Semiconductor Nanomaterials and Nanocrystals

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This article introduces an innovative synthesis of doped nanocrystals and aims at expanding the fundamental understanding of charge transport in these doped nanocrystal films. The list of semiconductor nanocrystals that can be doped is large, and if one combines that with available dopants, an even larger set of materials with interesting properties and applications can be generated. In addition to doping, another promising route to increase conductivity in nanocrystal films is to use nanocrystals with high ionic conductivities. This work also examines this possibility by studying new phases of mixed ionic and electronic conductors at the nanoscale. Such a versatile approach may open new pathways for interesting fundamental research, and also lay the foundation for the creation of novel materials with important application.

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1. SEMICONDUCTOR NANOCRYSTALS

The nano-scale ranges from about 1 nanometer (nm) to 100 nanometers corresponding to roughly 100 atoms to 10 million atoms. The upper and lower boundaries of this scale are not sharply defined, but are chosen such that one excludes individual atoms on the bottom end and micrometer-scale objects on the top end. This intermediate state of matter lies somewhere between the bulk phase and the atomic or molecular regime. Material properties in nano-sized systems can be controlled appreciably by tuning their size and give rise to potentially new phenomena. Electronic and optical properties of metals and semiconductors depend strongly on the crystallite size once one starts to venture into the nano-scale regime. The evolution of these size dependent fundamental properties can be attributed to the increased surface area in addition to quantum effects that become increasingly important with decreasing size. This change is quite impressive especially in the case of semiconductors. For instance, simply altering the size of CdSe nanocrystals can tune its band gap between 1.7 and 3 eV and hence, the material can absorb and emit across the entire visible spectrum. It is fascinating that the properties in a material of a single chemical composition can be varied so significantly, simply by tailoring bulk material parameters such as size.

A semiconducting crystallite, which is a few nanometers in scale, with sizespecific optical and electronic behavior, is referred to as a semiconductor nanocrystal (NC) or a quantum dot (QD). Semiconductor (SC) NCs are a promising technological material because the ability to control their optical and electronic properties can be exploited for a diverse range of applications, such as light-emitting diodes, bio-labels, single molecule transistors and solar cells.

1.1 Doping Semiconductor Nanocrystals

The introduction of trace intentional impurities (or doping) is central to controlling the behavior of SC materials. Dopants possess the ability to modify strongly the optical, magnetic, and electronic properties of bulk SCs. A dopant, with one more valence electron than the host atom it substitutes for, can donate its extra electron to the SC for electronic charge transport. Similarly, an impurity atom with one less electron can donate a hole to the SC. Modern SC-based technology owes its existence, in large part, to the fact that these materials can be doped. It is the ability to control precisely the number of carriers available in the SC by doping, which has expedited the advance in SC-based electronic and optoelectronic technology. The advantage of doped SCs is that they provide the device engineer with a wide range of mobilities, so that materials are available with properties that meet specific requirements. Hence, it is natural to extend the versatility of nanocrystals by adding dopants. Doping can expand the range of properties in SC NCs substantially; thus opening up a plethora of applications ranging from solar cells 9 and bio-imaging 10 to wavelength tuned lasers.

However, while the field of bulk-doping can be traced back many decades, the first breakthrough in nanocrystal doping came in 1994 when Bhargava et al. observed interesting luminescent properties in manganese-doped zinc selenide NCs. Since then, several II-VI SC NCs have been doped by transition metals and rare earth elements. However, until now, no group has managed to dope SC NCs with electronic dopants that have proved as useful as their analogues in bulk SCs.

1.2 Challenges and Issues in Doping Nanocrystals

NCs represent one of the most promising classes of nanotechnology. Over the last two decades, most of their intrinsic properties have been mapped out. Adding dopants to NCs further extends their properties and possible applications. However, the ability to incorporate dopants successfully and efficiently into NCs faces several challenges. One of the major bottlenecks is the non-existence of any specific or reliable synthetic

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technique which can ensure controlled dopant incorporation. Due to the high surface-to volume ratios of NCs, a large percentage of the total dopant population is at the NC surfaces. Dopants at the surface sites may differ considerably from those in the NC cores. Dopant atoms inside the NC also do not distribute uniformly throughout the NC. Moreover, any ensemble of doped NCs will always have a statistical distribution of dopants per NC. This inhomogeneity may lead to an adverse effect on the targeted properties of the doped material.

Furthermore, how does one know for sure that the NCs have been successfully doped? NC doping suffers from the intrinsic problem that only an extremely small fraction of the product is the impurity, and hence, the doped NC is virtually indistinguishable from its pure analogue if one uses X-ray crystallographic techniques and microscopy (Scanning Electron Microscopy and Transmission Electron Microscopy).

Hence, these materials are considerably more challenging to probe experimentally. Due to these challenges, attempts at doping SC NCs have been largely unsuccessful. However, even if one manages to incorporate dopants inside a NC and introduces extra charge carriers by some technique, there is a high probability that one might run into additional problems. NCs with an extra electron (hole) can behave as a strong reducing (oxidizing) agent. This leads to a redox reaction at the surface, which can consume the extra charge carrier and render it unavailable for conduction [5, 6]. Also, it has been observed that wide band gap II-VI SCs (ZnTe, ZnSe, CdSe, CdS) exhibit a strong proclivity for only one type of doping – either p-type (extra holes) or n-type (extra electrons) – which restricts their use in practical applications such as light-emitting diodes and lasers [7]. An intricate understanding of the doping mechanism is required to circumvent the above mentioned problems and achieve successful doping in SC NCs.

This study aims at trying to understand the fundamental science behind doping mechanisms, developing new techniques for incorporating dopant molecules into NCs, using appropriate spectroscopic techniques to verify the presence of dopants and finally characterizing the location of the dopants. The thesis focuses largely, but not exclusively, on doping of II-VI (CdSe) and IV-VI (PbSe) colloidal SC NCs because these are the mostly widely and thoroughly studied NC-systems to date. Moreover, these NCs hold enormous potential for applications in light-emitting diodes, field effect transistors and solar cells. The use of dopants for enhancing the luminescence and magnetic properties of SC NCs has already been demonstrated. To date, however, no one has presented evidence of electronically doped NCs. By electronically doping NCs, we hope to fill this gap and complete the entire set of optical, magnetic and electronic properties for SC NCs. This exciting opportunity to research and further advance the understanding of doping SC NCs has motivated the submission of this thesis. Electronic doping of NCs might also provide a niche for opening new pathways for interesting fundamental research, and lay the foundation for the creation of novel materials with important applications.

