Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Layer-By-Layer Growth in Solution Deposition of Monocrystalline Lead Sulfide Thin Films on GaAs(111)

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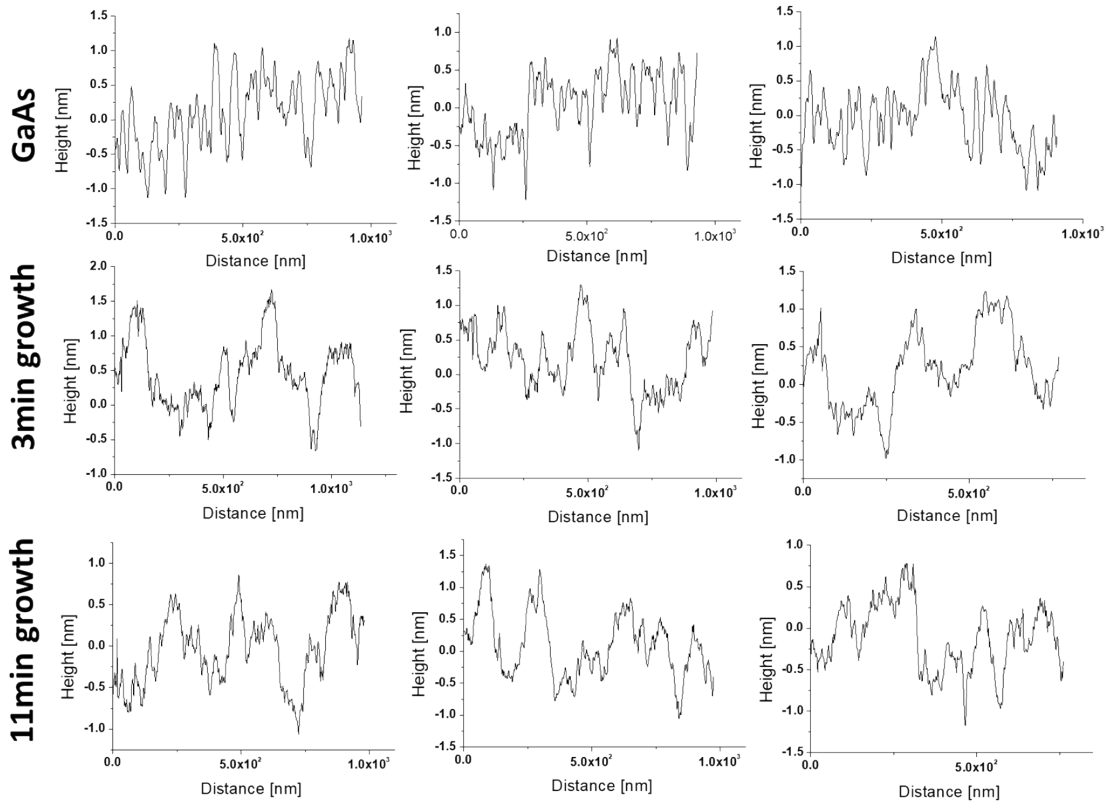
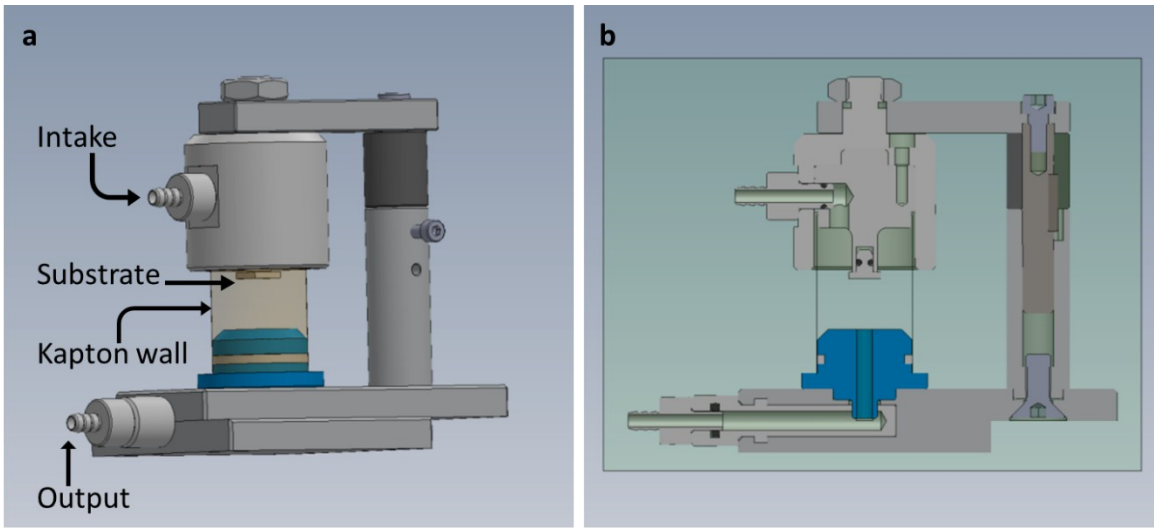


