Van der Waals Heteroepitaxy of GaSe and InSe, Quantum Wells, and Superlattices

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Bandgap engineering and quantum confinement in semiconductor heterostructures provide the means to fine-tune material response to electromagnetic fields and light in a wide range of the spectrum. Nonetheless, forming semiconductor heterostructures on lattice-mismatched substrates is a challenge for several decades, leading to restrictions for device integration and the lack of efficient devices in important wavelength bands. Here, it is shown that the van der Waals epitaxy of 2D GaSe and InSe heterostructures occur on substrates with substantially different lattice parameters, namely silicon and sapphire. The GaSe/InSe heteroepitaxy is applied in the growth of quantum wells and superlattices presenting photoluminescence and absorption related to interband transitions.

1. Introduction

III–VI post-transition metal chalcogenides (PTMC), like GaSe, GaS, GaTe, InS, InSe, and InTe, crystallize in a hexagonal lattice of four monoatomic sheets known as tetralayers (TL), bonded by vdw forces and surface lattice parameter ≈4 Å (Figure 1a). Its bulk form has been known since the 1970s, and they have been used for some non-linear optical applications in the infrared,[1,2] second harmonic generation[3] (SHG), or circular dichroism[4] in the meantime. Despite the unexplored properties as thin films, in the bulk form, the chemical, optical and electronic properties are already well studied. The bulk PTMC types with similar formation energy,[16] appearing depending on the synthesis method. The most common polytypes are formed by non-centrosymmetric TL (D3h), named as α-(P63/mmc), β-(P63/mmc), γ(R3m), and ε-(P63/mmc), based on different stacking sequences between the adjacent layers along the [0001] orientation.[16–19] Dissimilar polytypes present small differences in some of the PTMCs can be found in several phases or polymorphs. Indium Selenide, for example, appears as InSe, α-In2Se3, β-In2Se3, In3Se4, etc.,[6] which makes the synthesis of these materials challenging, but at the same time it opens the possibility of exploiting specific properties of each phase and the phase changes itself. Few memory devices based on phase transformation have been already reported,[7–9] β-In2Se3 and α-In2Se3 present robust ferroelectricity[10] at room temperature, which is a building block for energy harvesting/storage and neuromorphic devices, and still a rare property in the 2D material world.[11] The InSe, which we deal in this paper, apart from the already mentioned high-mobility, exhibited quantum hall effect,[12] good photoresponsivity, good mechanical strength, and flexibility,[13] exotic properties when strained,[14] and low lattice conductivity (<2 Wm−1K−1)[15] together with high Seebeck coefficient,[6] important for thermoelectric (TE) materials, being the perfect definition of multifunctional material. Due to lattice and electronic band similarities, the equivalent properties are expected in GaSe and all PTMCs.

Yet, GaSe and InSe have several known polymorphs or polytypes with similar formation energy,[16] appearing depending on the synthesis method. The most common polytypes are formed by non-centrosymmetric TL (D3h), named as α-(P63/mmc), β-(P63/mmc), γ(R3m), and ε-(P63/mmc), based on different stacking sequences between the adjacent layers along the [0001] orientation.[16–19] Dissimilar polytypes present small differences in...
band structure, electronic and optical properties particularities due to the presence or lack of special symmetries.

Ab initio studies and ARPES direct measurements have found Mexican-hat valence band (MHVB) dispersions in the valence band of many few-layer PTMCs. The uncommon MHVB result in step-like and delta-like density of states (DOS), large transport velocity due to the flatness and steepness of the band, and electronic instabilities that lead to tunable superconductivity, ferroelasticity, and ferromagnetism. MHVB is present in the most efficient TE materials, that is, Bi$_2$Se$_3$ and Bi$_2$Te$_3$. It is anticipated that PTMC TE figures-of-merit can be improved when thinned to TL scale, due to the increment of the density of states (DOS) when the band structure turns into MHVB. Such thin PTMCs in theory would present enhanced $zT$ as high as 2.0; as good as the reference Bi$_2$Te$_3$ alloys.

Most importantly, it was demonstrated that heterostructures from InSe and GaSe flakes exhibit optical transitions that densely cover the spectrum from violet to infrared, something that was rarely achieved with any other material system.

Decades ago, Esaki and Tsu used the Molecular beam epitaxy (MBE) of two semiconductor compounds with distinct bandgaps, GaAs and AlAs, to create the first man-made artificial crystal using ultrathin layers of material. Layers with few nm forming QW and SL succeed on explore the effect of quantum tunneling and quantum confinement with unprecedented control since the carrier’s potential barrier is determined by the bandgap difference, band offset, and the precisely chosen layer thickness. In the first few years, using the same materials, high-mobility transistors and optoelectronic devices (diode lasers and photodetectors) were invented, and the following years were devoted to expanding the family of the III–V alloys (Ga, In, Al with P, As, and Sb) with similar lattice sizes. Unfortunately, those heterostructures only reach efficiently the infrared and the red part of the visible spectrum, up to 1.5 eV. Widegap III–V technology over sapphire substrates was developed only in the 1990s using Ga, In, and Al nitrides, when the first blue light-emitting diodes were invented. However, several important wavelengths and a whole region of the spectrum still lack a material with good properties for device fabrication. Even with new compound semiconductors developed for the green region, like the II–VI family (Zn, Mg, Cd with S, Se, and Te), we are still unable to achieve the required material quality, since doping and epitaxial growth of II–VI never prospered as expected. Figure 1b shows the lattice parameter and the bandgap of those materials where some observe the lack of direct bandgap materials in the green, orange and yellow window, and the complete void in the lattice parameter from 3.5 to 5.2 Å. As result, the only viable high-power alternatives in this color region make use of frequency down or up-conversion in complex non-linear solid-state systems, which price, size, limitations in power, and wavelength coverage results unsuitable for wide exploitation.