1.3 Phase Transitions in Nanocrystals

While the main focus of this thesis is to study the effect of a few dopant atoms (especially silver) on the properties of cadmium and the lead chalcogenide NCs, we were also interested in looking at the effects of these impurity atoms at the other end of the spectrum *i.e.*, in the high doping limit, where one would have the silver chalcogenides mostly, with minute amounts of lead and cadmium atoms as the impurities. While cadmium and lead chalcogenide NCs have been extremely well studied, very few reports exist that study silver chalcogenide NCs. Hence, this lack of information about the silver chalcogenide NCs motivated us to pursue a detailed study of their properties.

Apart from tuning the material properties of NCs by changing their size and adding impurities, another way is to vary their temperature and tap into new crystal phases of the same material that exhibit different properties. One such material system, which shows rich phase behavior, is the silver chalcogenides. As a bulk material, silver chalcogenides are a class of semiconductor with many intriguing properties. They are mixed conductors with high electronic and ionic mobility, i.e., both electrons and silver ions can travel rapidly within the semiconductor. They undergo a reversible phase transition [e.g., water undergoes phase transitions from solid (ice) to liquid (water) to gas (water vapor)] from a low-temperature phase (α-phase) to a high-temperature phase (β-phase) at temperatures varying from 135-180 °C (depending on whether it is silver sulfide, silver selenide or silver telluride) with a strong change in electronic properties [8].

Whilst all these materials have been very well studied in the bulk, very few studies have been conducted at the nano-scale. By shrinking the size of the material into the nanoscale, new metastable crystal phases can be observed which are not seen in bulk crystals [8, 9]. By varying the size of the material and the temperature of the same, one might expand the possible range of structures further and hence derive novel properties

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The Purple of Cassius consisting of a mixture of tin oxide and Au nanocrystals (NCs) 1 and the Lycurgus cup, with Au and Ag NCs in its walls, are two classic examples. Maya blue, with metal and oxide NCs, 2 and metal nanoparticles in the glass windows of medieval cathedrals demonstrate that nanoparticles have been used for ages without any clear knowledge of nanoscale phenomena.

Despite some early work in the 17th century, systematic studies on nano-sized materials did not really begin until the 1800s. Finally in 1857, Michael Faraday3 realized the role of metal particles in the color of church windows followed by Einstein, Gustav Mie and Gans, 4-7 who proposed several theories for the properties of nanoparticles. However, colloidal nanoparticle science was fairly neglected until the early 20th century. This prompted Ostwald8 to title his 1915 book on colloids as "The World of Neglected Dimensions." Feynman's lecture 9 at the American Physical Society

in 1960, entitled "There is Plenty of Room at the Bottom," led to a revived interest in generating nanoparticles of various materials. Despite the identification of unique properties in metal nanoparticles, similar exciting properties were not observed in semiconductor (SC) nanoparticles until early 1980's when Ekimov and Brus *et al.* observed a size dependent shift in energy of the HOMO (Highest Occupied Molecular Orbital) – LUMO (Lowest Unoccupied Molecular Orbital) transition in SC NCs [10, 11]. This breakthrough generated a renewed interest and led to rapid advancements in the field of SC NCs. The progress has been aided by advances in instrumentation, which help in characterizing these nanomaterials. Today, it is possible to prepare and study NCs of metals, SCs and other substances by various means. Rapid advances in both experimental and theoretical methods have led to a much better understanding of the properties of NCs than ever before.

2. PHYSICS OF SEMICONDUCTOR NANO-CRYSTALS

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Nanoparticles can either be amorphous or crystalline. Crystalline nanoparticles can again exist as single crystalline or polycrystalline particles. The term "nanocrystals" is used for those nanoparticles which have a single crystalline domain [12]. The focus of my work, and hence, this chapter will be on semiconductor (SC) NCs.

2.1 Surface

The dimensions of NCs are so small that a substantially high fraction of the total atoms is present on their surfaces as compared to the bulk. The surface of the NCs plays an essential role in determining the properties exhibited by the nanocrystal. Typically, the surface is passivated by attaching long-chained molecules. However, more often than not, there exist lots of dangling bonds due to incomplete passivation. Hence, the surface is dynamic and chemically accessible, with the surface atoms sufficiently mobile. The poor knowledge of the surface has typically impeded the study of these NCs. Many important properties of the NCs, such as the fluorescence quantum yields [12] carrier trapping [13] and energy relaxation14 are affected by the surface. Therefore, it is essential to achieve surface control for these colloidal NCs, since it is this surface that governs many of their versatile properties.

2.2 Strong Quantum Confinement Effect

The gap that separates the conduction and the valence energy bands is characteristic of any semiconductor (SC) material. In bulk SCs, it is fixed. Additionally, it can either be direct or indirect. Direct-gap SCs can absorb a photon, when an electron is promoted directly from the valence band into the conduction band; thus creating an electron-hole pair (or exciton). Indirect-gap SCs require the assistance of a phonon to absorb or emit light. However, when the size of the SC material decreases to a level where the electrons, the holes and the excitons start to feel the physical boundary of the particle, the material starts to adjust its energy levels in response to this change in size and thus exhibits a phenomenon known as quantum confinement.
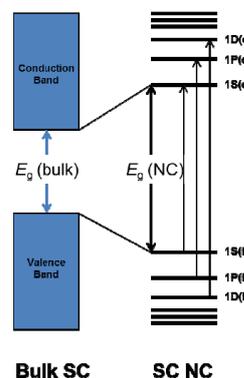

Fig. 2.1 – Comparison of bulk SC electronic states with NC electronic states. *Eg* (bulk) is the band gap in the bulk and *Eg* (NC) is the effective band gap in the NC

The conduction and valence bands in bulk SC collapse to discrete atomic-like states in SC NCs (1S, 1P, 1D etc.). The "e" and "h" in brackets refer to electron

and hole states respectively. Any particles that exhibit quantum confinement are named quantum dots (QDs). Typical features of quantum confinement include an increase in band gap and a collapse of the continuous valence and conduction bands of the bulk material into discrete energy levels. This leads to sharp features in the absorption spectra of QDs instead of a continuous absorption spectrum observed in bulk SCs (Fig. 2.1) [15] It can also lead to an indirect-gap material in bulk converting to a direct band-gap material at the nano-scale.

