Atomically Smooth Defect-Free III-As Heterostructures on InP(111) Substrate for Next-Generation Electronic Devices

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ABSTRACT: Research into Zinc Blende III–V compound semiconductors has focused almost entirely on growth on (001)-oriented substrates for more than five decades. This is because high-quality epitaxial layers can be achieved relatively smoothly when III–Vs are grown on (001) substrates. However, emerging technologies generated renewed interest in the growth of high-quality III–Vs on (111)-oriented substrates. Prime examples of these applications are devices based on spin transport, and low-anisotropy tensile-strained quantum dots for quantum computing applications. Growth on (111) substrates could also help understand the growth of complex chalcogenides. Exploring these applications requires high-quality epitaxial thin films on (111) substrates. Here, we demonstrate for the first time the atomically smooth and defect-free growth of nanoscale InGaAs/InAlAs superlattice on InP(111)-oriented substrate using molecular beam epitaxy (MBE). This was achieved by optimizing the substrate misorientation angle and growth conditions. The growth optimization was guided by scanning transmission electron microscopy Moiré geometrical phase analysis and density functional theory calculations. It is shown that ensuring the step-flow growth mode for each ternary layer is the most effective way of achieving high-quality epitaxial structures on (111)-oriented substrates. This work sets the stage for developing InGaAs/InAlAs/InP(111) electronic and photonic structures with properties that can be tuned with strain-mediated piezoelectric effects. The reported observations should help optimize epitaxy in other Zinc Blende material systems for the structure that could benefit from the tunable piezoelectric effects.

KEYWORDS: molecular beam epitaxy, InP(111)B, migration length, phase instability, stacking faults, vicinal surfaces

INTRODUCTION

Epitaxial growth on (111) substrates, using both molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD), was mainly studied in the 1970s, 1980s, and 1990s with a focus on GaAs. However, since most growth conditions resulted in a defective and rough surface, McFee et al. concluded that growth on (111) substrates is too difficult; therefore, efforts should focus on (001) surfaces for reproducible device quality epitaxial layers. The decline in funding and research in this field followed. However, in recent years, growth on polar (111) surfaces has generated renewed interest due to the emergence of new applications for which switching to (111) substrates would offer significant advantages. Prime examples are devices based on spin transport novel, low-anisotropy tensile-strained quantum dots for quantum computing applications. Growth on (111) substrates could also help understand the growth of complex chalcogenides.

InGaAs/InAlAs material system grown on (001) InP substrates has received much interest due to its application in optoelectronics. Also, MBE-grown short-period InGaAs/InAlAs superlattices (SLs) on (001) InP have been successfully used for THz transmitters (Tx) and receivers (Rx) in photoconductive antennas for terahertz time-domain spectroscopy (THz-TDS) systems. Unlike the more established MBE-grown low-temperature GaAs (LT-GaAs), InGaAs can be efficiently excited over optical fibers at a wavelength of 1.55 μm using compact and relatively inexpensive telecom femtosecond lasers. However, in this case, MBE growth conditions must be separately optimized for emitter and receiver structures, adding to cost and complexity. Recently, InGaAs/InAlAs SLs grown on InP(111) substrates were proposed as a next-generation material system, combining the advantages of LT-GaAs and nonpolar InGaAs/InAlAs material systems. By tailoring strain in (111) InGaAs and InAlAs SL layers, strong piezoelectric fields can be embedded in the material, bringing further enhancement of the Tx and Rx antennas’ performance.
Figure 1. Schematics showing (a) the step-flow growth mode on vicinal surfaces and (b) the multilayered structures studied.

Figure 2. STEM images of sample A on (a–c) singular (111) and (d–f) vicinal surface. (d) Tilt of 7.6° with respect to the (111) atomic plane at the edge of the substrate where the lamella was cut. (e) Moiré fringes enhancing the visibility of the defects over a large field of view. A stacking fault and a twin are circled in (e) and (b), respectively. HRSTEM images of a few stacking faults in the smooth region (f) and a high density of stacking faults at the center of the wafer (c).

RESULTS AND DISCUSSION

Growth on singular (111) substrates is challenging due to the formation of three-faced surface islands that lead to surface roughening. Helping attachment of the adatoms to the surface steps, i.e., promoting the step-flow growth mode, is an effective way to avoid the formation of surface islands (Figure 1a). Such surface steps can be introduced in a controlled manner by engineering the optimum substrate misorientation angle. The complexity arises because such optimum substrate misorientation angle depends on the adatoms incorporation length, thus the material composition.

