ADVANCED MATERIALS INTERFACES

Supporting Information

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Hints for a General Understanding of the Epitaxial Rules for van der Waals Epitaxy from Ge-Sb-Te Alloys

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SUPPORTING INFORMATION

Hints for a general understanding of the epitaxial rules for van der Waals epitaxy from Ge-Sb-Te alloys

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InAs(111) surfaces

Zincblende {111} surfaces are intrinsically polar and can be cation (A) and anion (B) terminated; in this paper three different substrate surface reconstructions were considered: InAs(111)A-2×2 and InAs(111)B-2×2 and -1×1. The surface unit cell of the InAs(111)A-2×2 reconstruction contains one In vacancy and three surface In atoms, this surface is self-passivated having no half-filled dangling bonds.[1,2] The InAs(111)B surface exhibits a 2×2 reconstruction at As-rich conditions and a 1×1

unreconstructed surface at As-poor conditions. [3,4] The surface unit cell of the 2×2 As-rich reconstruction has one As-trimer in the adlayer; even in this case no unsaturated dangling bonds are present on the surface reconstruction, which can be considered self-passivated. [3,4] Conversely, the 1×1 surface structure does not satisfy the electron counting rule, [5,6] it would be meta-stable or stabilized by surface defects, as actually observed by STM experiments; [3] this surface is expected to be un-passivated. In the case of InAs(111)A substrates, a 2×2 reflection high energy electron diffraction (RHEED) pattern can be obtained after annealing the samples at 400 °C. Depending on the time of annealing the RHEED pattern quickly deteriorates from quite streaky (sample A1, see Fig. S1 and Tab. 1 in the main text), where an intensity modulation is visible, to an almost spotty pattern for longer annealing (sample A2).

The desorption temperature for the native oxide on InAs(111)B is higher than the maximum temperature of congruent evaporation at which the surface starts decomposing. As a result, the surface cannot be cleaned by a simple annealing in UHV, while sputtering will usually degrade and alter the surface. To overcome this problem, thick layers (~250 nm) of InAs were grown on InAs(111)B substrates in a separate MBE dedicated to III-Vs. After the growth, the samples were capped at room temperature with an amorphous layer of As and transferred, under ambient conditions, to the MBE system dedicated to GST epitaxy. Then, by means of a short annealing at about 260 °C the As-cap was removed and a very sharp 2×2 streaky pattern appeared (Fig. S1, sample B1). A longer annealing at the same temperature leads to a further As desorption and the surface reconstruction changes from 2×2 to the less As-rich 1×1. A very long annealing of the sample at 300 °C no longer changes the surface reconstruction, but the surface quality deteriorates as can be observed by the blurring of the streaks and the increase of the background in the RHEED pattern (Fig. S1 sample B2).

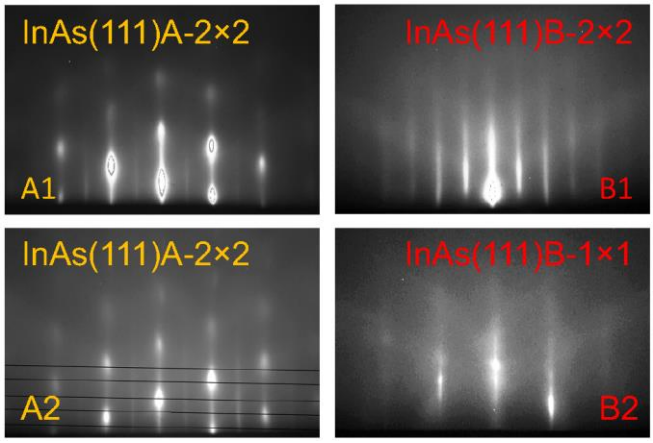

Figure S1. RHEED patterns along the $\langle 1\bar{1}0 \rangle$ direction of InAs(111)A and InAs(111)B substrate surfaces for samples A1 (top left panel), B1 (top right panel), A2 (bottom left panel) and B2 (bottom right panel). Patterns are typical of flat surfaces (B1 and B2) as well as mixed flat/rough surfaces (A1 and A2).

For annealing temperatures as high as 500 °C of InAs(111)A substrates a 2×2 streaky pattern was again obtained but, at these high temperatures, the surface undergoes a partial melting and recrystallization, which gives rise to the formation of nuclei with orientations other than (111) (see XRD characterization in Fig. S2). Besides, for such a treatment the formation of 60° rotated domains of 2D InAs islands (crystal structure from ZB to WZ) has been observed. [3] The presence of grain boundaries between the twin defects can influence the epitaxy of GST on InAs, which makes this surface interesting in our context (sample A3).

