The quantum-well turn into van der Waals: epitaxy of GaSe and InSe heterostructures for optoelectronic devices

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Abstract

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 has been a challenge for several decades, leading to restrictions for device integration and the lack of efficient devices in important wavelength bands. Here, we show that the van der Waals epitaxy of two-dimensional (2D) GaSe and InSe heterostructures occur on substrates with substantially different lattice parameters, namely silicon and sapphire. The GaSe/InSe heterostructures were applied in the growth of quantum wells and superlattices presenting photoluminescence and absorption related to interband transitions. Moreover, we demonstrate a self-powered photodetector based on this heterostructure on Si that works in the visible-NIR wavelength range. Fabricated at wafer-scale, these results pave the way for an easy integration of optoelectronics based on these layered 2D materials in current Si technology.

Main

Semiconductor heterostructures are ubiquitous in all aspects of modern life governed by electronics and photonics, including applications such as high-speed communication1, energy2, defence3, health4,5, or interplanetary exploration6. The most widely used semiconductor heterostructures for optoelectronic device applications are based on compound semiconductors, commonly from the III-V family but also from Si-Ge and II-VI families, as their bandgap can be engineered by choosing the composition of the alloys. Since their invention by Esaki and Tsu7 in the 1970s, ultrathin semiconductor layers in the form of quantum wells (QW) and superlattices (SL), have provided additional degrees of freedom to the device engineer based on the concept of quantum confinement, and have rapidly evolved from the fundamentals of quantum mechanics concepts into wealth-creating semiconductor devices.8,9 Bandgap engineering and quantum confinement enable the fabrication of heterostructures with unprecedented specificity in
properties such as light emission and absorption, which can be tuned to specific wavelengths ranging from THz to ultra-violet. A fundamental constraint in the development of efficient heterostructures is the requirement of epitaxial growth for the deposition of the layer stacks. The interplay between material composition, crystal lattice parameters, and optoelectronic properties (Figure 1a) is what limits in practice the accessible range of operating semiconductor heterostructures. Lattice mismatch beyond tight limits of tolerance incurred by adjacent materials creates local strain that typically prevents epitaxial growth. Furthermore, even minimum strain accumulation, while permitting epitaxy, can still severely create defects or affect the band structure and thus the performance of the optoelectronic devices, such as target wavelength, optical gain, linewidth, and quantum efficiency. As a result of the limited access to certain parameter ranges due to material incompatibility, we still lack, e.g., electrically-pumped solid-state lasers and light emitters at important wavelengths. For example, the only viable laser alternatives in the yellow range make use of amplification and frequency conversion in solid-state systems, but the complexity, price, size, limitations in power and wavelength coverage results unsuitable for wide exploitation.

The two-dimensional (2D) semiconductors GaSe and InSe belong to the group of layered III-VI post-transition metal chalcogenides (PTMC), which are a more recent class of materials with great potential for optoelectronic applications due to the properties of thin films that cannot be found in well-known bulk materials, including high electron mobility, quantum Hall effect, and anomalous optical response. They crystallize in a honeycomb-type lattice of four monoatomic sheets (Se-Ga(In)-Ga(In)-Se), known as tetralayers (TL), which are bonded together only by weak van der Waals (vdW) interactions. They do not carry out strain, which means that they can, in principle, lay on any substrate, including TLs of a different PTMC and thereby opening the path for the growth of QWs and SLs with confined electron wavefunctions and transitions with intermediary and tuneable transition energies. In contrast to most 2D transition metal dichalcogenides (TMDs), both GaSe and InSe possess direct bandgaps in bulk form of 1.98 eV and 1.26 eV at room temperature, respectively. Yet, when reduced to few layers (<7 TL), a transition to a quasi-direct bandgap with Mexican-hat valence band and a notable increase of bandgap occurs. Taking advantage of the increase of the bandgap up to ~3 eV within thin films, Terry et al. recently demonstrated that heterostructures from InSe and GaSe flakes exhibit optical transitions that densely cover the spectrum from violet to infrared, something hard to achieve with any other material system. Therefore, GaSe and InSe as bulk or standalone TLs fill the void in the bandgap vs. lattice parameter diagram (Figure 1a). Moreover, the electron and hole confinement should be observed in more complex heterostructures containing quantum wells, dots, wires and superlattices, like the structure presented in the Figure 1b, which was simulated using already know material parameters as bandgap, effective mass and band offsets.
Figure 1. a) Bandgap vs. lattice parameter diagram of the most common semiconductors and the PTMCs. 
b) Simulated band profile (purple and green) along the growth direction, wavefunctions (modulus, colorful), and energies in the same sample using the function envelope and effective mass approximation (EF/EMA) c) High-angle annular dark field (HAADF) STEM image of the 2.5/2.5 superlattice (SL) + 4/4/4 quantum well (QW) grown on c-sapphire. d) Photoluminescence spectrum at 15 K of the 2.5/2.5 SL + 4/4/4 QW and 4/4 SL + 5/5/5 QW also grown on c-sapphire.

In comparison to the micromechanical exfoliation and manual restacking process, which is versatile for proof-of-concept demonstrations, direct growth of vdW heterostructures would have the advantage of producing clean interlayer interfaces, better control over the orientation of the stacking layers and providing the possibility for scaling up device fabrication of complex devices with bandgap engineering based on vdW heterostructures.9 Direct growth of 2D materials, including InSe and GaSe, has been demonstrated by chemical vapor deposition17 (CVD), pulsed-laser deposition18 (PLD) and molecular beam epitaxy13,19,20 (MBE). Using these growth methods, fabrication at wafer-scale of 2D material devices has become possible21,22, which enables the transfer of the 2D materials technology to industrial applications. Such direct growth methods are usually referred to as van der Waals (vdW) epitaxy23, since vdW forces are the only bond between the substrate and the layers. Despite these examples of vdW epitaxy of selected 2D materials and their heterostructures24, the controllable growth of PTMC heterostructures has not been demonstrated yet.

