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Device Applications of Band-Structure-Engineered Nanomaterials Current Status and Future Trend - Review

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Abstract

A variety of nanostructured materials are now available with precise control of their energy band structures due to quantum-confinement of electrons caused by changing morphologies and constituent materials due to recent developments of nanotechnology. These band-structure-engineered nanomaterials, possessing significantly modified physical and chemical properties against their bulk counterparts, in turn, are offering low-cost options of realizing altogether newer classes of electronic/opto-electronic devices by involving nanocrystals in place of atomic and molecular species as building blocks. The progress made in fabricating a number of useful devices such as light emitting diodes, photodetectors, solar cells, laser diodes, field effect transistors, memory and thermoelectric devices based on nanocrystals is reviewed here to assess their advantages in terms of the optimal use of the electronic wave functions of the modified discrete and extended electron energy states involved therein.

Current status and future trend in preparing solution-grown nanocrystals for producing such devices are discussed here by citing the latest experimental results. The trend of realizing these devices in the last few years shows their imminent industrial applications in near future. The impact of this kind of device technology development is expected to complement the microelectronics technology to have more profound impact on human society.

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1. Introduction

Solution grown metallic and semiconducting nanocrystals (NCs) have been extensively explored, in recent past, for fabricating conventional microelectronic devices including rectifying diodes, photo-resistors, field-effect transistors, memory elements, light-emitting diodes and photovoltaic solar cells (Talapin, et al, **2010**). Size-dependent electronic structures (Chelikowsky, et al, **1994**), charging energies (Alivisatos, **1996**), melting temperatures (Talapin, et al, **2010**) and many other physical and chemical properties that are possible to modify by changing the morphology of the NCs are the features that have attracted the attentions of the device engineers for their future explorations. Besides, adequately stabilized NCs offer newer ways of reducing the device fabrication costs by

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solution-based techniques like spin-coating, dip-coating, doctor blading; inkjet and a whole variety of printing techniques, which are very appropriately applicable in roll-to-roll type processing for large-scale productions (Talapin, and Murray, **2005**). This is one of the reasons that solution-grown NCs based large area solar cell development is currently being targeted for significant economic returns in harnessing the renewable energy from solar radiation (Krebs, et al, **2009**). Similarly, solution grown NC-FETs, exhibits reasonable carrier mobilities compared to the best known devices made from organic electronic materials, offer great potentials in developing flexible and wearable electronics of tomorrow (Kim, et al, **2008**). Indeed, for the progress in developing commercially successful NC-FETs needs very strong collaborative efforts of chemists, material scientists, device engineers and device fabrication technologists to optimize the processes involved in material preparation, device designs, device fabrication as well as their commercial production. Unprecedented improvement in the quality at reduced cost is foreseen in near future developments because of the inherent flexibilities present there in these futuristic nanomaterials that are yet to be fully explore.

The current status of the ongoing developments in the area of different NC-devices is highlighted in the following that will be helpful to assess the situation regarding future developments accordingly. The experimental results reported in the most recent publications are included, as far as it has been possible, in order to assess the situation regarding intelligent design of these band-structure-engineered nanomaterials and their device applications in the coming times.

2. Exploration of NC-Devices

For fabricating active electron devices, employing a large variety of NCs for their system applications in the field, it is necessary to form reasonably good electrical contacts that are capable of efficiently injecting and extracting charge carriers to and from the NC thin film. They are organized for realizing a given device structure in isolated discrete and integrated forms (Swisher, **2012**). Reliability and reproducibility of the contacts and interconnects are of prime importance for a reliable device function. On the basis of experience gained during the development of semiconductor devices based on monocrystalline semiconductors in past, it is anticipated that ohmic contacts will be equally applicable in case of nanocrystals as well. This is why it is necessary to examine contact formation to the basic material involving NCs before discussing the related device fabrications.

Proper electrical contacts are necessary for realizing low-loss interconnects among a number of active electronic devices with the external circuitry in which the device characteristics are put to use while taking care of the assigned circuit functions. Reasonably low loss electrical contacts, formed during device fabrication, help in accomplishing this task.

For efficient injection/extraction of the charge carriers in/from a device, respectively, it is not only necessary that the work functions of the metal layers involved should coincide with either the conduction or valence band edges of the semiconductor region in immediate contact but also there should be sufficient vacant states for these charge carriers in conduction and valence bands accordingly (Ahmad, **1998**; Swisher, **2012**). In order to accomplish this in case of classical example of a metal-semiconductor ohmic contact, the work function of the metal should be close/equal to either the electron affinity of n-type semiconductor or more than the sum of electron affinity and band gap in case of p-type semiconductor (Ahmad, **1998**; Swisher, **2012**). In case, these conditions are not met, the formation of potential barrier takes place involving depletion or accumulation of charge carriers that leads to poor injection or extraction of charge carriers resulting in a non-ohmic contact resistance (Ahmad, **1998**). This non-ohmic behavior of the contact is ultimately reflected in form of a combination of slowly increasing current at lower bias voltages followed by super-linear increase at larger bias voltages in the measured I-V characteristics (Ahmad, **1998**). Consequently, higher potential barriers formed at the metal-semiconductor interface combined with low semiconductor doping levels leads to the formation of non-ohmic or blocking/rectifying contacts (Ahmad, **1998**), which do not permit easy charge carrier injection and extraction into and from the semiconductor respectively.

There is an alternate scheme to fabricate a good contact even in case there is no appropriate metal available to form a low-barrier contact. In such cases, a tunnel contact is formed between a metal thin film and a heavily doped semiconducting layer, where the formation of an extremely thin potential barrier allows the charge carriers to tunnel across easily (Ahmad, **1998**; Swisher, **2012**).

Since the device behavior is a manifestation of the charge carrier transport across the active regions, injection and extraction efficiency of charge carriers becomes a critically important parameter for fuller utilization of the device capability. For instance, in case of a solar cell or photodetector the extraction efficiency of photo-generated carriers from the NC-solid would ultimately determine the overall performance. Similarly, the contact resistance in a solar cell would limit the corresponding fill factor (Brabec, et al, **2001**).

