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Interface effects in molecular beam epitaxy of SrMnSb₂ on InAs and GaSb: segregation and endotaxy

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Epitaxial growth of the topological semimetal SrMnSb₂ is demonstrated using InAs and GaSb substrates. The growth is studied by reflection high energy electron diffraction, X-ray photoemission spectroscopy and electron microscopy. The epitaxial orientation is SrMnSb₂ (001)||III–V (001), with the epilayer <010> axes parallel to substrate <110>. The relaxed in-plane lattice parameter of the epilayer depends on the vicinal miscut of the substrate and results in an overall volume expansion of the unit cell compared to bulk crystals, along with a possible lifting of the bulk orthorhombic distortion. Segregation of substrate atoms through the growing film is observed, along with Mn-driven endotaxial growth of secondary phases. Interface control methods to suppress endotaxial growth are discussed.

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1 Introduction

Semimetallic materials with topologically protected electronic states attract intense research effort because they show a range of new physical effects and could be exploited in novel electronic devices. The family AMnPn₂ (A = alkaline earth metal, Pn = pnictogen Sb or Bi) is of great interest¹ as a class of potential Dirac semimetals. For example, tuneable spin-valley coupling of Dirac nodes has been observed in BaMnPn₂.² Additional non-symmorphic crystal symmetries or magnetic order may induce Weyl physics. SrMnSb₂ is an antiferromagnetic semimetal which has been studied both theoretically and in bulk single crystal form.^{1,3–10} A gapped Dirac dispersion is predicted at the Y-points of the Brillouin zone of SrMnSb₂, with a gap around 200 meV.^{3,4} Remarkably, the material supports a coherent A_g phonon mode with frequency 4.4 THz which is predicted to narrow and, at sufficient amplitude, close the Dirac gap on femtosecond timescales 4. This offers unique possibilities for ultrafast control of Dirac and Weyl physics.¹¹

Epitaxial thin film material is preferable to bulk single crystals for device applications: not only does it allow

efficient device processing and improved compatibility with existing electronic materials, but additional control is possible *via* quantum size effects, strain engineering and magnetic proximity effects. Crucially, the effects of the coherent phonon could be studied by ultra-fast pump-probe spectroscopy of thin-film SrMnSb₂.¹¹ Although the related materials SrMnBi₂ (ref. 12 and 13) and MnSb (ref. 14) have been grown using molecular beam epitaxy (MBE), thin-film SrMnSb₂ has not yet been grown and characterised. The MBE growth of transition metal pnictides such as MnSb,^{15–18} CrSb (ref. 19) and NiSb (ref. 20) is quite well established.²¹ In many respects the surface chemistry of the epitaxy appears to follow that of the III–V semiconductors, at least in respect of the pnictogen. At sufficiently high substrate temperature, incorporation of the group V element is self-limiting, leading to stoichiometry between the transition metal and pnictogen components. At too low a substrate temperature, excess pnictogen may be incorporated. Excessively high substrate temperature leads to the group V element re-evaporating before incorporation.¹⁸ However, the growth window between these two extremes is wide (at least 200 °C for MnSb) and so there is scope for MBE optimisation on different substrates. Endotaxial growth of secondary phases has been noted for MnSb grown on both GaSb (ref. 22) and InP, (ref. 23) and for MnP on GaP,²⁴ *i.e.* these phases form as nano-crystals *below* the initial substrate surface. This is potentially

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problematic for SrMnSb_2 , whose antiferromagnetism may be masked by ferromagnetic secondary phases such as MnSb or MnAs .

In this paper we describe the MBE growth of $\text{SrMnSb}_2(001)$ on InAs and $\text{GaSb}(001)$ substrates. The primary interfacial effects of segregation and endotaxy are explored using structural and chemical analysis.

2 Crystal structure and heteroepitaxy

Our choice of InAs and GaSb as substrates was motivated by minimisation of epitaxial strain and symmetry mismatch. The SrMnSb_2 lattice structure is illustrated²⁵ in Fig. 1. The orthorhombic unit cell⁷ (shown as the rectangular frame in the figure) has c much larger than a or b , which are not quite equal. Note that we choose to denote the long axis as c so that $[001]$ is the epitaxial growth direction; the space group of bulk SrMnSb_2 is then $Pcnm$.¹ The bulk unit cell dimensions were measured as (4.41, 4.46, 23.10) Å for recent stoichiometric bulk material.¹⁰ The $[001]$ layering arrangement can be described as MnSb_4 tetrahedra separated by checkerboard pattern Sr-Sb in sandwich structures. Mn and Sr atoms share no bonds with each other and are separated by intermediate Sb planes. The Sr-Sb arrangement is slightly different in each $c/2$ half of the unit cell, which is also observed in SrZnSb_2 .^{5,26} The $\text{Sb}(1)$ layer differs from structures such as the equivalent $\text{Bi}(1)$ layer of SrMnBi_2 by

a subtle distortion in the otherwise 2D square lattice,²⁷ incurred *via* a Peierls distortion,²⁸ and results in a buckled atom arrangement with orthorhombic symmetry. Under external stress, the unit cell structure can instead maintain a square $\text{Sb}(1)$ lattice *via* the same mechanism as SrMnBi_2 , in which the strong spin-orbit coupling (SOC) suppresses the distortion. The weaker SOC in Sb interactions can overcome the buckling phenomenon by inducing a compression of the total cell volume by 10%, forcing the interatomic distances to contract and thus flattening the Sb layer and closing the band gap.³ It is plausible that epitaxial strain could also affect the orthorhombic distortion.