By varying the size of the QD, one can have only the electron confined or the hole or the electron-hole pair (exciton). The regime where the exciton, the hole and the electron are all confined is referred to as the strong confinement regime. Correspondingly, when only the exciton is confined, but not the hole and the electron, it is referred to as the weak confinement regime.

In the strong confinement regime, the electron and hole can be treated as independent carriers. To model this system using the effective mass approximation, one assumes parabolic conduction and valence bands with bulk effective masses for the electron and hole [11]. Using a simple particle in a sphere model, the electron and hole in the NC can then be described by hydrogenic wave functions. By solving the Schrodinger equation while including the electron-hole Coulomb interaction, the band gap of the SC NC (NC bandgap E) as a function of its size can be approximated as:

$$E_{bandgap}^{NC}(R) = E_{bandgap}^{bulk} + \frac{h^2 \pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 R}$$

where R denotes the radius of the NC, bulk bandgap E the band gap in bulk, h the Planck's constant, ε the dielectric constant of the material, ε_0 the vacuum permittivity, and m_e and m_h are the effective masses of the electron and hole, respectively.

2.3 Synthesis of Nanocrystals

Nano-science is characterized by a close interplay between physics, chemistry, biology and materials science. This is demonstrated vividly by a wide range of synthetic techniques that have been developed and used extensively for nano-scale materials. All these various techniques can be grouped into two broad schemes – the top-down and the bottom-up approaches. The top-down methods involve starting with bulk materials and breaking them down to smaller and smaller particles. Conversely, the bottom-up methods start from the respective atoms and progressively build up the nanoparticle. The topdown and bottom-up approaches are also at times broadly categorized into physical and chemical methods, respectively. While physical methods produce large quantities of nanoparticles, chemical synthesis techniques offer much better reaction control, provide higher quality nanocrystals and can be easily tailored to produce different materials.

2.4 Physical Methods

A characteristic feature of any physical method is a high input of energy which is used to evaporate the bulk solid material forming a supersaturated vapor. Owing to the supersaturation, nucleation of nanoparticles takes place. It is extremely hard to control the particle size and distribution as the growth is extremely fast (on the order of milliseconds). Some popular examples of physical processes include molecular-beamepitaxy (MBE), metal organic-chemical-vapor-deposition (MOCVD) [15-19 [and vapor-liquid solid (VLS) approaches [20, 21]. However, our emphasis is on low-energy input colloidal chemical syntheses of SC NCs.

2.5 Chemical Methods

Chemical methods are generally carried out under much milder conditions than the physical methods. The focus of these methods lies on the development of different means of producing NCs, which are then dispersible in solvents. These are better known as colloidal NCs. My entire work on NCs revolves around these colloidal NCs. Any chemical reaction that leads to formation of colloidal NCs consists of three basic steps – nucleation, growth, and termination. One usually starts with a mixture of the NC constituents (precursors containing the elements forming the NC), capping agents (for colloidal stability), and the solvent (to control the growth temperature and manipulate precursor concentrations). NCs of different dimensions can be obtained from the same reaction mixture by manipulating relative rates of the various steps, which, in turn, are altered by changing precursor concentrations and temperature.

An important process that one needs to consider during the growth of a colloidal NC is Ostwald ripening [15]. It is a growth mechanism wherein smaller particles with higher surface energy dissolve, and thus release monomers or ions which are consumed by larger particles. This, however, leads to defocusing of the size distribution of synthesized NCs during early periods of growth and hence, severely limits the ultimate size distribution. One way to avoid this scenario is to keep adding reaction precursors during growth to ensure that monomer concentrations are never depleted.

The important factors that determine the quality and success of any NC synthetic procedure are the crystallinity, surface passivation, dispersity in various polar or nonpolar solvents, and the size distribution of the NCs obtained. Since the properties of nanoparticles are strongly size-dependent, it is highly desirable to have nanoparticles of nearly the same size, in order to be able to distinguish and study the properties that arise due to quantum size effects. Although the definition of monodispersity in its strictest sense requires identical or indistinguishable particles, colloidal NC samples, with a standard deviation, $\sigma < 5$ % in diameter, are nominally termed as fairly monodisperse. NCs produced by chemical means can either be dispersed in aqueous media (sterically or electrostatically stabilized) or in organic solvents (sterically stabilized).

Sterically stabilized NCs are redispersible, *i.e.* the NCs in the solvents can be precipitated, filtered, and dispersed again in a solvent. Furthermore, NCs in a sterically stabilized solvent can be dispersed in a wide range of concentrations. Most of the NCs used in this thesis are sterically stabilized.

Following La Mer and Dinegar's studies [12, 22] Murray et al. pioneered a high temperature NC synthesis method in the early 1990s which yielded fairly monodis-

perse NCs with high crystallinity. This technique involved a rapid injection of organometallic precursors of the target NCs into a coordinating solvent maintained at a high temperature.

Hence, it is popularly known as the hot-injection method. This rapid injection was essential to achieve a discrete nucleation event and separate it from the growth process. Immediately after the injection, the precursor concentration is forced above the solubility limit which leads to a nucleation burst. The nucleation event decreases the precursor concentration below the threshold following which nucleation is suppressed.

Subsequently, the leftover precursors add to the existing nuclei and growth proceeds [23] In this growth regime where the monomer concentration is relatively high, small particles grow faster than larger particles resulting in focusing of the size distribution. Once the monomer concentration is sufficiently depleted, growth proceeds by Ostwald ripening. If nucleation is fast, *i.e.* the concentration of the precursors falls below the threshold concentration quickly, then nucleation can be separated from growth. The separation of nucleation and growth is imperative for monodispersity since particles that nucleate simultaneously will grow at similar rates and will eventually end up the same size.

To produce high quality colloidal NCs, the size and size dispersion of these NCs needs to be controlled precisely. Growth time, temperature, and precursor concentrations are the key variables. Longer reaction times, in general, imply a larger average particle size. Injection and growth temperatures have a huge impact on the final size of the NCs.

Lower injection temperatures lead to a smaller number of nuclei and thus yield larger sized particles with similar precursor concentrations. When one has sufficiently high precursor concentrations in the reaction solution, higher growth temperatures generate larger particles after the same period of growth compared to lower growth temperatures due to enhanced reaction rates.