InGaAs and InAlAs layers and superlattices were grown on InP(111)B substrate. A schematic illustration is shown in Figure 1b. It is expected that InGaAs and InAlAs epilayers may require different substrate misorientation angles to promote the desirable step-flow growth mode. Alternatively, growth conditions on a misoriented substrate may have to be separately optimized for the two types of epilayers. For the growth of InGaAs on InP(111)B, we showed that a minimum misorientation angle of 0.4° is needed to avoid surface hillocks at the optimized growth conditions. However, the optimum misorientation angle for InAlAs on InP(111)B was not optimized.

To further investigate the underpinning of hillock formation on (111) surface, the growth of a dual-layer InGaAs/InAlAs (sample A) was performed. Figure 2 shows cross-sectional HAADF STEM images of sample A. The specimen was oriented along the [011] zone axis with the [111] growth direction pointing upward. Figure 2a–c shows the STEM images from the center of the wafer corresponding to the exact (111)B surface. Hillocks and resulting surface roughening were seen on the surface. V-type twinning (Figure 2b) and a high density of stacking faults (Figure 2c) were observed below the hillocks. This shows that the stacking faults and twins are the underpinnings of at least some of the hillocks when growth is done on the exact (111)B surface. Many stacking faults originate from the substrate/film interface and persist as the film grows. A stacking fault in a Zinc Blende (ZB) structure is formed by a missing B bayer in a stacking sequence of ABCABC, resulting in a stacking sequence of ABCAIA. The CACA sequence represents a single segment of the Wurtzite (W) phase. Hence, a stacking fault in a ZB (111) structure is an insertion of one monolayer of W structure between two ZB structures that have been rotated 60° along the growth direction. The formation of stacking faults was attributed to a small energy difference for forming ZB and W crystalline phases in the [111] growth direction, and a lower nucleation barrier for W compared to ZB. Such energetics leads to the reversal of ZB and W phases during epitaxial growth and, hence, phase instability.

Twinning, as seen by STEM in this study, were reported to have a V-shape characteristic due to the formation of a twin complex. Twinning was seen before in MBE-grown GaAs on GaAs(111)B substrate. The formation of growth twins was attributed to the ease of the rotation of the group III atoms’ three dangling bonds when attached to the terrace by a single bond. A 60° rotation of these bonds from their perfect ZB position leaves the in-plane surface structure unchanged, with
only the stacking sequence altered, resulting in a twin. However, at surface step edges, the group III adatoms attach to the substrate by more than one bond. In that case, the possibility of rotation and twin formation is vastly reduced. Therefore, by locking the orientation of the bonds to the ZB phase, the step-flow growth mode is an effective way to avoid phase instability and resulting stacking faults and twins.

Figure 2d–f shows the cross-section micrographs of a lamella cut from the rounded edge region of the wafer, i.e., vicinal (111) surface. The (111) atomic planes are horizontal, and a 7° surface tilt from the (111) planes was measured at this specific cut. As shown in Figure 2f, very few stacking faults were observed, and no hillocks were seen at this misorientation angle. STEM Moiré fringes, as seen in Figure 2e, were used to identify the defects, such as stacking faults. A local change in the atomic arrangement modifies the Moiré fringes’ spacing, phase, and orientation, making them very sensitive to a deformation field in the sample.26 The strength of the STEM Moiré interferometry technique in mapping the strain field is its inherent capability to display the Moiré fringes over a large lamella area.

Besides stacking faults and twinning, phase separation is another growth challenge in this material system.27 Phase separation leads to a local strain inhomogeneity in the structure, giving rise to the STEM Moiré contrast. Figure 3b–d shows the result of strain analysis on the smooth region of Sample A, grown on the exact (111)B surface. Globally, the SMG deformation maps confirm that the InAlAs/InGaAs epitaxy is nearly lattice-matched to the InP substrate with the in-plane strain tensor component close to zero (εzz ≈ 0) on average. The deformation profile along the [111] growth direction, εzz (Figure 3d) shows the presence of a very small elastic strain in both the InAlAs and InGaAs layers. The εzz map in the InAlAs layer shows several prominent reddish lines going along [111] direction. These are In-rich regions (purple arrows in Figure 3c,d), indicating the presence of phase separation. In the InGaAs layer, the εzz map appears more uniform (except around crystallographic defect), indicating a much better uniformity of In and Ga atoms distribution. The relative deformation profile in Figure 3d also depicts the presence of a strain spike at the InP/InAlAs interface. This confirms the formation of an InAs layer at the interface, resulting from substituting desorbed P atoms with As atoms during the substrate oxide desorption under As flux. The presence of phase separation in the InAlAs layer demonstrates that the Al atoms behave differently than Ga, confirming the need for optimizing growth conditions for the InGaAs and InAlAs layers separately. Figure 3f–h shows the EELS maps taken from the InAlAs layer within sample A, confirming the presence of In-rich regions related to phase separation in the InAlAs layer.