Fig. 1 shows a possible epitaxial arrangement on $\text{InAs}(001)$. The (a, c) axes of the SrMnSb_2 align with the $[110]$ and $[1\bar{1}0]$ primitive surface mesh axes of the InAs with average lattice mismatch 3.2%. This is indeed the observed epitaxial relationship, although the precise interfacial atomic structure is not known. The figure illustrates the lower $\text{Sb}(1)$ layer of the SrMnSb_2 adopting the approximate atomic positions of the surface As atoms in bulk-like $\text{As-terminated InAs}(001)$. The vertical black bar represents the $a/2 \approx 3$ Å step height on $\text{InAs}(001)$, which is far smaller than the c lattice parameter of SrMnSb_2 . Short grey lines joining In to Sb atoms represent interfacial bonds with an exaggerated in-plane epitaxial mismatch.

Epitaxial mismatches (% change between film and substrate lattice parameter, normalised to the latter) are shown in Table 1 for several common semiconductor materials. Negative values indicate that the SrMnSb_2 must be compressively strained to match the substrate, and the positive values (for InSb only) would require tensile strain in the SrMnSb_2 . The (a, b) column uses the averaged in-plane lattice parameter of SrMnSb_2 and this quantity will be discussed subsequently. A good lattice match to the average (a, b) spacing of bulk SrMnSb_2 could be achieved by growing on the ternary materials $\text{InAs}_{0.5}\text{Sb}_{0.5}$ or $\text{Ga}_{0.6}\text{In}_{0.4}\text{Sb}$.

The critical thickness d_c for plastic relaxation *via* misfit dislocations is also tabulated. This was estimated using the People-Bean model²⁹ evaluated in closed form using the Lambert W-function.³⁰ Elastic constants are taken from first-principles calculations reported in Materials Project.³¹ Because the Burgers vectors of misfit dislocations in SrMnSb_2 are not known, a range from $a\sqrt{2}$ to a is used. The three high-mismatch substrates are out of the range of validity of the continuum elastic model. The calculation suggests that pseudomorphic SrMnSb_2 should be observable on $\text{GaSb}(001)$,

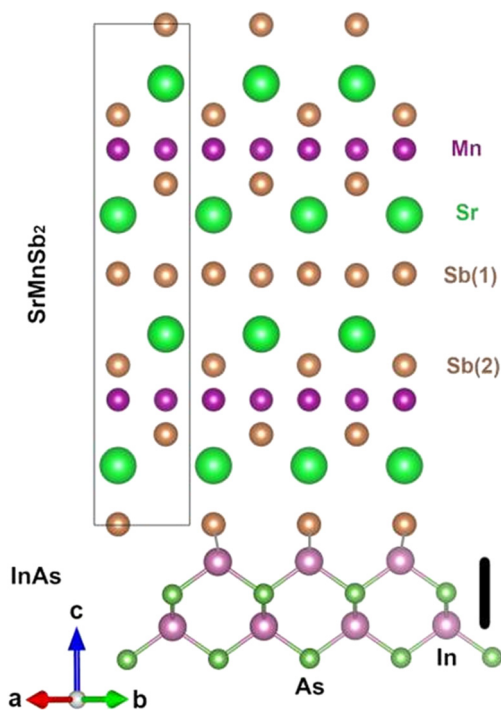


Fig. 1 SrMnSb_2 crystal structure and possible epitaxy on $\text{InAs}(001)$. The crystallographic axes refer to the substrate and colour-coded atoms are labelled in the figure. The SrMnSb_2 is shown in the ac -plane and the InAs in a $[110]$ plane. The vertical black bar represents the surface atomic step height on $\text{InAs}(001)$.

Table 1 Epitaxial mismatch and critical thickness d_c for SrMnSb_2

Substrate	% (a)	% (b)	% (a, b)	d_c (nm)
InAs	-2.6	-3.7	-3.2	4.8–11.4
GaSb	-2.0	-3.1	-2.5	9.9–22.5
InSb	4.1	3.0	3.5	3.6–8.7
GaAs	-9.9	-11.1	-10.5	
Si	-14.5	-15.7	-15.1	
SrTiO_3	-12.9	-14.2	-13.6	



but that relaxation may occur on InAs(001) before even 2 ML film thickness (here defining 1 monolayer, ML, of SrMnSb₂ as one bulk unit cell, 2.3 nm height).

3 Experimental methods

The two readily available low-mismatch substrates, InAs and GaSb, were used, with and without GaSb buffer layers. Miscut (vicinal) substrates are often used in MBE to promote layer-by-layer growth or suppress anti-phase boundaries, and several vicinal miscuts of InAs(001) were also investigated. Substrate wafers were cleaved to roughly 8 mm square pieces and mounted to sample transfer flags using spot-welded Ta strips. Preparation of clean, reconstructed, III-terminated surfaces was achieved by a combination of chemical cleaning (dip in HCl:isopropanol mix) immediately before loading to vacuum under dry nitrogen, argon ion sputtering (500 eV ion energy, 1 μ A beam current) and annealing. The types of substrate and buffer layer are summarised in Table 2. For all substrates, SrMnSb₂ growth was performed either directly on the cleaned substrate or on a GaSb buffer layer.

The MBE growth was performed using shuttered effusion cells for Ga, Sr, Mn and Sb₄. These were calibrated using beam equivalent pressure (BEP) from a retractable ion gauge, and *via* scanning transmission electron microscopy (STEM) measurements of total film thicknesses. Growth was monitored using reflection high energy electron diffraction (RHEED) with a 12.5 keV beam. The fluxes and substrate temperature were initially based on our experience with MBE growth of MnSb,^{17,32} treating the summed Sr and Mn fluxes as equivalent to the Mn flux for MnSb. Optimising the quality of the RHEED patterns from this starting point led to the following standard growth conditions: substrate temperature $T_{\text{sub}} = 340$ °C, BEP ratios Sr:Mn:Sb approximately 1.0:1.2:6.5, total growth rate 0.6 nm min⁻¹, film thickness between 12 and 120 nm (5 to 50 ML). Any variations on these conditions are discussed in the individual results sections. The GaSb(001) buffer layers were grown at $T_{\text{sub}} = 360$ °C and 0.7 nm min⁻¹.

