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Mapping the Interfacial Electronic Structure of Strain-Engineered Epitaxial Germanium Grown on $In_xAl_{1-x}As$ Stressors

Michael B. Clavel, Jheng-Sin Liu, Robert J. Bodnar, and Mantu K. Hudait*

ABSTRACT: The indirect nature of silicon (Si) emission currently limits the monolithic integration of photonic circuitry with Si electronics. Approaches to circumvent the optical shortcomings of Si include band structure engineering *via* alloying (*e.g.*, $Si_xGe_{1-x-y}Sn_y$) and/or strain engineering of group IV materials (*e.g.*, Ge). Although these methods enhance emission, many are incapable of realizing practical lasing structures due to poor optical and electrical confinement. Here, we report on strong optoelectronic confinement in a highly tensile-strained (ε) Ge/$In_{0.26}Al_{0.74}As$ heterostructure as determined by x-ray photoemission spectroscopy (XPS). To this end, an ultra-thin (~10 nm) ε-Ge epilayer was directly integrated onto the $In_{0.26}Al_{0.74}As$ stressor using an *in-situ*, dual-chamber molecular beam epitaxy approach. Combining high-resolution x-ray diffraction and Raman spectroscopy, a strain-state as high as ε ~ 1.75% was demonstrated. Moreover, high-resolution transmission electron microscopy confirmed the highly-ordered, pseudomorphic nature of the as-grown ε-Ge/$In_{0.26}Al_{0.74}As$ heterostructure. The heterointerfacial electronic structure was likewise probed *via* XPS, revealing conduction- and valence-band offsets (ΔE_C and ΔE_V) of 1.25 ± 0.1 eV and 0.56 ± 0.1 eV, respectively. Lastly, we compare our empirical results with previously-published first-principles calculations investigating the impact of heterointerfacial stoichiometry on the ε-Ge/$In_xAl_{1-x}As$ energy band offset, demonstrating excellent agreement between experimental and theoretical results under an $As_{0.5}Ge_{0.5}$ interface stoichiometry exhibiting up to two monolayers of heterointerfacial As–Ge diffusion. Taken together, these findings reveal a new route towards the realization of on-Si photonics.

KEYWORDS: *Ge, InAlAs, Heterostructure Laser, Band Structure, Strain Engineering, Bandgap Engineering*

INTRODUCTION

With the increasing ubiquity of computing devices and corresponding rise in bandwidth requirements, high-speed, large-bandwidth optical data transmission has been proposed as a cost-effective, low-loss solution for intra- and inter-chip communication.[1–3] Consequently, extensive research has been conducted in order to realize the monolithic integration of photonic circuitry with state-of-the-art silicon (Si) electronics.[4–7] Although Si-based optoelectronics[8] offer a desirable solution due to the ease with which they can be integrated into current complimentary metal-oxide-semiconductor (CMOS) process flows, the indirect bandgap of Si limits its radiative recombination efficiency and thus its suitability for on-chip light sources.[4] In order to overcome these challenges, researchers have focused on alternative integration approaches that employ direct or pseudo-direct bandgap materials attained through band structure engineering,[9–11] strain engineering,[12–14] wafer bonding,[15–17] or novel lasing structures.[18] In particular, the band structure engineering of group IV-based elemental, binary, and ternary semiconductors (*e.g.*, Ge, $Ge_{1-y}Sn_y$, $Si_xGe_{1-x-y}Sn_y$) has seen rapid progress, with recent demonstrations of Ge nanomembrane and micro-disk light-emitting diodes and lasers,[19–21] laser structures fabricated from heavily-doped and tensile-strained Ge directly grown on Si,[22,23] and $Ge_{1-y}Sn_y$ waveguide lasers.[24] Although several of these efforts have been successful in achieving enhanced emission from group IV, predominately Ge-based, materials,[19,21,24–26] none are compatible with the development of a group IV-based quantum well (QW) laser due to their inability to control optical and electronic confinement. Thus, the difficulty in realizing low threshold current group IV-based quantum well lasers is two-fold: (i) sufficient band structure and/or strain engineering must be introduced such that the emitting material is direct-gap in nature, and (ii) sufficient optical and electronic confinement must be provided such that recombination is strictly limited to the gain medium.

In order to address these challenges, this work leverages the capacity of group IV/III-V heterostructures to impart modular, epitaxial stress on overlying group IV thin-films,[27–30] while simultaneously providing sufficient optical[18,31,32] and electronic confinement[33] so as to realize practical lasing structures. Using solid-source molecular beam epitaxy (MBE), we demonstrate the low-defect, pseudomorphic epitaxy of a highly tensile-strained Ge (ε-Ge) epilayer on an $In_xAl_{1-x}As$ stressor. It is anticipated that such strain-engineered group IV materials could serve as the

gain medium in future QW heterostructure lasers, whereas the high-bandgap $In_xAl_{1-x}As$ stressor could function as the cladding.[34] Moreover, characterization of the ε-Ge/$In_xAl_{1-x}As$ heterostructure material and electronic properties reveal energy band offsets (ΔE_C = 1.25 ± 0.1 eV; ΔE_V = 0.56 ± 0.1 eV) conducive to electro-optical confinement. Lastly, we elucidate the role that heterointerface stoichiometry has on the interfacial energy band alignment through a comparison of our measured heterointerfacial electronic structure with that explored *via* extensive first-principles calculations reported in ref. 35. Through the synthesis of our empirical findings with the reported *ab-initio* modeling of the ε-Ge/$In_xAl_{1-x}As$ heterointerface, we provide a new route towards the realization of group IV-based photonic devices.

