Supplementary Information
Wafer-Scale Two-dimensional Semiconductors for Deep-UV Sensing

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1 X-ray photoelectron spectroscopy of GaSe on sapphire

X-ray photoelectron spectroscopy (XPS) was acquired using a SPECS DeviSim near ambient pressure XPS (NAP-XPS) instrument operating in ultra-high vacuum (UHV) mode at a pressure less than 1×10^{-9} mbar. Spectra were measured using a Phoibos 150 NAP hemispherical analyzer with 20 eV pass energy and monochromatic Al Kα X-rays (1486.7 eV). The samples were transported between the EPI2SEM system and XPS using a vacuum suitcase at a pressure less than 1×10^{-10} mbar. Figure S1**a** shows the XPS spectra of GaSe on sapphire under different conditions: at room temperature (T = 300 K), at T = 300 K under a flood gun (30 µA), and at T = 350 K. The XPS spectra associated with specific atomic orbitals of Ga and Se are shown in Figure S1**b-c-d** and Figure S1**e-f**, respectively.

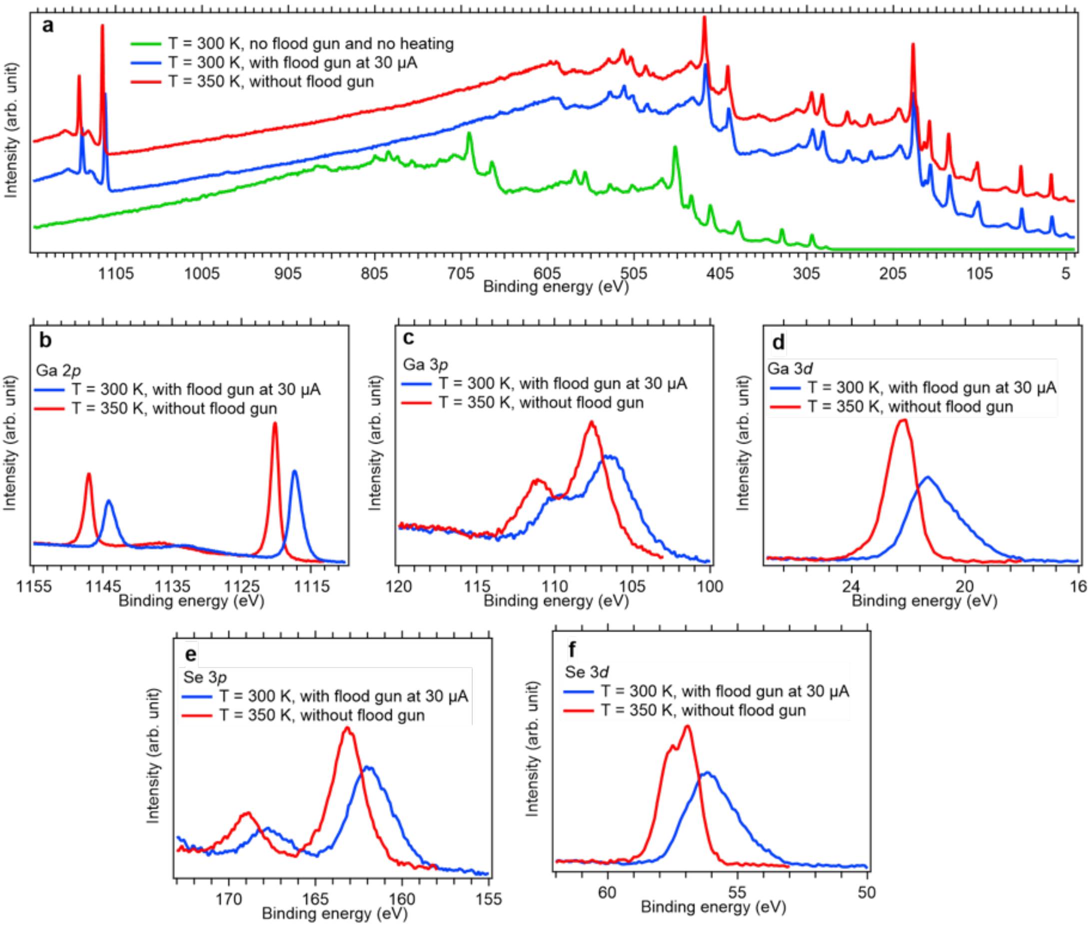

Figure S1: **a**. XPS spectra of GaSe on sapphire under different conditions: at room temperature (T = 300 K), at T = 300 K under a flood gun (30 µA), and at T = 350 K. **b-f**. XPS spectra for **b** Ga 2p, **c** Ga 3p, **d** Ga 3d, **e** Se 3d and **f** Se 3p under a flood gun (30 μA) at T = 300 K and at T = 350 K without flood gun. The XPS measurements show a shift of the peaks due to charging. Before applying the flood gun the peaks are shifted by around 274 eV to high binding energy. Under the flood gun all peaks shift to low binding energy towards the expected values. These were first reached under a flood gun (30 μA) at room temperature, but were not stable. Under heating at T = 350 K, the peaks were found to be instead stable even without a flood gun. The XPS findings indicate that in all spectra the Ga:Se ratio is 1.