Most recently, since the interest in 2D PTMC resurged due to its novel properties as 2D materials and its promises for optoelectronics, few groups report the growth of thin films by CVT, PVT, CVD, PLD, or MBE. However, these efforts, with few exceptions, have been limited to small area characterization or few devices, rather than large-area, pretty much like as it is done with 2D material flakes,
suggesting challenges in achieving wafer-scale uniformity. A fairly general trend in vdW epitaxy. The epitaxy by MBE of bulk PTMCs has been reported without constancy since the 1990s and unfortunately, most of them reported only the homoepitaxy, or then, the standard heteroepitaxy on GaAs substrates, which results in rough interfaces and growth in other orientations than the \([0001]\), which cannot be directly applied to form the atomic defined interfaces as required for QWs and SLs. Only recently, Sorokin demonstrate the growth of GaTe/GaSe heterostructures that could be used for this goal, however, up to now, no one succeed to grow high-quality InSe/GaSe heterostructures or to demonstrated quantum confinement on PTMC large-area heterostructures.

Recently, we presented the epitaxial growth of high-quality and single-phase \(\beta\)-In\(_2\)Se\(_3\) by MBE on a 2-inch wafer scale. Thin layers down to two QLs were uniformly obtained and photodetectors were fabricated using photolithography and other standard semiconductor processing. In the same work, we demonstrated that changing substrate temperature and Se flux is possible to obtain different Indium Selenide phases, including the InSe phase. We also optimized the growth of GaSe and obtained high-quality thin layers on two completely different substrates: c-sapphire (4.7 Å) and Si (111) (3.85 Å). Using atomic-resolution scanning transmission electron microscopy (STEM), we investigated the formation of its multiple polytypes during the growth and correlated defects. It was observed that, far from the substrate, the GaSe and InSe relax and assume their original lattice parameter (3.75 and 4.0 Å, respectively). We also reported the first structural observation of a new polymorph (R\(_3\)m) (named as \(\gamma\)-polymorph) characterized by a distinct atomic configuration with centrosymmetric TL (D\(_{3d}\)).

In this work, after deal with the segregation effects, we have combined both GaSe and InSe epitaxy in heterostructures, growing short-period (~2 TL) InSe/GaSe SLs and QWs in both substrates (sapphire and Si). They presented photoluminescence that emission wavelength can be tuned changing the QW widths, demonstrating quantum confinement. It was observed that the InSe and GaSe lattices are commensurable in the SL, making both materials strained (with 3.88 Å) with the D\(_{3d}\) polymorph dominant that probably presents enhanced properties in comparison with the non-centrosymmetric TL (D\(_{3h}\)). Finally, we were able to fabricate a simple photodetector based on this heterostructure at wafer scale, to demonstrate the applicability of the GaSe/InSe heteroepitaxy by MBE.

2. Results and Discussion

2.1. Large-Area Growth by MBE

Since gallium selenide (GaSe\(_2\)) and indium selenide (In\(_2\)Se\(_3\)) exist in various solid phases, and form a complex phase diagram, a precise control on stoichiometry and growth conditions is required. As demonstrated earlier by our group and others, MBE provides the necessary means to control the III and VI material fluxes to obtain the desired pure phase, and in addition, to monitor the growth in situ by Reflection High-Energy Electron Diffraction (RHEED). For our samples, the MBE growth proceeds from elemental indium (6N) and gallium (6N) sources, evaporated from Knudsen cells, and selenium (5N), provided from a valved cracker cell wherein the flux is controlled by a valve with an adjustable aperture. The III–VI ratio is controlled by the Se cracker cell valve aperture, and the growth rate by the In and Ga Knudsen cell temperature. The lowest value of surface roughness was obtained within the window of substrate temperatures between 450 and 600 °C for (thickness > 60 nm) multilayer growth. Starting the growth beyond this temperature range usually results in randomly oriented polycrystalline films, or their complete vaporization, as observed by in situ Reflection High Energy Electron Diffraction (RHEED). Within this temperature window, three phases of In\(_2\)Se\(_3\) were selectively obtained by varying the Se flux through the valve aperture (linear relation in the range used). InSe was obtained with the valve at 0.75 mm or less, \(\gamma\)-In\(_2\)Se\(_3\) from 1 to 3 mm and \(\beta\)-In\(_2\)Se\(_3\) from 2 to 5 mm. GaSe was obtained with the valve at 1.2 mm or less, and Ga\(_2\)Se\(_3\) beyond this value. In general, to obtain single-phase InSe (GaSe), In-rich (Ga-Rich) growth conditions are required. Despite the narrow growth window, the valve aperture is finely tuned for each temperature and material by monitoring the RHEED pattern.

