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Description	

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A nitride-based epitaxial surface layer formed by ammonia treatment of silicene-terminated ZrB₂

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We present a method for the formation of an epitaxial surface layer involving B, N, and Si atoms on a ZrB₂(0001) thin film on Si(111). It has the potential to be an insulating growth template for 2D semiconductors. The chemical reaction of NH₃ molecules with the silicene-terminated ZrB₂ surface was characterized by synchrotron-based, high-resolution core-level photoelectron spectroscopy and low-energy electron diffraction. In particular, the dissociative chemisorption of NH₃ at 400 °C leads to surface nitridation, and subsequent annealing up to 830 °C results in a solid phase reaction with the ZrB₂ subsurface layers. In this way, a new nitride-based epitaxial surface layer is formed with hexagonal symmetry and a single in-plane crystal orientation. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4944579>]

INTRODUCTION

Currently, the growth on insulating substrates is one of the largest challenges faced by research on 2D semiconductors, in particular, for silicene^{1–3} and germanene,^{4–6} as these materials have so far only been synthesized on metal substrates. Silicene and germanene are single-atom thick layers of Si or Ge atoms, respectively, in a buckled honeycomb lattice. Their growth on an insulating substrate is highly sought after in order to explore the rich physics of these materials that are predicted to exhibit, for example, the quantum spin Hall effect.⁷

In this article, a method is presented to form an epitaxial surface termination involving B, N, and Si atoms on the surface of ZrB₂(0001) thin, epitaxial films on Si(111). The ZrB₂(0001)/Si(111) system has already been extensively studied in the context of 2D materials since it has been demonstrated that an epitaxial layer of silicene is formed through surface segregation upon annealing at 750–800 °C.² However, the electrical characterization of the silicene layer is hindered by the metallic ZrB₂ substrate. For that purpose, an ordered, electrically insulating surface layer would make an ideal template. Many oxides and nitrides show the desired insulating behavior. We use a combination of exposure to ammonia (NH₃) gas and annealing to convert the silicene-terminated surface into a new, nitride-based, epitaxial termination layer involving B, N, and Si atoms. The evolution of the surface was characterized at several stages of the process using synchrotron-based, high-resolution core-level photoelectron spectroscopy (HR-PES) and low-energy electron diffraction (LEED).

The newly created surface layer presents itself as a candidate template for the heteroepitaxial growth of 2D materials. Based on the inclusion of B, N, and Si atoms, resembling boron nitride and silicon nitride, the layer has the potential to be electrically insulating. Furthermore, the single in-plane crystal orientation may promote this same property in a heteroepitaxial layer. This in turn may allow anisotropic properties to be probed of, for example, the electrical conductivity. In this work, the layer is thin enough to enable surface characterization techniques that depend on the electrical conductivity of the surface region. The nitride-based surface layer, as presented in the current work, provides a way towards growing a 2D semiconductor on an insulator. This in turn would enable electronic transport measurements and utilization in electronic devices.

EXPERIMENTAL

Single-crystalline ZrB₂ epitaxial thin films were grown on Si(111) substrates by ultra-high vacuum chemical vapor epitaxy, as described elsewhere.⁸ All subsequent sample preparation steps and measurements were carried out at beamline D1011 of the MAX-lab synchrotron radiation laboratory in Lund, Sweden. The experimental arrangement in this beamline consists of (i) a loadlock, (ii) a preparation chamber (base pressure below 5×10^{-9} mbar), and (iii) an analysis chamber (base pressure below 4×10^{-10} mbar) equipped with a Scienta SES200 hemispherical analyzer for HR-PES measurements. Annealing is performed in the preparation chamber by means of e-beam heating while the temperature was measured using a thermocouple (mounted on the sample holder) and a pyrometer. The same chamber is equipped with a LEED system and a variable leak valve for exposing the sample to NH₃ gas (99.98% purity).

All HR-PES measurements were performed with the sample normal directed towards the photoelectron analyzer,

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and with the photon source at a 45° angle to the surface normal. The binding energies of Si $2p$, N $1s$, and B $1s$ core-levels were measured using a photon energy of 500 eV. The binding energy of the Zr $3d$ core-level was measured using a photon energy of 700 eV. In addition, the binding energy of the Si $2p$ core-level was also measured using a photon energy of 130 eV. The photon energy resolutions are 187 meV, 170 meV, and 25 meV, for the 700 eV, 500 eV, and 130 eV photon energies, respectively. Initially, the binding energy scale of the Si $2p$ spectrum measured with a photon energy of 130 eV is calibrated using the dominant peak of the pristine silicene that is related to the β -component (98.98 eV) in the Si $2p_{3/2}$ levels of silicene on ZrB_2 .⁹ The possible errors in binding energy caused by varying conditions of the beamline and storage ring are corrected for by measuring the Si $2p$ levels using a photon energy of 130 eV immediately before and after any sample treatment. These spectra are also used to calibrate the Si $2p$ and Zr $3d$ spectra measured using a photon energy of, respectively, 500 eV and 700 eV by aligning the overall shape. The calibration values for the Si $2p$ spectra are also applied to the B $1s$ and N $1s$ spectra measured with the same photon energy. All spectra are normalized to the photon flux as measured with the total electron yield of a gold grid mounted in the beam line.