2 Atomic Force Microscopy of thin GaSe layers

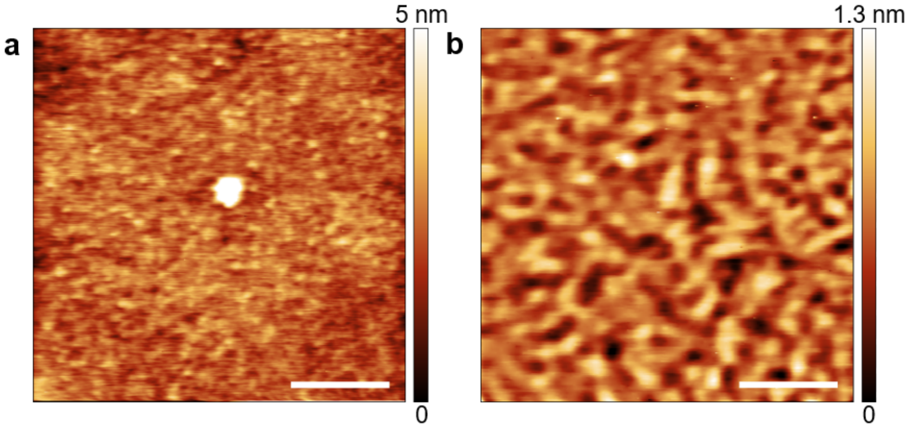

Figure S2: ncAFM of ∼ 1 nm **a** and ∼ 5 nm **b** thick GaSe layers (scale bars = 500 nm).

3 Scanning transmission electron microscopy

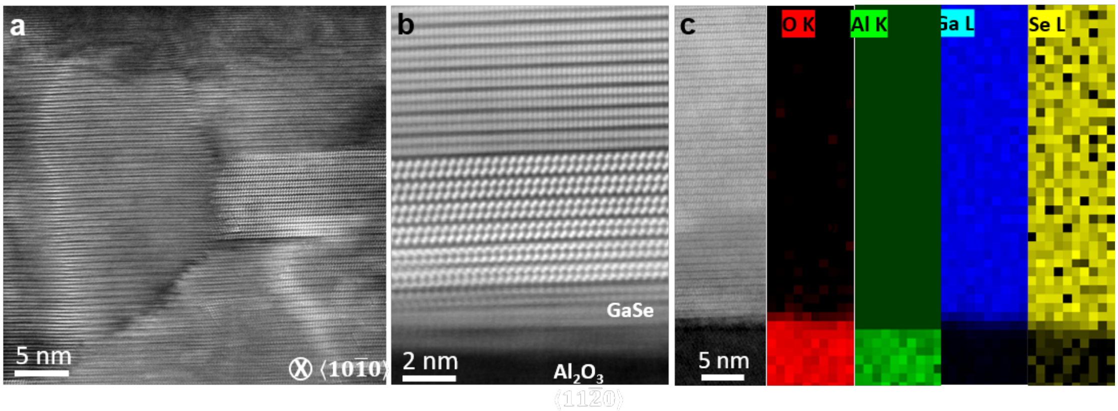

Figure S3: **a**. Cross-sectional HR-HAADF image of a 55 nm-thick GaSe layer on sapphire registered at $\langle 10\bar{1}0\rangle$ zone axis. The GaSe layer is formed by the confluence of grains. **b**. HR-HAADF image showing a γ'-GaSe structure in the $[10\bar{1}0]$ (bottom) and $[11\bar{2}0]$ (top) orientations on sapphire $\langle 11\bar{2}0\rangle$ zone axis. **c**. HAADF image of the GaSe/sapphire interface region and the corresponding electron energy loss spectroscopy (EELS) elemental maps for O, Al, Ga and Se.

