CHARACTERIZATION OF CHARGE CARRIER BEHAVIORS IN II-VI AND IV-VI

NANOCRYSTAL ASSEMBLIES

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To my family

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ABSTRACT

CHARACTERIZATION OF CHARGE CARRIER BEHAVIORS IN II-VI AND IV-VI NANOCRYSTAL ASSEMBLIES Qinghua Zhao

Cherie R. Kagan

Nanostructures (NSs), including nanocrystals (NCs), nanowires (NWs), and nanosheets, are composed of inorganic cores with size <100 nm in at least one dimension. Their electronic structure and properties can be tailored by size and shape. NSs can serve as building blocks to create functional NS assemblies, with coupling from weak to strong by controlling the interparticle distance. In strongly coupled NC assemblies, properties emerge from collective interactions and offer great opportunities for designing materials with properties inaccessible in materials 'on the shelf'. For semiconductors NSs with applications in electronics and optoelectronics, it is important to understand the behavior of carrier statistics and transport.

In this thesis, we first use NWs, rather than NCs, to avoid inter-NC barriers and investigate the efficiency of doping and thus charge carrier statistics in NSs through measurements of charge transport in the platform of the field-effect transistors (FET). We show the doping efficiency of n- or p-doped PbSe NWs is increased as the permittivity of the surrounding environment increases and develop a theoretical model that agrees with our experimental data for both NW array and single NW devices. Then we investigate carrier transport in epitaxially-fused, CdSe NC arrays with wide necks between neighboring NCs synthesized by a cation exchange (CE) reaction from PbSe NCs through an intermediate. Time-resolved microwave conductivity measurements

probe carrier transport at nanometer length scales and show a photoconductance of 0.28 cm² V⁻¹ s⁻¹, the highest among CdSe NC solids reported with little or no necking. FET measurements probe carrier transport at micron length scales and realize a high electron mobility of 35(3) cm² V⁻¹ s⁻¹ with on-off ratios of 10⁶ after doping. Last, we show that residual Pb impurities from CE reactions have detrimental effects on device turn-on, hysteresis, electrical stability, and carrier transport of CE-obtained CdSe NC films. The selection and surface functionalization of the gate oxide layer and low-temperature atomic-layer deposition encapsulation can suppress these detrimental effects. By converting the NC thin films layer-upon-layer, impurities are driven away from the gate-oxide interface and mobilities increase by 10 times.

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CHAPTER 1 Introduction

1.1. Nanoscale semiconductors

Semiconductors have energy gaps between occupied and unoccupied states in a typical range of 0.1 - 4 eV and conductivities intermediate between those of metals and insulators. The charge carriers in semiconductors are named electrons and holes. Adding dopants – donors or acceptors of electrons – is used to alter the population of charge carriers and shift the Fermi level towards the conduction band or the valance band, respectively.¹

Quantum physics provides powerful toolkits to understand semiconductors. Based on the Schrödinger's equation of an approximate one-electron system and the Bloch theorem, the energy-momentum (*E-k*) relationship for carriers of a crystalline semiconductor follows $E(k) = \sum \frac{\hbar^2 k_i^2}{2m^*}$, where \hbar is the reduced Planck constant and m^* is the effective mass of the carrier. The allowed momentums $k_{i|i=x,y,z}$ are $\frac{n\pi}{d_i}$, where *n* is $\{0, \pm 1, \pm 2, ...\}$ and d_i is the length in a given dimension. Whereas d_i is infinite in an infinite crystal and thus *k* takes a continuum of values, k_i becomes discrete when the crystal is confined in a given dimension.² Depending upon the number of dimensions in which charge carriers are confined, nanoscale semiconductors are categorized as 0D, 1D, and 2D. The density of states describes the allowed states at each energy and Figure 1.1 depicts the functional form for each degree of confinement.³ As a result of the spatial confinement, the band structure of a nanoscale semiconductor depends on the length in the confined dimensions, granting tunable excitonic and electronic properties by size and shape.



Figure 1.1 Density of states in 3D, 2D, 1D, 0D semiconductors³ [Adapted from reference 3]

Colloidal low-dimensional materials include 0D nanocrystals (NCs), 1D nanowires (NWs), and 2D nanosheets and can be described as having inorganic cores covered by ligand shells. Ligands can be large and fatty, such as oleic acids or oleylamine, for steric stabilization or can be charged, such as cetyltrimethylammonium bromide, to allow electrostatic stabilization. In this thesis, binary metal chalcogenide NCs and NWs are studied.

Thanks to the large surface to volume ratio in nanoscale semiconductors, their electronic structures and thus electronic properties are sensitive to surface treatments such as modifying the surface atoms and, in colloidal nanostructures, the ligands.⁴ Take colloidal 0D PbSe NCs and 1D NWs for example, remote doping has been employed to realize n- and p-type NC thin films and NWs, by exposing the NCs or NWs to hydrazine or oxygen, or by tuning their stoichiometry by adding atoms or ions to their surfaces

[Figure 1.2].^{5–9} The tunable electronic structures of nanoscale semiconductors makes them potential building blocks in device engineering.¹⁰



Figure 1.2 N-doping or p-doping of PbSe nanocrystal by tuning the stoichiometry⁷ [Adapted from reference 7]

1.2. Nanocrystal assemblies

1.1.1 Self-assembled superlattices and epitaxially-fused superlattices

Akin to atoms comprising atomistic solids, NCs are the building blocks of NC solids. By slowly evaporating the solvent of a NC dispersion, ordered NC assemblies, namely "superlattices", can be prepared [Figure 1.3A].¹¹ Akin to atomistic crystalline solids, NC solids can be single crystalline, polycrystalline with observable grain boundaries,¹² polymorphic,¹³ and doped superlattices.¹⁴ In single component superlattices, composed of a single type of NC, the structure of assemblies can be adjusted, for example, to form rods, honeycomb sheets, or square sheets, by controlling the assembling conditions, such as temperature, noncoordinating solvent, and ligand.¹⁵ In multicomponent superlattices formed by two or more types of NCs of different

shape,¹⁶ size,^{17,18} or composition [Figure 1.3B],^{17,19} the crystal structure can be affected by the charge as well as the relative size and concentration of the constituent NCs.¹⁶



Figure 1.3 (A) Single-component superlattice.¹¹ [Adapted from reference 11] (B) Binary and ternary NC superlattices.¹⁹ [Adapted from reference 19]

Long ligands are typically used in assembly processes to sterically stabilize the NCs in solvents and control superlattice structure.²⁰ Though long ligands in NC superlattices allow for collective effects based on weak dipolar interaction (i.e. electrostatic²¹ or magnetic dipole-dipole interactions²²), electronic communication between neighboring NCs is poor for reasons to be explained in Section 1.2.2.²³ Long ligands can be replaced with short ligands or removed in NC assemblies to improve electronic communication in single-component systems, although often at the cost of

sacrificing the film continuity and at the risk of introducing disorder.^{24,25} Pb-chalcogenide NCs have the advantage of forming epitaxially-fused superlattices spontaneously, where neighboring NCs are connected with atomically matched interfaces, believed to form from dipole-dipole interactions between neighboring NCs.^{26,27} PbSe NC superlattices can form square-packed structures with NCs oriented along the <100> direction [Figure 1.4] and silicene-like honeycomb structures with NCs oriented along <100>, <110>, or <111> directions²⁸ [Figure 1.5]. Square and honeycomb structures coexist in some cases and the proportion of honeycomb structures increases up to 70% by slowing NC assembly in a saturated vapor of the solvent (toluene) used to disperse the NCs.²⁹ Studies have proposed that the phase diagram of honeycomb and square PbSe NC superlattices is governed by competition among NC-NC attraction between neighboring {100} facets where ligands are the most likely to desorb, NC-solvent interaction, and fluid-fluid interfacial forces.³⁰ The computational results have shown that the energy barrier of the transformation between two structures is small, that strong NC-solvent interaction favors the honeycomb structure, and that large NC-NC interaction yields a square structure and accordingly suggests the use of large particles for preparation of square structures.³⁰



Figure 1.4 PbSe NC square-ordered superlattices.



Figure 1.5 Honeycomb structured PbSe NC superlattice²⁸ [Adapted from reference 28]

In epitaxially-fused superlattices, structural disorder can be classified as "inplane" and "out-of-plane" disorder. "In-plane" disorders include atomic defects at the interface between two attached NCs³¹, and misaligned facets, in which case the central axes parallel to the substrate of two attached NCs are different or not aligned.³² "Out-ofplane" disorder describes the axis of a NC normal to the substrate and misalignment that is different from one NCs to its neighboring NCs.³²

1.1.2 Electronic structures of semiconductor NC assemblies

In an ideal semiconductor NC array, with uniform size and no disorder, the potential energy diagram in real space is a series of identical potential wells [Figure 1.6A]. The potential has been well described by the Woods-Saxon model [Figure 1.6B] for hard-sphere like NCs³³, $U(r) = -\frac{U_0}{1+e^{\frac{r-a}{\lambda}}}$, where U_0 is the depth of a potential in vacuum, *a* is the NC radius, and parameter λ is on the order of the interatomic distance. The depth of the potential well becomes smaller than U_0 when the inter-NC distance is less than $(2a + \lambda)$. The potential becomes more complex in soft-sphere like particles where short-range repulsive potentials are not negligible.³⁴ Electrons with energy higher than U_0 are nearly free electrons moving through a continuous band³³ and lower energy states form narrow bands as shown by discrete shaded stripes in Figure 1.6A.

In an ideal semiconductor NC array with an inter-NC distance $d \ge 2a$, the dispersive relation (*E-k*) of the lowest energy band, formed by the lowest energy states of NCs, is theoretically calculated as $E_{k} = E_{0} - \Delta E_{0} - 2\gamma U_{0} \sum_{i|x,y,z} \cos(k_{i}b)$, where E_{0} is the ground-state energy, *b* is the inter-NC distance, ΔE_{0} is the energy band shift proportional to $\frac{6a^{2}U_{0}}{b(b-a)}$ due to wavefunction overlapping between the nearest neighbors,

and γ is the overlapping parameter proportional to $\frac{2a}{b}$. The corresponding bandwidth is $12U_0\gamma$ for a NC array with a simple cubic structure and $16U_0\gamma$ with a *fcc* or *hcp* close-packed structure. Pictorially, ground-state electrons are localized at E_0 when $b \gg 2a$ and the ground-state extends to form a band as *b* approaches 2a [Figure 1.6C]. The parameter γ is inversely dependent on m^* in the NC and therefore the bandwidth is wider for a lighter carrier and normally the bandwidth of the conduction band is larger than that of the valence band except for semiconductors like the Pb-chalcogenides where m^* of electrons and holes are comparable.³⁵ Experimentally, it has been demonstrated in PbSe NC solids that as the length of ligands and thus the inter-NC distance are reduced, the carrier mobility μ and the strength of electronic coupling $\hbar\Gamma$ in a NC array is enhanced, where Γ is the hopping rate between two NCs [Figure 1.6D].³⁶



Figure 1.6 (A) Schematic of a 3D ideal NC solid and an energy diagram of a periodic array. (B) Scattering function and the confined Woods-Saxon potential.³³ [Adapted from reference 33]. (C) Energy diagram as a function of the inter-NC distance in an ideal NC array.²³ [Adapted from reference 23] (D) Carrier mobility and the coupling strength as a function of the ligand length.³⁶ [Adapted from reference 36]

In an ideal epitaxially-fused NC superlattice, the dispersion relation depends on the interfaces' width between attached NCs, namely, the neck width. The band is more dispersive, and the electronic coupling is stronger with a wider neck width. Figure 1.7 shows the results of a theoretical study on square-packed NC arrays with one layer of zinc-blende-CdSe epitaxially fused along <100>. The bandwidth of the lowest conduction band (1S) and the highest valence band increases with the neck width. In the extreme case where the neck width is equal to the size along the <100>, the superlattice become an 2D CdSe film. ³⁷ As the neck widens, the carrier mobility increases. In a model described by Shklovskii, μ is proportional to $l^2/2a$ where l is the neck width.³⁸



Figure 1.7 The bandwidth of (A) the lowest conduction band (1S) and (B) the highest valence band (VB) as a function of the number of atoms in the neck (Nat) in a square-packed, epitaxially-fused CdSe NC array. The legend lists the diameter of NC.³⁷ [Modified from reference 37]

In real semiconductor NC assemblies, nonidealities including structural disorder, size distribution, and differences in surface atoms and ligands result in inhomogeneities in the energy of NC electronic states, smaller bandwidths, and shallow trap states that

extend from the band edge or deep trap states in the mid-gap as shown in Figure 1.8. The strength of electronic coupling and carrier behaviors are governed by the interplay between the inter-NC distance and nonidealities. Reducing the inter-NC distance improves electronic coupling and favors carrier delocalization, whereas nonidealities reduce the coupling strength and increase carrier localization. For example, in real NC assemblies with a small number of trap states, an extended electronic state can form as the inter-NC distance becomes small enough that the delocalization term wins over the localization term.²³



Figure 1.8 Comparison of schematic energy band diagrams and density of states of strongly-coupled ideal and real NC solids cases.²³ [Adapted from reference 23]

1.2.3 Carrier transport in nanocrystal assemblies

In a semiconductor NC assembly with extended electronic states and trap states in the band gap, charge carrier transport occurs in extended states with bandlike transport behavior, described by $\frac{d\mu}{dT} < 0$, when the Fermi level is close to the conduction/valence band and trap states are filled. Bandlike carrier transport has been observed in CdSe NC solids,^{39,40} Pb-chalcogenide NC solids,^{7,41} and HgTe NC solids⁴² after ligand exchange. Band transport behavior is also expected in NC superlattices,⁴³ but has not been realized yet, ascribed to structural disorder.⁴⁴

In other cases where the bandwidth of electronic state is too narrow to support band-like transport behavior or there is a minimal number of carriers in the extended states because carriers are trapped in localized states within the band gap, carrier transport in NC assemblies occurs by thermally activated hopping. Depending upon the density of states, the occupation of transport sites, and the temperature, the temperature dependence of the hopping rate can be described by variable range hopping (VRH)⁴⁵ and nearest-neighbor hopping models. VRH can be further described by either the Mott model or the Efro-Shklovskii model. In Mott's model, the temperature dependence of conductance is $\ln G \propto T^{-\frac{1}{D+1}}$, where *G* is the conductance and *D* is the dimensionality.⁴⁶ In the Efros-Shklovskii model, the temperature dependence is dimensionless, $\ln G \propto T^{-\frac{1}{2}, 47}$ Variable range hopping has been shown to evolve from Mott's VRH to Efros-Shklovskii(ES) VRH as temperature drops.⁴⁵ Nearest-neighbor hopping requires $kT \ge \Delta E_{NC}$, where ΔE_{NC} describes the bandwidth of the NC energy distribution caused by predominantly the size distribution or differences in surface composition. Therefore, nearest-neighbor hopping occurs at higher temperatures than VRH in a given system. Nearest-neighbor hopping follows the Arrhenius' relation, $\ln G \propto T^{-1}$ and the mobility is described as $\mu = \mu_0 \exp\left(-\frac{0.865d}{l_c}\right) \exp\left[-\frac{\Delta E_{NC}}{kT}\right]$, where l_c is the average delocalization length of carriers.³⁶

1.3. Field-effect transistor

1.3.1 Measuring mobility, threshold voltage and subthreshold slope

Field-effect transistors (FETs) can be used as a platform to probe charge transport and thus collect information about the electronic structure in NC assemblies. FETs are composed of drain and source electrodes, a semiconductor, an insulator, and a gate electrode [Figure 1.9]. NC thin-film FETs can be fabricated by coating a thin film of NCs, to form the semiconductor channel, on a stack of an insulator and a metal or a heavily-doped semiconductor, that serves as the gate insulator and electrode, respectively. FET behavior is characterized by the drain-source current as a function of gate voltage $(I_D - V_G \text{ curve})$ or as a function of drain-source voltage at various gate voltages ($(I_D - V_D \text{ curves})$). The characteristics of NC thin-film FETs are well described by the equations developed for metal-oxide-semiconductor FETs (MOSFETs), $I_D =$ $\frac{\mu_{FET}C_{ox}W}{L} \left(V_G - V_{th} - \frac{V_D}{2}\right) V_D$ in the linear regime ($V_D < V_{Dsat}$, $V_G \ge V_{th}$) and $I_D =$ $\frac{\mu_{FET} C_{ox} W}{2L} (V_G - V_{th})^2$ in the saturation regime $(V_D \ge V_{Dsat}, V_G \ge V_{th})$, where μ_{FET} is the field-effect mobility, C_{ox} is the capacitance of the gate oxide, W is the width of the channel, L is the length of the channel, and V_{th} is the threshold voltage, or more appropriately in thin-film FETs, the turn-on voltage. By fitting $I_D - V_G$ curves, μ_{FET} and V_{th} can be extracted.