RESULTS AND DISCUSSION

Figure 1 shows the spectra of Si $2p$, N $1s$, B $1s$, and Zr $3d$ core-level regions of a silicene-terminated ZrB_2 sample

before and after several consecutive annealing treatments. These treatments are divided into three phases based on annealing temperatures and exposure to NH_3 molecules. The first phase covers sample preparation by annealing at 780°C to remove the native oxide. In the second phase, the sample is annealed while exposed to a low and constant pressure of NH_3 gas, in order to nitridize the surface. In the third and final phase, the sample is annealed in ultra-high vacuum at a higher temperature after which a new epitaxial surface termination layer was found.

In the first phase, the thin $\text{ZrB}_2(0001)$ epitaxial film on Si(111) is annealed at 780°C resulting in the formation of a pristine monolayer of silicene at the surface by segregation of Si atoms originating from the Si(111) substrate. The Si $2p$ spectrum (Fig. 1(a), spectrum 1) shows the characteristic “fingerprint” of silicene on the $\text{ZrB}_2(0001)$ surface.⁹ The Zr $3d$ spectrum shows a single doublet where Zr $3d_{3/2}$ is 181.5 eV and Zr $3d_{5/2}$ is 179.0 eV corresponding to Zr atoms in the ZrB_2 crystal (Fig. 1(d), spectrum 1). The B $1s$ spectrum has a single peak at a binding energy of 188.1 eV associated with the B atoms in the ZrB_2 crystal (Fig. 1(c), spectrum 1). Note that the outermost B atoms are below the Zr atoms that are in contact with the silicene layer.² The pristine silicene sample shows a flat background in the N $1s$ core-level region indicating the absence of N atoms at the surface. Annealing the sample at 300°C for 2 min while exposed to an NH_3 partial pressure of 1.0×10^{-6} mbar (90 L exposure) did not result in a chemical change of the surface. This is in contrast with the Si(111)^{10,11} and Si(100)¹¹ surfaces where dissociative