The STEM experiments were performed in a double aberration-corrected JEOL ARM200f TEM, operated at 200 kV. This TEM is equipped with an Oxford Instruments SDD energy dispersive X-ray analysis (EDX) detector, and elemental maps were obtained for the main elements in the heterostructures. Additional standard TEM images were obtained using a JEOL 2100 microscope, also operating at 200 kV. Samples were transferred either through air or *via* vacuum suitcase to separate chambers for study by X-ray

photoelectron spectroscopy (XPS). X-ray diffraction (XRD) was also performed on selected films (Panalytical X'Pert Pro MRD, Cu K α radiation). Samples transferred by air were protected from oxidation by arsenic caps deposited in a side chamber on the MBE vacuum system. Some samples were also capped with Sb by cooling in the MBE chamber under Sb₄ flux. Caps were not completely removed in XPS since the maximum annealing temperature used was set at the MBE substrate temperature.

4 Results and discussion

4.1 General results

Before discussing the individual interfaces, we show a selection of results to highlight common features. Fig. 2 shows RHEED patterns for SrMnSb₂ grown on a GaSb(001) buffer layer on InAs(001). Row (a) shows the initial InAs surface, which displays a (4 \times 2) periodicity as expected for an In-stable surface prepared without As flux. Strong Kikuchi features characteristic of the zincblende B3 structure are visible. Row (b) shows the GaSb buffer layer surface (20 nm grown) with (1 \times 3) surface periodicity. The GaSb is pseudomorphic to the InAs substrate and the Kikuchi features are identical. Row (c) shows the SrMnSb₂ surface (12 nm or 5 ML grown). The in-plane lattice parameters have relaxed to larger values, slightly larger than the bulk (*a*, *b*) lattice parameters of SrMnSb₂. The Kikuchi features have vanished and there is no surface reconstruction. The RHEED pattern is streaky but the background is higher and some modulation and spots are visible on the streaks. In general, the background intensity and spottiness of the RHEED

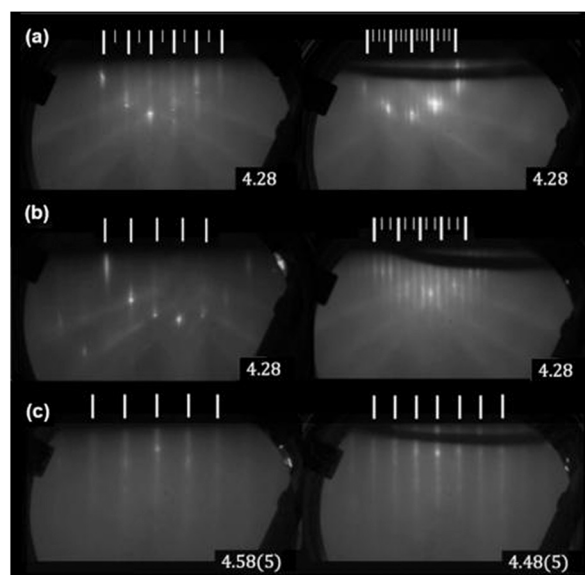


Fig. 2 RHEED patterns for SrMnSb₂ grown on GaSb buffer on InAs(001) in the [110] and [110] azimuths. Long white dashes indicate integer order surface streaks, while short dashes highlight fractional orders. Inset numbers show the lattice parameter in Å. Row (a) shows the as-prepared InAs(001) surface. Row (b) shows the completed GaSb(001) buffer layer. Row (c) shows the completed SrMnSb₂ layer.

Table 2 Substrate types for SrMnSb₂ heteroepitaxy

Material	Miscut (°)	Buffer (nm)	Section
InAs	0 \pm 0.1, 0.5, 1, 2	None	4.1, 4.2
InAs	0 \pm 0.1, 0.5, 1, 2	GaSb 10–20 nm	4.1, 4.4
GaSb	0 \pm 0.1	None	4.1, 4.3
GaSb	0 \pm 0.1	GaSb 10–20 nm	SI



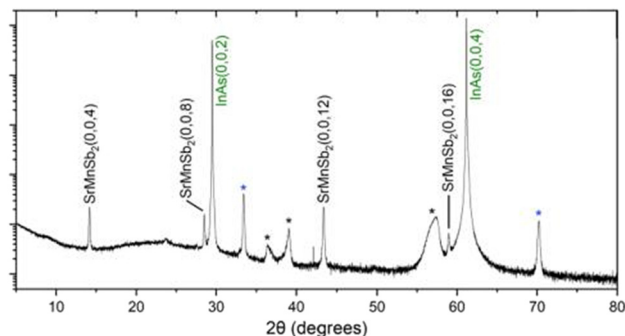


Fig. 3 XRD data for 80 nm SrMnSb_2 grown directly on $\text{InAs}(001)$. Substrate and SrMnSb_2 peaks are labelled. The asterisks denote secondary phases.

patterns increased at higher SrMnSb_2 film thicknesses. It was not possible to distinguish between the a and b lattice parameters in RHEED, although the precision of the relative lattice parameter measurement should be sufficient (SI). For all SrMnSb_2 films studied, the streak spacings in orthogonal the $[10]$ and $[01]$ directions were identical within the measurement uncertainty. This is compatible with tetragonal rather than orthorhombic symmetry.