Precursor and surfactant concentrations play a pivotal role in both nucleation and growth. Analogous to higher injection temperatures, a high precursor concentration leads to a large number of nuclei while lower precursor concentrations imply fewer nuclei. The final particle size would depend on the interplay between the precursors consumed during nucleation and the amount left for growth. Surfactants can have an adverse effect on the growth of the NCs. A higher concentration of surfactants implies lower growth rates and hence smaller NCs with similar growth times. On one hand, if the surfactant binds too strongly to the NC, it will hinder NC growth while a very weakly coordinating surfactant can lead to uncontrolled growth resulting in agglomerates which cannot be dispersed in solvents [23].
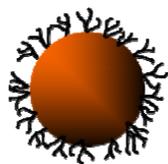
Fig. 2.2 – Cartoon showing the ligands surrounding a colloidal nanocrystal

Alkylphosphines (tri-octylphosphine, diphenylphosphine, tri-butylphosphine), alkylphosphine oxides (tri-octylphosphine oxide), alkylamines (hexadecylamine, octadecylyamine, oleyl amine), alkylthiols (dodecanethiol), alkylphosphonic acids (dodecylphosphonic acid) and fatty acids (oleic acid) are typical examples of surfactants or coordinating solvents used during high temperature NC syntheses. They contain a lyophilic polar head group which is attached to the surface atoms of the nanocrystal, and a lyophobic tail which is exposed. These surfactant molecules, thus, act as ligands and form an organic capping shell around the NC core (Figure 2.2). The lyophobic tail renders the NCs soluble in common nonpolar solvents like hexane, octane, chloroform, toluene, carbon tetrachloride. The ligands also help to prevent aggregation of individual NCs by keeping them apart. Finally, the ligands can reversibly attach or detach from the NC surface which explains the fact that the NC nuclei can grow even when ligands are present in solution during growth. Also this permits ligand exchanges post synthesis by exposure of the NC to an excess of a different desired surfactant [12]. Moreover, these ligands serve to passivate the surface trap sites which result due to uncoordinated or dangling bonds from the surface atoms [24]. Hence, NCs with well passivated surfaces and high crystallinity exhibit high photoluminescence (PL) yields, i.e. higher quantum efficiencies [25, 26]. Crystallinity is important because defects in the crystal can scatter phonons and / or photons. However, the ligand shell lends an insulating potential barrier to charge transport between NCs, and thus, has an adverse effect on electrical properties [27]. Reduction, reverse-micelle, and high-temperature injection are the three most prominent chemical methods employed for NC syntheses. The first two techniques are simpler and use less toxic reagents. The advantages of high temperature injection are that it produces nearly monodisperse particles with fewer trap states, and they form stable dispersions. Even though the high temperature route is more difficult, the higher-quality material which it yields is better for fundamental studies. Since many nanoparticle properties are size dependent, polydisperse samples make characterization difficult.

Polydisperse samples usually show broadened peaks in their spectra, so it is hard to pinpoint the energy of a particular transition. Therefore, it is desirable to study nearly monodisperse samples. The high-temperature synthesis method pioneered by Murray et al. produces a low polydispersity by separating nucleation from growth. In general, the low temperature methods suffer from relatively poor size dispersions ($\sigma > 20\%$) and often exhibit significant, if not exclusively, trap-state PL. The latter is inherently weak and broad compared to band-edge PL, and it is less sensitive to quantum-size effects and particle-size control. The high-temperature technique relies on surfactant ligands to transport atoms to the correct location in the crystal, so that the NC surface is coated with a layer of stabilizing ligands. In reduction-based syntheses, since ligands are added after the crystal is grown, it becomes much harder to attach these ligands; hence resulting in more trap states [28]. Moreover, high-temperature injection provides the atoms plenty of thermal energy to move around and find the best location in the crystal, thus resulting in fewer defects. NCs prepared

by the low-temperature routes do not have the energy to find the most thermodynamically favorable bonding, resulting in poor crystallinity. Any potential application or study involving NCs calls for stable NC dispersions.

If NCs continue to grow and/or ripen after synthesis, all measurements must be taken immediately after synthesis to have a consistent set of data. Any industrial application such as printing or ink-jetting requires stable dispersions. This is another area where the high-temperature injection methods are preferable to the incomplete surface ligand coverage (which leads to unstable dispersions) of alcohol-based syntheses (reduction-based). Further, low-temperature aqueous preparations (reverse-micelle) are limited in their applicability to mostly ionic NCs. In general, higher temperatures are required to synthesize covalent NCs and have them crystalline as well. Thus, II-VI compounds, which are more ionic compared to III-V compounds, have been successfully prepared at relatively low temperatures, whereas III-V compound SCs have not [29] For all the reasons mentioned, the high-temperature synthetic method provides the best route to small quantities of high quality material for study.

3. SEMICONDUCTORS AND DOPING

The ability to introduce precise amounts of impurity atoms (dopants), to control the behavior of SC materials, is central to the SC industry. Without these impurities, negligible charge transport occurs through the SC crystals. To enhance this transport and render the materials benign for applications in devices, the concept of "doping" was developed. It involves controlled addition of impurity atoms to obtain desired conductivity in a given device. While conductors will always show high electrical conductivities, insulators will always possess low conductivities. The ability to manipulate the conductivity of the material by tuning the level of doping with additional donor or acceptor atoms distinguishes SCs from both conductors and insulators. Modern SC technology thrives due to the ability to exert precise control over the number of carriers (electrons and holes) available in the SC crystal. By controlling the carriers, the electrical properties of the SC can be precisely tailored for a particular application. However, this adaptability of doped SCs to various applications comes at a price. Since minute concentration of dopants have a huge effect on their electronic properties, inevitably, one runs into the risk of unintentional doping of these SCs. Thus, these SC materials need to handled with utmost care to prevent any contamination. Apart from their electrical properties, since SCs possess a finite band gap, they can also be used to absorb and emit light efficiently.

However, the band gap is fixed and depends on the identity of the material. Thus, applications that require light at certain fixed wavelengths demand materials with matching optical properties. Thus, new materials need to be synthesized to exploit the potential of SCs for optical applications. This is where SC NCs can aid with their unique size tunable properties.