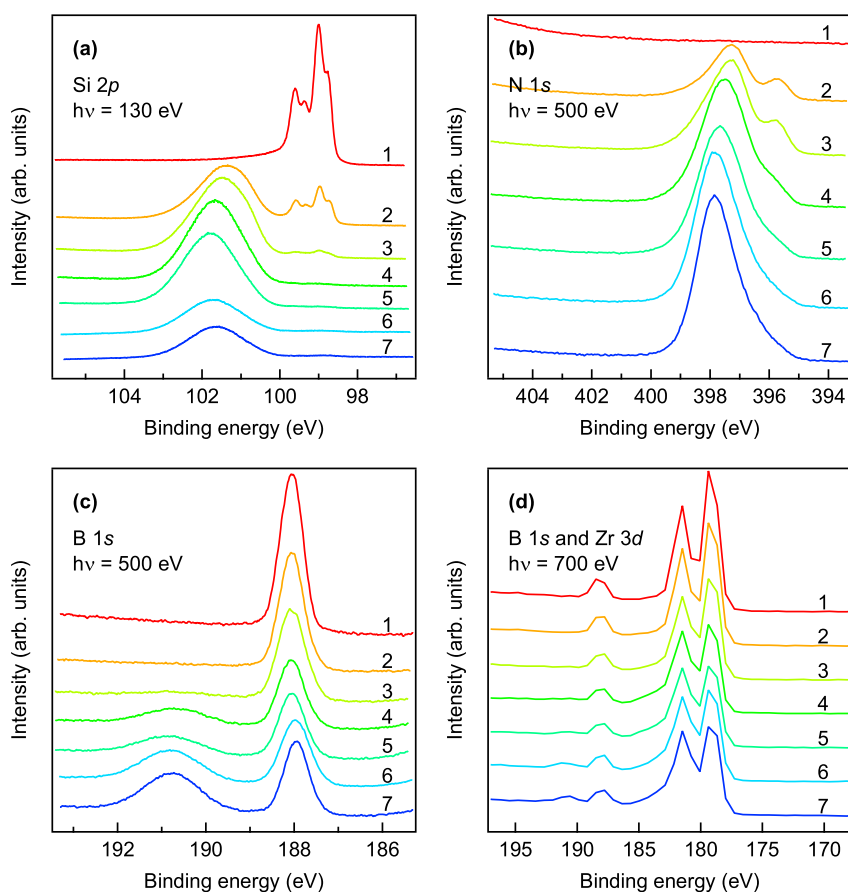


FIG. 1. HR-PES of (a) Si $2p$, (b) N $1s$, (c) B $1s$, and (d) Zr $3d$ core-level regions detailing the results of chemical reactions on the silicene-terminated ZrB_2 surface exposed to NH_3 . The spectra are presented in chronological order: (1) pristine silicene, (2) annealed for 30 min at 400°C in 1.0×10^{-6} mbar of NH_3 gas, further annealed for a total time of (3) 60 and (4) 90 min at the same temperature and pressure, and subsequently annealed in ultra-high vacuum for (5) 30 min at 470°C , (6) 30 min at 800°C , and (7) 30 min at 830°C .

chemisorption of NH_3 is already observed at room temperature and for a lower amount of exposure. It is thus apparent that the silicene-terminated surface is less reactive to NH_3 molecules. This is similar to its lower sensitivity towards oxidation by O_2 molecules.^{12,13} As demonstrated, NH_3 molecules do not react with silicene-terminated surfaces at a temperature of 300 °C. This means that, at these temperatures, NH_3 can possibly be used in a deposition process of an encapsulation layer.

During the second phase, the sample is annealed three times for a total of 90 min at 400 °C and at an NH_3 partial pressure of 1.0×10^{-6} mbar (equivalent to a total dose of 4050 L), with spectra recorded after every 30 min (Figs. 1(a)-1(d), spectra 2-4). During this process, the Si 2*p* silicene fingerprint remains visible while its integrated intensity (henceforth referred to as just the intensity) quickly diminishes. At the same time, a new, broad Si-related peak forms at a higher binding energy of 101.4 eV. These changes are due to dissociative chemisorption of NH_3 molecules on the surface where the N atoms chemically bond with Si atoms from the silicene layer. Because the presence of chemisorbed N atoms strongly affects the binding energy position of the individual Si components characteristic for silicene, it is suggested that the nitridation of the silicene starts out with a nucleation process, and the newly formed nuclei grow laterally consuming the silicene. After 90 min annealing, nearly all of the silicene has reacted and the new Si 2*p* peak shifts towards a higher binding energy of 101.7 eV (Fig. 1(a), spectrum 4) while its intensity saturates.

After annealing for 30 min at 400 °C, two broad peaks form in the N 1*s* spectrum (Fig. 1(b), spectrum 2). The major and minor peaks are centered at 397.3 eV and 395.7 eV, respectively. The peaks are attributed to newly adsorbed species resulting from the dissociative chemisorption of NH_3 molecules. In this way, drawing upon an analogy with the Si(111) and Si(100) surfaces,^{10,11,14} three species can possibly form: $\text{Si}-\underline{\text{N}}\text{H}_2$, $\text{Si}_2=\underline{\text{N}}\text{H}$, and $\text{Si}_3\equiv\underline{\text{N}}$. This notation describes the neighboring atoms bound to a central atom (i.e., $\underline{\text{N}}$) with covalent bonds. The N core-level binding energies of the species can be assigned according to their initial state binding energies. Since H is more electronegative than Si, substituting a N—H bond with a N—Si bond will decrease the core-level binding energy.¹⁰ This ranks the species in the following order from the highest to lowest in core-level binding energy: $\text{Si}-\underline{\text{N}}\text{H}_2$, $\text{Si}_2=\underline{\text{N}}\text{H}$, and $\text{Si}_3\equiv\underline{\text{N}}$.¹¹ While at least two of these three configurations are formed, B atoms are not involved in the bonding at this stage of nitridation, as the B 1*s* binding energies are unaffected (Fig. 1(c), spectrum 2).

The binding energies of the $\underline{\text{N}}\text{H}_x$ species in the N 1*s* spectrum (Fig. 1(b), spectrum 2) are lower compared to those on the surface of bulk Si substrates.^{10,11,14} Since the silicene layer is structurally and electronically very different, this can be expected to result in a different range for the binding energies of the $\underline{\text{N}}\text{H}_x$ species. In addition, the ZrB_2 substrate is metallic and is expected to have a different final state effect on the N 1*s* core-level due to its higher polarizability compared to a semiconducting Si substrate.

