

This work was written as part of one of the author's official duties as an Employee of the United States Government and is therefore a work of the United States Government. In accordance with 17 U.S.C. 105, no copyright protection is available for such works under U.S. Law.

Public Domain Mark 1.0

<https://creativecommons.org/publicdomain/mark/1.0/>

Access to this work was provided by the University of Maryland, Baltimore County (UMBC) ScholarWorks@UMBC digital repository on the Maryland Shared Open Access (MD-SOAR) platform.

Please provide feedback

Please support the ScholarWorks@UMBC repository by emailing scholarworks-group@umbc.edu and telling us what having access to this work means to you and why it's important to you. Thank you.

Optimization of sensor materials using physical vapor transport growth method

**Christopher Cooper, Sonali Saraf, Dan Kazal, Brian Cullum,
Fow-Sen Choa, Bradley Arnold, Lisa Kelly and N. B. Singh**

University of Maryland, Baltimore County, Baltimore, MD

and

Ching Hua Su

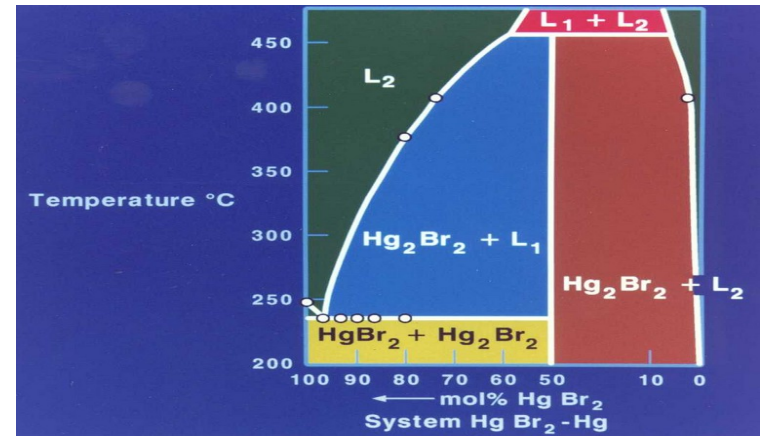
NASA Marshall Space Flight Center, Huntsville, AL

NASA Headquarters and Marshall Space Flight Center for financial

Optimization of sensor materials using physical vapor transport growth method

Outlines

- Objectives
- Background
 - Effect of growth parameters
 - Effect of fluid flow
- Experimental design, methods
 - Horizontal vs vertical configuration
- Experimental method
- Results
- Conclusion



Decomposing melt and high vapor pressure prohibits melt growth and PVT is good method

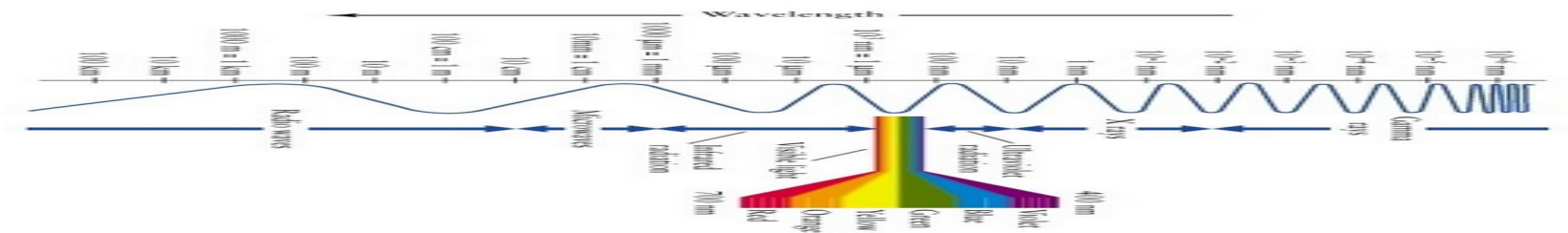


PVT grown crystals

PVT is an excellent method when there is decomposition during growth

Thrust on bioinspired sensors

There is a great need for a sensor with potential ultraviolet vision of birds, IR heat sensing of snakes, photoreceptors of scorpions sensing from deep UV to LWIR, and aquatic life in the UV through the red.



Concept for bioinspired sensing

biosensor designs are based on:

- Animals have great sensing ability before storms, tsunami, earthquake etc. (Piezo sensing, dog nose, skin changes)
- Large fishes do not get hit with boats, ships etc. (Piezo)
- Imaging capability (changing color of sensor e.g. eyes)
- Changing skin for sensing as change of weather (dyes)
- Contact sensors (contact potential, thermal, mechanical and chemical)

Bio sensors and bio inspired sensors can be designed based on novel materials

Optimization of sensor materials using physical vapor transport growth method

Background on materials growth methods

- Bridgman method (BM)
 - Vertical BM
 - Horizontal MB
 - Czochralski method (CZ)
 - Moving crucible
 - Moving seed
 - Vapor transport method
 - Physical vapor transport
 - Molecular beam assisted
 - Laser assisted (PLD etc.)
 - Chemical vapor transport (CVD)
 - Molecular organic CVD
 - Solution growth method
 - Travelling solvent/heater method (TS/TM)
- In decomposing materials with incongruent systems and high vapor pressure systems:
 - Melt growth methods such as BM, CZ can not be used since melt decomposes
 - Solution growth can not be used due to insolubility
 - TS/TM can not be used due to miscibility or solubility

Method depends on the material and size

Growth of bio sensor materials using physical vapor transport growth method

Objectives

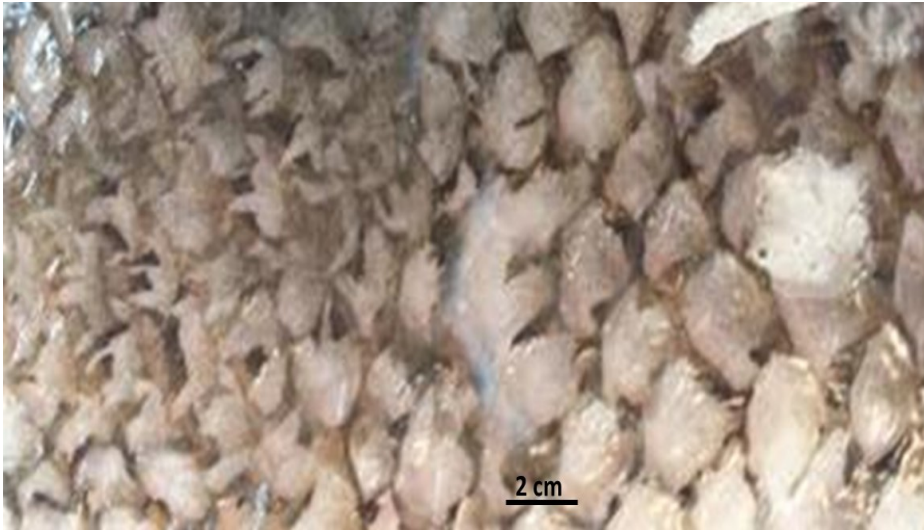
The objectives are to evaluate feasibility of physical vapor transport method for the growth of sensor materials and to determine effect of parameters on the quality of grown materials.

- Process used by Su et al will be used; Opt. Eng. 56(7), 077106 (2017), J. Crystal Research and Technology, 180023, 1-10 (2019)., Optical Materials 60, 474-480 (2016), J. Materials Today 4, 4 5478-5487 (2017).