RESULTS AND DISCUSSION

Strain and Structural Characterization of the ε-Ge/$In_xAl_{1-x}As$ Heterostructure. Figure 1a presents a cross-sectional schematic diagram of the ε-Ge/$In_{0.26}Al_{0.74}As$ heterostructure investigated in this work. As demonstrated by Figure 1b, epitaxial-induced biaxial tensile stress results in an expanded in-plane lattice constant ($a_{\parallel}$) and compressed out-of-plane lattice constant ($a_{\perp}$) within the overlying epilayer. For strained epilayer thicknesses below the critical layer thickness (h_c), it is expected that the strained layer and stressor in-plane lattice constants will be lattice matched, *i.e.*, $a_{\parallel,epilayer} = a_{\parallel,stressor}$. Correspondingly, the optical and electronic properties of the overlying strained layer can be tuned within a wide range by tailoring the InAs mole fraction of an $In_xAl_{1-x}As$ stressor in order to vary the stressor lattice constant (a_{AlAs} = 5.661 Å ≤ $a_{In_xAl_{1-x}As}$ ≤ a_{InAs} = 6.0583 Å) and therefore the epitaxial strain ($\varepsilon_{Ge/AlAs}$ = +0.05% ≤ ε ≤ $\varepsilon_{Ge/InAs}$ = +7.07%).

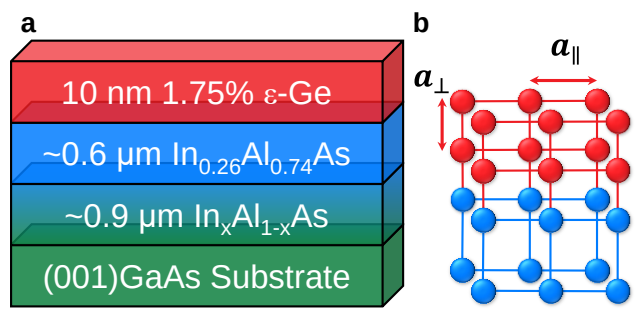

Figure 1. (a) Cross-sectional schematic diagram of the ε-Ge/$In_{0.26}Al_{0.74}As$ heterostructure grown on (001)GaAs. (b) Graphic representation of the influence of biaxial tensile stress on the in-plane ($a_{\parallel}$) and out-of-plane ($a_{\perp}$) lattice constants of a pseudomorphic thin-film (red) grown onto a lattice-mismatched stressor (blue).

For this study, a target InAs mole fraction of 0.25 was chosen, corresponding to a nominal ~1.8% tensile strain with respect to the relaxed Ge lattice constant. Such a relatively high Ge strain state was selected in order to increase

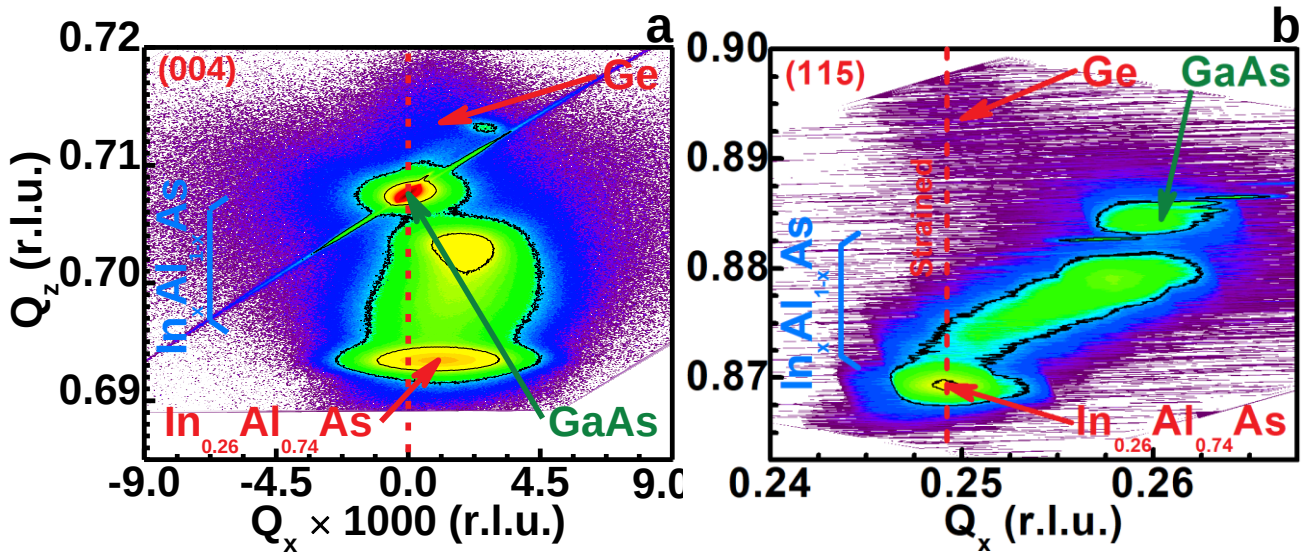

Figure 2. High-resolution reciprocal space maps (RSMs) taken along the (a) symmetric (004) and (b) asymmetric (115) crystallographic orientations. The separation between the Ge reciprocal lattice point (RLP) and that of the substrate (GaAs) in the Q_z coordinate is indicative of compressive out-of-plane stress, and thus tensile in-plane stress.

the likelihood of direct-gap recombination within the Ge epilayer (gain medium), prompted by a reduction in the ε-Ge Γ-valley conduction band minimum (CBM) by ~26 meV below that of the L-valley CBM.[36,37] Likewise, the Ge epilayer thickness (10 nm) was determined so as to reduce the likelihood of strain relaxation within the Ge thin-film (h_c ~ 30 nm).[29] High-resolution x-ray diffraction (HR-XRD) data of the as-grown heterostructure reveal that the Ge epilayer was indeed pseudomorphic with respect to the underlying $In_xAl_{1-x}As$ stressor. Figures 2a and 2b show the symmetric (004) and asymmetric (115) reciprocal space maps (RSMs), respectively, recorded from the ε-Ge/$In_xAl_{1-x}As$ heterostructure. We note that the reciprocal lattice contour (RLC) centroid for each epilayer has been highlighted for clarity. As can be seen from the symmetric (004) RSM shown in Figure 2a, the strain-induced compression of $a_{\perp,Ge}$ was observed directly as a modification to the (004) Bragg angle of the ε-Ge film, and thus, a corresponding change in the Q_z component of the ε-Ge RLC. Further examination of the asymmetric (115) RSM (Figure 2b) revealed a close alignment in the Q_x components of the ε-Ge and $In_xAl_{1-x}As$ RLCs, indicative of coherent strained layer epitaxy.[38] Moreover, the Q_x-Q_z symmetry of the ε-Ge RLC suggested a uniform crystallinity absent of substantial mosaicity-inducing crystal defect scattering. By the same token, the relatively low Bragg diffraction intensity of the Ge epilayer can be ascribed to its minute diffraction volume, as opposed to crystal defect-induced

