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On the feasibility of silicene encapsulation by AlN deposited using an atomic layer deposition process

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Since epitaxial silicene is not chemically inert under ambient conditions, its application in devices and the *ex-situ* characterization outside of ultrahigh vacuum environments require the use of an insulating capping layer. Here, we report on a study of the feasibility of encapsulating epitaxial silicene on ZrB_2(0001) thin films grown on Si(111) substrates by aluminum nitride (AlN) deposited using trimethylaluminum (TMA) and ammonia (NH_3) precursors. By *in-situ* high-resolution core-level photoelectron spectroscopy, the chemical modifications of the surface due to subsequent exposure to TMA and NH_3 molecules, at temperatures of 300 °C and 400 °C, respectively, have been investigated. While an AlN-related layer can indeed be grown, silicene reacts strongly with both precursor molecules resulting in the formation of Si–C and Si–N bonds such that the use of these precursors does not allow for the protective AlN encapsulation that leaves the electronic properties of silicene intact. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4907375]

INTRODUCTION

Due to its predicted exceptional electronic properties, silicene, the silicon counterpart of graphene, has drawn increasing attention from theorists and experimentalists.[1–6] Similar to graphene, the so far hypothetical freestanding silicene is predicted to feature massless Dirac fermions near the Fermi energy.[1] However, contrary to graphene, since silicene is buckled at the atomic scale, under an out-of-plane electric field, the two sub-lattices forming the buckled structure of freestanding silicene are no longer equivalent and a band gap can be induced.[7,8] This makes silicene a promising material for future electronic applications. 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 SOC-induced topological phase transition to the quantum spin Hall insulator phase[2,3] should occur at much higher temperatures.

So far, freestanding silicene has not been synthesized and may not even be the most stable 2D Si allotrope,[9] but epitaxial silicene layers could be grown on several metallic surfaces such as Ag(111),[4,10,11] ZrB_2(0001),[5] Ir(111),[6] and ZrC(111).[12] This progress allows for the experimental investigation of many intriguing properties of the associated epitaxial silicene phases under ultra-high vacuum (UHV) conditions. However, in order to explore the electronic *transport* properties of silicene and its potential applications in electronic devices, the growth of silicene on semiconducting or insulating substrates is highly desired. Although several semiconducting substrates such as h-BN,[13] SiC,[13] aluminium nitride (AlN),[14] and ZnS[15] have theoretically been investigated and proposed, this task remains as one of the main challenges for experimentalists. In addition, as silicene is not chemically inert, a capping layer is needed for any *ex-situ* characterization, i.e., for handling outside UHV environments. Recently, it has been suggested that aluminum oxide (Al_2O_3) could be a suitable encapsulation material for silicene on Ag(111).[16] However, we have shown that forming such capping layers by exposing epitaxial silicene on ZrB_2 to Al atoms and O_2 molecules actually leads to enhanced oxidation of the silicene layer (as compared to the case where there are no Al atoms present at the surface).[17] This can be attributed to the dissociative chemisorption of O_2 molecules producing reactive atomic oxygen species.[18,19]

Besides Al_2O_3, another dielectric material, commonly used in, e.g., III-V semiconductor devices, is AlN. A theoretical study by Houssa *et al.* predicted that the sp^2-hybridization of the buckled silicene layer can be preserved when it is sandwiched by two thin graphite-like AlN layers.[14] This form of AlN has recently been synthesized on the Ag(111) surface.[20] Understanding the chemical interactions of silicene with AlN and/or with chemical precursors that can be used to grow thin AlN capping layers is, therefore, of particular importance and forms the main motivation of this work.

Here, we report on the feasibility of encapsulating epitaxial silicene on thin ZrB_2 films grown on Si(111) wafers by an AlN thin film, deposited by an atomic layer deposition (ALD) process. As is common in ALD of AlN films,[21] we employed subsequent exposure of the sample to the volatile precursors trimethylaluminum (TMA, $Al(CH_3)_3$) and ammonia (NH_3).[21] The evolution of the chemical bonding states of the relevant elements (i.e., Si, C, N, and Al) has been studied using *in-situ* high-resolution core-level photoelectron spectroscopy (PES).