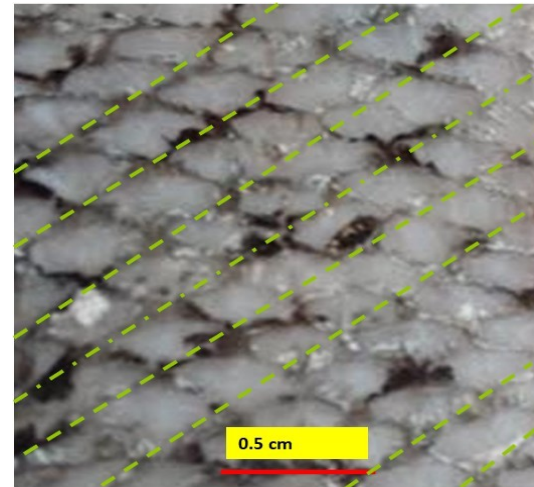
Method depends on the material and size

Optimization of sensor materials using physical vapor transport (PVT) growth method

- During the growth of nano-, micro-, thin film and bulk crystals, in addition to growth parameters, fluid flow is most important factor.
- Fluid flow affects the morphology and hence performance



(a)



(b)

Irregular pattern on the skin of a typical pond salmon fish and (b) regular patterns on the skin of a typical salmon fish. Both were almost identical in size.

Method depends on the material and size

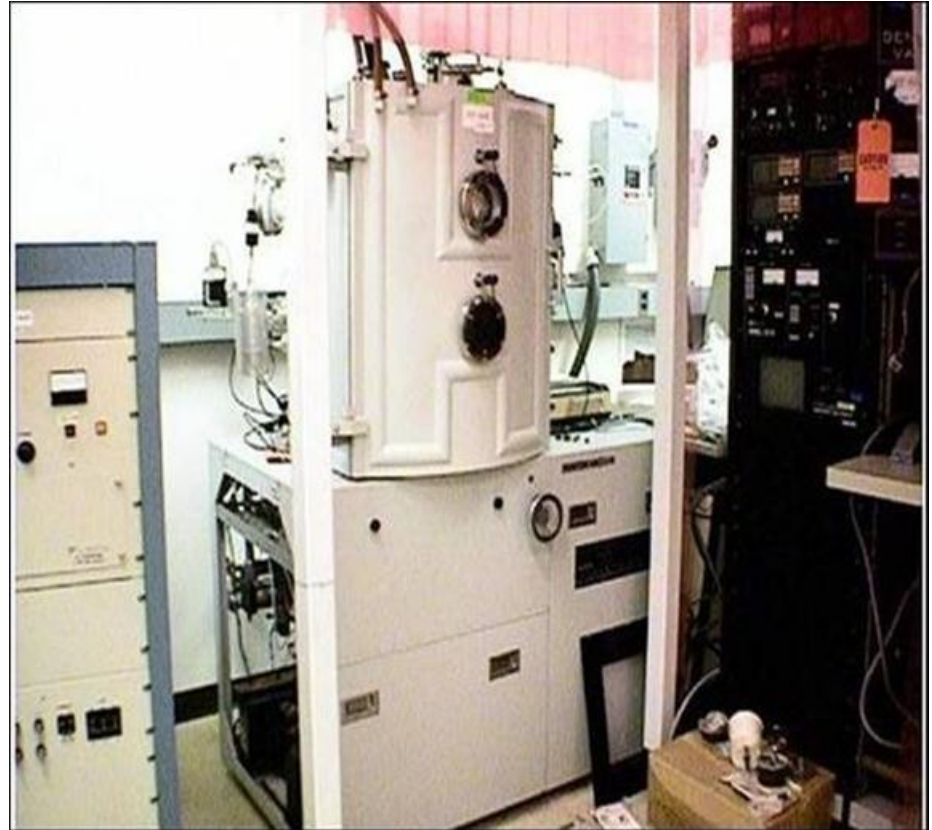
Previous research using PVT on IR detector materials in our lab

- Growth studies: PbSe pure and Sn doped
- Studies are performed with physical vapor deposition on silicon substrates
 - Effect of growth temperature
 - Morphologies
 - Resistivity
 - Effect of annealing
 - Transition of morphologies
- There is limited data for Sn-doped materials on various substrates for MWIR detectors

Papers published in Optical Eng. And SPIE proceedings

Commercial PVT DENTON system used by us

- Materials System
 - PbSe and PbS, 99.9999% purity used as source material
 - Tantalum boat
 - Resistively heated
- Substrate
 - Si (111)
 - Dilute HF etch to remove native oxide
- Process
 - Base vacuum in 10^{-7} Torr range
 - Stationary, resistively heated 2' substrate mount
 - Temperature of substrate varied
 - PVD process
 - PbSe sublimation
 - 1 K/sec Deposition Rate
- Characterization
 - SEM, X-ray, 4-point probe
 - D^* (sensitivity) TBD