Figure 1.9 A representative $I_D - V_G$ curve of CdSe nanocrystal FETs. The inset depicts the FET structure.³⁹ [Adapted from reference 39]

Ohmic contacts are required in FETs to extract μ_{FET} . μ_{FET} can be gate-voltage dependent because of traps being filled electrostatically when the Fermi level in the channel is shifted by the applied gate voltage.⁴⁸ In some cases, μ_{FET} is distinguished from intrinsic μ of carriers at the band edge because it has contributions from both trapped and free carriers.⁴⁹

 V_{th} is the minimum V_G that is required to create a conducting path between the source and drain electrodes. In nonideal cases, threshold voltage is $V_{th} = V_{th0} + \phi_{MS} + \gamma_M \frac{Q_M}{C_{ox}} - \frac{Q_{IT}}{C_{ox}}$, where V_{th0} is the ideal threshold voltage, ϕ_{MS} captures the workfunction difference between metal and semiconductor, Q_M is the charge of mobile ions in the NC thin films, γ_M depends on the distance of the mobile ions to the NC-oxide interface, and Q_{IT} is the charge trapped by interfacial trap states at the semiconductor-oxide interface under an applied gate voltage of $V_G = V_{th}$.¹ With other parameters fixed, V_{th} is larger (smaller) when negative (positive) charges are trapped at the interface at $V_G = V_{th}$.

measure charge carrier concentration difference between two systems with the difference of the threshold voltage.⁵⁰

By fitting $\log_{10} I_D - V_G$ curves in the subthreshold regime ($V_G < V_T$), subthreshold slope (S^1) can be extracted.¹ The subthreshold slope $S^{-1} = \frac{d \log I_D}{d V_G}$ is related to the interface trap density by $S = \ln 10 \frac{kT}{q} (1 + \frac{e}{C_{ox}} N_{trap})$, where N_{trap} is the trap density per area per volt. Considering subthreshold regime data is used to extract N_{trap} , it only describes the interface trap density below the Fermi level, below threshold.

1.3.2 Capacitance-voltage measurements in FET structures

Capacitance-voltage measurements can be conducted in FET structures where the drain and source electrodes are grounded.⁵¹ A DC bias voltage is applied across the capacitor while probing the capacitance with an AC signal and usually sweeps from negative (positive) to positive (negative) to drive a p-type (n-type) semiconductor from depletion to accumulation. The capacitance is $C_{ox} = \frac{\epsilon_0 \epsilon_{ox} A}{t_{ox}}$ in accumulation and is $\frac{C_{ox}}{1+\frac{\epsilon_{ox} W}{\epsilon_s t_{ox}}}$ in depletion, where ϵ_0 is the vacuum permittivity, ϵ_{ox} is the dielectric constant of the gate oxide, ϵ_s is the dielectric constant of the semiconductor, t_{ox} is the thickness of the gate oxide, W is the depletion width in semiconductor, and A is the area. Dopant concentration can be determined from the slope of $\frac{1}{c^2} - V$ in depletion. Nonidealities can arise from leakage or parasitic components in the system, contacts, and series resistance and inductance. When the equivalent resistance parallel to the capacitor is too small, the signal to noise ratio becomes low due to the large leakage current. The integration of the capacitance over the voltage gives the amount of charge involved in the process [Figure 1.10B]. ^{1,39}



Figure 1.10 (A) Schematic of MOS⁵² [Modified from reference 52] (B) Capacitance and gate voltage measurements in FET structures³⁹ [Modified from reference 39]

1.4. Time-resolved microwave conductivity

Contactless carrier transport measurements include terahertz (THz) conductivity measurements and time-solved microwave conductivity (TRMC) measurements where no electrodes are required and the conductance of photogenerated carriers is probed with electromagnetic fields at THz or GHz frequencies. In contrast to channel lengths up to micrometer scales in FETs, THz and TRMC probe the AC mobility and length scales (L_{detect}) in tens of nanometers, estimated by $L_{detect} = \sqrt{\frac{kT}{q}\mu(\omega)\frac{2\pi}{\omega}}$, where ω is the oscillation frequency of the electromagnetic field. AC mobility can be much larger than DC mobility in NC solids because of fewer hopping steps, $\frac{L_{detect}}{d}$, in smaller regions.⁵³

Our group has a home built TRMC spectrometer. An HP 8671B Synthesized CW generator is used to create microwaves (~9 GHz). A Quantel Ultra Nd:YAG laser is used to generate 5 ns FWHM, 532 nm laser pulses. The diameter of the laser spot at the sample is 9 mm. Microwave power is converted to voltage through a Herotek

DTM180AA Schottky diode and digitalized on a Keysight DSO-S 054A oscilloscope. Power is converted by a Schottky diode: $P = V^n$, n = 1.31, when the change is small, $\frac{\Delta P}{P} = \frac{n\Delta V}{V}$. When measuring photoinduced microwave transients, the detected voltage is amplified 10x by a HP 462A pulse amplifier.

TRMC measures transient photoconductance (ΔG) by probing the interaction of microwave and photogenerated carriers, $\Delta G = -\frac{F_I}{K}\frac{\Delta P}{P}$ where $F_I = 2$ is a correction for partial illumination of the sample by the 9-mm laser spot and the sensitivity factor K is obtained through numerical simulations of the microwave cavity loaded with a glass substrate using CST Microwave Studio. The product of the carrier yield and the sum of the carrier mobilities $\phi \Sigma \mu$ is equal to $\frac{\Delta G}{\beta q I_0 F_a}$, where β is the aspect ratio of the waveguide, and $I_0 F_a$ is the number of absorbed photons.⁵⁴

Real $\phi \Sigma \mu$ is needed to take the instrumental response time (*IRF*) into consideration. The measured spectra are fit to the convolution of *IRF* and exponential functions to extract $\phi \Sigma \mu$ and lifetime, *Signal* \propto *IRF* $\otimes \Delta G$. An exponentially modified Gaussian function is adapted to represent instrumental response function, *IRF* = $\frac{\sigma_{laser}}{\tau_{RC}} exp \left(0.5 * \left(\frac{\sigma_{laser}}{\tau_{RC}} \right)^2 - \frac{t-t_0}{\tau_{RC}} \right) \times erfc(\frac{1}{1.41} * \left(\frac{\sigma_{laser}}{\tau_{RC}} - \frac{t-t_0}{\sigma_{laser}} \right) \right).^{54}$ The temporal profile of the laser is Gaussian and σ_{laser} is found to be 2.144(2) ns [Figure 1.11A]. τ_{RC} and *Q* are found from a fit of the cavity response curve, which can be written as R(f) =

$$\frac{R_0 + \left(\frac{2(f_0 - f)}{\Delta W}\right)^2}{1 + \left(\frac{2(f_0 - f)}{\Delta W}\right)^2} + mf + b, \text{ where } \tau_{RC} = 1/f_0 \text{ and } Q = \frac{f_0}{\Delta W} \text{ [Figure 1.11B]}.^{54,55}$$


Figure 1.11 (A) Laser pulse (blue) and the fitted curve (orange) (B) Normalized microwave power reflected from a cavity loaded with a representative sample (blue). The orange line represents the fitted curve.

1.5. Thesis overview

This thesis investigates elements fundamentally critical to the performance of optoelectronic and electronic devices built from semiconductor NCs and NWs: a) carrier statistics, b) carrier transport pathways, and c) impurities.

Chapter 2 introduces a new method to investigate the doping efficiency in the platform of FETs. PbSe NWs are n-doped with elemental Pb or In or p-doped with elemental Se by thermal evaporation. Polymeric and oxide materials of varying dielectric constant (ϵ) are subsequently deposited to control the dielectric environment surrounding the NWs. The doping efficiency in each case is estimated by analyzing the FET characteristics and is shown to increase as the ϵ of the surrounding medium increases. A theoretical model is built to describe the doping efficiency in PbSe NWs embedded in different dielectric environments, which agrees with our experimental data for both NW array and single NW devices.

Chapter 3 investigates carrier transport in epitaxially-fused, CdSe NC arrays with wide necks between neighboring NCs using TRMC and FET measurements. The CdSe

NC arrays are prepared by cation exchange reactions using PbSe NC epitaxially-fused arrays as the starting materials and Cu₂Se NC arrays as the intermediates. TRMC measurements probe carrier transport at nanometer length scales and show a photoconductance of 0.28 cm² V⁻¹ s⁻¹ in such epitaxially-fused CdSe NC arrays, the highest among CdSe NC solids reported with little or no necking. We fabricate field-effect transistors to study carrier transport at micron length scales and realize a high electron mobility of 35(3) cm² V⁻¹ s⁻¹ with on-off ratios of 10⁶ after doping.

Chapter 4 studies how residual Pb impurities in cation-exchange obtained CdSe NC films affect charge transport and thus the device performance including device turnon, hysteresis, electrical stability, and the activation energy for carrier transport. The selection and surface functionalization of the gate oxide layer and low-temperature atomic-layer deposition encapsulation can suppress these detrimental effects. By converting the NC thin films layer-upon-layer, impurities are driven away from the gate-oxide interface and mobilities increase by 10 times.

Chapter 5 presents preliminary results of preparing other epitaxially-fused, metal chalcogenide NC assemblies and propose future studies. Cation exchange reactions in PbTe NC solids and replacing Cu⁺ with other cations (Ge²⁺, Sn^{2+/4+}, Ag⁺, and Zn²⁺) in Cu₂Se NC solids are explored. We show preliminary results of fabricating epitaxially-fused NC arrays in honeycomb- and stripe-like structures with the size of ordered regimes in μ m. This chapter also includes the TRMC results of InP and persoskite in a collaborative project. The last section of Chapter 5 concludes the thesis.

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CHAPTER 2 The Effect of Dielectric Environment on Doping Efficiency in Colloidal PbSe Nanostructures

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2.1. Introduction

Colloidal lead chalcogenide nanostructures, including nanocrystals (NCs) and nanowires (NWs), are promising building blocks for solution-based deposition of high mobility and narrow bandgap semiconductor devices, such as electronic transistors and circuits, infrared photodetectors and photovoltaics, and thermoelectrics.¹⁻⁹ The design and operation of such devices require control over the free carrier type and concentration in assemblies of the nanostructures.¹⁰ The electron and hole concentrations in lead chalcogenide NC and NW assemblies have been manipulated through "remote doping," *i.e.*, by the addition of atoms, ions, or ligands at the surface of the nanostructures, ¹⁷ Although different methods have been developed to dope lead chalcogenide nanostructures, the doping efficiency is extremely low, such that only approximately 1% of dopants yield carriers.^{11,18} Therefore high concentrations of dopants have been required to reach high conductances, at the anticipated expense of increasing carrier scattering, and hence reducing achievable carrier mobilities.

The low doping efficiency in these nanostructures can be attributed to dopants that are ineffectively bound,^{11,19} and/or consumed by surface redox reactions, unidentified

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traps,¹⁰ or self-compensation^{10,20,21} and/or effectively bound but not ionized.¹⁸ The concentration of inactive dopants may be increased in nanostructures, compared to their bulk analogues, as the dopant ionization energy can be enhanced by quantum and/or dielectric confinement effects.^{22–24} For a given size nanostructure, where quantum confinement effects are fixed, theoretical and experimental studies of silicon nanowires (SiNWs) have shown that the ionization energy of dopants increases as the dielectric mismatch between the NW and its surrounding increases.^{25,26} Lead chalcogenides have larger Bohr radii for electrons and holes and a higher dielectric constant than Si, suggesting that lead chalcogenide nanostructures should experience more significant dielectric confinement effects that act to increase dopant ionization energies.

Here we study the doping efficiency in PbSe nanostructures and show that by tailoring the surrounding dielectric environment we can greatly increase doping efficiency. We choose to probe the doping efficiency of both NW arrays and single NWs integrated in the device platform of the field effect transistor (FET), as the wires span device electrodes and thus provide a simplified picture of carrier transport, in comparison to that for NC arrays, where there are a large number of interfaces created by intervening ligands at the NC surface in the transport pathway. The NW channel in the FET platform is also accessible, allowing us to modify the NW doping and dielectric environment of completed devices. Dopant atoms (Pb, In, Se) are introduced to remotely dope PbSe NW devices and different dielectric constant polymeric and oxide materials are deposited to encapsulate the FET devices. We measure the device characteristics to probe the majority carrier type and concentration in the NWs and to calculate the doping efficiency and ionization energy of dopants. As the dielectric constant of the surrounding

medium increases, the doping efficiency increases significantly by 5-10 fold and the ionization energy approaches 0 eV, consistent with the theoretical prediction.

2.2. Experimental section

Materials: Lead acetate trihydrate is purchased from Fisher Scientific Co., Tri-noctylphosphine (TOP, 90%), oleic acid (OA, 90%), diphenyl ether (99%), lead chloride (PbCl₂, 99%), amorphous selenium pellets (99.999%), (3-

Mercaptopropyl)trimethoxysilane (MPTS) (95%), anhydrous isopropyl alcohol, anhydrous acetonitrile, anhydrous hexane, anhydrous chloroform, and anhydrous toluene are bought from Aldrich. N-tetradecylphosphonic acid (TDPA, 97%) is purchased from Strem.

Methods: *PbSe NW synthesis*. Colloidal PbSe NWs15 nm in diameter and >10 µm long are synthesized a following established method.²⁷ By using standard Schlenk line techniques, 0.76 g of lead acetate trihydrate is dissolved in 2 mL of oleic acid and 10 mL of diphenyl ether at 150 °C for 30 min under nitrogen flow. Then the solution is cooled down to 60 °C and 4 mL of 0.167 M TOPSe is slowly added to form PbSe "seeds" for later NW growth. Meanwhile, a solution of 0.2 g of TDPA and 15 mL diphenyl ether is heated at 255 °C. The seed solution is swiftly injected causing the temperature to drop to 190-210 °C. After 60 s of growth, the reaction is quenched with a water bath. NWs are precipitated by centrifuging the crude dispersion at 4000 rpm for 5 min inside a glovebox, washed with hexane, then with chloroform and finally re-dispersed in 5 mL chloroform.

PbSe NW array FET fabrication. The fabrication of PbSe NW array FETs is reported previously.²⁷ Briefly, source and drain electrodes (2 nm Cr/18 nm Au) are

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defined by photolithography on top of n⁺ silicon wafers with a 250 nm-thick silicon oxide layer to form FET channels 10 μ m in length and 150 μ m in width. The substrate is treated by MPTS before use. The NW dispersion is further diluted in octane to a concentration of 100 g/mL and dropped onto the substrate while a dc electric field of 10⁵ V/cm is applied between source and drain electrodes for ~30 s, creating NW arrays aligned across the channel. NW array devices are immersed in a 10 mg/mL NH₄SCN solution in acetone for 30 s to carry out ligand exchange.²⁸ The device is rinsed with acetone and chloroform to remove excess ligands and organics.

PbSe single NW FET fabrication. The fabrication of PbSe single NW FET is similar to the literature reports.²⁹ Large metal contact pads (5 nm Cr/ 135 nm Au) are defined by photolithography and thermal evaporation on n⁺-Si wafers with 250-nm SiO₂. The substrate is cleaned and treated by 1% MPTS of toluene. 100 g/mL NW dispersion in octane is dropcast between the contact pads and the same NH₄SCN ligand exchange process is performed as described above for the array devices. PMMA e-beam resist is spincast on the sample and the location of single wires within the contact pairs is recorded by an optical microscope. E-beam lithography is used to define source and drain electrodes (2 nm Pb/18 nm Au) and are customized for each single NW to connect them with the pre-patterned, large contact pads. The channel dimensions are designed as 1 μ m: 4 μ m (W: L).

Doping of PbSe NW FETs. Using NW and NC doping methods previously developed by our group, we evaporate metal on top of the NWs to tune NW surface stoichiometry or introduce impurities. ^{11,12,30} Thermally depositing elemental Pb or In is used to n-dope NWs and elemental Se to p-dope NWs. The thermal deposition of In is followed by a 5-minute annealing at 250 °C to "activate" the dopants.

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Dielectric encapsulation of PbSe NW devices. NW Devices are coated by three different dielectric media. The procedure for encapsulating NW array and single NW devices is identical. Commercial PMMA (495K, 2% in anisole) and PVDF (10% in dimethylformamide) is spincast onto devices and annealed at 200 °C for 2 min to achieve thickness of 180 nm and 2000 nm, respectively. 50-nm HfO₂ layer is grown by atomic layer deposition at 200 °C for 3 hours.

Characterization: *FET characterization.* The cross-section sample is prepared by focused-ion beam lithography (FIB, FET Strata DB235) and imaged by a high-resolution SEM (JEOL 7500F). FET measurements are conduct at room temperature with a Karl Suss PM5 probe station mounted in glovebox or at variable temperature (230 – 320 K) with a Lakeshore Cryotronics vacuum probe station. Both probe stations are equipped with model 4156C semiconductor parameter analyzers. Capacitance is measured by an HP 4276A LCZ meter.

2.3. N-type and p-type PbSe NW FETs



Figure 2.4 Top-view SEM image of a NW array FET and inset, schematic of the device geometry.

Highly n-doped, oxidized Si wafers are patterned with Au electrodes to serve as the gate electrode, gate oxide, and source and drain electrodes of the FET platform. All

following fabrication steps are carried out inside a nitrogen filled glovebox, unless otherwise noted. To fabricate PbSe NW array FETs, 15 nm diameter, colloidal PbSe NWs capped with oleate and tri-n-octylphosphine are synthesized and dispersed in octane. A drop of the NW dispersion is deposited and the NWs are directed to align across the 10 µm channel of bottom-contact FETs by applying a DC electric field between the pre-fabricated Au source and drain electrodes, as shown in Figure 2.1.8 To remove the long organic ligands at the surface of as-aligned NWs and better passivate the NWs and improve their contact to devices electrodes, device substrates are immersed in a 10% NH₄SCN solution in acetone for 30 s.^{27, 30} NW devices are annealed at 180 °C for 20-40 s to desorb surface-bound oxygen and water, which are known to act to p-dope PbSe NWs,¹³ following procedures previously developed by our group.²⁷ After annealing, the SCN-capped NW FETs show ambipolar behavior [black curves in Figure 2.2]. Devices are doped remotely by modifying the NW stoichiometry via thermal evaporation of Pb (n-type) or Se (p-type) on the surface of NWs, following our group's previous work on lead chalcogenide NCs and NWs.^{11,12,32} We also provide an example of n-type impurity doping by thermally evaporating In onto the PbSe NWs, consistent with reports of In serving as a donor in bulk PbSe.³¹ A film of Pb, In or Se, varying from 3 Å to 15 Å is evaporated onto the NWs array channel [Figure 2.2 and Figure 2.3]. Pb- and Se- doped NW devices are used as is, however, In-doped NW devices are annealed at 250 °C for approximately 5 min to "activate" the dopants.³³



Figure 2.2 Representative $I_D - V_G$ characteristics of PbSe NW array FETs doped by various amount of Pb deposited by thermal evaporation in the saturation regime ($V_D = 20 V$) (A) and in linear regime ($V_D = 0.25 V$) (B) and by various amount of In in the linear regime. Inset: Calculated change in carrier concentration as a function of the amount of thermally-deposited Pb or In. Colors represent 0 Å (black), 3 Å (red), 6 Å (green), 10 Å (blue), and 15 Å (cyan) of thermally-deposited Pb or In. In (B), solid lines represent scans from $V_D = +50 V to - 50 V$ and dashed lines are scans from $V_D = -50 V to + 50 V$.