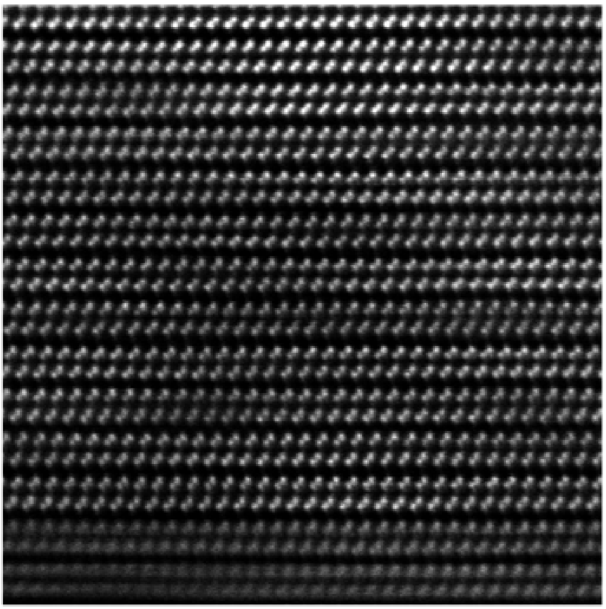

Figure S4: Cross-sectional high-angle annular dark-field imaging (HAADF) scanning transmission electron microscope (STEM) image of a 55 nm-thick GaSe layer on sapphire filtered by fast-Fourier transform (FFT). This type of images were used to estimate the lattice parameters in Table S1.

	Ga-Ga (Å)	Ga-Se (Å)	Layer thickness (Å)	In-plane lattice constant (Å)
STEM	2.87	2.48	4.70	3.87
D_{3h} [1]	2.49	2.50	4.88	3.81
D_{3d} [1]	2.49	2.50	4.87	3.82
D_{3h} - This work	2.44	2.48	4.81	3.78
D_{3d} - This work	2.44	2.49	4.79	3.79

Table S1: Lattice parameters and lengths of bonds (Ga-Ga and Ga-Se) in epitaxial GaSe on sapphire, as derived from high-resolution TEM studies in this work. Lattice parameters and bonds for the D_{3h} and D_{3d} polymorphs are taken from the literature[1] and this work.

4 Raman spectroscopy and stability of GaSe

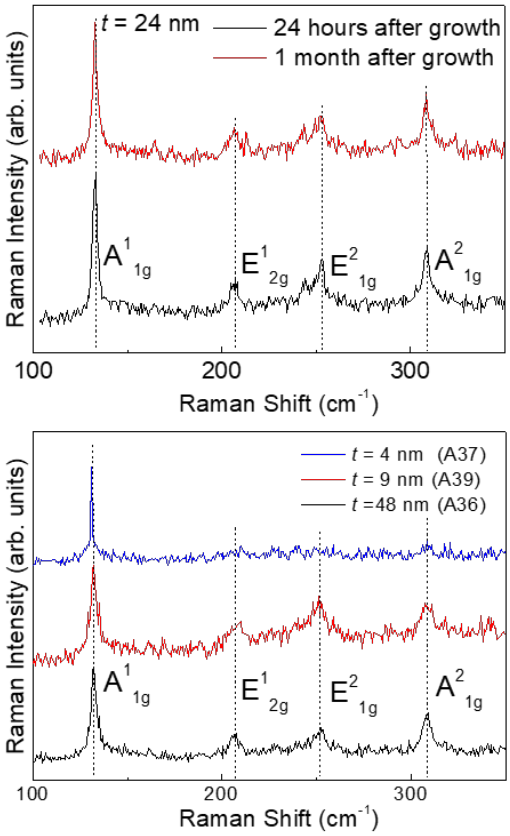

Figure S5: (Top) Raman spectrum for a 24 nm thick GaSe layer 24 hours after growth and after 1 month of storage in a nitrogen environment.(Bottom) Raman spectra for thick (t = 48 nm) and thin (t = 4 and 9 nm) GaSe layers.

5 Spectroscopic ellipsometry: modelling and dielectric permittivity of GaSe

The dielectric permittivity functions of the GaSe (figure S6) were modelled in CompleteEase v6.70 (J.A. Woollam Co.) as a summation of generalized oscillator functions consisting of two Tauc-Lorentz oscillators and a Gaussian oscillator [2]. The energy gap of the Tauc-Lorentz oscillators was taken to be 2 eV. In addition, a UV pole centred at 11 eV was included to model the DUV response that was not captured in the measurements. The model allowed for a roughness layer – however this layer only made a significant contribution to the fit for the thickest GaSe layer. Table S2 contains mean oscillator parameters determined for the 55 nm thick sample by measuring the sample at 49 points across the surface.