Here, we show that the vdW epitaxy of GaSe/InSe heterostructures was achieved using molecular beam epitaxy with TL precision, on both Si and c-Sapphire substrates, which have substantially different lattice
parameters. GaSe/InSe heterostructures are applied to the growth of quantum wells and superlattices (Figure 1c) as the one presented in Figure 1b. Those heterostructures exhibited photoluminescence (Figure 1d) and absorption from interband transitions involving electrons confined in InSe and holes in GaSe, due to a type II InSe/GaSe alignment. We also demonstrate the wafer-scale fabrication of a self-powered photodetector based on this heterostructure that works in the visible wavelength range and that paves the road for an easy integration of these 2D materials in current Si technology.

Large-area growth by MBE

Both gallium selenide (Ga$_x$Se$_y$) and indium selenide (In$_x$Se$_y$) exist in various solid phases, GaSe or Ga$_2$Se$_3$, InSe or α-In$_2$Se$_3$, β-In$_2$Se$_3$ and In$_3$Se$_4$, and form a complex phase diagram. As demonstrated earlier by our group and others, MBE provides the necessary control over the III and VI material fluxes that permits obtaining the desired pure phase and stoichiometry, and monitor them in-situ by reflection high energy electron diffraction (RHEED) (Figure S1 in Suppl. Info.). 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 (more details in Section 1 of Suppl. Info.). 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 approximately 1 TL/min. The Raman spectrum shows peaks at 133 cm$^{-1}$, 205 cm$^{-1}$, and 307 cm$^{-1}$, corresponding to the $A_1^1$, $E_1$, and $A_2^1$ vibration mode of GaSe, respectively, while the peaks located at 115cm$^{-1}$, 177 cm$^{-1}$, and 227 cm$^{-1}$ are attributed to the same modes for InSe. No evidence of other phases, namely Ga$_2$Se$_3$ or In$_3$Se$_4$ 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 (Figure 2b). The surface topography obtained by atomic force microscopy (AFM) exhibits atomic terraces with triangular shape, as expected for these hexagonal crystals (Figure 2c), wherein the crystal grows laterally along the [211] or [121] directions.
GaSe and InSe can assume several polytypes with very similar formation energy, corresponding to different stacking sequences between the adjacent layers. All polytypes have unit cells, which are similar along the [0001] orientation, but differ in the number and lateral placement of the stacked double (or triple) TL. They are obtained either by rotation and/or translation operations. In addition to these polytypes, a new polymorph presenting centro-symmetric symmetry (D$_{3h}$) within the Se-Ga(In)-Ga(In)-Se stack in the TL can also be found in the growth by MBE, together with the well-known polymorph D$_{3h}$. The coexistence of all these polytypes and polymorphs and their grain boundaries are present in samples grown on both substrates. It results in the observed contrast between regions of the same material in Bright Field (BF) of scanning transmission electron microscopy (STEM) (Figure 2d and f), and is expected to occur after twinning and stacking sequence changes, as happens in most of vdW-layered materials. The impact of these defects in future devices is still unknown, and attempts to reduce their formation in 2D materials, including GaSe, are under study.

Regardless of the rotation and twinning along the c-axis (around multiples of 30°), the GaSe and InSe vdW layers stack nicely across the surface, as observed in the selected area electron diffraction (SAED) pattern.
(Figure 2f and g) and the high-magnification HAADF-STEM image (Figure 2h). Nevertheless, the interface between InSe and GaSe is well defined, over a region of 1 to 3 TL (see Figure 2h). This result confirms that both materials grow epitaxially layer-by-layer on both substrates and with minimal In-Ga inter-diffusion, differently from a previous report\textsuperscript{34}. 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 in Section 4 of Suppl. Info.) at their interface (Figure 2h).

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 quantum well failed due to segregation of In, a well-known MBE-effect reported also for InGaAs/GaAs QWs.\textsuperscript{35} As the In segregation is proportional to the growth temperature and Se flux\textsuperscript{36,37}, we modified the growth process for the heterostructures and grew at a substrate temperature of 380 °C on top of buffer layers (grown at 500-550 °C as before). At such low temperatures, there is a slight increase in the surface roughness. On the other hand, the In segregation is significantly reduced, and flat vDW layer-by-layer growth is possible again. A more detailed discussion about the In segregation and the growth of QWs is presented section 2 of the Suppl. Info.

With these conditions, we have grown thick (>120 nm) superlattices containing alternating layers of approximately 2.5 and 4 TL (4 and 7 nm) of InSe and GaSe with an InSe/GaSe/InSe double quantum well in the center with an extra TLs (4/4/4 and 5/5/5 QW, respectively) as the one presented in the Figure 1b. The QW in the center is aimed to work as a preferential recombination center to obtain enhanced photoluminescence (PL). STEM shows sharp Ga and In distribution along the SL and QW (Figure 3a-c), with very well-defined interfaces and the expected layer thicknesses. In the heterostructure, the distinct layers exhibit in general the μ-polymerorph (D\textsubscript{3d} TL – See Figure 3d), with a common in-plane lattice parameter (more details in the Section 4 of Suppl. Info.). However in some locally-confined spots, others polytypes(e- and β-polytype) and polymorphs (γ with D\textsubscript{3h} TL) are found. 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. In fact, the strain likely causes the abundant presence of the rare μ-polymerorph\textsuperscript{38} (Figure 5B). 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. Nonetheless, as in the bulk layers, the structure is indeed fully relaxed when the whole SL supercell is considered, due to strain compensation. SL lattice parameters similar to the experimental ones were obtained in simulations.