Extending a similar concept in case of forming good contact to NC-solids, the availability of unoccupied energy state for the electrons and holes should be ensured around lowest unoccupied states and highest occupied states near conduction and valence band edges in the NCs, respectively.

Further, it is natural to anticipate significant influence of the potential barriers present at the interfaces due to the difference in the work functions of contact material and the lowest unoccupied (electron conductors) or highest occupied (hole conductors) states of the NCs. Ensuring for good ohmic contact to such a NC-solid, the metal work function should be close to the highest occupied or lowest unoccupied states of the nanocrystal (Ishii, et al, **1999**). In case of NCs, the size plays a significant role in determining the quality of contact formed. For instance, gold film forms a hole injecting contact with the bulk as well as larger size PbS NCs having larger than 6 nm diameters (Konstantatos, et al, **2006**; Lee, et al, **2008**), whereas, a potential barrier is formed at the interface between Au and smaller size PbS nanocrystals smaller than 2nm in diameters. Generally, electrons and holes flow easily from smaller into larger size NCs, whereas the reverse is not true. The presence of surface ligands also affects the position of energy levels in semiconductor NCs. For instance, tuning of the electronic levels with respect to the vacuum level in InAs NCs was demonstrated by changing to different surface ligands (Soreni-Harari, et al, **2008**) suggesting that both size and ligand effects must be taken into account while designing NC based solar cells and other optoelectronic devices (Weiss, et al, **2008**). It has also been observed that In-Ga eutectic (EGaIn) injects electrons into the NCs, but not vice versa. Whereas, PEDOT: PSS neither injects electrons nor holes forming a blocking contact. Similarly, a rectifying contact was observed in CdSe NC films sandwiched between PEDOT: PSS and EGaIn in a device configuration of ITO/PEDOT: PSS/CdSe-nanocrystal /EGaIn (Weiss, et al, **2008**).

In case of Au-PbSe contact, the gold work function (~5.1 eV) being quite close to $1S_h$ state of 7 nm PbSe nanocrystals (~4.7 eV) should result into a low contact resistance unlike that in case of Au and 4 nm CdSe nanocrystals, where the available electrons and holes states are: $1S_e$ (- 4.6 eV) and $1S_h$ (- 6.5 eV) as compared to vacuum level; the contact resistance is naturally high. Au formed non-ohmic contacts to 4 nm CdSe NCs (Morgan, et al, **2002**; Drndic, et al, **2002**), preventing the current flow in the NC film. At the same time, gold electrode injects holes into $1S_h$ state of CdTe NCs film due to lower ionization potential of CdTe as compared to the CdSe phase (Porter, et al, **2008**). Ohmic contacts have been observed between Au and PbS (Konstantatos, et al, **2006**; Clifford, et al, **2007**; Lee, et al, **2008**; Clifford, et al, **2009**), PbSe (Talapin & Murray, **2005**; Law, et al, **2008**; Luther[1], et al, **2008**), and PbTe (Urban, et al, **2006; 2007**) NC-solids. Hole-injecting ohmic contacts between indium-tin oxide (ITO) electrodes and PbS (Clifford, et al, **2007**), PbSe (Luther[1], et al, **2008**; Barkhouse, et al, **2008**) NCs are also reported.

Once again, drawing a parallel from the metal-semiconductor system involving bulk semiconductors (Ahmad, **1998**), doping of NC-solids was noted to influence the contact resistance as the doping of CdSe NCs by potassium evaporation or by electrochemical charging resulted in ohmic electron-injecting contacts with Au and even Pt (5.6 eV) electrodes (Yu, et al., **2003)**.

Often, the presence of an additional dipole barrier at the interface has been observed to change the metal work function and the interface barrier height (Vazquez, et al, **2004**; de Boer, et al, **2005**). Consequently, intentionally introduced dipoles at the metal surface, using self-assembled monolayers (SAMs), were employed to improve charge injection into organic semiconductors (de Boer, et al, **2001**; Hamadani, et al, **2006**). Similarly, the density of electronic states in metal and NC-solids are expected to influence the I-V characteristic as the electronic structure of NC- solids with sharp spikes in the density of states should lead to unusual electronic properties. For example, a tunnel diode like behavior with pronounced negative differential resistance was reported in case of Au/SAM/CdSe-NCs/SAM/Au structures (Kim, et al, **1999**).

In a recent report, vacuum deposited low work-function metal electrodes comprising of Ca, Mg and Al on a film of PbS or PbSe NCs exhibited Schottky barrier (SB) at the interface (Luther[1], et al, **2008**; Johnston, et al, **2008**; Barkhouse, et al, **2008**; Klem, et al, **2008**; Clifford, et al, **2009**). Technology of preparing high quality Schottky contacts to NC-solids, in addition to the ability to form ohmic contacts, would be of significant advantages for the device applications in this area. For instance, the SB created built-in electric field causes fast separation of electrons and holes in photovoltaic devices and photo-detectors (Luther, et al, **2008**; Barkhouse, et al, **2008**; Clifford, et al, **2009**). Moreover, metal-semiconductor Schottky barriers possess rectifying I-V characteristics, suitable for a number of applications (Clifford, et al, **2007**). Compared to more traditional p-n junction diodes, the Schottky diodes exhibit very fast switching times, with essentially nonexistent reverse recovery, when the diode switches from non-conducting to conducting state and vice versa (Ahmad, **1998**; Zaban, et al, **2003**). Some of these options are very well possible to extend in case of Schottky-NC-solids contacts as well.

Some interesting observations were made while attempting to form ohmic contacts on NCs solids as described in the following. In the process of trying to form good electrical contacts to NCs and a large variety of branched nanostructured species, CdSe nanorods (NRs), attached with solution grown Au-tips, showed five orders of magnitude increase in conductance due to 75% reduced barrier height at the interface between gold and NR tips. These experimental findings (*Sheldon, et al, 2009)* emphasize the importance of interface conditions in deciding the quality of ohmic contacts to the NC-solids in general. It was further noted in another experiment (Mishra, et al, **2012**) that it is possible to selectively deposit metal on branched semiconductor nanostructures like asymmetrically tipped CdSe seeded CdS tetrapods with cone like arms that may be useful in preparing good electrical contacts to the tips in a complex nanostructured sample for using these individual units in certain specific ways.