PVD Growth of material

We are using several systems for the growth of materials for PVT



DENTON Evaporator

We have several growth chambers available at UMBC

PVD Furnace used for deposition in present study



DENTON
Furnace



Crucible and
holder



Example of Lead tin selenide
sample grown by PVD on a
glass substrate

Temperature and transport path can be controlled during deposition

PVD Furnace used for deposition of PbSe, ZnSe, and several other materials



DENTON Furnace



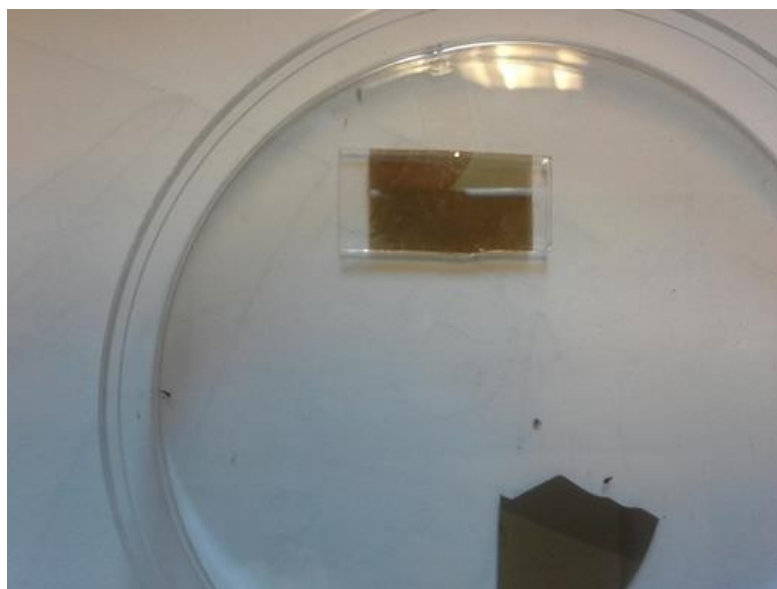
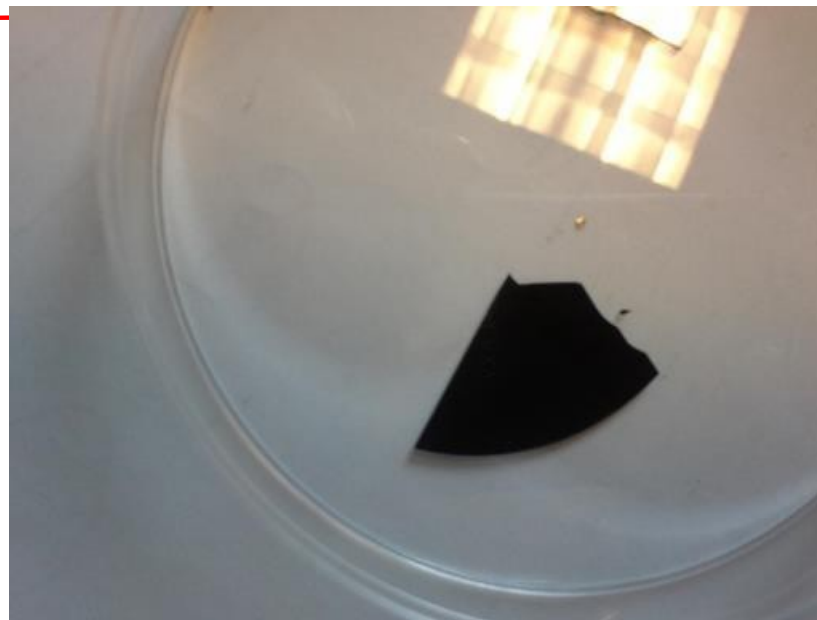
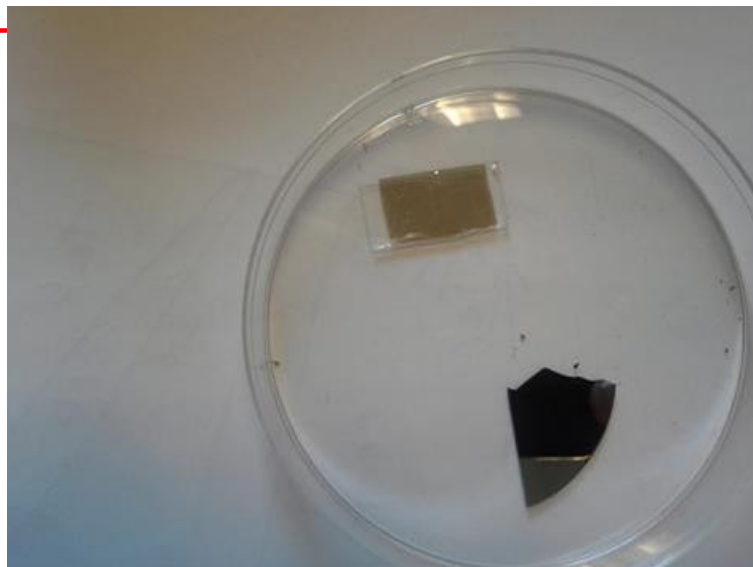
Crucible and holder



Example of Lead tin selenide sample grown by PVD on a glass substrate

Temperature and transport path can be controlled during deposition

We used high resistivity Silicon and glass as substrates



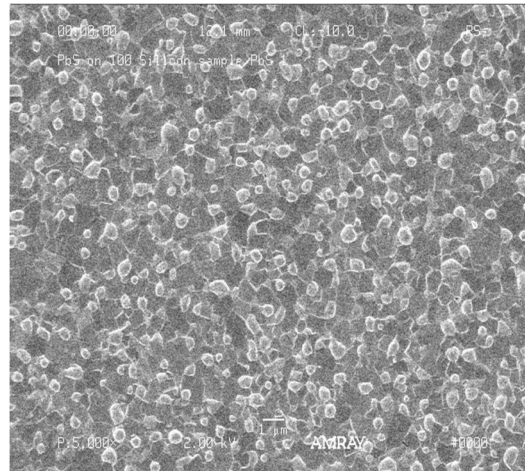
- We cut the Si wafers in 4 pieces
- Several deposition runs were performed using PbSe and tin doped PbSe source materials
- Time of deposition was 5-10 minutes

Present attempt was to study effect of tin on PbSe

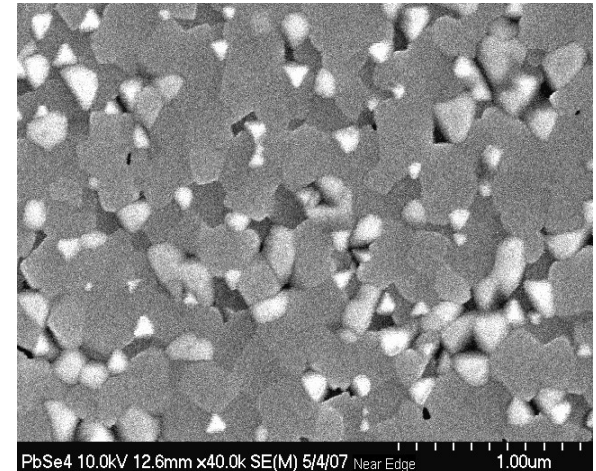
Growth of PbSe, an IR sensing material in two different conditions