The most important observation in the PL spectra (Figure 1d are the emission lines in the infrared region, peaked at 1.06 and 1.20 eV. 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-QW (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. 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\textsuperscript{39} and the spatially indirect transitions due to the GaSe-InSe type II band alignment. The PL values are similar to the value predicted by the function envelope and effective mass approximation\textsuperscript{40} (EF/EMA), which is strong evidence of carrier confinement in our heterostructures. Yet, in the same spectrum, it is possible to identify another peak that corresponds to the
calculated 2.5/2.5 SL miniband energy in the EF/EMA model. More details about the band structure model is given in the supplementary information.

Figure 3. a) HAADF-STEM image and b) energy-dispersive X-ray spectroscopy (EDX) map of indium and gallium in the same image of the 2.5/2.5 superlattice (SL) + 4/4/4 quantum well (QW) grown on c-sapphire. c) Compositional profile of Ga and In obtained from the EDX along the white arrow in (b). d) Atomic resolution HAADF-STEM image 2.5/2.5 SL region.

With the aim of determining 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). Despite DFT typically underestimates the bandgap and is not always accurate for calculations of the conduction bands, DFT is a suitable tool to investigate ground state properties and therefore gives reliable values of the valence band alignment (or valence band offset) between at the GaSe/InSe interfaces. We have performed DFT-LDA simulations of a 4 TLs of InSe quantum well with 4 TLs of GaSe as barrier and optimized the atomic distances and the in-plane lattice parameter. As measured previously by TEM, we find an intermediate lattice parameter, with the value of 3.88 Å.

Figure 4 shows the electronic structure (a), density of states (b) and relevant wave functions of the GaSe/InSe superlattices. 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 blue (red) color. As evidenced from the calculations, the electronic states near the bandgap are hybridized 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 4d). On the contrary, the second valence band state (Figure 4c) 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.

Our DFT-LDA calculations are also useful to estimate the valence band alignment. Thus, 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. This definition works well for quantum wells 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. 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 is compatible with the value found using the function envelope and effective mass approximation considering the strain and the PL measured energies.

Figure 4: (a) Electronic structure of the 4/4 TLs GaSe/InSe SL. The color map represents the weight corresponding to atomic orbitals from the 4 TLs of each material. (b) Projected density of states (pDOS) on GaSe (red line) and InSe (blue line). The electronic wave functions of the first conduction band state (c) and the first valence band state (b) are represented with isosurfaces in grey. Note that the wave functions are mostly localized around the selenium atoms (green).

Photodiodes at wafer-scale

To demonstrate the capabilities of our MBE growth process, proof-of-concept photodiodes were fabricated at wafer scale using standard microfabrication techniques. 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 layer stack and expected band diagram in Figure 5a). 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 Al₂O₃. The processed wafer with several identical devices is presented in Figure 5b.
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$^{-3}$.[42,43,47] 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,[48] the fabricated device shows the existence of a rectifying junction (Figure 5c) that behaves as a photodiode with very-low-threshold voltage (and $V_{oc}$) and responsivity peak of 60 mA/W at 800 nm without voltage bias (Figure 5d). This value is 2.5 times higher than the responsivity previously observed on similar devices based on flakes[42] and 1/10th of commercial p-i-n Si diodes, which usually have much thicker active regions, in the range of micrometers. 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) which corresponds to a VBO of 170meV.

Discussion and outlook

Van der Waals epitaxy of GaSe/InSe heterostructures containing quantum wells and superlattices 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\textsuperscript{49-52}, 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 superlattices, 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.

**Methods**

**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 °C 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. The stand-by base pressure of the MBE system is 2.6x10^{-10} 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-side polished 2-inch c-sapphire (0001) and p-Si (111) substrates were used, with a specified and confirmed roughness of ~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 (nm/min) 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\textsubscript{2} and formation of the Si (111) 7x7 surface reconstruction was observed by RHEED. The samples presented in Figure 2 show 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 1.15 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 quantum-well 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 1.10 mm, plus 4 min while the temperature linearly ramps down to 380 °C, and the valve follows the temperature ramp from 1.1 mm to 0.65 mm. The InSe QWs were grown at the same temperature with Se valve at 0.7 mm. The following GaSe layers were grown at 380 °C and 0.65 mm. In the superlattice with embedded quantum well, the GaSe buffer layer is grown on c-sapphire for 23 min at 600 °C with Se at 1.15mm, 6 min at 550 °C with Se at 1.1 mm, and cooldown to 380 °C with Se at 0.7 mm, all the temperature changes occur during the growth at the rate of 60 °C/min and the Se valve changes follow linearly the temperature. Without pauses, the SL is grown at 380 °C alternating 15 (10) times 2 min (3 min) of GaSe and InSe in the case of the 2.5/2.5 TL (4/4 TL) SL with Se at 0.7 mm for GaSe and 0.65 for
InSe. The 4/4/4 (5/5/5) QWs are grown depositing each layer for 3 (4) min. The cap layer of 10 nm GaSe on top of the superlattice is grown at the same Se aperture yet at 380 °C.

**Material characterization:** Raman spectroscopy was measured at room temperature in a Witec alpha300 R confocal microscope, using a 50X objective lens, and a solid-state 532 nm excitation laser. X-ray diffraction (XRD) measurements were performed in a PANanalytical Xpert PRO MRD diffractometer with 5-axis cradle, standard Bragg-Brentano (BB) geometry, Cu anode X-ray tube operated at 45 kV accelerating voltage and 40 mA filament current to generate X-rays (Cu K-alpha). Soller and collimation 0.5" slits were used in the source side and a CCD detector (PiXcel) inline (1D) model with additional Soller slit. Atomic force microscopy (AFM) measurements were taken under ambient air conditions with a BRUKER Dimension Icon in tapping mode using PPP-NCH (Nanosensors™) cantilevers with a nominal tip radius of < 20 nm, force constant of 42 N/m, and ~ 265 kHz resonance frequency.