The ever-evasive phenomena of doping of impurities in NCs was very recently studied in a doctoral program (Wills, **2011**) with very interesting findings for device applications in future. Out of several precursors, chosen for doping studies, Mn doping was realized successfully using dimethyl manganese as source (Wills, **2011**). Further experiments were conducted using a core-shell configuration to incorporate of impurities like Al and In into CdSe NCs by optimizing the three steps of nucleation, dopant binding and growth of high quality NCs. Finally, for preparing conducting thin films, appropriate for surface coatings, dithiocarbamates ligands were used to stabilize CdSe and PbSe/CdSe core/shell NCs, where these ligands bind well to metals initially but are broken on gentle heating resulting in bonding to the NCs. After ligand removal, the inter-particle spacing was noted to shrink yielding reduced barriers for electron transport as evidenced from the measurement (Wills, **2011**). Though, these observations initially appeared to be of ad-hoc nature, but ultimately it clearly showed the way to go about in understanding metal-NC-solid contact formation by extending the search on these lines as mentioned above.

3. Solution Grown NC based Devices

Optoelectronic and electronic devices based on surface passivated/functionalized NCs based 2 and 3-D hierarchical structures, considered in the present review, include light emitting diodes (LEDs), laser diodes (LDs), photo detectors (PDs), solar cells (SCs), field effect transistors (FETs), memory and thermo-electric (TE) devices. In order to explore charge carrier confinements and superlattices induced modifications resulting in collective behavior of electrons in metal, semiconductor and insulator NCs, it is better to know the limitations/challenges met in developing these devices further.The understanding the challenges of either utilizing the inorganic or organic semiconductors is essential, so that newer ways are explored while using NCs based solids in place of monocrystalline semiconductor bulk materials. It is quite likely that the devices realized using NC-solids would be complementary to the existing devices instead of replacing them directly. The major advantage foreseen in using NC-solids would be the additional flexibility achievable in optical response and electronic conduction mechanisms, which are otherwise missing in conventional bulk materials. For example, in case of TE materials, the involvement of phonon excitations is a fairly complex phenomena and therefore lumping the whole influence in form of mobility alone is not sufficient. The role of nanostructuring needs to be examined exclusively for minimizing the phonon thermal conductivity besides not affecting the electronic conductivity beyond certain level. This illustrates that every device based on NC-solids should be considered from an altogether different angle, where additional features of quantum confined charge carriers are used prominently.

3.1 LEDs

Basic structure of a light emitting diode (LED) involves a thin layer of luminescent material sandwiched between electron and hole-transport layers (E/HTL) (Morgado, et al, **2003**). When forward biased, electrons and holes are injected from the corresponding layers from the either side leading to recombination that generates photons with the energy corresponding to the gap between highest occupied $1S_h$ and lowest unoccupied $1S_e$ states. There is a requirement in understanding the processes involved in optimizing for improved device performances to be able to choose right kind of electron and hole transport layers and developing highly luminescent and stable semiconductor material.

Single or multiple core-shell configurations are preferred over simply surface stabilized NC based structure in case of LED development due to their enhanced photoluminescence and electroluminescence quantum efficiencies and their ruggedness during device processing. Solution grown, CdSe/ZnS core-shells or $Cd_{1-x}Zn_xSe$ recombination layer are used as emitters for NC-LEDs. This is achieved by putting the active layer between electron and hole transport layers responsible for carrier injection. Though, still lagging far behind the organic light emitting diodes (OLEDs) in terms of the efficiency; NC-LEDs otherwise possess high color purity and tunability of the emission right from UV to near-IR region of spectrum. However, for a better performance compared to OLEDs, both brightness and lifetime of NC-LEDs need further improvements. In addition, the future developments should address to the problems of incorporating better stability in the core-shell structures and electron and hole-transport layers based on the understanding of the chemical and physical processes involved at the interfaces along with optimization of the energy transfer and carrier injection from the organic molecules into the NCs.

The device structure of the first hybrid polymer-NC LEDs (Colvin, et al, **1994**) involved five monolayers of hexane-dithiol capped CdSe nanocrystals on top of the spin coated p-paraphenylene vinylene (PPV) layer. The recombination of the holes injected into the PPV layer with the electrons injected into the multilayer film of CdSe NCs resulted in light emission with very low external quantum efficiency of the order of 0.001 to 0.1% that was attributed to either low PL efficiency of the CdSe core or the poor electron conduction through the five layer thick NC film. It was also observed that the hexane-dithiol capping added impurities causing exciton quenching (Rizzo, et al, **2010**).

Considerable improvements were made while using CdSe (CdS) core/shell type NCs in confining the holes but still leaving the electrons delocalized (Schlamp, et al, **1997**). This modification gave higher PL quantum yield > 50% in solution at room temperature and improved the photo-oxidative stability compared to the bare CdSe cores. These devices emitted wavelengths from red to green with external quantum efficiency ~ 0.22% at a brightness of 600 cd/m^2 @ 1 A/cm^2. The basic cause of poor efficiency noted in these QD-LEDs was due to the poor conductivity of the NCs compared to semiconducting materials (Rizzo, et al, **2010**). These observations indicated that possibly a multilayer device configuration was needed to allow for an independent optimization of materials for charge injection, transport and emission.

In a subsequent modification (Coe, et al, **2002**), a monolayer of CdSe/ZnS core/shell NCs was sandwiched between HTL and ETL so that the NCs acted as source of light emission but did not participate in the carrier conduction. Rather, the organic layers transported the charge carriers to the NC monolayer from where the luminescence originated. The device fabrication process used simple colloidal NCs and organic small molecules spin coated onto the surface of ITO anode. The thickness and the coverage of the NC layer were optimized to have a single close packed monolayer. Devices having this configuration (Coe, et al, **2002**) exhibited high luminance emissions in the red-green region at a maximum external quantum efficiency ~ 2% and maximum luminescence over 7,000 cd/m^2.