3.1 Doping Semiconductor Nanocrystals

In light of the importance of doping in bulk SCs, it is interesting to consider their potential impact on SC NCs. NCs differ significantly from their bulk counterparts, since they possess a different band structure. Also, their carriers behave differently due to quantum confinement. Recently, concentrated efforts have started to explore the possibility of combining quantum confinement with the introduction of extra carriers by doping, to obtain a completely novel set of properties in these materials. Intrinsic SCs need to be doped to modify their charge transport characteristics. Doping of nanocrystals (NCs) can be used for entirely different reasons as well. SC NCs can be doped with a low percent of foreign atoms to create impurity centers that interact with the electrons and holes. A valuable effect of this interaction is that the mid gap states arising from surface species can be shifted outside the gap region. Dopants (when added in trace amounts) do not affect the absorption spectra; however, the intensity of emission is vastly increased.

Doping enhances the properties of NCs by providing another means to control and subsequently tailor their remarkable electronic, optical, transport, and magnetic properties. In this sense, the development of doped nanocrystalline materials is progressing along the same lines as bulk SCs did half a century ago. In general, dopants have been incorporated into nanocrystals for three main applications: to act as luminescence activators, to create improved dilute magnetic semiconductors, and to alter the electronic properties of NCs. Electronic dopants are those that introduce carriers by acting as either shallow donors or acceptors within the SC band structure. Typically, donor atoms are substitutional impurities with one more valence electron than the host atoms they replace. They can be ionized by thermal energy and provide additional electrons in the conduction band, which help in charge transport ("n-type" doping since we have extra electrons). In the same way, acceptor atoms incorporated into a SC crystal create holes (missing electrons) in the valence band which aid charge transport by acting as positively charged particles (thus "p-type doping). The promise of NCs, as a technological material for applications which often require thin conducting films, depends in many cases on the ability to introduce these carriers. Although electronic doping of NCs has not yet been widely explored, it is clear that this area will play a major role in the future of nanotechnology as self-assembled device structures become more accessible. High absorption coefficients, high quantum yields and narrow line widths make NCs exciting candidates for optical applications like bio-imaging applications [30].

Manipulation of the luminescent properties of NCs, by doping with impurities, has the potential to broaden the range of spectroscopic properties that can be achieved currently from these materials. Lasers based on NC emission are intrinsically inefficient [14]. Introducing dopants, which provide carriers, might help to achieve higher mobility in colloidal quantum dot films and higher injection currents. A threefold reduction in the lasing threshold in CdSe nanocrystals is observed by eliminating induced absorption through addition of extra electrons [31]. In solar cells, unwanted reactions and photooxidation might occur on the nanocrystal surface due to

protracted exposure. This can be avoided by adding dopants which can absorb the energy from adsorbed photons thus localizing the excitation [30]. Giant Zeeman effects observed in SCs containing magnetic impurities or "diluted magnetic semiconductors" (DMSs) [32, 33] sparked a huge interest in these materials. DMSs hold the potential to pave the way for applications in optical gating [34] and future spintronic and spin-based electronic devices [32, 33].

3.2 Challenges in Doping

Difficulties in doping wide band gap II-VI SCs (ZnTe, ZnSe) were encountered as early as the 1950's. These SCs, unlike group IV SCs (Si, Ge) exhibited a strong proclivity for only one type of doping – either *p*-type or *n*-type – which restricted their use in practical applications such as light-emitting diodes and lasers. CdSe, CdS, ZnSe and ZnS were resistant to *p*-type doping, whereas ZnTe could be doped *p*- but not *n*-type.

Although dopants would not be expected to behave exactly the same way in SC NCs as they do in bulk SCs, basic complexities (like deep defect levels scavenging the charge carriers provided by dopants, donor-acceptor compensation etc.) encountered while doping bulk SCs are inherent to doping at the nanoscale too. In addition to these issues, challenges which are specific to nanoparticles are discussed below.

3.3 Host Material

New challenges arise when nanoscale materials are doped with small quantities of impurities. The high surface / volume ratios of NCs and the inherent statistical inhomogeneities of any ensemble of doped NCs play a key role in determining the dopant behavior. A 5-nm diameter CdSe NC would consist of around 2400 atoms, $\sim 30\%$ of which are on the surface, where they are exposed to surface ligands and / or solvent [35]. Assuming a Poissonian distribution, a mean concentration of 1 dopant per 1000 atoms is necessary to ensure almost every NC is doped. Comparing this doping level to heavily doped bulk SCs, which might have 1 dopant atom per 10,000 atoms; one concludes that dopant concentrations must be inhe-rently much higher in NCs than in the bulk. The number of dopants at the NC surfaces comprises a large percentage of the total dopant population. Dopants, substituting for host ions at the surface sites, may differ considerably from those in the NC cores in terms of their geometries, electronic structures, redox potentials, and interactions with the SC [35]. Since surface-exposed dopants and those within the NC core (Figure 2.3a) can show starkly different behavior, this may obscure the origin of the physical properties of doped NCs, and even compromise some of the target physical properties of the doped material. Two diverse approaches have been employed to remove dopants from the NC surface. The first technique uses coordinating solvents or ligands, such as pyridine or tri-octylphosphine oxide, as surface cleaning agents.36-38 The second method, demonstrated to eliminate surface-exposed dopants successfully, is the isocrystalline core-shell (ICS) procedure [36, 38]. This procedure involves purifying the as-synthesized NCs to remove excess dopants from the

growth solution, followed by epitaxial growth of additional layers of the pure host material to coat the surface-exposed dopants and encapsulate them.
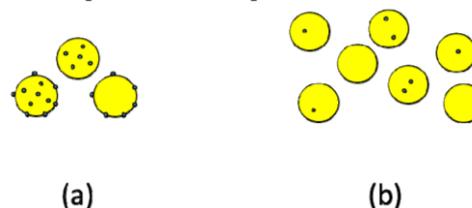

Figure 2.3 – (a) Cartoon showing the inhomogeneity in location of dopants in a sample of doped NCs (b)

Cartoon depicting the stochastic fluctuations in dopant distributions within a sample of doped NCs. In addition to inhomogeneities introduced in doped NCs due to surface-exposed dopants and those inside the NC core, any sample of doped NCs will also exhibit a statistical distribution of dopant populations per NC (Figure 2.3b). While the dopant concentration may be well defined on average, the number of dopants in any individual NC cannot be controlled or determined. A NC with a single dopant might show significantly different behavior than one with two or more dopants. Due to this heterogeneous distribution of dopants in any NC sample, it becomes complicated to draw conclusions from subsequent physical measurements. This feature could significantly impact single quantum dot electronics or photonics measurements that rely on doped NCs. While purification to ensure size uniformity is possible (size-selective precipitation), no purification method has yet been developed for ensuring uniform dopant concentrations in an ensemble of NCs.

