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Absence of Dirac cones in monolayer silicene and multilayer Si films on Ag(111)

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ABSTRACT

Monolayer silicene and multilayer silicon films on Ag(111) have been the subject of many investigations within the last few years. For both systems, photoemission data have been interpreted in terms of linearly dispersing bands giving rise to the characteristic Dirac cone features, similar to graphene. Here we demonstrate, on the basis of angle-resolved valence band and core level photoemission data that this assignment is not correct. The bands previously attributed to states with Dirac fermion character are shown to derive from Ag(111) interface and bulk states in the silicene monolayer and from the well-known Ag-($\sqrt{3}\times\sqrt{3}$)R30°-Si(111) structure in Si multilayers. These results question the validity of the claim that graphene-like silicene and silicene multilayers are in fact formed on Ag(111).

1. Introduction

The discovery of graphene with its rich physical properties has sparked tremendous interest towards the study of other two-dimensional (2D) materials with honeycomb structure [1]. It was believed that a free-standing 2D sheet with long range order cannot exist in nature due to the thermal fluctuations, inducing melting of the 2D sheet into a three-dimensional (3D) material [2]. However, graphene has been shown to be stable as a 2D material and has emerged with a different physics that connects quantum electrodynamics and condensed matter physics [3]. This has motivated exploration of the electronic structure of other group IV elements, in the form of either free-standing or supported monolayers. In this context, silicene, a 2D honeycomb lattice of silicon, has been studied extensively in the last few years.

Silicene [4] is theoretically predicted to be stable as a free standing monolayer in a low buckled geometry and is expected to display Dirac cones like graphene [5–8] with a comparable group velocity [9], and thus may form the basis for a multitude of applications [10]. While free-standing silicene has not so far been realized, Si deposition on different surfaces has been pursued as an alternative method to synthesize silicene. The formation of honeycomb silicene monolayers (ML) has been reported on Ag(111) [11–21], $ZrB_2(0001)$ [22,23], and Ir(111) [24] surfaces. Si films on Ag(111) [13–21,25] have been studied most extensively. In the monolayer and sub-monolayer range, Si forms a mixture of (4 × 4), ($\sqrt{13}\times\sqrt{13}$)R13.9° and ($2\sqrt{3}\times2\sqrt{3}$)R30° (w.r.t. Ag(111) unit cell) reconstructed phases [26], depending on the growth parameters. Such structures present different atomic buckling, arising from the registry relations between silicene and the Ag lattice.

A main open question in silicene research concerns the strength of interfacial interactions and how silicene electronic structure is affected by them. In particular, it has been debated whether the characteristic Dirac cones formed by the π-symmetry bands [16], showing linear dispersion similarly to graphene, are preserved for the case of supported silicene [27]. Even though we show that honeycomb lattice of Si monolayer on Ag(111) does not exhibit such features in their band structure, we will adhere to the usage of "silicene" for these structures in line with the literature, but this point should be kept in mind in the discussion.

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The most simple and best characterized monolayer silicene phase on Ag(111) shows a (4 × 4) structure. Angle-resolved photoemission spectroscopy (ARPES) on this phase allowed a substrate-modified Dirac cone of π-band at the $\bar{K}_{Si}$ point to be identified as opening a gap at 0.3 eV below Fermi energy (E_F) [16]. A similar π-band Dirac cone feature was also claimed to be found at the $\bar{M}_{Ag}$ point of the Ag surface [28] and at the equivalent points of the (4 × 4)-silicene Brillouin zone centers. However, the absence of Landau levels in scanning tunneling spectroscopy (STS) measurements under high magnetic field [21], and theoretical calculations [21,29–31] questioned this interpretation. In addition to the monolayer case, ARPES studies on multilayer Si films on Ag(111) assigned certain spectral features observed near E_F to the presence of Dirac cones. This claim was taken as evidence for a weak interaction between the Si planes, and led to the description of the film as multilayer silicene [32–35]. Such Si films, in excess of one ML, present a $(\sqrt{3} \times \sqrt{3})$R30° reconstructed surface in low energy electron diffraction (LEED) with respect to an ideally flat silicene lattice [15,17–19,32]. Theoretical studies have proposed that the multilayer structure consists of a stacking of dumbbell patterned Si layers with a $(\sqrt{3} \times \sqrt{3})$R30° periodicity [36], with stronger in-plane than out-of-plane bonding. However, the calculated band structure presents a band gap larger than in diamond-like Si, in contrast with the ARPES results [32]. Moreover, scanning tunneling microscopy (STM), STS, atomic force microscopy (AFM), core level photoemission, LEED-IV and Raman measurements, indicate that the Si films have a Ag terminated diamond-like Si(111) structure [37–44]. In order to dispute the ARPES results that were in conflict with the silicene multilayers, it was suggested that multilayer silicene on Ag(111) might only be fabricated in a narrow temperature range [45].

To assess whether silicene and Si multilayers display Dirac cones, as claimed by other photoemission investigations, we have performed extensive ARPES investigations, complimented by LEED, low-energy electron microscopy (LEEM), core level photoemission measurements as well as band structure calculation analysis. Our experiments allowed us to unambiguously clarify the nature of Si-Ag interfacial interactions and their relation to the silicene electronic structure. ARPES on a (4 × 4) silicene monolayer highlights the effects of Si-Ag interaction at the interface. In the following, we will show that, due to hybridization with the Ag states, the silicene states with π-symmetry lose their 2D character, resulting in the disruption of the Dirac cone. For Si multilayers grown on Ag(111) we find that the band structure of the films closely corresponds to the one of the $(\sqrt{3} \times \sqrt{3})$R30°-Ag terminated Si(111) surface, in line with the conclusions of structural investigations.