Representative source-drain current–gate voltage $(I_D - V_G)$ characteristics for Pb-doped PbSe NW array FETs are shown in the and saturation [Figure 2.2A] and linear [Figure 2.2B] regimes. All the $I_D - V_G$ measurements are carried out by sweeping forward from $V_D = +50$ V to -50 V and backward from $V_D = -50$ V to +50 V. As we increase the number of Pb atoms deposited on the channel, the device behavior changes from ambipolar to increasingly n-type and to eventually heavily n-type. Correspondingly, the threshold voltage (V_T) shifts in the negative direction and the onstate electron currents first increase and then decrease. From the shifts in the device threshold voltage (ΔV_T) of the linear characteristics, we calculate the concentrations of excess carriers (Δn) provided by added donors or acceptors as,

$$\Delta n = \frac{\Delta V_T C_{ox}}{q V_{NW}} \tag{1}$$

where V_{NW} is the volume of the active channel and C_{ox} is the unit capacitance of the gate oxide. The linear regime characteristics ($V_D = 0.25$ V) are used in calculations to avoid the non-uniform distribution of charges across the channel at high V_D in the saturation regime. The thin-film model is applied to find a C_{ox} of 13 nF/cm² in array FETs. We note that the NWs do not completely cover the channel area defined by the source and drain electrodes (*i.e.*, the NWs occupy ~10% of the area, as seen in Figure 2.1), therefore simply treating the NW arrays as thin films may give rise to an underestimation of Δn . A comparison between the thin film and cylinder-on-a-plate models is discussed below. The capacitance and the change of carrier concentration calculated by thin-film model is,

$$C_{ox,1} = \frac{\epsilon_0 \epsilon_{r,ox} A}{t_{ox}}, \ \Delta n_1 = \frac{\Delta V_T C_{ox,1}}{2RAq}$$
(2)

by the cylinder-on-plate is,34

$$C_{ox,2} = \frac{2\pi\epsilon_0\epsilon_{r,ox}L}{\ln\left[\frac{2(t_{ox}+R)}{R}\right]}, \ \Delta n_2 = \frac{\Delta V_T C_{ox,2}}{LR^2 \pi q}$$
(3)

where $C_{ox,1}$ and $C_{ox,2}$ are the gate oxide capacitance by thin-film model and cylinder-onplate model, respectively, $\epsilon_{r,ox}$ is the dielectric constant of the gate oxide, *A* is the area, *L* is the channel length, *R* is the radius of NW, and t_{ox} is the thickness of the gate oxide layer. To compare the two models, the ratio of Δn_1 to Δn_2 is calculated, $\frac{\Delta n_1}{\Delta n_2} =$

$$\ln\left(\frac{2t_{ox}}{R}\right)\frac{R}{2t_{ox}} = 0.06$$
. If NWs sparsely span the channel such that there is no coupling

between any two of the NWs, as is the case for the single NW FET, the cylinder-on-plate model is suitable. However, if the channel is entirely filled by NWs with interactions among them, then the thin-film model is more appropriate. Our NW array FETs are in between the two cases, as they are not dense films, but they are also not arrays of isolated NWs. We choose the thin-film model to capture the presence of bundles and overlap of NWs across the channel. We use this model consistently for NW array FETs to make comparisons in Δn as a function of doping and as a function of dielectric environment.

For Pb-doped NW array channels, as the amount of Pb increases upon evaporation of 3 Å to 10 Å thick films, the carrier concentration change calculated from the linear (Δn) regime characteristics increases from 10^{17} cm⁻³ to 3 × 10^{17} cm⁻³ [inset of Figure 2.2B]. At higher doping levels of 15 Å of deposited Pb, Δn reaches ~ 10^{18} cm⁻³ and the gate modulation of the current is weak.² Given the ~ 10^{14} cm⁻³ intrinsic carrier concentration of PbSe NWs with a 0.4 eV bandgap is negligible¹² compared to Δn (> 10^{17} cm⁻³), the free electron concentration (n) is approximately equal to Δn .

Similar behavior is also observed in In-doped devices [Figure 2.2C]. V_T shifts in the negative direction, consistent with *n* increasing from 10^{16} cm⁻³ to 2.5×10^{18} cm⁻³ as the amount of In increases upon evaporation of 3 Å to 10 Å films. We also demonstrate an example of p-type doping on PbSe NWs by evaporating 10 Å of Se. The resulting V_T of the $I_D - V_G$ curve shifts positively and the hole concentration increases by 7×10^{17} cm⁻³ [Figure 2.3].



Figure 2.3. $I_D - V_G$ characteristics of PbSe NW array FETs as made (black), doped by 10 Å of Se (red), and encapsulated by PMMA (blue) at $V_D = -20$ V.

2.4. Dielectric encapsulation of PbSe NW FETs

We investigate the effect of dielectric environment on the doping efficiency of PbSe NWs. Doping efficiency is defined as the percentage of ionized impurities, N_D^+/N_D or N_A^-/N_A , where N_D^+ or N_A^- is the concentration of ionized donors or acceptors and N_D or N_A^-/N_A , where N_D^+ or N_A^- is the concentration of ionized donors or acceptors and N_D or N_A is the concentration of total impurities. Unencapsulated PbSe NW array FETs are first doped with Pb, In, or Se and then are coated with either Poly(methyl methacrylate) (PMMA), Polyvinylidene fluoride (PVDF), or HfO₂ [Figure 2.4]. 180 nm PMMA or 2 µm PVDF is spin-cast on top of the Pb- or In-doped devices and annealed at 200 °C for 2 min to evaporate the solvent. For Se-doped samples, evacuation at -0.1 MPa is used to remove residual solvent to avoid possible Se loss during annealing. 50 nm HfO₂ is deposited on top of NW array FETs *via* atomic layer deposition (ALD) at 200 °C for 3 hours. The relative dielectric constants ϵ_r for PMMA, PVDF and HfO₂ insulators are

found to be 3, 9, and 20, respectively, by fabricating and characterizing their metal/insulator/metal capacitors [Table 2.1].



Figure 2.4 Cross-sectional SEM image of a NW array FET encapsulated by HfO2 at low and (inset) high magnification.

ε _r	PMMA	PVDF	HfO ₂
Reference	2.7 ^{Ref.104}	8.2-10.5 ^{Ref.105}	20-30 ^{Ref.106}
Measured	2.9 ± 0.2	8.5 ± 0.5	17 <u>+</u> 4

Table 2.1. Measured relative dielectric constants at 15 kHz

For example, Figure 2.5A shows the $I_D - V_G$ characteristics of unencapsulated, PbSe NW array FETs before (black) and after (red) n-doping by 3 Å of Pb, to yield $n \sim 10^{17} \text{ cm}^{-3}$, as described above. The FET is then coated with PVDF (blue). Embedding the NW array channel in the high- ϵ PVDF matrix increases the source-drain current and shifts V_T to more negative voltages, consistent with an increase in the accumulated electron concentration at the same gate voltage. As V_T shifts to more negative voltages with an increase in NW carrier concentration, the $I_D - V_G$ curves of the covered NW array FETs show lower gate modulation in the scanned voltage range. Likewise shown in Figure 2.5A and Figure 2.5C, both the PMMA and HfO₂ coatings enhance the current and negatively shift the V_T , suggesting more electrons are introduced from the 3 Å of Pb deposited. It is worth mentioning that the n-type NW array device covered with 50 nm of HfO₂ maintains its $I_D - V_G$ characteristics after being exposed to air for 24 hours with only a small change of its performance [Figure 2.5C].

PbSe NW array FETs n-doped by 5 Å of In deposited show similar effects of PMMA [Figure 2.5D], PVDF [Figure 2.5E] and HfO₂ [Figure 2.5F] encapsulation on the device characteristics, as described above for Pb doping, leading to an increase in current and a negative shift of V_T . PbSe NW array FETs p-doped by evaporation of 10 Å Se, show a positive shift of V_T after PMMA coating [Figure 2.3]. The doping efficiency for both n-and p-type dopants increases for NW arrays embedded in high- ϵ media.



Figure 2.5. Representative $I_D - V_G$ characteristics of n-type PbSe NW array FETs as aligned (black), with 3 Å of Pb or with 5 Å of In deposited (red), and further covered by dielectric materials(blue). In (B) and (E), solid lines represent scans from $V_D = +50$ V to -50 V and dashed lines represent scans from $V_D = -50$ V to +50 V. In (C), pink curves represent HfO₂-encapsulated NW FETs after air exposure overnight (magenta).

We calculate the Δn in the n-type NW array devices before and after encapsulation of the Pb- and In-doped devices by PMMA, PVDF, and HfO₂ media. Δn is equal to the free electron concentration (*n*), as discussed above. The initial doping state of the NWs varies, as NW synthesis yields Pb-rich unintentionally n-doped NWs, and trace (<1 ppm) amounts of oxygen in the nitrogen glovebox p-dope the NWs. Therefore, we collect data from 3 different samples for each type of dopant and encapsulating layer. For devices doped by 3Å of Pb, the average *n* increases by 3.3, 9.4, and 11 fold with PMMA, PVDF, and HfO₂ coating, respectively [Figure 2.6, black]. In-doped devices show a similar trend [Figure 2.6, purple] as the average *n* increases by 1.9 fold after PMMA coating, but saturates at ~8 fold for PVDF and HfO₂ encapsulation. In the case of Sedoped p-type devices, the hole concentration increases by 3 fold for NWs embedded in a PMMA matrix.



Figure 2.6 Change in carrier concentration (Δn) in the NW arrays created by either 3 Å of Pb (black) or 5 Å of In (purple) before ($\frac{\epsilon_{out}}{\epsilon_0} = 1$) and after encapsulation by PMMA ($\frac{\epsilon_{out}}{\epsilon_0} = 3$), PVDF ($\frac{\epsilon_{out}}{\epsilon_0} = 9$) and HfO₂ ($\frac{\epsilon_{out}}{\epsilon_0} = 20$), respectively.

2.5. A theoretical model of the dielectric confinement effect in PbSe NWs

In n-type semiconductors, the free electron concentration equals the ionized donor concentration (N_D^+) , *i.e.*, $n = N_D^+$. However, for the same concentration of donors (N_D) introduced by Pb- or In-deposition, $n = N_D^+$ increases as the dielectric constant of the surrounding environment increases. In other words, the same amount of thermal energy can promote more electrons into the conduction band from the same concentration of donor states, suggesting the ionization energy (E_I) for donors decreases when NWs are encapsulated in a higher- ϵ matrix [Figure 2.7A]. The stronger screening effect of charge in the NWs embedded in a higher- ϵ environment results in a weaker Coulomb interaction between free carriers and ionized impurities [Figure 2.7B]. ³⁵

Theoretically, doping efficiency can be derived from the ionization energy and density of states.^{26,36} The calculation details are presented below for the theoretical model we build to describe doping efficiency in terms of the enhanced ionization energy as a function of environment dielectric constant for PbSe NWs. In Delerue's semianalytical effective mass model for self-energy correction, an isotropic effective mass approximation is used. For <111>-oriented Si nanowires, ³⁶

$$\langle \varphi | \Sigma | \varphi \rangle = \frac{e^2}{\varepsilon_{in} R} \frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + \varepsilon_{out}} F_{Si} \left(\frac{\varepsilon_{in}}{\varepsilon_{out}} \right)$$
(4)

where Σ is self-energy correction, φ is the corresponding wavefunctions for which an effective mass ansatz is used, ϵ_{in} and ϵ_{out} are the dielectric constants of the NW and its surrounding environment respectively, $F_{Si}\left(\frac{\varepsilon_{in}}{\varepsilon_{out}}\right)$ is a positive numerical function of $\left(\frac{\varepsilon_{in}}{\varepsilon_{out}}\right)$ for silicon. The electron effective mass of <111>-oriented Si nanowire is 0.40 m₀. Because $E_I - E_I^0 \approx 2\Sigma$ for a free-standing silicon NW (SiNW), the ionization energy enhancement of a donor is,

$$E_{I} - E_{I}^{0}(Si) \approx \frac{2e^{2}}{\varepsilon_{in}R} \frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + \varepsilon_{out}} F_{Si}\left(\frac{\varepsilon_{in}}{\varepsilon_{out}}\right)$$
(5)

where $E_I - E_I^0(Si)$ are the ionization energies of the impurities in the NWs referenced to that for bulk Si. The bulk value $E_I^0(Si)$ is used as the reference because in Delerue's work the diameters of SiNWs are large enough to neglect quantum confinement effects. However, 15 nm diameter PbSe NWs are smaller than the 23 nm Bohr radius for electrons and holes and quantum confinement effects are not negligible. Therefore, in our studies E_I is referenced to the ionization energy without dielectric confinement E_I^0 (PbSe). In this model, the dispersion of the impurity band is below 0.1 meV and there is one dopant per supercell. The ionization energy enhancement in PbSe NW is derived by modifying *eq.* 4 for SiNWs to account for the increase in the electron Bohr radius (equivalently the reduction in the electron effective mass) for PbSe, since an effective mass model is applied to calculate the electron wavefunction, such that

$$E_{I} - E_{I}^{0}(\text{PbSe}) \approx \alpha \ \frac{2e^{2}}{\varepsilon_{in}R} \frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + \varepsilon_{out}} F\left(\frac{\varepsilon_{in}}{\varepsilon_{out}}\right), \ \alpha = \frac{a_{0}(\text{PbSe NW})}{a_{0}(\text{SiNW})}$$
(6)

where $E_I - E_I^0$ is the difference in the ionization energies of the donor in the NWs with and without dielectric confinement effects, respectively, $a_0 = \frac{\hbar^2 \epsilon}{m_e^* e^2}$ is the effective electron Bohr radius, α is a scaling factor to capture the broader extension of the electron Bohr radius of PbSe (a_{PbSe}) relative to that for Si (a_{Si}). In a 1D system, $\alpha = \left(\frac{\epsilon_{out}}{0.124}\right): \left(\frac{\epsilon_{out}}{0.4}\right) \sim 3.^{37,38}$ The electron effective mass of the <100>-oriented PbSe NW is 0.124 m₀.^{37,39} The E_I^0 for most of the donors are less than 50 meV.

Using E_I and the density of states, the probability of ionization (doping efficiency), and the Fermi level can be estimated at 300 K. A supercell with a length twice larger than the Bohr radius is used to meet the 'lightly-doping' condition mentioned above.^{26,37} In addition, the band structure (and density of states) can be different when the free electron concentration is above the Mott criterion. Above the Mott criterion, the NW is metallic and the doping efficiency can be treated as a unity. Here we only calculate the doping efficiency and Fermi level when the free electron concentration is below the Mott criterion. The Fermi energy and doping efficiency can be determined from³⁸

$$n = \frac{1}{1 + 2\exp(\frac{E_F - E_D}{kT})} N_D = \frac{1}{1 + 2\exp(\frac{E_F - E_C + E_I}{kT})} N_D$$
(7)

$$n = \int_{E_c}^{\infty} g(E)f(E) dE = \int_{0}^{\infty} g(E) \frac{kT}{1 + \exp\left(\frac{E_F - E_C}{kT} - x\right)} dx \qquad x = \frac{E - E_c}{kT}$$
(8)

$$g(E) = \frac{1}{\hbar\pi} \sqrt{\frac{m^*}{2(E - E_c)}} \tag{9}$$

where N_D is the concentration of dopants, f(E) is the Fermi-Dirac distribution of electrons, E_F is the Fermi energy, E_C is the conduction band edge, g(E) is the one dimensional density of states. Calculated ionization energy enhancements as a function of medium dielectric constant are listed in Table 2.2. The ionization energy decreases as ϵ_{out} increases, and approaches a constant value E_I^0 when ϵ_{out} is higher than 20 (closer to or higher than $\epsilon_{in} \sim 23$). There is predicted to be a polaron shift of ~10 meV in HfO₂coated NWs due to the response of the ions in HfO₂. ⁴⁰ Ignoring the polaronic effect introduces a 3-10% error in calculating doping efficiency. Given the relative variations in the doping efficiency for experimental HfO₂-coated NWs are ~20%, the polaronic effect is not significant enough to be observed.

Table 2.2. Theoretical Prediction of Ionization Energy Enhancement

€ _{out,r}	1	3	6	9	15	20
$E_I - E_I^0$ (eV)	0.24	0.105	0.054	0.033	0.012	0.004

To make a clear comparison between our theoretical model and experimental results, the calculated doping efficiencies for each E_I^0 (E_I^0 from 0.01 to 0.07 eV) are normalized by its value at $\epsilon_{out} = 20$ [Figure 2.7C, yellow]. The experimental *n* of NW array FETs before encapsulation and after encapsulation by PMMA and PVDF are normalized by *n* for the device covered by HfO₂, for each of the 3 devices [Figure 2.7C, black and green]. Normalization also cancels out variations in Δn (or *n*) from device-to-

device differences in channel coverage and in the number of unbound dopants introduced in the fabrication process. As shown in Figure 2.7C, the carrier concentration increases in both Pb- and In-doped PbSe NWs as ϵ_{out} increases, indicating the doping efficiency is improved by reducing the dielectric mismatch between the NWs and their surroundings. The experimental results lie in the range of our theoretical prediction.