Cross-sectional TEM samples were prepared using standard lift-out procedure in a dual-beam FEI Helios NanoLab 450S focused ion beam with EUHELIM FEG-SEM. To protect the In$_2$Se$_3$ layers from oxidation, a Mo layer was deposited by sputtering immediately after MBE growth. Additionally, two protective Pt layers were deposited by electron beam and ion beam, respectively, to prevent Ga ion implantation and consequent damage during FIB preparation. Bulk milling and lamella thinning down to 100 nm was carried out using a 30 kV ion beam, while final thinning was performed using a 5 kV ion beam. The structural characterization was performed by STEM imaging using a FEI Titan Cubed Themis 60-300 kV double-corrected TEM/STEM at acceleration voltage 200 kV and a convergence angle of 19 mrad. The high-angle annular dark field STEM (HAADF STEM) images were acquired on the HAADF detector with 50.5 mrad inner and 200 mrad outer detection angles at a beam current of ~ 150 pA. Energy-dispersive X-ray (EDX) maps were acquired with a super-X EDX (FEI) system with simultaneous high-angle annular dark field (HAADF) image acquisition with 71.6 mrad inner to 200 mrad outer detection angles on the FEI HAADF STEM detector at a beam current ~ 500 pA to assure a satisfactory signal-to-noise ratio.

The XPS spectra were acquired with a hemispherical analyzer with pass energies 20 eV 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 ultra-high vacuum (UHV) system ESCALAB250Xi (Thermo Fisher Scientific). The base pressure in the system was below 5·10$^{-10}$ 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 the monoatomic ion source (MAGCIS, Thermo Fisher Scientific). The sputtering rate established for Ta$_2$O$_5$ film was used to estimate the sputtering rate on the surfaces under study. 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 to 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 spectrophotograph 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 of \( 10^{-3} \) 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\(^5\). The DFT-LDA calculations have been done in 4GaSe/4InSe superlattices using an energy cutoff of 100 Ry and using a 9x9x1 k-grid. In the suppl. Info the entropy was calculated have optimized lattice parameters and atomic positions until forces in each atom are smaller than 0.01 eV/Å. The basis-set cutoff energy is 160 Ry and the Brillouin zone integrated with 15x15x6 Γ-centered Monkhorst-Pack grid of k-points in the self-consistent calculations with convergence criteria of \( 1 \times 10^6 \) 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 = \( 10^{-1} \) 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 1.15 mm. The 10 nm 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 Kenosystec multi-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 photoresist using a 405 nm laser (DWL2000 - Heidelberg Instruments) and AZ400K developer. The etch depth is monitored by ion mass spectrometry (SIMS). Without removing the photoresist, 200 nm of Al₂O₃ was deposited in a Singulus Four-Target-Module (FTM) physical vapor deposition cluster tool, base pressure \( 6 \times 10^{-9} \) mbar, 1500W 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 ash and acetone bath. The top 5 nm Ni/35 nm Au metallic contacts were deposited in the same multi-target UHV sputtering system and defined by lift-off using a similar photolithography procedure. The ohmic bottom contact is formed by welding indium metallic balls on the substrate surface with an iron tip at 380 °C.

**Device Characterization:** Photocurrent and IV curves were measured by a Keithley 6487 picoamperemeter in DC mode. For these experiments illumination was provided by a QuantumDesign MLS-450-300 monochromator which light power density was measured using a calibrated Si PIN photodiode (Thorlabs DSD2).

**DATA AVAILABILITY**
The samples and data that support this paper and other findings of this study are available from the corresponding author upon reasonable request.

AUTHOR INFORMATION

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 to write the manuscript.