3.4 Impurity Atom and Characterization of Doped Nanocrystals

Another category of challenges concerns the impurities themselves and how one knows when the NCs have been doped successfully. X-ray diffraction studies of doped crystals yield predominantly the characteristic diffraction features of the host, and provide little reliable indication of the success or failure of doping (except at extremely high doping). NC doping suffers from the intrinsic problem that only an extremely small fraction of the product is the impurity, and consequently a doped NC is virtually indistinguishable from its pure analogue by microscopy techniques, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Hence these systems are more challenging to probe experimentally. Solving this problem requires using other analytical techniques. Spectroscopic methods that are sensitive to some physical property inherent to the dopants themselves can prove to be extremely successful. For instance, if they absorb light within the forbidden gap of the SC, then absorption spectroscopy may be applied to probe the dopants selectively. The existence of a manganese (Mn) luminescence peak has been reported in Mn-doped ZnS and ZnSe. Optical absorption spectroscopy has been used to verify cobalt (Co) doping in CdS and ZnS NCs. If the dopant is magnetic, then magnetic spectroscopic techniques may be applied to probe them selectively within the diamagnetic hosts. Unusual phenomena, such as giant Zeeman splittings, observed in

the case of Mn-doped NCs by magnetic circular dichroism (MCD) studies, can be used as an effective tool to verify Mn doping (e.g. CdS). Another challenge in the synthesis of doped NCs is to ensure that the impurity is in the NC core, rather than at the surface or the interface. Impurities on the surface are always plausible, since the NC is only a few lattice constants in size. Very few analytical techniques possess the ability to distinguish impurities on the surface from those inside the core of the NC. Spectrum changes, in an electron paramagnetic resonance (EPR) study, can reveal whether Mn is incorporated or surface-bound. EPR spectroscopy has been the primary tool to confirm Mn doping in ZnS [43] CdS [44] and ZnSe. Mikulec et al. studied the distribution of dopants in NCs [36]. They synthesized Mn-doped CdSe NCs. EPR spectroscopy revealed a four-fold decrease in Mn concentration, when the NC surface was cleaned with pyridine, which implies that most of the Mn was on the surface, rather than in the core. After the ligand exchange with pyridine and trioctylphosphine oxide, they gradually etched away the NCs with tripyrrolidinophosphine oxide. They observed a decrease from 2.9 Mn / NC on an average to 0.5 Mn / NC, when the NC was etched from 4.0 nm to 3.3 nm in diameter. This proves that dopant molecules do not always distribute uniformly throughout the NC.
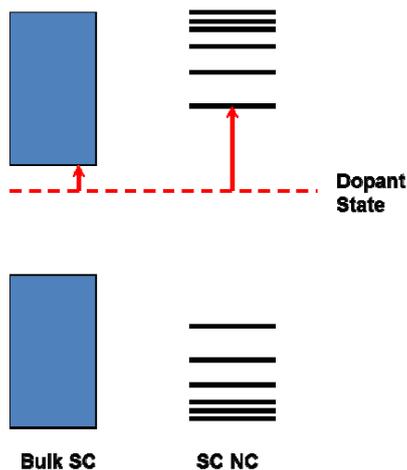

Fig. 2.4 – Schematic describing how a shallow dopant level in a bulk SC could potentially turn into a deep defect level in the corresponding SC NC

3.5 Quantum Confinement

Addition of extra charge carriers in bulk SCs is generally achieved by substitution of a host atom with a dopant atom. In bulk, this electronic impurity atom introduces a shallow dopant state which lies within a few tens of meVs of the corresponding band edge (valence band for *p*-type and conduction band for *n*-type doping) thus facilitating thermalization into the band even at room temperature. Now the incorporation of this dopant atom in the corresponding NC of the same material does not necessarily guarantee stable electronic doping. Due to quantum confinement, this favorable alignment of the dopant state and the bulk band edge can be entirely distorted for the doped NC case (Figure 2.4).

Two situations can potentially arise in such a situation. Firstly, the depth of the dopant state can increase

due to increase in band gap of the NC as a direct result of quantum confinement. Hence the probability to thermalize a free charge carrier drops down drastically. Secondly, when the hydrogenic Bohr radius of the charge carrier in the NC becomes comparable to the size of the NC, the dopant starts to feel the effect of the confinement and shifts to higher energies. These two effects compete against one another. If the dopant state shifts into the band states of the NC, the dopant would undergo auto ionization and provide charge carriers to the NC. The interplay of all these effects complicates electronic doping in SC NCs.

3.6 Instability of Electronically Doped Nanocrystals

The stability of excited state carriers also needs to be taken into account when doping NCs. These carriers have relatively high energies and NCs have much more surface area as compared to bulk crystals, at which reactions may occur. These reactions might scavenge the carriers, which would make them unavailable for conduction.

It has been shown that CdSe and CdS NCs produce free radicals from the surrounding solution when they are exposed to UV light. Ipe et al. noted that CdS NCs produced both superoxide (O^{2-}) and hydroxide ($OH\cdot$) radicals, while CdSe NCs only produced the lower energy hydroxide radicals. Shim and Guyot-Sionnest observed that chemically reduced CdSe and ZnO NCs showed peaks correlated with conduction band electrons which disappeared in the presence of oxygen. These results imply that *n*-type NCs, with an extra electron, behave like reducing agents. Extending this idea to *p*-type NCs, they would behave as strong oxidizing agents with an excess of holes. To avoid surface redox reactions and confine the carriers within the NC, one might coat the doped NC core with a shell of a wide band gap SC material. However, this would lead to a huge potential barrier which would hinder the transport of the carriers and ultimately result in low conductivity.

4. NANOCRYSTAL DOPING MODELS

A number of models, which try to explain the mechanism of doping in SC NCs, have been proposed. Some of them are discussed in this section.

4.1 Turnbull Model

Turnbull argued that, for uniform constant defect density, small crystals are statistically less likely to contain defects than large crystals and hence they tend to be pure [48]. This model assumes that dopant solubility in the NC is the same as in bulk. Therefore if an impurity is highly soluble in the bulk, it should still exist in fairly small NCs. This is contrary to what is actually observed; particularly in the case of Mn doping in II-VI SCs. Mn concentrations in II-VI SC NCs such as ZnSe are 1-2 orders of magnitude lower than in their bulk counterparts.