When the valve is found at the optimized value, the RHEED diffraction pattern (Figure 2a) is bright and streaky even after the growth of several layers, otherwise, the pattern fades in intensity and the streaky lines become diffuse. Advantageously, a single c-sapphire substrate could be used for calibration of the fluxes using the RHEED diffraction, as the substrate surface is immutable even after several growths and desorption cycles. Very similar patterns are obtained on Si(111) substrates without specific surface treatments (completely vdW epitaxy). In these patterns (Figure 2a), it is visible the superposition of [11\(\bar{2}\)0] and [10\(\bar{1}\)0] signaling the mix of both orientations and typical twinning defects of vdW epitaxy. It presents in-plane registry within the substrate, sharing the same crystallographic directions. Highly-oriented GaSe can be obtained on Si (111) substrates taking advantage of the Ga–Se passivation/termination layer wherein the [11\(\bar{2}\)0] and [10\(\bar{1}\)0] patterns are distinct and obtained rotating the substrate by 60° as it would be expected in a twinning-free crystal (see Figure 2b), which is usually called quasi-vdW epitaxy. Despite the improvement in the passivated Si(111), the crystallographic order was in general not sustained along with several TLs or within heterostructures, resulting back in the patterns of Figure 2a, or worse, resulting in relaxation by dislocations in specific conditions. It points the importance of the defects for the lattice relaxation in the vdW epitaxy at mismatch found in sapphire and Si(111).

Initially, single heterostructures consisting of thick layers (~30 TL) of single phase InSe on top of thick (~60 TL) GaSe were grown on Silicon (111) and c-Sapphire substrates at the growth rate of ~1 TL min\(^{-1}\). The Raman spectrum (Figure 2c) shows peaks at 133, 205, and 307 cm\(^{-1}\), corresponding to the A\(_1\), E\(_1\), and A\(_2\) vibration mode of GaSe, respectively, while the peaks located at 115, 177, and 227 cm\(^{-1}\) are attributed to the same modes for InSe. No evidence of other phases, namely Ga\(_2\)Se\(_3\) or In\(_2\)Se\(_3\) is inferred. In addition, distinct and narrow peaks in X-ray diffraction (XRD) support the high quality of growth, including high-quality single phase InSe, which could not be obtained directly on bare Si and sapphire substrates,
without a GaSe buffer layer\textsuperscript{[58]} (Figure 2d). The surface topography obtained by atomic force microscopy (AFM) exhibits atomic terraces with triangular shape, as expected for these hexagonal crystals (Figure 2e), wherein the crystal grows laterally along the [1120] or [1100] directions. The minimum step height is 8 Å, meaning that the TLs are formed at full height and then grown laterally in those directions, fundamentally different from the covalent epitaxy wherein the growth occurs monolayer-by-monolayer. The full-layer TL growth is also evidenced by the absence of alternative surface reconstruction\textsuperscript{[65]} as a unique RHEED pattern in all temperatures and III/VI flux ratios. In the AFM is noted a small accumulation of Se in the surface, which appears in the AFM as tall round particles, and which will be discussed later.

We observe the coexistence of all the non-centrosymmetric TL (D\textsubscript{3h}), named as ε-(P6\textsubscript{3}m2), β-(P6\textsubscript{3}mmc), γ-(R3m), and δ-(P6\textsubscript{3}mc) polytypes and centrosymmetric TL (D\textsubscript{3d}) polymorphs and their grain boundaries in samples grown on both substrates. This results in distinct regions, as shown by changes in contrast observed by Bright Field (BF) scanning transmission electron microscopy (STEM) (Figure 2f,h), which is expected to occur after twinning and changes in stacking sequence, as
occurs in most of layered materials and was observed in the RHEED patterns. The impact of these defects in future devices is still unknown, and attempts to reduce their formation in 2D materials,[61,66] including GaSe,[47] are under study.

Regardless of the rotation and twinning along the c-axis (around multiples of 60°),[59] the GaSe and InSe vdW layers stack nicely across the surface, as observed in the selected area electron diffraction (SAED) patterns (Figure 2g,i) and the aberration corrected HAADF-STEM image (Figure 2j). Moreover, the interface between InSe and GaSe is well defined, over a vertical region of 1 to 3 TL. These results confirm that both materials grow epitaxially layer-by-layer on both substrates and with minimal In–Ga inter-diffusion, differently from previous reports.[49] In fact, layer rotation, translational shear fault, and local changes in the vdW interplanar distance are important mechanisms of stress release, which allows the quick change in the in-plane lattice parameters. Both materials are unstrained and exhibiting their natural lattice parameters (further discussed below) at their interface presented in Figure 2i.

2.2. Quantum-Wells and Superlattices

Even though high-quality InSe on GaSe could be obtained with the conditions used above, the growth of GaSe on InSe and the growth of a GaSe/InSe/GaSe QW failed. In the trials to grow heterostructures using the same conditions used in the thick growth of a GaSe/InSe/GaSe QW failed. In the trials to grow the conditions used above, the growth of GaSe on InSe and the enhancement of PL in these expected type-II heterostructures. STEM shows sharp Ga and In distribution along the SL and QW (Figure 4b–f), with very well-defined interfaces and the expected layer thicknesses. In the Figures 2e,f and 4c,d is observed a mixing of In and Ga of \( \approx 1 \) TL (0.8 nm) in the interface. It is expected as the growth occurs in full TL steps and there are always incomplete TLs in the surface, which will be completed by the following material in the heterostructure. Similarly, such mixture also occurs on heteroepitaxy of covalent compounds, nevertheless, in PTMCs, the interface has the width of a TL instead of a monolayer. Though the islands size and density can be further optimized, it reflects in limitations of QW width and interface roughness or steepness. Nonetheless, it is also common on covalent materials to have interface with several monolayers due to segregation, like in InGaAs/GaAs interfaces,[69] and due diffusion, as InAs/GaSb interfaces.[71] In perspective, many of useful III–V heterostructures present interface with similar characteristics as the observed in the GaSe/InSe SL.

