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Engineering multiple topological phases in nanoscale Van der Waals heterostructures: realisation of $\alpha$-antimonene

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Abstract

Van der Waals heterostructures have recently been identified as providing many opportunities to create new two-dimensional materials, and in particular to produce materials with topologically-interesting states. Here we show that it is possible to create such heterostructures with multiple topological phases in a single nanoscale island. We discuss their growth within the framework of diffusion-limited aggregation, the formation of moiré patterns due to the differing crystallographies of the materials comprising the heterostructure, and the potential to engineer both the electronic structure as well as local variations of topological order. In particular we show that it is possible to build islands which include both the hexagonal $\beta$- and rectangular $\alpha$-forms of antimonene, on top of the topological insulator $\alpha$-bismuthene. This is the first experimental realisation of $\alpha$-antimonene, and we show that it is a topologically non-trivial material in the quantum spin Hall class.

Introduction

Van der Waals heterostructures consist of multilayers of weakly-coupled few-monolayer-thick sheets of materials [1–4]. This weak coupling means that the intrinsic properties of individual layers of the material of interest may be preserved, only mildly perturbed by interactions with other layers, and so provides potential for realisation of new topologically-interesting materials [4]. Topological insulators are materials in which strong spin–orbit coupling (SOC) leads to an inversion of the usual band structure, and hence to unusual topologically protected boundary states [5, 6]. In the two-dimensional (2D) systems of interest here, the topologically protected states are electronic edge states in which spin and momentum are locked together so that backscattering is forbidden. The dissipationless 1D spin currents in these systems provide a platform for the fabrication of spin-selective electronic devices [7, 8].

To date, only a very limited range of van der Waals heterostructures have been reported, and the materials that have been investigated have almost exclusively hexagonal symmetry [1–3, 9–11]. While such graphene-like [12] structures are very promising, an ability to engineer heterostructures with different crystal symmetries could open up significant new opportunities in both fundamental physics and electronic device fabrication. Moreover, incommensurate moiré structures, which modulate the electronic states in 2D materials, can lead to the emergence of a fractal spectrum of electronic states containing new Dirac points [13, 14], and could provide a platform for the observation of predicted spatial modulation of local topological phases [8].

Bismuth is a key ingredient in many topologically interesting materials because of its strong SOC. As a thin film, Bi exists in two forms: the [Black Phosphorous (BP)-like, rectangular symmetry] $\alpha$-form and the [hexagonal (111)-oriented] $\beta$-form which are
both called ‘bismuthene’. It has been shown recently that \(\alpha\)-bismuthene \([17]\), \(\beta\)-bismuthene \([18]\) and even bulk Bi \([19]\) are topological insulators. Antimony, which sits above Bi in group 15 of the periodic table, has similar allotropes but is much less well explored. It is known that multilayer \(\beta\)-antimonene is a topological insulator, but that coupling between the surfaces destroys the topological states in few-monolayer-thick films \([20, 21]\), unless sufficient strain is applied \([22]\). In contrast, despite significant theoretical interest \([23–27]\), \(\alpha\)-antimonene has never been realized experimentally and its topological properties have not been investigated. The \(\alpha\)-phases of Sb and Bi are particularly interesting because they have structures that are homologous to those recently used to build novel BP transistors \([28]\). If similar transistors could be fabricated with built-in strong SOC their topologically-protected edge states could be used in spin-selective devices allowing manipulation and robust transport of quantum information—the present antimonene / bismuthene structures, grown on microelectronics-compatible substrates, are a significant step towards this goal.

We report the realisation of van der Waals heterostructures comprising multiple bismuthene and antimonene allotropes. These include: (i) \(\alpha\)-bismuthene, (ii) one monolayer (ML)\(^6\) thick sheets of \(\beta\)-antimonene (1 ML-\(\beta\)-Sb) and (iii) 2 ML thick sheets of the never previously experimentally observed \(\alpha\)-antimonene (2 ML-\(\alpha\)-Sb). We investigate these structures using scanning tunnelling microscopy (STM), scanning tunnelling spectroscopy (STS), and density functional theory to show that the new allotrope 2 ML-\(\alpha\)-Sb is topologically non-trivial and energetically preferred over 2 ML-\(\beta\)-Sb because of interactions with the underlying Bi islands. All three allotropes exhibit distinctive moiré patterns that provide potential for engineering spatially dependent topological order \([8]\).

