

Curriculum Vitae

DR. SUCHETA SENGUPTA

DST-Inspire Faculty Fellow

Amity Institute of Advanced Research and Studies (Materials and Devices)

Amity University, Noida

Previous experience:

2017-2018: Department of Physics, University of Mumbai, Mumbai.

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PERSONAL DETAILS:

DATE OF BIRTH	NATIONALITY	SEX	MARITAL STATUS	LINGUISTIC ABILITY
6 th February, 1984	Indian	Female	Married	English, Bengali, Hindi

WORK EXPERIENCE (Post PhD):

November, 2018-till present: DST Inspire Faculty Fellow, Amity Institute of Advanced Research and Studies (Materials and Devices), Amity University, Noida

February, 2017-October, 2018: DST Inspire Faculty Fellow, Department of Physics, Mumbai University, India

March, 2013-June, 2016: Post doctoral researcher, Department of Materials Engineering, Ben Gurion University, Israel

RESEARCH INTEREST:

Synthesis of hybrid metal chalcogenide nanostructured thin films for different photovoltaic and photothermal activation

EDUCATION:

2013-2016: Post Doctoral Research Associate

Advisor: Professor Yuval Golan

Director, Ilse Katz Institute for Nanoscale Science and Technology, and Professor, Department of Material Engineering, Ben Gurion University of Negev, Israel

2007-2013: PhD, Calcutta University, India

Thesis Title:

OPTICAL MODULATION, ASSEMBLY AND ADVANCED APPLICATIONS OF ULTRA NARROW NANOMATERIALS AND HETEROJUNCTIONS

Thesis Advisor:

Dr. Somobrata Acharya

Centre for Advanced materials,
Indian Association for the
Cultivation of Science, Kolkata,
India

Professor Dipankar Das Sarma

Solid State & Structural
Chemistry Unit,
Indian Institute of Science
Bangalore, India

2005-2007: Post B.Sc Integrated Fellow in Chemical Sciences,

S. N. Bose National Centre for Basic Sciences and Indian Association for the Cultivation of Science, Awarded by West Bengal University of Technology, India

2002-2005: B.Sc (Chemistry (Honours.))

Presidency College, Calcutta University, India

2002: Higher Secondary level (85.2%), Patha Bhavan, Kolkata

2000: Secondary level (88.5%), Gokhale Memorial Girls School, Kolkata

ACADEMIC AWARDS:

2005: Post B.Sc Integrated Fellow in SNBNCBS and IACS

2011: MRSI Young Scientist Award by Material research Society of India, Kolkata Chapter

2012: Post Doctoral Research Fellow under PBC Program for Outstanding Post-doctoral Researchers from China and India

2016: INSPIRE Faculty Award (Material Science), Ministry of Science & Technology, Government of India

PROFESSIONAL PREFACE:

Thirteen years of research experience in chemical synthesis and analysis of high quality metal and semiconductor nanoparticles at relatively high temperature with the decomposition of organometallic precursors. I have also worked about one year on time resolved ultrafast spectroscopy (mainly, TCSPC) during my M.Sc project. The wet lab chemical synthesis in IACS and BGU enabled me to synthesize both high quality metal and semiconductor nanoparticles maintaining proper standards of a chemical laboratory and laboratory safety regulations.

I am also possessing exposure in different instrumental techniques, such as:

- * XRD (Powder X-ray diffractometer by Bruker D8 Advance),
- * PL (Photoluminescence Spectroscopy by Fluoromax 3, Fluoromax 4)
- * TCSPC (Time Correlated Single Photon Counting)
- * UV (Ultraviolet spectroscopy by Shimadzu)
- * ICP-OES (Optical Emission Spectroscopy by Perkin Elmer)
- * FTIR (Fourier Transfer Infra Red Spectroscopy by Nicolet)
- * FE-SEM (Field Emission Scanning Electron Microscopy by JEOL),
- * HRTEM (High Resolution Transmission Electron Microscopy by JEOL)
- * High speed centrifuge
- * Rotary evaporator by EYELA
- * Ultra-sound sonicator
- * Computational techniques

I have also the experience in performing *in-situ* SAXS and GISAXS measurements in synchrotron beamline once in Elettra, Trieste, Italy in November, 2009 and in ESRF, Grenoble, France in April, 2015. The experiments were intended to study the growth mechanism of the colloidal nanocrystals and nanocrystalline epitaxial thin film grown from the solution.