a



b

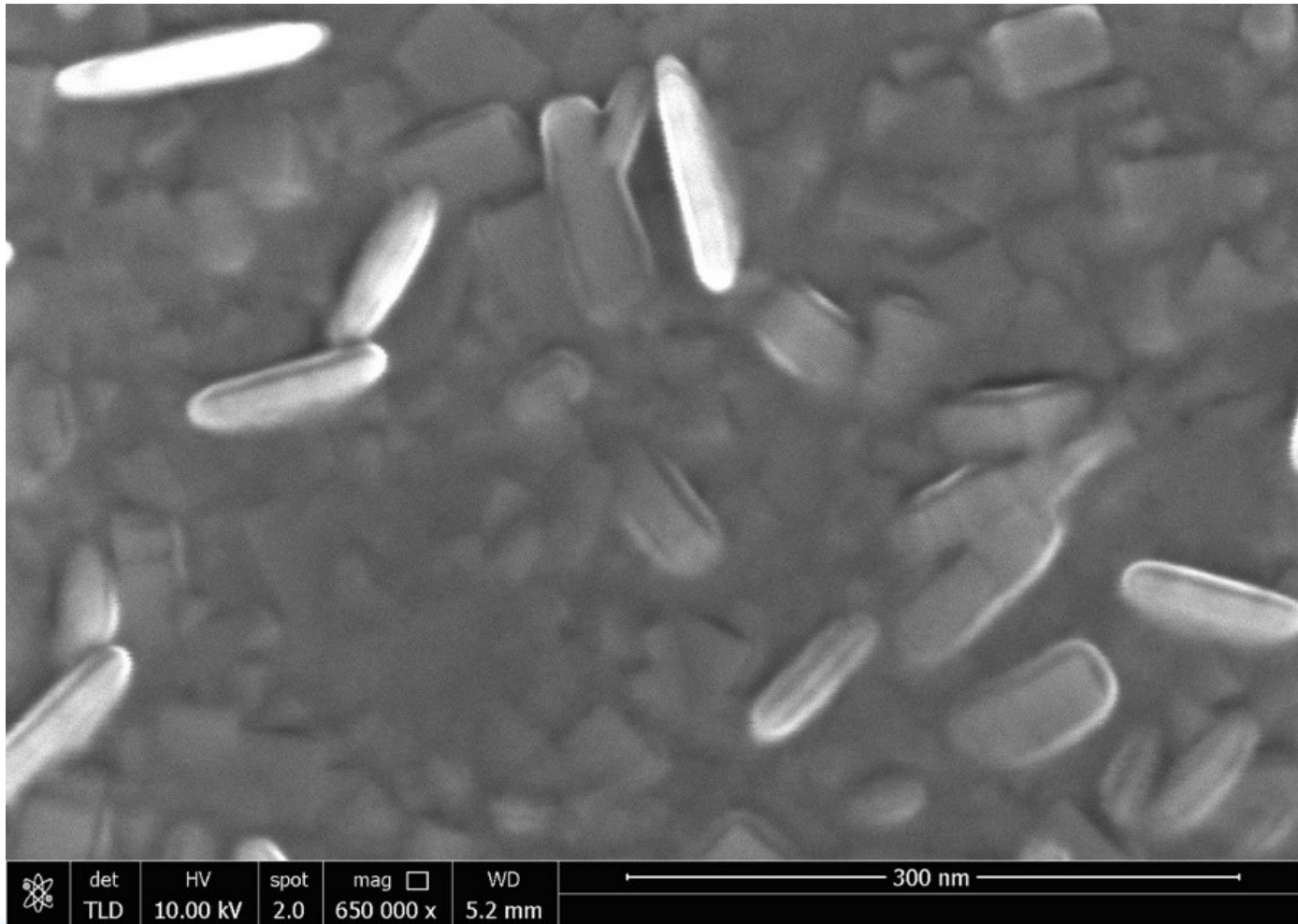


c

- (a) film grown on Silicon substrate
- (b) morphology at low ΔT showing uniform morphology
- (c) large ΔT showing different shaped grains and nonuniformity

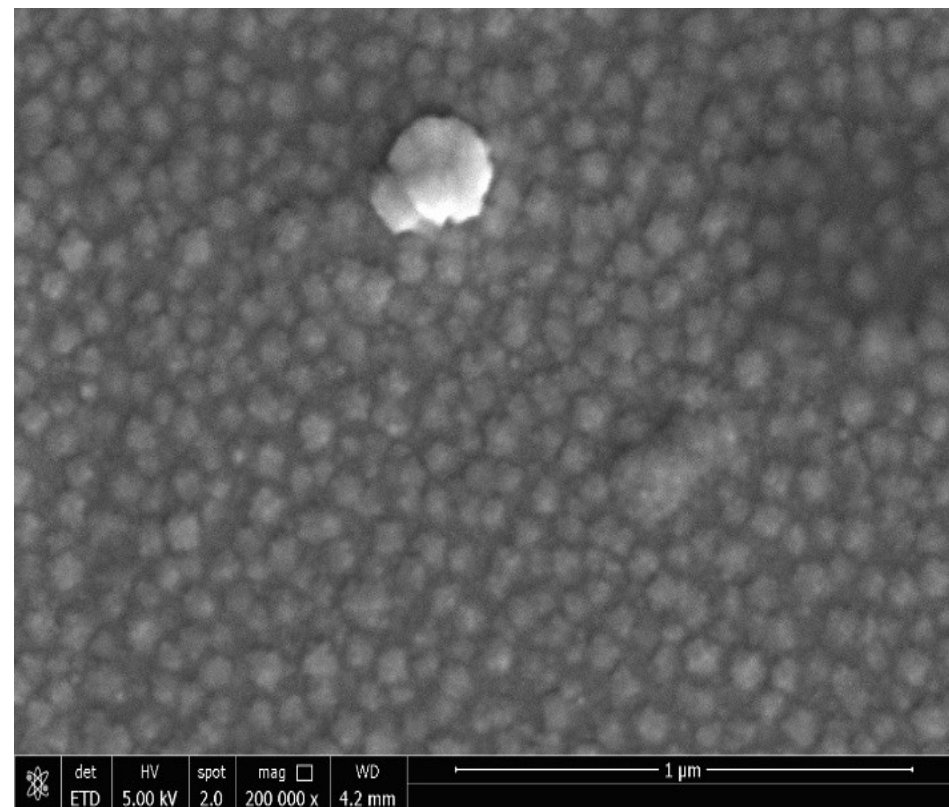
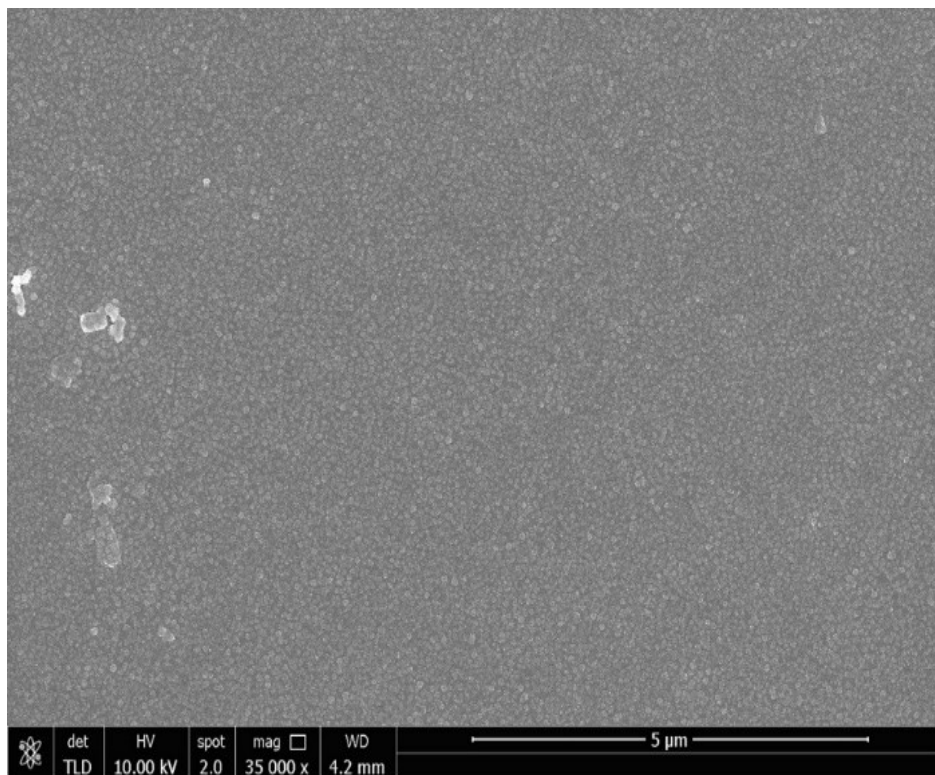
Morphology is different and varies with growth condition