4.2 Self-Purification Model

This model, proposed by Dalpian and Chelikowsky, takes into account the thermodynamics of the system to understand the incorporation of dopants in NCs. They

consider the case of thermodynamic equilibrium and examine the formation energies of impurities as the NC gets smaller. They observe that, as the NC size decreases, the formation energy increases. This suggests that it will cost more energy to insert impurities into small NCs than the larger ones, i.e. the impurity will be less stable in the small NCs. Hence, the impurities can be easily annealed out owing to the material's limited size since the distance the impurity must move, to be ejected from the NC, is much smaller than in bulk materials. In the limit of large NCs, the formation energy will approach, asymptotically, the value for bulk. According to Dalpian et al., this provides clear evidence that doping NCs should be more difficult than doping bulk materials.

However, a significant assumption in this model is thermodynamic equilibrium, which implies that impurity atoms can readily diffuse in and out of the NC. But in the case of Mn, the bulk diffusion coefficient at typical colloidal growth temperatures of around 300 °C is negligible [50]. Therefore, the assumption of thermodynamic equilibrium, on which the model is based, is difficult to justify. Furthermore, Du et al. showed that the increase in impurity formation energy with decreasing size of CdSe NCs is fairly small (~ 0.03 eV) and hence, almost independent of size.

4.3 Trapped Dopant Model

Du et al. [33] suggested that non-equilibrium kinetic effects, such as activation barriers for substitutional impurities, will control doping at the low temperatures commonly used in liquid-phase colloidal syntheses. They argue that, since diffusion of the impurity through the NC is strongly inhibited, doping depends on the surface adsorption of the impurity during growth. If the dopant atom binds strongly to the surface, it can be subsequently "trapped" when overgrown by additional material. If a dopant molecule adheres to the crystal long enough to be overgrown, it will be incorporated into the NC. Impurity adsorption, in turn, depends strongly on the surface morphology, the shape of the NC, and surfactants in the growth solution. Knox et al. [39] explained Mn doping in II-VI SC NCs, based on these factors, which earlier were not considered significant to the doping mechanism. They argued that successful doping in NCs depends on the "stickiness" of the crystal facets. They noted that all SC NCs that had been successfully doped with Mn adopt the zinc-blende crystal structure. Density-functional theory (DFT) computations suggest that the (001) facets of zinc-blende structure crystals provide stable binding sites for Mn. These facets consist solely of anions and therefore strongly attract cationic dopants. They, then, proceeded to grow Mn-doped CdSe around ZnSe cores. The ZnSe core (which commonly exists in the zinc blende structure) topotaxially forced the CdSe [which commonly exists in the wurtzite structure and hence lacks (001) facets] into a zinc-blende crystal structure, and Mn was successfully incorporated throughout the shell. Previous attempts to dope wurtzite CdSe nanoparticles with Mn had failed. Their model establishes the importance of kinetics in NC doping.

5. DOPING SUCCESSES

The most studied systems have been Mn-doped colloidal QDs of ZnS, CdS, and ZnSe. Early efforts to dope Mn into CdSe, the most-studied NC system, failed to incorporate any impurities but Erwin et al. were successful in doping this system with Mn. Gamelin and co-workers have been successful in doping CdSe with Co and ZnO with Mn and Co. The problem with Mn and Co doping in all of these II-VI SCs is that they are isovalent with the cation. Thus, no extra carriers are obtained and no net electronic effect can be observed. Recent efforts aim at achieving electronic doping of NCs. Knox et al. tried to dope CdSe NCs with indium (In^{3+}) but succeeded only in coating the surface with indium that could easily be removed by pyridine exchange. Colloidal Mn-doped InAs and Li-doped ZnO have also been synthesized. By co-doping aluminium (Al) and copper (Cu) into ZnS NCs, Manzoor et al. reported a new luminescence peak, which they ascribe to an Al^{3+}-Cu^+ transition. However, the resulting NCs would show unaltered electronic properties since their method is based on stoichiometric inclusion of n-type and p-type dopants. More recently, Cd-doped InAs NCs showed changes in their electronic behavior. However, these dopants were most likely coating the surface. Viswanatha and coworkers managed to incorporate Cu dopants into ZnSe / CdSe core-shell NCs but the Cu dopant existed primarily as Cu^{2+} as proven by optical spectroscopy studies and hence was isovalent with the host atom replaced. Using a "core-shell doping" approach, Wills et al. were able to dope In and Al into CdSe NCs, with the Al-doped NCs showing n-type doping. Recent progress has been made by incorporating rapidly diffusing electronically active dopant atoms [Cu, silver (Ag) and gold (Au)] in InAs, CdSe and PbSe NCs. An alternative approach to control the number of carriers (electrons and holes) in SC NCs is through charging which involves the use of applied electric fields to manipulate carrier densities near an interface or junction.

6. CHARGING NANOCRYSTALS

The conventional approach of obtaining n- and p-type NCs, by doping with a heterovalent impurity, such as In in bulk CdSe, has not been successful in colloidal quantum dots (QDs) to date, possibly because of difficulties in introducing the impurity, or in eliminating surface traps that can capture the extra carrier. An alternative approach involves obtaining n- and p-type NCs, by direct injection of charge carriers into undoped NCs. For example, oxidizing or reducing agents, gates, or electrochemical processes can be used.This method is also referred to as remote doping.

Colloidal QDs can be charged n-type by electron-transfer from a strongly reducing species (e.g., sodium and sodium biphenyl). However, for such charge transfer to occur, the lowest unoccupied electronic state of the NC, the $1S_e$ state, should be below the reduction potential of the reducing species. Optical measurements confirm the n-type character of such NCs. Upon reduction, if the extra electron occupies the $1S_e$ state, then the exciton transitions that involve this state should be bleached. Shim et al. observe this bleach in the absorption spectra of CdSe / ZnS core-shell colloidal QDs after charge transfer

doping. However, trap states or other phenomena could produce a similar bleach. Conclusive evidence of the n-type character is obtained from the appearance of a new intraband peak in the IR spectrum of the NCs, which can be ascribed to a transition from the 1Se to the 1Pe state. These n-type NCs are stable indefinitely at low temperatures, but they lose their n-type character under ambient conditions due to oxidation. Close-packed films of NCs were more permanently doped n-type, by the evaporation of potassium, in a high vacuum chamber. However, a more practical approach involves electrochemical doping of colloidal QDs, in which a thin film of NCs is put in contact with a metal electrode in an electrochemical cell. By controlling the potential to the cell, electrons could be reversibly injected into the colloidal QD, as confirmed by changes in visible and IR spectra. However, in the remote doping experiments, many traps need to be filled by the injected electrons, before the 1Se level can be occupied. The number of these unknown traps could not be quantified. This has a serious implication for n-type impurity doping, since these traps might consume all the electrons donated by the dopants. Therefore, even if successful n-type doping is achieved, one might still not have any free carriers in the doped NCs.

