a distance between the nearest neighbor bright protrusions of about 1nm. We observe that the stripes are either isolated or assembled in pairs (Figure 1b). In addition, in domain C, we observe a small area with a 2D hexagonal arrangement and a 1nm unit cell (Figure 1c). This latter structure corresponds to the (√13x√13)R13.9° type I already reported [22,43]. Therefore, we can conclude that these stripes are precursors during the growth of the (√13x√13)R13.9°-type I structure.

Figure 2a shows another area of the sample. In addition to the 4x4 reconstruction and the new silicon stripes, domains corresponding to the (√13x√13)R13.9°-type II structure can be seen. It has been shown that both the type I and type II structures can coexist on the same surface [22]. However, an important new aspect is present. We observe areas of bare silver and silicene structures coexisting on the same terrace. The line scan L1 in Figure 2b shows a weak corrugation (around 0.02 nm) indicating that the silicon and Ag atoms are in the same plane. In comparison, the line scan L2 shows a step with a height of 0.22 nm height which is the expected value for an inter-atomic layer on Ag(111).

These experimental results indicate that the silicene does not form on the Ag (111) surface by adsorbing on the unmodified silver substrate. We observe that the bare silver regions are always located within the
terrace, away from the step edge. In other words, below the edge of a higher terrace. In addition, some islands are observed close to the step edges or among the silicene region, but never on the bare silver surface. Therefore, we can assign these islands to the silver atoms expelled from their initial location. This can be explained by the diffusion of the expelled silver atoms across the terrace to the step edge. This implies that an exchange between the silicon and silver atoms has taken place so that the silicene structures develop on the same level as the silver. Such a scenario has been proposed in the literature [24]. It was argued that the released adsorption energy of a Si atom allows the diffusion of this atom on the Ag(111) surface and its substitution with a Ag atom of the topmost layer. The excess energy may also favor the diffusion of the expelled Ag atoms, explaining the propagation of the silver step edges during the growth of silicene [25]. Recent studies of germanium adsorption on Au(111) and Al(111) using ion scattering techniques show that the Ge atoms coexist with the metal atoms in the topmost layer [44-45]. These results support a number of previous studies that had proposed or raised the question of the formation of a 2D surface silicide or germanicide on the Ag, Al, Au, and Pt surfaces [11,16,18-19,38,40].

The present STM measurements confirm a mechanism of exchange between Si and Ag atoms leading to the growth of silicene on Ag(111) substrate at temperatures higher than room temperature. In addition, our data suggest that the first steps of silicene growth start at the step edges. The silicene domain then extends further across the whole terrace. Therefore, silicon atoms are likely to exchange with silver atoms located at the step edges. Thus, it is quite reasonable to propose that at elevated sample temperatures, expulsion and diffusion processes produce an intermediate mixed top layer that evolves into the commonly observed 2D silicene reconstructions.

Figure 2: (a) 60x60nm² STM image recorded at -1.7V and 0.3 nA showing the coexistence of the bare silver with the striped silicon structures on the same terrace. The expelled silver atoms form islands that are highlighted by the black circles. (b) and (c) show the line profiles of the bare silver surface and the step height, respectively.

4. Conclusion

We have studied the growth of silicene on Ag(111) substrate in the sub-monolayer range using STM. It was possible to identify different domains of silicene, as well as domains of bare silver substrate, within the same topography. A detailed analysis of these domains reveals that silicon atoms exchange with surface silver atoms. In addition, the growth mechanism of silicene starts from the step edges of the substrate. Different nucleation sites on the step edges are probably responsible for the formation of different domains of silicene of nanometric size. This study shows that the initial growth of the silicene structures proceeds via the expulsion and diffusion of the metal atoms during an intermediate stage.
where a mixed topmost layer containing both Si and Ag exist. This supports the observations in a number of recent studies of mixed Si-metal or Ge-metal surface 2D alloy phases.

5. References

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