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Interaction of epitaxial silicene with overlayers formed by exposure to AI atoms and O2 molecules

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Interaction of epitaxial silicene with overlayers formed by exposure to AI atoms and O₂ molecules

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As silicene is not chemically inert, the study and exploitation of its electronic properties outside of ultrahigh vacuum environments require the use of insulating capping layers. In order to understand if aluminum oxide might be a suitable encapsulation material, we used high-resolution synchrotron photoelectron spectroscopy to study the interactions of Al atoms and O₂ molecules, as well as the combination of both, with epitaxial silicene on thin $ZrB_2(0001)$ films grown on Si(111). The deposition of Al atoms onto silicene, up to the coverage of about 0.4 Al per Si atoms, has little effect on the chemical state of the Si atoms. The silicene-terminated surface is also hardly affected by exposure to O₂ gas, up to a dose of 4500 L. In contrast, when Al-covered silicene is exposed to the same dose, a large fraction of the Si atoms becomes oxidized. This is attributed to dissociative chemisorption of O₂ molecules by Al atoms at the surface, producing reactive atomic oxygen species that cause the oxidation. It is concluded that aluminum oxide overlayers prepared in this fashion are not suitable for encapsulation since they do not prevent but actually enhance the degradation of silicene. (© 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4878375]

INTRODUCTION

A new quasi-2D crystalline form of silicon, featuring Si atoms in a honeycomb lattice with a characteristic out-ofplane atomistic buckling, is currently receiving a lot of attention from theorists and experimentalists alike.¹⁻⁷ In analogy with its carbon-based analogue, graphene, this 2D form has been coined silicene.⁸ The interest in silicene is mainly due to its predicted exceptional electronic properties, which have much in common with those of graphene but also exhibit several important differences. Like in graphene, the electronic bands in yet hypothetical free-standing silicene host Dirac fermions near the Fermi energy. Unlike graphene, however, silicene is buckled at the atomic scale due to the relative instability of the sp^2 -hybridized state, such that the two sublattices that make up the hexagonal sheet are displaced in the out-of-plane direction. Hence, under application of an out-ofplane electric field, a band gap can be induced in silicene, but not in graphene. In addition, spin orbit coupling (SOC) in silicene is much larger than in graphene (SOC scales with the fourth power of the atomic number) such that the SOCinduced topological phase transition to the quantum spin Hall insulator (QSHI) phase^{3,4} should occur at much higher temperatures. The QSHI, characterized by helical edge states, is of particular interest, since it may lead to the emergence of Majorana fermions,9 and to a spin accumulation at the edges of a sheet when a charge current is passed through. The former may have far reaching implications for topological quantum computing, while the latter is highly interesting for spintronics.

Free-standing silicene has not yet been fabricated, but epitaxial silicene layers, also characterized by a buckled honeycomb lattice of Si atoms, have been prepared on several metallic surfaces, such as Ag(111),^{5,10,11} ZrB₂(0001),⁶ and Ir(111).⁷ This progress allows for the experimental investigation of many intriguing properties of such 2D Si lattices that are different from those of free-standing silicene.⁶ In this work, we focus on the chemical properties of epitaxial silicene on thin ZrB₂(0001) films prepared on Si(111) wafers.

Unlike graphene, silicene is not chemically inert, and it will have to be protected from degradation if it is to be used (or studied) outside ultra-high vacuum environments. Therefore, the silicene sheet will have to be sandwiched between other materials, ideally without perturbing its electronic properties. For any future electronic application exploiting quantum effects, the use of semiconducting or insulating (dielectric) substrates and capping layers is desired. As suggested recently, based on a study of epitaxial silicene on Ag(111) covered by a few nanometers of oxidized aluminum,¹² capping layers may possibly prevent oxidation of the electronically active silicene layer under ambient conditions.

Here, we report on the results of an experiment designed to reveal the details of the individual interactions of Al atoms as well as of O_2 molecules, and of the combination of both, with epitaxial silicene on thin $ZrB_2(0001)$ films grown on Si(111). The evolution of chemical changes of the epitaxial silicene layer resulting from these interactions was studied by high-resolution core-level photoelectron spectroscopy (PES), while the surface reconstruction was monitored with low energy electron diffraction (LEED).

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EXPERIMENTAL

Single-crystalline zirconium diboride films were grown on Si(111) substrates by ultra-high vacuum chemical vapor epitaxy, as described elsewhere.¹³ All subsequent sample preparation steps and measurements were carried out at beam line D1011, located at the MAX-lab synchrotron radiation facility in Lund, Sweden. The end station at D1011 is comprised of (i) an analysis chamber (base pressure $< 10^{-10}$ mbar), equipped with a Scienta SES200 hemispherical analyzer for PES measurements, (ii) a preparation chamber (base pressure $<10^{-10}$ mbar) allowing for sample treatment by ebeam heating, Al deposition, and exposure to oxygen gas, and (iii) a load lock (base pressure $<10^{-7}$ mbar) for fast sample transfer. Following the ex situ transfer of samples to beam line D1011, native oxides were removed by annealing at about 780 °C resulting in the formation of a well-defined silicene layer by surface segregation.⁶ The samples, held at room temperature, were exposed to an Al flux produced by a well-degassed, mini e-beam evaporator. A quartz crystal microbalance was used to monitor the Al flux, while absolute flux calibration was carried out in a separate experiment, using the well-documented Si(111)-(7 × 7) to $\sqrt{3} \times \sqrt{3}$ phase transition at a coverage of about 1/3 of an Al monolayer (ML), occurring upon annealing at 800 °C.^{14,15} The error in the absolute flux calibration is conservatively estimated as $\pm 15\%.$

