Applied Surface Science 291 (2014) 93–97

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Silicene on metal substrates: A first-principles study on the emergence of a hierarchy of honeycomb structures

D. Kaltsas [a,*], L. Tsetseris [a], A. Dimoulas [b]

[a] Department of Physics, National Technical University of Athens, GR-15780 Athens, Greece
[b] National Center for Scientific Research "Demokritos", GR-15310 Athens, Greece

ARTICLE INFO

Article history:
Received 21 June 2013
Received in revised form
15 September 2013
Accepted 18 September 2013
Available online 25 September 2013

Keywords:
Silicene
Graphene
Deposition
Ab-initio
DFT
Monolayer

ABSTRACT

Experimental studies have reported several types of Si monolayer structures that are formed on metal surfaces. These structures typically show the topology of a honeycomb bonding network, but differ in terms of corrugation and surface coverage. Using first-principles calculations, we identify atomic-scale mechanisms that underlie the appearance of different configurations as coverage increases during Si deposition on silver. The key point is that any extra Si adatoms that land on preformed silicene films can be incorporated in the honeycomb network and form bonds with underlying Ag atoms. As a result, the corrugation profile changes, giving rise to varying overlayer geometries. We also show that the same set of mechanisms control the appearance of silicene films on an iridium substrate. The results address available experimental data, but also probe the stability and properties of silicene wetting films that have not been observed yet.

1. Introduction

Silicene, the Si-based analog of graphene, has received intense interest lately, driven mostly by the observation [1–7] of Si honeycomb films on silver substrates. Given that the honeycomb geometry is related to some of the exceptional properties of graphene [8–10], there is strong motivation to investigate whether changing the type of atom from carbon to silicon (or germanium) might give rise to novel physical phenomena. Naturally, a first step in this direction is the actual growth of honeycomb silicon and the characterization of its physical traits.

Important knowledge about silicene can be derived through studies of free-standing films that have no interactions with other systems. In this respect, density-functional theory (DFT) calculations have shown that honeycomb silicon, though not the lowest energy monolayer configuration of Si [11], is a stable structure [12,13] with linear electron dispersion at the K points of the first Brillouin zone (BZ) [13–16]. In contrast to graphene, silicene is not flat, but has a certain buckling profile [12]. According to scanning tunneling microscopy (STM) pictures [1–5,17], Si overlayers on silver and other metal substrates have even higher levels of corrugation than free-standing silicene. Variations in the registry of the Si overlayer atoms with respect to the underlying sites of the metal surface affect the buckling pattern and give rise to distinct two-dimensional Si lattices. DFT studies [1–5] have confirmed the stability of several different Si honeycomb overlayers, proposed partial Si–Ag hybridization [18,19], and found corrugated profiles in satisfactory agreement with experiments. One key issue, however, that ought to be clarified is the mechanism (or mechanisms) that is responsible for the plethora of Si overlayer structures on silver and, possibly, other metals.

In a recent study [20] we used DFT calculations to address the issue of polymorphism for Si wetting layers on silver surfaces. We found that the arrival of Si atoms on top of existing overlayers, or on bare Ag surface parts, is followed by the incorporation of these adatoms within a honeycomb network. In this article, we extend the scope of the study by examining the feasibility of the adatom incorporation process for other Si wetting polymorphs on Ag. Furthermore, we show that a similar scenario holds true for the case of silicene formation on iridium. Overall, the results reveal that the moderate levels of interaction between Si and Ag or Ir, combined with the flexibility of the Si wetting layer in accommodating Si adatoms through variations in buckling, account for the formation of a hierarchy of honeycomb overlayers as surface density increases during Si deposition.

2. Method

The results were obtained with the DFT code VASP [21], a plane-wave basis with an energy cutoff of 250 eV, and

* Corresponding author. Tel.: +30 210 7722906.
E-mail address: kaltsasd@gmail.com (D. Kaltsas).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.09.115

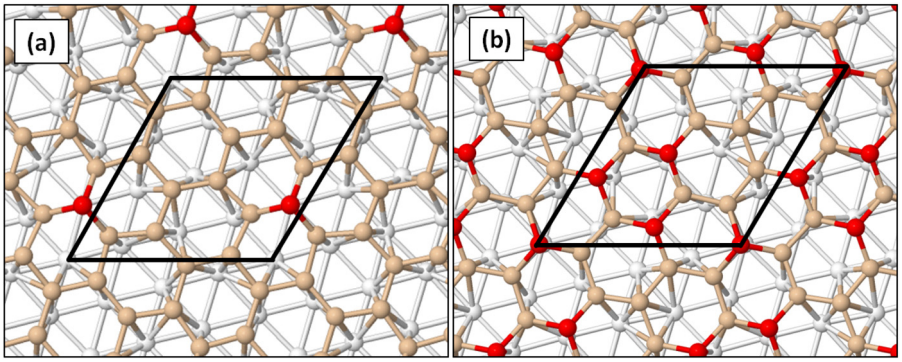

Fig. 1. (a) Type I, and (b) type II structures of $\sqrt{13} \times \sqrt{13}$ R13.9° monolayers on Ag with areal density $\lambda = 0.149$ Si atoms/Å^2. Lines show the unit cell and dark (red) spheres represent Si atoms at higher positions [Si: gray (dark yellow) and dark gray (red), Ag: light gray spheres]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