7. STABILITY TRENDS IN DOPED / CHARGED NANOCRYSALS

In the remote doping experiments conducted by Shim and Guyot-Sionnest, they observed that the lifetime of injected electrons decreased from ZnO to CdSe to ZnSe [46]. N-type doping of ZnO with Li impurities has also been achieved 61. This suggests that ZnO is somehow amenable to n-type doping while ZnSe is not. A simple approach to determine which systems can be doped n-type was proposed by Guyot-Sionnest et al. They explained this behavior by looking at the reduction potential of the NCs and of their constituent elements. An extra electron in the bulk crystal sits at the bottom of the conduction band. They noted that the conduction band electron stability in the NCs was inversely proportional to the energy of the conduction band minimum. This energy increases from ZnO to CdSe to ZnSe; and from larger to smaller NCs. Accordingly, smaller n-type NCs, with a larger degree of confinement, were also observed to be less stable. Since they carried out their experiments in oxidant-free conditions, they hypothesized that redox reactions might be occurring within the NC. N-type ZnSe NCs may be less stable, because the reduction potential of Zn^{2+}/Zn [– 0.762 V versus Standard Hydrogen Electrode (SHE)] is below the conduction band minimum of ZnSe (– 1.5 V versus SHE) 71. Therefore, it is energetically favorable for conduction band electrons to undergo the electrochemical reaction and reduce Zn^{2+} to form Zn atoms, which can then break apart from the crystal by corrosion, if other factors such as lattice binding energies

are ignored. On the other hand, ZnO, with a conduction band minimum far below the reduction potential of Zn, is expected to be more stable, if auto-corrosion were the cause of instability. Similarly, in the bulk, an extra hole will sit at the top of the valence band.

In a NC, the hole will be pushed lower in energy by confinement. The lower the hole, the more likely that the hole might become less stable compared to the competing electrochemical reactions. Despite the simplistic nature, the predictions from this theory correlate roughly with results to date in bulk as well as NC doping of II-VI SCs. However, this data excludes many factors such as crystal binding energies. The reduction potentials are for aqueous conditions, while colloidal NCs are generally dispersed in organic solvents.

Details such as the surroundings of NCs and kinetic barriers to reactions have not been taken into account. Bulk band gap values are used, except for PbSe, which is estimated from NC results and includes some confinement. This theory thus represents a lower bound for stability. It seems that the limited amount of data on band offsets in NCs matches this theory, but the theory fails for several cases in the bulk. In the bulk, all II-VI SCs except ZnTe can be doped n-type. The theory predicts that ZnTe should be very unstable when doped n-type, but so should ZnS, which, however, can be doped n-type. Similarly, ZnTe and CdTe can be doped p-type in the bulk, which agrees with the theory, but so can ZnSe, which should be unstable following this hypothesis. This theory may, however, give a qualitative explanation, and a general guide to select appropriate SCs for obtaining stable carriers.

8. CONCLUSIONS

Semiconductor nanocrystals are a promising technological material because their size-dependent optical and electronic properties can be exploited for a diverse range of applications such as light-emitting diodes, bio-labels, transistors, and solar cells. For many of these applications, electrical current needs to be transported through the devices. However, while their solution processability makes these colloidal nanocrystals attractive candidates for device applications, the bulky surfactants that render these nanocrystals dispersible in common solvents block electrical current. Thus, in order to realize the full potential of colloidal semiconductor nanocrystals in the nextgeneration of solid-state devices, methods must be devised to make conductive films from these nanocrystals. One way to achieve this would be to add minute amounts of foreign impurity atoms (dopants) to increase their conductivity. Electronic doping in nanocrystals is still very much in its infancy with limited understanding of the underlying mechanisms that govern the doping process.

Напівпровідникові наноматеріали і нанокристали

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Дана стаття присвячена огляду нових методів синтезу та легування нанокристалів і спрямована на розширення фундаментального розуміння переносу заряду в цих легованих нанокристаллічних структурах. Список напівпровідникових нанокристалів, які можуть бути легованими є досить великим, тому якщо об'єднати отримані раніше результати, можна згенерувати набір матеріалів з цікавими властивостями. Окрім легування, ще одним перспективним шляхом для збільшення провідності в нанокристаллічних структурах є використання нанокристалів з високою іонною провідністю. Стаття також розглядає цю можливість, вивчаючи нові фази змішаних іонних і електронних провідників на нанорівні. Такий універсальний підхід може відкрити нові шляхи для цікавих фундаментальних досліджень, а також закласти основу для створення нових матеріалів з важливим застосуванням.

Ключові слова: Нанокристали, Нанотехнології, Домішки, Легування, Легуючі добавки, Наночастинки, Квантовий ефект.

Полупроводниковые наноматериалы и нанокристаллы

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Данная статья посвящена обзору новых методов синтеза и легирования нанокристаллов и направлена на расширение фундаментального понимания переноса заряда в этих легированных нанокристалличных структурах. Список полупроводниковых нанокристаллов, которые могут быть легированными довольно большой, поэтому если объединить полученные ранее результаты, можно сгенерировать набор материалов с интересными свойствами. Кроме легирования, еще одним перспективным путем для увеличения проводимости в нанокристаллических структурах является использование нанокристаллов с высокой ионной проводимостью. Статья также рассматривает эту возможность, изучая новые фазы смешанных ионных и электронных проводников на наноуровне. Такой универсальный подход может открыть новые пути для интересных фундаментальных исследований, а также заложить основу для создания новых материалов с важным применением.

Ключевые слова: Нанокристаллы, Нанотехнологии, Примеси, Легирование, Легирующие добавки, Наночастицы, Квантовый эффект.

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