Both pristine silicene, as well as silicene covered with about 0.4 Al per Si atoms, were exposed to O_2 gas at particular doses, leaked into the preparation chamber of the end station using a variable leak valve. After each sample preparation step, the samples were characterized by LEED and by PES. Si 2p and Al 2p spectra were recorded with the photon energy hv = 130 eV, while O 1s spectra were measured with hv = 600 eV. For the spectra taken with hv = 130 eV, intensity variations and energy offsets caused by varying beam line settings and ring conditions have been traced by taking several Si 2p spectra for each preparation step. In between sample preparation steps, beam line settings remained unchanged. Additionally, the intensities have been normalized to the photon flux as measured with a gold grid mounted in the beam line.

RESULTS AND DISCUSSION

Fig. 1 shows the Si 2p and Al 2p spectra of Al on silicene with increasing Al coverage up to the Al/Si ratio $x = 0.38 \pm 0.06$. For comparison, the Al 2p spectrum of 0.35 ± 0.05 MLs of Al on a Si(111) surface is also shown. Note that a



FIG. 1. (a) Si 2*p* spectra of epitaxial silicene on ZrB₂(0001) thin films for several stages of Al coverage, from x = 0 (pristine) to $x = 0.38 \pm 0.06$ Al per Si atoms. (b) The corresponding Al 2*p* spectra, plus an Al 2*p* spectrum of 0.35 ± 0.05 MLs of Al atoms (corresponding to x = 0.175) on the Si(111) surface. (c) Zoom-in of the Si $2p_{3/2}$ feature of the spectra in (a), where all spectra have been normalized to the same maximum height to allow for an easier observation of small peak shifts. Arrows indicate the order of increasing *x*, dashed lines are guides to the eye. All spectra have been offset for clarity.

bilayer at the Si(111) surface corresponds to a honeycomb layer of silicene, assuming similar areal densities. Therefore, 0.35 MLs of Al on Si(111) correspond to x = 0.175 Al per Si atoms of the bilayer.

As we have discussed in detail previously,¹⁶ the Si 2*p* doublet of pristine silicene is composed of at least four components that correspond to different atomic positions within and at the boundaries of stress-related stripe domains of silicene on the ZrB₂ surface. Only two of these components are resolved in the Si 2*p* spectrum. The most intense $2p_{3/2}$ feature, at the binding energy of 98.98 eV, has major contributions from Si atoms in bridge-positions near Zr-atoms, in so-called "B sites" while the weaker component at 98.72 eV derives largely from Si atoms occupying hollow sites ("A sites").^{6,16} Only slight traces of surface oxides could be detected within the high binding energy tail of the spectrum. LEED images (not shown) exhibited a similar (2 × 2) pattern as observed previously for silicene on ZrB₂ consistent with a ($\sqrt{3} \times \sqrt{3}$) reconstruction of the silicene sheet.¹⁷

As shown in Figs. 1(a) and 1(c), the effects of Al deposition on the Si 2p spectra are rather small, indicating a weak interaction between the Al atoms and silicene. Besides a suppression of the integrated Si 2p intensity, due to inelastic scattering of photoelectrons by Al atoms on top the silicene layer, the main effect is a broadening of the spectrum. This is likely due to the inhomogeneous bonding between Al and Si atoms. Note that, in contrast to previous experiments on rather thick Al capping layers prepared on silicene on Ag(111) substrates,¹² no Al-related peak at the high-binding energy side of the Si 2p lines (at the binding energy of about 103.5 eV) is present in our spectra. This particular spectral feature is likely due to a bulk-related electron energy loss peak, characteristic for metallic aluminum,¹⁸ and associated with the Al 2p line. Note that this bulk plasmon feature is quenched upon oxidation.¹⁹ Since it is a feature related to the bulk of metallic aluminum, it is not expected to occur for both fully oxidized aluminum films and sub-monolayer thin films studied in our experiment.

The Al 2p lines themselves are very broad (Fig. 1(b)), which reflects the presence of different chemical states of Al atoms on top of silicene. In contrast, for the $(\sqrt{3} \times \sqrt{3})$ phase of Al on Si(111), obtained after annealing, 14,15 the sharpness of the Al 2p lines (see lower panel of Fig. 1(b)) is associated with a well-defined chemical environment of the Al atoms. It can thus be concluded that at room temperature, Al atoms adopt various adsorption sites on the atomically buckled silicene lattice. The integrated Al 2p intensity as a function of the deposition time is shown in Fig. 2. Since the intensity is not proportional to x, we conclude that either some clustering of Al atoms occurs or that the line is suppressed by a small amount of oxygen atoms that are present due to the high reactivity of Al atoms. Note that with increasing x, the Al overlayer gets oxidized to a minor degree, most probably due to a small amount of oxygen-containing species released by the Al source. Exposure to O₂ molecules, on the other hand, results in the complete oxidation of the Al overlayer, as is shown further below.