To elucidate the origins of the observed difference in the behavior between Ga and Al atoms during the film growth, we study the potential energy surface (PES) for Ga and Al adatoms on InAs(111)B. Calculating PES is a technique that has been employed by many researchers to study surface phenomena, such as adatom adsorption and diffusion, and to understand epitaxial growth on solid surfaces.28–35 Here, we present the adsorption energies and diffusion barriers for Ga and Al adatoms to gain insight into optimizing the growth parameters.

As shown by SMG (Figure 3d) and will be discussed further below (referencing to the HRXRD analysis), about one monolayer of InAs is formed on the InP substrate during the oxide desorption process. The InAs layer is fully strained to lattice match to the underlying InP substrate as shown by SMG and confirmed by the rocking-curve analysis by dynamical simulation (RADS). Thus, we use an InAs(111)B slab model in our calculation that is laterally compressed by 3.2% to match the lattice constant of InP (5.867 Å). Since the base surface under consideration is InAs, the calculations are particularly relevant to the adsorption of the first layer of the InGaAs and InAlAs films on an InAs(111)B surface. However, since about half of the bonds in the grown layers are In-As, the results are expected to give a good qualitative description of what to expect during the growth on InGaAs and InAlAs(111)B surfaces. The InAs(111)B surface is an unreconstructed As-terminated polar surface. While most III–V semiconductor polar surfaces exhibit various reconstructions, the bulk-truncated InAs(111)B surface is stable even though it does not comply with the electron counting rule.36,37 An earlier ab initio calculation study38 has explained this surface stability to be driven by the removal of charge from the surface to the bulk. Similar behavior was also observed for InP(111)B and InGaAs(111)B.
GaP(111)B surfaces. The observation that strained InAs(111) B surface formed on the InP(111)B surface follows the 1 × 1 unreconstructed pattern of the underlying InP substrate, was also confirmed during the in situ RHEED monitoring. Using first-principles density functional theory calculations, we have studied the kinetics of Al and Ga adatoms on the unreconstructed As-terminated (111) plane of InAs.

The PES plots for Al and Ga adsorption on InAs(111)B (Figure 4a,b) show similar patterns qualitatively. Deep minima appear at point A1, the fcc threefold hollow sites where the cation adatom is bonded to three As atoms, as indicated in Figure 4a,b. The second minimum appears at the hcp site (A2 in Figure 4). Therefore, the most stable adsorption sites are located at the positions where the coordination number of the adsorbate is maximized, i.e., the number of Al(Ga)-As bonds is the highest. A global minimum at the fcc sites has been reported for a number of other polar surfaces with threefold surface symmetry, including GaN(0001).39 To move to a neighboring minimum (A3), the adatom must hop through the transition site (T) from another minimum (A2). The diffusion barrier for this movement is much higher for Al (0.59 eV) than Ga (0.39 eV). As the diffusion length is proportional to \((D\tau)^{1/2}\) [where \(D\) is the diffusion coefficient and \(\tau\) is the adatom lifetime before incorporating in the crystal] and \(D\) is proportional to \(\exp(-E_d/k_BT)\) [where \(E_d\) is the diffusion barrier and \(k_B\) and \(T\) are the Boltzmann constant and temperature, respectively], the migration length of Al atoms is much shorter than that of Ga. Hence, smaller surface terrace sizes are required for the step-flow epitaxial growth of Al-containing layers. Alternatively, since the incorporation time equals the monolayer growth time, a much slower growth rate of InAlAs compared to InGaAs is needed to achieve step-flow growth mode for the same terrace length.