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References

1. Zhou, H., Xu, H. & Duan, J. an. Review of the technology of a single mode fiber coupling to a laser diode. Opt. Fiber Technol. 55, 102097 (2020).
2. Ekins-Daukes, N. J. Quantum well solar cells. in Advances in Solar Energy: An Annual Review of Research and Development in Renewable Energy Technologies vol. 17 45–73 (2015).
3. Razeghi, M., Dehzangi, A. & Li, J. Multi-band SWIR-MWIR-LWIR Type-II superlattice based infrared photodetector. Results Opt. 2, 100054 (2021).
4. Guina, M., Rantamäki, A. & Härkönen, A. Optically pumped VECSELs: review of technology and progress. J. Phys. D. Appl. Phys. 50, 383001 (2017).
5. Goodrich, J. Lasers in Aesthetic Surgery. in Facial Plastic and Reconstructive Surgery 351–359 (Springer International Publishing, 2021). doi:10.1007/978-3-030-45920-8_24.
6. Manrique, J. A. et al. SuperCam Calibration Targets: Design and Development. Space Science Reviews vol. 216 1–27 (2020).
7. Esaki, L. & Tsu, R. Superlattice and negative differential conductivity in semiconductors. IBM J. Res. Dev. 14, 61–65 (1970).
8. Fox, M. & Ispasoiu, R. Quantum Wells, Superlattices, and Band-Gap Engineering. in Springer Handbook of Electronic and Photonic Materials 1–1 (Springer International Publishing, 2017). doi:10.1007/978-3-319-48933-9_40.
9. CAPASSO, F. Band-Gap Engineering: From Physics and Materials to New Semiconductor Devices. Science (80-. ). 235, 172–176 (1987).
10. Kantola, E. et al. VECSEL-Based 590-nm Laser System With 8 W of Output Power for the Treatment of Vascular Lesions. IEEE J. Sel. Top. Quantum Electron. 25, 1–8 (2019).
11. Bandurin, D. A. et al. High electron mobility, quantum Hall effect and anomalous optical response in atomically thin InSe. Nat. Nanotechnol. 12, 1–18 (2016).
12. Norkus, R., Nevinskas, I. & Krotkus, A. Terahertz emission from a bulk GaSe crystal excited by above bandgap photons. J. Appl. Phys. 128, 225701 (2020).
13. Chen, M.-W. et al. Large-grain MBE-grown GaSe on GaAs with a Mexican hat-like valence band dispersion. npj 2D Mater. Appl. 2, 2 (2018).
14. Hamer, M. J. et al. Indirect to direct gap crossover in two-dimensional InSe revealed by angle-resolved photoemission spectroscopy. ACS Nano 13, 2136–2142 (2019).
15. Brotons-Gisbert, M. et al. Nanotexturing To Enhance Photoluminescent Response of Atomically Thin Indium Selenide with Highly Tunable Band Gap. Nano Lett. 16, 3221–3229 (2016).
16. Terry, D. J. et al. Infrared-to-violet tunable optical activity in atomic films of GaSe, InSe, and their heterostructures. 2D Mater. 5, 041009 (2018).
17. Balakrishnan, N. & Balakrishnan, N. Epitaxial growth of γ-InSe and α, β, and γ-In2Se3 on ε-GaSe. 2D Mater. 5, 035026 (2018).
18. Bergeron, H. et al. Large-area optoelectronic-grade InSe thin films via controlled phase evolution. Appl. Phys. Rev. 7, 041402 (2020).
19. El Kazzi, S. et al. MoS2 synthesis by gas source MBE for transition metal dichalcogenides integration on large scale substrates. J. Appl. Phys. 123, 135702 (2018).
20. Lee, C. H. et al. Molecular beam epitaxy of 2D-layered gallium selenide on GaN substrates. J. Appl. Phys. 121, 094302 (2017).
21. Schram, T. et al. BEOL compatible WS2 transistors fully fabricated in a 300 mm pilot line. in 2017 Silicon Nanoelectronics Workshop, SNW 2017 vols 2017-Janua 139–140 (2017).
22. Claro, M. S., Grzonka, J., Nicoara, N., Ferreira, P. J. & Sadewasser, S. Wafer-Scale Fabrication of 2D β-In2Se3 Photodetectors. Adv. Opt. Mater. 9, 2001034 (2020).
23. Walsh, L. A. & Hinkle, C. L. van der Waals epitaxy: 2D materials and topological insulators. Applied Materials Today vol. 9 504–515 (2017).
24. Gong, Y. et al. Vertical and in-plane heterostructures from WS 2/MoS 2 monolayers. Nat. Mater. 13, 1135–1142 (2014).
25. Briggs, N. et al. A roadmap for electronic grade 2D materials. 2D Mater. 6, (2019).
26. Han, G., Chen, Z.-G., Drennan, J. & Zou, J. Indium Selenides: Structural Characteristics, Synthesis and Their Thermoelectric Performances. Small 10, 2747–2765 (2014).
27. Li, X. et al. Controlled vapor phase growth of single crystalline, two-dimensional gase crystals with high photoresponse. Sci. Rep. 4, 1–9 (2014).
28. Magorrian, S. J., Zólyomi, V. & Drummond, N. D. Structures of bulk hexagonal post transition metal chalcogenides from dispersion-corrected density functional theory. Phys. Rev. B 103, 094118 (2021).
29. Srour, J., Badawi, M., El Haj Hassan, F. & Postnikov, A. Comparative study of structural and electronic properties of GaSe and InSe polytypes. J. Chem. Phys. 149, 054106 (2018).
30. Sun, Y. et al. New Polymorphs of 2D Indium Selenide with Enhanced Electronic Properties. Adv. Funct. Mater. 2001920 (2020) doi:10.1002/adfm.202001920.
31. Grzonka, J., Claro, M. S., Molina-Sánchez, A., Sadewasser, S. & Ferreira, P. J. Novel Polymorph of GaSe. Adv. Funct. Mater. 2104965 (2021) doi:10.1002/adfm.202104965.
32. Levy, I., Garcia, T. A., Shafique, S. & Tamargo, M. C. Reduced twinning and surface roughness of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ layers grown by molecular beam epitaxy on sapphire substrates. *J. Vac. Sci. Technol. B, Nanotechnol. Microelectron. Process. Meas. Phenom.* **36**, 02D107 (2018).

33. Mortelmans, W., De Gendt, S., Heyns, M. & Merckling, C. Epitaxy of 2D chalcogenides: Aspects and consequences of weak van der Waals coupling. *Appl. Mater. Today* **22**, 100975 (2021).

34. Sorokin, S. V. et al. Molecular beam epitaxy of layered III metal chalcogenides on GaAs(001) substrates. *Materials (Basel)*. **13**, (2020).

35. Muraki, K., Fukatsu, S., Shiraki, Y. & Ito, R. Surface segregation of In atoms during molecular beam epitaxy and its influence on the energy levels in InGaAs/GaAs quantum wells. *Appl. Phys. Lett.* **61**, 557–559 (1992).

36. Martini, S. et al. Ex-situ investigation of indium segregation in InGaAs/GaAs quantum wells using high-resolution x-ray diffraction. *J. Appl. Phys.* **94**, 7050–7052 (2003).

37. Gajjela, R. S. R. et al. Cross-sectional scanning tunneling microscopy of InAs/GaAs(001) submonolayer quantum dots. *Phys. Rev. Mater.* **4**, 114601 (2020).

38. Nitta, H., Yonezawa, T., Fleurence, A., Yamada-Takamura, Y. & Ozaki, T. First-principles study on the stability and electronic structure of monolayer GaSe with trigonal-antiprismatic structure. *Phys. Rev. B* **102**, 235407 (2020).

39. Shubina, T. V. et al. InSe as a case between 3D and 2D layered crystals for excitons. *Nat. Commun.* **10**, 1–8 (2019).

40. Bastard, G. Superlattice band structure in the envelope-function approximation. *Phys. Rev. B* **24**, 5693–5697 (1981).

41. Zribi, J. et al. Strong interlayer hybridization in the aligned SnS$_2$/WSe$_2$ hetero-bilayer structure. *npj 2D Mater. Appl.* **3**, 27 (2019).

