ESRF	**Experiment title:** **Anomalous GIXD Studies of Ultrathin Nanocrystalline Films**	**Experiment number**: MA-128
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Names and affiliations of applicants (* indicates experimentalists):

(i) Dr. Yuval Golan, Dept. of Materials Engineering, Ben-Gurion University, Israel. ; (ii) Prof. Maria J.M. Gomes*, Physics Department, University of Minho, Braga, Portugal.*

Part I: Study of chemically deposited nanocrystalline lead chalcogenide films on GaAs(100)

This study was focused on preferred orientation within ultra-thin nanocrystalline PbSe and PbS films chemically deposited on GaAs(100) substrates. The preferred orientation was studied using GIXD radial scans of the films. Since PbSe has cubic (rocksalt) structure, the angle between (202), (220) and (022) planes is 60 degrees. When GIXD radial scan of 180 degrees was applied to single crystal PbSe film deposited on GaAs(100) we observed all three sharp peaks of the mentioned planes, indicating <111> orientation out of plane of the film, with <110> in plane orientation, in agreement with our previous electron diffraction measurements. Figure 1a shows GIXD radial scan of nanocrystalline PbSe films deposited on GaAs(100) using $PbCl_2$ precursor during 30 and 120 minutes. At 30 minutes sample scan we clearly see all three {110} peaks, but they are much weaker and broader then in single crystal sample, suggesting existence of <111> preferred orientation in nanocrystalline layer. At 120 minutes sample, the {110} peaks are much weaker, pointing to loss of preferred orientation with the film thickness, due adhesion of randomly oriented nanocrystals from solution. Figure 1b shows GIXD radial scan of nanocrystalline PbSe films deposited on GaAs(100) using $Pb(Ac)_2$ precursor during 10 and 60 minutes. For the sample deposited for 10 minutes, we see a picture similar to scan of single crystal film, pointing to same <111> out of plane orientation of all deposited nanocrystals within the film. At 60 minutes sample we do not see any {110} peaks, demonstrating absence of preferred orientation in thicker films, due adhesion of large amount of randomly oriented nanocrystals from solution. Figure 1c shows schematic illustration of the resulting nanocrystalline PbSe films deposited during longer deposition times (120 and 60 minutes) using both precursors.

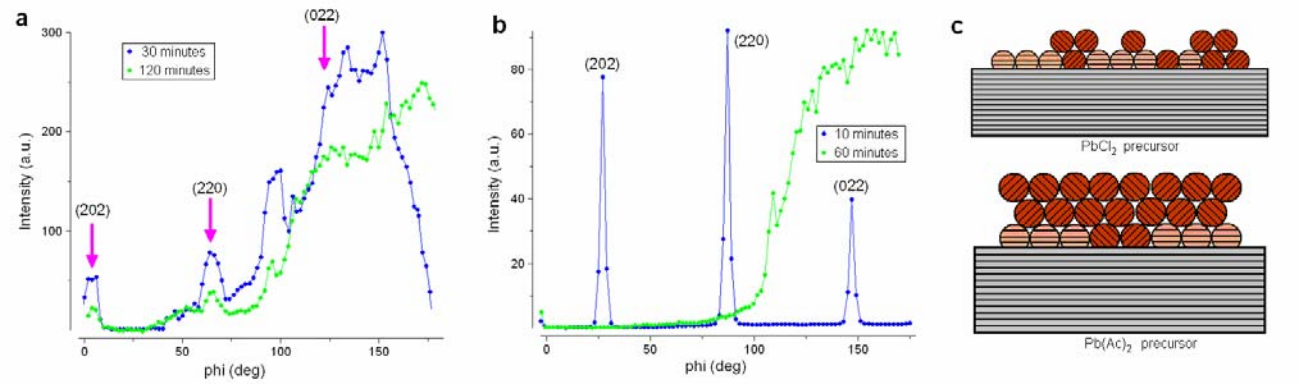


Fig. 1 GIXD radial scans of nanocrystalline PbSe films deposited using $PbCl_2$ precursor (a) and $Pb(Ac)_2$ precursor (b) during various periods of time. (c) Schematic illustration showing preferred orientation of the crystallites directly touching the substrate; where bright-colored crystallites have <111> orientation and dark-colored crystallites are randomly oriented. Crystallites deposited using $Pb(Ac)_2$ precursor are larger then crystallites deposited using $PbCl_2$, corresponding to FWHM measurements of Bragg (220) peaks (not shown).