LEED images do not show any changes upon Al deposition other than a slight suppression of the original spots of



FIG. 2. Al/Si ratio x as a function of the deposition time. Also shown are the O 1s and Al 2p intensities, normalized to the highest value, versus (a) Al deposition time and (b) O_2 exposure at two different doses. Dashed lines are guides to the eye.

the (2×2) -reconstructed ZrB₂ surface. The robustness of the LEED pattern as well as of the Si 2*p* line shape is consistent with only minor structural changes of the silicene sheet upon Al deposition at room temperature.

In addition to the spectral broadening of the Si 2p spectra of silicene upon Al deposition, subtle binding energy shifts can be observed in the zoom of the spectra in Fig. 1(c). After the first Al deposition leading to $x = 0.03 \pm 0.01$, the main $2p_{3/2}$ line, due to B-site Si atoms, shifts by about 0.03 eV towards higher binding energy, while a slightly smaller shift of 0.02 eV is observed for the low-binding energy peak that has major contributions from A-site atoms. This indicates that, initially, the Al ad-atoms prefer to interact with B-site rather than with A-site Si atoms, resulting in a slightly enhanced binding energy splitting of the corresponding peaks. As the Al coverage increases, this splitting again reduces, and all Si 2p lines shift back towards the initial binding energy positions of pristine silicene. The reduced splitting is most probably due to the occupation of less favorable bonding sites for Al atoms as the coverage increases, while the non-monotonic binding energy shifts may in part stem from changes in the electrostatic potential at the surface.

As shown above, deposition of Al atoms onto silicene leads to only minor changes in the Si 2p spectra and in the LEED pattern, indicating that the $\sqrt{3} \times \sqrt{3}$ -reconstructed and buckled silicene lattice remains largely intact. This behavior changes dramatically upon exposure of the Al-covered silicene to 4500 L of O₂ molecules. As visible in the disappearance of the low-binding energy, metal-like components in the Al 2p spectrum shown in Fig. 3(a), all of the Al atoms react with O atoms. Additionally, a broad Si 2p high-binding energy component appears (Fig. 3(b)) (at around 103 eV), indicating that a major fraction of between 1/3 and 1/2 of the Si atoms becomes oxidized. On the other hand, if pristine silicene is exposed to the same dose of O₂ molecules, the oxidized fraction is minor (Fig. 3(c)). This shows unambiguously that the presence of Al atoms at the surface of silicene



FIG. 3. (a) Al 2*p* and (b) Si 2*p* spectra of epitaxial silicene on $ZrB_2(0001)$ covered with Al atoms at Al/Si ratio $x = 0.38 \pm 0.06$, before and after exposure to particular O₂ doses: 100 L and 4500 L. (c) Si 2*p* spectra of pristine silicene before and after exposure to the same O₂ doses. All spectra have been offset for clarity.

increases the oxidation rate. It can thus be concluded that Al atoms act as a catalyst for the oxidation of silicene, rather than preventing it. This is most probably due to dissociative chemisorption of O_2 molecules by Al atoms at the surface, which is a well-known process for aluminum surfaces.^{20,21} The so-formed atomic oxygen species subsequently react with both Al and Si atoms, leading to the ternary surface oxides that we observe. In addition, an enhanced sticking probability for O_2 molecules could also play a role.

CONCLUSIONS

Using high-resolution synchrotron PES measurements, we have studied the interaction between epitaxial silicene on thin ZrB₂(0001) films on Si(111) substrates and Al atoms, O₂ molecules, and a combination of the two. The deposition of Al atoms onto silicene, up to a coverage of $x = 0.38 \pm 0.06$, has little effect on the chemical state of the Si atoms, the surface reconstruction and the buckling of silicene, indicating weak interactions between Al and silicene. The silicene-terminated surface is also hardly affected by an exposure to 4500 L O₂. Like for silicene nanoribbons²² and silicene sheets,¹² both prepared on Ag surfaces, our results show that silicene on zir-

conium diboride substrates resists oxidation to some extent as well. In contrast, when Al-covered silicene is exposed to the same O₂ dose, a large fraction of the Si atoms become oxidized. We ascribe this behavior to dissociative chemisorption of O₂ molecules due to the presence of Al atoms, producing reactive atomic oxygen species that cause the oxidation. Our results demonstrate unambiguously that, in contrast to conclusions drawn previously,¹² aluminum oxide overlayers formed by exposing silicene to Al atoms and O2 molecules simultaneously do not prevent, but actually enhance the degradation of silicene on $ZrB_2(0001)$ thin films. This clearly does not allow for an encapsulation of epitaxial silicene with so-prepared electrically insulating Al₂O₃ films, needed for the use in electronic devices under atmospheric conditions. This, however, does not exclude the possibility that another method for depositing Al₂O₃ could be less destructive to silicene.

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