I also maintain close relationship with the maintenance agency such as Perkin Elmer, Alfa aser, Sigma Aldrich, Merck, Rankem (RFCL), Julabo in respect to any fresh order or non-functioning of the instruments. Literature review and survey through **SciFinder**, **ISI Web of Knowledge**, and various journal browsing etc.

Working level knowledge in MS-OFFICE, Chem office, Microcal origin professional, ImageJ, Digital Micrograph, Crystal Maker, Adobe Photoshop, Corel draws, grapher 3, 3D Max etc.

PRESENT JOB DESCRIPTION:

- Taught courses (Surface and thin films) at the post graduation level

- Taught Physics Lab courses (General Physics and Electronics) at the post graduation level
- Setting up state-of-art laboratories with international standard equipment for synthesizing and characterizing semiconductor thin films.

PUBLICATIONS:

1. “An integrated and open-ended experiment: study of chemical waves in time and space”
Deb, B. M. ; Sadhukhan, M. ; Sinha, S. S. ; **Sengupta, S.** ; Biswas, R. *Resonance - Journal of Science Education*, **2008**, 13(1), 54
2. “Shape dependent confinement in ultrasmall zero, one and two dimensional PbS nanostructures”
Acharya, S.; Sarma, D. D.; Golan, Y.; **Sengupta, S.**; and Ariga, K. *J. Am. Chem. Soc.*, **2009**, 128, 9294
3. “Long-Range Visible Fluorescence Tunability Using Component-Modulated Coupled Quantum Dots”
Sengupta, S.; Ganguli, N.; Dasgupta, I.; Sarma, D. D.; Acharya, S. *Advanced Materials*, **2011**, 23, 1998
(Highlighted in Nature India doi:10.1038/nindia.2011.68)
4. “Coalescence of magic sized CdSe into rods and wires and subsequent energy transfer”
Sengupta, S.; Sarma, D. D.; and Acharya, S. *J. Mater. Chem.*, **2011**, 21, 11585
5. “ZnS nanorod as an efficient heavy metal ion extractor from water”
Malakar, A.; Das, B.; Sengupta, S.; Acharya, S.; and Ray, S., *J. Water Process Eng.*, **2014**, 3, 74-81.
6. “Insitu monitoring the role of citrate in chemical bath deposition of PbS thin films”
Sengupta, S., Perez, M., Rabkin, A. and Golan, Y. *CrystEnggComm*, **2016**, 18, 149
7. “Chemical epitaxy and interfacial reactivity in solution deposited PbS on ZnTe”
Sengupta, S., Templeman, T., Chen, C., Moon, E., Shandalov, M., Ezersky, V., Phillips, J. and Golan, Y. *J. Mater. Chem. C*, **2016**, 4, 1996
8. “Chemical Tailoring of Band Offsets at the Interface of ZnSe–CdS Heterostructures for Delocalized Photoexcited Charge Carriers”
Dalui, A., Chakraborty, A.; Thupakula, U.; Khan, A. H.; **Sengupta, S.**; Satpati, B.; Sarma, D.D.; Dasgupta, I. and Acharya, S. *J. Phys. Chem. C*, **2016**, 120, 10118
9. “The effect of short chain thiol ligand additives in chemical bath deposition of lead sulphide thin films: the unique behaviour of 1,2-ethanedithiol”
Sengupta, S.; Loutaty, H.; Petel, K.; Levin, E.; Lemcoff, G. and Golan, Y. *CrystEnggComm*, **2016**, 18, 9122