**Methods**

In our experiments Bi nanoislands (which have been intensively studied previously \([16, 30–34]\)) serve as a basis for the growth of the antimonenes. For growing those Bi islands we have used MoS\(_2\) substrates as well as the more usual graphite (HOPG) and obtain qualitatively similar results in both cases, but focus here on the MoS\(_2\) samples for three different reasons: (i) MoS\(_2\) is a semiconductor which provides opportunities for fabrication of electronic devices, (ii) the difference in the interactions between the Bi and the MoS\(_2\) (compared to HOPG) lead to subtle but interesting structural differences, and (iii) neither antimonene nor bismuthene have been reported on MoS\(_2\) before. Sample preparation was carried out in situ under UHV conditions; the nanostructures presented here were grown by first thermally evaporating 2 ML of Bi onto MoS\(_2\) substrates (held at 295 K), followed by 0.6 ML of Sb. STM/STS measurements were performed either at room temperature or \(\sim 50\) K using a commercial Omicron VT AFM/STM with Pt/Ir tips. Imaging and STS conditions are stated in the figure captions. The lateral resolution of the STM is calibrated using atomically resolved images of MoS\(_2\).

The first-principles calculations are similar to those used to predict the band structure of \(\alpha\)-Bi \([32, 35]\). They were performed with ABINIT package within plane-wave expansion and pseudopotential framework. In order to take relativistic effects into account, the Hartwigsen–Goedecker–Hutter (HGH) pseudopotential was used in the calculations. The cutoff of electron kinetic energy was set to be 400 eV. The \(k\)-sampling was carried out on a \(\Gamma\)-centered \(13 \times 13 \times 1\) grid based on Monkhorst-Pack method. The films were modelled by a periodic array of slabs separated by a 15 Å vacuum gap between neighboring layers. The atomic positions, including the in-plane lattice constants, were allowed to relax by energy minimization until the Hellmann–Feynman forces were reduced to below \(1.0 \times 10^{-3}\) eV Å\(^{-1}\).

**Results and discussion**

Figure 1(a) shows a typical STM image of a nanoscale Bi-island decorated with antimonene. The (110)-oriented Bi-island is 3 ML thick\(^7\) and exhibits three atomically flat regions of different height (line profile in figure 1(d)): the 3 ML bismuth island base (green), a 5 ML high region (pink), and a region which is 1 ML higher than the base (orange). On careful inspection the 5 ML high central region comprises a Bi stripe (arrowed) which is absolutely linear, with straight edges running parallel to the Bi \((1 1 0)\) direction \([29, 30, 36]\) surrounded by a laterally less well-defined Sb region of variable width. This Sb film is 2 ML high, and is supported by the 3 ML Bi island base. As described in detail below, based on atomic resolution images and spectroscopic data, the differently coloured regions can be identified as 2 ML-\(\alpha\)-Bi (green), 2 ML-\(\alpha\)-Sb (pink), and 1 ML-\(\beta\)-Sb (orange). Hence, in this one island, we see a heterostructure comprising three distinct topologically interesting materials (as shown schematically in figure 1(c)).

Figures 1(e)–(g) show magnified atomic resolution images obtained from examples of each of the three phases of interest (see also supplementary figure S1). In each case the symmetry of the lattice is indicated, alongside fast Fourier transforms (figures 1(h)–(j))

\(^6\)We define \([29]\) a monolayer to be a single sheet of atoms which in all cases is 3 Å to 4 Å thick; these monolayers are sometimes called a ‘bilayer’ in the literature because of puckering which results in atoms that lie in two separate planes (see figure 1(b)). We use the suffix ‘-ene’ to denote the thinnest possible films for each structure: 1 ML-\(\beta\)-Sb, 2 ML-\(\alpha\)-Sb, and 2 ML-\(\alpha\)-Bi.