Examples of nanomorphology of pure PbSe material on silicon substrate



***Purity had significant effect on the morphology:,
Elongated morphology on the nanocubes were observed***

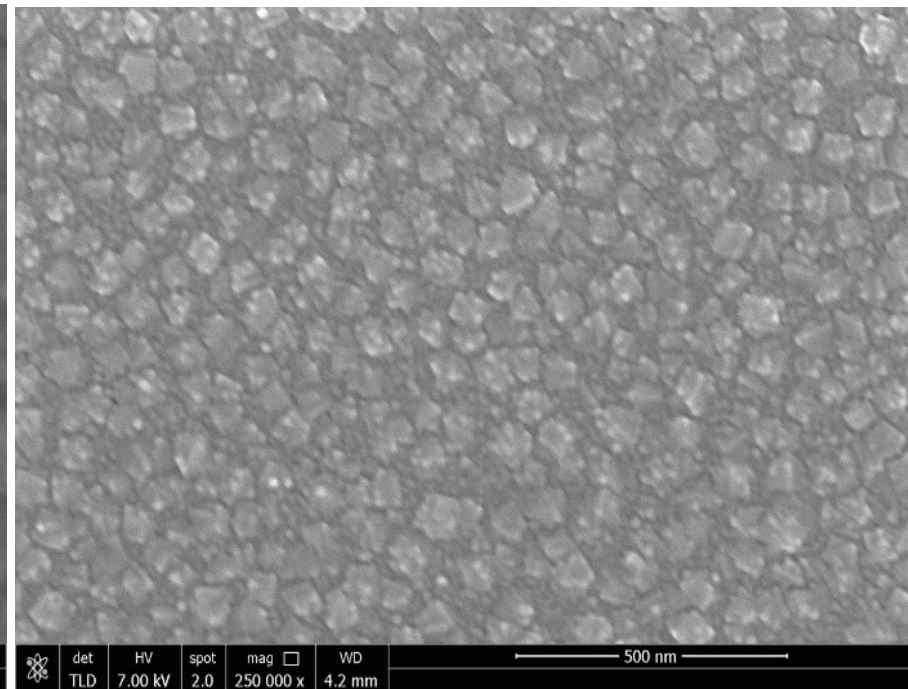
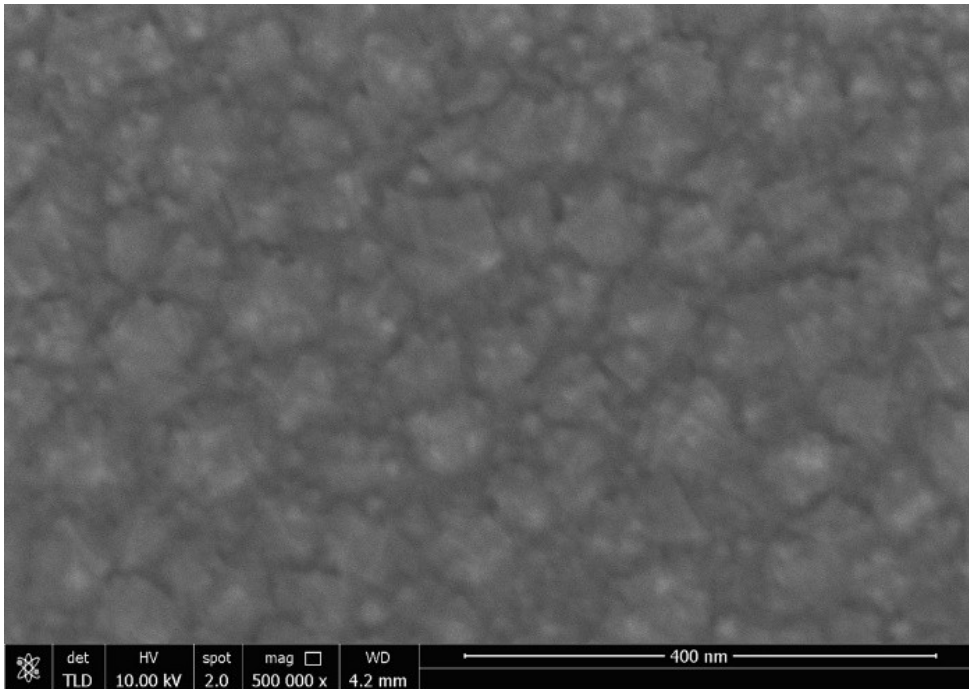
Morphology of PbSe material on silicon substrate: Slight variation in growth condition



Shiny tin rich phases were observed

Change in growth parameters did not change morphology

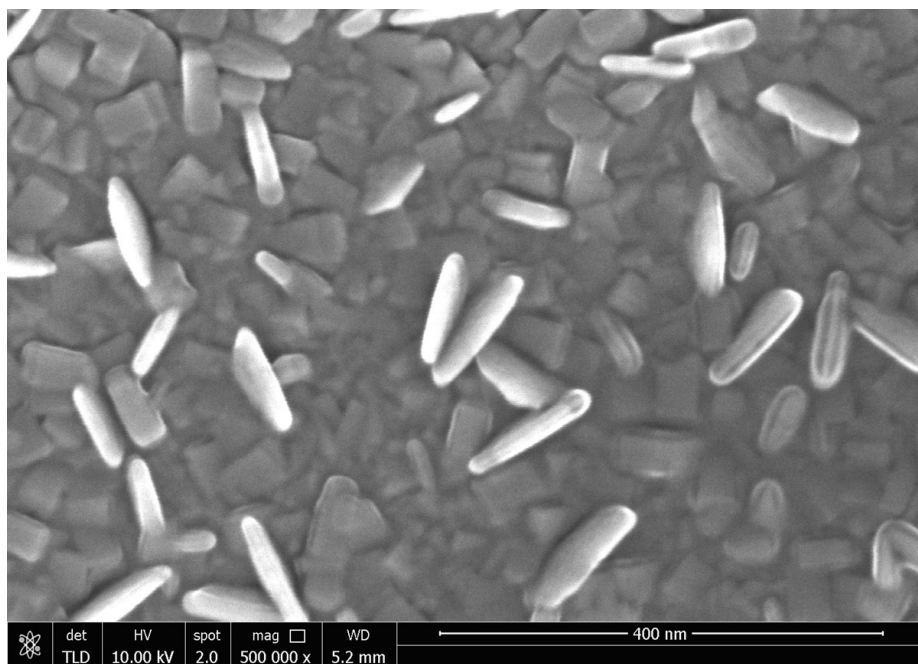
Doping of PbSe changed nanomorphology



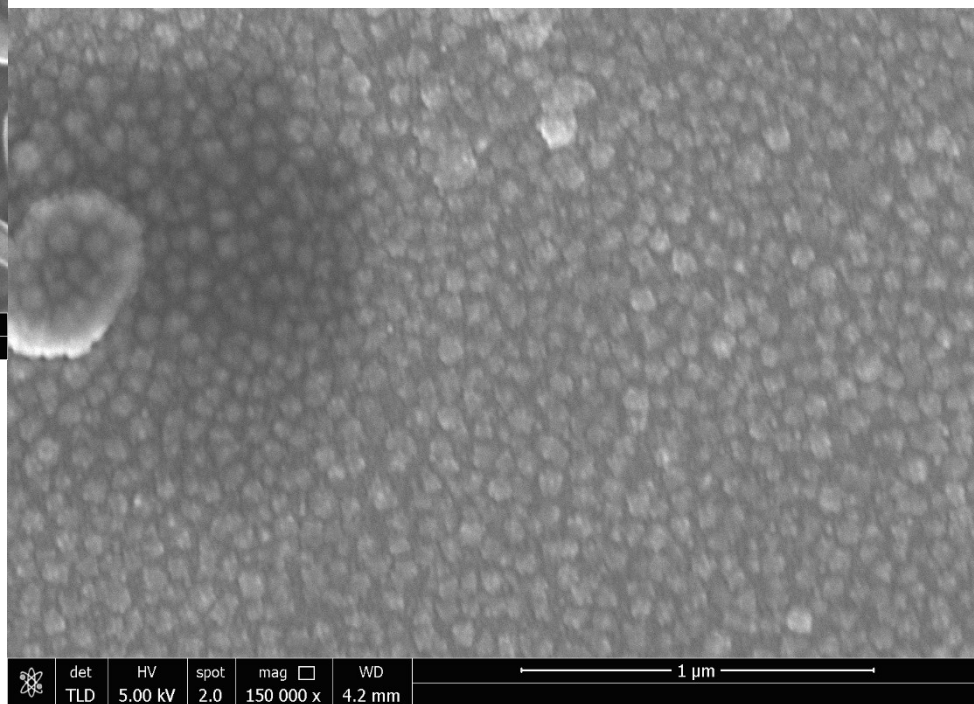
Morphology at two portion of the substrate
There was no sign of cubes or spheres

