	Experiment title: _In-situ_ GIXD studies of the solid-liquid interface during chemical bath deposition of PbSe thin films on GaAs(100)	**Experiment number**: MA-2608
Beamline: ID-10b	**Date of experiment**: from: 30/4/15 to: 4/5/15	**Date of report**: 15DEC2015
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Applicants _Prof. Y. Golan, BGU, Israel; T. Templeman, BGU, Israel;_

Dr. S. Sengupta, BGU, Israel; O. Friedman, BGU, Israel.

The overall aim of the project was _in-situ_ investigation of the solid-solution interface during GaAs surface pre-treatment and subsequent PbSe film growth. By monitoring grazing incidence X-ray diffraction (GIXD) structural variations, and particularly new phase formation at the interface were attempted. Following the chemical reaction initiation, morphology evolution and orientation relationship between the PbSe and the underlying substrate were investigated. Selenide pre-treatment parameters such as pH, duration, temperature and Se^{2-} concentration control the passivation kinetics and resulting initial film growth were studied _in-situ_.

In the experiment we made use of a modified version of the custom designed liquid cell built at ID-10 by Oleg Konovalov and co-workers (Figure 1c). Precursor solutions (all aqueous) were prepared by adding KOH followed by Na_2SeSO_3 and purging of the solutions with N_2 to remove dissolved O_2 and CO_2. GaAs (100) substrates were mounted in the cell and aligned with respect to the GIXD beam, followed by solution injection into the cell. After studying selenide passivation of GaAs, PbSe growth was initiated by one of two distinct methods; addition of Pb acetate (source of divalent lead cations) or rinsing of the cell followed by addition of KOH and Pb acetate. _In-situ_ GIXD 'snapshots' were taken during the very early stages of film formation until full surface coverage by PbSe film was achieved, and further to monitor the structural evolution of the film. The extremely slow growth rates (typically 0.03 nm/sec), combined with the enhanced brilliance at ID-

10b and ultrafast acquisition rates using Pilatus 300 2D plate detector allowed very good time resolution of the experiment.