10. "Oriented Attachment: a Path to Columnar Morphology in Chemical Bath Deposited PbSe Thin Films" Templeman, T.; **Sengupta, S.**; Maman, N.; Bar-or, E.; Shandalov, M.; Ezersky, V.; Yahel, E.; Sarusi, G.; Visoly-Fisher, I.; Golan, Y. *Crystal Growth & Design*, **2018**, 18 (2), 1227
11. "Chemical bath deposition of CdS thin films – Effect of complexing agents at lower pH" **Sengupta, S.** and Jain, V. K. (communicated) (Thin Films and Solids)
12. "Potential of CdS- Silicon nanowire heterojunction device as hygroelectric cells" **Sengupta, S.**, Kumar, A., Verma, A., Dhasmana, H. and Jain, V. K. (in preparation)
13. "Comprehensive study on the effect of different complexing agents during chemical bath deposition of metal chalcogenide thin films" **Sengupta, S.**, Aggarwal, R., Jain, V.K. and Golan, Y. (in preparation)
14. "On the probable mechanism of hierarchical assembly of ZnS in ODA matrix exploring in situ SAXS" **Sengupta, S.**; Santra, P.; Sarma, D. D.; and Acharya, S. (in preparation)
15. "Coalescence of ZnS wires into ultrathin wide surface nanosheets" **Sengupta, S.**; Thupakula, U.; Bal, J. K.; Sarma, D. D.; and Acharya, S. (in preparation)

CONFERENCE PROCEEDINGS:

1. "Tuning of Long range Visible Emissions Using Coupled Quantum Dots" Sengupta, S., Ganguli, N., Dasgupta, I., Sarma, D. D. and Acharya, S. *AIP Conf. Proc.* **2011**, 1349, 277

CONFERENCES/ SEMINAR ATTENDED:

1. **Poster presentation** at XXth International Workshop on the Physics of Semiconductor Devices (IWPSD-2019) held at Kolkata, India (December 17-20, 2019), Poster Title: Optimizing II-VI semiconductor heterojunction thin films by chemical bath deposition for photovoltaic and sensor applications (**Dr S. K. Agarwal Memorial Award 2019 for Best Poster Award**)
2. **Poster presentation** at 5th *International Nanotechnology Conference & Exhibition (NanoIsrael 2016)* held at Tel-Aviv, Israel (February 22-23, 2016), Poster Title: Chemical epitaxy and reactivity in solution deposited PbS on ZnTe for potential use in solar cells
3. **Poster presentation** at 4th *International Nanotechnology Conference & Exhibition (NanoIsrael 2014)* held at Tel-Aviv, Israel (March 24-25, 2014), Poster Title: Shape Dependent Confinement In Ultrasmall Zero, One, and Two Dimensional PbS Nanostructures.

4. **Oral presentation** at *Young Scientist Colloquium, MRSI Kolkata Chapter* held at IACS, Kolkata, India (August 04, 2011) Title: Asymmetric Coupled Heterostructures, Superlattices and Shape Evolution of Self Assembled Nanomaterials (**MRSI Young Scientist Award for best presentation**).

5. **Poster presentation** at International Conference on fundamental & applications of nano science & technology held at Jadavpur University, Kolkata, India (December 9-11, 2010), Poster Title: Synergistic tunability of Long Range Visible Fluorescence Using Component Modulated Coupled Quantum Dots

6. **Poster presentation** at 55th DAE Solid State Physics Symposium held at Manipal University, Karnataka India (December 26-30, 2010), Poster Title: Tuning of Long range Visible Emissions Using Coupled Quantum Dots

NAME AND ADDRESS OF THE REFEREES:

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In situ monitoring the role of citrate in chemical bath deposition of PbS thin films

Sucheta Sengupta, Maayan Perez, Alexander Rabkin and Yuval Golan*

Trisodium citrate (citrate) has been commonly used as a co-complexing agent during chemical bath deposition to improve film quality and control grain size, yet its precise role has not been elucidated to date. In this study, we have focused on the role of citrate in chemically deposited PbS thin films. Citrate effectively complexes the lead cation in solution thereby decreasing growth rate and inducing growth in the cluster mechanism. This was monitored in real time using laser light scattering and UV-vis absorption spectroscopy which quantitatively confirmed the retarded PbS formation in the cluster mechanism in the presence of citrate. Nano-crystalline PbS films formed in the presence of citrate show quantum confinement effects with blue shifted optical properties compared to the bulk, adding an important path for controlling film properties towards future infrared optoelectronic applications.