Figure 2.7. (A) Schematics showing the larger ionization energy ($E_I = E_C - E_D$) and therefore lower probability of promoting electrons from the donor state to conduction band at room temperature (low doping efficiency) in a low (red) dielectric constant medium in comparison to that for a high (blue) dielectric medium. (B) Coulomb interactions, depicted by the density of electric field lines, are not as readily screened between the ionized dopant and free electrons in a low, relative to a high- ϵ medium. (C) Theoretical doping efficiency (yellow) and measured doping efficiency (normalized Δn) of Pb (black squares) or In (green circles) in PbSe NWs as a function of the dielectric constant of the surrounding medium. From bright yellow to light yellow, the E_I^0 used in theoretical calculation change from 0.01 to 0.07 eV.

2.6. The effects of dielectric coatings on mobility, interface trap density, and doptant ioniziation energy

The study of doping efficiency in NW arrays is instructive for device engineering and the bottom-contact device geometry allows us to explore dielectric confinement effects on different dopants in PbSe nanostructures. However, the number and orientation of NWs that span the channel cannot be precisely controlled or counted. Therefore, we fabricate and measure single PbSe NW FETs with Pb as the dopant to gain a more on carrier concentration and transport. A dilute NW dispersion is drop cast on heavily n-doped, oxidized Si wafers, with the same thickness as array FETs, and e-beam lithography is used to write electrodes to the ends of the NWs. Different from the bottom contacts used in array FETs, 2 nm of Pb along with 18 nm of Au is evaporated onto the e-beam defined electrodes to form source and drain top contacts. Here the layer of Pb at the contact area is introduced to compensate for unintentional oxygen p-doping that is inevitable during the e-beam lithography process, and yield devices displaying ambipolar behavior [Figure 2.8A, black line]. SEM images are taken to confirm single NW channel FETs [Figure 2.8A, inset].

We deposit Pb on the single NW channel. $I_D - V_G$ characteristics at $V_D = 2$ V in the linear regime are collected for PbSe ingle NW FETs as a function of the amount of thermally-deposited, elemental Pb [Figure 2.8A]. Unsurprisingly, the evolution of $I_D - V_G$ characteristics observed for single NW FETs is similar to that for NW array FETs. The $I_D - V_G$ characteristic of the single NW FET doped by 1 Å of elemental Pb is still ambipolar, but with a more negative V_T . The characteristics become increasingly n-type with V_T monotonically shifting to negative voltages as more than 2 Å of elemental Pb is added. The cylinder-on-a-plate model, rather than thin-film model, is applied to find the gate capacitance when deriving Δn , as discussed in Section 2.3.



Figure 2.8. (A) Representative $I_D - V_G$ characteristics of a single PbSe NW FET as made (black) and with 1 Å (red), 2 Å (green), and 3 Å (blue) of evaporated Pb. (B) Representative $I_D - V_G$ characteristics of a single PbSe NW FET as made (black), with 5 Å of Pb (red), and PVDF encapsulation (blue). Inset: normalized doping efficiency and electron concentration change calculated based on theoretical model (dash line) and single PbSe NW FET data (dots).

Pb-doped single NW FETs are then coated by PMMA, PVDF, and HfO₂ and tested similarly as the array devices described above. Figure 2.8B shows representative $I_D - V_G$ characteristics of a PbSe single NW FET as made (black), doped by 5 Å of Pb (red) and covered by PVDF (blue). The high- ϵ surrounding PVDF increases the on-state

electron currents and shifts the V_T negatively, consistent with the trends exhibited by the NW array examples. As shown in Figure 2.9, PMMA and HfO₂ coating both enhance the current and negatively shift the V_T , yielding more electrons in the channel. Based on eq. 1 and 2, the *n* introduced upon doping with Pb and coating with PMMA are 2.7×10^{19} cm⁻³ and 6×10^{19} cm⁻³, doping with Pb and coating with PVDF are 2.3×10^{19} cm⁻³ and 1.1×10^{20} cm⁻³, and doping with Pb and coating with HfO₂ are 3×10^{19} cm⁻³ and 1.2×10^{20} cm⁻³. Akin to the behavior of array devices, in increasingly high- ϵ media, the number of electrons generated by a given amount of Pb increases and gradually saturates, suggesting the E_I in single NWs approaches E_I^0 [Figure 2.8B inset]. When n of single NW FETs in different dielectric surroundings are normalized by the n of the HfO_2 -covered FET, they match well with the normalized theoretical doping efficiency for E_1^0 of 0.03 eV. Considering the closed-packed structure of Pb, thermally-deposited, 5 Å films of Pb introduce 4.7×10^{20} Pb atoms/cm³ to the NW. Therefore, on average, the doping efficiency of Pb is 6% in uncoated single NWs, 13% in PMMA-coated single NWs, 23% in PVDF-coated single NWs and 25% in HfO₂-coated single NWs, respectively. While the doping efficiency of the NWs increases in high- ϵ environments, it is well-below 100% as would be expected for the low ionization energy. We attribute the loss in doping efficiency to ineffectively bound Pb atoms as discussed above.

Figure 2.9 shows the device characteristics of 9 individual Pb-doped single NW FETs before and after encapsulation by different dielectric media. After coating the NW channel with dielectric layers, the device hysteresis is reduced, while the current on-off ratio is improved. More specifically, for PMMA-covered FETs, the on-currents only slightly increase, but off-currents dropped from ~10⁻⁶ A to ~10⁻⁷ A. We also extract electron mobilities from the slope of $I_D - V_G$ curves in the high gate voltage region to

minimize contact resistance effects. For the set of samples we measure, electron mobilities of single PbSe NW FETs after being coated by PMMA and PVDF mostly decrease, while the mobility for all FETs encapsulated by HfO₂ increases. However, the variation in mobilities among individual single NW samples [Figure 2.10], as well as in NW array devices, is too large and we are unable to draw a conclusion regarding the effect of dielectric media on carrier mobilities in the PbSe NW devices.



Figure 2.9. $I_D - V_G$ characteristics of individual PbSe single NW FETs as made (black), doped by 3 Å of Pb (red), and embedded in (A)-(C) PMMA, (D)-(F) PVDF, and (G) –(I) HfO₂ (blue).



Figure 2.10. (A) Electron mobility extracted from PbSe single NW FETs in Figure S4 as made (black), with 3 Å of Pb (red), and embedded in left: PMMA, middle: PVDF, right: HfO₂ (blue). (B) Mobility enhancement of samples in (a) after doped by Pb (red) and encapsulated by the corresponding dielectric matrix (blue).

From the subthreshold slopes of the $I_D - V_G$ characteristics in Figure 2.9, we also calculate the interface trap density of single NW FET devices with different dielectric environments to exclude any effects of surface traps on calculated doping

concentrations. The subthreshold slope $S^{-1} = \frac{dlogI_D}{dV_G}$ is related to the interface trap density by,

$$S = \ln 10 \frac{kT}{q} \left(1 + \frac{e^2}{c_{ox}} N_{trap} \right)$$
(10)

where the C_{ox} is the gate oxide capacitance and N_{trap} is the trap density per area per unit energy. As the NW is only 15-nm thick and fully depleted, *S* measures all the traps at the NW surface, not only at the gate-NW interface. The calculated trap densities $(\frac{N_{trap}}{d})$, where *d* is the NW diameter) are listed in Table 2.3. Within the error of the measurement, there is no significant change in trap density upon encapsulating the NW devices in polymer or HfO₂ matrices.

cm ⁻³ V ⁻¹	PMMA	PVDF	HfO ₂
Before encapsulation	$(6 \pm 2) \times 10^{18}$	$(4 \pm 1) \times 10^{18}$	$(7 \pm 2) \times 10^{18}$
After encapsulation	$(7 \pm 4) \times 10^{18}$	$(4 \pm 2) \times 10^{18}$	$(4 \pm 2) \times 10^{18}$

Table 2.3. Trap Densities in PbSe NWs

The relative air-stability of HfO₂-coated n-type NW devices provides us with a platform to quantitatively study the ionization energy of Pb in PbSe NWs and investigate the electron barrier at the metal-NW contact. Representative temperature-dependent $I_D - V_G$ characteristics between 230 and 320 K for Pb-doped-single NW FETs with HfO₂ encapsulation are shown in Figure 2.11A. The Schottky barrier for electrons at the

metal-NW contact is extracted from temperature-dependent $I_D - V_D$ characteristics as 0.196 eV [Figure 2.11B], using the thermionic emission equation:³⁸

$$I = A^* T^2 \exp\left[-\frac{q\phi_{MS} - \left(\frac{qE}{4\pi\epsilon_{PbSe}}\right)^{0.5}}{k_B T}\right]$$
(11)

Where A^* is the effective Richardson's constant, k_B is Boltzmann's constant, ϕ_{MS} is the SB height, and *E* is the electric field at metal semiconductor interface. $\left(\frac{qE}{4\pi\epsilon_{PbSe}}\right)^{0.5}$ describes the image-force lowering effect and is proportional to $V_D^{1/2}$.



Figure 2.11 (A) $I_D - V_G$ characteristics of a HfO₂-covered, 5 Å Pb-doped single NW FET at $V_D = 2$ V at temperatures from 230 K to 320 K. (B) $\ln(I_D) - 1000/T$ plots at different

 V_D and the electron barrier at metal-semiconductor interface as a function of $V_D^{1/2}$. ϕ'_{MS} represents $\frac{q\phi_{MS} - \left(\frac{qE}{4\pi\epsilon_{PbSe}}\right)^{0.5}}{q}$. The extrapolation of the inset plot gives the SB height (0.196 eV). (C) Calculated free electron concentration (black symbols) as a function of temperature (*T*) and (red line) fit to $\ln(n)$ versus *T*.

As the barrier height is about half of the bandgap energy of PbSe NW despite its n-type doping, it suggests the Fermi level at the NW/metal contact interface is largely pinned, consistent with our group's previous report.³⁰ The electron concentrations at various temperatures are extracted from V_T and plotted in Figure 2.11C. The electron concentration (*n*) is exponentially proportional to the ionization energy of donors (E_I) and temperature (*T*) according to the following relation:^{25,38}

$$n \propto exp \ (-\frac{E_I}{2k_BT}) \tag{12}$$

Thus, the ionization energy of Pb atoms in HfO₂-covered PbSe NWs is extracted by fitting ln(*n*) against 1/T and found to be 0.04 ± 0.01 eV, consistent with our theoretical calculation results [Table 2.2]. The $I_D - V_G$ characteristics of two more HfO₂-covered single PbSe NW devices are measured between 80 K and 300 K and give E_I of $24 \pm 3 \text{ meV}$ [Figure 2.12A] and $30 \pm 10 \text{ meV}$ respectively, which are slightly smaller values than the measured E_I ($40 \pm 10 \text{ meV}$) for temperatures between 230-320 K. As shown in Figure 2.12B, the temperature dependence of the carrier concentration is different between the higher and the lower temperature ranges. Given the positive temperature-dependent coefficient of the bandgap for lead chalcogenides (*i.e.*, the bandgap is smaller at lower temperatures) and the dominance of the Schottky barrier at lower

temperatures (as evidenced by the dramatic shift in V_7 and lower currents) the lower and change in E_I found including a lower temperature range is not surprising. We hypothesize that this slightly smaller E_I is due to the temperature-dependent band structure of PbSe NWs and the dominance of the Schottky barrier at lower temperatures. Nevertheless, we observe a shallow ionization energy of Pb for HfO₂-coated NWs, which can be attributed to the considerable reduction in dielectric mismatch. Given the ionization energy of impurities in bulk lead chalcogenides is less than 0.01 eV,⁴⁰ quantum confinement effects are anticipated to cause a further increase in E_I of around 30 meV in our 15 nm-diameter NW system.



Figure 2.12. (A) $I_D - V_G$ characteristics of a HfO₂-covered, 5 Å Pb-doped single NW FET at $V_D = 2 V$ at temperatures between 80 K to 300 K. (B) Calculated free electron concentration (black symbols) as a function of temperature (*T*) and fits to ln(*n*) *versus T* over a lower *T* range (80 – 240 K, purple), a higher *T* range (155 -300 K, pink), and over the whole range (80-300 K, dashed grey line). The E_I calculated from fitted slopes are labeled with corresponding colors. The errors in the electron concentration and E_I are from fitting.

2.7. Conclusion and perspectives

This study showcases a strategy to study the ionization energy and efficiency of doping fundamentally and provides a simple approach technologically to enhance doping efficiency in nanostructures. We find both experimentally and theoretically that as the dielectric constant of the surrounding medium increases, the proportion of ionized dopants in PbSe NWs increases, both for n-type (Pb/In) and p-type (Se) dopants, which agrees with Law's observation of a higher electron concentration measured after Al₂O₃ coating of PbSe NC solids.⁴² More generally, the dielectric environment influences excitonic^{43–46} and impurity states in other low dimensional materials, such as zero-dimensional Si nanocrystals²³ and two-dimensional graphene.²⁴ Engineering the dielectric environment of low-dimensional materials integrated in the platform of the FET, as shown here, may provide a route to study dielectric confinement effects on the electronic properties in a broader range of low dimensional material systems, such as nanocrystals, 2D perovskites and 2D semiconducting transition-metal dichalcogenides.^{45,46}

2.8. Reference

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CHAPTER 3 Enhanced Carrier Transport in Strongly-coupled, Epitaxially-fused CdSe Nanocrystal Solids

This work has been prepared in manuscript, entitled "Enhanced carrier transport in strongly-coupled, epitaxially-fused CdSe nanocrystal solids" by Qinghua Zhao, Guillaume Gouget, Jiacen Guo, Shengsong Yang, Tianshuo Zhao, Daniel B. Straus, Chengyang Qian, Nuri Oh, Han Wang, Christopher B. Murray, Cherie R. Kagan.

3.1. Introduction

Colloidal nanocrystals (NCs) are promising solution-processable materials for electronic and optoelectronic devices.¹ High carrier mobility arising from strong coupling between NCs is essential to numerous applications such as high-speed circuits, highbandwidth photodetectors, and high-efficiency photovoltaic devices.^{2,3} Electronic coupling is enhanced exponentially as the distance between NCs is reduced⁴ and is strongest for the direct fusion of NCs. The strength of interdot coupling and thus carrier transport depend on the degree of fusion including the width,^{5,6} number,^{7–9} and atomic perfection^{10,11} of necking formed between adjacent NCs. For example, missing necks are one of the barriers preventing carrier delocalization in two-dimensional PbSe NC superlattices where terahertz mobilities probing distances of 30-40 nm exceed 100 cm² V⁻¹ s⁻¹, but carrier transport at longer length scales of 500 nm - 200 μ m, typical in devices such as diodes and field-effect transistors (FETs), remains less extraordinary.^{7-9,12} Post-assembly treatments like successive ionic layer absorption and reaction (SILAR) have been applied to increase neck width and film conductance.¹³ However, films after SILAR treatments are highly conductive and exhibit no gate modulation, likely due to over-doping. Loss of gate modulation prevents extensive applications of these materials as semiconductors in devices. It is important to fundamentally understand the impact of neck formation to achieve high mobility carrier transport and provide guidance in engineering NC materials for electronic and optoelectronic devices.

Compared to lead chalcogenides, which possess narrow bandgaps and thus undesirably high off currents in device measurements, CdSe has a larger bandgap and can offer a high current modulation (I_{ON}/I_{OFF}) for studies of charge transport and ultimately for application in electronics and optoelectronics. Here we take advantage of easily realized, epitaxially-fused structures in PbSe NC thin films and develop a two-step cation exchange (CE) method to create Cu₂Se thin-film intermediates to ultimately form zinc blende, epitaxially-fused CdSe NC films [Scheme 3.1]. The epitaxial necking considerably improves electronic communication and contributes to enhanced transient photoconductivity in the connected CdSe NC films by 10-200 fold compared to those reported in the literature for CdSe NC films with little or no measurable necking between NCs.^{14–20} A thin layer of Al₂O₃ is deposited by atomic layer deposition (ALD) to infiltrate the connected NC films and prevent the formation of a polycrystalline thin film during subsequent annealing at 200 °C. ALD encapsulation further increases the transient photoconductivity to 1.71 cm² V⁻¹ s⁻¹ and the diffusion length L_d for electrons to ~760 nm. We then use the platform of field-effect transistors (FETs) to study carrier transport at longer length scales of 100-240 µm. The epitaxially-fused, ALD-capped FETs exhibit onoff ratios of 10⁶ and electron mobilities of 35(3) cm² V⁻¹ s⁻¹ after doping.



Scheme 3.1. Cation exchange method

3.2. Experimental section

Materials: 1-octadecene (90%), oleic acid (90%), lead oxide (99.999%), trioctylphosphine (TOP, 90%), selenium pellets (99.999%), diphenylphosphine (98%), (3-mercaptopropyl) trimethoxysilane (MPTS, 95%), 11-mercaptoundecyltrimethoxysilane (MDPA, 95%), anhydrous iso-propanol (IPA), chloroform, hexane, methanol, toluene, dimethylformamide and acetonitrile are purchased from Sigma-Aldrich.

Substrate preparations: When using MDPA to form a self-assembly monolayer, substrates are immersed in 3 mM MDPA solutions in anhydrous IPA overnight inside glovebox after 30-min UV-ozone treatments. Then the substrates are rinsed with IPA 3 times, sonicated in ethanol for 5 min, blown dry with N_{2} , and then baked at 140 °C for 2 min inside a N_{2} -filled glovebox.