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We focused on the initial stages of AlN growth, i.e., surface reactions between TMA molecules and the silicene-terminated surface, and subsequent exposure to NH_3 molecules, in both cases until saturation was reached. The surface reactions depend critically on the substrate temperature, which were chosen such that (i) the chemisorption of TMA molecules was self-limiting and (ii) sufficiently rapid chemical reactions between the adsorbed TMA-related species and NH_3 molecules occurred. In case of Si(100) surfaces, while the latter can only be obtained at a temperature above 300 °C,[22] self-limiting adsorption of TMA occurs only below 370 °C.[21] Since the chemical reactivity of our silicene-terminated surface with respect to Si(100) is unknown, we adopted a safe margin and chose substrate temperatures of 300 °C and 400 °C, during the exposure to TMA and NH_3 gas, respectively.

EXPERIMENTAL

Single-crystalline ZrB_2 films have been grown on Si(111) substrates by ultra-high vacuum—chemical vapor epitaxy (UHV-CVE), as described elsewhere.[23] All subsequent sample preparation steps and measurements have been 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} millibars) equipped with a Scienta SES200 hemispherical analyzer for PES measurements, (ii) a preparation chamber (base pressure < 10^{-10} millibars) allowing for sample treatment by e-beam heating, and exposure to TMA and NH_3 gases, and (iii) a load lock (base pressure < 10^{-7} millibars) for fast sample transfer. Following the *ex-situ* transfer of samples to beam line D1011, the native oxides have been removed by annealing at about 780 °C in UHV, resulting in the formation of a well-defined silicene layer by surface segregation.[5] In each particular experiment, the sample held at a temperature of 300 °C has then been exposed stepwise to gradually increasing doses of TMA gas at a pressure of 10^{-6} millibars, until the adsorption of TMA reached saturation. After each single exposure, the sample has been transferred to the analysis chamber for the PES measurements. Following the exposure to TMA, NH_3 gas was introduced at the same pressure (i.e., 10^{-6} millibars), keeping the sample at a temperature of 400 °C. The NH_3 exposures and PES measurements have been performed again in a stepwise manner until saturation has been reached. Finally, the samples were annealed at 830 °C in UHV for 30 min and again subjected to PES measurements. The Si $2p$ and Al $2p$ spectra have been measured with the photon energy of $h\nu$ = 130 eV, whereas for the C $1s$ and N $1s$ spectra, $h\nu$ = 500 eV has been chosen. The intensities have been normalized to the photon flux as measured with a gold grid mounted in the beam line.

RESULTS AND DISCUSSION

The Si $2p$ spectrum of the pristine silicene sample, shown in Fig. 1(a), exhibits the features characteristic of silicene on ZrB_2 thin films.[5] As we have discussed in detail previously,[24] the Si $2p$ doublet contains at least four components that