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Introduction

Chemical bath deposition (CD) is by far the most effective method for reproducibly producing high quality semiconductor thin films.¹ Early studies focused on deposition of lead chalcogenide (PbS, PbSe) thin films by CD due to their technological importance as infrared radiation detectors and emitters predicted as early as 1964.^{2,3} Particularly, lead sulfide (PbS) has been the subject of considerable research due to its direct narrow bandgap energy (0.41 eV) and large exciton Bohr radius (18 nm) and useful optoelectronic properties for infrared detection and emission.^{4–6} Deposition of thin PbS films on GaAs provides the means for integration of PbS in optoelectronics with GaAs based technology.

We have previously showed that control over the microstructure of PbS thin films on GaAs (100) can be achieved by optimizing the deposition time, deposition temperature and the concentrations of the reactants present in the bath.^{7–9} PbS was deposited from a highly alkaline aqueous solution where the NaOH, besides affecting the rate of thiourea decomposition, also effectively complexes the Pb²⁺ metal ions. Trisodium citrate (citrate) has been commonly used as a co-complexing agent during CD especially for metal cations such as zinc (Zn²⁺) and tin (Sn²⁺) to produce high quality films with better uniformity and decrease in the grain size.^{10,11} In the particular case of PbS, it was observed that an increase in the concentration of citrate resulted in increased

film uniformity and decrease in the crystallite size, with the citrate ions being present as the functional group in the PbS film.^{12–14} In the presence of citrate, the hydroxyl citrate complex of Pb [Pb(OH)(cit)][−] (with variable co-ordination number depending on the pH of the solution¹⁵) would be expected to decompose differently from the common Pb-hydroxide complex. Thus, it would be important to study the effect of the co-complexant on film growth which can provide control over the growth mechanism and result in different film morphologies and physical properties.

The mechanism involved in the CD process is quite intriguing and holds the key for controlling film morphology. Generally, the role of the complexing agent is to bind with the metal ions to prevent rapid reaction and precipitation of the metal hydroxide; hence, in the absence of a complexant there is excessive and rapid precipitation with little or no film formation. The metal complex allows the slow release of the free metal ion to react with the slowly generated anion (usually formed by the controlled hydrolysis of the precursor) directly onto the substrate, a process commonly known as the ion-by-ion mechanism. Alternatively, the film growth can also occur by migration and adsorption of colloidal particles of either the metal chalcogenide, the metal hydroxide or the insoluble metal complexes generated in the solution onto the substrate, a process commonly known as the cluster mechanism. The change in the mechanism is manifested in a shift from the formation of a highly oriented monocrystalline film to a nano-crystalline cluster. Hodes *et al.* have previously demonstrated that this changeover in the mechanism can be affected by a change in the metal-complex ratio.^{16,17} They described that there is a particular critical ratio (R_c) between

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Chemical epitaxy and interfacial reactivity in
solution deposited PbS on ZnTeSucheta Sengupta,^a Tzvi Templeman,^a Chihyu Chen,^b Eunseong Moon,^b
Michael Shandakov,^c Vladimir Ezersky,^a Jamie Phillips^b and Yuval Golan^a

Despite their promise, the efficiency of quantum dot solar cells is currently low (<10%), where an improved understanding of interfaces and contact layers adjacent to the quantum dots is presently a major limitation. The present work aims at optimizing the conditions for growing PbS thin films on ZnTe in light of the solubility of ZnTe in the alkaline environment required for chemical bath deposition of PbS. The morphology and properties of these films are strongly affected by altering the solution pH, temperature and the reagent concentrations. A detailed structural and chemical analysis reveals the different orientation relationships present between the constituent layers and highlights the spontaneous formation of new, distinct intermediate layers in the unique local environment formed due to the simultaneous dissolution of the ZnTe layers in the presence of precursors for PbS thin film deposition.

Introduction

Lead chalcogenides have been the subject of considerable earlier research due to their unique optical and electronic properties and their technological importance for infrared radiation detection and emission and solar cells.^{1,2} Lead chalcogenide quantum dots are particularly suitable for incorporation into energy conversion architectures and are fundamentally interesting in light of their unusual photophysics.^{3,4} Analysis of the natural abundance of materials for solar cells shows that bulk PbS ranks favorably in terms of the cost and abundance of raw materials.⁵ Of the several techniques for fabricating high quality PbS thin films, chemical bath deposition is one of the simplest and cost effective methods. Chemically deposited PbS thin films can be easily integrated on almost any substrate and their band gap energy can be tuned from 0.41 eV of the bulk material to 0.8 eV in a shorter wavelength depending on the grain size due to the quantum confinement effect.^{6–12} PbS is a good alternative to other narrow band gap semiconductors for integration in electric and optoelectronic devices due to its relatively large Bohr radius of 18 nm so that quantum confinement effects can take place at a relatively large grain size.