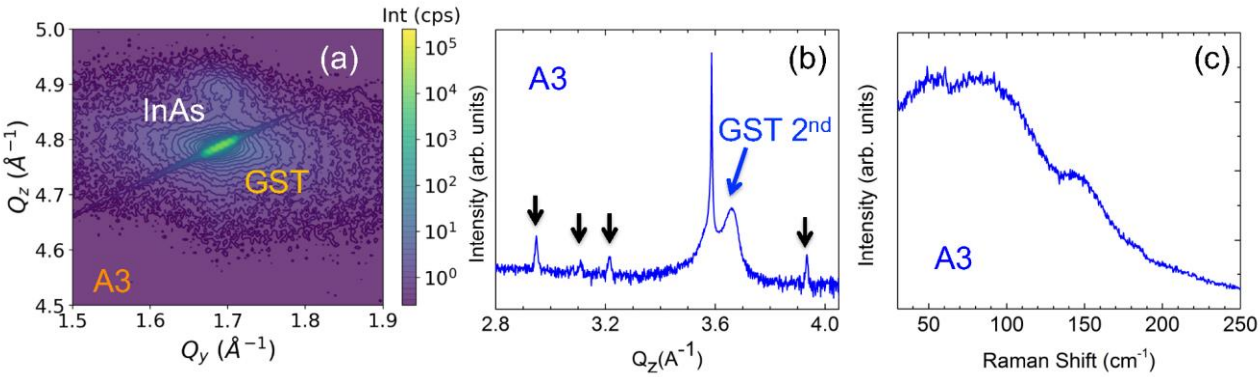

Figure S2. (a) Reciprocal space map around the asymmetric InAs(224) Bragg reflection in coplanar configuration of sample A3. InAs and GST reflection are almost completely superimposed (same lattice parameter) indicating that GST is growing pseudomorphically on InAs. (b) Symmetric XRD ω-2θ scan around the second order InAs and GST reflection of sample A3. The small sharp peaks (black arrows) arise from the presence of grains with orientations other than (111). (c) Raman spectrum of sample A3. As for sample A2, the spectrum shows almost no first order Raman modes with very broad features at ~80 and ~150 cm^{-1}, as the result of the partial breaking of symmetry in cubic rocksalt due to disorder and defects present in the crystal, suggesting that sample A3 is of cubic rocksalt structure. [7]

RHEED after GST growth

Here below we present the RHEED data along the $\langle 11\bar{2} \rangle$ azimuth for sample A2 and B2 after GST epitaxy. A2 RHEED pattern presents 2D streaks and a large diffused scattering background,

indicative of a lower surface quality. B2 RHEED pattern is 2D and streaky with a low background witnessing a good morphology after epitaxial growth.

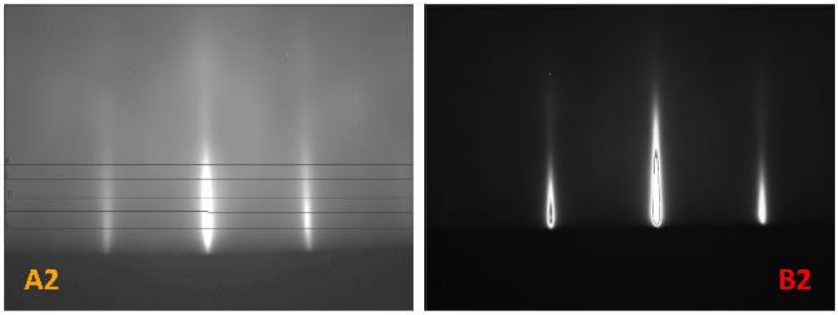

Figure S3. RHEED patterns along the $\langle 11\bar{2} \rangle$ direction after GST deposition InAs(111)A and InAs(111)B substrate surfaces for samples A2 (right panel), B2 (left panel).

Interplay between composition and strain in GST alloys

The GST 326 and 225 compositions differ from the structural point of view essentially only in terms of the out-of-plane lattice parameter, while both the in-plane lattice parameter and the out-of-plane Te-Te distance within the cell do not vary [8].

The different GST compositions (326 or 225) can be evaluated best when analyzing the distance between vdW/VL and the GST peak [9]. In fact, the distance between the vdW/VL and the GST peak relates to the out-of-plane lattice parameter, that for 326 and 225 varies of about 15%. The GST peak instead refers to the Te-Te distance that is not changing for both compositions, although could change in presence of strain. The same argument holds for the in-plane lattice parameters, that are the ones we evaluate from the RSMs, that are negligibly different for GST225 and GST326 (as also explained in the manuscript), thus the RSM peak positions of both compositions will be very close to each other, not allowing for composition evaluation. However, the presence of strain can be evaluated from the position of the GST peak in respect to the position of the substrate. This is indeed different from purely covalently bonded materials in which composition and strain are strongly related.

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