scattering. Similarly, the narrow and symmetric nature of the $In_xAl_{1-x}As$ stressor RLC suggested a strong confinement of lattice mismatch-induced defects within the metamorphic linearly graded $In_xAl_{1-x}As$ buffer, thereby minimizing dislocation propagation into the $In_{0.26}Al_{0.76}As$ stressor and hence, the active region (cladding). In order to quantify these observations, the measured RSM data were used to determine $a_{\parallel}$, $a_{\perp}$, and ε for the ε-Ge epilayer, as well as the InAs mole fraction of the $In_xAl_{1-x}As$ stressor, following the procedures outlined in ref. 38. Defining the in-plane epitaxial strain to be,

$$\varepsilon = \frac{a_{||} - a_r}{a_r}, \tag{1}$$

where $a_{||}$ and a_r correspond to the in-plane and relaxed epilayer lattice parameters, respectively, the strain-state of the ε-Ge epilayer was found to be ε = 1.76% utilizing the literature value of 5.658 Å for the relaxed Ge lattice constant[39] and the measured value of 5.7578 Å for $a_{||}$ ($a_{\perp}$ = 5.6051 Å). We note that the experimental $In_xAl_{1-x}As$ stressor InAs mole fraction (x_{exp} ~ 0.26) was slightly higher than the targeted value (x_{ideal} = 0.25), which was attributed to the competing add-atom surface mobilities of In and Al dimers. Additionally, the $In_{0.26}Al_{0.74}As$ stressor was found to be over 90% relaxed. From the 306 arcsec tilt measured along the (004) reflection, it can be posited that buffer relaxation occurred in a predominately symmetric nature, with only a minimal amount of observable anisotropy stemming from the disparity between α (group V-terminated core) and β (group III-terminated core) dislocation glide velocities oriented along the ⟨1$\bar{1}$0⟩ and ⟨110⟩ orthogonal directions, respectively.[40]

Atomic force microscopic (AFM) analysis of the as-grown ε-Ge/$In_{0.26}Al_{0.74}As$ surface (Figure 3)

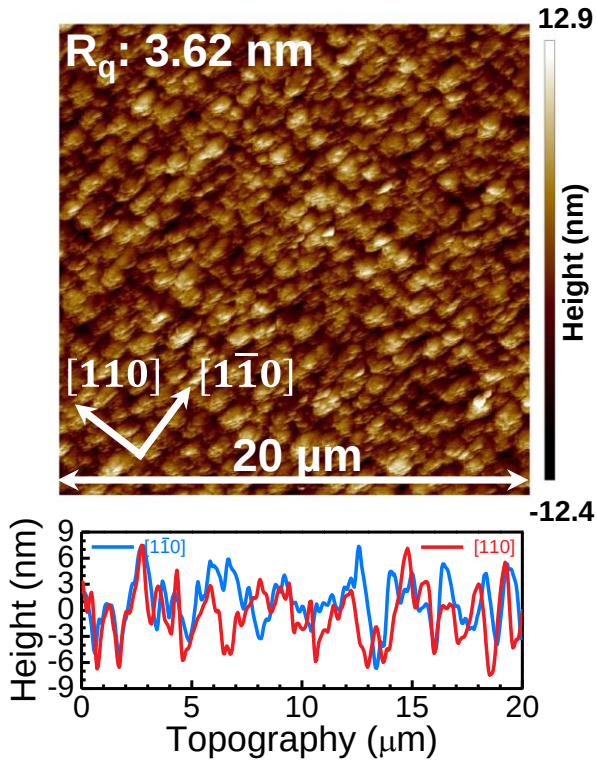

Figure 3. Atomic force micrograph of a representative 20 µm × 20 µm region of the as-grown ε-Ge/$In_{0.26}Al_{0.74}As$ surface and related line height profiles recorded along the two orthogonal ⟨110⟩ symmetric directions.

provided ancillary support for this conclusion, wherein the observed symmetric cross-hatch surface morphology was indicative of predominantly isotropic buffer relaxation. The relatively low measured *rms* surface roughness (R_q ~ 3.62 nm) was mirrored, with minimal deviation, along both $\langle 1\bar{1}0 \rangle$ and $\langle 110 \rangle$ orthogonal directions, from which the orientation-dependent R_q values of 3.30 nm and 3.41 nm, respectively, were obtained. It is well-known[29] that the uniformity of the surface topography can be directly correlated to the extent of (an)isotropic strain relaxation present in a film(s). This is a result of the origins of the cross-hatch morphology, wherein plastic relaxation processes within the growing film preferentially create dislocations within the (energetically favorable) $a/2\,\langle 110 \rangle\,\{111\}$ slip system. The successive process of strained film growth and relaxation, such as that which occurs in a metamorphic buffer, propagates surface morphology vertically *via* the formation of hillocks and valleys oriented along dislocation lines. As defects (threading and misfit dislocations) propagate laterally along $\langle 110 \rangle$ directions, analysis of the AFM surface morphology of a heterostructure can hence provide indirect evidence for the relaxation mechanism(s) present during epitaxy. It is within this lens that one can relate the uniform, cross-hatched surface of Figure 3 to the HR-XRD-derived tilt (306 arcsec), suggesting that the two-step $In_xAl_{1-x}As$ metamorphic buffer strategy successfully balanced the competing In and Al add-atom surface mobilities during buffer growth. Moreover, given the ultra-thin character of the ε-Ge epilayer (t_{Ge} = 10 nm), it is unlikely that subsequent ε-Ge epitaxy would quantitatively alter the $In_{0.26}Al_{0.74}As$ stressor surface morphology provided that the ε-Ge epilayer remained pseudomorphic.