Introduction of a single monolayer of CdSe/ZnS core/shell NCs, inserted between organic HTL and ETL, brought a dramatic improvement in NC-LED characteristics (Coe, et al, **2002**). These devices were fabricated by the phase separation of TOPO capped CdSe/ZnS core-shell NCs and TPD as HTL, while optimizing the concentration of TPD/NC to result in a single monolayer on top of continuous TPD film during spin-coating. ETL (Alq3) was thermally deposited on top of the NC layer followed by top electrode having a low work function like Al or its alloys. In this configuration, the holes are injected from the ITO contact into the TPD host matrix and are transported towards the single NC monolayer. Similarly, electrons are injected from the Mg:Ag cathode into the Alq3 and are transported to the NCs. Well-optimized HTL and ETL allow for balanced injection of carriers into the

NC-recombination layer. The external quantum efficiency of NC-LEDs with the configuration of glass/ITO/TPD/CdSe-NCs/Alq3/Mg was noted as ~ 0.4% for a broad range of luminance from 5 to 2000 cd/m^2, peaking at 0.52% at 10 mA/cm^2. A 100 cd/m^2 luminance was achieved at 5.3mA/cm^2 and voltage 6.1 V. At 125mA/ cm^2, the brightness of the device was 2000 cd/m^2, which was very significant improvement over previously reported NC-LEDs. To further improve the color purity, a thin hole-blocking layer (HBL) of TAZ was placed between the layer of NCs and Alq3 to suppress Alq3 emission by blocking transport of both holes and excitons into the Alq3 and allowing having devices with pure emission from CdSe/ZnS NCs.

In another scheme of CdSe/ZnS NC-LEDs (Zhao^2, et al, **2006**), a thermally cross-linked HTL of TPD - PFCB was followed by the deposition of the NC layer and the electron-transporting layer of TPBI by thermal evaporation. The maximum external quantum efficiency and brightness of these devices were 0.8% at 100 cd/m^2 and 1000 cd/m^2, respectively, was further improved to 1.6% at a brightness of 100 cd/m^2 after thermal annealing of the NC layer. Despite higher efficiency and lower turn-on voltage, observed in these devices, their output power, maximum luminance and color purity were limited owing to the low chromophore quantity and the poor confinement of excitons QD region (Zhao^2, et al, **2006**; Rizzo, et al, **2010**).

High-performance red, orange, yellow and green NC-LEDs were fabricated using CdSe core and a ZnS or CdS/ZnS shell resulting in maximum luminance of 9,064; 3,200; 4,470, and 3,700 cd/m^2, wherein the improved performances of the NC-LEDs was attributed to the preparation of purified, uniform and mono-dispersed core-shell NCs along with the optimized polymer HTL, the NC layer and the ETL (Sun, et al, **2007**; Rizzo, et al, **2010**).

For the performance optimization of the charge carrier transport layers in NC-LEDs, it was observed that these layers must be extra smooth with no large grain boundaries as in amorphous thin films, besides, having adjustable low carrier concentrations to minimize quenching of the NC EL through free-carrier Plasmon modes (Caruge, et al, **2008**). The most important consideration for choosing the ETL and HTLs is to have free carrier concentrations and energy-band offsets such that the electron and hole injections into the NC-layers are exactly equal in number otherwise any excess of one type of the carrier over the other will lead to charging, which will increase the likelihood of non-radiative three body Auger relaxations responsible for decreased EL-efficiency (Caruge, et al, **2008**). These requirements are possible from the metal oxides as charge transport layers as they offer a range of deposition specific morphologies and tunable conductivities through doping and physical co-deposition. Taking these options into account, NC-LEDs were fabricated using 5 ohm-cm resistivity 20-nm NiO film deposited on ITO by adjusting the Ar:O_2 ratio in plasma during deposition, while ensuring that as-grown film was not only amorphous but also extremely smooth (Caruge, et al, **2008**). Similarly, optically transparent, 10 ohm-cm resistivity and 50-nm film of ZnO: SnO_2 alloy film was chosen as ETL especially because ZnO or SnO_2 films, as such, are polycrystalline with large size grain boundaries whereas ZnO: SnO_2 alloy films are highly smooth and amorphous. This choice of ZnO: SnO_2 was also necessitated by the fact that the ETL could be sputtered directly onto the NCs without damaging NC-ligands as during sputter deposition only the ZnO: SnO_2 ratio determined the film conductivity. ZnCdSe NCs with 638 nm emission peak were spin-coated onto the NiO substrate so as to form a film consist of 3 - 4 close packed monolayers. These devices demonstrated a maximum efficiency of 0.1% with peak brightness of 1950 cd/m^2 at 3.73 A/cm^2 (Caruge, et al, **2008**).

In another approach, sol-gel based TiO_2 ETL was spin coated for preparing the NC-LEDs using an all-solution based process (Cho, et al, **2009**). The cross-linked NC-layer was spin-coated on a TFB based HTL. The linker molecule (1,7-diaminoheptane) was attached to NCs through exchange process followed by a post-deposition thermal anneal, where NC's crosslinking improved the luminance and luminous efficiency very significantly. It was noted that reducing the energy band offset between the NCs and the HTL from 1.5 to 0.9 eV led to 10-fold increase in the maximum luminous efficiency because of more efficient hole-injection and enhanced charge balance. Moreover, the TiO_2 layer showed an improved electron-injection superior to the standard organic Alq3 as a consequence of the lower band offset of 0.4 eV for Al/TiO_2 compared to that of 1.2 eV for Al/Alq3 in addition to the higher electron mobility of TiO_2 compared to that for Alq3. The overall device performance was improved resulting in a luminescence of ~ 12,380 cd/m^2 and a maximum power efficiency of 2.41 lm /W (Cho, et al, **2009**).