The most important and surprising conclusion from our study is following: Nanocrystals deposited from solution via the cluster mechanism (e.g., formed in solution and then adhered to the substrate) onto the single crystal GaAs(100) substrate clearly show a preferred orientation! Figure 2 shows GIXD radial scan of the PbS films deposited on GaAs(100) at 40ºC during 2, 4 and 6 minutes. Previous studies revealed that at certain deposition conditions thin PbS films tend to grow on GaAs(100) substrate with <110> out of plane orientation. GIXD radial scan of 180 degrees applied to ultra thin nanocrystalline PbS film deposited on GaAs(100) suggested coexistence of more than one in plane orientations (30 degree rotation of the <110> orientation) within the nucleation layer and transition to one dominant in-plane orientation with increasing film thickness .

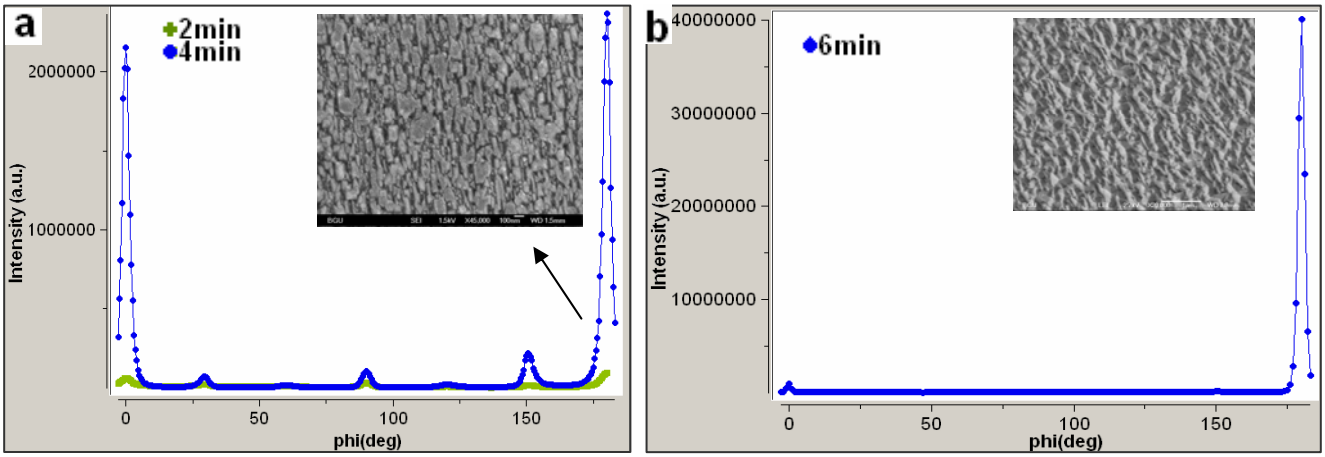


Fig. 2 GIXD radial scans of nanocrystalline PbSe films deposited using $Pb(NO_3)_2$ precursor for (a) 2, 4 and (b) 6 min. The insets show SEM micrographs emphasizing the morphology change with increasing thickness for samples deposited during 4 and 6 min.

Figure 3a shows 180 degree GIXD scan of PbSe deposited on GaAs(100) substrate at 30ºC for 30 min and PbS grown on the PbSe intermediate layer at 30ºC for 30 min. Figure 3b show 180 degree GIXD scan of PbS deposited on GaAs(100) substrate at 30ºC for 30 min and PbSe grown on the PbS intermediate layer at 30ºC for 30 min. In contrast with growth on GaAs(100), growth of PbS on PbSe (and vice versa) results in complete repetition of the orientation from the substrate (or, in this case, from the intermediate layer) to overgrown film, despite the fairly large (ca. 5%) mismatch between PbS and PbSe.