To this end, Raman spectroscopic data (Figure 4) further confirmed the nature of the ε-Ge epilayer strain, as demonstrated by the frequency shift observed in the measured ε-Ge/$In_{0.26}Al_{0.74}As$ Raman spectra. Explicitly, when a biaxial strain is applied to a (001) oriented diamond-cubic crystal, the threefold degenerate zone-center optical phonon modes are split into a doublet and singlet having eigenvectors perpendicular and parallel to the plane, respectively.[41] Consequently, considering the (001) backscattering geometry used in this work, application of the selection rules provided in ref. 41 implies that solely the longitudinal optical (LO) mode corresponding to the singlet is experimentally observable. Additionally, the inclusion of a lattice strain produces a hydrostatic shift of the phonon frequency (Ω_S), and therefore a relative shift in the measured Raman wavenumber ($\Delta\omega$) with respect to its relaxed value (ω_0). Thus, the strain-state of a material and the type of strain present are directly correlated with the

magnitude and sign of the wavenumber shift, *e.g.*, a positive (negative) Δω corresponds to compressive (tensile) stress.

As shown in Figure 4, the ε-Ge epilayer demonstrated a wavenumber shift of -7.27 cm^{-1} with respect to the Raman spectra recorded from a (001)Ge substrate. Previously,[42,43] we have utilized the relation $\Delta\omega = -b\varepsilon_{\parallel}$ to analyze the Raman shift as a function of strain ($\varepsilon_{\parallel} \leq 2.0\%$) in ε-Ge epilayers grown on (001)GaAs and (001)Si substrates, wherein Δω is the measured wavenumber shift, $\varepsilon_{\parallel}$ is the in-plane strain, and *b* is a material parameter dependent on the phonon deformation potentials, elastic constants, and unstrained phonon frequency (ω_0 ~ 300 cm^{-1} for Ge) of the material. Using a value of –415 for *b*,[27] the Raman-deduced in-plane strain was found to be ε = 1.75%, in good agreement with both the theoretical misfit (*f* ~ 1.8) as well as the strain determined *via* x-ray diffraction (ε_{XRD} = 1.76%).

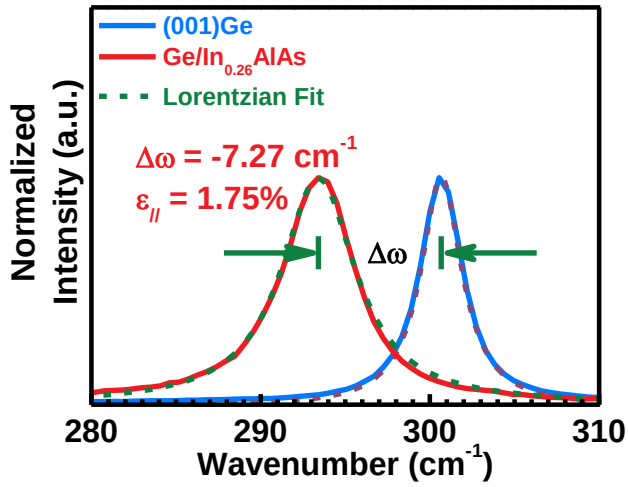

Figure 4. Raman spectra collected from a (001)Ge substrate and the ε-Ge epilayer grown on $In_{0.26}Al_{0.74}As$. The shift (Δω = -7.27 cm^{-1}) in the unstrained Ge longitudinal optical (LO)-related mode (ω_0 ~ 300 cm^{-1}) corresponds to an in-plane strain of 1.75%.

Lastly, to gain further insight into the material and structural properties of the ε-Ge/$In_xAl_{1-x}As$ heterostructure, low- and high-magnification cross-sectional micrographs from representative growth regions were captured *via* transmission electron microscopy (TEM). Figures 5a and 5b show the low- and high-magnification bright-field TEM micrographs corresponding to the complete heterostructure and the ε-Ge/$In_{0.26}Al_{0.74}As$ heterointerface, respectively. As can be seen from Figure 5a, the metamorphic linearly graded $In_xAl_{1-x}As$ buffer accommodated misfit strain (*i.e.*, lattice mismatch) *via* the formation and subsequent glide of threading dislocations, thereby inhibiting substantial defect propagation along the growth axis. Correspondingly, the constant-composition $In_{0.26}Al_{0.74}As$ stressor was observed to be absent of long-range microstructural defects or disorder, implicitly reinforcing the high degree of relaxation and crystallinity found *via* x-ray diffraction analysis. Examining Figure 5b, one can find that the epitaxial Ge and $In_{0.26}Al_{0.74}As$ strain template exhibited a highly uniform heterointerface.

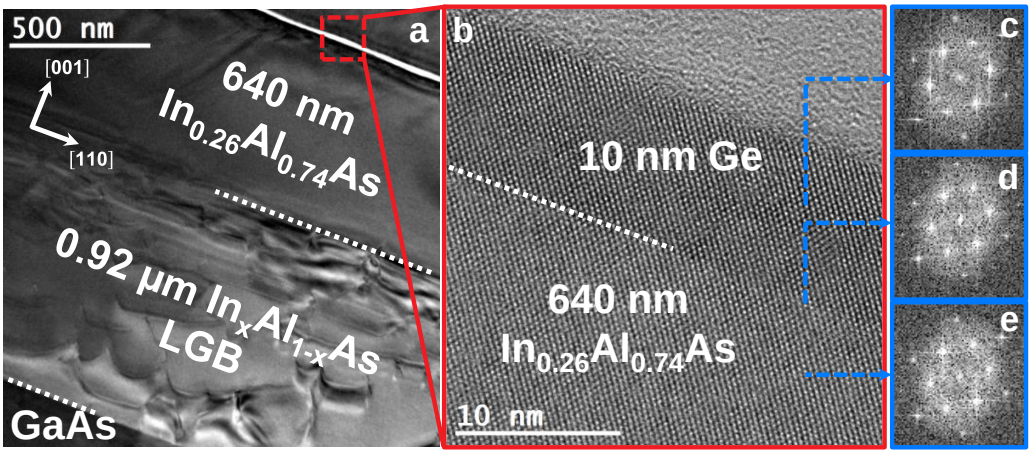

Figure 5. (a) Low magnification cross-sectional transmission electron micrograph (X-TEM) of the entire ε-Ge/$In_xAl_{1-x}As$/GaAs heterostructure, highlighting the confinement of lattice mismatch-induced defects below the region of interest. (b) and (c)–(e) High-magnification X-TEM of the ε-Ge/$In_{0.26}Al_{0.74}As$ heterointerface and associated Fast Fourier Transform (FFT) patterns, respectively, revealing coherent strained-layer epitaxy with no observable relaxation-induced interface defects.