A contact printing based device fabrication process produced high quality NC-LEDs by involving inking of an elastomeric stamp using spin coating of a NCs suspension to create a highly uniform NC monolayer on the stamp surface (Panzer, et al, **2012**). Subsequently, an organic thin film was pressed against the stamp surface, which resulted in an efficient transfer of the NC monolayer from the stamp to the LED device stack without exposing the organic film to any solvent. This process was found useful, in a sense, that the organic film was not exposed to solvent because the NC layer was already inked and dried on the stamp, and the conditions for inking the stamp with a uniform NC-monolayer optimized independently from the deposition of the underlying organic film, facilitating NC monolayer deposition on any thickness film desired. This procedure of contact printing NCs onto an organic semiconductor thin film involved fabricating PDMS stamp, inking the stamp with a single or multi-layer film of NCs by spin-coating, transferring the dried NC layer from the stamp to a substrate coated with an organic thin film via mechanical contacting and finally removing the stamp by peeling it apart from the substrate (Panzer, et al, **2012**). The PDMS stamp was prepared from a commercially available kit consisting of a base and curing agent, which were mixed in proper ratio followed by degassing the liquid mixture in vacuum for half an hour. The degassed mixture was poured into a shallow glass dish and cured either at 60^0C overnight or at room temperature for one week before cutting the proper size of the stamps from the cured film (Panzer, et al, **2012**).

Extra bright and efficient inverted NC-LEDs using ZnO NCs and electron injection/transport layer were reported recently exhibiting the maximum values of luminescence in red, green and blue region as 23, 040; 218, 800; and 2,250 cd/m^2, respectively, along with corresponding external quantum efficiency of 7.3, 5.8, and 1.7% (Kwak, et al, **2012**). Additionally, these NC-LEDs exhibited turn-on voltages as low as the band gap energy of each NC and relatively longer operational lifetime mainly attributed to the direct exciton recombination within NCs through the inverted device structure. This kind of improvement was realized by improving electron and hole injections into the NCs (Kwak, et al, **2012**), where an inverted device structure was employed by making the ITO the cathode with the help of ZnO NCs as an ETL, which injected charge carrier more efficiently. By patterning different size NCs on the layer of ZnO NCs, LEDs were fabricated for three different colors: red, green, and blue. However, the new blue NC-LEDs still displayed a lower brightness, which was the major drawback of both NC-LEDs and OLEDs. The newer values of efficiencies, mentioned above, were better than the previous values, but still lower than 20% efficiency of OLEDs (Kwak, et al, **2012**). Another major challenge, for both the NC-LEDs and OLEDs, is their shorter lifetimes. Till date, NC-LEDs lifetimes have not yet crossed over a few tens of hours as they degrade fast within a few hours of operation. Inverted type NC-LEDs, like those mentioned here, have half-lifetimes of up to 600 hours still falling behind tens of thousands of hours for OLEDs (Kwak, et al, **2012**).

In the development of white light sources, it generally involves stacking of different color pixels or down conversion. It was, however, demonstrated that the fabrication of a white LED was possible by incorporating a monolayer of balanced mix of red, green and blue NCs in a configuration having ITO/PEDOT: PSS/TPD/QDs/TAZ/Alq3 layers (Anikeeva, et al, **2007**). These NC-LEDs produced uniformly white luminescence, when biased at 9V. The independent processing of HTL and emitting layer of NCs in this processing offered the possibility of precisely tuning the emission spectrum by simply changing the color ratio of NCs without altering the device structure. Though, these results demonstrated, in principle, the promise of realizing electrically driven NCs in large area displays and lighting applications except they required right kind of packaging for preventing degradation of the organic transport layers in the presence of atmospheric O_2 and water vapor.

Further improvements were reported in white light hybrid NC-LEDs of ITO/PEDOT: PSS/PVK/CdS-QDs/(Al or Mg:Ag) configuration employing thermo-chemically prepared NCs with TGA capping resulting in higher intensity near white light emission (Molaei, et al, **2012**). Triton X-100 mediated 2 nm NCs spin coated on substrate demonstrated a broad-spectrum EL at 540 (170 nm width), which was about 50nm red shifted compared to PL spectra. Though, annealing up to 190 ^{0}C improved the device performance, possibly due to better contacts but replacing Al with Mg: Ag reduced the turn-on voltage from 7 to 6 V along with shift of EL peak to 525 nm, with a brightness of 15 Cd/m^2 at @ 15 V. The current efficiency and external quantum efficiency of these devices were 0.08 Cd/A and 0.03%, respectively, at >10 mA/cm^2 (Molaei, et al, **2012**).

A tandem combination of high luminescence NC-LEDs with bright and efficient single-crystal LEDs are used as down-converting medium, where a highly efficient emission from GaN LED is possible to down convert into the color of choice by NC-LED while offering superior performance to an LED based on direct injection of carrier into the NCs. Combining GaN LEDs with CdSe/ZnS NCs-polymer composites in combination with CdSe/ZnS NCs color converters were thus realized employing InGaN LEDs with high color stability. In 2008, Evident Technologies, Inc., commercially produced Christmas lights using III-V LEDs and luminescent nanocrystals as the down converter.

The device lifetime of a hybrid organic/NC-LED is primarily limited due to the onset of metal contact instability and organic compound degradations at higher operating currents. In order to remove these limitations, the organic hole and electron transport layers are replaced with more robust inorganic materials like p-type NiO films as hole transport layer demonstrating higher chemical, thermal, and electrical stability (Caruge, et al, **2008**). A maximum $\eta_{ext} \approx 0.18\%$ @ brightness ~3000 cd/m^2 was arrived at by optimizing NiO layer resistivity. In a subsequent attempt, all-inorganic NC LEDs were fabricated by replacing TAZ and Alq3 layers with sputtered amorphous ZnO: SnO_2 semiconductor (Caruge, et al, **2008**). The all-inorganic NC-LEDs, combined with p-type NiO layer, luminescent $Cd_{1-x}Zn_xSe$ NC emitting layer and n-type ZnO: SnO_2 electron transport layer, showed pure emission with the peak luminance of 1950 cd/m^2 and enabled very high injection currents of 3.5 A/cm^2 with maximum efficiency of 0.1%.

Intensive efforts were put in during last 15 years in the area of NC-LEDs, which are fast approaching maturity for commercial production, where these devices can very well compete with OLEDs and other emerging display and solid-state lighting technologies. For assured success in this context, it will be imperative to look into the performance, cost, lifetime and mass scale production technology. However, there is a serious problem of toxicity associated with NC-LEDs due to Cd-based raw material involved. Serious attempts were, thus, made to address to this issue by developing highly luminescent but nontoxic NCs like InP/ZnS core-shells or $CuInSe_2$ along with other combinations based on narrow gap semiconductor like InAs, PbSe and HgTe. Some recently reported results demonstrated solution-grown LEDs with the emissions at 1.3 and 1.55 μm of telecommunication wavelengths.

