

## Supplementary Pages (Optional)

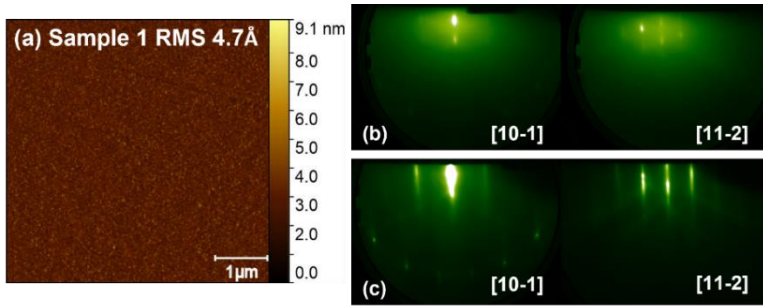


Fig. S1 (a) Atomic force microscope (AFM) image ( $5 \times 5 \mu\text{m}^2$ ) of sample 1, a deoxidized GaAs(111)B substrate. *In-situ* reflection high energy electron diffraction (RHEED) patterns of the GaAs(111)B before (b) and after (c) deoxidation. Root mean square (RMS) surface roughness of sample 1 is  $4.7 \text{ \AA}$ . [10-1] and [11-2] are the in-plane orientations of GaAs(111).

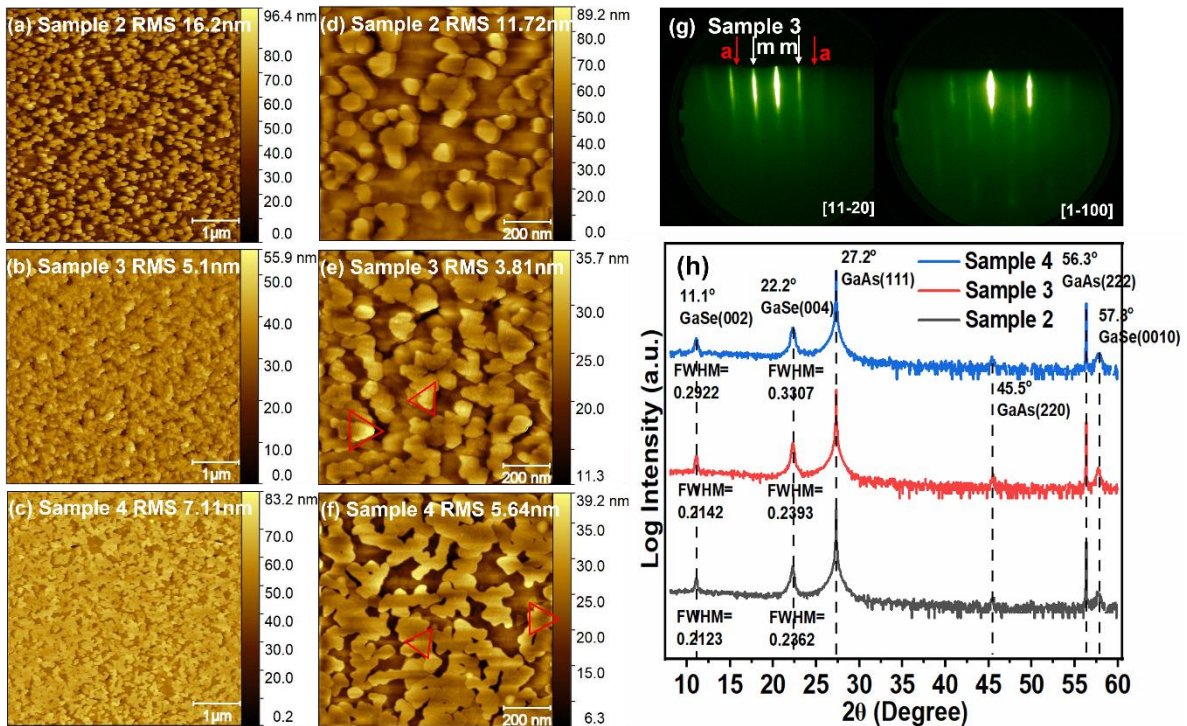


Fig. S2 AFM images ( $5 \times 5 \mu\text{m}^2$ ) of samples 2 (a), 3 (b), and 4 (c). AFM images ( $1 \times 1 \mu\text{m}^2$ ) of samples 2 (d), 3 (e) and 4 (f). The red triangle boxes mark typical GaSe nucleation domains. (g) *In-situ* RHEED patterns taken at the end of growth of sample 3, along two in-plane orientations of GaSe. The red and white arrows indicate a-plane and m-plane diffractions, respectively. (h)  $2\theta/\omega$  X-ray diffraction curves of samples 2-4. FWHM (full width at the half maximum) indicates the crystallite sizes. Samples 2-5 were grown using the same Se:Ga flux ratio and growth rate. Samples 2 and 3 were grown at  $375^\circ\text{C}$ , but sample 3 was annealed in Se at  $375^\circ\text{C}$  for 30min before growth. Sample 4 was grown via 2-step method: initially grew at  $375^\circ\text{C}$  for 8min, then grew at  $450^\circ\text{C}$  for 60min. Sample 5 was grown at  $375^\circ\text{C}$  for 8min (the first step of growing sample 4).

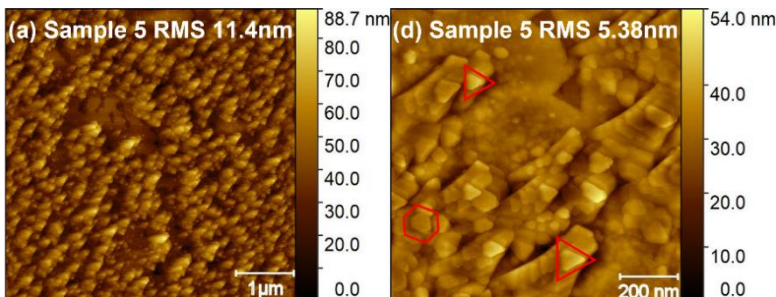


Fig. S3 AFM images ( $5 \times 5 \mu\text{m}^2$ ) (a) and ( $1 \times 1 \mu\text{m}^2$ ) (b) of sample 5. It used same growth conditions as sample 2, but used a freshly cleaved GaAs(111)B substrate. Red boxes mark GaSe nucleation domains.