Moreover, further inspection utilizing a two-step Fast Fourier Transform (FFT) noise filtering approach (*i.e.*, $\mathcal{F}^{-1}(\mathcal{F}(k))$) suggested an atomically abrupt heterointerface lacking substantive relaxation-inducing misfit dislocations. This conclusion was reinforced by the indistinguishable nature of FFT patterns taken from representative 6 nm × 6 nm regions of the (i) $In_{0.26}Al_{0.74}As$ strain template (Figure 5c), (ii) Ge/$In_{0.26}Al_{0.74}As$ heterointerface (Figure 5d), and (iii) epitaxial Ge layer (Figure 5e). The absence of satellite reflections in Figures 5c–5d indicated the contribution of a single lattice parameter (*i.e.*, $a_{In_{0.26}Al_{0.74}As} = a_{Ge}$) to the diffractogram, thereby reaffirming the pseudomorphic nature of the Ge epilayer as previously determined *via* HR-XRD and Raman spectroscopic analysis.

ε-Ge/$In_xAl_{1-x}As$ Heterointerface Band Alignment. Having demonstrated the feasibility of strained-layer Ge epitaxy on a large bandgap (*i.e.*, $In_xAl_{1-x}As$) stressor, we now address the nature of the energy band alignment at the Ge/$In_xAl_{1-x}As$ heterointerface. To this end, x-ray photoemission spectra were collected from three sample surfaces: (i) the 10 nm ε-Ge epilayer; (ii) the $In_{0.26}Al_{0.74}As$ stressor; and (iii) the heterointerface between ~1.5 nm ε-Ge and the $In_{0.26}Al_{0.74}As$ stressor. We note that surfaces (ii) and (iii) were realized *via* the *in-situ* sputtering of (i) by low-energy (≤ 1 kV) Ar^+ ion bombardment. Figures 6a–6c show representative spectra recorded from each sample surface,

respectively, wherein spectral fitting using a Lorentzian peak convolution of the spin-orbit coupled core levels (CLs) yielded the binding energy (E_B) positions for the Ge 3d$_{5/2}$ ($E_{Ge\,3d_{5/2}}^{\varepsilon-Ge}$) and As 3d$_{5/2}$ ($E_{As\,3d_{5/2}}^{In_{0.26}Al_{0.74}As}$) states. Likewise, the valence band maximum (VBM) binding energy for each material ($E_{VBM}^{\varepsilon-Ge}$ and $E_{VBM}^{In_{0.26}Al_{0.74}As}$) was determined by linearly fitting the onset of photoemission from the valence band density of states with respect to the experimental emission floor (inset of Figures 6a and 6b). Following the procedure introduced by Kraut *et al*, the valence band offset (ΔE_V) can be expressed as,[44]

$$\Delta E_V = \left(E_{Ge\,3d_{5/2}} - E_{VBM}\right)^{\varepsilon-Ge} - \left(E_{As\,3d_{5/2}} - E_{VBM}\right)^{In_{0.26}Al_{0.74}As} - \left(E_{As\,3d_{5/2}}^{In_{0.26}Al_{0.74}As} - E_{Ge\,3d_{5/2}}^{\varepsilon-Ge}\right)^{i} \quad (2)$$

where $\left(E_{Ge\,(As)\,3d_{5/2}} - E_{VBM}\right)^{\varepsilon-Ge\,(In_{0.26}Al_{0.74}As)}$ is the binding energy separation between the Ge (As) 3d$_{5/2}$ state and the VBM of the respective material and $\left(E_{As\,3d_{5/2}}^{In_{0.26}Al_{0.74}As} - E_{Ge\,3d_{5/2}}^{\varepsilon-Ge}\right)^{i}$ is the binding energy separation between the Ge and As 3d$_{5/2}$ states measured at the interface. Using the experimental binding energy separations of 29.19 ± 0.05 eV, 40.42 ± 0.05 eV, and 11.80 ± 0.05 eV, respectively, the corresponding ΔE_V at