Among alternative approaches to improve the efficiency of photovoltaic devices, the most notable is the multi-junction

(MJ) solar cell.^{13–15} MJ devices consist of stacked semiconductor junctions built in tandem; thus, material band gaps are tuned across a wide range of wavelengths in the solar spectrum. Since the constituent junctions can efficiently extract power from the different portions of the solar spectrum, their power conversion efficiency are much higher compared to single junction solar cells. Quantum dot solar cells also show promise, but their power conversion efficiency is currently low (<10%), where an improved understanding of interfaces and contact layers adjacent to the quantum dots is presently a major limitation. Layered structures of nanocrystalline thin films based on PbS quantum dot absorbers, along with electron and hole blocking layers based on compatible II–VI semiconductors, have been recently designed for improved solar cell efficiency.^{14–16} ZnTe is well suited as a selective contact for holes on one side with properties quite similar to CdTe (a well-established material in thin film solar cell technology) and highly compatible crystalline and electronic structure. Literature reports suggest that the epitaxial growth of PbSe on GaAs (211)B or Si(211) may be achieved using ZnTe as a buffer layer.^{17,18} Improvement in optical properties, minority carrier lifetimes, and interface quality may be possible using PbSe/ZnTe structures to provide enhancement in solar energy conversion.

Chemical bath deposition (CBD) offers a simple and cost effective method for the fabrication of high quality semiconductor films. Literature reports suggest the growth of epitaxial PbS single crystal films,^{19,20} where the term chemical epitaxy refers to the presence of a well-defined crystalline relationship between the CBD single crystal film and the substrate. Although epitaxy usually requires a certain degree of lattice match between the semiconductor film and substrate, chemical interactions between

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^b Department of Electrical Engineering and Computer Science, The University of Michigan, Ann Arbor, Michigan 48106, USA

^c Department of Physics, Nuclear Research Center Negev, Israel

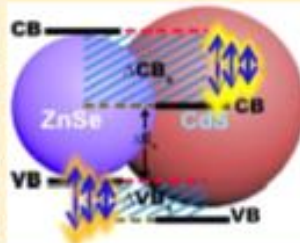
† These authors contributed equally to this work.

Chemical Tailoring of Band Offsets at the Interface of ZnSe–CdS Heterostructures for Delocalized Photoexcited Charge Carriers

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Supporting Information

ABSTRACT: Monocomponent quantum dots (QDs) possess limited electron–hole delocalization capacity upon photoexcitation that suppresses the efficiency of photomemory harvesting devices. Type II heterostructures offer band offsets at conduction and valence bands depending upon the band gaps of the constituent QDs which largely depend on their sizes. Hence, by keeping the size of one constituent QD fixed while varying the size of the other QD selectively, the band offsets at the interface can be engineered selectively. We report on the tuning of band offsets by synthesizing component size modulated heterostructures composed of a fixed sized ZnSe QD and size-tuned CdS QDs with variable band gaps. The resultant heterostructures show spontaneous charge carrier separation across the interface upon photoexcitation depending on the extent of band offsets. Formation mechanism, epitaxial relationship, and the intrinsic nature of interface of the heterostructures are investigated. Experimental results are corroborated with *ab initio* electronic structure calculations based on density functional theory. Spontaneous charge carrier delocalization across the interface depends on the magnitude of band offsets, which facilitates fabrication of QD sensitized solar cells (QDSSCs). Improved device performances of QDSSCs in comparison to the limited photon-to-current conversion efficiencies of monocomponent QDs demonstrate the significance of band offsets for natural charge carrier separation.