Supplementary Figure 1. **AFM surface topography images**: Typical AFM line profiles taken in air from the following samples: **(top row)** epi ready GaAs(111) wafer, **(second row)** PbS, 3 min growth duration and **(third row)** PbS, 11 min growth duration.



Supplementary Figure 2. **Schematic illustrations of the custom-built fluid cell used for *in-situ* GIXD characterization at ESRF ID-10**. (a) Cell overview and (b) Cell section.

Scattering model for VW (3D) growth

In the model of polycrystalline nucleation and growth, the film thickness t is composed of an assembly of M small single crystals having N repetition of $d_{(111)}$ arranged along z direction:

(1) $t = N \cdot d_{(111)} \cdot M$

Scattering intensity of individual crystals is proportional to N^2, as described in the main text, and the incoherent sum of scattering intensity from crystallites along the film thickness results in

(2) $$I_{\Sigma} = \sum_{i=1}^{M} I = I_S \cdot N^2 \cdot M$$

From (2) one can conclude the linear dependency of the intensity vs. film thickness.

Error calculations

Thickness:

Thickness is estimated from the formula

$$I = I_0 exp(-z/\tau) \rightarrow z = \tau[ln(I_0) - ln(I)]$$

Intensity error

$$\Delta I = \sqrt{I}$$

Following the theory of errors

$$\Delta z = \sqrt{(\frac{\partial z}{\partial \tau}\Delta\tau)^2 + (\frac{\partial z}{\partial I_0}\Delta I_0)^2 + (\frac{\partial z}{\partial I}\Delta I)^2} = \sqrt{(\Delta\tau[ln(I_0) - ln(I)])^2 + \tau^2(\frac{\Delta I_0}{I_0})^2 + \tau^2(\frac{\Delta I}{I})^2}$$

With $\frac{\Delta I}{I} \sim 3\%$ and $\Delta\tau \to 0$

We can write $\Delta z = \tau \cdot 0.03 \cdot \sqrt{2} \approx \tau \cdot 0.04$

Assuming $\tau \sim 4\ nm$, then $\Delta z \approx 0.17\ nm$

Thus we can say that the minimum of Δz is $0.2\ nm$

In-plane coherence length:

$$L_{xy} = 0.9\frac{2\pi}{fwhm_{q_{xy}}}$$

$$\Delta L_{xy} = \sqrt{\left(\frac{\partial L_{xy}}{\partial fwhm_{q_{xy}}}\Delta fwhm_{q_{xy}}\right)^2} = \frac{L_{xy}}{fwhm_{q_{xy}}} \cdot \Delta fwhm_{q_{xy}}$$

Width error taken from measurement resolution, $\Delta fwhm_{q_{xy}} = 1.1 \cdot 10^{-3} nm^{-1}$

resulting in a maximum value of $\Delta L_{xy} \sim 5\ nm$

Similarly ford-spacing:

$$d = \frac{2\pi}{q}$$

$$\Delta d = \sqrt{\left(\frac{\partial d}{\partial q}\Delta q\right)^2} = \frac{d}{q} \cdot \Delta q \approx 4 \cdot 10^{-4}\ nm$$