Fig. 3 shows XRD data for a thick SrMnSb_2 epilayer grown directly on $\text{InAs}(001)$. Apart from the substrate peaks, a family of sharp peaks is visible which can be assigned to $\text{SrMnSb}_2(0004n)$ reflections. Together with the RHEED data, this confirms the epitaxial orientation of SrMnSb_2 . The peak series can be fitted with a lattice parameter of $25.074(4) \text{ \AA}$, slightly larger than the c parameter of bulk crystals.¹⁰ Scherrer analysis (SI) gives a crystallite size of 10.7 nm , significantly smaller than the film thickness. This indicates that the epilayer contains domains or other extended defects, consistent with the poorer RHEED patterns for the thickest films. The XRD peaks labelled with asterisks correspond to secondary phases. The blue asterisk peaks (5.37 \AA) can be tentatively identified with strained orthorhombic MnAs .^{21,32} The remaining peaks, black asterisks, can be tentatively assigned to cubic MnSb (ref. 32) and InSb . Note that if the unit cell of the SrMnSb_2 epilayer is identified as tetragonal rather than orthorhombic, then the main peaks can be assigned to $(0002n)$ reflections with $c = 12.537(4) \text{ \AA}$.

Fig. 4 shows example STEM and EDX data. Panel (a) gives an annular dark field (ADF) STEM image of a well ordered region of a SrMnSb_2 film, which was grown on an $\text{InAs}(001)$ substrate miscut by 1° towards $(111)\text{B}$. The orthorhombic bulk unit cell is outlined by an orange box ($4.6 \text{ \AA} \times 24.1 \text{ \AA}$). Panels (b, c, d, e) show a STEM image and the corresponding EDX elemental maps, obtained from a SrMnSb_2 sample grown directly on $\text{InAs}(001)$. The SrMnSb_2 epilayer is less uniform and its interface to InAs , appearing as a dark horizontal band, is rougher. Furthermore, a triangular or dome-like feature is visible below the substrate surface. As shown by the elemental maps, Sr and Mn appear in the epilayer, as expected. However, the Mn signal follows the shape of the dome-like sub-surface feature. The As signal of

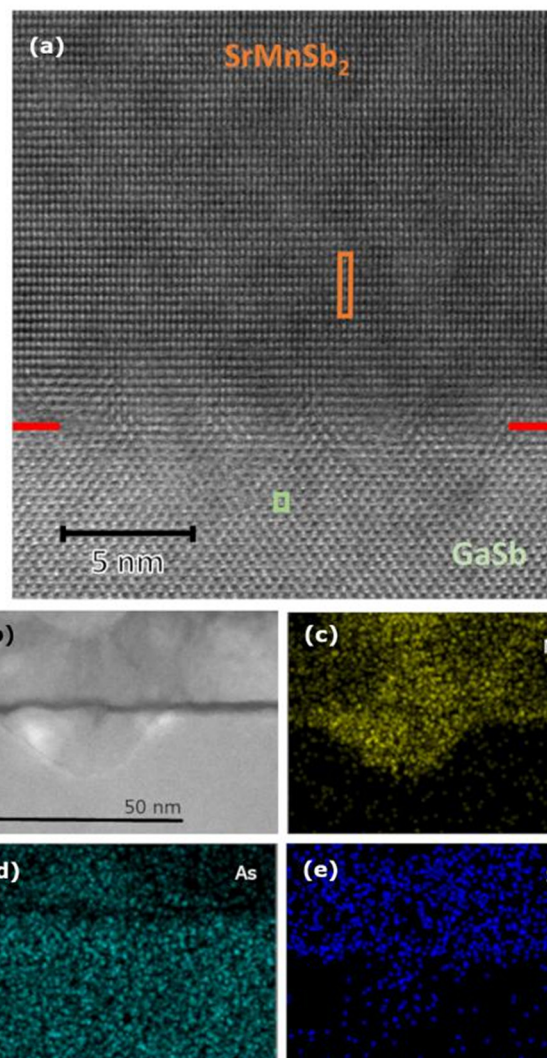


Fig. 4 Example STEM-EDX data. (a) ADF STEM image for SrMnSb_2 grown directly on $\text{GaSb}(001)$, with interface highlighted by red dashes. The bulk unit cells of GaSb and SrMnSb_2 are highlighted by coloured boxes. Panel (b) shows a BF STEM image of a sample grown directly on $\text{InAs}(001)$. The interface appears as a dark band and a triangular feature is visible below the substrate surface. EDX data are shown for Mn, As and Sr in panels (c), (d) and (e) respectively, identifying this feature as endotaxial MnAs .

the InAs substrate is quite uniform, allowing us to identify the subsurface nano-cluster as endotaxial MnAs . A small amount of Sr also appears in the endotaxial nano-cluster. Finally, a significant As signal [panel (c)] is observed in the SrMnSb_2 epilayer above the endotaxial cluster, indicating local segregation of As from the substrate into the growing film.

Fig. 5 gives XPS data for films grown directly on InAs and GaSb substrates. Panel (a) shows an XPS survey scan after vacuum suitcase transfer of a 35 nm thick film. No $\text{O } 1s$ or $\text{C } 1s$ peaks can be observed, indicating that the suitcase transfer did not introduce any surface contamination. The films have complete coverage and are sufficiently thick to prevent photoelectrons escaping from the substrate, and so



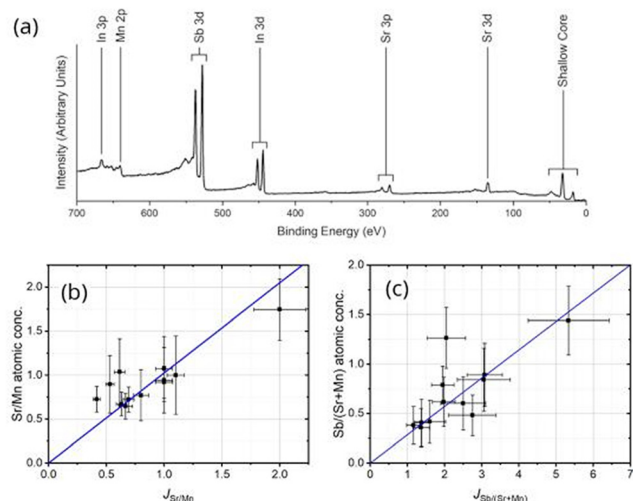


Fig. 5 (a) XPS survey scan for a SrMnSb_2 sample grown directly on $\text{InAs}(001)$, with all peaks indexed. (b) Sr/Mn composition ratio inferred from XPS as a function of Sr/Mn BEP ratio. (c) $\text{Sb}/(\text{Sr} + \text{Mn})$ composition ratio inferred from XPS as a function of $\text{Sb}/(\text{Sr} + \text{Mn})$ BEP ratio. In (b) and (c) the blue straight lines indicate stoichiometric incorporation.

the presence of clear $\text{In } 3d$ and $3p$ peaks implies that In has segregated through the SrMnSb_2 film.