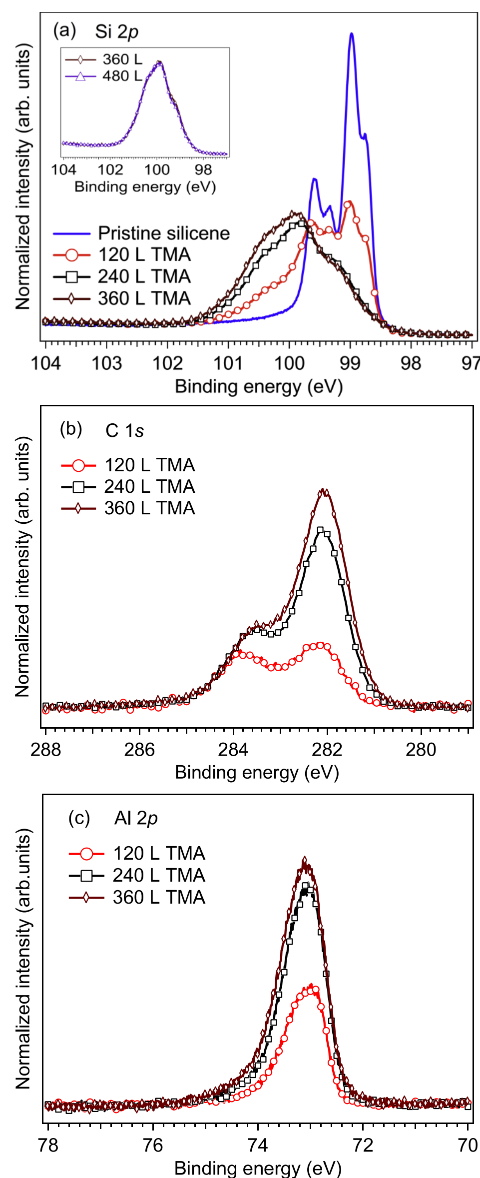

FIG. 1. (a) Si $2p$, (b) C $1s$, and (c) Al $2p$ spectra of epitaxial silicene on $ZrB_2(0001)$ thin films for different TMA exposures of up to 360 L, with the sample held at 300 °C. The inset in (a) shows the Si $2p$ spectra obtained after 360 and 480 L in total.

correspond to distinct chemical environments and positions of Si atoms on the $ZrB_2(0001)$ thin film surface, located either within or at the boundaries of stress-related stripe domains which are formed in order to avoid a critical phonon instability.[25] Only two of these components are resolved in the Si $2p$ 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 the so-called "B sites," while the weaker component at 98.72 eV derives largely from Si atoms occupying the hollow sites ("A sites").

The Si $2p$, C $1s$, and Al $2p$ spectra measured for different TMA doses (120, 240, and 360 Langmuir (L)) are plotted in Fig. 1. While after the exposure to 120 L of TMA, the Si $2p$ peaks of silicene (Fig. 1(a)) have been suppressed significantly, a broad shoulder appears at 100.4 eV. The presence of peaks related to unaffected silicene, albeit with reduced intensities,

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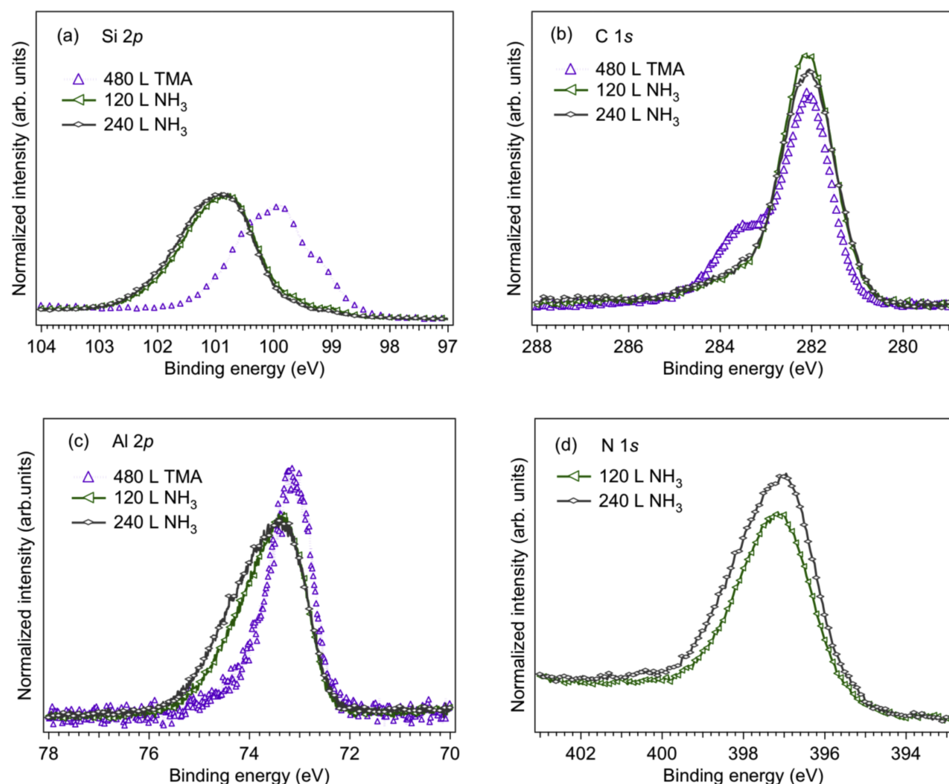

FIG. 2. (a) Si 2*p*, (b) C 1*s*, (c) Al 2*p*, and (d) N 1*s* spectra measured following the exposure to NH_3 gas at up to 240 L at a pressure of 10^{-6} millibars, the sample held at 400 °C. The up-triangles represent the spectra *prior* to the NH_3 exposure and are added for comparison.