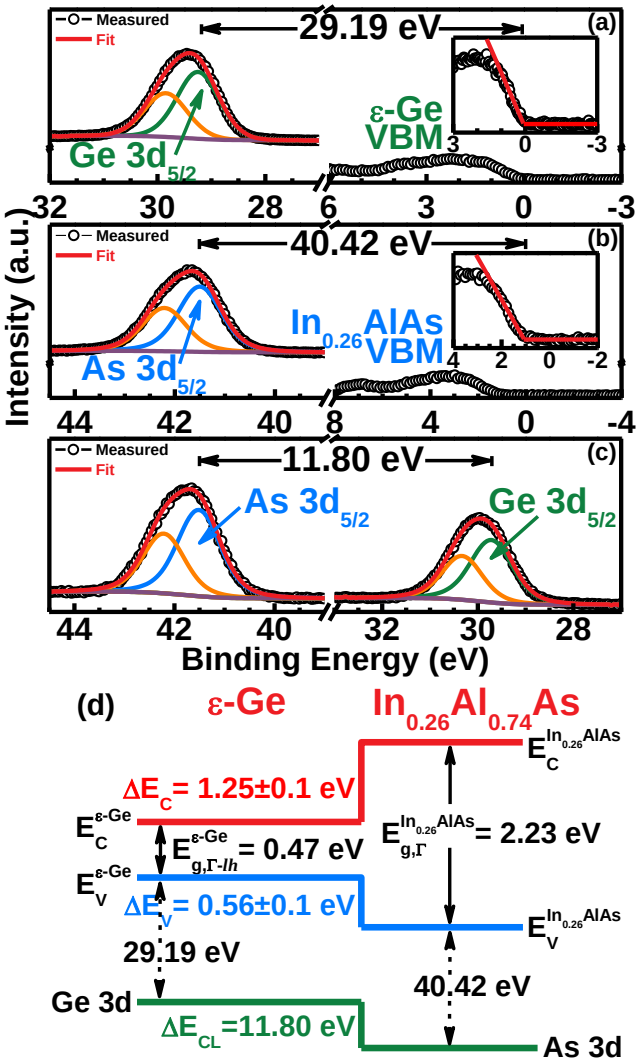

Figure 6. X-ray photoelectron spectroscopy (XPS) spectra of the (a) Ge 3d core level ($E_{Ge3d}^{\varepsilon-Ge}$) and valence band maximum ($E_{VBM}^{\varepsilon-Ge}$) from the ε-Ge thin-film, (b) As 3d ($E_{As3d}^{In_{0.26}Al_{0.74}As}$) and VBM ($E_{VBM}^{In_{0.26}Al_{0.74}As}$) from the $In_{0.26}Al_{0.74}As$ stressor, and (c) As 3d and Ge 3d core levels measured at the ε-Ge/$In_{0.26}Al_{0.74}As$ heterointerface. (d) Schematic flat-band diagram for the ε-Ge/$In_{0.26}Al_{0.74}As$ heterostructure illustrating the relatively large valence (ΔE_V = 0.56±0.1 eV) and conduction (ΔE_C = 1.25±0.1eV) band offsets found in this work.

the ε-Ge/$In_{0.26}Al_{0.74}As$ heterointerface was found to be 0.56 ± 0.1 eV. Similarly, the conduction band offset (ΔE_C) can be derived as,[44]

$$\Delta E_C = E_g^{In_{0.26}Al_{0.74}As} - E_g^{\varepsilon-Ge} - \Delta E_V \quad (3)$$

where $E_g^{In_{0.26}Al_{0.74}As}$ and $E_g^{\varepsilon-Ge}$ are the bandgaps of $In_{0.26}Al_{0.74}As$ and ε-Ge, respectively, and ΔE_V is the measured valence band offset. Using the calculated $In_{0.26}Al_{0.74}As$ and ε-Ge bandgaps of 2.23 eV[45] and 0.47 eV,[42,43] respectively, a value of 1.25 ± 0.1 eV was found for ΔE_C. Figure 6d summarizes these parameters in schematic form, illustrating a flat-band representation of the empirical Γ-valley energy band alignment at the ε-Ge/$In_{0.26}Al_{0.74}As$ heterointerface and highlighting the strong confinement to be expected in the ε-Ge epilayer. In the following section, we will correlate these empirical data with first-principles calculations of the electronic structure of ε-Ge/$In_xAl_{1-x}As$ heterojunctions;[35] and, in so doing, elucidate the nature of the bonding environment and stoichiometry at the experimental ε-Ge/$In_{0.26}Al_{0.74}As$ heterointerface reported herein.

Comparison of Empirical and Calculated Interfacial Electronic Structures. It has been well-established that atomic interdiffusion across semiconductor heterojunctions is capable of quantitatively modifying the heterointerfacial energy band alignment,[46–52] wherein variations in the local bonding environment at the interface can correspond to a significant range of possible interfacial electronic configurations. This is particularly true of IV/III-V heterointerfaces, more specifically, Ge/III-V heterointerfaces, which have been predicted to exhibit either staggered (type I) or straddling (type II) interfacial electronic structures depending on the heterointerfacial stochiometry.[31,35] Despite this remarkable result, relatively few studies have been reported on the experimental[29,42,54] or theoretical[31,35] investigation of the heterovalent Ge/III-V interface. Specifically, the first-principles-based systematic investigation of the heterovalent ε-Ge/$In_xA_{l-x}As$ interface by Greene-Diniz *et al*[35] remains the only reported theoretical inquiry into the ε-Ge/$In_xAl_{1-x}As$ interfacial electronic structure; *i.e.*, the same property of the ε-Ge/$In_xAl_{1-x}As$ material system studied in this work. In ref. 35, Greene-Diniz and co-workers employ density functional theory (DFT), utilizing the GW approximation, to calculate the ε-Ge/$In_xAl_{1-x}As$ interfacial electronic structure under abrupt and non-abrupt conditions. Expanding upon the latter, the ε-Ge/$In_xAl_{1-x}As$ heterointerface was then probed considering:

(i) variations in the stoichiometry of a mixed interfacial region; (ii) variations in the InAs mole fraction (up to x = 0.25) of the $In_xAl_{1-x}As$ stressor; and (iii), interdiffusion of atomic species across the heterointerface, as well as their relative stability in the extrinsic material.

A key finding of these investigations is highlighted in Figure 7, which graphically depicts the modification of the ε-Ge/$In_xAl_{1-x}As$ energy band alignment as a function of As up-diffusion length into a strained (ε ~ 1.76%) Ge epilayer overlying an As-terminated $In_{0.25}Al_{0.75}As$ stressor. We note that monolayer 0 (ML0) corresponds to an abrupt heterointerface with a singular mixed monolayer bridging the two disparate materials. Likewise, ML1 and ML2 correspond to the distance between the maximum extent of diffusion and the abrupt heterointerface, in monolayers; *i.e.*, the furthest such mixed monolayer from the abrupt interface case.