In addition, the on-top site (on top of the surface As atoms) is the global maximum for an isolated adatom. The energy differences between the global minimum (A1) and the on-top positions for Al and Ga are 1.96 and 1.00 eV, respectively. To follow the ABCABC stacking order of the InAs(111) substrate, the epitaxial sites for the Al and Ga adatoms must be the on-top sites. Since the ZB phase is energetically favorable in the bulk arsenides, at high coverages, this site must be the global minimum. Consequently, the cation adatoms must shift from the potential minima sites to the on-top positions with increasing coverage. Based on our PES plots, this process is kinetically hindered; therefore, the initial adsorption on A1 and A2 sites might be a potential source for stacking fault formation, and the probability of the stacking fault formation is higher for Al-based layers than the Ga-based layers. Table 1 summarizes the PES parameters explained above.

<table>
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<th>adatom</th>
<th>(A_1)</th>
<th>(A_2)</th>
<th>(T)</th>
<th>on-top</th>
<th>(E_{A1})</th>
<th>(E_{A2})</th>
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<td>Al</td>
<td>−5.09</td>
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<td>−4.50</td>
<td>−3.13</td>
<td>0.59</td>
<td>0.38</td>
</tr>
<tr>
<td>Ga</td>
<td>−4.03</td>
<td>−3.96</td>
<td>−3.64</td>
<td>−3.03</td>
<td>0.39</td>
<td>0.32</td>
</tr>
</tbody>
</table>

*The global potential energy at point \(A_1\), second minimum at point \(A_2\), transition site at point \(T\), and diffusion barriers \(E_{A1} = (A_1 - T)\) and \(E_{A2} = (A_2 - T)\). All values are in electronvolts (eV).*

It should be noted that the strain asserted by the underlying InP substrate onto the InAs monolayer not only provides the lattice match for the growth of InAlAs/InGaAs epitaxial superlattices but also affects the adatom kinetics. The effect of strain on adatom diffusion can vary depending on the surface structure and the nature of the adatoms.40,41 In our study, the compressive strain of 3.2% was seen to enhance the diffusion properties of both Al and Ga adatoms compared to their PES on the unstrained InAs(111)B slab. In general, the binding energies at all adsorption sites are lower on the strained slab compared to the relaxed one.

In accordance with the insights provided by DFT calculations, two different substrates with misorientation angles of 1 and 2° toward the [211] direction were used. In our previous study, we showed that the smooth epitaxy could occur on optimally misoriented substrates regardless of the misorientation direction. The misorientation direction only affects the shape of the hillocks (i.e., being completely symmetric or asymmetric).20 The [211] direction was used since the facets of the pyramids are tilted toward <211> azimuthal directions.18

To account for the lower mobility of the Al atoms compared to Ga atoms, the growth rates of InGaAs and InAlAs layers within the InGaAs/InAlAs superlattice were adjusted separately. The As valve opening was adjusted when switching between layers to keep the V/III ratio approximately constant throughout the growth. Sample B consists of an InGaAs/InAlAs SL grown on a 1° misoriented substrate, while for Sample C the same structure was grown on a 2° misoriented substrate. Figure 5 shows AFM images of these two samples. For the 1° misoriented substrate (sample B), pyramid-shaped surface features were still present even for the slowest growth rate used (Figure 5a), while they were entirely eliminated for growth on the 2° misoriented substrate (sample C) (Figure 5b,c). This is confirmed further on larger areas with Nomarski images, as shown in Figure 6. Also, long-range irregular undulations are revealed by AFM for sample B, even though the Nomarski image is featureless in between the pyramids. Closer inspection of the AFM scan of sample C (Figure 5c) reveals that the surface morphology is dominated by 1 ML atomic steps with a very uniform terrace width of ∼110 Å, and 3 ML-high macro steps (the light contrast) spaced on average by ∼1100 Å, conforming overall to the substrate’s 2° offcut. It appears, therefore, that for this material system and the growth conditions used, the epitaxy naturally establishes an optimum terrace width of ∼110 Å. This width is most likely stabilized by...
the strain fields generated by the atomic step ledges. A choice of offcut closer to 1.5° would probably eliminate the 3 ML-high macro steps still present on the surface. This is the first report of the atomically smooth growth of InGaAs/InAlAs SL on the InP(111) substrate. Since the top layer for this sample is made of 80 Å (approximately 27 MLs) of InAlAs, it is reasonable to assume that such a uniform pattern of atomic steps reflects the kinetics of surface formation for InAlAs material at these particular growth conditions. Nevertheless, as discussed further below, both cross-sectional STEM analysis and HRXRD show very high-quality superlattice throughout, indicating that the same atomic smoothness also characterizes the InGaAs layers.