\(^7\)Note that a wetting layer exists underneath the 2 ML-\(\alpha\)-Bi \([31, 32]\).
of the images which allow determination of the lattice constants of the surface unit cells. We obtain $a_{\text{Sb}}^\alpha = 404 \text{ pm}$, $a_{\text{Sb}}^\beta \times a_{\text{Bi}}^\alpha = 429 \text{ pm} \times 486 \text{ pm}$, and $a_{\text{Bi}}^\alpha \times a_{\text{Bi}}^\beta = 453 \text{ pm} \times 487 \text{ pm}$. These values agree well with the result of our calculations and existing literature values [17, 22, 23, 25, 34, 37–39]. Refer to supplementary table SI for full details, including experimental uncertainties.

In our topography images we observe apparent spatial modulations of the height $\leq 50 \text{ pm}$ that are hardly visible in figure 1(a); hence, we show them on expanded scales in figure 2 and supplementary figures S1 and S2. In figure 2(b) the $\alpha$-Sb fringes have a period of 7.3 nm $\pm 0.6$ nm and are perpendicular to the Bi (1 1 0) direction; the $\beta$-Sb fringes are inclined with respect to the Bi (1 1 0) direction at an angle of 20° $\pm 5^\circ$ and exhibit a period of 4.0 nm $\pm 0.4$ nm.

To show that these fringes are moiré patterns we have carefully modelled them by creating superpositions of the two lattices with the software VESTA [15] and by varying the lattice constants and relative angles. Supplementary figure S3 exemplifies that the observed period and angle of the moiré pattern are very sensitive to these parameters.

Figure 1. Morphology and atomic structure of the layered nanoislands. (a) Large-scale STM image of a typical van der Waals heterostructure comprising the $\alpha$-Bi island base (light green), 2 ML-$\alpha$-Sb (pink) and 1 ML-$\beta$-Sb (orange). (Imaging conditions: +400 mV, 10 pA, 295 K). The scale bar corresponds to 50 nm. The arrow indicates the location of an additional 2 ML thick Bi stripe on top of the base. The regions marked by rectangles are shown in detail in figure 2(b) (black rectangle) and supplementary figure S1(d) (stacks.iop.org/TDM/5/011002/mmedia) (blue rectangle). (b) Schematic top and side views (created with VESTA [15]) of the crystal structures of single sheets of $\alpha$-Sb and $\beta$-Sb, respectively; the unit cells are marked in black. (c) Schematic side view of the island showing the stacking of the different layers, with colors corresponding to the topography image in (a). The wetting layer (Bi WL) [16] is shown separately in dark green. (d) Height profile at the indicated position (red line in (a)). (e)–(g) Atomically resolved STM images of $\alpha$-Bi, 2 ML-$\alpha$-Sb, and 1 ML-$\beta$-Sb, respectively (scale bar: 1 nm; imaging conditions: 50 mV, 200 pA for (e); 100 mV, 50 pA for (f) and (g); all at 295 K.) Larger scale atomically-resolved images are presented in supplementary figure S1. (h)–(j) show the inner regions of the 2D Fourier transforms of the respective raw images. (Scale bar: 1.3 Å$^{-1}$).

Figure 2. Example of observed and simulated moiré patterns of 2 ML-$\alpha$-Sb and 1 ML-$\beta$-Sb on a 3 ML Bi island. In all three panels the black arrow represents the Bi (1 1 0) direction. Dashed white lines serve as guides to the eye. (a) Simulated moiré pattern of 2 ML-$\alpha$-Sb. The grey arrow indicates the $\alpha$-Sb (1 1 0) direction which is parallel to the Bi (1 1 0) direction in this case. (b) STM image (200 mV, 10 pA, scale bar: 20 nm) from inside the black rectangle in figure 1(a), enhanced to show both moiré patterns of $\alpha$-Sb and $\beta$-Sb. (supplementary figure S2 shows an example in which different moiré patterns are observed due to differing orientations of the overlayer and underlayer.) (c) Simulated moiré pattern of 1 ML-$\beta$-Sb. The grey arrow represents the $\beta$-Sb (1 1 0) direction, which is rotated by 10.5° with respect to Bi (1 1 0).
We begin by considering the pattern that is observed on the 3 ML-Bi bases due to the mismatch between the rectangular bismuth crystal structure and the underlying hexagonal MoS$_2$. We find that the best agreement with the experimentally observed moiré pattern (figure S1(a)) is achieved for Bi lattice constants that match exactly with those obtained from atomic resolution (453 pm $\times$ 487 pm). Hence, we use those lattice parameters to subsequently model the antimonene structures on $\alpha$-Bi.

