Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for "Allotropic Ga_2Se_3/GaSe nanostructures grown by van der Waals epitaxy: Narrow exciton lines and single-photon emission"

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Constituent materials

GaSe

The photoluminescence (PL) properties of GaSe have been actively studied earlier,[1–3] but there is still a discrepancy between the experimental results and their interpretation. The explanation for this lies partly in the difficulty of obtaining perfect layers and crystals, and partly in the insufficient completeness of the methods used in optical diagnostics. The published low-temperature spectra of bulk GaSe are, as a rule, inhomogeneous and contain a series of lines that were attributed to different states, such as direct-gap and indirect-gap excitons bound to donors and acceptors,[4] as well as to the presence of polytypes existing in the same sample.

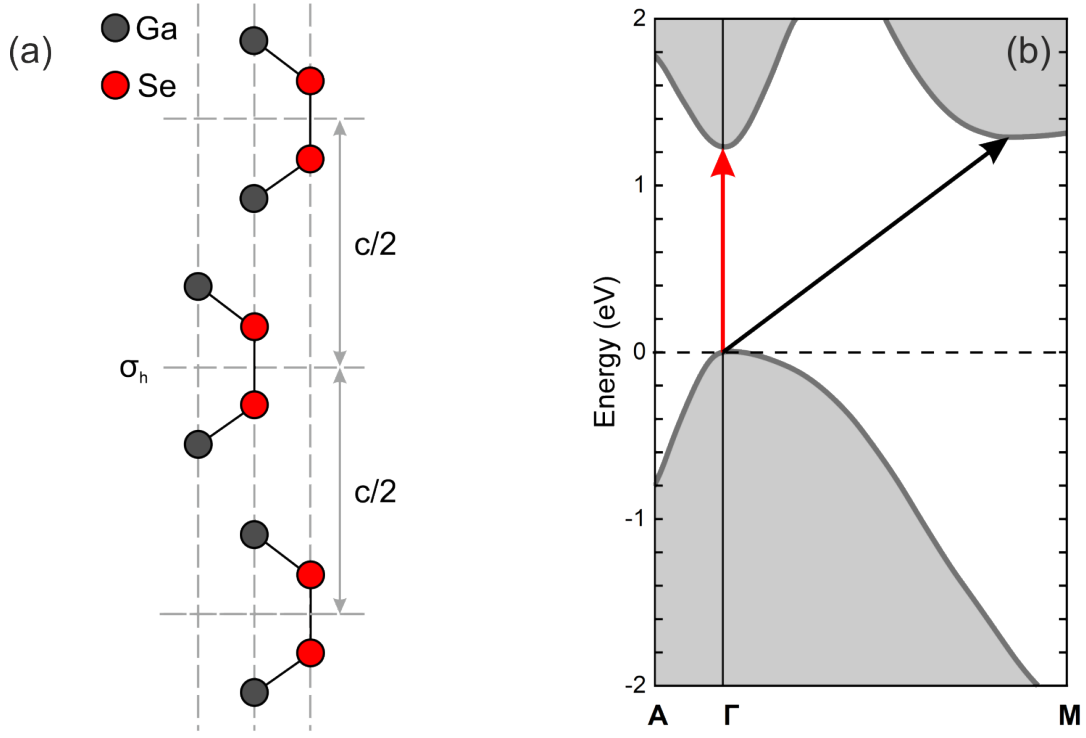

Figure S1: (a) Projection of the ϵ-GaSe in the [110] direction. (b) Band structure of ϵ-GaSe. Red and black arrows show direct and indirect transition, respectively.

Due to anisotropic nature, the band structure in GaSe has asymmetrical conduction band (CB), where the CB minimum is shifted in k-space. The difference in the band gap energy between direct and indirect transition is small. For instance, for the ϵ-GaSe, the energies are 2.12 and 2.10 eV for direct and indirect transitions respectively. The direct (Γ, k=0) and indirect transitions can occur between the valance band maximum and the close minima in CB (Fig. S1). Thus, the PL emission spectra measured in bulk GaSe sample exhibited two dominant peaks at 2.095 and 2.11 eV (Fig. S2a). The decay times of 80 nanoseconds, measured in the 2.095 eV peak at low temperature (Fig. S2b), and its sharp decay with increasing temperature, when there is a mixture of the indirect state and the overlying direct state, allows us to attribute this peak to an indirect exciton (X) transition. Theoretical calculations of the band structure of GaSe also have shown that this

semiconductor can indeed be indirect-gap.[5] Accordingly, the 2.11 eV peak is associated with the direct exciton, which agrees well with direct exciton emission at 2.109 eV reported by Cingolani et al.[6] Despite the fact that the band structure is indirect, the behavior of PL with a further increase in temperature resembles that in direct bandgap semiconductors due to the predominance of excitation relaxation through the direct bandgap channel due to the high recombination rate of direct exciton, as well as the increase in the population of this state with increasing temperature.