Only minor amounts of oxygen are introduced during the nitridation process (PES data not shown) when the

sample surface is exposed to NH_3 , and therefore oxide-related contributions to the N 1*s* and Si 2*p* features are disregarded. The small oxygen signal is likely caused by trace amounts of H_2O originating from the NH_3 gas bottle that have reacted with the sample surface. The O 1*s* intensity strongly decreases upon subsequent higher temperature annealing.

As exposure to NH_3 at 400 °C is continued for a total of 60 min, the remaining silicene reacts with NH_3 , except for a small fraction (Fig. 1(a), spectrum 3). After 90 min, the silicene peak has nearly disappeared and the peaks of Si 2*p* and N 1*s* (Figs. 1(a) and 1(b), spectrum 4) shift to higher binding energies. This coincides with the formation of a new peak in the B 1*s* spectrum (Fig. 1(c), spectrum 4), and a shoulder on the higher binding energy side of the Zr 3*d* doublet (Fig. 1(d), spectrum 4). The intensity of the major N 1*s* peak also continues to increase. However, this is rather marginal compared to the previous two annealing phases. The minor N 1*s* peak decreases in intensity, becoming a shoulder on the low binding energy side of the major peak (Fig. 1(b), spectrum 4).

As a result of annealing during exposure to NH_3 , the intensities of the B 1*s* (Fig. 1(c), spectra 1-4) and Zr 3*d* peaks (Fig. 1(d), spectra 1-4) decrease significantly. This is attributed to the aforementioned dissociative chemisorption of NH_3 molecules on the surface leading to a suppression of PES signals from subsurface elements. In contrast to the Si 2*p* and N 1*s* core-levels, the B 1*s* binding energies show a change, albeit small, only after annealing for 60 min (Fig. 1(c), spectra 3). At this point, a new, broad peak centered at a binding energy of 190.7 eV can be distinguished as a result of a solid phase reaction with the underlying ZrB_2 . The peak increases in intensity for continued annealing (Fig. 1(c), spectra 4).

Two consecutive processes can be suggested to explain the observations: (i) nitridation of the silicene initially and (ii) the subsequent solid phase reaction of B with N and/or Si atoms. Although it is clear that chemical interactions between B, N, and Si atoms occur, the exact attribution of the peaks to certain chemical species in Fig. 1 cannot be made unambiguously.

In the third phase, in order to test the behavior and chemical stability of this surface compound, the sample is annealed three times, for 30 min each, in ultra-high vacuum. This is done first at 470 °C, then at 800 °C, and finally at 830 °C, with spectra recorded after every step.

Annealing at 470 °C results in only minor changes in intensity, smoothing of the N 1*s* shoulder, and an additional small shift towards a higher binding energy for the Si 2*p*, N 1*s*, and new B 1*s* peaks (Figs. 1(a)-1(c), spectra 5). The Zr 3*d* doublet shows no significant change (Fig. 1(d), spectrum 5).

After annealing at 800 °C, the intensity of the N 1*s* peak increases and it shifts towards a higher binding energy. Furthermore, there is a large decrease in the Si 2*p* peak intensity (Fig. 1(a), spectrum 6) coinciding with a large increase in intensity of the new B peak at 190.8 eV (Fig. 1(c), spectrum 6). This can be explained by an exchange of some of the Si atoms by B atoms at the outermost surface. This is confirmed by increasing the photon energy. The Si 2*p* signal measured with 500 eV photon energy shows a relatively smaller decrease in intensity (data not shown) compared to

the measurement obtained with the photon energy of 130 eV. The Zr 3*d* doublet shows no significant change (Fig. 1(d), spectrum 6).

Annealing at 830 °C results in a further increase in intensity of the new B 1*s* peak. Furthermore, the ZrB₂-related B 1*s* peak at 188.0 eV and the major N 1*s* peak both become slightly narrower. This change is attributed to a more homogeneous chemical environment of the respective atoms. The Si 2*p*, N 1*s*, and new B 1*s* peaks are centered at 101.6 eV, 397.9 eV, and 190.8 eV, respectively (Figs. 1(a)-1(c), spectrum 7). The Zr 3*d* doublet shows no change (Fig. 1(d), spectrum 7).

Figure 2 shows the LEED pattern observed at room temperature after the final annealing treatment at 830 °C. It shows an epitaxial surface termination with hexagonal symmetry and a single in-plane crystal orientation.