Diffraction intensity maps of q_z vs. q_{xy} were obtained through the GIXD experiments at the substrate-solution interface, during which the substrate was rotated nearly parallel to the incidence beam (rotation angle φ, propagation vector k_0 – see figure 1c). Diffraction scattering patterns were recorded at 0.5^0 φ intervals in the range of 0^0 to 180^0. During the experiment not all φ rotation angles resulted in Bragg scattering; only specific crystallographic orientations coinciding with film/substrate zone axes appeared. Rotation angles which gave high intensity peaks were marked and analyzed by converting to d_{hkl} and compared to crystallographic powder database (ICDD# 06-0354 ; 32-0389, for PbSe and GaAs accordingly). Several minutes after reaction initiation, epitaxial relations between GaAs and PbSe were observed, specifically $(111)_{PbSe}\|(001)_{GaAs}$, $[110]_{PbSe}\|[110]_{GaAs}$. PbSe grown on GaAs(100) substrates under current growth conditions are well known to result in (111) textured films, therefore both these plain vectors are expected to be located on q_z (for any given φ). The angle between a given d_{hkl} peak and q_z was measured (Figure 1a-b) and by comparing Laue diffraction patterns, zone axes for both film and substrate were calculated. Rotating the substrate along φ confirmed this method as rotation angles matched the angles between varying zone axes.
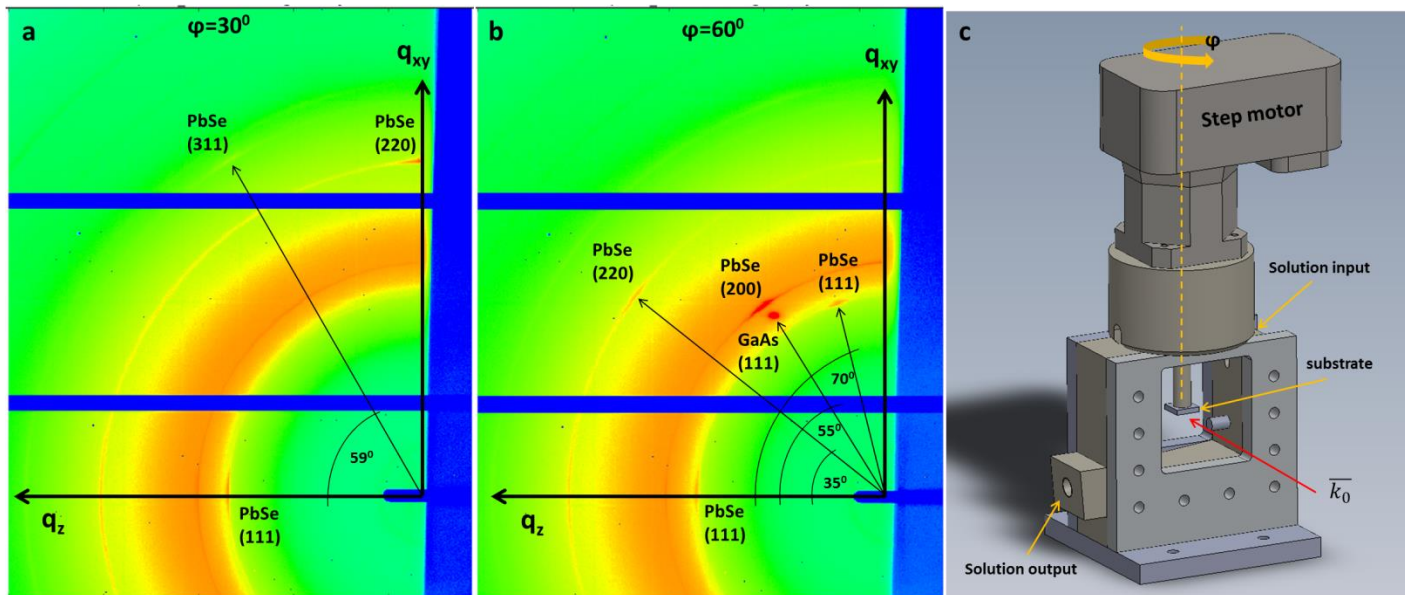

Figure 1. GIXD diffraction intensity maps of q_z vs. q_{xy} obtained at the substrate-solution interface. (a) Intensity map acquired at a rotation angle of 30^0 with [211] zone axis of PbSe. (b) Intensity map acquired at a rotation angle of 60^0 taken with PbSe zone axis [110] and GaAs zone axis [110]. (c) Schematics of the modified cell used throughout the experiments.

Figure 1a-b show the presence of weak powder rings which appeared at alternating strengths during the experiment. This we attribute to deposition of randomly oriented crystallites which dissolve during film growth (a kinetic process which continues throughout the growth). Considering that fully grown films show clear epitaxial relations (confirmed using ED in the TEM) this assumption is reasonable.

Several issues have risen during the experimental procedures, which were not unexpected considering the novelty of the method in use. Initiating the reaction through the standard chemical bath deposition protocol resulted in nucleation on the cell windows and in the solution itself. This in turn diffracted the incident beam at varying camera lengths and overlaid the intensity maps with strong powder rings. Solving this issue was accomplished by rinsing the cell using DI water prior to reaction initiation to remove selenide anions (so called "selenide starved conditions"). Once the lead precursor was added, reaction was limited to the selenide anions adsorbed on the substrate surface (due to the previous selenosulfate treatment), resulting in the formation of an ultrathin film of PbSe. More problematic to deal with was the mechanical stability of the rotation axis connecting the substrate to the motor (figure 1c). The cell was built to withstand extreme chemical environments (KOH solutions of pH=14), thus, all parts of the cell in contact with the solution were constructed of PTFE and cell windows out of polyimide films. Lack of stability in the PTFE rod introduced off axis wobbling which severely hampered data acquisition in the φ angle range (φ scans). Currently we have manufactured a PTFE coated stainless steel rod, which will be integrated in the cell on order to solve the issue based on in-house testing.