Annealing also changed the morphology

Nanomorphology of pure and doped PbSe

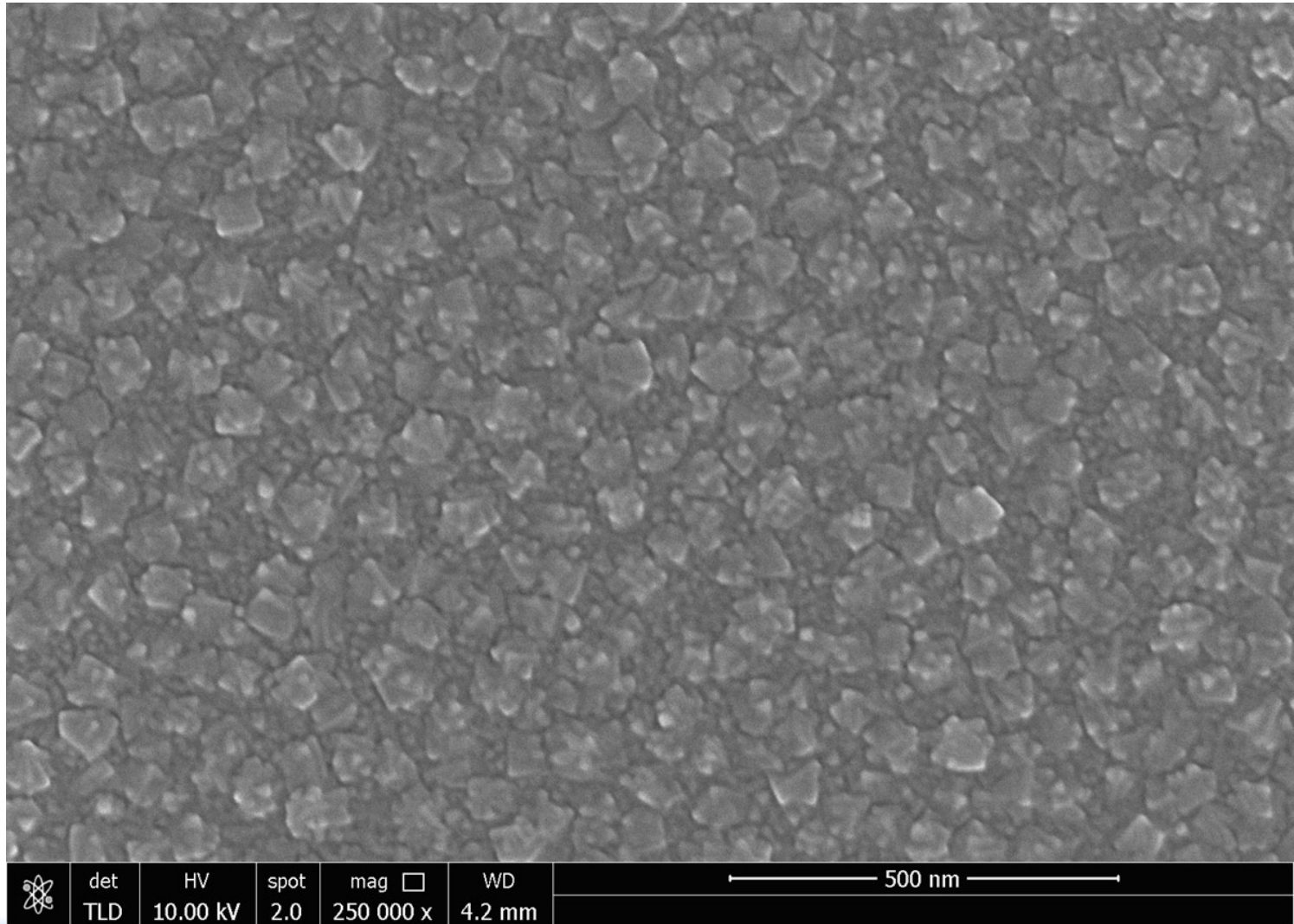


In CdSe doped grains grew on the top of thin films of grains, but morphology did not change



Morphology was different; but did not change

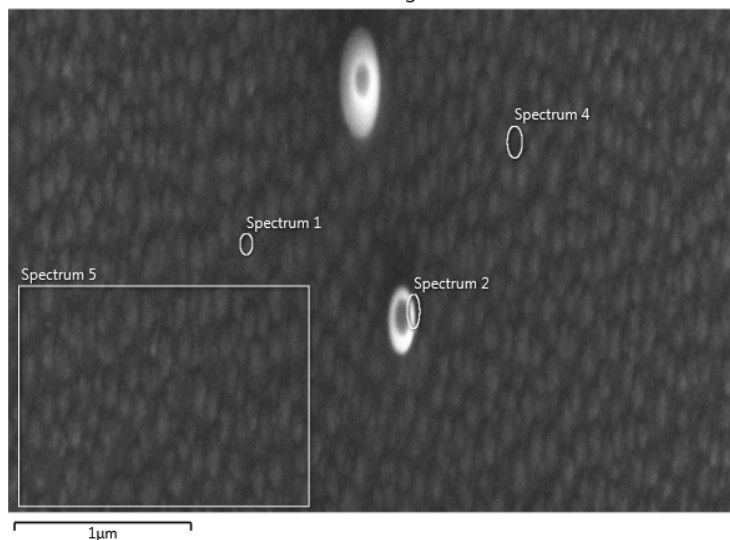
Grains had small instability and anisotropy at interface ; Size up to 50nm



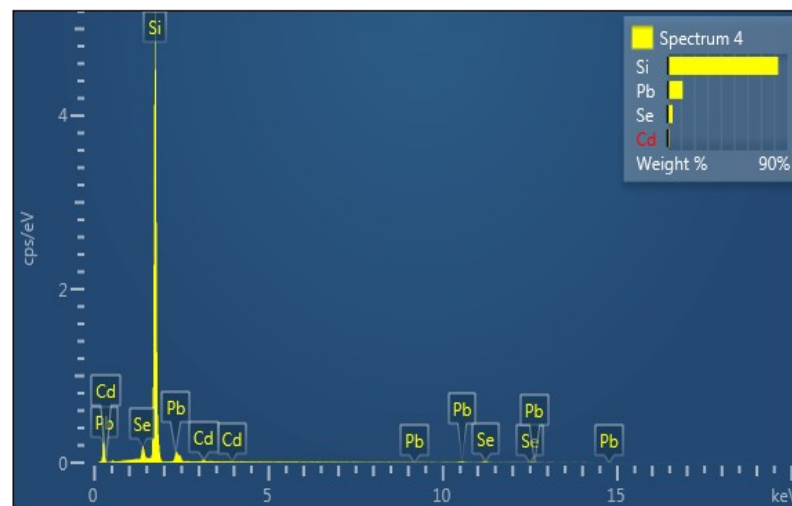
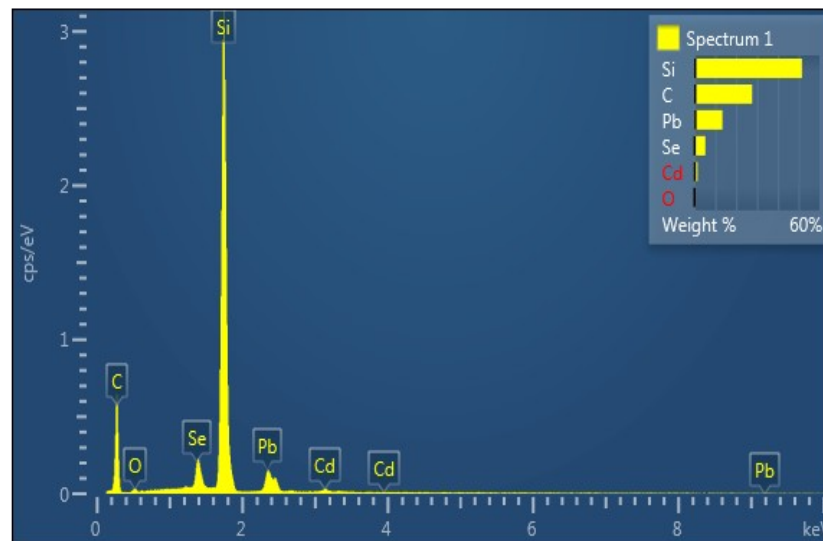
Tin doping had octahedral morphology