For the ZrB₂(0001)/Si(111) system, it has been reported^{15,16} that a different nitridation and annealing process leads to a surface termination of h-BN(0001)-(1 × 1). The two main differences with the current work are (i) the use of reactive nitrogen radicals formed in a nitrogen plasma instead of NH₃ gas, while (ii) the annealing is performed at a higher temperature of 900 °C instead of 830 °C. The B 1*s* and N 1*s* peaks measured in the current work (190.8 eV and 397.9 eV, respectively) correspond well to the B 1*s* and N 1*s* peaks from a h-BN monolayer on a SiO₂/Si substrate¹⁷ (190.6 eV and 398.2 eV, respectively), and to the B 1*s* peak related to h-BN on ZrB₂/Si reported by Wang *et al.* (190.4 eV).¹⁵ Similar to Wang *et al.*, the Zr 3*d* peaks observed in this work do not show a strong change after nitridation or annealing, except for a suppression of intensity and the formation of a shoulder at higher binding energy.

The formation of cubic phase ZrB_xN_{1-x} upon exposure of bare ZrB₂ to NH₃ at 1100 °C has been reported by Tomida *et al.*¹⁸ Formation of a cubic phase Zr_xB_yN_z alloy at temperatures as low as 385 °C has been suggested by Manandhar *et al.*¹⁹ The PES data of Manandhar *et al.* show

no new clearly resolved chemical states for either the Zr 3*d* or B 1*s* core-level, in which case the Zr 3*d* and B 1*s* binding energies must be the same in Zr_xB_yN_z and in the ZrB₂ underneath. This makes it difficult to observe and assign the Zr_xB_yN_z phase by PES alone. It is clear, however, from Fig. 1(d) that the intensities of the B 1*s* and Zr 3*d* peaks associated with ZrB₂ decrease in equal manner, consistent with a surface layer suppressing PES intensity from the ZrB₂ below. In contrast, this is not consistent with the formation of an intermediate layer of ZrB_xN_{1-x} as the ratio of Zr to B atoms is higher in this phase than in ZrB₂. The PES results should then show a change in the ratio of the B 1*s* and Zr 3*d* intensities, which is not the case. The surface layer involves then B, N, and Si atoms. This does not explicitly exclude Zr atoms, but based on the PES data in Fig. 1 there is no evidence to suggest their involvement.

Annealing for 30 min at 830 °C demonstrates that this new surface termination is stable at relatively high temperatures. In addition, the electronic properties of the surface have the potential to be insulating, resembling the properties of boron nitride and silicon nitride. This would make it an interesting candidate as a template for van der Waals epitaxy of 2D materials.

CONCLUSIONS

The chemical reaction of NH₃ with silicene-terminated ZrB₂ is investigated using synchrotron-based HR-PES and LEED. The results show that dissociative chemisorption of NH₃ on silicene takes place at 400 °C and nitridizes the surface. At 300 °C, no chemical reaction between silicene and NH₃ is observed which demonstrates that the silicene-terminated surface is less chemically reactive towards NH₃ molecules than a Si(111) or Si(100) surface for which dissociative chemisorption of NH₃ already occurs at room temperature. Furthermore, annealing the nitrided surface of the ZrB₂(0001)/Si(111) system to 830 °C involves a solid phase reaction that results in a new epitaxial surface layer with hexagonal symmetry and a single in-plane crystal orientation, involving B, N, and Si atoms.

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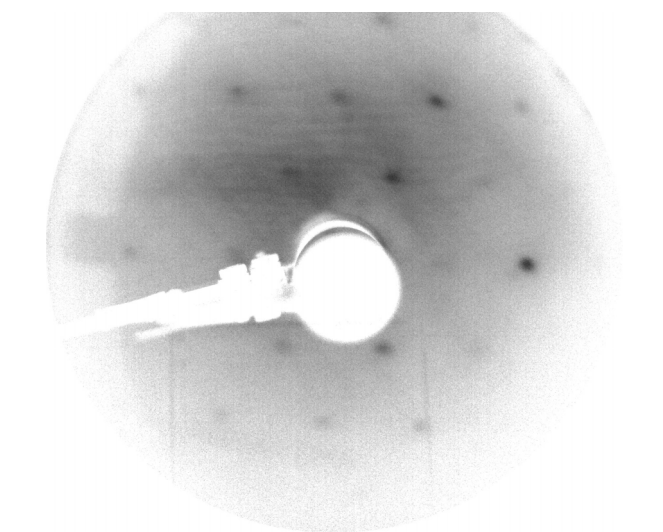


FIG. 2. The LEED pattern at room temperature using a kinetic energy of 115 eV for the incident electrons, following the final annealing treatment at 830 °C. It indicates the presence of an epitaxial surface termination with hexagonal symmetry and a single in-plane crystal orientation.

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