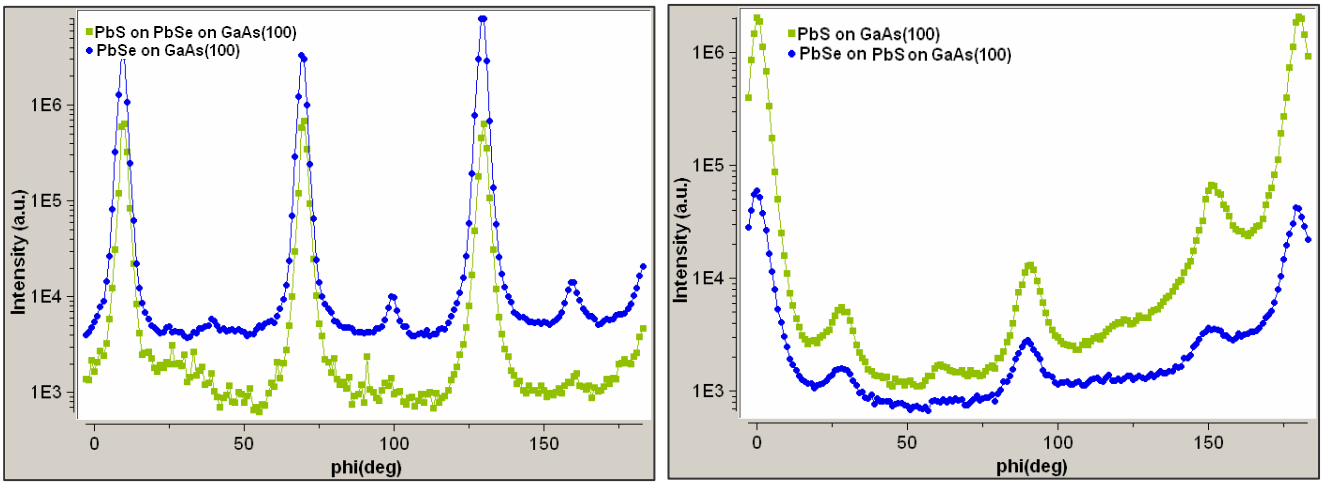
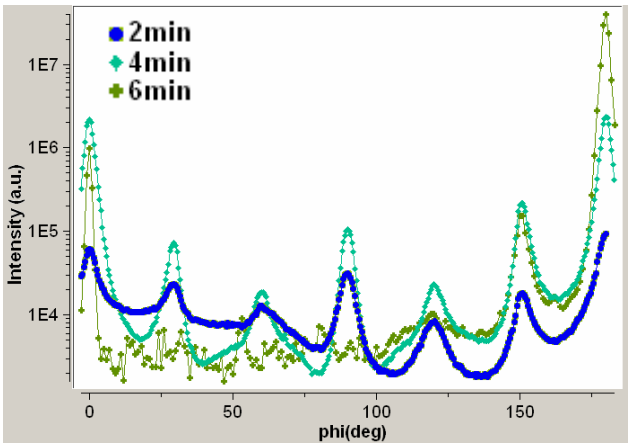


Fig. 3 (a) GIXD scan of PbSe deposited on GaAs(100) substrate at 30ºC for 30 min and PbS grown on the PbSe intermediate layer at 30ºC for 30 min. (b) GIXD scan of PbS deposited on GaAs(100) substrate at 30ºC for 30 min and PbSe grown on the PbS intermediate layer at 30ºC for 30 min. (Notice logarithmic y scale)



This angular relationship in the spectra could be explained by co-existence of <110> and <111> out of plane orientations while 0º and 180º peaks are from <110> out of plane orientated particles and 30º, 90º and 150º are from <111> oriented particles. These ultrathin samples will be measured also in the 2θ/θ geometry.

Part II. Nanocrystals within dielectric thin film matrices.

During this experiment we were able to obtain XRD spectra from our CdSe and Ge nanocrystals (NCs) dispersed on dielectric matrices: (i) alumina matrix - Al_2O_3; Ge NCs-doped Al_2O_3 ; and CdSe NCs- doped SiO_2 films. The flux at ID-01 provided sufficient signal-to-noise and therefore enhancements using anomalous scattering were not employed. Some of the results are presented below. From XRD spectra obtained using a Philips PW 1710 Diffractometer using CuK_α radiation and Bragg-Brentano geometry it is very difficult to tell which of delta or gamma (or both) Al_2O_3 phase is/are present in the annealed films. From X-ray diffraction data from the same samples shown in Fig.4, obtained with the synchrotron radiation (θ_{inc} =0.15º) it became clear that both delta and gamma Al_2O_3 crystalline phases are present in annealed films, while as-gown ones are basically amorphous.

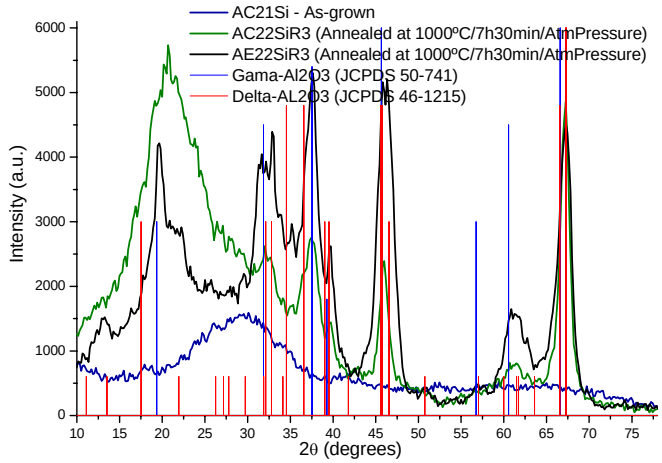


Fig. 4 alumina matrix Al_2O_3;