projector-augmented waves [22]. The exchange and correlation interactions were described with a generalized-gradient approximation (GGA) functional [23]. Supercells were used to simulate the growth of Si overlayers by including the metallic substrate in the form of a four-layer slab. The atoms of the bottom slab layer were not allowed to relax, whereas all other atoms were equilibrated so that the total energy of the system converged within 10^{-4} eV. Selected calculations with a five-layer Ag slab led to the same conclusions. The first BZ of the system was sampled [24] with a grid of $4 \times 4 \times 1$ k-points, wherein the third component is associated with the direction that is normal to the surface. As in previous DFT studies [25,26] on graphene and Si-based systems [27,28], total energy differences were used to assess the relative stability of structures and, concomitantly, the thermodynamic tendency for transformations between different geometries as deposition proceeds. Selected tests showed that the energy differences are well converged with respect to the energy cutoff and the size of the k-grid.

3. Results and discussion

In the following we describe the results for various Si overlayer structures on Ag(1 1 1) and Ir(1 1 1) substrates. We start with results on the stability of a number of structures that have been reported in previous studies about Si deposition on Ag. We then present results on the relative stability of these structures on Ir.

3.1. Silicon on silver

Fig. 1 shows two possible monolayer films with 14 Si atoms over a $\sqrt{13} \times \sqrt{13}$ R13.9° Ag surface area (hereafter denoted as $\sqrt{13} \times \sqrt{13}$-I for Fig. 1(a) and $\sqrt{13} \times \sqrt{13}$-II for Fig. 1(b)). This coverage corresponds to an areal (surface) density $\lambda = 0.149$ Si atoms/Å^2, the lowest value for all structures discussed in this work. General structural features of the configuration shown in Fig. 1(a) are in agreement with those in previous DFT studies [5,6], in particular the existence of a continuous honeycomb network and the periodicity. Small differences exist with respect to buckling. We found that one Si atom lies at a height of 3.25 Åabove the substrate, whereas the heights of the remaining Si atoms are 2.26 Å. Their difference of 0.99 Ådefines the buckling (or corrugation) level as the vertical distance between the highest and lowest Si atoms of the structure. The type II configuration of Fig. 1(b) has four protruding Si atoms per unit cell with a buckling of around 0.80 Åas in other DFT studies [5,7]. Type II structure is marginally more stable than Type I configuration by 0.14 eV per unit cell.

Next in line for Si mono-layer structures with increasing coverage is the 4×4 configuration. In fact, two such structures [3,4] have been reported in STM experiments and analyzed with DFT studies [3,4,20]. Their surface density is 0.155 Si atoms/Å^2 with 18 Si atoms in a unit cell. In the case of Si deposition of Ag these two configurations have almost the same energy. For this reason, we will not differentiate between the two in the following discussion about transformations between Si overlayer films.

Finally, the densest Si honeycomb monolayer observed [1] is the $2\sqrt{3} \times 2\sqrt{3}$R30° structure (or simply $2\sqrt{3} \times 2\sqrt{3}$), the structural features of which have been analyzed with DFT calculations [1,20]. It has 14 Si atoms in its unit cell and an areal density of 0.161 Si atoms/Å^2.

In order to understand the reason why polymorphism occurs for Si monolayers on Ag(1 1 1) we need to analyze the main processes active during deposition of silicon. These processes are the arrival of Si atoms on the surface (either on bare parts of the metallic substrate, or on silicene patches), and their subsequent interactions among themselves and with the Si wetting film. It is well known that adatoms play an important role for various processes on graphene and other nano-systems [29,30]. In the systems of interest here they also play a key role as they facilitate transformations from Si structures of lower areal densities to configurations with higher surface coverage.

Theoretical calculations [20] have shown that when two Si adatoms on top of the 4×4 structure interact, they form a stable dimer with a binding energy of around 0.39 eV. For the $\sqrt{13} \times \sqrt{13}$ structure the opposite was found to be true, i.e. isolated adatoms where found to be more stable than an ad-dimer pair with an energy difference of around 0.17 eV. In both cases, these extra atoms on top of the overlayer can then interact further with the silicene sheet and be incorporated in the honeycomb network. Though the actual details of how this incorporation proceeds can be complex (they relate to a phase transition with long-range changes that cannot be probed with DFT calculations), there is a simple test to decide whether a particular transformation of a low-density structure A to a denser configuration B is energetically favorable. This test is the sign of the following energy difference

$$\Delta E_A^B = \alpha \times E_B - (\beta \times E_A + \gamma \times E_C), \quad (1)$$

where E_A and E_B are the total energies (absolute values) of the unit cells of structures A and B. E_C is the total energy (absolute value) of a unit cell of structure A with a Si ad-dimer (for the 4×4 case) or a Si adatom (for the $\sqrt{13} \times \sqrt{13}$ case). The multiplicative factors α, β, and γ (normalized with the total number of silicon atoms) are selected for each particular A–B pair so that a number of α unit cells of structure B contains the same number of Si and Ag atoms as the combination of β unit cells of pristine structure A and γ unit cells of structure A with a Si ad-dimer (adatom) for the 4×4 ($\sqrt{13} \times \sqrt{13}$) case. Positive ΔE_A^B values indicate that it is