The most important observation in the PL spectra (Figure 4g) is the emission lines in the infrared region, peaked at 1.06 and 1.20 eV depending on the QW thickness. Particularly, we associate these PL lines to the optical interband transitions from the ground electron subband of the InSe/GaSe/InSe 5/5/5 and 4/4/4 TL QWs to the ground hole subband now confined in GaSe-QWs (5 and 4 TL thick). Given the lower value of the electron effective mass in the conduction band, most of the difference between those PL peak energies (140 meV) will be due to the difference in the electron confinement energy when the InSe QW narrows from 5 to 4 TLs according to our models. 1.06 and 1.20 eV are energies that cannot be associated to any other transition coming from the substrates (Sapphire and Si) and are below the bandgap of both bulk InSe and GaSe and must come from the heterostructure.
Both PL lines are weak, as compared to the signal measured in III–V semiconductor heterostructures, which is consistent with low absorption in InSe and GaSe materials and the spatially indirect transitions due to the GaSe–InSe type II band alignment. The narrow peaks at 1.8 eV come from the usual Chromium defects in sapphire and from the gray selenium accumulated in the surface. The experimental peak at 1.45 eV is attributed to the transition to the SL miniband and the peaks at 2.0 eV to the GaSe buffer layer.

To obtain the direct (or quasi-direct) bandgap resulting from carrier confinement in the SL and QWs and compare them to the experimental data (Table I) we used methods based on the function envelope and effective mass approximation (EF/EMA) and the transfer-matrix method (TMM). The EF/EMA with TMM model is widely used for Si–Ge and III–V semiconductors with high success and precision. The required values of the bandgap, effective mass ($m^*$), and valence-band offset (VBO) were collected from the limited literature available for

![Figure 3.](image-url)
PTMC heterostructures (Table 2) and from the first principles calculations shown in Fig 4 h. Strain is considered through deformation potential. Despite its simplicity, the method is accurate for wide QW\(^{[25]}\) (>2 nm), showing a difference of only 4% to the experimental value or ab-initio calculations obtained from a 2/2 TL SL system.

Noteworthy, the comparison between InSe/GaSe/InSe 5/5/5 and 4/4 TL QWs using EF/EMA model (Figure S1, Supporting Information) fully represent the observed in the PL measurement. The PL values similar to the value predicted by the EF/EMA model is strong evidence of carrier confinement in our heterostructures. Yet, in the same spectrum, it is possible to identify another peak (1.45 eV) that corresponds to the calculated 2.5/2.5 SL miniband energy in the EF/EMA model. Unfortunately, Photoreflectance (PR) measurements (Figure S2, Supporting Information) performed at room temperature exhibited poor signal-to-noise ratios, likely due to the inertia of vdW interfaces and the absence of significant band bending modulation upon excitation. Additionally, Fabry–Pérot interference turns it difficult to clearly define the peaks and their position. Nonetheless, there are indications of absorption in the energies pointed by the calculations and PL between 1.0 and 1.5 eV, as well as, the absorption by the GaSe buffer.

Table 1. Experimental and calculated direct (Γ–Γ) bandgap for the bulk GaSe and InSe, its short-period superlattices, and embedded quantum wells.

|                  | Experimental [eV] 15 K | EF/EMA [eV] 15 K |
|------------------|------------------------|------------------|
| GaSe             | (at RT) 2.0\(^{[a,b]}\) | (at RT) 1.97\(^{[c]}\) |
| InSe             | (at RT) 1.26\(^{[d]}\) |
| 2.5/2.5 TL SL    | 1.45\(^{[a]}\)          | 1.46             |
| 4/4 TL SL        | 1.13\(^{[a]}\)          | 1.23             |
| 4/4/4 QW         | 1.20\(^{[a]}\)          | 1.15             |
| 5/5/5 QW         | 1.05\(^{[a]}\)          | 1.09             |
| 10/10 TL         | 1.08\(^{[a]}\)          | (1.08)\(^{[a]}\) |

\(^{[a]}\)Photoluminescence; \(^{[b]}\)Photoreflectance; \(^{[c]}\)Photocurrent; \(^{[d]}\)Reference\(^{[76]}\) and \(^{[77]}\); \(^{[e]}\)Used for VBO determination
Table 2. Parameters used in the function envelope and effective mass approximation (EF/EMA). $m^\ast_e$ and $m^\ast_h$ are the electron and hole effective mass in the c-axis, respectively. $\alpha$ and $\beta$ are the Varshini coefficients for temperature-dependent bandgap calculations.[76] $\alpha_\gamma$ and $\alpha_\sigma$ are the deformation potential for conduction and valence band in strained lattices.