Ge NC's doped-Al_2O_3 films

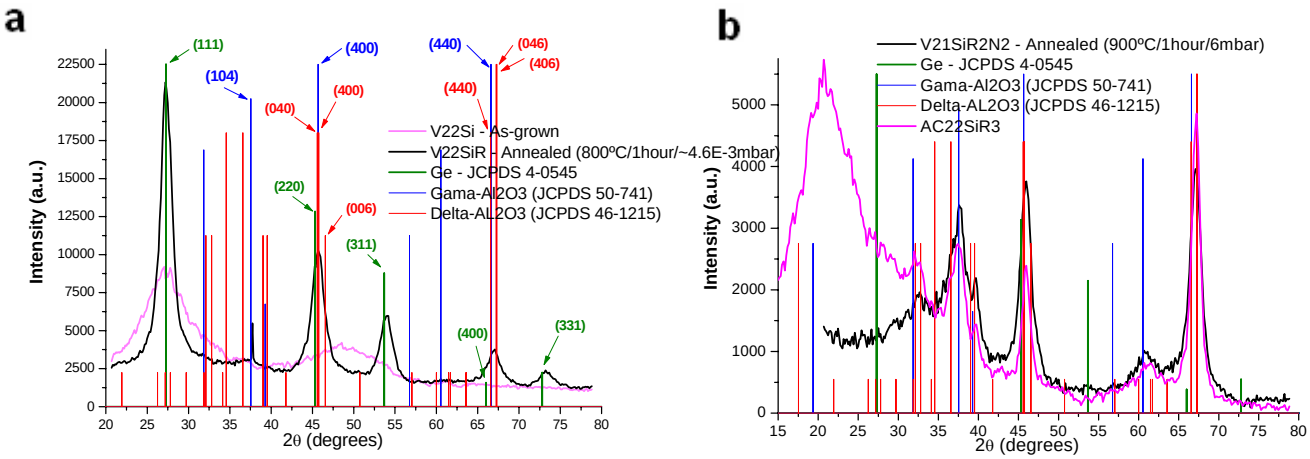


Fig. 5 (a) XRD spectrum of V22Si (as-grown) vs V22SiR (annealed in air) samples. (b) XRD spectrum of one annealed sample under a Nitrogen atmosphere ($V12SiR2N_2$) obtained at ESRF.

Ge NC size of approximately 4.8nm could be estimated from the annealed sample after a Lorentzian fitting of (311) reflection peak. In as-grown sample only amorphous Ge phase is present (Fig 5a).
It seems to indicate that nitrogen atmosphere is not a good one to anneal Ge NC's. We do not believe that the fact that this annealing had been done at a higher temperature (900ºC) is enough to cause such a drastic difference, when comparing XRD spectra $V21SiR2N_2$(Fig 5b) to V22SiR (Fig.5a).

Conclusions

The annealing of Al_2O_3+Ge films under N_2 atmosphere favours the formation of crystalline alumina phases (gamma+delta) instead of the c-Ge phase. Argon atmosphere was used to anneal Ge NCs doped- Al_2O_3 films but not a big improvement in the NC's size was revealed. Until know, annealing at low air pressure seems to be the more effective atmosphere to grow and control the size of the Ge NCs inside a matrix.

The changing of growing parameters of CdSe NCs dispersed on SiO_2 films (results not shown here) does not influence too much to the NC's formation during the deposition at RT or low temperatures. The as grown samples contain already formed CdSe NC's with both hexagonal and cubic phases with size of 0.8 – 1.5 nm.

The formation of the CdSe NC's occurs mainly due to the post-deposition annealing treatments. It is possible to change the NC's sizes by varying the annealing conditions, particularly the annealing atmosphere. The samples that had been annealed under the Ar (P=1 mbar) atmosphere have NC's of 1.6 - 2.5 nm sizes mostly in the cubic phase. And the samples annealed under vacuum ($P=2x10^{-2}$ mbar) have have NC's of 25 nm size in the hexagonal phase. Changing the annealing pressure it is possible to tune the NC's size and phase distribution.

However, different annealing conditions are being carried out at present using Argon, Nitrogen and Air atmospheres, and at different pressure values. So, further measurements at ESRF would be of great interest in order to complete our study of the effect of annealing.