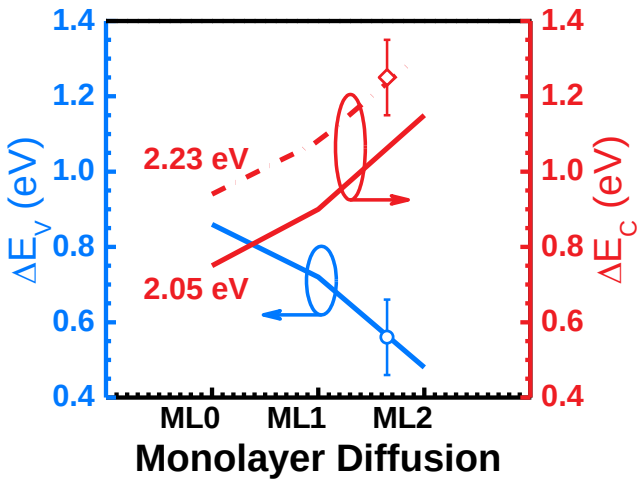

Figure 7. Calculated valence band offset (ΔE_V, left, blue) and conduction band offset (ΔE_C, right, red) as a function of arsenic (As) diffusion length into a ε-Ge epilayer overlying an As-terminated $In_{0.25}Al_{0.75}As$ stressor. Solid lines have been adapted from ref. 35, whereas dashed lines represent ΔE_C when recalculated using the $In_xAl_{1-x}As$ bandgap provided in ref. 45. Symbols (and associated error) correspond to the experimental energy band offsets as determined *via* XPS and reported in this work. The experimental data (symbols) were overlaid with the modeled "trend" (lines) to approximate the extent of As diffusion in the as-grown (empirical) ε-Ge/$In_{0.26}Al_{0.74}As$ heterostructure studied herein.

The stoichiometry of these mixed monolayers is modeled as an equal number of As and Ge atoms, *i.e.*, $As_{0.5}Ge_{0.5}$, based on previous correlations between theoretical and empirical data from the lattice-matched Ge/AlAs(001) heterointerface.[54] As shown in Figure 7, an increase in up-diffusion of As atoms (into the epitaxial Ge layer) corresponded to a substantial decrease in ΔE_V from 0.86 eV (in the abrupt case) to 0.48 eV (in the two-monolayer diffuse case, ML2). Utilizing the *ab-initio* calculated bandgaps for 1.76% ε-Ge (0.43 eV) and $In_{0.25}Al_{0.75}As$ (2.05 eV), Greene-Diniz *et al*[35] determined a concomitant increase in ΔE_C from 0.75 eV to 1.15 eV.

Comparing these data with the energy band offsets determined in this work *via* XPS (ΔE_V = 0.56 eV; ΔE_C = 1.25 eV), one can find that the first-principles calculations suggest an empirical diffusion window of up to two monolayers. This is in excellent agreement with the experimentally-determined diffusion window for Ge/AlAs(001) heterointerfaces as demonstrated by atom probe tomography (APT) analysis, which was found to be ~6 Å (approximately two monolayers).[54] Moreover, the predominance of As–Ge bonds within the mixed monolayers is supported by the epitaxy conditions utilized herein, wherein an As_2 overpressure was maintained post-III-V growth and prior to wafer transfer into the isolated Ge epitaxy chamber (see Materials and Methods for additional growth details). Furthermore, investigations into the thermodynamic stability and formation energies of As–Ge and Al–Ge bonds in Ge and AlAs materials[35] indicate that under the vast majority of epitaxy conditions, As–Ge bonds exhibit lower formation energies than Al–Ge bonds, and are thus more likely to form. Additionally, for the case of As-rich growth conditions, the As–Ge bond formation energy remains negative, suggesting the spontaneous formation of As–Ge bonds under thermodynamic equilibrium. This finding has important consequences for the design of future ε-Ge/$In_xAl_{1-x}As$ heterostructure-based optical devices, as it has been previously shown that a negative linear relationship exists between As (V) diffusion length and ΔE_V.[35] Likewise, a similar relationship exists between increasing As content in the mixed As_bGe_{1-b} monolayer, *i.e.*, as the mixed monolayer becomes more As-rich, the corresponding heterointerfacial ΔE_V decreases.[54] As such, the synthesis of experimental and theoretical findings herein indicate that careful control over stressor (III-V) atomic diffusion into the overlying Ge epilayer is of utmost importance in order to maintain sufficient carrier confinement and functioning optical devices.

CONCLUSIONS

Our experimental results demonstrate that highly tensile-strained Ge epilayers can be realized on large bandgap (*e.g.*, $In_xAl_{1-x}As$) metamorphic buffers while maintaining coherent, atomically abrupt heterointerfaces. Key to accomplishing this is careful control over the growth temperature and growth rate, wherein low growth temperatures and rates allow for the minimization of both atomic interdiffusion and relaxation of the epitaxially induced lattice stress. Following these measures, we demonstrated a ~1.75% biaxial tensile stress in an overlying Ge epilayer grown atop an $In_{0.26}Al_{0.74}As$ stressor. High-resolution x-ray diffraction (HR-XRD), transmission electron microscopy, and

Raman spectroscopy were used to verify the epilayer crystallinity, heterointerface long- and short-range uniformity, and strain-state of the Ge thin-film. Likewise, atomic force microscopy demonstrated smooth surface morphologies (*rms* roughness ~ 3.6 nm) and the development of a uniform, cross-hatched surface; the latter of which was indicative of symmetric metamorphic buffer relaxation, mirroring the HR-XRD results. Employing x-ray photoemission spectroscopy analysis, valence and conduction band offsets (ΔE_V = 0.56 ± 0.1 eV and ΔE_C = 1.25 ± 0.1 eV) were determined in order to project the extent to which large bandgap $In_xAl_{1-x}As$ confines carriers to the ε-Ge epilayer. Moreover, a comparison of these findings with first-principles calculations of the ε-Ge/$In_xAl_{1-x}As$ interfacial electronic structure not only validated the empirical band alignment results, but also highlighted the critical role in which heterointerface stoichiometry plays in determining band offsets and the need to control interfacial atomic species diffusion.

More generally, our results demonstrate how the atomic structure at the Ge/III-V heterointerface can be engineered to realize a wide range of energy band alignments. Selective termination of the III-V stressor surface, *i.e.*, with either group III or group V atoms, is expected to have a substantial impact on valence and conduction band offsets.[31,35,54] However, great care must be taken during crystal growth to control heterointerface interatomic diffusion and prevent the unintentional transition from one band alignment type to another (*e.g.*, straddling to staggered). This is particularly important when designing photonic structures in which optical and electrical confinement are critical to device operation. Correspondingly, these results provide a unique pathway for the realization of group IV-based optoelectronic and photonic devices.