The XPS was quantified using standard atomic sensitivity factors, with results for $[\text{Sr}]/[\text{Mn}]$ ratios and $[\text{Sb}]/([\text{Sr}] + [\text{Mn}])$ ratios shown in Fig. 5(b) and (c) respectively. The $[\text{Sr}]/[\text{Mn}]$ ratio inferred from XPS follows stoichiometric incorporation of the fluxes as measured by BEP, with a slight excess of Sr possible at low BEP ratio. The Sb incorporation shows a similar trend with BEP ratio. Although the Sb incorporation does not seem to show clear self-limiting behaviour, as is the case for MnSb ,²¹ only two data points lie above the line $[\text{Sb}]/([\text{Sr}] + [\text{Mn}]) = 1$. The BEP standard ratios used aim to provide stoichiometric SrMnSb_2 and the average $\text{Sr}:\text{Mn}:\text{Sb}$ atomic ratios inferred from XPS for samples grown close to the standard conditions were 1:0.89:1.95.

To summarise these general results, the RHEED and XRD confirm that the epitaxial orientation of the SrMnSb_2 has the long $[001]$ axis out of plane and the $[100]$ and $[010]$ axes aligned with substrate $[110]$ and $[1\bar{1}0]$ bulk axes (*i.e.* the primitive surface mesh $[10]$ and $[01]$ axes). Diffraction results are compatible with relaxation of the orthorhombic distortion of bulk material towards a smaller tetragonal unit cell. The standard growth conditions produce SrMnSb_2 films with close to stoichiometric composition. For growth on InAs substrates, indium surface-segregates through the films. Furthermore, endotaxial growth of MnAs nano-clusters within the substrate occurs, accompanied by some local diffusion of As into the epilayer and Sb -related secondary phases.

4.2 Direct growth on $\text{InAs}(001)$

Fig. 6 shows a sequence of RHEED patterns for direct deposition of SrMnSb_2 on $\text{InAs}(001)$ [$T_{\text{sub}} = 360^\circ\text{C}$]. The

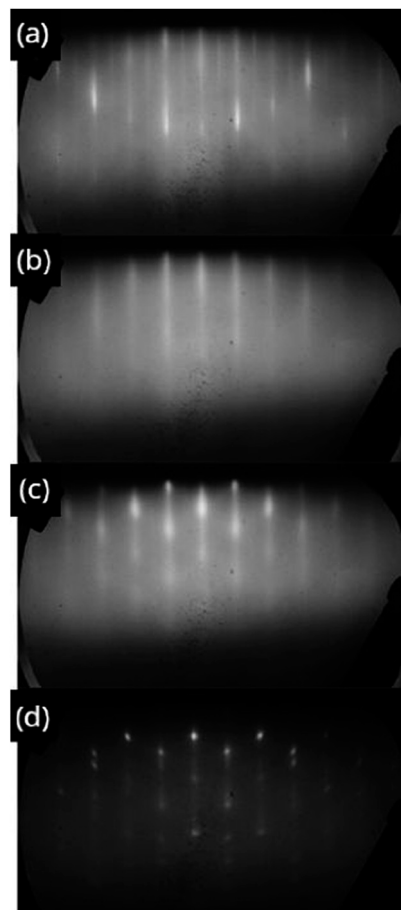


Fig. 6 RHEED patterns in the $[110]$ direction for SrMnSb_2 grown directly on $\text{InAs}(001)$. (a) As-prepared $\text{InAs}(001)$ surface, with $2\times$ periodicity; (b) 1 minute SrMnSb_2 deposited ($0.6\text{ nm} \approx 0.25\text{ ML}$); (c) 4 nm deposited; (d) 50 nm deposited.

as-prepared InAs surface shows the expected (4×2) or $c(8 \times 2)$ periodicity, with half-order streaks clearly present in the $[110]$ RHEED pattern [Fig. 6(a)]. These fractional order streaks vanish almost immediately when SrMnSb_2 growth is initiated by opening all three shutters simultaneously. Panel (b) shows only integer order streaks after just 0.25 ML SrMnSb_2 coverage (0.6 nm). This is also true for the $[110]$ azimuth; indeed, throughout the experiments no surface reconstruction of SrMnSb_2 was observed, *i.e.* (1×1) periodicity only. As growth proceeds, modulation appears along the diffraction streaks, which evolves into a mixed spotty/streaky pattern (c, d). This indicates increasing roughness leading to transmission diffraction. The spots lie on the surface streaks which indicates that the material growing as 3D islands is the same as that growing in layer-by-layer fashion, and is co-epitaxial.