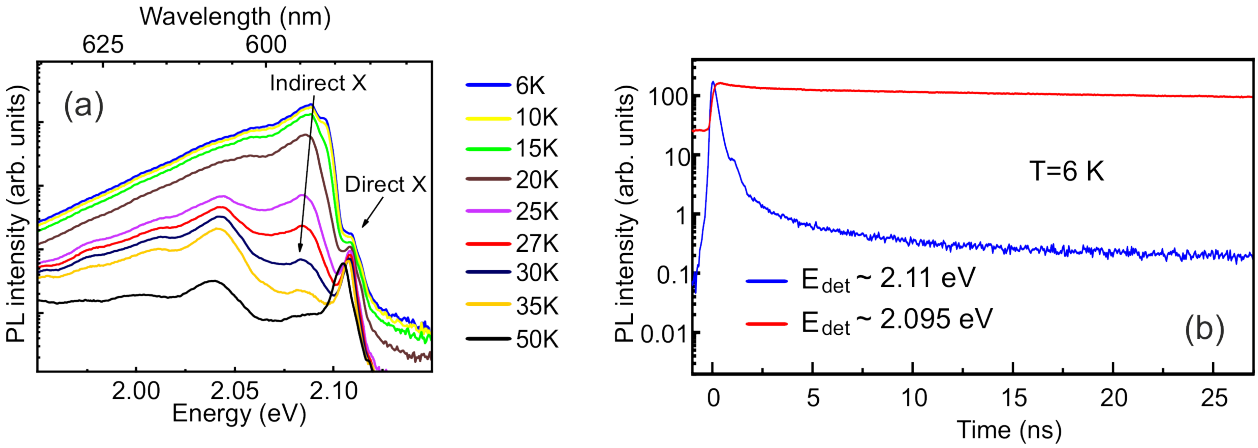

Figure S2: (a) PL spectra of a bulk GaSe measured at different temperatures. The sharp peak at 2.11 eV is attributed to direct free exciton emission. The peak located at 2.095 eV is attributed to an indirect-gap exciton. (b) The decay curves of PL in GaSe measured from the peaks: (a) direct X ∼2.11 eV and (b) indirect X ∼2.095 eV.

Ga_2Se_3

The Ga_2Se_3 compound has a sphalerite structure, where, due to the not completely compatible valency of gallium and selenium, one third of the gallium positions are not filled and represent structural vacancies.

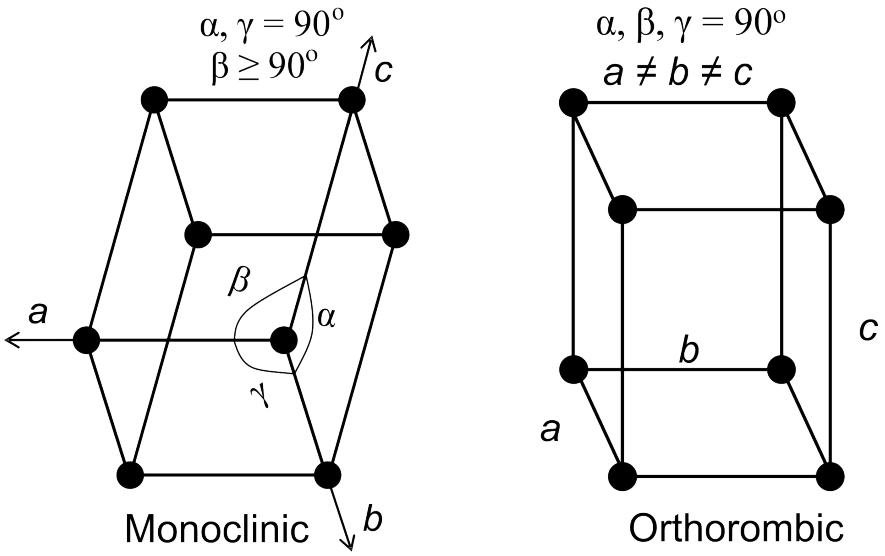

Figure S3: Monoclinic and orthorombic crystal systems that can be implemented in Ga_2Se_3.