The moiré fringes for 2 ML-$\alpha$-Sb on $\alpha$-Bi are perpendicular to the $\alpha$-Bi stripe, consistent with atomic resolution results which show that (1 1 0)$_{\text{Bi}}$ is parallel to (1 1 0)$_{\text{Sb}}$ (supplementary figure S1(d)). This means that $a_{\alpha}^{\text{Sb}} \approx a_{\alpha}^{\text{Bi}} = 487$ pm, and only $a_1^{\text{Sb}}$ is to be determined. We find an optimal match (figure 2(a)) to the observed moiré pattern in figure 2(b) using $a_1^{\text{Sb}} = 426$ pm, in good agreement with the atomic resolution value.

In the case of 1 ML-$\beta$-Sb on $\alpha$-Bi, we find the best match (figure 2(c)) for the moiré pattern in figure 2(b) by using a lattice constant of 413 pm. This is slightly larger than the result from atomic resolution and calculations but still in reasonable agreement. Supplementary figure S4 shows the modelled moiré patterns for both $\alpha$-Sb and $\beta$-Sb in more detail.

We now consider the growth mechanism of these van der Waals heterostructures. It is well-established that both Sb and Bi nanostructures grow by diffusion and aggregation on atomically-flat substrates like HOPG [30, 32, 36]. The present bismuth structures are very similar to those grown on HOPG but subtle differences include predominance of narrower 5 ML stripes and broader 3 ML island bases, and a shorter wavelength moiré pattern (supplementary figure S1(a))—these differences originate from the different MoS$_2$ and HOPG lattice constants.

The growth of the antimonene layers on top of the bismuth structure is rather remarkable. It is known [36] that Sb prefers to form three-dimensional structures in comparison to the planar 2D structures preferred by Bi, and this is manifested in the present islands by up-diffusion of Sb from the MoS$_2$ substrate onto the Bi island bases; no Sb is observed on the MoS$_2$. The amount of Sb that is directly deposited onto the top surface of the Bi islands is very small, and so the amount of Sb observed on top of the Bi island reflects the size of the capture zone on the MoS$_2$ substrate (e.g. the bottom left of the island shown in figure 1(a) is covered with a thicker layer of Sb because of a large open MoS$_2$ terrace on that side of the island).

In the vast majority of islands the Bi base was covered by either antimonene or an additional 2 ML-Bi stripe. Bare 3 ML Bi regions were scarce and hence we conclude that on the Bi bases the antimony prefers to form a complete layer first before growing thicker layers. In particular, the 1 ML-$\beta$-Sb regions often covered the whole width of an island whereas 2 ML-$\alpha$-Sb was mostly observed adjacent to the additional Bi stripe. After the formation of a 1 ML-$\beta$-Sb layer the arrival of further Sb leads to a restructuring into 2 ML-$\alpha$-Sb. The necessary nucleation can occur directly on the 1 ML-$\beta$-Sb but is greatly facilitated by the presence of the Bi stripes. According to this scenario, we believe that the disordered regions on the left of figure 1(a) are yet to be fully-crystallized as $\alpha$-Sb. Additional data (not shown) shows that these disordered regions re-order into the $\alpha$-phase over a period of weeks because they were only found close to the $\alpha$-Sb and only within a few days after deposition. As explained in the next paragraph this phase transformation is likely driven by energetics, but the atomic scale mechanisms are not well understood at present.

Thicker layers of $\beta$-Sb, such as 2 ML-$\beta$-Sb, were never observed in our experiments, which strongly indicates that 2 ML-$\alpha$-Sb is energetically preferred. Our first principles calculations find that the energies of free-standing slabs of these two structures are identical within the numerical accuracy of the simulations. The preference for the $\alpha$-phase in 2 ML thick films can therefore be attributed to the weak interaction with the underlying Bi which has rectangular symmetry. Interestingly it is known that Bi grows initially in the $\alpha$-phase but re-orients into the $\beta$-phase at a critical thickness that depends on the substrate [33, 40]. Sb also grows in the $\beta$-phase for thicknesses greater than ~20 ML [20] which suggests that the $\alpha$-phase is preferred only for an intermediate thickness range. Deposition of additional Sb will likely lead to observation of $\alpha$-Sb in the sequence of thicknesses 4 ML, 6 ML, 8 ML etc. (as for Bi) [16, 30–34], but it will be interesting to see at what thickness the transition to the $\beta$-phase occurs.