|                | InSe       | GaSe       |
|----------------|------------|------------|
| $m^\ast_e$    | 0.14[76]   | 0.17[79]   |
| $m^\ast_h$    | 0.74[76]   | 0.87[76]   |
| Direct bandgap ($0$ K) | 1.35[76] eV/1.35[76] eV | 2.10[77] eV |
| $\alpha$ (meV) | 0.475[76] | 0.66[77]   |
| $\beta$ (K)   | 224[76]    | 181[77]    |
| $\alpha_\gamma$ (eV) | 8.9[80]    | 5.3[81]    |
| $\alpha_\sigma$ (eV) | 2.0[80]    | 2.3[81]    |
| Valence band offset (VBO) | $-0.17$ eV [see82] | Reference |

and cap layer at 2.0 eV. With the aim of better understand the band structure and valence band alignment of the heterostructure, we have performed ab-initio calculations using density functional theory (DFT) within the local-density approximation (LDA). DFT typically underestimates the band gap and is not always accurate for calculations of the conduction bands; and at this stage cannot be used to calculate sub-bands and transitions in the conduction band. The inherent bandgap underestimation of DFT-LDA can be corrected either using hybrid functionals or the GW method.[83] However, DFT is a suitable tool to investigate both materials (Figure 2i). Measured interplanar distance of the peaks (003) and (T11) in reciprocal space were used to calculate $a = b$ and $c$ lattice parameters in real space. $a = b = 3.77$ Å and $c = 24.5$ Å for GaSe; and $a = b = 3.93$ Å and $c = 25.2$ Å for InSe.

Figures 4h–k shows the electronic structure (h), density of states (i) and relevant wave functions of the GaSe/InSe SLs. In order to observe the band alignment, we have represented the band structure using a color code that represents the weight of the atomic orbitals of each tetralayer. An electronic state totally localized at the GaSe (InSe) tetralayer will have a dark red (blue) color. As evidenced from the calculations, the electronic states near the bandgap are hybridized[84] between the two layers with a slightly larger localization on the GaSe layer. For instance, the wavefunction of the top of the valence band state is clearly more localized on the GaSe layer (Figure 4j). On the contrary, the second valence band state is more localized on the InSe layer but still with a relevant hybridization. The conduction band state (Figure 4k) is expanded along both GaSe and InSe layers, because the electronic density is localized on the selenium atoms, which facilitates delocalization along the $c$-direction.[85]

Our DFT-LDA calculations are also useful to estimate the valence band alignment, including strain effect. The valence band offset at the interface of two semiconductors is the energy difference between the top of the valence band of the two semiconductors resulting from the alignment of the Fermi level.

Table 2. Parameters used in the function envelope and effective mass approximation (EF/EMA). $m^\ast_e$ and $m^\ast_h$ are the electron and hole effective mass in the c-axis, respectively. $\alpha$ and $\beta$ are the Varshini coefficients for temperature-dependent bandgap calculations.[76] $\alpha_\gamma$ and $\alpha_\sigma$ are the deformation potential for conduction and valence band in strained lattices.

This definition works well for QWs of a thickness of many atoms but it might be less precise when dealing with systems of few atoms, as in the present case. As established in our calculations, there is a non-abrupt change in the electron density and the wavefunctions are rather hybridized in the two layers.[84] Nevertheless, we can estimate the valence band offset (VBO) to 0.25 eV for a 4/4 TL SL and to 0.42 eV for a 3/3 TL SL, the difference between the state on top of the valence band and the next valence band state. This VBO value re-enforces the value found using the function envelope and effective mass approximation considering the strain and the PL measured energies.[84]

2.3. Structure, Strain, and Sample Homogeneity

The lattice parameters of GaSe and InSe in the thick (bulk) film are obtained through fast-Fourier transform (local-FFT) (Figure 5a,b) of each part of the image of the interface containing both materials (Figure 2i). Measured interplanar distance of the peaks (003) and (T11) in reciprocal space were used to calculate $a = b = c$ lattice parameters in real space. $a = b = 3.77$ Å and $c = 24.5$ Å for GaSe; and $a = b = 3.93$ Å and $c = 25.2$ Å for InSe.

A similar method was used for the 2.5/2.5 SL in Figure 5c. A profile of the (00n) and (m00) directions of the FFT (Figure 5d–f) points to a common in-plane lattice parameter $a = b = 3.88$ Å (single peak), and distinct $c = 24.9$ Å for GaSe and $c = 26.9$ Å for InSe. The SL lattice parameters similar to the experimental ones were obtained in the previous DFT relaxations. Thereby, GaSe is in tensile strain and the InSe in compressive strain, assuming individually new interplanar distances and c-lattice parameters, larger than the relaxed bulk structure. Accordingly, a biaxial strain as high as 3% should be considered in precise theoretical models, the main effect is the increase of the valence band offset (VBO) and decrease of the type-II indirect bandgap (Figure 4f; Figure S3, Supporting Information). Nonetheless, as in the thick layers, the structure is indeed fully relaxed when the whole SL supercell is considered, due to strain compensation and relaxation.