According to theoretical considerations,[7] only two types of short-range order are possible in the ordered Ga_2Se_3 - a monoclinic structure, mono-Ga_2Se_3 and an orthorhombic structure, ortho-Ga_2Se_3 (Fig. S3). They correspond to the arrangement of vacancies along a zigzag line in mono-Ga_2Se_3 and along a straight line in ortho-Ga_2Se_3 (Fig. S4). It has been shown theoretically that the band gap of mono-Ga_2Se_3 is E_g∼2.07-2.56 eV, while for ortho-Ga_2Se_3 it is in the range of 1.75-2.0 eV for room temperature.[8–10] Published experimental data are correspond rather to the lower limits.[11,12]

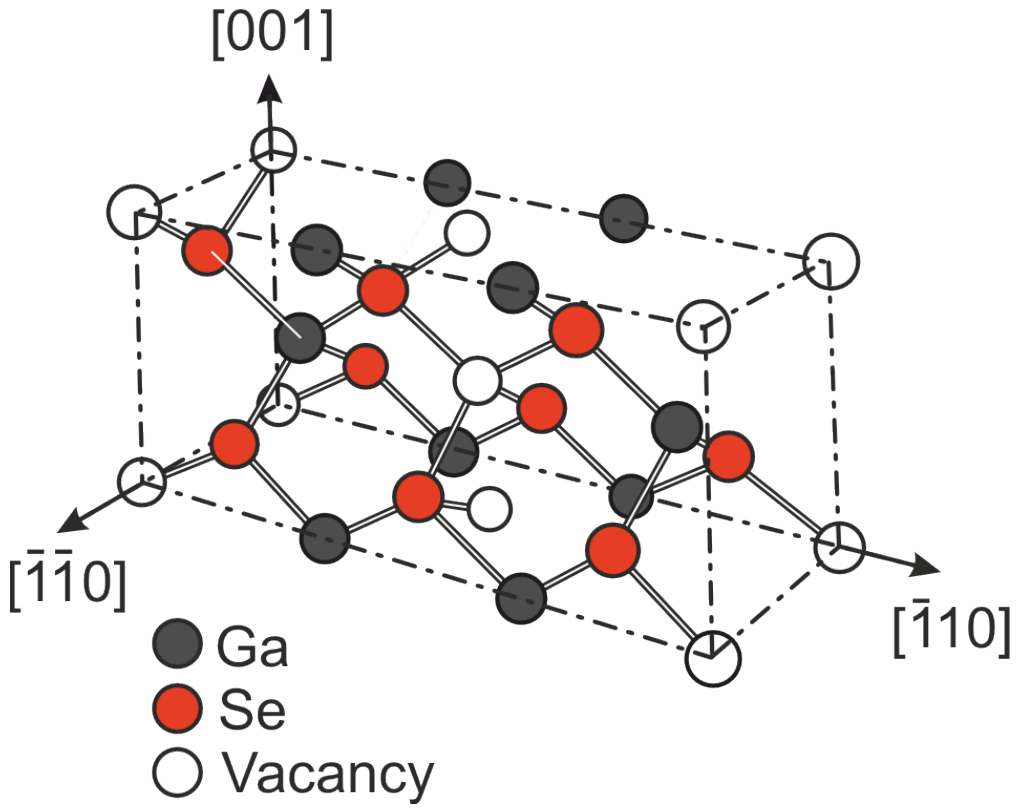

Figure S4: Scheme of the crystal structure of vacancy-ordered Ga_2Se_3.

X-ray diffraction analysis

The X-ray powder diffraction patterns of GaSe layers grown on GaAs(001) substrate under strong Se-rich conditions at T_S=400°C are presented in Figure S5. A standard Ga cell and Se valve cracking cell with the cracking zone temperature $T_{Se}(cr)$=500°C were used as molecular beam sources. The P_{Se}/P_{Ga} (BEP) flux ratio is as high as 42 and 34 for the GaSe layers corresponding to the upper and lower curves, respectively. An additional peak in the angle range ∼28.4° can be associated with the inclusions of the Ga_2Se_3 phase since its position is in a good agreement with Ga_2Se_3(111) reflection.[13] The intensity of this peak is higher for the layer grown at higher VI/III flux ratio.