2. Experimental methods

The clean Ag(111) surface was prepared by cycles of Ar^+ sputtering and UHV annealing at ~830 K. The order and cleanliness of the surface was confirmed by LEED. Si was deposited by resistive heating of a Si wafer at a rate of 0.01 ML/min on Ag(111), in accordance to the rate used in other studies [12,13,17,18,21]. Here one monolayer of Si is defined as the quantity corresponding to the completion of the Si wetting layer at ~500 K, according to Ref. [26]. Multilayer Si films were grown at ~470 K. The $(\sqrt{3} \times \sqrt{3})$R30°-Ag/Si(111) surface was prepared by deposition of ~1 monolayer of Ag onto clean Si(111)-(7 × 7) surface at room temperature, followed by annealing to ~870 K.

LEED and LEEM measurements were carried out using the SPELEEM (Spectroscopic PhotoEmission and Low Energy Electron Microscope) instrument at the Nanospectroscopy beamline of the Elettra synchrotron [46]. The electron source is a LaB_6 cathode, with 0.4 eV energy spread. The transfer width of the instrument is about 130 Å. In the diffraction mode, the incident electron beam is limited to a micron-sized area by using an illumination aperture. In LEEM imaging, the lateral resolution is about 10 nm. By inserting an angle-selecting aperture in the diffraction plane, dark-field imaging (df-LEEM) can be performed in order to map out structural domains characterized by distinct LEED patterns.

The ARPES and core level photoemission spectroscopy measurements reported here were performed at the VUV-Photoemission beamline of the Elettra synchrotron using a Scienta R4000 electron spectrometer. In these measurements the spectrometer was placed at an angle of 45° with respect to the direction of the p-polarized photon beam. Photoelectrons were collected within the light scattering plane. All photoemission measurements were performed at room temperature with an angular resolution better than 0.3° and an energy resolution of 30 meV. Core level data were acquired at photon energy of 150 eV for the Si 2*p* and 430 eV for the Ag 3*d* core level. ARPES spectra of monolayer and multilayer Si were measured using 126 eV and 135 eV photon energy. The binding energy was calibrated by determining E_F on a clean Ag(111) surface. Ab-initio band structure calculations were performed using the VASP code [47] with the GGA-PBE exchange-correlation potential [48] and including van der Waals interactions in the semi-empirical method of Grimme [49].

3. Results and discussion

3.1. Growth characterization: (4 × 4) and $(\sqrt{13} \times \sqrt{13})R13.9°$ structures

Silicene on Ag(111) presents a mixed phase structure, with proportions depending on coverage and deposition temperature [26]. In LEED, all these structures exhibit the same lattice constant, but may be rotated at different angles with respect to the Ag(111) substrate. Fig. 1 shows the evolution of the LEED pattern taken at electron energy of 31 eV as a function increasing Si coverage at 500 K. As can be seen, the initial (1 × 1) pattern of the clean Ag substrate quickly evolves into a superposition of several hexagonal patterns closer to the specular (00) spot, matching the lattice unit of Si. At 1ML Si coverage, two prominent structures are clearly visible: a (4 × 4) pattern aligned with the Ag(1 × 1) unit vectors, and a $(\sqrt{13} \times \sqrt{13})$R13.9° pattern with two equivalent domains symmetrically placed close to the (4 × 4) spot. The angle between the $(\sqrt{13} \times \sqrt{13})$R13.9° and the (4 × 4) lattices is about 5°. At higher temperature, another rotational silicene domain, $(2\sqrt{3} \times 2\sqrt{3})$, becomes visible (not shown in the figure). Importantly, the surface is never uniformly covered with a single silicene phase at any temperature or coverage. Upon completion of the silicon monolayer, additional spots appear at locations corresponding to the $(\sqrt{3} \times \sqrt{3})$R30° structure in the basis of the Si lattice. The new spots are marked in Fig. 1(d) by a dashed hexagon. A close inspection of the azimuthal profile of the new pattern clearly reveals the emergence of this $(\sqrt{3} \times \sqrt{3})$R30° structure, corresponding to each rotational Si domain ((4 × 4) and $(\sqrt{13} \times \sqrt{13})$R13.9°). The $(\sqrt{3} \times \sqrt{3})$R30° structure is identified with two layer silicene on Ag(111) [26]. A detailed structural study on the growth of different phases of silicene on Ag(111) as a function of the deposition temperature and coverage using LEED, LEEM has been reported elsewhere [26].

Fig. 2(a) displays the LEED pattern of silicene on Ag(111) grown at ~500 K comprising intense (4 × 4) and relatively broad and weaker $(\sqrt{13} \times \sqrt{13})$R13.9° spots, due to azimuthally disordered domains. Fig. 2(b) shows maps of different Si rotational domains. The LEEM image on the right panel highlights the (4 × 4) and $(\sqrt{13} \times \sqrt{13})$R13.9° domains, which cover almost the entire surface. Note that the two rotational $(\sqrt{13} \times \sqrt{13})$R13.9° domains are seen with

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