Cation exchange reactions: PbSe NCs with diameters from 5.5-7.5 nm are synthesized at various conditions following reported recipes.²¹ Cation exchange reactions are performed in an N₂-filled glovebox. In the first step, PbSe NC films with a thickness of 5-20 nm are obtained by spin-coating 5-20 mg mL⁻¹ PbSe NC dispersions in toluene at 800 rpm for 20 s and 2000 rpm for 5 s. The films are then treated by 10 mg mL⁻¹ NH₄SCN solutions in methanol for 60 s and rinsed with methanol 3 times to replace oleate ligands. In the second step, PbSe NC films are then soaked at 80 °C in cation reaction solutions of 0.03 mg mL⁻¹ [Cu(CH₃CN)₄]PF₆ in DMF with 1 %v/v methanol. Then films are treated with 1M Na₂Se solutions in methanol for 10 min to make nonstoichiometric Cu_{2-x}Se thin films, followed by three times rinsing with methanol and by blowing dry with N₂. In the fourth step, Cu_{2-x}Se NC films are then soaked in a mixture of toluene, TOP, and methanol with

50-100 eq. of CdI₂ at 80 °C overnight. CdSe NC films are then rinsed by methanol three times and blown dry by N_2 .

Characterizations: Room temperature FET measurements are conducted with a Karl Suss PM5 probe station mounted in glovebox, equipped with an Agilent model 4156C semiconductor parameter analyzer. Transistor and time-resolved microwave conductivity (TRMC) measurements are performed on NCs with a diameter of 6 nm in N₂-filled environments. TEM images are taken by a JEOL F200 scanning/transmission electron microscopy equipped with a cold field emission source operating at 200 kV.

Details of TRMC measurements: Our group's TRMC set-up is an updated version of the one reported in previous work.²² In the current setup, an HP 8671B Synthesized CW generator is used to generate X-band (~9 GHz) microwaves. The microwave signal is converted to voltage by a Herotek DTM180AA Schottky diode and then digitalized on a Keysight DSO-S 054A oscilloscope. The conversion follows $\frac{\Delta P}{P} = n \frac{\Delta V}{V}$, n = 1.31, when the change of voltage is small. The detected voltage is amplified by a CLC100 amplifier and a HP 462A pulse amplifier. A Quantel Ultra Nd:YAG laser is used to generate ~5 ns, 532nm laser pulses, which are then focused through an aperture into the resonant cavity. The expanded laser spot at samples has a diameter of 9 mm. To prevent oxidation, samples are loaded into the resonant cavity in the nitrogenfilled glovebox. The change in conductance ΔG equals to $\frac{K\Delta P}{P_IP}$, where the sensitivity factor K is -34000(1000) and the correction factor F_I is 2 for the illuminating spot of 9 mm in diameter. Quantum yield-mobility product can be calculated from the change of conductance,

$$\Sigma \phi \mu = \Delta G / \beta q I_0 F_a$$
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where the aspect ratio of the wave guide β is 0.9/0.4, I_0F_a is absorbed photons per pulse per area. F_a is measured by an integrating sphere. The experimental signal is a convolution of an instrumental response function (*IRF*) and exponential decays, *Signal* \propto *IRF* $\otimes \Delta G$.²³

$$IRF = \frac{\sigma}{\tau_{RC}} exp\left(0.5 * \left(\frac{\sigma}{\tau}\right)^2 - \frac{t - t_0}{\tau}\right) \times erfc\left(\frac{1}{1.41} * \left(\frac{\sigma}{\tau} - \frac{x - t_0}{\sigma}\right)\right)$$

where σ_{laser} is 2.144(2) ns for the Gaussian beams and the cavity response time τ is 18-19 ns in this work.

3.3. Sequential cation exchange in epitaxially-fused NC solids

3.3.1 TEM characterization of PbSe, Cu₂Se, and CdSe epitaxially-fused NC solids

Oleic acid capped, PbSe NC dispersions, tailored in diameter from 5.5 nm to 7.8 nm, are deposited *via* spin-coating to form thin films and subsequently treated by NH₄SCN ligand exchange to realize epitaxially-fused NC structures.²¹ Quasi-square packing of the PbSe NCs with predominate fusion along the <100> atomic lattice is confirmed by high-resolution transmission electron microscopy (HRTEM) lattice imaging and fast Fourier transforms (FFTs) of the lattice orientation [Figure 3.1A]. In assemblies of Pb- and Cd-chalcogenide NCs, {100} attachment is more favorable to achieve strong electronic coupling than other attachment orientations considering the higher proportion of defect-free necks^{24,25} and theoretically stronger wavefunction overlap.²⁶ The angles of intersection between spots in the FFTs [insets of Figure 3.1A, D] show the angle between the <100> and <010> NC lattice slightly deviates from 90°.²⁷



Figure 3.5. (A)-(C) High resolution and (D)-(F) low-resolution TEM images of a PbSe NC (black, (A) and (D)), a Cu₂Se NC (green, (B) and (E)), and a CdSe NC (red, (C) and (F)) film. Schematics in (A)-(C) show epitaxially connected NCs along <100> atomic lattices with a diameter *d* and a necking width *l*. Insets in (A)-(C) show corresponding FFT of the atomic lattice images with representative high-resolution reflections labeled. Insets in (D)-(F) show FFT of NC lattices imaged in highlighted regions (red ellipses). Scale bars are (A)-(C) 2 nm and (D)-(F) 100 nm.

Out-of-plane misalignment due to orientational mismatch is observed and leads to narrower necks, as shown in Figure 3.2 where a {100} facet contacts a {110} facet.²⁴ {100} facets can fuse with adjacent {100} facets, rotating n/4 π along the symmetric axis through atomic matching. In most cases, n is even and the orthogonal facet in plane is a

{100} facet, for instance the connection between NC a with NC b or NC c Figure 3.2.
When n is odd, the orthogonal facet in plane is {110} instead of {100}, for example the connection between NC b and NC d, and orientational mismatch and a narrower neck is observed.



Figure 3.2. High resolution TEM of four connected PbSe NCs, fast Fourier transform (FFT) patterns of the assembly (up) and of each NC (sides) with lattice fringes labeled. On the right FFTs, common (020) orientation of **NC b** and **NC d** is highlighted with dashed circles.

Diameter (nm)	Neck width (nm)	l/d
5.7 ³¹	2.5	0.44
7.8 ³¹	3.5	0.45
6.2 ¹³	3.1	0.50

Table 3.1. PbSe NC diameter and neck widths reported in the literature

Consistent with literature values [Table 3.1],^{13,28–30} the average necking width to NC diameter ratio l/d is 0.49(7) [histograms in Figure 3.3A] and shows little dependence on the size of the NCs for diameters ranging from 5.5 nm to 7.8 nm [Figure 3.3B, C].



Figure 3.3. Histograms of l/d in PbSe NC films with diameters from 5.5 nm to 7.8 nm (A), a diameter of 7 nm (B), and 5.5 nm (C). The bin is 0.05, approximately equal to half of the ratio between lattice constant and diameter. (D) HRTEM images of epitaxially connected PbSe NC films with a diameter of 5.5 nm.

Lateral grains are observed within which NCs are aligned like in superlattices [Figure 3.1D].³² The size of epitaxially-connected, ordered NC grain is measured on Image J. The number of particles per grain is obtained by calculating the ratio between grain surface area and the surface area of the crystal motif. The histograms are shown in Figure 3.4. Grain sizes are averaged on at least 50 grains. On average, there are 344 ± 202 particles per grain in PbSe NC films. 98% of lateral grains contain 100 NCs or more, 10 times smaller than that for PbSe NC superlattices assembled at the liquid-air interface, but the corresponding domain size is over 50 nm and is thus larger than reported coherence lengths in such superlattices.^{7,29}



Figure 3.4 Histograms of the number of particles per grain in PbSe NC films

To avoid high reaction temperatures exceeding 170 °C^{33–35} as required in direct Pb²⁺-to-Cd²⁺ exchange which can degrade connected films, Cu₂Se nanocrystals (NCs) with a binding energy between PbSe and CdSe are sought as intermediates to lower the thermodynamic barrier (PbSe: 302.9 kJ/mol, Cu₂Se: 255.2 kJ/mol, CdSe: 127.6 kJ/mol)

to CE. PbSe NC films are soaked in solutions of 0.03 mg mL⁻¹ [Cu(CH₃CN)₄]PF₆ in dimethylformamide (DMF) with 1 %v/v methanol at 80 °C. Methanol binds more strongly to the binary cation Pb²⁺ and thus promotes the replacement. The solvent DMF is chosen for its high polarity and its boiling point which exceeds the CE temperature. In comparison, film delamination is observed when using toluene or oleylamine as the solvent and CE is extremely slow in octadecene because of the low Cu-precursor solubility in nonpolar solvents. The Cu-precursor concentration of 0.03 mg mL⁻¹ is optimized to yield the best film quality, with minimal film delamination and no observation of precipitated copper. The Se lattices, the neck width, and the assembly structure remain unchanged after CE to form the Cu₂Se NC intermediates [Figure 3.1B, E and Figure 3.5A].



Figure 3.5. Histograms of the ratio between neck width and NC diameter l/d in Cu₂Se (A), and CdSe (B) NC films. The bin is 0.05, approximately equal to half of the ratio between lattice constant and diameter.

Next, Cu⁺-to-Cd²⁺ reactions are adapted from literature methods for $Ag^+ \rightarrow Cd^{2+}$.³⁶ TOP is necessary to bind Cu⁺ and facilitate CE, but can strip surface Se atoms.³⁷ To offset the loss of Se, Cu₂Se NC films are treated by Na₂Se before the second CE. Non-stoichiometric Cu_{2-x}Se NCs are confirmed by energy-dispersive X-ray spectroscopy (EDX). Cu_{2-x}Se NC films are then soaked in a mixture of toluene, TOP, and methanol with 50 to 100 eq. of CdI₂ at 80 °C overnight. The quasi-square connected structure is well preserved [Figure 3.1B, F] throughout the CE method. The neck l/d grows from ~0.5 to 0.71(8), further improving connectivity between NCs. The increased neck width is likely attributed to the methanolic Na₂Se treatments of Cu₂Se NC films. Chalcogenide treatments alone have been shown to facilitate fusion.³⁸ In addition to CE, treatment in Se²⁻ and Cd²⁺ solutions completes one SILAR cycle.¹³

Figure 3.6A shows that there are 168 ± 96 particles per grain and 121 ± 67 particles per grain in CdSe NC films, giving average grain sizes larger than 50 nm for NCs with 6 nm in diameter. Figure 3.6B gives an example of CdSe NC films where multiple grains can be seen in TEM images. Note that film delamination is more severe on TEM grids, which causes material loss and a reduction in the number of NCs in the grains. The glass substrates and SiO₂/Si wafers used for carrier transport measurements are treated with self-assemble molecules as adhesives and thus no film delamination is observed.



Figure 3.6. (A) Histograms of the number of particles per grain. (B) Low-resolution TEM images of CdSe NC films and corresponding FFT patterns highlighting random orientation of the grains.

3.3.2 Absorption and X-ray diffraction measurements of PbSe, Cu₂Se, and CdSe NC films

The first exciton peak of PbSe NC films broadens and redshifts after fusing but is still confined as PbSe has a large Bohr radius [Figure 3.7A, black and blue curves]. Green curves in Figure 3.7A show the broadband infrared optical absorption of Cu₂Se NC films after Na₂Se treatments indicative of the Cu deficiency and high p-doping.³⁹ The absorption spectrum of CdSe NC films has one broad shoulder at ~670 nm, approaching the bulk CdSe band edge, indicating excitons are at best weakly confined in such epitaxially-fused CdSe NC films [Figure 3.7A, red curves].

X-ray diffraction (XRD) measurements are performed on drop cast samples with a film thickness of ~ 100 nm to obtain a sufficient signal-to-noise ratio and plotted in Figure 3.7B. Peak positions and lattice constants are labeled in Table 3.2. As shown by XRD, the crystal structure is rock-salt for PbSe NCs, berzelianite for Cu₂Se NCs, and zinc-blende for CdSe NCs is rock-salt.



Figure 3.7. (A) Absorption spectra of a PbSe NC film before (blue) and after (black) NH_4SCN treatment, a $Cu_{2-x}Se$ NC film (green), and a CdSe NC film (red) across broad and narrow spectral ranges to highlight excitonic and band edge features. (B) XRD of PbSe, Cu_2Se and CdSe NC films. *Si

Sample	2 <i>θ</i> ₁₁₁	a_{exp} (Å)	a _{ICSD*} (Å)
PbSe	25.14	6.13	6.121
Cu₂Se	27.08	5.70	5.694
CdSe	25.42	6.06	6.077

Table 3.2. Peak positions of {111} facets and corresponding lattice constants

*ICSD: Inorganic Crystal Structure Database. Cif file collection codes 63097 (PbSe),

41140 (Cu₂Se) and 41528 (CdSe).

3.4. Partial cation exchange of PbSe NC films



Figure 3.8. HRTEM images of NCs after 30 s (A)-(C) and 60 s (D) of the Pb^{2+} -to-Cu⁺ cation exchange reaction. Scale bars in (B)-(D) are 2 nm. (E) Percentage of residual Pb atoms in Cu₂Se NC films with different film thickness after CE at 80 °C for 4 h (dark grey) and 12 h (light grey).

As a nature of solid-state CE, reaction kinetics rely on film thickness. We monitor the progress of Pb²⁺-to-Cu⁺ CE over time for both monolayers and multiple layers of NCs. The amount of Pb in selected areas is measured by EDX analysis in the TEM for NC monolayers. In a monolayer of NCs after 30 s CE, lattice fringes of the parent PbSe NCs are still observed and are unevenly distributed in the film, in contrast to homogenous products found in solution CE [Figure 3.8A]. As indicated by TEM images of partially exchanged particles [Figure 3.8B, C], the two phases, PbSe and Cu₂Se, are immiscible and the replacement of Pb^{2+} by Cu^+ starts from more than one site, otherwise, alloy or Janus structures would form.⁴⁰ After 60 s CE at 80 °C, HRTEM shows the entire NC has the crystal structure of Cu₂Se [Figure 3.8D] and the amount of residual Pb in the NCs falls to the level of background noise. In NC multiple layers, EDX in the SEM instrument is used to qualitatively compare the amount of Pb and the elemental composition is determined by inductively coupled plasma - optical emission spectrometry (ICP-OES) after digestion. The reaction is slowed as film thickness increases [ICP results in Figure 3.8E]. The amount of Pb quickly drops in the first 2 h of the Cu⁺ CE reaction, but then slowly plateaus in the next 4 hours as the concentration of Cu⁺ precursor drops to levels too low to continue to drive the reaction [EDX results in Figure 3.9]. The Pb to Cu ratio is obtained by ICP-OES and is 0.054 for a 10-nm-thick film, 0.081 for a 20-nm-thick film, and 0.139 for a 30-nm-thick film after 4 h CE. Adding 1%v/v of 3 mg mL⁻¹ [Cu(CH₃CN)₄]PF₆ in methanol can further push the equilibrium forward and reduce the Pb to Cu ratio. The Pb to Cu ratio is 0.021 for a 10-nm-thick film and plateaus to ~0.057 for thicker films after 12 h CE. In transport studies, we spin coat 20-nm-thick films with 6 nm PbSe NC in diameter and run Pb²⁺-to-Cu⁺ CE for 12 h. Then following procedures mentioned above, CE-obtained CdSe NC films have negligible Cu, <3% Pb, and Cd to Se ratio is 1.26, confirmed by ICP-OES and EDX.

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Figure 3.9. The amount of Pb measured by energy-dispersive X-ray spectroscopy in a 20-nm-thick NC film as a function of time.

3.5. TRMC measurements of charge carrier transport in CE-obtained CdSe NC films



Figure 3.10. (A) TRMC transients of CdSe NC films after CE (black solid line), ALDcapped NC films after 200 °C annealing for 10 min (blue solid line), and NC films after 300 °C annealing for 10 min (red solid line) and then after ALD encapsulation (red dashed line). (B) TEM of a 300 °C annealed film. The scale bar is 20 nm. (C) TEM of an ALD-capped NC film after 200 °C annealing for 10 min. The scale bar is 10 nm. The time-resolved microwave conductivity (TRMC) technique²³ is applied to probe carrier transport *locally* (100-500 nm) and the photoexcited carrier lifetime in epitaxially-fused CdSe NC films. Representative photoconductance transients are plotted in Figure 3.10A. The product of the carrier yield and the sum of the carrier mobilities $\phi \Sigma \mu$ is equal to $\frac{\Delta G}{\beta q I_0 F_a}$, where ΔG is the change in film conductivity, β is the aspect ratio of the waveguide, and $I_0 F_a$ is the number of absorbed photons. The measured spectra are fit to the convolution of the instrumental response function and an exponential decay to extract $\phi \Sigma \mu$ and lifetime τ , as described in Section 3.2.

In pristine connected CdSe NC films, the $\phi\Sigma\mu$ is 0.28(1) cm² V⁻¹ s⁻¹ under a photoexcitation of 10¹⁵ photons/pulse/cm² at 532 nm, the lowest photoexcitation density that generates signal above the instrumental detection limit. The $\phi\Sigma\mu$ is > 10 times higher than that of wurtzite or zinc-blende CdSe NC films with limited epitaxial necking between NCs reported in the literature [Table 3.3].^{14–18} We attribute the enhanced carrier transport to the epitaxially-fused structure. The photoconductance $\phi\Sigma\mu$ is lower than FET mobilities because samples are measured without an external gate bias. Lifetimes τ of the bi-exponential decay are found from fits to be 2-16 ns and 130-170 ns [Figure 3.11A], similar to reported values in spin-cast wurtzite CdSe NC films.^{14,18} The diffusion length (L_d) is calculated as:

$$L_{d} = \sqrt{\langle D\tau \rangle} = \sqrt{\frac{k_{B}T}{q}} \Sigma f_{i} \tau_{i} \mu_{i}$$
(1)

where k_B is the Boltzmann constant, *T* is the temperature, *q* is the elementary charge, *D* is the diffusivity equal to $\frac{\mu k_B T}{q}$ according to Einstein's relation and f_i is the steady-state

population fraction of the decay. Assuming ϕ is 1, L_d is ~35 nm in as-made NC films, which is comparable to the connected NC grain size.