suggests that, after this particular exposure, only part of the silicene surface is covered by TMA molecules. The shoulder at 100.4 eV is attributed to the formation of Si–C bonds caused by the dissociative adsorption of TMA molecules.[26] At 240 L, the characteristic silicene features are no longer observed. Instead, a new broad peak at 99.9 eV and a shoulder at 99.3 eV are found. The disappearance of the silicene features indicates not only that the surface is covered by TMA molecules or its fragments but also that a significant chemical reaction between the silicene surface and the adsorbing species occurred. The resulting Si 2*p* spectrum, showing main contributions at 100.4, 99.9, and 99.3 eV, clearly contains several components that originate from a number of chemical states of Si atoms formed due to interactions with adsorbed groups. Only minor changes have been observed after a total exposure of 360 L. At this point, the TMA adsorption has reached saturation. Following the further exposure up to 480 L, as shown in the inset of Fig. 1(a), the spectrum is unaffected. The observed saturation is evidence for the self-limiting nature of TMA adsorption on the silicene surface under the conditions studied. This is similar to the behavior reported by Mayer *et al.*[22] of self-limiting adsorption of less than 1 monolayer of TMA molecules on the Si(100) surface at temperatures below 370 °C.

In the C 1*s* spectra (Fig. 1(b)), two broad peaks at 283.8 and 282.2 eV are observed following the exposure to 120 L of TMA gas. These two peaks are assigned to distinctly different bonding configurations of C atoms. In analogy to previously reported studies of TMA adsorption on Si(100) surfaces at comparable temperatures,[22,27] upon dissociative adsorption of TMA molecules, one or more $–CH_3$ groups may split off. Based on these studies, the following peak assignments can be made: The peak at ~283.8 eV corresponds to C atoms in $–CH_3$ groups that are still attached to Al atoms, whereas the peak at ~282.2 eV may be attributed to C atoms in the split-off reaction products, involving $–CH_x$ groups bound to Si atoms. This picture is also consistent with the changes in the Si 2*p* spectra described above. The intensity ratio of the two C 1*s* peaks clearly changes with increasing TMA exposure. This suggests that the abundance of C atoms in the Si–CH_x species increases relative to the amount of $–CH_3$ groups that remain bound to Al atoms and may be explained by the release of volatile methane (CH_4) molecules formed in reactions between two or more of such $–CH_3$ groups. These reactions become more probable at higher adsorbate coverage. This mechanism is similar to the one proposed by Gow *et al.*[27] for TMA on Si(100), where the release of CH_4 molecules was detected by mass spectrometry.

A single broad Al 2*p* peak, centered at a binding energy of 73.1 eV (Fig. 1(c)), has been recorded for all TMA doses. Since the width of the Al 2*p* line of about 1.0 eV is slightly larger than that of Al atoms in a single chemical environment (like that of Al atoms adsorbed on the Si(111) surface of 0.8 eV[17]), it reflects the presence of various chemical states of Al atoms caused by the chemisorption of dissociative products on silicene. As expected, the C 1*s* and Al 2*p* peak intensities increase with longer TMA exposure, until saturation has been reached after a total dose of 360 L.

The observations described above are qualitatively similar to the adsorption of TMA on surfaces of diamond-structured silicon. On Si(100) substrates and at temperatures above 170 °C, TMA adsorption produces strong Si–C bonds (chemisorption of CH_x groups on Si sites) and weaker Al–Si bonds (chemisorption of $Al(CH_x)_y$ groups).[22,27,28] This might suggest