MATERIALS AND METHODS

Materials Synthesis. The unintentionally-doped ε-Ge epilayers studied in this work were grown using an *in-situ*, dual-chamber molecular beam epitaxy (MBE) growth process leveraging separate III-V (composite) and group IV semiconductor growth reactors connected *via* an ultra-high vacuum transfer chamber. The isolation of each growth phase is expected to minimize the likelihood of atomic interdiffusion at the ε-Ge/$In_xAl_{1-x}As$ heterointerface during subsequent epitaxy of the ε-Ge epilayer following $In_xAl_{1-x}As$ stressor growth. Reflection high-energy electron diffraction (RHEED) was used to analyze epilayer surface reconstruction at key points throughout the surface

cleaning and subsequent heterostructure growth. A (001)GaAs substrate offcut 2° towards the ⟨110⟩ direction was first desorbed of native oxide at 750°C under an arsenic (As_2) overpressure of ~10^5 Torr as supplied by a valved As cracking source. It should be noted that substrate offcut has been previously demonstrated[55–59] to minimize the formation of anti-phase domain boundaries during polar-on-non-polar epitaxy. As the ε-Ge/$In_{0.26}Al_{0.74}As$ heterojunction investigated herein was envisioned as a double heterojunction (*i.e.*, $In_xAl_{1-x}As$/ε-Ge/$In_xAl_{1-x}As$) in practical (future) applications, this work utilized offcut (001)GaAs substrates to expand the applicability of the results. Following oxide desorption, 0.25 µm of homoepitaxial GaAs was grown at 660°C, after which a ~0.9 µm graded $In_xA_{l-x}As$ metamorphic buffer was grown at 420°C in order to balance the dissimilar add-atom mobilities of indium (In) and aluminum (Al) surface dimers. After $In_xAl_{1-x}As$ buffer growth, a 15 minute, 540°C annealing step was introduced to provide sufficient thermal energy for the annihilation of in-grown dislocations resulting from the large lattice mismatch between the active region and substrate. A ~0.6 µm constant composition $In_xAl_{1-x}As$ (x_{exp} ~ 0.26) stressor was then grown at 525°C, after which the sample was cooled (under a decreasing As_2 overpressure) and transferred to the group IV reactor for Ge growth. During cooling of the sample following $In_xAl_{1-x}As$ virtual substrate (VS) epitaxy, the As needle valve was closed at a rate of ~10% every 25°C. As such, the low temperature at which the As_2 supply was terminated (~275°C) ensures that the III-V surface is As-terminated. A 10 nm thick Ge epilayer was then grown at 400°C using a growth rate of ~0.067 Å/s in order to maintain an abrupt heterointerface. Following Ge epilayer growth, the sample was gradually cooled to ~25°C using a low 5°C/min ramp rate in order to prevent the formation of defects due to the dissimilar thermal expansion coefficients between each epilayer.

Materials Characterization. The heterostructure crystal quality, $In_xAl_{1-x}As$ stressor composition, and epilayer relaxation and strain-states were characterized using high-resolution x-ray diffraction (HR-XRD). X-ray rocking curves (*i.e.*, ω-2θ scans) and reciprocal space maps were recorded using a PANalytical X-pert Pro system equipped with PIXcel and proportional detectors and a monochromatic Cu Kα (λ = 1.540597 Å) x-ray source. Analysis of the diffraction data was performed following the methods introduced in ref. 38. Independent corroboration of the ε-Ge strain-state was provided by Raman spectra collected in the (001) backscattering geometry. All Raman spectra were captured using a JY Horiba LabRam HR800 system equipped with a 514.32 nm Ar laser source and calibrated

using the Si LO mode at $\omega_0 \sim 520$ cm^{-1}. The surface morphology of the as-grown ε-Ge/$In_xAl_{1-x}As$ heterostructures was investigated using a Bruker Dimension Icon atom force microscope (AFM) in tapping mode. Lastly, high-resolution cross-sectional transmission electron microscopy (HR-TEM) was performed on a JEOL 2100 TEM in order to study the structural quality, ε-Ge/$In_xAl_{1-x}As$ heterointerface uniformity, and lattice coherence of the strained layer/stressor heterointerface. The requisite electron transparent foils were prepared *via* standard polishing techniques, *i.e.*, mechanical grinding, dimpling, and subsequent Ar^+ ion beam milling at low temperature (~150 K) in order to prevent the re-deposition of milled material on the imaging surface.

Heterostructure Band Alignment Characterization. The band alignment between the ε-Ge epilayer and the $In_{0.26}Al_{0.74}As$ stressor was investigated using a PHI Quantera SXM XPS x-ray photoelectron spectroscopy (XPS) system with a monochromatic Al Kα (E = 1486.7 eV) x-ray source. A low-energy electron flood gun was utilized to compensate positive charge accumulation in the samples due to photoelectron generation during sample x-ray irradiation. All core level (CL) and valence band binding energy spectra were collected with a pass energy of 26 eV and an exit angle of 45°. Correction for residual surface charging on each sample surface was performed by adjusting the experimental carbon 1s CL peak position to the literature value of 285.0 eV. Curve fitting of the recorded spectra was performed using CasaXPS v2.3.14 utilizing Lorentzian peak shapes convolved over a Shirley-type background. The CL energy position was defined to be the center of the peak width at half the peak height (*i.e.*, the FWHM). Additionally, the valence band maximum for each bulk-like semiconductor was determined using a linear extrapolation of the onset of valence band photoemission. Finally, statistical deviation in the Au $4f_{7/2}$ CL binding energy of a Au standard was used to derive an experimental uncertainty of ±0.04%, wherein subsequent uncertainty was estimated using a root-sum-square approach.

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M.K.H. and M.B.C. conceived of the research and performed the epitaxial heterostructure growths. M.B.C. and J.–S.L. performed the materials characterization and analysis, including the XRD, Raman, AFM, and TEM characterization. M.B.C. performed the XPS measurements and analysis. M.K.H. and R.J.B. supervised the research. All authors discussed the results and contributed to the writing of the manuscript.

Notes

The authors declare no competing financial interest.

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