42. Yan, F. et al. Fast, multicolor photodetection with graphene-contacted $p$-GaSe/$n$-InSe van der Waals heterostructures. *Nanotechnology* **28**, 27LT01 (2017).

43. Balakrishnan, N. et al. Room Temperature Electroluminescence from Mechanically Formed van der Waals III-VI Homojunctions and Heterojunctions. *Adv. Opt. Mater.* **2**, 1064–1069 (2014).

44. Cheng, K. et al. 2D lateral heterostructures of group-III monochalcogenide: Potential photovoltaic applications. *Appl. Phys. Lett.* **112**, 143902 (2018).

45. Balakrishnan, N. et al. Engineering $p$–$n$ junctions and bandgap tuning of InSe nanolayers by controlled oxidation. *2D Mater.* **4**, 025043 (2017).

46. Kim, J., Min, K. A., Cha, J. & Hong, S. Contact properties of 2D/3D GaSe/Si(1 1 1) heterostructure. *Appl. Surf. Sci.* **516**, 145969 (2020).

47. Shigetomi, S. & Ikari, T. Electrical and photovoltaic properties of Cu-doped $p$-GaSe/$n$-InSe heterojunction. *J. Appl. Phys.* **88**, 1520–1524 (2000).

48. De Cesare, G., Caputo, D. & Tucci, M. Electrical properties of ITO/crystalline-silicon contact at different deposition temperatures. *IEEE Electron Device Lett.* **33**, 327–329 (2012).

49. Micocci, G., Molendini, M., Tepore, A., Rela, R. & Siciliano, P. Investigation of the electrical properties of Cd-doped indium selenide. *J. Appl. Phys.* **70**, 6847–6853 (1991).

50. Shigetomi, S., Ikari, T. & Nishimura, H. Photoluminescence spectra of $p$-GaSe doped with Cd. *J. Appl. Phys.* **69**, 7936–7938 (1991).

51. Micocci, G., Serra, A. & Tepore, A. Electrical properties of $n$-GaSe single crystals doped with chlorine. *J. Appl. Phys.* **82**, 2365–2369 (1997).

52. Segura, A., Martínez-Tomás, M. C., Mari, B., Casanovas, A. & Chevy, A. Acceptor levels in indium
selenide. An investigation by means of the Hall effect, deep-level-transient spectroscopy and photoluminescence. *Appl. Phys. A Solids Surfaces* **44**, 249–260 (1987).

53. Hamann, D. R. Optimized norm-conserving Vanderbilt pseudopotentials. *Phys. Rev. B - Condens. Matter Mater. Phys.* **88**, 085117 (2013).
Supplementary Materials for
The quantum-well turn into van der Waals: epitaxy of GaSe and InSe heterostructures for optoelectronic devices
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Supplementary text

1. Growth conditions
The lowest value of surface roughness was obtained within the window of substrate temperatures between 450 to 600 °C for (thick) 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 \( \text{In}_x\text{Se}_y \) 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, \( \gamma\text{-In}_2\text{Se}_3 \) from 1 to 3 mm and \( \beta\text{-In}_2\text{Se}_3 \) from 2 to 5 mm.\(^1\) GaSe was obtained with the valve at 1.2 mm or less, and \( \text{Ga}_2\text{Se}_3 \) beyond this value. In general, to obtain single-phase InSe (GaSe), In-rich (Ga-Rich) growth conditions are required. Despite the narrow growth window\(^2\), 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 S1) is bright and streaky even after the growth of several layers, otherwise, the pattern fades in intensity and the streaky lines become more diffuse. A single c-sapphire substrate could be used for calibration as the substrate surface is immutable even after several growths and desorption cycles.
2. In segregation and quantum-well

In the trials to grow heterostructures using the same conditions used in the thick films as soon as the Ga shutter is open, a sudden change in the RHEED is observed: the streaky diffraction pattern changes to a spotty pattern, typical of a rough surface and very similar to the pattern observed in the growth of Ga$_2$Se$_3$ (Figure S1). The accumulation of In at the surface explains the change in the RHEED pattern that cannot result from simple diffusion.

A sample intended to have two 10 nm InSe quantum-wells separated by 20 nm GaSe barriers exhibited approximately a constant Indium signal along with the whole sample thickness (Figure 4a) when observed by X-ray photoelectron spectroscopy (XPS) depth profiling, indicating the formation of an In$_x$Ga$_{1-x}$Se alloy. In fact, in a separate experiment, where a 10 nm InSe layer is exposed to Ga for sufficient time (~20 min), it transforms into (InGa)Se with very low In content (Figure S2c). Rather than diffusion, the exchange of Ga-In atoms during the growth is attributed to a well-known segregation MBE-effect as reported in InGaAs/GaAs QWs: impinging Ga atoms replace In in the grown lattice, the replaced In stays on the surface, where it is incorporated in the following layers (Figure S2a). The accumulation of In at the surface explains the change in the RHEED pattern that cannot result from simple diffusion.

As the In segregation is proportional to the growth temperature and Se flux\(^4,5\), a similar stack was grown with two 10 TL InSe quantum-wells but at a substrate temperature of 380 °C during the growth of the InSe QW and GaSe capping layers. At such low temperatures, the RHEED diffraction pattern loses part of its brightness, which points to an increase in the surface roughness. On the other hand, the RHEED remains streaky even after the growth of GaSe on InSe proceeds, indicating the continuity of flat vdW layer-by-layer growth and that the In segregation is significantly reduced. In comparison, the XPS depth profile of this sample shows In concentrated in the QW region (Figure S2b).
Figure S2. a) Representation of In segregation during MBE growth. b) X-ray photoelectron spectroscopy (XPS) depth profile of two 20nm GaSe/10nm InSe QWs grown at 500 °C (red) and at 380 °C (black). c) Raman spectrum of 10 nm InSe exposed to Ga for 5 min without Se, which confirms the In segregation induced by Ga.