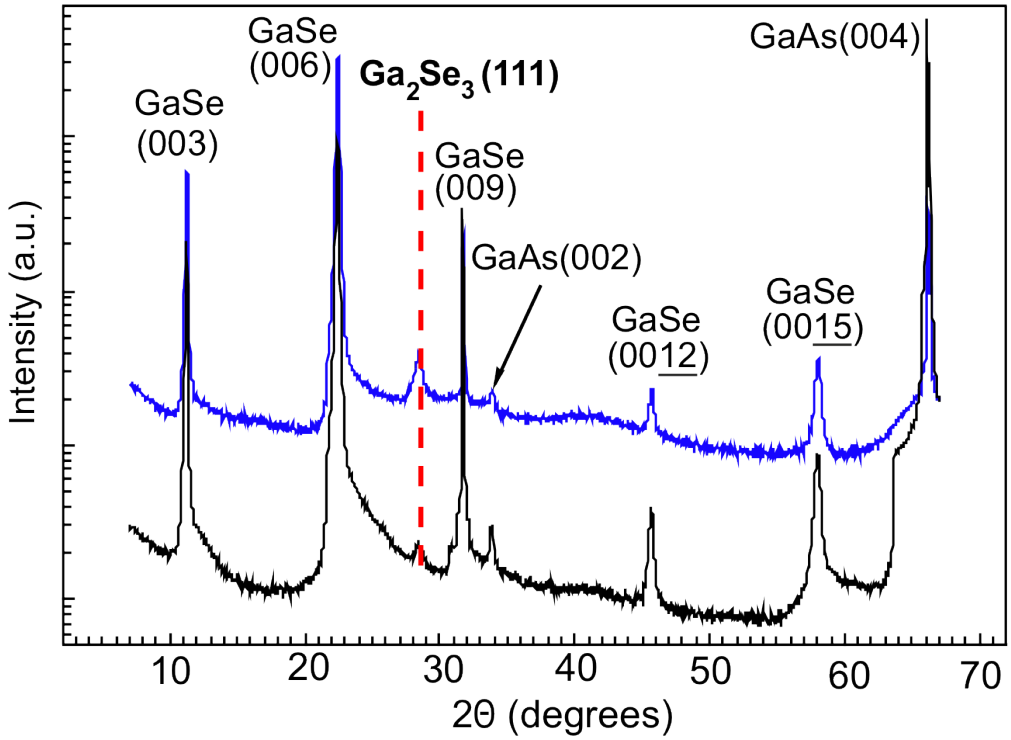

Figure S5: The X-ray powder diffraction patterns of the GaSe layers grown on GaAs(001) substrate. The BEP ratio was as high as 42 and 34 for the GaSe layers corresponding to the blue and black curves, respectively.

The study of MBE in the van der Waals growth mode made it possible to control the composition of GaSe-based layers. Figure S6 shows the dependence of the BEP on the substrate temperature. The cracking zone temperature of the Se valve cell is $T_{Se}(cr)$=500°C. Depending on the MBE growth conditions, the formation of either pure GaSe or enriched with inclusions is observed, which can be Ga droplets (at low VI/III ratio and high T_S) or Ga_2Se_3 (at high VI/III ratio). GaSe/GaAs(001) layers containing inclusions of the Ga_2Se_3 phase are indicated by the red circles. The XRD patterns of these layers are presented in Figure S5. The dashed line corresponds to the nearly stoichiometric conditions on the growth surface.