3.2 Laser Diodes

Semiconducting NCs possess excellent light-emitting properties as discussed in the earlier section and are therefore destined to emerge as an optical amplification medium, which is possible to process with solution grown material synthesis. The basic requirement for realizing optical gain in a NC-solid is that there should be minimum two excitons. Though, the excitons, generally, annihilate each other before any optical amplification occurs, but this is possible to overcome using core-shall type NCs made from different semiconductor materials and constructed in a way that the electrons and holes are separated from each other. Under this condition, it is possible to have optical gain based on single excitons, significantly enhancing their promise as a practical optical gain material for laser applications.

Historically, quantum confinement of electrons and holes in form of a two-dimensional electron and hole gas sheets (2DEG and 2DHG) did improve the performance of bulk semiconductor lasers significantly (Han, **2009**). Compared to the bulk semiconductors, the quantum well (QW) structures possess a higher density of electronic states near the edges of the conduction and valence bands and therefore a higher concentration of carriers are available for the band-edge emission for the lasing action (Dupuis, et al, **1978**). Consequently, QW lasers operate at lower threshold current density demonstrating improved thermal stability and a narrower emission line.

Semiconducting NCs of few nm diameters prepared by solution grown synthesis were currently viewed as promising candidates for the next phase of advancement over those of the QW lasers mentioned above (Klimov, **2003**). Theoretically, it is established that a 3-d confinement of the charge carriers in a semiconductor NC gives rise to a size and shape dependent discrete energy spectrum with an inter-level energy difference inversely proportional to square of its diameter. It is, therefore, anticipated that in very small NCs, it is quite possible that the larger value of inter-level energy difference exceeding the thermal energy - k_BT would not favor the thermal depopulation of the lowest electronic states. In case, such NCs are used for lasing action, it would definitely have a temperature independent lasing threshold at an ideal excitation level of only one electron-hole pair per NC (Klimov, **2003**).

The very first lasing action in 10 nm CdSe semiconductor NCs was experimentally demonstrated in 1991 using high-temperature precipitation of NCs in the molten glass (Vandyshev, et al, **1991**). Subsequently, lasing action was also reported in case of NCs grown epitaxially (Ledentsov, et al, **1994**). These NC-lasers did demonstrate improved performance of reduced threshold and enhanced temperature stability in comparison to QW-lasers. These early results prompted to develop sub-10nm NC based laser structures, wherein the inter-level differences could be size tuned up to an eV. However, after a decade of intensive research and development with enough hints of optical gain, semiconducting NCs did not demonstrate any lasing action while such a failure could be attributed to material defects or dangling bonds existing invariably on the NC-surfaces. Such surface defects created electronic states within the energy gap causing electrons relax while going through non-radiative or radiative decay to the ground state eventually ending into carrier losses that inhibited the optical gain. Another concern was the reduced efficiency of electron-phonon interactions that reduced the ability of carriers to enter into the band-edge states and reduced luminescence efficiency. Besides, multi-particle Auger recombination was finally considered as the main hindrance for lasing action (Klimov, et al, **2000**).

For stimulated emission of radiation necessary for lasing action, it is necessary to create population inversion, wherein larger numbers of electrons occupy the excited state as compared to the lower energy states. In smaller NCs, considering the simplest two-level system involving two electrons in ground state for stimulated emission, to affect population inversion, both the ground state electrons should move to the excited state. This amounts to a basic requirement that the NCs should have two excitons for optical gain as mentioned in the start of this section. Generally, the intrinsic decay of singly excited NC is due to the electron-hole recombination and the emission of a photon, but two electron-hole pair states relax predominantly by nonradiative Auger recombination (Klimov, et al, **2000**), wherein instead of a photon generation the energy is transferred to a third particle (an electron or a hole) that is re-excited to a higher energy state. Auger recombination is relatively less efficient in bulk semiconductors because of restrictions imposed due to energy and momentum conservation conditions whereas in NCs the translational momentum conservation does not apply and consequently the Auger effect becomes significantly enhanced. Because of having the same electron-hole pairs for both Auger recombination and population inversion for lasing action, it is natural to expect adverse effect of Auger recombination in return. However, the adverse effect of Auger recombination was eliminated subsequently by the end of the Century (Klimov, et al, **2000**) when in a NC-solid, having a fill factor of 0.2 to 1%, it became possible to enhance the stimulated emission from Auger recombination (Klimov, et al, **2000**). Subsequently, optical gain was demonstrated for the first time by using close-packed, matrix-free films of CdSe NCs. Though, initial experiments were conducted at lower temperature but with improvement in NC synthesis, room temperature lasing action was also demonstrated subsequently (Mikhailovsky, et al, **2002**).

For demonstrating true lasing action, the NCs gain medium was transferred into micro-capillary tubing that served as cavity (Klimov, et al, **2001**; Malko, et al, **2002**) to provide positive feedback for optical gain. After several attempts, it became possible to uniformly fill the tube with the NCs and demonstrate the first lasing action (Klimov, et al, **2001**; Malko, et al, **2002**). Several types of cavities have demonstrated NC based lasing actions, including polystyrene microspheres (Klimov and Bawendi, **2001**) and distributed-feed-back resonators (Eisler, et al, **2002**).

Using the concept of band alignments in superlattices to separate charge carriers across band offsets, CdTe-CdSe and CdSe-ZnTe core-shell type of NCs were studied wherein it was demonstrated that optical transitions corresponding to energies different from the band gap energies were possible by designing the core and shell structures appropriately (Kim^2, et al, **2003**). This concept was pursued further (Ivanov and Achermann, **2010**) in understanding single and multi-exciton emission energies and their decay in CdS/ZnSe core/shell NCs that exhibited spatially separated charge carriers resulting in long radiative exciton lifetimes, repulsive bi-exciton interactions and reduced Auger recombination efficiencies. The spectral and dynamic properties of bi-excitons varied with the shell thickness. The different sensitivity of exciton and multi-exciton characteristics on the ZnSe shell thickness provided a method to tune them independently. More recently, using a two band effective mass model and perturbation theory, the control of exciton parameters in type I/II configurations was studied to offer proper design of core-shell NCs, where radiative and nonradiative decay rates could be enhanced or suppressed for their uses in NC based laser applications (Tyagi and Kambhampati, **2012**).