The strain observed in these layers reinforces the strong interlayer coupling on PTMCs,[85] and that the epitaxy in these materials is an intermediary case between covalent compound semiconductors and weakly bonded vdW layers. The interlayer force is also demonstrated by the ratio of elastic coefficients in in-plane and cross-plane directions of these materials, $C_{11}$ and $C_{44}$, respectively. While in covalent semiconductors $C_{11}/C_{44} = 1$ and graphite $C_{11}/C_{44} = \infty$, on PTMC this value is $\approx 3$.[86]

This intermediary condition allows a force between layers to be weak enough to relax strong substrate mismatch, damping strain along the vdW bonding or through localized defects, but strong enough to induce epitaxial growth of 2D materials with reduced defects when compared with ordinary vdW epitaxy, when the substrate lacks order or the surfaces are not commensurable.

In the heterostructure, the distinct layers exhibit in general the $\gamma$-polymorph (D$_{4h}$ TL—see Figures 3d and 4e), with a common in-plane lattice parameter. However, in some locally-confined spots, others polytypes($\varepsilon$ and $\beta$-polype) and polymorphs ($\gamma$ with D$_{3h}$ TL) are found. In fact, the strain likely
causes the abundant presence of the rare \( \gamma' \)-polymorph.\(^{[60]} \) The enthalpy of each GaSe polymorph, \( \gamma' \) (D\(_{3d}\) TL) and \( \gamma \) (D\(_{3h}\) TL), was calculated using density functional theory for fully relaxed GaSe lattice, strained GaSe/InSe SLs, and InSe surface lattice parameters (Figure S3, Supporting Information). Similarly to observed on isolated TL,\(^{[60]} \) it was observed that the strain makes the \( \gamma' \)-polymorph slightly more stable and explains the abundance of the rare \( \gamma' \) (D\(_{3d}\) TL) form in the SL.

In the Raman spectrum (Figure 5g), the interfacial Raman mode (125 cm\(^{-1}\)) that is present in the previous single QWs sample (Figure 3h) is now enhanced. A new peak at 264 cm\(^{-1}\) that corresponds to grey Se is visible. Again, the shift or splitting of the E peak indicates the presence of D\(_{3d}\) TL polymorphs.\(^{[59]} \)

The MBE growth results in an overall film of uniform thickness with smooth surface morphology. The XRD (Figure 5h), which is taken in an area of 1 cm\(^2\), present well defined SL satellite peaks, which assures the SL periodicity and interface quality over this extent. The BF-STEM images (Figure 2e,g) reveal the rotation of some of the GaSe and InSe domains, as well as the formation of grain boundaries between the domains, created during growth on both substrates. However, the selected area electron diffraction patterns (Figure 2f,h) obtained from the interfacial region between the InSe/GaSe films and the substrates show the following crystallographic relationships: InSe(001)/GaSe(001)/Si(111), GaSe(110)/Si(110), InSe(001)/GaSe(001)/sapphire(001) and GaSe(110)/sapphire(110). The same relationship is observed within 15° (full-width at half-maximum–FWHM) in the \( \phi \)-scan of the peak (107) of the shortest period SL (Figure 5i). It states that notwithstanding the twin and polytypes grain boundaries, it is indeed a single crystal.

Despite the contrast variations in STEM (that is part due to the lamella thickness variation and the grains slight off the
after growth, or just avoided controlling the cracker valve with higher precision.

It is also noticeable that defects (mostly polytypes/polymorphs grain boundaries, stacking faults, and dislocations) are more visible close to the substrate, in the 30–40 nm buffer layer, or just above it. It is related to the mismatch between the substrate and the GaSe lattice. Indeed, the first layers presented stretched in-plane lattice parameters (3.89 Å) to fit the sapphire lattice, which tends to relax creating the observed defects. However, these defects did not reach the QW and cause the complete suppression of PL signal as would be expected in some classical compound semiconductors. Nonetheless, there is room for improvements in the buffer layer that could reflect the PL and future device’s performance. Considering that a fast relaxation was observed due to the vdW stack, a simple increase of the buffer layer thickness could be enough for initial improvements.

2.4. Photodiodes at Wafer-Scale

Only to demonstrate the capabilities of our MBE growth process, proof-of-concept photodiodes were fabricated at wafer scale using standard microfabrication techniques (CMOS compatible). Our photodiodes are based on the vdW epitaxy of a 10 nm GaSe and 10 nm InSe heterojunction on boron doped p^+Si (111) substrates and a transparent indium-tin oxide (ITO) top contact deposited by magnetron sputtering (see Figure 6b). In order to protect the heterojunction from oxidation and preserve its properties, the photodiode area is defined by etching the stack perimeter by argon-ion milling until the substrate, and encapsulating with 200 nm of amorphous Al_{2}O_{3}. The processed wafer with several identical devices is presented in Figure 7b.

Unintentional doping is expected in GaSe and InSe grown by most methods, largely due to selenium vacancies, leading naturally to p-GaSe and n-InSe with majority carrier concentrations ranging from 10^{15} to 10^{17} cm^{-3}. Consequently, the p-GaSe/n-InSe heterojunction is expected to show strong photoresponse due to the built-in potential. Self-driven photodetectors that can detect light without any external voltage bias are important for low-power applications, including future internet of things, wearable and flexible electronics. 2D materials exhibit good optoelectronic properties; nonetheless, their extraordinary properties have not been fully exploited to realize high-performance, self-driven photodetectors due to the difficulties of producing such heterostructures at large scale.