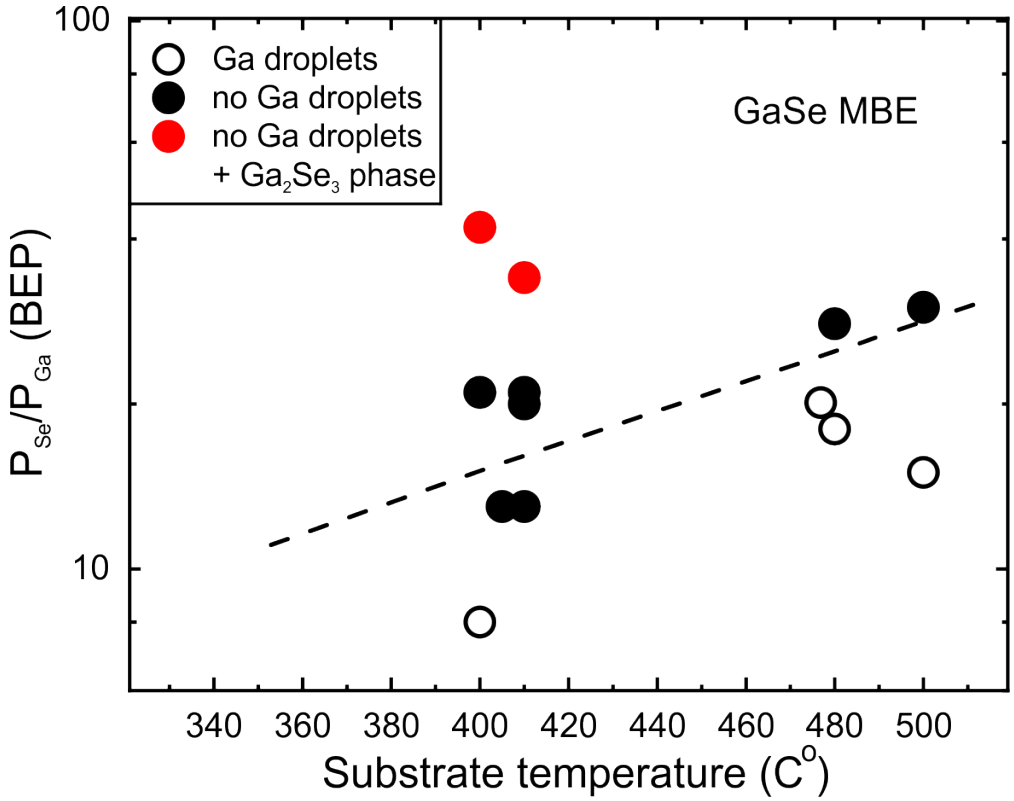

Figure S6: The map in P_{Se}/P_{Ga} (BEP) vs substrate temperature coordinates illustrating the properties of GaSe/GaAs(001) layers grown by MBE using a standard Ga cell and Se valve cracking cell with the cracking zone temperature $T_{Se}(cr)$=500°C as molecular beam sources. GaSe layers containing inclusions of the Ga_2Se_3 phase are indicated by the red circles. The line is guide for eye only.

Micro-photoluminescence spectroscopy

The emission spectra measured in Ga_2Se_3/GaSe allotropic nanostructure at T=10 K and spatial resolution $\sim$ 1 μm demonstrate ultra-narrow lines (black line in Fig. S7). It should be noted that such narrow lines can only be detected at certain locations on the sample. Even with a slight shift of the laser spot by a few micrometers, the narrow lines first broaden (red line in Fig. S7) and then disappear completely (blue line in Fig. S7).

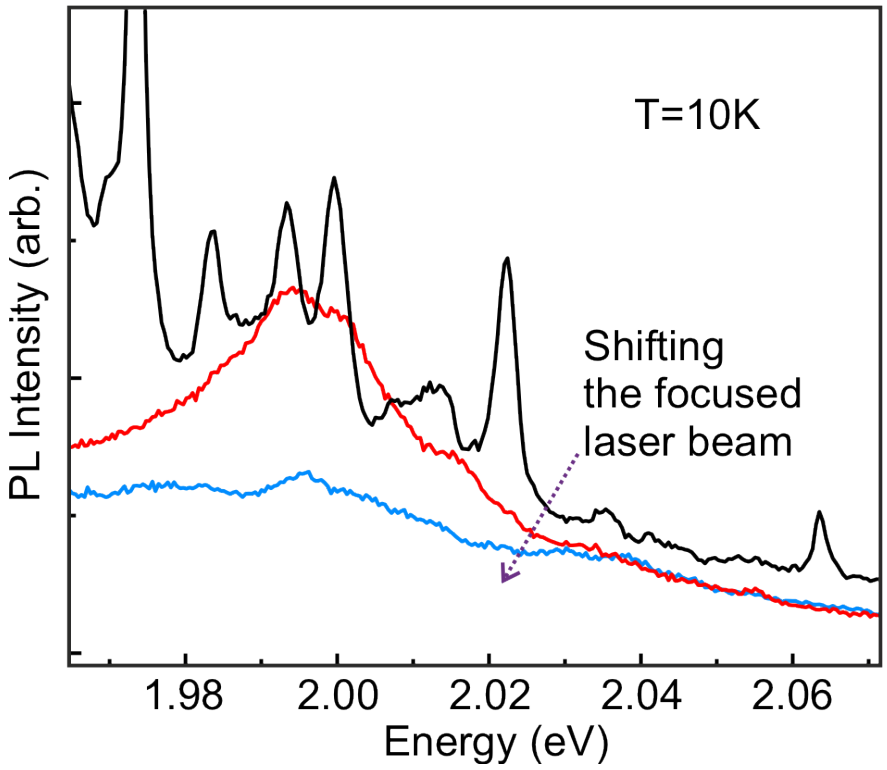

Figure S7: Micro-PL spectra of an allotropic Ga_2Se_3/GaSe nanostructure, measured at T=10 K in three closely spaced spots.

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