INTRODUCTION

Heterostructures composed of chemically distinct semiconductor components are unique class of materials suitable for a number of applications based on the principle of charge carrier migration mechanism at the interface.^{1–10} Unlike tuning the electronic properties by changing the size or shape of monocomponent nanocrystals,^{9,11} the electronic properties of heterostructures rely on the energy states at the interface.^{1,6–11} Heterostructures consisting of two different monocomponent semiconductor quantum dots (QDs) possesses band offsets at conduction band (CB) and valence band (VB) depending upon the relative alignments of the energy levels. The presence of band offsets results in a spatially indirect band gap for type II heterostructures which is smaller than the band gaps of both constituent QDs. The band offsets at the CB and VB are determined by the band gaps of the constituent QDs which largely depends on the sizes of the QDs.^{12–25} Hence, by varying the size of one of the constituent QDs while retaining the other size unchanged, the band offset at the interface can be tuned selectively. Such nanostructures allow spontaneous charge carrier (electron and hole) delocalization across the interface depending on the band offset retarding the charge

recombination, which is beneficial for photovoltaic applications.^{26–28} Additionally, superior band gap tunability, in comparison to the monocomponent QDs, can be achieved in heterostructures depending upon the extent of band offsets leading to improved photon conversion efficiencies in the solar spectrum. Both the band offset and band gap tunable features are beneficial for fabricating QD sensitized solar cells (QDSSCs) where electron injection rates into oxides or hole transport in the QD/radon electrolyte plays the key role for improving device efficiencies.^{29–34} However, creating such heterostructures with selective band offset at the interface is synthetically challenging.

We report on the band offset control at the interface by synthesizing a fixed sized ZnSe QDs (~4.5 nm) and three different sized CdS QDs (2.6, 4.2, and 5.6 nm). Synthesis of size-tuned CdS QDs allowed us varying the band gaps of CdS component selectively while the fixed size of ZnSe QDs predefines the band gap of the other component within the hetero-

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The effect of short chain thiol ligand additives on chemical bath deposition of lead sulphide thin films: the unique behaviour of 1,2-ethanedithiol

 Sucheta Sengupta,* Rachel Loutaty,* Keren Petel,* Efrat Levin,^b
 N. Gabriel Lemcoff^b and Yuval Golan**

Chemical bath deposition is an effective method for depositing semiconductor thin films with a wide range of compositions and microstructures. While it is widely accepted that organic additive molecules can play a very important role in chemical bath deposition, their role has not been systematically studied. In the present work, we have comparatively studied the effect of four common water-soluble molecules, 1,2-ethanedithiol, mercaptosuccinic acid, cysteamine and mercaptoethanol, on the chemical bath deposition of lead sulfide. The effect of 1,2-ethanedithiol was shown to be markedly different, resulting in a significantly increased film thickness. We show the effect of each additive on the growth rate, microstructure and optical properties, and provide insights on their mechanism of operation.

Introduction

Chemical bath deposition (CBD) is a popular cost effective process for production of high quality and potentially useful semiconductor thin films.¹ Literature reports suggest significant improvement in optimization of the growth of different metal chalcogenides of which lead sulfide (PbS) is of particular importance since it has a narrow band gap energy (0.41 eV) and large exciton Bohr radius (18 nm) and has useful optoelectronic properties for infrared detection.^{2–4} Deposition of PbS thin films on GaAs provides the means for integration of PbS IR optoelectronics with GaAs based technology.

Earlier studies from our group suggest that by varying the deposition time, deposition temperature and the concentrations of the reactants, a variety of microstructures of PbS over the GaAs (100) substrate can be achieved.^{5–7} PbS is usually deposited from an alkaline aqueous solution where the NaOH, besides affecting the rate of thiourea decomposition, also effectively complexes the Pb²⁺ metal ions. The metal complex allows the slow release of the free metal ion to react with the slowly generated anion (usually formed by the controlled hydrolysis of the precursor) directly in the substrate, a process commonly known as the ion-by-ion mechanism.⁸ Alternatively, film growth can also occur by migration and adsorption of colloidal particles of the metal chalcogenide, the

metal hydroxide or the insoluble metal complexes generated in the solution onto the substrate, a process commonly known as the cluster mechanism.⁹ The mechanism involved in the CD process holds the key for controlling the film morphology. The change in the mechanism is manifested in a shift from the formation of a highly oriented monocrystalline film to a nanocrystalline cluster. Our recent study has shown that the presence of a co-complexant like citrate ions in addition to the hydroxide in the growth solution has a prominent effect on the CD of PbS thin films.⁸ For conditions favoring film growth via the cluster mechanism, the presence of citrate results in a strong texturing along the (100) direction along with a substantial increase in the activation energy which results in retardation of the rate of cluster formation in solution and hence a smaller film thickness. Upon increasing the temperature and the pH, the ion-by-ion mechanism becomes dominant and the citrate has less influence on the deposition and on the resulting film morphology.