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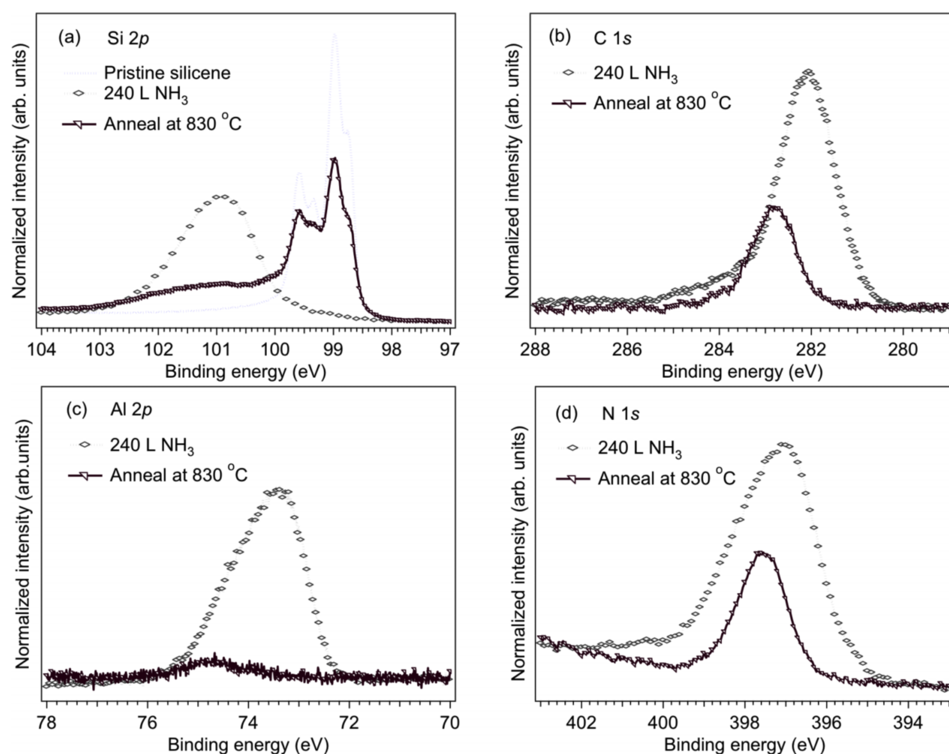

FIG. 3. (a) Si 2p, (b) C 1s, (c) Al 2p, and (d) N 1s spectra (solid lines) after annealing at 830 °C. The diamond markers represent spectra measured after NH_3 exposure and are added for comparison.

that the surface reactivity of epitaxial silicene on ZrB_2(0001) thin films towards TMA is not very different from that of the Si(100) surfaces. The comparison should be made with care, however, since the temperature that we used for the TMA exposure (300 °C) is considerably higher than the onset temperature for chemisorption of TMA on the Si(100) surface.

A following exposure of the sample to NH_3 gas at 300 °C showed extremely slow reactions between the TMA fragments and the NH_3 molecules. This motivated the choice of a higher temperature of 400 °C. Following the subsequent exposure at 400 °C to 120 L of NH_3 gas, as shown in Fig. 2(a), a broad Si 2p peak centered at 101.2 eV has been measured. This represents a significant shift of about 1.0 eV of the center of the spectral weight with respect to the spectra obtained after exposure to TMA molecules. At even longer exposure times, additional changes have then been minor which indicates that saturation has already occurred at 120 L.

On the other hand, when under identical experimental conditions, similar pristine silicene samples are directly exposed to NH_3 gas (without the prior exposure to TMA molecules), a broad Si 2p peak centered at about 101.2 eV has been measured (not shown).[29] It is obvious that this peak must originate from Si–N bonds. Since the peak maximum is located at lower binding energy for the case in which the surface has previously been exposed to TMA molecules, the direct reaction of NH_3 molecules with the TMA-exposed silicene surface cannot be the sole origin of the new feature. The Si 2p peak at 101.7 eV is then attributed to the presence of a mixed compound, also involving reactions between NH_3 molecules and previously formed Si–CH_x species.

Considerable changes are also observed in the C 1s and Al 2p spectra, as shown in Figs. 2(b) and 2(c). The C 1s peak at 283.8 eV (related to –CH_3 groups bound to Al atoms, see above) has been strongly attenuated, while the intensity of the peak at 282.2 eV (related to Si–CH_x species formed by the dissociative chemisorption of TMA) has been somewhat increased. This can be explained by (i) reactions between NH_3 molecules and the Al–CH_3 species on the surface, and (ii) the higher substrate temperature during the NH_3 exposure (400 °C). On one hand, reactions between the Al–CH_3 species and NH_3 result in partial replacement of Al–C by Al–N bonds, consistent with the shift and broadening of the Al 2p spectra shown in Fig. 2(c). This exchange reaction releases CH_4 as a by-product.[22] On the other hand, the increase of the substrate temperature might cause further dissociation of Al–CH_3 moieties and therefore an increased amount of Si–CH_x species. In addition, at this temperature, the NH_3 molecules can react with these Si–CH_x species, forming a mixed compound involving Si, C, and N atoms.[30] The broad N 1s spectra centered at 396.9 eV (Fig. 2(d)) suggest a distribution of chemical states of N atoms, which could include Si–N and Al–N bonds.