The in-plane lattice parameter measured by RHEED rapidly increases from the substrate value as growth proceeds, as shown in Fig. 7 for two different substrate miscuts. At the earliest stages of growth, up to 1 ML SrMnSb_2 coverage, the lattice parameter remains at the



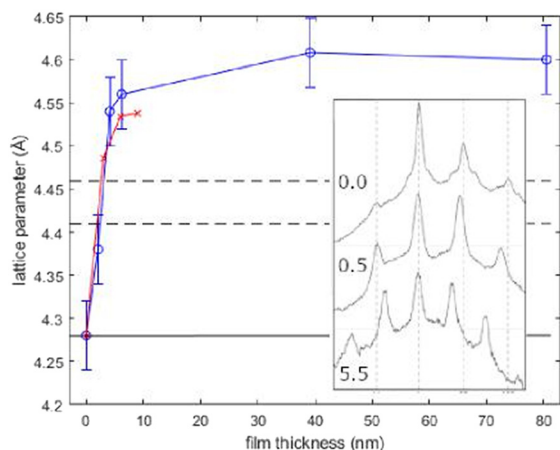


Fig. 7 In-plane lattice parameter as a function of film thickness, as inferred from streak spacings in RHEED. The InAs in-plane lattice parameter is highlighted by the solid horizontal line, while the dashed lines shown bulk (*a*, *b*) parameters for SrMnSb₂. Blue open circles correspond to SrMnSb₂ directly grown on InAs(001) miscut by 2°, while red crosses shown a sample miscut by 1°. Inset are typical RHEED intensity profiles for 0, 0.5 and 5.5 ML SrMnSb₂ growth. Vertical dashed lines on the inset represent substrate streak spacing.

substrate value (SI). Full relaxation occurs by around 5 to 10 ML coverage (10 to 20 nm). These values are broadly in line with the estimated critical thicknesses (Table 1). However, the lattice parameter clearly increases *past* the nominal bulk values. The “over-relaxation” is unusual, especially when considered alongside the out-of-plane lattice expansion relative to bulk material inferred from XRD (Fig. 3). Combining the two expansions, the unit cell volume of the epitaxial material ($4.6 \times 4.6 \times 25.074 \text{ \AA}^3$) is increased by 16% compared to the bulk crystal ($4.41 \times 4.46 \times 23.1 \text{ \AA}^3$).¹⁰ This is not compatible with a biaxial distortion from the substrate mismatch. The different strain relaxation for growth on two different InAs(001) miscuts is suggestive of strain relaxation *via* vicinal surface epitaxy, as previously observed for III-nitride growth on SiC,^{33,34} Ga₂O₃ on sapphire³⁵ and chalco-genide films on Si.³⁶

When the RHEED patterns become spotty, it is possible to measure the out-of-plane lattice parameter of the film (SI). These measurements give values close to *c*/2. This agrees with the X-ray diffractogram (Fig. 3), which shows the (0 0 *4n*) family of peaks (*n* = 1, 2, ...) rather than the (0 0 2*n*). This can be interpreted as a lifting of the distortions which distinguish the two halves of the full *c* = 23.10 Å unit cell and split the (*a*, *b*) lattice parameters, and is consistent with observation by RHEED of equal (*a*, *b*) values. This smaller tetragonal unit cell is very close in energy (1 meV per atom (SI)) to the orthorhombic ground state³¹ and could readily be stabilised by epitaxial strain or the presence of segregated substrate atoms in the structure.

The crystallite size was inferred from XRD as being smaller than film thickness, and this is confirmed by TEM. Fig. 8 shows example images from SrMnSb₂ grown directly

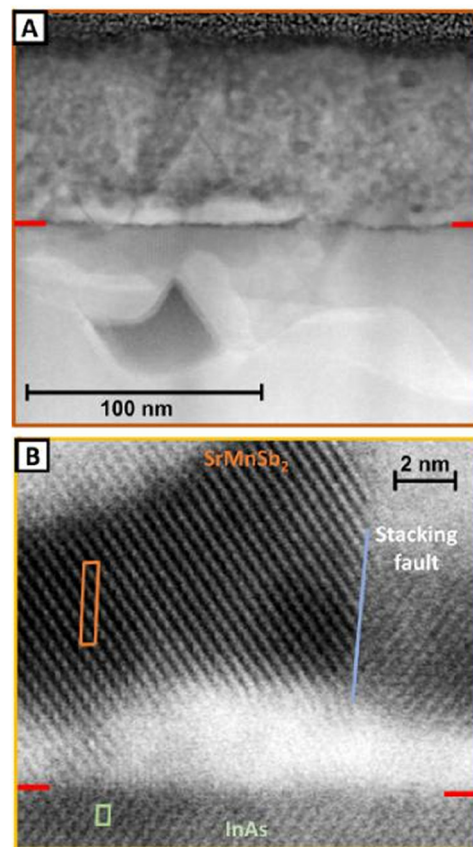


Fig. 8 TEM and STEM images for SrMnSb₂ grown directly on InAs(001), with interface highlighted by red dashes. The large scale image A shows some disruption at and below the interface (red dashes), and grain structure in the film. Image B at high magnification shows the unit cells of film and substrate (orange and green rectangles). A stacking fault is highlighted by a blue line.

on InAs(001). Image A shows a region of crystallographic disruption at the interface and grain-like structures above in the film. There is also clear endotaxial disruption below the interface. Atomic scale imaging is shown in B, with unit cells highlighted. The TEM data supports the epitaxial relationship and lattice parameters inferred from RHEED and XRD. However, a clear grain boundary is visible, most likely associated with a stacking fault. There is also a significant loss of atomic scale contrast close to the interface. The effective grain size is inevitably less than the film thickness for such samples. Smaller and more crystallographically diverse grains are observed in films with poorer RHEED patterns and a higher degree of endotaxial disruption (SI).

Three methods to suppress the endotaxial growth were investigated: (1) low temperature seed layer, (2) Sb soak, and (3) Sr-Sb growth initiation (delayed Mn flux). For (1), the substrate temperature was reduced to the range 30 °C to 200 °C for initial SrMnSb₂ growth up to a few ML thickness. However, this resulted in rapid and unrecoverable degradation of the RHEED pattern and was abandoned. For the Sb soak (2), the InAs(001) surface was



exposed to Sb flux for several minutes at the standard substrate temperature prior to initiation of SrMnSb_2 growth. The intention was to allow any excess In atoms at the surface to react with Sb and hence suppress surface segregation of In. This procedure caused the fractional order RHEED streak intensity of the initial (4×2) to be reduced but did not degrade the RHEED pattern of the subsequent SrMnSb_2 epilayers. However, segregated In was still observed in XPS, suggesting that the out-diffusion of In is not just a consequence of In nano-clusters or adatoms left from the surface cleaning process.³⁷ For procedure (3), the Sr shutter was opened 30 s before the Mn shutter (since the predominant endotaxial species was MnAs, it was hoped to discourage direct Mn interaction with the substrate). The SrMnSb_2 RHEED patterns were marginally better, and TEM data suggest that there is an overall reduction in secondary phase formation (SI). In addition, the delayed Mn flux reduced the concentration of surface-segregated indium by around 20%, according to XPS, and so this simple procedure was retained.