While it is well accepted that the presence of surface-active molecules in solution can greatly affect the deposition, there are very few reports on their effect on chemical bath deposition.^{10,11} Literature reports suggest that the presence of surfactants in the standard CBD bath resulted in a reduction in the rate of deposition and an increase in the terminal thickness.¹⁰ The possible explanation that was suggested was that surfactants adsorb onto surfaces (both the substrate and colloidal particles in the solution) resulting in a retarded growth rate. Simultaneously, the adsorption of the surfactant onto colloidal particles can also prevent rapid flocculation and precipitation, thereby increasing the precursors available for deposition and hence resulting in increasing the terminal

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Oriented Attachment: A Path to Columnar Morphology in Chemical Bath Deposited PbSe Thin Films

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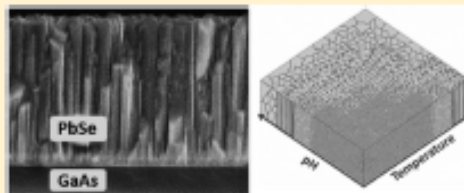
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Supporting Information

ABSTRACT: We have studied columnar PbSe thin films obtained using chemical bath deposition. The columnar microstructure resulted from an oriented attachment growth mechanism, in which nuclei precipitating from solution attached along preferred crystallographic facets to form highly oriented, size-quantized columnar grains. This is shown to be an intermediate growth mechanism between the ion-by-ion and cluster growth mechanisms. A structural zone model depicting the active growth mechanisms is presented for the first time for semiconductor thin films deposited from solution. The columnar films showed well-defined twinning relations between neighboring columns, which exhibited 2D quantum confinement, as established by photoluminescence spectroscopy. In addition, anisotropic nanoscale electrical properties were investigated using current sensing AFM, which indicated vertical conductivity, while maintaining quantum confinement.



INTRODUCTION

Thin films with tailored microstructure for desired anisotropic physical properties play an important role in many fields of technology. Applications, such as magnetic storage media, optical components (birefringent filters, tunable laser mirrors, linear polarizers, etc.) and gas sensors, all rely on microstructural control for their unique anisotropic physical properties.^{1–4} The potential for directly grown anisotropic film growth is quite promising as it cuts back on both time and costs of post growth processing, which would otherwise be required. With the emergence of nanotechnology-based applications, there has been increasing interest in complex nanoscale structures and their incorporation into state-of-the-art devices.^{1–7} Applications relying on nanoscale components require control over the growth mechanisms, achievable by understanding the fundamental processes leading to nanostructured films. Mass production of nanoscale devices will always prefer simplicity and lower costs relative to the conventional, currently available growth methods.

To date, the most commonly used technique for the growth of structured films is physical vapor deposition (PVD), which originates as far back as 1886.⁸ Growth of columnar thin films (CTF) has been achieved by controlling the angle of incident vapor flux while maintaining low temperature and pressure. Ordered growth of CTF requires control over the arriving

atoms, namely surface diffusion length, angular distribution, and incoming flux angle, which are all crucial for achieving columnar microstructure.^{9,10} Predicting film microstructures based on deposition parameters has been demonstrated by the structural zone model (SZM), established by Thornton for films deposited using PVD.⁹ Thornton presented a general model describing the effect of growth conditions in PVD, in which CTF was achieved by maintaining low substrate temperatures and low chamber pressure. Both of these conditions resulted in low adatom mobility, preventing lateral grain growth. However, high values of angle distribution of the incoming vapor flux and adatom angle of incidence might still perturb CTF growth by self-shadowing effects, where the growing columns prevent adatoms from reaching neighboring grains and expanding. Maintaining both low adatom surface mobility and a uniform angular distribution will result in well-ordered CTF. An alternative, simpler and less expensive technique for the growth of columnar thin films is by chemical solution deposition.

Chemical solution deposition (CD) is one of the simplest and least expensive methods for the growth of high quality thin films.^{11–14} In contrast to PVD, CD does not require stringent

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