Table 3.3. Summary of TRMC literature values

Figure 3.11. Representative TRMC transients of (A) as-made 20-nm-thick CdSe NC films, (B) ALD-encapsulated NC films, (C) NC films after 300 °C annealing for 10 min, and (D) 300 °C annealed films after ALD encapsulation. Solid lines represent experimental signals and dashed lines represent the fit.

Annealing is known to further improve fusion and carrier transport.^{16,25,41} Annealing the epitaxially-connected NCs at 300 °C leads to the formation of

polycrystalline thin films with voids [Figure 3.10B]. In films annealed 300 °C for 10 min, $\phi \Sigma \mu$ is measured to be 1.42(7) cm² V⁻¹ s⁻¹ in thin films and L_d is ~370 nm [Figure 3.10A and Figure 3.11C]. Lifetimes τ of the bi-exponential decay is 13 ns and 130 ns. To prevent grain growth to form polycrystalline thin films [Figure 3.12], 1-3 nm Al_2O_3 is deposited to infiltrate the epitaxially-connected NC films via ALD at 80 °C before annealing at 200 °C for 10 min [Figure 3.10C]. A tri-exponential decay is used in fitting the measured spectra since a bi-exponential decay fails to fit the data within 10% error. In ALD-capped NC films, $\phi \Sigma \mu$ is 1.71(5) cm² V⁻¹ s⁻¹ and L_d is ~760 nm, making the structure promising for optoelectronic devices. Lifetimes τ of the tri-exponential decay are 16 ns, 155 ns, and 1.58 µs. The improvement of transient photoconductivity and electron lifetime time benefits from both the strongly coupled structure and ALD encapsulation. Previous studies have suggested that ALD encapsulation can lower the tunnel barrier to carrier transport and passivate traps in NC films.^{42,43} ALD encapsulation, following these same deposition conditions, for 300 °C annealed polycrystalline thin films also beneficially increases the transient photoconductivity to 2.43(7) cm² V⁻¹ s⁻¹ and L_d to ~720 nm. Lifetimes τ of the tri-exponential decay are 10 ns, 97 ns, and 720 ns. Increased carrier lifetime after ALD encapsulation is consistent with reports that improved optoelectronic performance in PbSe NCs⁴² and Si nanowires.⁴⁴

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Figure 3.12. Low resolution TEM of CdSe NC films, (A) annealed at 80 °C for 10 min, (B) annealed at 100 °C for 10 min, (C) annealed at 200 °C for 10 min, and (D) annealed at 300 °C for 10 min. Low resolution TEM of an ALD-capped CdSe NC film, (E) annealed at 80 °C for 10 min, (F) annealed at 100 °C for 10 min, (G) annealed at 200 °C for 10 min, and (H) annealed at 300 °C for 10 min. ALD Al₂O₃ is 1-3 nm thick.





Figure 3.13. (A) A schematic of the FET structure. (B) Representative $I_D - V_G$ curves at $V_D = 50 V$ of as-made CdSe NC FETs with Au contacts (black), ALD-capped CdSe NC FETs with Au contacts (blue), CdSe NC FETs with In/Au contacts after ALD encapsulation (green), TOP-InCl₃ doped CdSe NC FETs with Au contacts after ALD encapsulation (orange), and TOP-InCl₃ doped CdSe NC FETs with In/Au contacts after ALD encapsulation (cyan). (C) Transmission line measurements of contact resistance for as-made CdSe NC FETs with Au contacts (black) and CdSe NC FETs with In/Au contacts after ALD encapsulation (green) at $V_G = 50 V$.

Back-gate, top-contact field-effect transistors (FETs) are fabricated to explore carrier transport at longer length scales up to 240 μ m [Figure 3.13A]. 20 nm Al₂O₃ is deposited by ALD on n⁺-Si wafers with 300 nm thermally-grown SiO₂ and treated with MDPA. NCs are spincast on top of the Al₂O₃/SiO₂/Si stack. 40 nm Au is deposited onto NC films as electrodes by thermal evaporation unless otherwise indicated. The asexchanged zinc-blende CdSe NC films have n-type behavior as shown by the black I_D – V_G curve in Figure 3.13B. Devices shown in Figure 3.13B have a fixed channel width to length ratio of 15 for comparison. On-currents at $V_D = 50 V$ are below 100 nA. The extracted linear and saturation mobilities are $\mu_{FET_lin} = 0.2(1) \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for $V_D = 2 V$ and $\mu_{FET_sat} = 2.4(6) \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at $V_D = 50 \text{ V}$, respectively. The lower μ_{FET_lin} than μ_{FET_sat} is due to a large Au/CdSe NC contact resistance R_c , which is found by the transmission line method to be 700 Ω -m at $V_G = 50 V$ [Figure 3.13C]. NC films are then encapsulated by 50 nm ALD Al₂O₃. The first 10 nm is deposited at 80 $^{\circ}$ C and then an additional 40 nm is deposited at 200 °C. On-currents increase by 10⁴ and off-currents stay below 1 nA after ALD encapsulation [blue curve in Figure 3.13A]. Consistent with TRMC results, 77

ALD encapsulation benefits carrier transport such that μ_{FET_lin} at $V_D = 2 V$ is 0.82(9) cm² V⁻¹ s⁻¹ and μ_{FET_sat} rises to 8(2) cm² V⁻¹ s⁻¹.

We then dope the NC films to reduce the contact resistance. We adapt the thermal-diffusion In doping method previously reported by our group.⁴⁵ 120 nm In/ 70 nm Au electrodes are deposited. Then the NC film is encapsulated by 50 nm ALD Al_2O_3 , 10 nm at 80 °C first and 40 nm at 200 °C. R_c is reduced to 1 Ω -m at $V_G = 50 V$ [Figure 3.13B]. FET mobilities improve and show negligible V_D dependence, consistent with the small contact resistance, as $\mu_{FET \ lin}$ is 23(3) cm²V⁻¹s⁻¹ and $\mu_{FET \ sat}$ is 24(2) cm²V⁻¹s⁻¹. Off-currents remain at ~100 pA and I_{on}/I_{off} increases to ~10⁷. Additional doping of the NC channel by depositing 1 nm In across before ALD encapsulation, with the same In/Au contacts, does not change $\mu_{FET sat}$, 21(1) cm²V⁻¹s⁻¹ but reduces I_{on}/I_{off} to ~10³ as the NC films more conductive. Considering In diffusion is thermally-driven by the increased temperatures during the ALD process,⁴⁵ the In doping process can be hindered by the growth of Al_2O_3 . To more efficiently dope the NC channels, we perform a solution doping process following an unpublished method in our group using TOP-InCl₃ as the source of dopants and the doped CdSe forms Ohmic contacts with Au electrodes. The efficient doping of TOP-InCl₃ is confirmed by the smaller threshold voltage (V_{th}) of 6(1) V, compared to 19(3) V in films with 120 nm In at contacts and 18(1) V in films with 120 nm In at contacts and 1 nm In across the channel. For TOP-InCl₃ treated NC channels and with Au contacts, the FETs have higher $\mu_{FET \ sat}$ of 35(3) cm²V⁻¹s⁻¹ with on/off ratio of 10⁶ [orange curve in Figure 3.13A]. The mobility is the highest among CdSe NC films with comparable on-off ratios, which can be attributed to the epitaxiallyfused structure.^{45,46} Depositing In in the contacts and treating the channel with TOP-InCl₃ [cyan curve in Figure 3.13A] increases the on-currents at $V_D = 50 V$ to 10 mA, but the NC films lose the gate modulation because of the heavily doping.

3.7. Conclusion and perspectives

In conclusion, we combine the advantages of the easily-obtained, epitaxially-fused structure in PbSe NC films and the wide bandgap in CdSe NC through a sequential CE process and demonstrate a notable, structure-induced enhancement in charge transport both at the length scales of 30-800 nm and at 100-200 μm. These epitaxially-fused CdSe NC thin films possess a diffusion length of 760 nm and a high FET electron mobility of 35 cm² V⁻¹ s⁻¹ with off-currents below 10 nA, allowing for applications in high-speed circuits and efficient optoelectronic devices. As the intermediates-Cu₂Se nanocrystals-have been widely explored as starting materials for CE, the sequential solid-state CE can be employed to expand the library of epitaxially-fused nanostructures and study their collective properties.

3.8. References

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CHAPTER 4 Impurities in Nanocrystal Thin-film Transistors Fabricated by Cation Exchange

This work is under preparation for manuscript, entitled "Impurities in Nanocrystal Thinfilm Transistors Fabricated by Cation Exchange" by Qinghua Zhao, Shengsong Yang, Christopher B. Murray, and Cherie R. Kagan*

4.1. Introduction

Cation exchange (CE) is a powerful tool in preparing nanostructured materials, in which parent cations are replaced with guest cations while maintaining the anion framework and shape of the starting materials. Cations can be exchanged completely, opening up access to a wider composition range of size- and shape- engineered nanostructures,¹ or partially, enabling the preparation of nanostructures hard to access *via* direct syntheses, such as core-shell structures,² heterostructures,^{3,4} and alloys.⁵ CE-obtained nanostructures show great potential in catalytic,⁶ photonic,^{2,7,8} and electronic applications.⁵ However, residual parent cations in the product material can limit the performance of CE-obtained materials in devices. Studies show that the luminescence quantum yield is lower for nanocrystals (NCs) obtained by CE than by direct synthesis.^{1,9} Yet, few studies have explored the effects of inherited chemical impurities on electronic device performance.

In this work, we report the effects of residual cation impurities in CE-nanostructures on the device performance of back-gate, top-contact, thin-film transistors (TFTs) [Figure 4.1A].¹⁰ CdSe NC thin films are synthesized from epitaxially-fused PbSe NC films *via* a sequential CE process. Residual Pb impurities impede the TFT turn-on, as measured by an increase in subthreshold swing (*SS*); increase TFT hysteresis, quantified by the difference in the sweep direction threshold voltage (ΔV_{th}); and increase bias stress effects, measured by the decline in the on-state, drain-source current $(I_{D,ON})$. By modifying the gate oxide composition and surface chemistry and by ALD encapsulation, the detrimental effects of Pb impurities are reduced. Temperature-dependent TFT measurements show residual Pb increases the band tail and thus the activation energy for carrier transport from 35 meV to 62 meV, as the amount of Pb impurities increases from 2% to 7%. Finally, we find the effect of impurities depends on the impurity distribution vertically away from the semiconductor/oxide interface and is reduced as the impurities are removed from the interface, increasing TFT electron mobilities by 10x

4.2. Experimental section

Materials: 1-octadecene (90%), oleic acid (90%), lead oxide (99.999%), trioctylphosphine (TOP, 90%), selenium pellets (99.999%), diphenylphosphine (98%), (3-mercaptopropyl) trimethoxysilane (MPTS, 95%), 11-mercaptoundecyltrimethoxysilane (MDPA, 95%), anhydrous solvents are purchased from Sigma-Aldrich.

Substrate preparations: substrates are immersed in 3 mM MDPA solutions or 5% MPTS in anhydrous IPA overnight after 30-min UV-ozone treatments. The substrates are rinsed 3 times with IPA, sonicated for 5 min in ethanol, and then blown dry with N₂.

Characterizations: Room temperature FET measurements are conducted with a Karl Suss PM5 probe station mounted in glovebox, equipped with an Agilent model 4156C semiconductor parameter analyzer. Cryogenic FET measurements are conducted with a Lakeshore Cryotronics vacuum probe station. The cross-section sample is prepared by focused-ion beam lithography (TESCAN S8000X FIB/SEM) and imaged by a highresolution TEM (JEOL F200). Calculation of the interface trap density and hysteresis: SS can be used to find the interface trap density as:

$$SS = \frac{k_B T ln 10}{q} \left(1 + \frac{N_{INT} q}{C_{ox}} \right),$$

where k_B is the Boltzmann constant, *T* is temperature, N_{INT} is trap density, and C_{ox} is the oxide capacitance.¹¹ The additional interface trap density introduced in the devices with 7% Pb, compared to <2% Pb, is estimated by the difference in their SS (ΔSS). To quantitively describe the hysteresis, we calculate the difference between the turn-on voltage (V_{th}) extracted from the $I_D - V_G$ curve of the forwarding and backward scans (ΔV_{th}). ΔV_{th} is calculated from sweeps at a fixed scan rate of 4 V/s between 50 V and -50 V, noting hysteresis is sensitive to sweep conditions. Hysteresis between the backward $I_D - V_G$ scans and the forwarding scans.

4.3. TFT performance in CdSe NC films with chemical impurities from cation exchange

6 nm, oleic-acid capped, PbSe NCs are synthesized, dispersed, spin-cast and exchanged with thiocyanate ligands to form 10-nm-thick, epitaxially-connected NC films [Figure 4.1A]. The films are deposited on thermally-oxidized, n⁺-Si substrates treated with MPTS unless otherwise stated. Sequential CE of PbSe NC films, first with Cu⁺ and then with Cd²⁺, is used to form CdSe NC films [Figure 4.1B]. By controlling the Cu⁺ reaction time, we prepare CdSe NC films containing 2% and 7% residual Pb, as measured by inductively coupled plasma mass spectrometry. Au/In source-drain electrodes are deposited to complete the TFTs [Figure 4.1C].



Figure 4.1 Transmission electron microscopy images of (A) a PbSe NC film, (B) a cation-exchange obtained CdSe NC film. (C) Schematic of the NC thin-film transistor configuration. (D) Representative $I_D - V_G$ curves at $V_D = 50 V$ of a CE-obtained CdSe NC FET with 2% (black) and 7% residual Pb (blue). Comparison to a CE-obtained CdSe NC FET with 2% residual Pb and 6 Å of Pb deposited on the channel (red). Forward scans from 50 V to -50 V (solid) and reverse scans from -50 V to 50 V (dashed).

Drain current (I_D) versus gate voltage (V_G) characteristics of TFTs with thin-film channels having 2% (black) and 7% (blue) residual Pb are shown in Figure 4.1D. Both $I_D - V_G$ curves exhibit n-type behavior with similar off- and on-state I_D . However, the $I_D - V_G$ characteristics differ in the subthreshold region, where the NC channel is depleted. The subthreshold swing $SS = \left(\frac{dlogI_D}{dlogV_G}\right)^{-1}$ is larger in devices having channels with more residual Pb atoms, *i.e.*, 13(3) V/dec (for 7% residual Pb) versus 6.6(7) V/dec (for 2% residual Pb). From the difference in *SS*, we calculate the additional interface trap density introduced by residual Pb, which is ~0.008(4) additional interface traps per Pb considering a 10-nm thick, square-packed NC channel. Greater residual Pb also creates a larger hysteresis. ΔV_{th} is 10(3) V in devices with 7 % Pb, larger than 6(2) V in devices with 2% Pb for a scan rate of 4 V/s between 50 V and -50 V, noting hysteresis is sensitive to sweep conditions. ΔV_{th} approximately linearly decreases with the amount of residual Pb [Figure 4.2]. When the amount of Pb is ~10%, the films are seen to be composed of CdSe NCs containing smaller PbSe NCs [Figure 4.2] and ΔV_{th} varies from 68 V to 212 V.


Figure 4.2 Hysteresis (ΔV_{th}) as a function of the amount of residual Pb atoms in films. Inset: transmission electron microscopy images of a partially exchanged PbSe NC film by Cu⁺.

To compare the effects of residual Pb inherited from the parent NCs and Pb introduced after CE, control samples are made by thermally depositing 6 Å of elemental Pb onto the surface of NC channels with 2% residual Pb [the red curve in Figure 4.1D]. Assuming cubic close-packing of Pb, 6 Å Pb adds 1×10^{15} cm⁻² atoms, comparable to the Pb concentration difference in 10-nm thick CE films with 2% and 7% Pb. Thermally-deposited Pb atoms substantially increase ΔV_{th} by 30 – 50 V, but lead to a small rise in *SS* of 1.3(3) V, and thus, in interface traps per Pb of 0.0016(4), considerably lower than that from residual CE Pb. We hypothesis that the small change in *SS* is because of the lack of interaction between deposit Pb and the gate oxide surface.

4.4. The effects of residual Pb on SS and ΔV_{th} in TFTs with different interfaces

We modify the interface to understand the correlation between the interface and the impact of Pb impurities. Two methods are investigated to reduce the interface trap density, and thus the *SS* [Figure 4.3A]. First, we replace the short-chain, MPTS self-assemble monolayer (SAM) modifying the SiO₂ gate oxide layer with a long-chain, MDPAmfunctionalized Al₂O₃/SiO₂ stack to reduce the -OH density at the gate oxide surface, which are a large source of interface electron traps in TFTs.^{12,13} Untreated Al₂O₃ is less acidic and has a lower -OH density ^{14,15} compared to SiO₂.¹⁶ SAMs are widely used to passivate gate oxide surfaces. MPTS reacts with silanol groups on SiO₂ to partially, but not completely, passivate the surface.¹⁷ Longer-chain SAMs pack more

densely, better passivating surface -OH and increase the barrier width for charge carrier tunneling to unreacted -OH.^{18,19} TFTs with MDPA-modified AI_2O_3/SiO_2 oxide stacks (in comparison to MPTS-modified SiO_2) have a lower *SS* of 4.5(4) V/dec in channels with 2% Pb and of 8(1) V/dec in channels with 7% Pb. The additional interface trap density introduced by Pb is reduced by half to 0.004(1) traps per Pb.