Indeed, the characterization of this sample by STEM confirms the formation of a QW with well-defined interfaces within 1 to 2 TL and well-aligned layers. In the HAADF-STEM (Figure S3a) the contrast between InSe and GaSe matrix is clearly visible, and the composition is confirmed by energy-dispersive X-ray spectroscopy (EDX) in Figures S3b and S3c. In the XRD of 2x QW (Figure S3d), we note the appearance of satellites corresponding to its period (30 nm). The Raman spectrum (Figure S3e) exhibits some changes in comparison to the bulk/thick layers: a new mode at 125 cm$^{-1}$, the blue shift of $\sim$3 cm$^{-1}$ in the GaSe $A_2$ mode, and in the InSe $E$ mode, which could be attributed to the interaction between the distinct layers, similar to observations in WS$_2$/MoS$_2$ heterojunctions$^6$. The shift or splitting of the $E$ peak could also indicate the presence of D$_{3d}$ TL polymorphs$^7$ which is amply present in the STEM images (Figure S3a).

Figure S3. a) HAADF-STEM image and the energy-dispersive X-ray spectroscopy (EDX) map of b) indium and c) gallium in the same image of the GaSe/InSe/GaSe QW grown on c-sapphire. d) X-ray diffraction and e) Raman spectrum of the 2x InSe/GaSe QWs grown on c-sapphire.
3. Superlattice properties

Figure S4. a) Raman spectrum of the 2.5/2.5 SL. b) X-ray diffraction of both samples which exhibit SL peaks with satellites that closely correspond to the expected SL period and c) φ-scan of the peak (107) of the 2.5/2.5 TL SL.

In the Raman spectrum (Figure S4a), the interfacial Raman mode (125 cm$^{-1}$) which is present in the previous single QWs sample (Figure S3a) is now enhanced. A new peak at 264 cm$^{-1}$ which corresponds to grey Se is visible. More discussion about sample homogeneity and Se in the surface is below.

Photoreflectance (PR) measurements (Figure S5) performed at room temperature exhibited poor signal-to-noise ratios, likely due to the inertness 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 and cap layer at 2.0 eV.

Figure S5. Photoreflectance spectra of a,b) 2.5/2.5 TL SL with 4/4/4 TL QW and the c,d) 4/4 TL SL with 5/5/5 TL QW on Si(111) (a and c) and c-sapphire (b and d) substrates. e) Shows the lock-in phase which helps to identify the multiple peaks.
4. Structure and Strain

The lattice parameters of the thick (bulk) film are extracted from localized diffraction (Figure S6), which is obtained through area-selected fast-Fourier transform (local-FFT) of the image of the interface containing both GaSe and InSe (Figure 2h in the main article). Measured interplanar distance of the peaks (003) and (111) were used to calculate $a=b$ and $c$ lattice parameters. A similar method was used for the 2.5/2.5 SL. A profile of the (00n) and (nnn) directions of the FFT (Figure S7) of the whole Figure 3d (main article) points to a common in-plane lattice parameter $a=b=3.88\,\text{Å}$ (single peak), and distinct $c=24.9\,\text{Å}$ for GaSe and $c=26.9\,\text{Å}$ for InSe.

Figure S6. Area-selected fast-Fourier transform (local-FFT) and measured interplanar distance (in colors) of GaSe and InSe in Figure 2h of the main article.

Figure S7. a) HAADF-STEM image of the InSe/GaSe interface with the corresponding b) fast-Fourier transform (FFT), respectively. c) and d) The intensity profiles along the (00n) and (nnn) planes are shown by the line arrows in b.

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 superlattices, and InSe surface lattice. Similarly to
observed on isolated TL, 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 superlattice.

Figure S8: Ab-initio calculation of the enthalpy of fully and partially relaxed GaSe unit cell in the form of the \( \gamma' \)-polymorph (\( D_{3d} \) TL) and the \( \gamma \)-polymorph (\( D_{3h} \) TL).

5. Sample Homogeneity and Se in the surface

The MBE growth results in an overall film of uniform thickness with smooth surface morphology. The BF-STEM images (Figure 2d and 2f in the main article) 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. The selected area electron diffraction patterns (Figure 2e and 2g in the main article) 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(1-10), 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.

Despite the contrast variations in STEM (which is due to the FIB sample preparation, lamella thickness variation, and the grains slight off the zone-axis) it is noticeable that the homogeneity of the QW layer along the wafer is very satisfactory, as typical for the MBE method. Figure S9 shows the homogeneity of thick QW (10 nm) when seen at low magnification.
On the other hand, in the SL + QW sample, dark spots were visible on the surface, even in the optical microscope. The homogeneity of the photoluminescence signal from the QW (1.06 and 1.20 eV) means that it does not affect the core of the heterostructure and the variations are restricted to the surface. It was observed that in some of these spots, the PL signal attributed to grey selenium (1.74 eV) and its Raman (264 cm$^{-1}$) are stronger, pointing to an accumulation of Se on the surface. In fact, selenium “bumps” were spotted on the surface in the STEM image (Figure S9) and confirmed by local electron diffraction. The accumulation of Se at the surface is an issue for thick samples grown at low temperatures. It could be expected considering that the SL growth temperature is reduced, reducing also the re-evaporation of the excess of Se. It demonstrates the importance of precise control of the III/VI flux ratio. We believe that in the future the Se droplets on the surface can be removed with flash annealing inside the chamber during growth pauses or 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 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 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.
6. Band structure calculation

To obtain the direct (or quasi-direct) bandgap resulting from carrier confinement in the superlattice and QWs and compare them to the experimental data (Table 1) we used methods based on the function envelope and effective mass approximation\(^9\) (EF/EMA). The EF/EMA 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 PTMC heterostructures (Table 2). Strain is considered through deformation potential. Despite its simplicity, the method is accurate for wide quantum wells\(^{10}\) (> 2 nm), showing a difference of only 4% to the experimental value or ab-initio calculations obtained from a 2/2 TL SL system.