Parameter	Parameter Value	Standard deviation
Roughness (nm)	3.34	0.21
Thickness (nm)	54.50	0.36
UV Pole amplitude (eV^2)	119.3	5.2
Tauc-Lorentz 1 amplitude (eV)	18.86	0.48
Tauc-Lorentz 1 width (eV)	0.549	0.015
Tauc-Lorentz 1 energy (eV)	4.7772	0.0057
Tauc-Lorentz 2 amplitude (eV)	12.96	0.36
Tauc-Lorentz 2 width (eV)	0.6579	0.0046
Tauc-Lorentz 2 energy (eV)	3.6453	0.0045
Gaussian amplitude (fixed)	12	-
Gaussian width (eV)	2.153	0.020
Gaussian energy (eV)	5.477	0.018

Table S2: Dielectric function parameter values for the 55 nm thick sample determined by VASE measurements at 49 points over the sample surface.

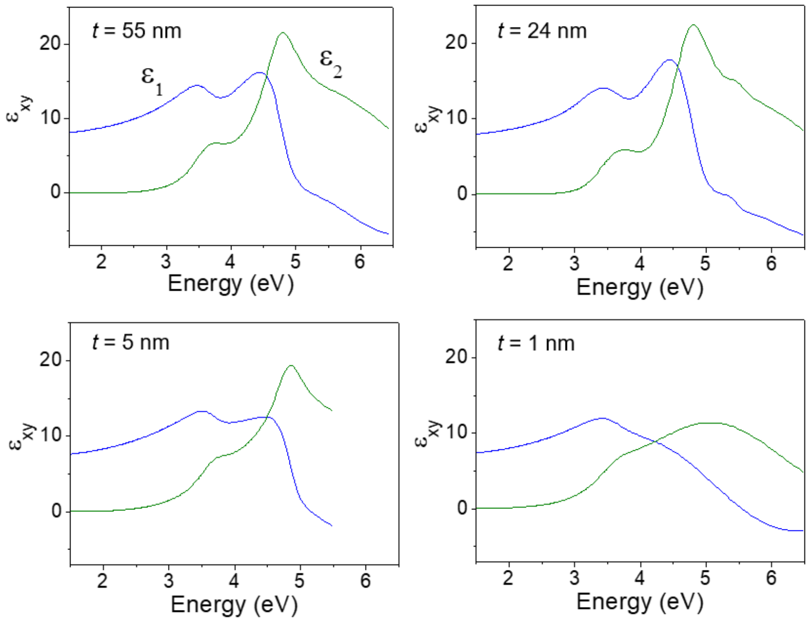

Figure S6: Dielectric permittivity of MBE-grown GaSe layers of different thickness t (t = 1, 5, 24 and 55 nm), as measured by ellipsometry. Since GaSe is a uniaxial crystal, the permittivity measured by ellipsometry corresponds to the tensor component ε_{xy} (*i.e.* the electric field dipole is in the layer plane).

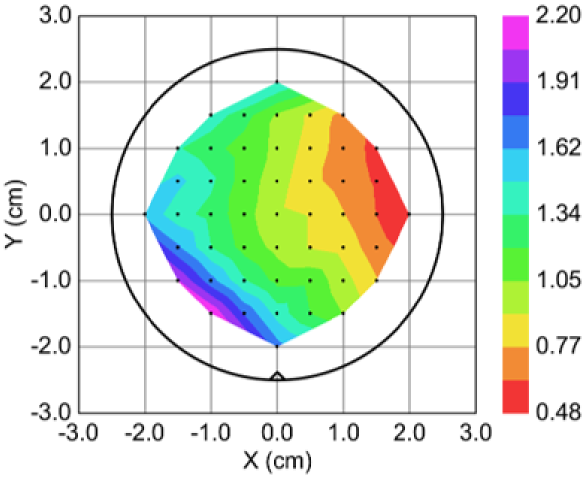

Figure S7: Ellipsometry map of the layer thickness for a representative MBE-grown GaSe of average thickness t = 1.1 nm. The map is formed from measurements taken on a 5 mm square grid over the central region of a 2-inch diameter wafer using focus probes. A parameter uniqueness test at single points in the map suggests that the thickness values are certain to ± 0.5 nm. The central values shown lead to dielectric permittivity values comparable to those measured on thicker layers.