While practically exploring the realization of lasing action in core-shell type of NCs, it was possible to demonstrate lasing action at room temperature in CdS/ZnS NCs stabilized in a sol-gel derived silica matrix coated microspheres over long duration of continuous excitation (Chan, et al, **2005**). In a subsequent attempt (Klimov, et al, **2007**), core/shell type

NCs were prepared in type-II heterostructures configuration that ensured separation of electrons and holes between the core and the shell and produced a strong local electric field, which disturbed the balance between absorption and stimulated emission. This led to successful demonstration of single exciton based lasing action in NCs (Klimov, et al, **2007**).

3.3 Photodetectors

The current IR-detector technology is primarily based on mercury cadmium tellurium (MCT-HgCdTe) - a material that is relatively difficult to grow with reasonable quality and yield facing problems in having a viable production technology that ultimately translated into overall very high costs (Rogalski, **2005**). Because of these limitations, alternate technologies were examined involving III–V compound semiconductor strained layer superlattice with a type-II band lineup, quantum well (QW) and NC based structures where it was expected to increase the operating temperature of these devices.

A direct comparison of three families of photo-detectors involving MCT, QWs and NCs was made sometime back in terms of dark current and detectivity by taking into account the basic material parameters in which the NCs based devices were found to be much superior to QW based detectors while having equal or even better performance in comparison to MCT detectors provided the required uniformity in NCs sizes could be achieved for which fabrication technology needs drastic improvements to minimize inhomogeneous broadening (Phillips, **2002)**.

While comparing QWs versus NCs for optical detection, it was felt necessary to consider the difference in the nature of the confinement in the two cases. In the QWs, the confinement is only along the growth direction, while in the NCs, it is a continuum like situation in all the three directions making the corresponding devices distinctly different from those involving QWs. Consequently, the NCs based devices were found better photo-detectors compared to QWs based structures (Martyniuk and Rogalsky, **2008**). It was also observed that in QWs, at normal incidence of radiation signal, only transitions having polarization perpendicular to the growth direction were allowed for inter-sub-band absorption as compared to completely different selection rules in NCs. On the other hand, the thermal generation of electrons in NCs is significantly reduced due to the energy quantization in all the three dimensions and consequently, the relaxation time of the excited electron states increases due to phonon bottleneck. This prohibition is not there in QWs, since the energy levels are quantized exclusively in the growth direction and a continuum existed in the other two directions. Thus, it is expected that signal to noise (S/N) ratio in NC-based devices would be significantly higher than those in QWs based devices. Similarly, lower dark current is expected in NC- based devices as compared to MCT and QW based detectors due to 3-D quantum confinement of the electron states (Martyniuk and Rogalsky, **2008**).

Theoretical calculation of QDs based detector performance under dark and illuminated condition was carried out in detail, assuming that both thermionic emission and field-assisted tunneling mechanisms were involved in generating the dark current. The relevant detector parameters such as - dark current, current gain; average number of electrons in NCs, photocurrent, detector responsivity and detectivity were estimated as function of the structural parameters providing a good design base for detector development (Martyniuk and Rogalsky, **2009**).

MCT is a variable-gap semiconductor that has been in use as detector in different ranges of IR spectrum. Detailed theoretical analysis (Martyniuk and Rogalsky, **2008**) indicated that only type-II superlattice photodiodes and NCs based devices would compete with MCT photodiodes. For example, the measured performance of NC photodiode detectivities @ 77 K were found inferior to the current MCT performance mainly due to two reasons - non-optimal band structure and non-uniformity in NCs size (Martyniuk and Rogalsky, **2008**). Comparison of NCs based detectors with MCT and type-II superlattice based detectors indicated that the NCs based devices are suitable for high temperature operation. It was, therefore, expected that improvement in fabrication technology and device design of NCs based detectors would finally achieve both high sensitivity and fast response useful for practical applications in room temperature focal plane arrays (FPAs). This new generation of room temperature FPAs would eventually compete with silicon micro bolometers that dominate at present (Martyniuk and Rogalsky, **2008**).

Despite a variety of sensitive photon detection systems available currently for the visible region based on photomultiplier tubes, monocrystalline Si detectors and CCD cameras; the situation in the IR-region is not that good as most of these systems are especially of array type having lower sensitivity and very high costs. One of the reasons for this kind of situation is attributed to the use of Si charge coupled devices (CCDs) and avalanche photo-diodes (APDs), which could not operate beyond 1.1 μm besides the other materials, were quite noisy and difficult to process using standard microfabrication technology. For all of those areas like telecommunication, night-vision, bio imaging, environmental sensing, spectroscopy and chemical analysis, it was, therefore, highly pertinent to look for the newer materials that possessed higher detectivity at a reasonable cost. Recent developments in NC based solids for photo-detectors offer better prospects, in this context, because of tunable confinement of charge carriers and associated charge carrier transport properties.

Exploring the phenomenon of photo-detection in NC solids is, essentially, driven by a number of reasons including easy access to size-tunable electronic structures, appropriate surface chemistry for stabilization and charge carrier trapping, compositional flexibility and simpler device manufacturing using low cost solution grown materials technology. Keeping the relevance of these important parameters in view in this context, narrow band gap semiconductors like PbS, PbSe, PbTe, HgTe, InAs and InSb emerged strongly for light absorption and emission in the near-IR region as their band gaps were possible to tune from the visible region to 3.5 micron wavelength (Talapin, et al, **2010**).

In photo-conducting detectors, the change in conductivity of the illuminated photoconductor arising due to photogenerated electron-hole pairs is precisely measured. Though, the phenomenon of photoconductivity, in general, is observed in almost every semiconductor; however, the development of one particular device with characteristic features appropriate for specific application is a difficult task. This is primarily so due to a number of parameters such as responsivity, spectral response, noise-equivalent power, detectivity, response time and frequency response are involved in characterizing the detector figure of merit, which is rather difficult to meet in terms of the characteristic requirements of a specific application (Talapin, et al, **2010**).