Materials spots selected to evaluate for the composition

Electron Image 1



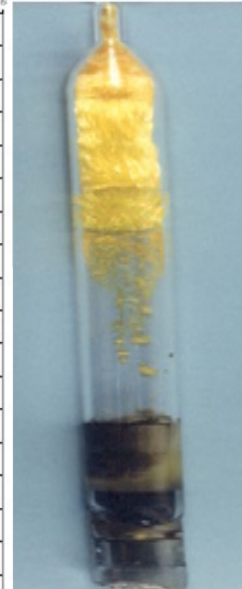
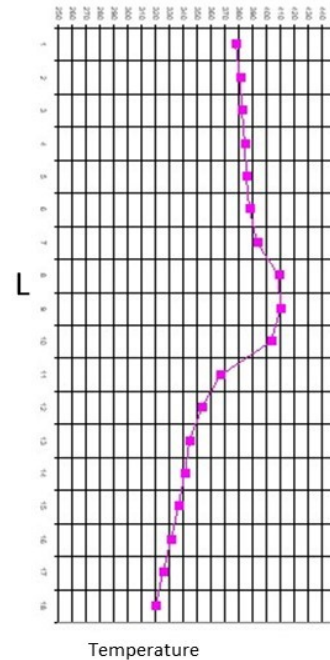
Composition of each components for the selected spots 1 and 4 shown in Figure.



We did not find CdSe rich phases in the matrix

We have furnaces in our laboratory for controlled PVT growth

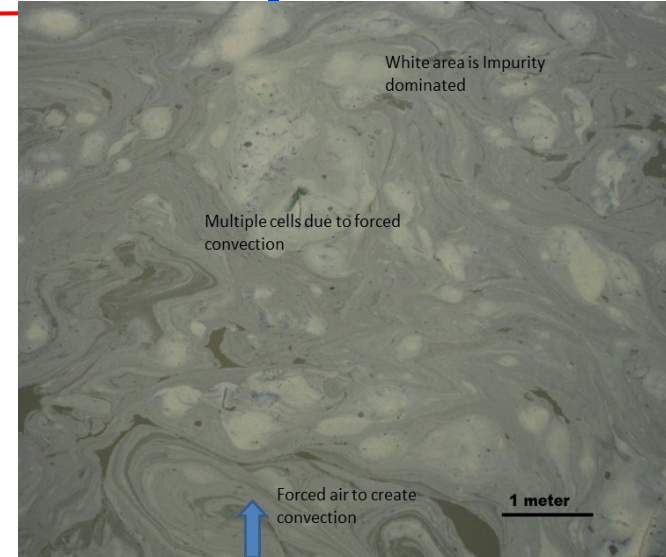
PVT vertical furnace, a typical thermal profile and a grown crystal



Vertical PVT is commonly used for the growth of bio, organic and inorganic material

Nano-, micro-, thin film and bulk crystals can be grown by PVT
Singh et al (>30 papers)

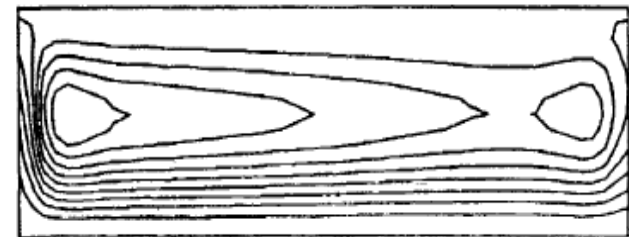
Optimization of PVT: Fluid flow is very important parameter in PVT process



Effect of fluid flow and pattern formation in (a) fire (Bottom hot top cold) and (b) a 15x 20-meter size (1.5-meter-deep) pond created by steady dynamic flow air blowing from bottom



a



b

. Streamline flow for gravity level of (a) $10^{-1}g$ and (b) $10^{-2}g$ in horizontal configuration (Singh et al)

Instabilities can be controlled by modelling fluid flow during PVT

PVT method in controlled condition has shown good quality materials

The velocity profile across the circular duct is derived by substituting the general expression for shear stress into Newton's law of viscosity and integrating by applying the no-slip condition at the wall. The average velocity is defined as:

$$\alpha = \frac{\pi a^4}{8\eta l} (P_s - P_c)$$

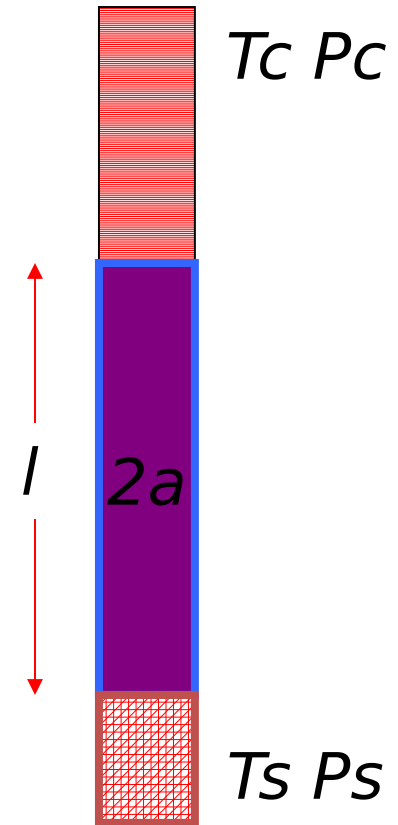
α = Volume Flow Rate

η = Viscosity

Number of Moles per second through cross section

$$N = \frac{\pi a^4}{8\eta l R} \left(\frac{P_s^2 - P_c^2}{T_s + T_c} \right)$$

where $\Delta P = P_s - P_c$, P_s and P_c are the vapor pressure at the source and crystal interfaces, η is the viscosity, $8\eta L a$ result which is Hagen-Poiseuille equation. In spite of the fact that this equation is only applicable to incompressible fluids, one can derive the number of moles, N , flowing each second through the cross sectional area, which is given as:



The model shows that pressure, temperature, path and diameter affects the number of molecules travels from hot to cold end