Figure 7 shows the HRXRD ω-2θ double- and triple-axis scans around InP (222) X-ray reflection of sample C. The HRXRD pattern of the SL structure shows a few prominent features. First, the most intense peak at zero arcsec belongs to the (222) Bragg reflection of the InP substrate. The second feature is the characteristic periodic superlattice reflections. The relative intensities of all of these peaks closely match the intensities obtained with dynamical simulation. The angular position of the zero-order SL peak (n = 0) reflects the average lattice constant of the InGaAs/InAlAs SL stack. Here, the zero-order SL peak, SL₀, is to the left of the substrate peak and is separated from it by 206 arcsec, indicating that the average lattice constant of the SL layers is only slightly larger than that of the InP substrate. The exact Bragg angle for SL₀ is set by the vertical size of the tetragonally distorted average unit cell of the SL. The third feature is the appearance of additional fringes in between the SL peaks caused by the interference of X-rays reflected from the sample surface and the base of the SL. They are commonly referred to as interference or Pendelloßung fringes. The presence of strong SL satellite peaks and clearly visible Pendelloßung fringes is an indication of high structural quality and excellent thickness and compositional homogeneity within this multilayer since structural imperfections such as interface roughness, poor periodicity, or crystallographic defects result in damping of the characteristic features in the SL HRXRD pattern. The HRXRD data were used to fit a model using RADS software. The layers’ parameters that were obtained from the model are shown in Table 2. The experimental data could fit the dynamical model by assuming a tetragonal distortion of the epilayers’ lattices. The simulation result suggested the presence of a ~6 Å (~1 ML) thick InAs layer at the interface between the buffer layer and the substrate, confirming the deformation map analysis discussed above. The finer features visible in the triple-axis scan as slightly washed out on the double-axis scan. The latter offers a better S/N ratio but is sensitive to (i) lattice tilts around dislocations and structural defects, (ii) the wafer bowing resulting from small residual strain, and also (iii) diffused scattering from point defects that are present on the layer surface. A comparison of the triple-axis and double-axis scans points to a negligible contribution from (i) and the dominant role of the latter two factors (ii) and (iii).

Cross-sectional STEM investigations were carried out on sample C to characterize the microstructure. The micrographs in Figure 8 confirm that the SL has excellent crystalline quality and smooth interfaces. The crystalline lattices of the FCC crystal structure (oriented along the [011] direction with the [111] growth direction aligned vertically) are recognizable in Figure 8d. It is seen in Figure 8d that the InGaAs-on-InAlAs
interface is atomically abrupt, while the InAlAs-on-InGaAs interface appears diffuse over a thickness of the order of 2–3 ML. This is attributed to the slower growth rate of InAlAs, favoring Ga for Al atom exchange and segregation at the interface. The effect is exacerbated by the higher tendency of Ga to segregate, compared to the Al atoms in III/V semiconductors.\textsuperscript{32} The STEM image in Figure 8c focuses on the buffer layer between the InP and the SL layers. It is noticed that the buffer layer/InP interface is rough, but the InP surface roughness is mitigated by the buffer layer offering a smooth surface for the SL epitaxial growth. No defects, such as stacking faults or twins, were observed within the whole lamella analyzed. In addition, no sign of phase separation was present. Since this structure was grown at a slower growth rate than sample A, this observation may indicate that the phase separation in InAlAs is not thermodynamically driven and can be suppressed by optimization of the growth conditions on stepped surfaces.