Methods

Materials and Chemicals

Sodium hydroxide (Gadot, AR), lead nitrate (Aldrich, analytical 99.99+%) and thiourea (Aldrich, ACS≥99.0%) were used without further purification. Single crystal GaAs(111)A substrates were purchased from AXT (epi-polished, undoped, ±0.1° miscut). The films were deposited from a solution with a final composition of 30 mM lead nitrate, 50mM thiourea and 1.2M sodium hydroxide at a final pH > 14. For ex-situ experiments, films were deposited in a thermostatic bath into which a 50 ml Pyrex beaker was placed. The beaker was equipped with a custom-built Teflon stage for mounting the substrates. The substrates were placed epi-side down in the solution, at an angle of ca. 70° with respect to the air–solution interface. The beaker was covered using a glass Petri dish. Under these conditions a linear growth regime is obtained up to a duration of 2hr after which saturation impedes continuous film growth. Note that several minutes after reaction initiation homogenous precipitation is observed within the beaker.

Structural and Chemical Characterization

X-Ray Diffraction (XRD)

The crystallographic phase and texture of the films were studied by XRD. A Panalytical Empyrean diffractometer equipped with a PIXcel linear detector and monochromator on diffracted beam was used. Data were collected in the 2θ/θ geometry using Cu Kα radiation (λ = 0.15405 nm) at 40 kV and 30 mA. Diffraction scans were taken during 8 minutes in a 2θ range of 20-65° with a step size of ~ 0.033°. Rocking curves were obtained using a parabolic X-ray mirror for Cu Kα radiation installed on the incident beam, providing a quasi- parallel beam with divergence less than 0.05 of a degree.

Field Emission Gun Scanning Electron Microscopy (FEG-SEM)

The morphology of the films was observed using an ultrahigh resolution JEOL JSM-7400F FEG-SEM without coating of the surface. Acceleration voltage was 3.5 kV and signal was collected using an in-lens secondary electron detector. Film thickness was measured from cleaved cross sections (X-sec) while surface topography was observed in plan-view.

Transmission Electron Microscopy (TEM)

Cross sections were prepared by cutting the sample into slices normal to the interface and gluing them together face-to-face using M-Bond 610 adhesive (Allied HighTech Ltd.). The samples were polished with a precision small-angle tripod holder on a series of diamond polishing papers (Allied HighTech Ltd) until a nominal thickness of 30μm was achieved, and glued to a Mo slot grid (1×2 mm^2). Final thinning was done by Ar ion milling using a Gatan PIPS-2 precision ion polishing system. TEM, HAADF STEM and HRTEM were carried out using a JEOL JEM-2100F instrument operating at 200kV.

Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) measurements were performed in AC-mode with an MFP-3D AFM from Asylum Research (Oxford Instruments). Analyses were performed on 1X1 μm^2 scans obtained at a scan rate of 1.5 Hz.

XPS

An ESCALAB 250 spectrometer with a monochromatic Al X-ray source (excitation energy 1486.6 eV) at a base pressure of 1×10–9 mbar was used for XPS measurements. Wide-scan survey spectrum for all elements and high-resolution spectra of selected elements were recorded.

GIXD Characterization

X-ray scattering measurements were performed at ID10 beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France), which is especially designed for studies of liquid-solid interfaces using GIXD. A beamstop was used for detector protection in the position of direct and specularly reflected beams. GIXD data were obtained using monochromatic X-rays with an energy of 22 keV. The 2D GIXD patterns were recorded with a Pilatus 300k detector (487x619 pixels with a pixel size 172x172 μm^2) from Dectris (Baden, Switzerland) at a distance of 284 mm from the sample. The beam grazing angle was 0.08°, 80% of the GaAs critical angle (0.1°), and 67% of the PbS critical angle (0.12°). Phi scan rate was 0.02 [deg/sec].