While the p-Si/ITO junction exhibits an ohmic behavior, the fabricated device shows the existence of a rectifying junction (Figure 7c) that behaves as a photodiode with very-low threshold voltage (and \(V_{oc}\)) and responsivity peak of 60 mA W^{-1} at 800 nm without voltage bias (Figure 7d). This value is 2.5 times higher than the responsivity previously observed on similar devices based on flakes and 1/10th of commercial p-i-n Si diodes, which usually have much thicker active regions, in the range of micrometers. Despite some can find reports of much higher responsivities, caution should be taken, since the interface defects can be the cause of the amplified responsivity usually
seen in the 2D devices based on flakes and nanosheets (photogating). Furthermore, the analysis of the photocurrent onset indicates that carrier photogeneration takes place at the type-II GaSe/InSe interface with the energy of 1.08 eV (1146 nm) that corresponds to a VBO of 170 meV.

3. Conclusions

vdW epitaxy of GaSe/InSe heterostructures containing QWs and SLs has been demonstrated on Si and sapphire substrates using molecular beam epitaxy. Control of the crystalline phase and indium segregation was achieved by monitoring in situ the surface properties by RHEED with simultaneous fine-tuning of the III/VI ratio and substrate temperature. The obtained interfaces are sharp and can be applied in the design of a large set of optoelectronic devices requiring quantum confinement, relaxing the requirement of lattice matching of mainstream Si–Ge, III–V, or II–VI semiconductors.

These 2D materials not only cover a wide range of bandgap values, but more importantly, they form a novel class of materials exhibiting unparalleled properties such as high electron mobility, quantum Hall effect, or non-linear optical properties, and many other properties yet to be discovered. A significant improvement in the level of understanding about the doping, band structure, and defects in the GaSe/InSe system is still required before optoelectronic devices of similar quality as those based on Si or III–V technology can be fabricated. Nonetheless, our work presents a breakthrough as it demonstrates the controlled epitaxial growth of functional heterostructures and SLs, thereby paving the way for a further rapid development. In fact, a disruptive displacement of Si technology by 2D materials is not to be expected, but instead, rather their coexistence and mutual benefits will prevail. The wafer-scale fabrication of a 2D self-driven photodetector on a Si substrate that can be included in the back-end of the line process flow is one proposal to realize it.

4. Experimental Section

MBE Growth: The growth of GaSe and InSe was performed in an EVO-50 molecular beam epitaxy (MBE) system (Omicron Nanotechnology GmbH). Indium (6N) and gallium (6N) are evaporated from Knudsen cells at ≈750 and ≈850 °C, respectively. Selenium (5N) is evaporated from a valved cracker cell with reservoir maintained at 285 °C, while the flux is controlled by a valve with an adjustable aperture ranging from 0 to 8 mm. Before entering the growth chamber, large selenium molecules are cracked by the cracker stage kept at 900 °C.
stand-by base pressure of the MBE system is $2.6 \times 10^{-30}$ mbar and during the growth, when the Se valve is open, the pressure increases to $10^{-8}$ to $10^{-7}$ mbar. All growth processes are monitored by reflection high-energy electron diffraction (RHEED, Staib Instruments), which was operated at 15 kV. Epi-ready single-sided polished 2-inch c-Sapphire (0001) and p-Si (111) substrates were used, with a specified and confirmed roughness of $\approx 0.2$ nm. Substrate temperatures are nominal (thermocouple at the heated surface) and close to the temperature of the Si substrate surface as measured by a two-color infrared pyrometer. The growth rate of GaSe and InSe is 1 TL min$^{-1}$ (nm min$^{-1}$) calibrated ex situ by X-ray reflectometry (XRR).

Each substrate was annealed in vacuum inside the growth chamber for 30 min at 950 °C just before the growth. Particularly in the Si substrate, the desorption of native SiO$_2$ and formation of the Si (111) 7 × 7 surface reconstruction was observed by RHEED. The samples presented in Figure 2 shows GaSe layers grown on sapphire for 30 min. at 600 °C and 30 min. at 550 °C, and on silicon for 30 min. at 520 °C and 30 min. at 470 °C, with Se valve aperture of 1.1 mm. InSe thick layers were grown for 30 min. at 500 °C on sapphire and 450 °C on Si, with selenium valve aperture of 0.75 mm.

In the QW samples, the first GaSe layer was grown on sapphire substrate for 10 min at 600 °C, 6 min at 550 °C with Se valve at 1.3 mm, plus 4 min while the temperature linearly ramps down to 380 °C, and the valve follows the temperature ramp from 1.1 to 0.65 mm. InSe layers were grown for 30 min at 500 °C on sapphire and 450 °C on Si, with selenium valve aperture of 0.75 mm.