Upon increasing the NH_3 dose up to 240 L, the Si 2p spectrum has been hardly affected while the Al 2p peak has been broadened such that its spectral weight shifted slightly towards higher binding energy. The intensities of the Si 2p and Al 2p peaks remained nearly unchanged. No significant changes in the peak shapes of the C 1s and N 1s spectra have been observed although the N 1s and C 1s intensities increased and decreased, respectively, which points to the ongoing partial replacement of C by N atoms.

To sum up the results of the experiments at intermediate temperatures (of 300 °C to 400 °C) discussed so far, it becomes clear that the use of TMA and NH_3 precursors does not allow for the protective encapsulation of silicene on ZrB_2 thin film substrates that leaves the electronic properties of silicene intact.

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Instead of a capping layer, Si atoms form a complex compound that includes C, N, Al, and likely also H atoms; the details of which could not be resolved in our experiments.

After subsequent annealing of the sample in UHV at 830 °C, the Si 2p spectrum shown in Fig. 3(a) shows again the peaks characteristic of silicene at 98.98 and 98.72 eV while a broad feature remains at the high binding energy side. Strikingly, the Al 2p peak is almost completely suppressed (Fig. 3(c)), and the intensities of the C 1s and N 1s peaks are significantly reduced (Figs. 3(b) and 3(d)). This indicates that a considerable amount of Al, C, and N atoms have been removed. The decrease in intensity of the C 1s and N 1s peaks, the significant shifts of about 0.6 eV and 0.7 eV of these peaks towards higher binding energy, respectively, and the strong attenuation of the Al 2p signal and the broad feature between 100 and 103 eV in the Si 2p spectrum (Fig. 3(a)) all suggest that the remaining C and N atoms are bound to Si atoms. The reappearance of the characteristic Si 2p peaks at 98.98 and 98.72 eV, although with a lower intensity, indicates that silicene has been (partially) recovered on the ZrB_2 surface. The fact that the silicene-related features appear at the exact same binding energy as on the clean silicene-terminated surface strongly suggests that they correspond to silicene forming on the top-most surface, instead of being buried below the retained Si-C-N compound. The recovery of silicene might be explained by surface segregation of Si atoms upon annealing which may serve as a surfactant during the process of the removal of adatoms. This process is imagined to be similar to the initial silicene formation process where Si segregation is accompanied by the removal of surface oxides.[5] However, in this case, the annealing step does not completely remove the N and C species, which apparently are strongly bound to surface Si atoms. It is then impossible to control the creation of new silicene all over the surface. In any case, the high-temperature treatment does not lead to the non-reactive encapsulation of silicene either.

CONCLUSIONS

Using *in-situ* high-resolution core-level PES, we have investigated the feasibility of depositing an AlN capping layer on top of epitaxial silicene on ZrB_2 thin films on Si(111) substrates, using TMA and NH_3 as precursors. Exposing the sample held at 300 °C to TMA molecules leads to the dissociative chemisorption of TMA which results in the presence of various reaction products on the surface, and in particular of Al–CH_3 and Si–CH_x species. For TMA doses larger than 360 L, the PES spectra are unaffected which shows that the chemisorption process is self-limiting. Upon subsequent exposure to NH_3 at 400 °C, nitridation of the surface is observed involving the formation of Al–N and Si–N bonds. While some loss of C atoms is observed in this process, most probably due to the formation of volatile CH_4 in reactions between NH_3 and Al–CH_3 species, the majority of surface carbon remains. The disappearance of the silicene-related features and the formation of stable Si–C and Si–N bonds suggest that the use of TMA and NH_3 precursors to realize AlN capping layers for silicene on ZrB_2(0001) thin film surfaces, without affecting its electronic properties, should be avoided.

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