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\(^a\) |
| InSe          | (at RT) 1.26\(^a\)   |                  |
| 2.5/2.5 TL SL | ~1.3\(^b\)           | 1.23             |
| 4/4 TL SL     | 1.20\(^a\)           | 1.15             |
| 5/5 QW        | 1.05\(^a\)           | 1.09             |
| 10/10 TL      | 1.08\(^b\)           | (1.08)\(^a\)     |
a) Photoluminescence
b) Photoreflectance
c) Photocurrent
d) Reference 11 and 12
e) Used for VBO determination

Table 2. Parameters used in the function envelope and effective mass approximation (EF/EMA). $m^*_{e}$ and $m^*_{h}$ are the electron and hole effective mass in the c-axis, respectively. $\alpha$ and $\beta$ are the Varshini coefficients for temperature-dependent bandgap calculations\textsuperscript{11}. $a_c$ and $a_v$ are the deformation potential for conduction and valence band in strained lattices.

|                  | InSe          | GaSe          |
|------------------|---------------|---------------|
| $m^*_{e}$        | 0.14\textsuperscript{13} $m_e$ | 0.17\textsuperscript{14} $m_e$ |
| $m^*_{h}$        | 0.74\textsuperscript{13} $m_e$ | 0.84\textsuperscript{14} $m_e$ |
| Direct bandgap (0 K) | 1.35\textsuperscript{11} eV | 2.10\textsuperscript{12} eV |
| $\alpha$ (meV) | 0.475\textsuperscript{11} | 0.66\textsuperscript{12} |
| $\beta$ (K)     | 224\textsuperscript{11} | 181\textsuperscript{12} |
| $a_c$ (eV)      | 8.9\textsuperscript{15} | 5.3 \textsuperscript{16} |
| $a_v$ (eV)      | 2.0\textsuperscript{15} | 2.3\textsuperscript{16} |
| Valence band offset (VBO) | -0.17 eV (See \textsuperscript{17}) | reference |

Figure S10. Simulated band profile (purple and green) along the growth direction, wavefunctions (modulus, colorful), and energies in the 2.5/2.5 SL + 4/4/4 QW (left) and 4/4 SL + 5/5/5 QW (right) samples which were calculated using the function envelope and effective mass approximation (EF/EMA).

References

1. Claro, M. S., Grzonka, J., Nicoara, N., Ferreira, P. J. & Sadewasser, S. Wafer-Scale Fabrication of 2D β-In2Se3 Photodetectors. Adv. Opt. Mater. 9, 2001034 (2020).
2. Sorokin, S. V. \textit{et al.} Molecular beam epitaxy of layered group III metal chalcogenides on GaAs(001) substrates. Materials (Basel). 13, (2020).
3. Muraki, K., Fukatsu, S., Shiraki, Y. & Ito, R. Surface segregation of In atoms during molecular beam epitaxy and its influence on the energy levels in InGaAs/GaAs quantum wells. *Appl. Phys. Lett.* **61**, 557–559 (1992).

4. Martini, S. *et al.* Ex-situ investigation of indium segregation in InGaAs/GaAs quantum wells using high-resolution x-ray diffraction. *J. Appl. Phys.* **94**, 7050–7052 (2003).

5. Gajjela, R. S. R. *et al.* Cross-sectional scanning tunneling microscopy of InAs/GaAs(001) submonolayer quantum dots. *Phys. Rev. Mater.* **4**, 114601 (2020).

6. Gong, Y. *et al.* Vertical and in-plane heterostructures from WS 2 /MoS 2 monolayers. *Nat. Mater.* **13**, 1135–1142 (2014).

7. Grzonka, J., Claro, M. S., Molina-Sánchez, A., Sadewasser, S. & Ferreira, P. J. Novel Polymorph of GaSe. *Adv. Funct. Mater.* 2104965 (2021) doi:10.1002/adfm.202104965.

8. Nitta, H., Yonezawa, T., Fleurence, A., Yamada-Takamura, Y. & Ozaki, T. First-principles study on the stability and electronic structure of monolayer GaSe with trigonal-antiprismatic structure. *Phys. Rev. B* **102**, 235407 (2020).

9. Bastard, G. Superlattice band structure in the envelope-function approximation. *Phys. Rev. B* **24**, 5693–5697 (1981).

10. Harrison, P. & Valavanis, A. *Quantum Wells, Wires and Dots: Theoretical Computational Physics of Semiconductor Nanostructures*. (Wiley, 2016).

11. Abay, B., Efeoğlu, H. & Yoğurtçu, Y. K. Low-temperature photoluminescence of n-InSe layer semiconductor crystals. *Mater. Res. Bull.* **33**, 1401–1410 (1998).

12. Isik, M. & Gasanly, N. M. Temperature-tuned band gap characteristics of InSe layered semiconductor single crystals. *Mater. Sci. Semicond. Process.* **107**, 104862 (2020).

13. Segura, A. Layered Indium Selenide under High Pressure: A Review. *Crystals* **8**, 206 (2018).

14. Mooser, E. & Schlüter, M. The band-gap excitons in gallium selenide. *Nuovo Cim.* **18**, 164–208 (1973).

15. Xia, C. *et al.* Two-dimensional $\text{InSe}/\text{GeSe(SnS)}$ van der Waals heterojunctions: High carrier mobility and broadband performance. *Phys. Rev. B* **97**, 115416 (2018).

16. Zhou, B. *et al.* A type-II GaSe/GeS heterobilayer with strain enhanced photovoltaic properties and external electric field effects. *J. Mater. Chem. C* **8**, 89–97 (2019).

17. Yan, F. *et al.* Fast, multicolor photodetection with graphene-contacted $\text{p-GaSe}/\text{n-InSe}$ van der Waals heterostructures. *Nanotechnology* **28**, 27LT01 (2017).