SMG strain characterization was carried out to map the strain within the layers in Sample C. Figure 9a,b shows the $\varepsilon_{xx}$ and $\varepsilon_{zz}$ relative deformation maps, and Figure 9c highlights the averaged $\varepsilon_{xx}$ and $\varepsilon_{zz}$ vertical deformation profiles within the layers. In general, $\varepsilon_{xx} \approx 0$ throughout the film, as expected from a good lattice matching to InP and fully elastically strained lattice. The $\varepsilon_{zz}$ deformation map shows a slightly positive strain within both the buffer layer and the SL, indicating a slight mismatch between the epitaxial structure and the substrate, accommodated by a tetragonal distortion of the lattice, i.e., the layers remained unrelaxed ($\varepsilon_{xx} \neq \varepsilon_{zz}$). This is consistent with the observed separation of the 0th-order SL peak from the substrate peak in Figure 7. It is seen from the $\varepsilon_{zz}$ strain map that the InAlAs layers are slightly better lattice-matched to the substrate than InGaAs layers. Note that InAlAs are the darker layers, and InGaAs are the lighter layers in the SL. This is in accordance with the HRXRD simulation data and the lattice, i.e., the layers remained unrelaxed ($\varepsilon_{xx} \neq \varepsilon_{zz}$). This is consistent with the observed separation of the 0th-order SL peak from the substrate peak in Figure 7. It is seen from the $\varepsilon_{zz}$ strain map that the InAlAs layers are slightly better lattice-matched to the substrate than InGaAs layers. Note that InAlAs are the darker layers, and InGaAs are the lighter layers in the SL. This is in accordance with the HRXRD simulation data tabulated in Table 2. The sharp spike in the $\varepsilon_{zz}$ deformation map at the substrate/SL interface shows the presence of an InAs layer formed at the interface that is also consistent with the HRXRD simulation results.

### SUMMARY AND CONCLUSIONS

Epitaxial growth on polar surfaces of the Zinc Blende family of semiconductors has been studied in detail using an important case of MBE growth of InGaAs/InAlAs on InP(111)B surfaces. With the help of high-resolution scanning transmission electron microscopy analysis along with the Moiré Geometrical Phase analysis and electron energy loss spectroscopy, we showed that the epilayer layers grown on on-orientation substrates are prone to forming high density of stacking faults and twins along with phase separations, the latter particularly prominent in the InAlAs layers. The presented results of the density functional theory calculations bring new insights into the atomistic origin of these defects and help develop strategies for their elimination. The key element for eliminating these problems is growth on vicinal surfaces, ensuring at the same time conditions supporting step-flow growth mode. Because of the much higher energetic barriers for the diffusion of Al adatoms on (111)B surface compared to Ga adatoms, the growth conditions must be separately optimized for InGaAs and InAlAs layers. In the case of superlattices of these materials, this can be achieved using a sufficiently slow growth rate for InAlAs, avoiding being prone to stacking fault generation InAlAs islands on the (111)-oriented terraces. Ensuring attachment of group III atoms to the step edges on the vicinal surface also minimizes the tendency for phase separation in these ternary compounds. We demonstrate the validity of these observations in nanoscale by growing high-quality, defect-free InGaAs/InAlAs superlattice on the 2° offcut InP(111)B surface. The high-resolution STEM images show atomically abrupt InGaAs on InAlAs interfaces and evidence of some Ga segregation at the InAlAs on InGaAs interfaces. The high-resolution X-ray diffraction measurements, along with dynamical simulations, confirm the high structural perfection of the superlattice. Inspection of the surface morphology with Nomarski DIC microscopy shows a very smooth, featureless surface. At the same time, AFM scans reveal the existence of a regular array of single atomic steps interspaced with 3 ML-high macro steps to fully accommodate the 2° substrate offcut. Such remarkable self-organization of the surface points toward a role of stain-mediated interaction
between the step ledges, stabilizing the terrace width. To the best of our knowledge, this is the first report of a highly perfect, defect-free InGaAs/InAlAs heterostructure on an InP(111)-oriented substrate.

Our work sets the stage for developing InGaAs/InAlAs/InP(111) high-quality epitaxial thin films for fundamental studies and device demonstrations as has been long-established for growth on (001) substrates. Notably, the epitaxial growth in polar crystallographic directions offers access to new properties tunable by embedding piezoelectric fields in the layers. The strength and direction of such fields can be engineered by deliberate choice of indium composition and thus strain in the layers. In general, the work advances the understanding of growth on polar surfaces. The reported observations should help optimize epitaxy in other Zinc Blende material systems for the electronic and photonic structures that could benefit from the tunable piezolectric effects.