Second, we encapsulate the NC TFT channel by low temperature Al₂O₃ ALD encapsulation, first depositing 10 nm at 80 °C, to ensure infiltration, and then an additional 40 nm at 200 °C, to increase thickness. Note: ALD encapsulation by 50 nm Al₂O₃ above 150 °C does not reduce SS [Figure 4.3B]. ALD encapsulation does not change the SS on MPTS-modified SiO₂ significantly, in comparison to the variation among samples, suggesting the interface traps are dominated by surface -OH. On MDPA-modified Al_2O_3 , the SS is reduced to 5.7(5) V/dec in channels with 7% Pb and 4.2(2) V/dec in channels with 2% Pb, and thus the additional interface trap density from residual Pb is reduced to 0.0019(7) interface traps per Pb. The additional interface traps introduced by one Pb atom decrease as the total interface trap density is reduced [Figure 4.3A, inset]. We hypothesize the correlation is due to a weak bond that forms between Pb and binding sites on the gate oxide, such as -OH, adding to the interface state density. The impact of Pb impurities on hysteresis and bias stress is reduced after reducing the interface trap density. ΔV_{th} displays no difference within variation after replacing the oxide and/or ALD encapsulation and decreases as the density of -OH groups decrease [Figure 4.3C].



Figure 4.3 Subthreshold swing (*SS*) (A) and hysteresis (C) of NC TFTs composed of channels on MPTS-modified SiO₂ before (black) and after ALD encapsulation (grey), of films on MDPA-modified Al₂O₃ before (blue) and after (green) ALD encapsulation. Solid bars represent channels with 7% Pb atoms and empty bars represent channels with 2% Pb atoms. The inset of (A) depicts the additional interface trap density introduced by Pb as a function of the interface trap density in channels with 2% Pb atoms (N_{INT}). (B) The difference of subthreshold slope before and after ALD encapsulation (SS). ALD process is conducted at 250 °C (left panel) and at 80 °C for the first 10 nm and at 200 °C for the rest (right panel).

4.5. The effect of residual Pb on charge carrier transport

Temperature-dependent TFT measurements are then conducted to investigate the influence of residual Pb atoms in the electronic structure of the CE-obtained CdSe NC film. ALD-capped CE-obtained 10-nm-thick CdSe NC films on MDPA-modified Al₂O₃ are used. Representative transfer curves at temperatures in a range of 160–300 K are plotted in Figure 4.4. On-currents increase as temperature increases and are higher in channels with less Pb impurities at a given temperature. Mobilities (μ_e) are the average between mobilities calculated from the forwarding and backward sweeps in the linear regime. More Pb impurities in channels lead to a greater device-to-device variation in μ_e .

At 290 K, μ_e averaged among at least 12 devices is 0.5(4) cm² V⁻¹ s⁻¹ in channels with 2-5% Pb atoms and is 0.8(2) cm² V⁻¹ s⁻¹ in channels with <1% Pb atoms.

 μ_e shows a positive dependence on temperature and the temperature-dependence is altered by residual Pb [Figure 4.4C]. Carrier transport is thermally activated, which is not supersizing in 10-nm-thick film with μ_e below 1 cm² V⁻¹ s⁻¹. The temperatures dependence deviates from a simple linear relation between $\ln \mu_e$ and T^{-1} at temperatures below 240 K. Studies have shown that the carrier transport mechanism is nearest-neighbor hopping (NNH) with Arrhenius behavior at higher temperatures and transfers to Mott or Efro-Shklovskii variable range hopping (VRH) at lower temperatures, depending upon the density of states and the temperature.^{20,21} However, given the CdSe NC films are intentionally doped by In in all devices and unintentionally doped by Pb in films with residual Pb, the ionization process of dopants can alter the proportion of occupied states in the transport regime and thus the probability of hopping between states, making it hard to extract the hopping barrier at lower temperatures. Thus, we use $\mu = \mu_0 \exp\left(-\frac{E_a}{k_BT}\right)$, where μ_0 is a prefactor and E_a is the activation energy required for hopping to the activation energy for NNH transport in 240-290 K. E_a is averaged among at least 3 devices. E_a is 35(5) meV in films with <1% Pb atoms and 62(2) meV in films with 2-5 % Pb at on-states. Higher E_a suggests that residual Pb increases the density of localized tail states below the conduction band, pinning the Fermi level at a lower energy level under a given applied gate bias. The picture of a larger band tail in the presence of Pb echoes the larger SS mentioned above. Except for Pb^{2+} at the gate oxide surface, Pb²⁺ in bulk NC films and on the gate oxide surface should also be accused of the larger band tails, since disorder in semiconductor lattice has shown to generate localized states.22



Figure 4.4. $I_D - V_G$ curves in linear regime ($V_D = 2 V$) at various temperatures in films with (A) 2% and (B) 7% Pb atoms. (C) Extracted μ as a function of temperature.

4.6. Residual Pb and the bias stress effects

The bias-stress effects are more significant in channels with 7% Pb than 2% Pb, as shown by a larger positive (negative) shift of V_{th} , under a positive (negative) gate bias [Figure 4.5].



Figure 4.5 Drain-source current and gate voltage $(I_D - V_G)$ curves at $V_D = 50 V$ of CdSe NC films with 2% Pb (A) and 7% Pb (B).

Bias stress effects are further examined by monitoring drain current over time under a continuous drain and gate bias of TFTs with MDPA-modified Al₂O₃ [Figure 4.6]. We use the ratio of $I_{D,ON}$ at t = 300 s to $I_{D,ON}$ at t = 0 s to quantify electrical instabilities. In channels with 2% Pb atoms, $I_{D,ON}(300 \text{ s}) / I_{D,ON}(0 \text{ s})$ is 0.5 and rises to 0.9 after ALD encapsulation, consistent with reported behaviors in as-synthesized CdSe NCs.²³ Increasing Pb from 2% to 7% reduces $I_{D,ON}(300 \text{ s}) / I_{D,ON}(0 \text{ s})$ by 5 times in uncapped channels and by 2.3 times with encapsulation, suggesting ALD encapsulation reliefs the detrimental effects of Pb on electrical instability.

The current decays under bias stressing at temperatures in a range of 280-330 K are plotted in Figure 4.6B and 4.6C. The bias-stress effect is more significant for devices operating at higher temperatures. For example, $I_{D,ON}(300 s)/I_{D,ON}(0 s)$ is 0.69 in channels with 2% Pb atoms and is 0.17 with 7% Pb atoms at 330 K. The decay can be fit into a stretched exponential function $I_{D,ON}(t) = I_{D,ON}(0 s) \times \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]$, where τ is relaxation time and β is exponent between 0 and 1. τ is plotted and fit against temperature, The relaxation time extracted from the current decay is fit by $\tau = v^{-1} \exp\left(\frac{E_T}{k_BT}\right)$. Frequency prefactor v is used to compare the reliability phenomenologically and lower v is correlated with higher electrical stability phenomenologically.^{24,25} With Pb increasing from 2% to 7%, v increases from 10⁶ Hz to 10⁷ Hz. E_T is 0.49(6) eV with 2% Pb atoms and is 0.52(2) eV with 7% Pb atoms.

Though the current physical picture of the bias-stress effects and E_T is unclear in nanocrystal TFTs, here list a few examples of mechanisms in organic FETs: (a) undesired diffusion of dopants,²⁶ (b) diffusion of H₂O or O₂ into the gate dielectric,²⁷ (c) trapped charge carriers accumulated at the gate dielectric surface,²⁸ (d) metastable deep traps

created by gate bias over time,^{29,30} and (e) mobile charges tunneling across the interface into the gate dielectric.^{31,32} E_T is the average energy required for such processes to occur, which means the diffusion barrier of carriers in example (a)-(c), the energy for creating the traps in example (d), and the energy cost for charge tunneling in example (e). In example (e), experiments show that increasing the energy barrier between the material and the polymer gate dielectric results in slower charge transfer from the channel to the dielectric surface under gate bias and a lower activation energy calculated from the temperature dependent decay.³²



Figure 4.6. (A) I_D/I_{D0} as a function of time at $V_G = 50V$ and $V_D = 5V$ in films with 2% Pb atoms before (grey) and after (red) ALD encapsulation and in films with 7% Pb atoms before (black) and after (wine) encapsulation. Current decays at $V_G = 50V$ and $V_D = 5V$ (B) in films with7% Pb atoms and (C) in films with 2% Pb atoms at temperatures from 330 K (dark red) to 280 K (light pink) with a step of 10 K. Insets: relaxation time as a function of temperature.

4.7. Reducing the effects of Pb impurities by driving them away from nanocrystalgate oxide interfaces

We explore methods to reduce the effect of residual Pb by driving impurities away from the semiconductor-oxide interface. The films are divided into two layers with a

thickness of t_1 for the first layer and t_2 for the second layer. We deposit the second layer of parent NC films after the first layer has been converted and then run the CE reaction for the same amount of time. Representative transfer and output curves are plotted in Figure 4.7A and Figure 4.7B for a 40-nm-thick film obtained by converting 20-nm-thick NC film each time. The CE-obtained CdSe thin film TFTs present a better performance in all aspects than those of being transformed as a whole [Table 4.1], with μ_e of 32(3) cm² V⁻¹ s⁻¹ v.s. 3(1) cm² V⁻¹ s⁻¹, ΔV_{th} of 21(2) V v.s. 50(10) V, SS of 5.4(2) V/dec v.s. 5.6(3) V/dec, and I_{on}/I_{off} of 10⁵-10⁶ v.s. 10⁴. We conduct an elemental mapping of the cross-section using TEM-EDX of a film with a total thickness of 40 nm and $t_1 = t_2 = 20$ nm. As the profile of cation distribution [Figure 4.7C] shown, Cd atoms are evenly distributed across the layer, while Pb atoms are concentrated on the second layer and no signal of Pb is detected at the interface. Schematics are drawn in Figure 4.7D to help explain the phenomena. When the films are converted as a whole, the diffusion pathway is longer than that for a slice of the film, thus slowing down the CE reaction and leaving more impurities at the interface. When the transformation is performed in two sections, the diffusion pathway is shortened for a more effective CE reaction. In the meanwhile, since the diffusion is driven by the concentration gradient, cations can diffusion into the first layer such that a week signal from parent cations is found in the first layer near the interface of two layers. Accordingly, a combination of $t_1 = 10 nm$ and $t_2 = 30 nm$ will result in the existence of Pb starting from 10-away from the oxide-semiconductor interface. The corresponding films have μ_e of 5(1) cm² V⁻¹ s⁻¹, ΔV_{th} of 29 (V), and SS of 5.6(3) V/dec. The surge of μ_e when increasing t_1 from 10 nm to 20 nm indicates that the Debye length is in 10-20 nm and in films with $t_1 = 20 nm$, the impurities in the active transport region are significantly reduced. Comparable SS between films with t_1 of 10

nm and 20 nm is consistent with results of the control sample described earlier, where impurities away from the interface do not contribute to the interface trap states.



Figure 4.7. (A) A representative $I_D - V_G$ curve at $V_D = 50 V$ and (B) $I_D - V_D$ curves for V_G from 0 to 50 V in steps of 10 V for a 40-nm-thick CdSe NC film TFT channel after ALD encapsulation. (C) Dark-field TEM and cation distribution profile of the cross-section of a 40-nm thick film with $t_1 = t_2 = 20 nm$. (D) Pb²⁺ diffusion pathways in a thick NC film during CE in a multilayer film (left) and layer-by-layer CE of two layers (right).

Table 4.1. TFT met	ics
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t ₁ +t ₂ (nm)	40+0	10+30	20+20
$\mu_e \left(cm^2 V^{-1} s^{-1} \right)$	3(1)	5(1)	32(3)
$\Delta V_{th}\left(V ight)$	50(10)	29(2)	21(2)
<i>SS</i> (V dec ⁻¹)	5.2(9)	4.2(3)	4.0(5)

4.8. Conclusion and perspectives

To summarize, we comprehensively study the influences of residual Pb on transistor performances and provide methods to reduce the detrimental effects. The interaction between the interface trap and residual Pb is found to play a key role in the impact of residual Pb. By reducing the interface trap density by replacing the gate oxide with MDPA-modified Al₂O₃ and applying low-temperature ALD encapsulation, Pb induced interface traps is reduced from 0.008(4) to 0.0019(7) cm⁻² per Pb and Pb induced hysteresis is eliminated. ALD encapsulation reduces the detrimental impact of Pb on bias-stress effects. Temperature-dependent studies further show that the mean activation energy of relevant trapping processes stays unchanged after encapsulation. The band tail is found to extend deeper into the bandgap in films with residual Pb, responsible for the poor carrier transport. Since the active region for carrier transport is close to the NC-oxide interface, the influence of Pb atoms greatly diminishes as Pb atoms are driven away from the oxide-semiconductor interface after conducting CE layer upon layer. The results we report in this letter offer general guidelines to optimize electronic device performance and pave the way for applying numerous CE-obtained materials as electronic or optoelectronic devices.

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CHAPTER 5 Future works and conclusions

5.1. Preparation of metal chalcogenides nanostructures by cation exchange

Over the past 100 years, materials have been evolving much faster than at any time in human history. The library is quickly expanded by modifications of natural materials, and mostly, by new materials developed for specific purposes. Yet, materials have been so far constrained in their properties by the chemistry, abundance, and stability of elements in the periodic table. Nanocrystals (NCs) with tunable properties can serve as 'artificial atoms' to build single/multiple-component NC assemblies. In strong coupled NC solids, properties emerge from collective interactions within assemblies at the mesoscale [100 –1000 nm] and offer great opportunities for designing materials with novel, orthogonal physical properties inaccessible in materials 'on the shelf'. It is therefore helpful to expand the library of strongly-coupled NC assemblies.

Cation exchange (CE) is a powerful post-synthetic method to synthesize desired nanostructures from an existing nanoscale template. In a CE reaction, parent cations are fully or partially replaced by guest cations while the anion lattice and the shape remain unchanged.¹ Nanostructures not readily accessible through conventional synthetic methods can be made *via* CE, such as in metastable phases (*e.g.* rock-salt CdSe² and *hcp* Cu₂Se³), heterostructures (*e.g.* nanorods with up to 8 segments⁴), or hollow structures (*e.g.* Cu₂S toroids⁵ and hollow CuInS₂ nanodisks⁶).

Thermodynamic and kinetic concepts have been used to predict the feasibility and outcome of a CE reaction. Take a CE with Cu⁺ for example, written as:

$$A_x E_y(s) + my Cu^+(sol) \rightarrow y Cu_m E(s) + \frac{x}{n} A^{n+}(sol)$$

The CE process can be broken down into 6 steps: $A_x E_y$ dissociation, $Cu_m E$ association, A^{n+} solvation, Cu⁺ desolvation, Cu⁺ diffusion inwards, and A^{n+} diffusion outwards.

To forecast if the reaction is thermodynamically allowed, the bulk lattice energy, widely accessible in literature, is employed to estimate the Gibbs free energy of the reaction. Based on calculated Gibbs free energies of aqueous reaction. The solvation process needs a more comprehensive understanding of solution environments to predict, including hardness, solubility product constant, and affinity to coordinating solvents.^{7,8} For example, CdSe and ZnSe have a higher solubility in polar solvents than Cu₂Se.⁸ Methanol is commonly used to favor the replacement of binary metal cations with Cu^{+ 3}or Ag^{+ 1} because methanol binds more strongly with multivalent cations than monovalent cations.

Chapters 3 and 4 have shown the transformations of epitaxially-fused PbSe NC films to Cu_{2-x}Se and CdSe NC films. Here are preliminary results of more CE reactions to prepare epitaxially-fused metal chalcogenides.

5.1.1 From PbTe NC solids to Cu₂Te NC solids

PbTe NCs are synthesized by Dr. Chenjie Zeng following established recipes.⁹ PbTe NC films are prepared by spin-casting or drop-casting. The films are treated with 1 mg/ml NH₄SCN solutions in methanol for 1 min. The films are Te-rich with a Pb to Te ratio of 1:1.24(2). The films are then soaked in reaction solutions containing 0.06 mg/ml $[Cu(CH_3CN)_4]PF_6$, 2%v methanol and 3%v TOP at 120 °C in N,N-dimethylformamide overnight. After reacting for 2 hours, the same amount of $[Cu(CH_3CN)_4]PF_6$ and methanol is added to push the reaction forward. The films are washed with acetonitrile three times and then with methanol three times. The stoichiometry of the product film is Cu_2 Te. The residual Pb is 2.8%. 5.1.2 Replacing Cu⁺ in Cu₂Se NC solids with Ge²⁺, Sn^{2+/4+}, Ag⁺, and Zn²⁺

Based on $Cu_2Se \rightarrow CdSe$ CE reactions described in Chapter 3 and Chapter 4, four other cations (Ge, Sn, Ag, and Zn) are employed to test the generality of the approach. In the reactions, metal halide solutions in methanol are mixed with toluene and trioctylphosphine (TOP). TOP is used to stabilize Cu⁺ in solution and can potentially be replaced with tributylphosphine to make the reaction faster.⁸ The reaction temperature and the concentration of metal halide and TOP are adjusted to control the composition and morphology of the products. The composition of the product is characterized by energy-dispersive X-ray spectroscopy (EDX) in the scanning electron microscopy (SEM) unless stated otherwise. All the reactions are carried in N₂-filled gloveboxes.