The XPS spectra were acquired with a hemispherical analyzer with pass energies 20 and 200 eV for high resolution and survey spectra, respectively. The XPS spectra were generated by an Al monochromated and a twin Al/Mg anode non-monochromated X-ray sources operated at 15 keV and power 200 W. The experiments were carried out in an ultrahigh vacuum (UHV) system ESCALAB250Xi (Thermo Fisher Scientific). The base pressure in the system was $<5 \times 10^{-10}$ mbar. XPS spectra were peak-fitted using Avantage (Thermo Fisher Scientific) data processing software. For peak fitting Smart-type background subtraction was used. Quantification has been done using sensitivity factors provided by Avantage library. Elemental composition depth profiling was carried out by means of an ion source (MAGGIS, Thermo Fisher Scientific) operated in the monoatomic mode. The sputtering rate established for Ta$_2$O$_5$ film. The sputtering rate estimated for the surfaces under study was $0.03$ nm s$^{-1}$. The Ar$^+$ beam was raster-scanned over a 2 mm x 2 mm area. A dual beam charge neutralization technique with 0.5 eV Ar ions and 0.5 eV electrons was used for eliminated surface charging during the XPS measurements. PL experiments at near infrared wavelengths (900–1700 nm) were carried out in backscattering geometry at low temperatures (15 K) by placing the samples in the cold finger of a closed-cycle cryostat (ARS model DE-202AE). The pumping was made at 532 nm by using a continuous wave DPSS green laser. Emitted light is coupled into a multimode optical fiber and detected by means of a NIRQuest512 spectrograph from Ocean Optics.

Room-temperature PR was carried out using the light beam of a quartz-tungsten-halogen lamp operated at 200 W. This probe light is passed through a monochromator (1/8 m Cornerstone–Newport) and focused with optical lenses on the sample. Light directly reflected with intensity $I_0(\lambda)R(\lambda)$ is focused on a solid-state detector, either Si or Peltier-cooled InGaAs. Two laser sources served as pump excitation, the lines at 325 nm of a 15 mW He–Cd laser (Oriel) and 632.8 nm of a 30 mW He–Ne (Melles–Griot). The pump beam is mechanically chopped at 777 Hz and superimposed onto the light spot of the probe on the sample, providing the periodic modulation. The current signal at the detector, containing the dc average signal $I_0(\lambda) R(\lambda)$ and the ac-modulated contribution $I_0(\lambda) \Delta R(\lambda)$ (where $\Delta R(\lambda)$ is the modified reflectance resulting from the modulated perturbation) is transformed into a dc-voltage and preamplified (Keithley). The complete signal feeds a lock-in amplifier (Stanford Instruments), which tracks the ac signal at the chopping frequency. The relative change in reflectance is obtained thereof by normalizing the ac signal with respect to the dc component, with typical values in the range from $10^{-4}$ to $10^{-6}$.

**Computational Method:** The function envelope and effective mass approximation (EF/EMA) model was calculated using the transfer-matrix method (TMM) in a customized open-source software previously tested on III–V and II–VI heterostructures. The ab-initio calculations were done using density perturbation theory (DFT) within the local-density approximation (LDA) and the norm-conserving pseudopotentials.[9] The DFT-LDA calculations has been done in GaSe/InSe SLs using an energy cutoff of 100 Ry and using a 9 × 9 × 1 k-grid. In the supral, the entalpy of formation have been optimized lattice parameters and atomic positions until forces in each atom are $<0.01$ eV Å$^{-1}$. The basis-set cutoff energy is 160 Ry and the Brillouin zone integrated with 15 × 15 × 6 Γ-centered Monkhorst-Pack grid of k-points in the self-consistent calculations with convergence criteria of $1 \times 10^{-8}$ eV.

**Device Fabrication:** The GaSe/InSe heterostructure was grown by MBE in a similar way as described in the Supplementary Information. The boron-doped p-Si(111) (resistivity = $10^2$ Ω cm) substrate was annealed inside the MBE growth chamber for 30 min at 950 °C just before the growth. The first 10 nm GaSe layer was grown for 3 min at 520 °C and 7 min at 470 °C with Se valve aperture of 1.1 mm. The 10 mm InSe layer was grown for 10 min at 450 °C with selenium valve aperture of 0.75 mm. The 37 nm ITO is deposited in a Kenoys multicell-target UHV sputtering system with 2” diameter magnetrons in confocal geometry, using 60 W RF plasma with pure argon atmosphere. The pressure in the chamber during the depositions was $3 \times 10^{-2}$ mbar. The wafer was transferred from one system to the other within few minutes of air exposure.
The device active area is then defined by argon ion milling (Nordiko 7500) after direct photolithography with AZ1505 photosist using a 405 nm laser (DWL2000 – Heidelberg Instruments) and AZ400K developer. The etch depth is monitored by secondary-ion mass spectrometry (SIMS). Without removing the photoresist, 200 nm of Al2O3 was deposited in a Singulius Four-Target-Module (FTM) physical vapor deposition cluster tool, base pressure $6 \times 10^{-6}$ mbar, 1500 W RF plasma with pure argon atmosphere and pressure of $5 \times 10^{-3}$ mbar during deposition. The photoresist and Al2O3 (lift-off) are removed from the active area surface with a O2 plasma asher and acetone bath. The top 5 nm Ni/35 nm Au photoresist and Al2O3 (lift-off) are removed from the active area surface corresponding author upon reasonable request.

The data that support the findings of this study are available from the Cook & Calligaro database. All authors contributed in writing the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

M.S.C. coordinated the study, designed and executed the MBE growth, device processing, Raman spectroscopy, AFM, XRD, EF/EMA calculations and device characterization. A.M.-S. prepared the DFT calculations. A.B. performed the XPS depth profile, J.G., P.J.F., and K.E.H. executed the HR-STEM sample preparation and measurements. J.P.M.P and A.P.A performed the PL and D.F.M. the PR. S.S. supervised the study. All authors contributed in writing the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2D materials, epitaxy, GaSe, InSe, photoluminescence, quantum-wells, superlattices

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