### EXPERIMENTAL SECTION

#### MBE Growth.
Three types of InP(111)B semi-insulating substrates were used in this study: (i) singular (111) with rounded edge, giving access to the entire range of vicinal surfaces for this orientation; (ii) substrates misoriented toward [211] by 1° and (iii) substrates misoriented toward [211] by 2°. Nominally lattice-matched InGaAs/InAlAs and InGaAs/InAlAs epilayers and superlattices were grown at a temperature of 460 °C using a Veeco GEN10 MBE system. The superlattices consisted of 10 repeats of InGaAs (12 nm)/InAlAs (8 nm), for a total thickness of 200 nm. A buffer layer of 50 nm InGaAs nominally lattice-matched to the substrate was grown prior to the superlattice growth. The growths were done with As4 using Veeco Mark V arsenic cracker cell with a cracking zone temperature of 650 °C. Several structures were grown at various growth conditions with the aim of achieving an atomically smooth surface morphology. The structures discussed in this work, along with the growth conditions, are listed in Table 3. All of the growths were done with 20 rpm substrate rotation. A Staib 15 keV electron gun and a final 5 keV clean-up process was performed to remove most of the amorphized parts on each side of the lamellae. High-resolution STEM (HRSTEM) imaging was done using an FEI Titan Cubed 80–300 operating at 200 keV and equipped with CEOS correctors on both the probe and image-forming lens systems. The STEM acquisition conditions were set to obtain Z-contrast type imaging using a high-angle annular dark-field (HAADF) detector. Energy electron loss spectroscopy (EELS) was used to map the elemental distribution. An EELS spectrum-image dataset (i.e., a spectrum at every pixel of an image) was acquired along the growth direction to identify different layers. The spectrum was taken over an energy range covering the phosphorus K edge at 2146 eV, gallium L2 and L3 edges at 1142 and 1115 eV, respectively, aluminum K edge at 1560 eV, arsenic L2 and L3 edges at 1359 and 1323 eV, respectively, and indium M4,5 edge at 443 eV. Strain characterization was performed based on Moiré interferometry in STEM and geometrical phase analysis (GPA) method called STEM Moiré GPA (SMG) technique and processed using the STEM-Moiré_GPA Python script.

#### DFT Calculations.
The first-principles total energy density functional theory (DFT + U) calculations were carried out to obtain the adsorption energies of Al and Ga atoms on the strained InAs(111)B substrate using the projector augmented wave (PAW) method.44,45 Vienna Ab initio Simulation Package (VASP, version 5.4) with the Materials Exploration and Design Analysis (MedeA, version 2.19, Materials Design, Inc.) platform was used to perform the calculations. The Hubbard correction U = 3.3 eV was applied to the As atoms.46 The generalized gradient approximation (GGA) with the exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE)47 was incorporated. A cutoff energy of 500 eV was used for the convergence of the plane wave expansion. The electronic structure and ionic geometry were optimized using the conjugate-gradient algorithm. The Brillouin zone was sampled at the Γ point with a k-point spacing of 0.5 Å⁻¹. The convergence criteria of 0.01 eV/Å and 10⁻⁵ eV were employed for the self-consistent ionic and electronic energy optimization, respectively. The Methfessel-Paxton smearing of 0.2 eV was used. The unreconstructed As-terminated InAs(111)B surface was modeled by a slab geometry consisting of five InAs double layers, and the bottom-most In layer was terminated by pseudo-H atoms (Z = 1.25) with a vacuum gap of 20 Å perpendicular to the slab surface. All In and As atom positions were relaxed before the optimization. A periodic supercell composed of 4 × 4 surface unit cells was used to calculate the adatom adsorption energies. The potential energy surface (PES) calculation was done by placing an adatom above six adsorption sites in the symmetrically irreducible triangle inside the unit cell. The upper three bilayers and adatom height were fully relaxed at each position. The calculated potential values were then interpolated on a mesh using cubic interpolation.

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#### Table 3. Summary Information on Epitaxial Structures Discussed: Nominal Layer Thicknesses, Substrate Offcut, and Growth Rates

<table>
<thead>
<tr>
<th>sample</th>
<th>nominal structure InGaAs/InAlAs</th>
<th>substrate misorientation</th>
<th>growth rate (Å/s) InGaAs/InAlAs</th>
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<tr>
<td>A</td>
<td>200 nm/200 nm</td>
<td>singular InP with rounded edge</td>
<td>1/1</td>
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<tr>
<td>B</td>
<td>10 repeats of InGaAs (12 nm)/InAlAs (8 nm)</td>
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</tbody>
</table>

gallass beam. A final 5 keV clean-up process was performed to remove most of the amorphized parts on each side of the lamellae.
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