 $Cu^+ \rightarrow Ge^{2+} \rightarrow Ge^{2+} / Sb^{3+}$

1 mg/ml Gel₂ solution in toluene with 4% methanol and 3% TOP in volume is used as the reaction solution. The reaction is run at 80 °C overnight and the films are then washed with methanol three times. Using a 20-nm-thick film, the product is Ge_{1.23}Se where Cu is below the detection limit of EDX. Using a 100-nm-thick film, the product is Cu_{0.22}Ge_{1.25}Se as shown in Figure 5.1. In the 100-nm-thick film, 9% of Pb is inherited from the reactants which can be reduced by increasing the concentration of Cu when preparing Cu₂Se NC solids or sequential deposition and CE of multiple, thinner NC layers as mentioned in Chapter 4. Running the reaction in a 20-nm-thick film at room temperature yields Cu_{0.37}Ge_{0.58}Se.



Figure 5.1 EDX spectrum of NC films with a thickness of 100 nm after exchanging with Ge²⁺ at 80 °C

Bulk Ge₂Sb₂Se₅ with an fcc lattice structure is a phase transition material.¹⁰ Two Sb³⁺ precursors are tried. TOP-SbCl₃ precursors are prepared by stirring the mixture of 0.5 g SbCl₃ and 2.5 ml TOP at 75 – 100 °C for 1 h. TOP-SbCl₃ is then dissolved in 7.5 ml octadecene and degassed at 120 °C for 1 hour. GeSe NC films are soaked in Sb³⁺ solution at 125 °C overnight and then rinsed with hexane and methanol, each for three times. Films are heavily delaminated and only Sb is measured in films by EDX [Figure 5.2].



Figure 5.2 The product of reaction with GeSe NC films and TOP-SbCl₃

Methanolic solutions of SbCl₃ are then tested as the precursor. Various concentrations and reaction temperatures are tested. After soaking GeSe NC films in 100 mM methanolic SbCl₃ solutions at 60 °C for 30 min, the films are examined under SEM. As Figure 5.3 shown, the film is not uniform. Some parts are coral-like and some are flat NC islands similar to the starting materials. In Figure 5.3A, the spindle-like part is purely Sb₂Se₃ with no Ge, Cu, or Pb signal detected and in the dark parts with small spheres, suggesting the GeSe NCs in these regions become a Se source to react with SbCl₃ rather than being cation exchanged. In contrast, the composition is pretty uniform in areas like Figure 5.3B, Ge_{0.27}Sb_{0.55}Se. Reducing the concentration of SbCl₃ to 1mM produces films with uniform composition, Ge_{0.5}Sb_{0.3}Se [Figure 5.4]. No spindle structure is observed in these films. Running the reaction at room temperature only adds up to 2% Sb to the films.



Figure 5.3 SEM images of different areas in one sample prepared by soaking the GeSe NC film in 100 mM SbCl₃ solutions of methanol at 60 °C for 30 min.



Figure 5.4 SEM images of different areas in a NCs film prepared by soaking GeSe NC films in 1 mM SbCl₃ solutions of methanol at 60 °C for 30 min.

 $Cu^+ \to Sn^{2+} \ / \ Sn^{4+}$

Tin selenides have been explored as semiconductors for photovoltaic devices and photodetectors.¹¹ 0.05 ml of 30 mg/ml methanolic solutions of SnCl₂ is mixed with 0.15 - 0.3 ml TOP and 5 ml toluene. Cu₂Se NC films obtained from CE, details in

Chapter 2, are treated with Na₂Se solutions and then soaked in the Sn(II) solution overnight at room temperature (~20 °C). The composition of the product is measured in 20-nm-thick NC films. Increasing the amount of TOP from 0.15 ml to 0.3 ml strips off more Cu⁺ and changes the composition from Cu_{0.24}Sn^{II}_{1.43}Se to Cu_{0.15}Sn^{II}_{1.43}Se. It has been reported that Cu⁺ can be completely replaced by Sn²⁺ in a mixture of SnCl₂, oleylamine, and octadecene at 100 °C in 1 min.¹² In the future, we can try to gradually increase the reaction temperature and reduce the reaction time to completely remove the Cu impurities.

The work of preparing Cu-Sn(IV)-Se NC solids is collaboratively done with a former master student in Kagan group, Chenyang Qian. The hydrolysis of SnCl4 is so severe that it smokes when opening inside an N₂-filled glovebox. Instead, Sn(CH₃COO)₂Cl₂ is used to prepare an Sn⁴⁺ precursor solution following an established recipe that has been reported to prepare Cu₂Sn^{iV}Se₃ NCs from Cu_{2-x}Se NCs in solutions at 100 °C.¹² 60 mg/ml Sn(CH₃COO)₂Cl₂ is dissolved in octadecene with 1 ml of 1dodecanethiol and the mixture is degassed at 120 °C for 30 to 90 min until the solution is clear and no bubbling is observed. Then the Sn⁴⁺ precursor is dissolved in toluene with 3% by volume of TOP. The reaction is run at various temperatures for 1 hour. The concentration of Sn⁴⁺ is tested from 0.024 mg/ml to 0.096 mg/ml in steps of 0.024 mg/ml in reactions at room temperature. As the concentration increases above 0.072 mg/ml, the signal of Sn in the NCs increases above instrumental noise and a slight increase in the ratio of Sn to Cu as the concentration increases to 0.096 mg/ml is seen [Table 5.1]. Running the reaction at 60 °C with a 0.048 mg/ml Sn⁴⁺ solutions yields Cu_{1.52}Sn^{IV}_{1.36}Se, suffering from a significant loss of Se. In the future, reducing the reaction time and the concentration of TOP may reduce the loss of Se. Potentially we can adopt the published

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CE reaction at 100 °C without TOP if no film delamination happens.¹²

The resistance of the reactant and the products are measured by the four-probe methods [Table 5.2]. With the amount of Sn in Cu-Sn-Se NC increasing, the resistance becomes larger.

Sn precursor	0 mg/ml	0.024 mg/ml	0.048 mg/ml	0.072 mg/ml	0.096 mg/ml
Cu _x Sn ^{IV} ySe	Cu _{2.3} Sn _{0.23} Se*	Cu _{2.85} Sn _{0.25} Se	Cu _{2.85} Sn _{0.21} Se	Cu _{2.83} Sn _{0.30} Se	Cu _{2.89} Sn _{0.36} Se

Table 5.1 The composition of products at room temperature

*The signal of Sn comes from the instrumental noise.

Table 5.2 The resistance of the reactant and products

Sample	<r> (Ω- cm)</r>
Cu _{2-x} Se NC solids	232
After reacting with 0.048mg/ml Sn ⁴⁺ solution at room temperature for 1 hour	404
After reacting with 0.072mg/ml Sn ⁴⁺ solution at room temperature for 1 hour	1269
After reacting with 0.048mg/ml Sn ⁴⁺ solution at 60 °C for 1 hour	2206

$Cu^+ \rightarrow Ag^+ or Zn^{2+}$

 0.6 mg/ml AgNO_3 solutions in toluene with 1% methanol and 3% TOP in volume is used to react with Cu_{2-x}Se NC films at room temperature overnight. The product is Ag_{0.24(4)}Se. Another treatment by Na₂Se solutions in methanol can compensate for the loss of Se.

 0.5 mg/ml ZnCl_2 solutions in toluene with 1% methanol and 6% TOP in volume is used to react with Cu_{2-x}Se NC films for 12 hours. The reaction is tested at 80 °C and 100 °C. The Zn : Cu ratio is 2.7 : 1 at 80 °C and 4.4 : 1 at 100 °C, measured by inductively

coupled plasma spectroscopy. It has been reported that $Cu_{2-x}Se$ NCs can be completely exchanged to ZnSe NCs in solutions at 250°C but the reaction temperature is too high to use in solid-state CE reactions without film delamination.³

5.2. Epitaxially-fused NC assemblies in silicene-like and stripe-like structures

PbSe NCs with size in 4 – 9 nm are synthesized at temperatures from 150 – 200 °C using a hot-injection recipe modified from a reported method [Details of synthesis and washing steps in Chapter 3].¹³ To prepare PbSe NCs with an average diameter up to 7 nm and a first excitonic peak (λ_{1S}) up to 2040 nm, the molar ratio of oleic acid to Pb (OA/Pb) is 2:1. Increasing OA/Pb yields larger PbSe NCs [Figure 5.5].¹⁴ PbSe NCs with an average diameter of 7.7 nm and 9 nm are prepared with OA/Pb of 3:1 and 4:1, respectively, at 180 °C. λ_{1S} is 2400 nm for NCs in 9 nm and 2170 nm for NCs in 7.7 nm [Figure 5.5]. NCs are then spincast onto TEM grids and ligand exchanged with NH₄SCN following methods described in Chapter 3. As shown in TEM images [Figure 5.5], larger NCs with $\lambda_{1S} \ge 2040$ nm only form quasi-square arrays. In arrays formed by NCs with size in 5 – 7 and λ_{1S} of 1730 – 1920 nm, a mixture of square structures and a small fraction of honeycomb structures observed in single-layer regimes. As NCs become smaller than 5 nm, NCs tend to be less ordered.



Figure 5.5 PbSe NC films formed by NCs in various sizes.

In washing steps that are used to prepare NCs in Figure 5.5, antisolvents and solvents are both added into the "out-of-pot" solution, and precipitates are collected. We test a different washing method where only a small amount of hexane (5% in volume) is added into the "out-of-pot" solution. The mixture is then centrifuged at 6000 rpm for 5 min. Its precipitate and supernatant are separated into two centrifuge tubes. Isopropanol (IPA) is added to the supernatant to collect NCs. NCs from the precipitate (NC-p) and supernatant (NC-s) are redispersed in hexane, following by more washing steps to adjust the ligand concentration. λ_{1S} is 1920 nm for NCs-s and 1960 nm for NCs-p of a reaction at 180 °C for 60 s. The bandwidth of the first excitonic peaks is ~ 150 nm for both NCs-s and NCs-p. The grain size of the ordered regime in NC-p arrays is larger than that NCs prepared using common washing steps, as shown by Figure 5.6. In samples washed by a solvent/antisolvent (hexane/IPA) ratio of 1:5, multiple layers are silicene-like honeycomb NC-s arrays and in strip-like NC-p arrays. In single-layer regimes, square structures are observed. The grain size of the square-ordered regime of

NC-p arrays is larger than NC-s arrays [Figure 5.6A, B]. Compared to square- and honeycomb- ordered NC arrays,^{15,16} there is little report about stripe-like NC superlattices, and more structural analyzations such as high-resolution TEM and XRD are needed. Presumably, the square, honeycomb, and strip-like structure can be pictured as a slice of a 3D simple cubic structure as shown by the green, blue, and red plane in Figure 5.6C, respectively. In this case, NCs are attached through {100} facets in all three structures.



Figure 5.6 PbSe NC arrays formed by NCs collected from the supernatant (A) and the precipitate (B). (C) Schematics of NC arrays.¹⁷ [Modified from reference 17]

One of the possible reasons for the structural difference is the concentration of ligands in NC solutions. The thermal-gravimetric analysis shows that the concentration of organic ligands is 23% in weight in NC-s and 17% in NC-p. As we increase the ratio of IPA in washing steps and more ligands are washed away, more stripe-like regimes are

observed in multiple-layer NC-s arrays [Figure 5.7]. However, the honeycomb-structure is not always reproducible even using the same condition, potentially caused by other unconscious perturbations in assembling conduction, such as the temperature of the lab.



Figure 5.7 PbSe NC arrays formed by NCs collected from the supernatant. The antisolvent/solvent ratio used in washing varies from 5:1 to 20:1.

Following CE reactions described in Chapter 3, the honeycomb-structured PbSe NC array can be converted to the honeycomb-structured CdSe NC array [Figure 5.8].



Figure 5.8 Honeycomb-structured CdSe NC arrays prepared by CE

5.3. Time-resolved microwave conductivity measurements

Time-resolved microwave conductivity (TRMC) and terahertz (THz) conductivity measurements are contactless techniques that probe transient mobility and lifetime of charge carriers at GHz and THz frequencies, respectively [details in Chapter 1]. Compared to other techniques such as Hall measurements, time-of-flight measurements, and field-effect transistor measurements, they are fairly new techniques and need more studies to establish standards to collect and interpret the data. We participate in a project collaborated by 8 THz labs and 8 TRMC labs to compare the results among labs and between TRMC and THz measurements. The samples distributed to the 16 labs are a piece of semi-insulating InP wafer and a piece of quartz substrate with a perovskite thin film. The perovskite film is prepared by one of our collaborators following an established recipe.¹⁸ While the integrated report is on its way, here are results from our group.

Perovskite thin films are cast on a piece of quartz with 25.11 mm in length, 9.22 mm in width, and 1.08 mm in thickness. The sensitivity factor *K* is obtained through numerical simulations of the microwave cavity loaded with a quartz substrate using CST Microwave Studio, $K = -37300 \pm 1000$. The sample is illuminated under 3×10^{11} photos / pulse / cm² at 532 nm. The percent of light absorbed is 77% at 532 nm. The mobility yield product calculated by the maximum AC power is 22.2(9) cm² V⁻¹ s⁻¹. Real $\phi \Sigma \mu$ is fit well by a convolution of the instrumental response function (IRF) and exponential functions. The cavity response time of the perovskite sample τ_{RC} (*perovskite*) is found as 23 ns by fitting the cavity response curve. The signal is well fit by a sum of two exponential terms, suggesting there are two first-order decay processes [Figure 5.9]. Assuming ϕ is 1, the sum of mobility is 25(1) cm²V⁻¹s⁻¹.

lifetime is 1.646(3) μ s for the slower decay process and is 0.5063(3) μ s for the faster decay process.



Figure 5.9 Product $\phi \Sigma \mu$ as a function of time in the perovskite thin film

InP wafer with 22.5 mm in length, 9 mm in width, and 0.33 mm in thickness is loaded into the cavity. The sensitivity factor is $K = -26000 \pm 1000$, determined from numerical simulation using CST Microwave Studio. The sample is illuminated under 1×10^{10} photons / pulse / cm² at 532 nm. The transmission of the InP wafer at 532 nm is <<1%, measured by a UV-Vis-NIR absorption spectrometer. The reflectance index (n) of InP at 532 nm is 3.63.¹⁹ The percent of light absorbed by InP is calculated to be 68% and the reflectance is 32%. The mobility yield product calculated by the maximum AC power is 133(7) cm²V⁻¹ s⁻¹. $\tau_{RC}(InP)$ is extracted to be 21 ns

When the signal is fit with an exponential decay convolved with the IRF, the peak is underfit [Figure 5.10]. Assuming $\phi = 1$, $\Sigma \mu$ of the carrier is 390(20) cm²V⁻¹s⁻¹. τ is ~14 ns.



Figure 6.10 Product $\phi \Sigma \mu$ as a function of time in the InP wafer, fit with a single exponential decay.

The signal can be better fit with a sum of two exponentials, slightly misfit at the early time [Figure 5.11] though. $\phi\Sigma\mu$ of the carrier is 4700 (200) cm²V⁻¹s⁻¹. The lifetime of the two decay processes are 24 ns and 641 ps. We are not confident in the mobility or lifetime values for this sample because of the short decay compared to the instrument response.

$$f = 116 \exp\left(-\frac{t}{24 ns}\right) + 4600 \exp\left(-\frac{t}{641 ps}\right) + 3$$



Figure 5.11 Product $\phi \Sigma \mu$ as a function of time in the InP wafer, fit with a sum of two exponentials.

5.4. Concluding remarks

This dissertation investigates the electronic structures of nanocrystal (NC) assemblies by characterizing the carrier behaviors. Chapter 1 introduces NC and NC assembles, their electronic structures in theory, and two methods - field-effect transistor (FET) and time-resolved microwave conductivity (TRMC) - to study their carrier behaviors.

Chapter 2 experimentally demonstrates the dielectric confinement effect on dopants' ionization energy in PbSe nanowires (NWs) and propose a mathematical description of the effects by modifying a theoretical equation developed on Si NWs. The knowledge we learn in PbSe NWs can be further transferred to other low-dimensional systems, including but not limited to, the strategy we develop to study the dielectric confinement effect, the method we show to improve doping efficiency, and the model we use to modify the theoretical work. As a result of large sample-to-sample variations in mobility, we can not build a correlation between carrier mobility and the dielectric (ϵ_{out}) mediums, leaving an open question on whether carrier transport and the dispersion relation (E - k) of NWs are affected by ϵ_{out} .

In Chapter 3, we introduce a sequential cation exchange (CE) method to prepare epitaxially-fused CdSe NC assemblies from PbSe NC arrays *via* Cu₂Se NC intermediates and study the carrier transport in epitaxially-fused CdSe NC arrays. We show a $\phi\Sigma\mu$ of 0.28 cm² V⁻¹ s⁻¹ by TRMC, up to two orders of magnitude higher than reported with little or no necking and a high FET electron mobility of 35(3) cm² V⁻¹ s⁻¹ with on-off ratios of 10⁶ after doping. The grain size of ordered regimes in this work is only ~50 nm. There is a chance in the future we can potentially demonstrate extended electronic bands and band transport in ordered NC structures with a larger grain size by using similar CE methods and characterization techniques. Chapter 4 is a derivative project studying the effects of residual parent cations on FET performance and the electronic structure in CE-obtained NC solids, which can serve as guidelines for engineering CE-obtained NC devices.

Sections 5.1 – 5.2 of this chapter describe the preliminary results of the work to expand the library of the epitaxially-fused structures. Following similar formulas described in Chapters 3 and 4, CE reactions in lead telluride NC solids as well as replacing Cu⁺ with other cations (Ge²⁺, Sn^{2+/4+}, Ag⁺, and Zn²⁺) are explored. By modifying the washing steps in the synthesis of PbSe NCs, we fabricate epitaxially-fused NC arrays in geometries other than a square – honeycomb- and stripe-like structures with the size of ordered regimes in μ m. Section 5.3 of this chapter includes a collaborative study on comparing TRMC and terahertz conductivity.

With that, I hope this dissertation can contribute to the understanding of carrier behaviors and electronic structures in NC assemblies.

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