Clearly, the endotaxial growth of MnAs and related phases, along with concomitant segregation of In and As into the epilayer, has a deleterious effect on the uniformity of the SrMnSb_2 and the quality of the interface. Furthermore, MnAs is ferromagnetic²¹ and could easily mask the desired antiferromagnetic response of the SrMnSb_2 . We therefore consider GaSb substrates.

4.3 Direct growth on GaSb(001)

GaSb offers the lowest lattice mismatch (Table 1) as well as avoiding any problems arising from As segregation into the SrMnSb_2 . For direct growth on the as-prepared GaSb(001) substrates, an Sb soak was used to improve the initial GaSb(001) surface reconstruction and the delayed Mn flux protocol was employed. The evolution of RHEED patterns was very similar to that observed on buffer layers (Fig. 2) though with slightly worse quality and a higher tendency to show transmission diffraction spots. Despite this, the interface quality was generally improved over growth on InAs(001). Fig. 4(a) shows a STEM image of the $\text{SrMnSb}_2/\text{GaSb}$ interface at high resolution. While not atomically abrupt, the interface is reasonably sharp, transitioning between structures within a few unit cells either side of the nominal interface. There is no evidence of dislocations or other extended defects in this region of the film.

However, some segregation and endotaxial growth were observed. Fig. 9 shows a STEM image and selected (SI) EDX elemental maps for a $\text{SrMnSb}_2/\text{GaSb}(001)$ interface. On this wider view, the interface is still quite abrupt but some evidence for endotaxial growth and segregation. Two dome-like protrusions of Mn some tens of nm into the substrate can be seen in the centre of the Mn EDX map. The corresponding Sb map is quite uniform, suggesting that a MnSb phase has formed. There is a noticeable Ga

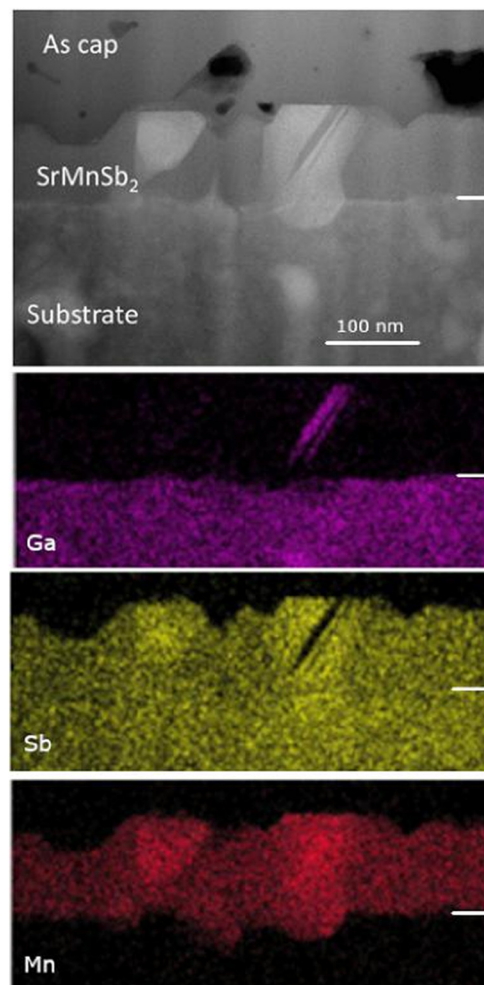


Fig. 9 STEM image and three EDX maps (Ga, Sb, Mn) for SrMnSb_2 grown directly on GaSb(001). The interface is highlighted by white dashes on the right in each panel.

deficiency close to the interface above the right hand side MnSb endotaxial nano-cluster, and above that a sharp “streak” of Ga can be seen within the SrMnSb_2 film. This shows that local Ga segregation has occurred. Sb is deficient on this streak, and there is a slight excess of Mn. The surface of the SrMnSb_2 film is defined by the Mn and Sb EDX maps. It is not planar but rather comprises mesa-like structures with flat tops. This morphology is consistent with the spotty RHEED patterns observed at higher film thicknesses.

The over-relaxation of the SrMnSb_2 epilayer also occurs on this substrate. Estimating unit cell dimensions from STEM (Fig. 4) gives a volume of $(4.6 \times 4.6 \times 24.1 \text{ \AA}^3)$, a volume expansion of 12% compared to bulk material.

4.4 Growth on GaSb buffer layers

GaSb(001) buffer layers were grown on both InAs(001) and GaSb(001) substrates. These were thin (10 to 20 nm) and were pseudomorphic on InAs(001) as expected. Typical