We have performed first principles calculations of the electronic states for both the experimentally observed 2 ML-$\alpha$-Sb and 1 ML-$\beta$-Sb structures (supplementary figure S5). The band structure for 1 ML-$\beta$-Sb is similar to that reported previously in [23–26], and it is known to be topologically trivial [20, 21] (although under sufficient strain it becomes non-trivial [22]). We now focus on the 2 ML-$\alpha$-Sb films since their topological properties have never been reported previously. Our calculations show that there exists an indirect negative band gap separating the conduction and valence bands which allows the $Z_2$ topological invariant to be defined: the crystal structure is centrosymmetric and thus the wavefunctions at each time reversal invariant momentum point carry definite parity eigenvalues. By using the Fu–Kane formula [41] the $Z_2$ invariant can be straightforwardly calculated from the parity data in supplementary table SII. Our results show that 2 ML-$\alpha$-Sb films are topologically non-trivial, belonging to the quantum spin Hall class.

In figure 3, we compare the calculated and measured density of states (DOS) Figure 3(a) shows experimental STS spectra (black, grey) for 2 ML-$\alpha$-Sb which
have deep minima at zero bias and weak peaks whose positions vary by $\sim \pm 0.1 \text{ V}$ (see the histogram). There is generally good agreement between positions of the peaks in the histogram and the peaks in the calculated DOS (which is shifted by 140 mV to account for charge transfer from the substrate [32]) demonstrating that the calculated electronic structure matches that obtained experimentally.

Figure 3(b) shows the measured STS data for 1 ML-\(\beta\)-Sb (grey curve). At first sight, there is no agreement between the experimental data and the calculated DOS (green curve). However, we find that the spectrum for 1 ML-\(\beta\)-Sb is strikingly similar to that for the 3 ML-Bi island base (brown curve) in the bias range $\pm 0.5 \text{ V}$. As it is already known that \(E_F\) lies in a band gap in 1 ML-\(\beta\)-Sb, we assign the features in our spectra to the underlying Bi layers. And indeed, when the measured DOS for 3 ML Bi is subtracted from that for the 1 ML-\(\beta\)-Sb the result (black) is in very good agreement with the calculated DOS.

The agreement between the calculated and measured DOS for both 1 ML-\(\beta\)-Sb and 2 ML-\(\alpha\)-Sb confirms that neither phase is significantly perturbed by interactions with the underlying Bi, and that the structures shown in figure 1(a) are indeed van der Waals heterostructures.

A remaining challenge is to clearly visualise edge states at the boundaries of all the structures of interest, and especially the topological states that are expected for the new \(\alpha\)-Sb phase. Such edge states were, however, only weakly observed in the DOS of 2 ML \(\alpha\)-Bi films [17] and are likely weaker in \(\alpha\)-Sb where there
is no band gap. We intend to perform detailed calculations of the edge state dispersion and DOS for α-Sb nanoribbon structures to guide future experiments.

Summary

One of the merits of our deposition technique is that it allows straightforward fabrication of heterostructures comprising materials with different thicknesses and different lateral dimensions [30, 36], and exhibiting a variety of moiré patterns. The combined influence of the moiré periodicity [8], inter-layer coupling, and strain on each of the materials within the heterostructures could allow exquisite control of the topology of their electronic states, and—as demonstrated in the present work—the realisation of new topological phases such as alpha-antimonene.

Finally, we note that the α-phases of Bi and Sb have a BP-like structure which has not previously been employed in van der Waals heterostructures, and in which the absence of surface dangling bonds means the structure is resistant to oxidation [16]. Together with the semiconducting nature of the MoS2 substrate, and potential to fabricate similar structures on a range of other substrates (especially those with rectangular symmetry), these features open up many new possibilities for the engineering of spintronic / topological devices.

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Notes

The authors declare that they have no competing financial interests.

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