6 Model of the photoresponsivity

We consider the planar sensor of figure S8. The GaSe channel has width w, thickness t, and length l, with ohmic contacts across the length l. When light of power P and energy $h\nu$ larger than the band gap energy of GaSe falls on the surface xy of the GaSe film, electron-hole pairs are generated. In a thin channel of the film with thickness Δz_i, the densities of photo-created electrons and holes generated are equal, *i.e.* $\Delta n_i = \Delta p_i$, and, at steady state, they can be expressed in terms of the carrier lifetime, τ_l, and the rate of carrier generation by light G_i, *e.g.*

$$\Delta n_i = \Delta p_i = G_i \tau_l, \tag{1}$$

where $G_i = \exp(-\alpha z_i)(\alpha \Delta z_i)(P/h\nu)(wl\Delta z_i)^{-1}$ and α is the absorption coefficient of GaSe at the energy $h\nu$. Since the mobility of electrons is much larger than that of holes, we express the photocurrent ΔI_i along the x-direction in the thickness channel Δz_i in terms of the dominant electron current, *e.g.*

$$\Delta I_i = \Delta n_i e v_d (w \Delta z_i), \tag{2}$$

where $v_d = l/\tau_t$ is the electron drift velocity and τ_t is the electron transit time across the length l of the channel. Using equations 1-2 and the relations for G_i and v_d, we express ΔI_i as

$$\Delta I_i = \exp(-\alpha z_i)(e\alpha\Delta z_i P/h\nu)(\tau_l/\tau_t), \tag{3}$$

from which we derive the photoresponsivity R

$$R = \Sigma_i \Delta I_i/P = (e\alpha/h\nu)(\tau_l/\tau_t)\int \exp(-\alpha z)dz = (e/h\nu)(\tau_l/\tau_t)(1-\exp(-\alpha t)). \tag{4}$$

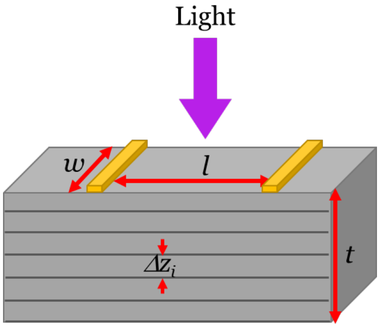

Figure S8: Schematic diagram of a planar GaSe device under optical illumination.

7 Optimisation of MBE growth of GaSe on sapphire

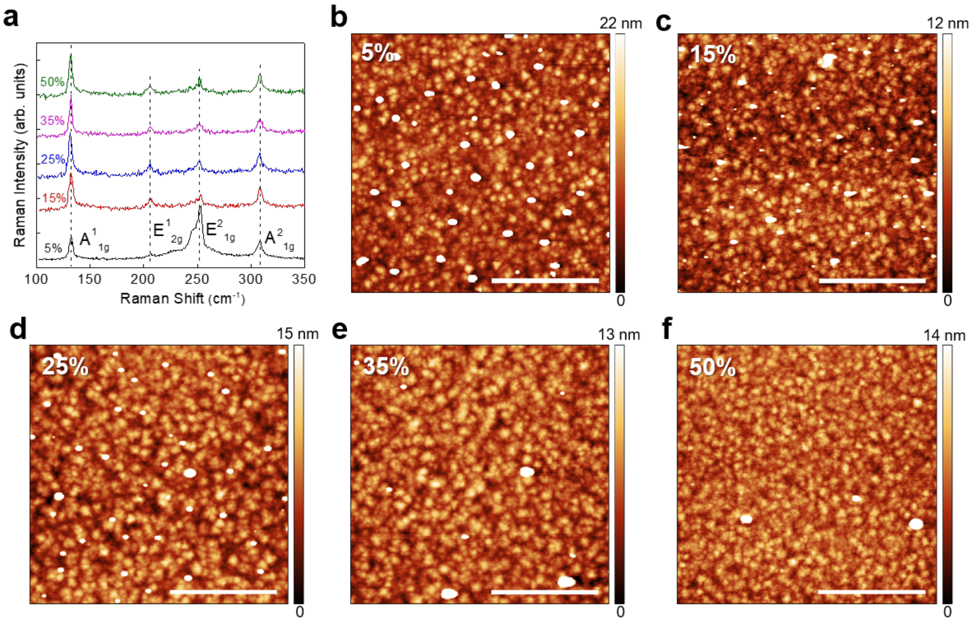

Figure S9: Raman spectroscopy **a** and tapping mode AFM **b-f** of 55 nm thick GaSe layers grown with varying Se:Ga flux ratios. The flux ratios are controlled by the opening of the Se cracker valve, ranging from 5% to 50%.

References

[1] H. Nitta, T. Yonezawa, A. Fleurence, Y. Yamada-Takamura, T. Ozaki, *Phys. Rev. B.* **2020**, *102*, 23 235407.

[2] H. Fujiwara, *Spectroscopic ellipsometry: principles and applications*, John Wiley & Sons, **2007**.