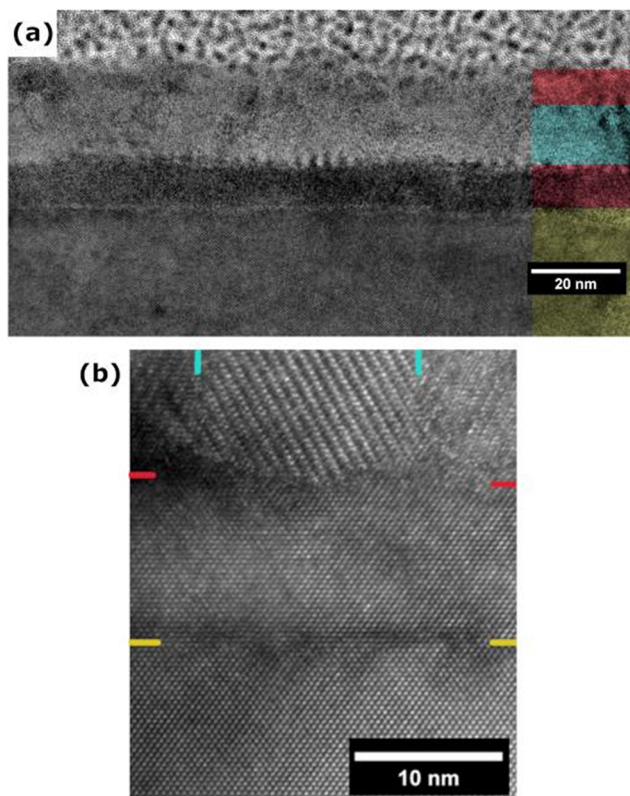


Fig. 10 TEM images of a SrMnSb_2 sample grown on a GaSb buffer layer on $\text{InAs}(001)$. Panel (a) shows an overview with colour blocks on the right highlighting the layer structure (yellow InAs , red GaSb , teal SrMnSb_2). Panel (b) shows a higher resolution image of the GaSb buffer layer interfaces to the underlying InAs (yellow dashes) and the overgrown SrMnSb_2 (red dashes). Vertical teal dashes show two grain boundaries in the SrMnSb_2 epilayer.

RHEED results were already shown in Fig. 2 for a sample grown using standard conditions. In such conditions, the SrMnSb_2 RHEED patterns were less spotty on GaSb buffer layers than when grown directly on as-prepared $\text{GaSb}(001)$. This is in line with the results on $\text{InAs}(001)$, where a poorer starting surface led to poor and unrecoverable SrMnSb_2 RHEED. Indium segregation is expected for the GaSb-on- InAs interface^{38–40} and segregated In was observed in XPS for these buffer layers (SI).

Two TEM images of a sample grown on 15 nm GaSb- $\text{InAs}(001)$ buffer layer are shown in Fig. 10. In panel (a), the InAs -to-GaSb interface appears as a lighter band, with the GaSb buffer layer darker than the substrate (colour highlights on the right guide the eye). The interface between the GaSb buffer and the SrMnSb_2 is not atomically abrupt. However, there is no evidence for significant endotaxial phase formation. Available measurements over several samples suggest that endotaxial growth was significantly less prevalent for samples growth on buffer layers compared to direct growth on GaSb. Note that this sample was capped with a thin GaSb layer, which shows a granular structure (top layer highlighted in red). Panel (b) shows a higher magnification image of the

interfaces. Yellow dashes highlight the abrupt GaSb-on- InAs interface, with the GaSb showing a continuous pseudomorphic crystal structure. The red dashes show the SrMnSb_2 -on-GaSb interface, which is less abrupt and fluctuates by several atomic layers. The SrMnSb_2 film shows three domains. The TEM images and RHEED (Fig. 2) confirm the improved SrMnSb_2 film quality when grown on GaSb buffer layers, even when they are thin (as low as 10 nm).

Conclusions

Thin epitaxial films of $\text{SrMnSb}_2(001)$ have been grown on $\text{GaSb}(001)$ and $\text{InAs}(001)$ substrates. The in-plane epitaxial orientation has epilayer $\langle 010 \rangle$ axes parallel to substrate $\langle 110 \rangle$. The in-plane strain is relaxed rapidly, with only around 1 ML of pseudomorphic growth. Films typically “over-relax”, with unit cell volume expansion up to 16% above the nominal bulk values, and the overall relaxation is affected by the vicinal miscut of the substrate. In diffraction, $(0004n)$ peaks are observed and the (a, b) lattice parameters cannot be distinguished. This is compatible with the orthorhombic distortion present in bulk crystals being lifted in epilayers, which could adopt a tetragonal structure with c lattice parameter around half the bulk value. Further study of the crystal structure of the epilayers using synchrotron XRD would be valuable.

Growth is hampered by the formation of endotaxial secondary phases alongside segregation of atoms from the substrate. This is particularly severe for direct growth on InAs substrates, where MnAs nanoclusters and other phases are formed. Both In and As segregate into the SrMnSb_2 films, the former surface-segregating through the films to give a prominent In signal in XPS. Arsenic segregation appears to associated more with local defect phases, as does Ga segregation for growth on GaSb. Controlled interface formation by Sb soak and delayed Mn exposure helped to limit endotaxial phase formation. Overall, in order of prevalence of endotaxial growth, direct growth on InAs substrates was worst, followed by direct growth on GaSb, with growth on GaSb buffer layers the most favourable.

A promising method for reliably suppressing endotaxial growth is remote epitaxy *via* the inclusion of an ultra-thin amorphous carbon layer.⁴¹ This acts to decouple the growing film from the substrate while maintaining the epitaxial relationship. A key advantage of amorphous carbon is that it can be grown *in situ* on any III-V substrate and does not require wet or dry transfer, as would be the case for a 2D material such as graphene. To our knowledge, this application of remote epitaxy has not yet been studied. A longer Sb soak for interface optimisation of GaSb buffer layers³⁹ may also improve the surface quality for SrMnSb_2 epitaxy. Atomic exchange models with multiple species,³⁸ extended to include Mn, may be useful in understanding endotaxial growth.



Author contributions

Bell, Rehaag: conceptualization, writing – original draft, formal analysis, methodology. Bell: supervision. All authors: investigation, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data for this article, including RHEED and TEM, are available at Warwick Research Archive Portal at <https://wrap.warwick.ac.uk/192906>.

Supplementary information: this includes additional analysis of RHEED, XRD, TEM and XPS. See DOI: <https://doi.org/10.1039/d5lf00284b>.

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