PVT growth optimization

Velocity Equation

$$V = \frac{9.6a^2 M}{\eta l \rho_s} \left(\frac{P_s^2 - P_c^2}{T_s + T_c} \right)$$

a and l in cm

M in g/mole

η in Poise

ρ_s in g/cm³

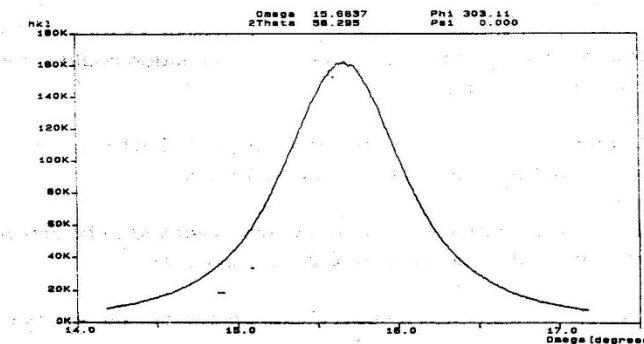
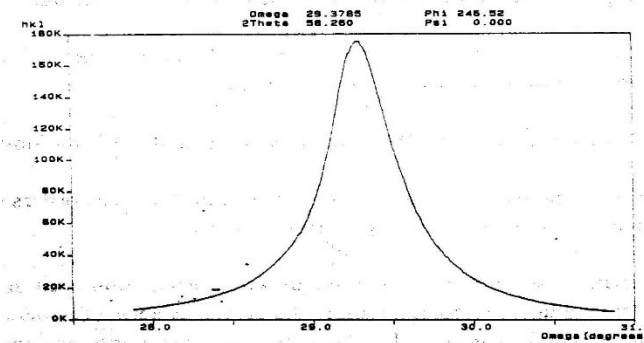
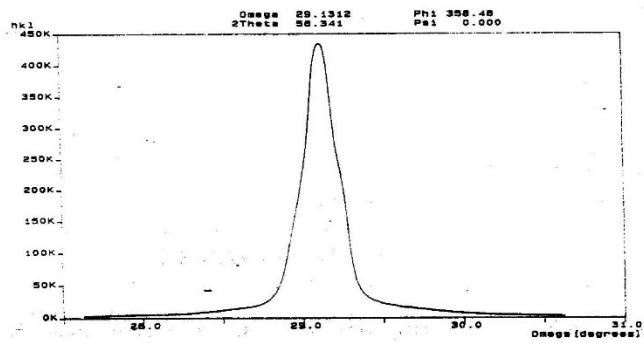
Pc and Ps in Torr

Tc and Ts in K

A growth rate higher than 5 cm/day was predicted.

Growth velocity can be predicted from parameters

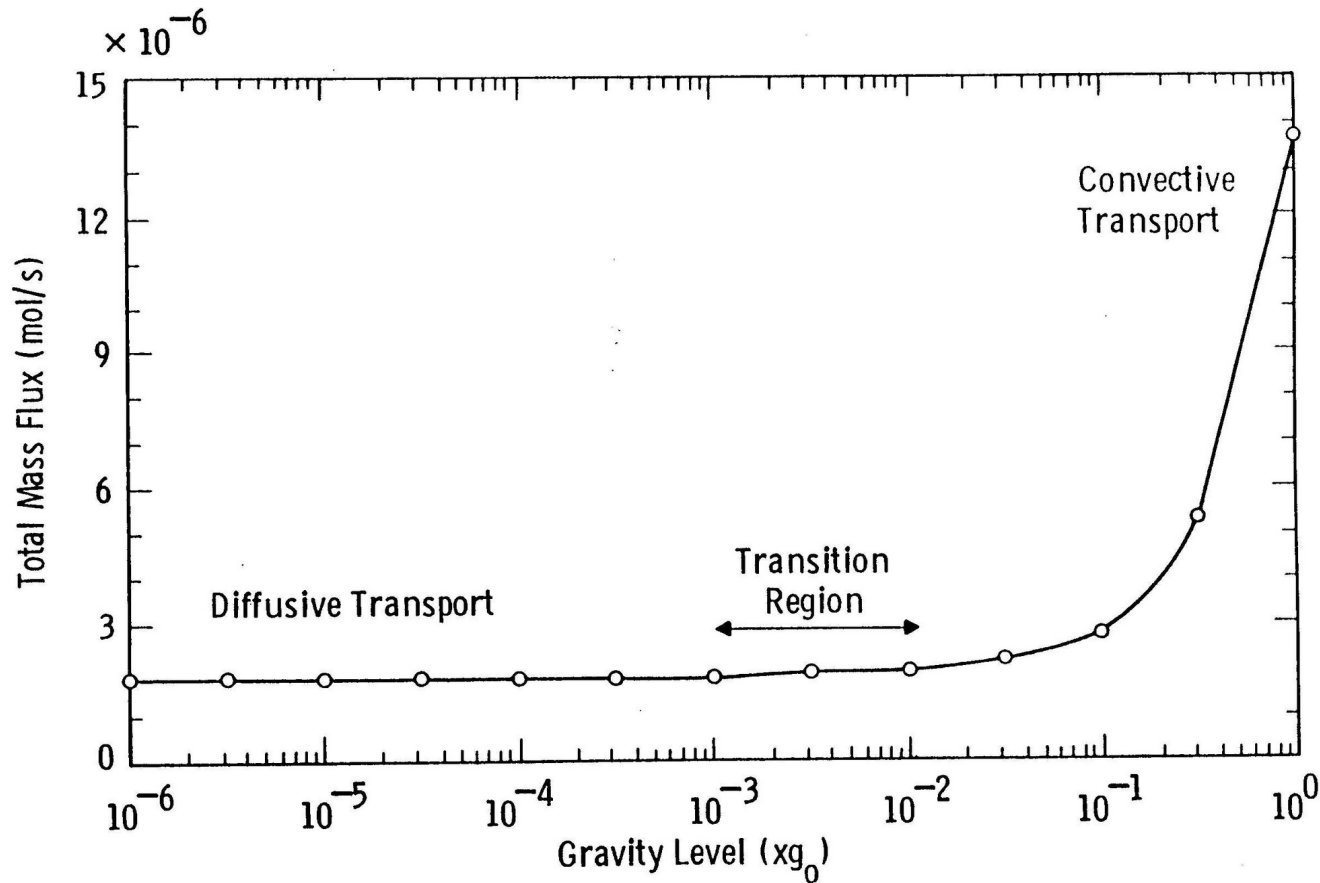
Fluid flow controls quality: X-Ray demonstrates that materials quality decreases if flow increases



Good material grown in very low flow

Flow affects the quality, proven by X-ray FWHM

Gravity controls diffusion: Transport Region as the Function of Gravity Level



For achieving good quality, pure diffusive growth can be achieved in $<10^{-4} g$ level

Summary

- **Controlled PVT method is an excellent method for growth of biosensor materials**
- **Bulk, thin films and nanocrystals can be grown by PVT method**
- **Fluid flow has significant effect on the materials and hence sensors performance**
- **Variety of materials including oxides, selenides, sulfides (major sensor components) can be grown by PVT**
- **Further study to optimization is based on materials for the growth**
- **We have established variety of growth methods and characterization methods for the sensors, lasers, rad detectors and microelectronic materials**

Morphology of material controls the performance of sensors

Thank You Very
Much