The basic structure of the photo-conducting detector involves ohmic contacts to a semiconducting thin film with preferably smaller electrode spacing appropriate for efficient collection of photo generated charge carriers. For NC based photo detectors, thin film geometry is more convenient as a homogeneous sub-micrometer thick NC thin film is easily prepared from colloidal solutions having right kind of constituents. Incidentally, photoconductivity measurements required for the material characterization are quite similar to those used for solar cells (Talapin, et al, **2010**).

While examining NC solids for photoconducting detector applications (McDonald, et al, **2004**), it is noted that the photo-generated mobile charge carriers that modulate the conductivity of NC solids are essentially the electron-hole pairs generated within individual NCs. The process of separating these photo-generated charge carriers is generally slower than their inter-band relaxations and they follow hopping transport dominated by inter-dot tunneling.

Thus, considering such prevailing conditions, it becomes clear that for better detection sensitivity, the dark current should be as low as possible. For designing NCs for low dark currents, the presence of large inter-particle spacing, insulating surface ligands and higher exciton binding energy of ~200 m eV belonging to 2 nm CdSe NCs (Jarosz, et al, **2004**; Yu, et al, **2006**) were found appropriate for realizing sub-pA dark currents. However, for improving the charge carrier transport, CdSe NC solids were treated with alkyl amines or strong bases (Jarosz, et al, **2004**; Yu, et al, **2006**), which resulted in highest photocurrents in CdSe NC solids. This improvement was noted after soaking TOPO-TOP capped CdSe NC solid films in butyl amine or sodium hydroxide followed by 70□□ drying, which substantially decreased inter-particle separations as well as improved the surface passivation. Using butyl amine-treated CdSe NC solids, photo detectors were fabricated (Oertel, et al, **2005**) by putting NC solid layer between ITO/PEDOT: PSS and Ag electrodes and under illumination, these devices exhibited a gain of 10^3 at zero bias and 50 Hz bandwidth.

In one of the experiments, higher performance devices were realized after treating the NC films with methanol under inert atmosphere followed by controlled surface oxidation resulting in high detectivity of ~2 × 10^{13} Jones @ 30 Hz modulation frequency, showing even better performance compared to InGaAs photodiodes having more than 60 dB linear dynamic ranges (Konstantatos, et al, **2006**). The gains in the range of 10^2-10^4, measured in these devices, were primarily attributed to the presence of long-living electron traps generated by chemical treatment of the NCs surfaces. This was followed by another report of detectors based on 2 nm PbS NCs with cutoff wavelengths of 850-900 nm, suitable for sensing in the visible spectral region (Konstantatos, et al, **2007**). To explore the advantageous role of the long-living trap states in PbS NCs for improving the response time of PbS-based detectors, a detailed investigation was carried out (Konstantatos, et al, **2008**) in which it was concluded that treating NC-solid films with different compounds like butyl amine, formic acid and small thiols could possibly controlled the chemistry of surface sites acting as the traps to influence the detector response time. In this context, the shortest time constant of 33 ms was reported after treating the films with ethanethiol in acetonitrile, which led to the formation of $PbSO_3$ at the surface upon exposure to air.

After a careful screening for finding out an appropriate material for detector applications, HgTe turned out to be a better material. For instance, efficient photocurrent generation and spectral response up to 1.8 μm wavelength was demonstrated in thio-glycerol-capped HgTe NC thin films (Kim[1,2], et al, **2006**). By tuning the NCs size in the range of 3-10 nm, in an inkjet printed class of photodetectors with ink containing dodecane-thiol-stabilized HgTe NCs in chloro benzene on pre-patterned glass slides, the devices exhibited extended spectral response from mid-infrared to 3 μm (Böberl, et al, **2007**).

Considering the importance of the current trend of promoting the uses of “greener” materials and processes; Pb, Cd, and Hg free devices are becoming more favorable, especially for their large-scale consumer applications. In this context, very efficient Bi_2S_3 nanorods (NRs) based photo detectors were successfully developed having characteristics very much similar to the above-described PbS detectors (Konstantatos, et al, **2008**).

It is already known that photodiodes offer significantly higher response speed than the photoconductors (Talapin, et al, **2010**). One of the recent reports described about the development of IR photodiodes using PbS NC solid layer sandwiched between ITO and Al contacts forming Schottky barrier at the NC-metal interface. The electric field due to built-in potential across the Schottky barrier helped in separating photo generated charge carriers as expected. Taking into consideration the higher carrier velocity in the depletion region as compared to that in the diffusion layer of photoconducting materials, it enabled optimization of the device performance by adjusting the thickness of NC layer such that it was just sufficient for holding the depletion layer with no extra homogeneous region causing diffusive transport. The sensitivity-bandwidth product of such a photodiode was found □□□□ fold improved over that found in similar photoconducting NC solids. This kind of device optimization resulted in much faster device operation with 3dB bandwidth of 35 kHz, while their detectivities were very much similar to those of previously reported photo conducting detectors (Sargent, **2008**).

Using the concept of adjustable photoresponse and charge carrier transport by invoking proper designs of organic molecules along with those of NCs, attempts were made to develop nanocomposites wherein optimization of both the features could be put to use in the present context. Following this approach, it became feasible to take care of the basic drawback of spectral response limited to the optical region in case of smaller molecules involving fullerene derivatives or π-conjugated polymers, which are otherwise very useful light-sensitive materials for solar cells and photo-detectors. It is therefore anticipated that the blending of narrow band gap NCs as sensitizer with the above mentioned organic semiconducting materials would produce superior hybrid organic-NCs devices involving the synergistic combination of light harvesting and charge transport (Talapin, et al, **2010)**. This scheme was duly verified in case of CdSe NC solid blended with crystalline arrays of fullerene C_{60}, which exhibited three orders of magnitude enhancement in photocurrent (Biebersdorf, et al, **2006**). This could be possible only due to efficient light absorption in CdSe NCs combined with faster electron transfer from NCs to C_{60} wherein the carrier mobilities were relatively higher within the C_{60} molecules. A similar concept, in case of IR range devices, was also implemented successfully by combining PbS NCs and soluble C_{60} derivative PCBM (Szendrei, et al, **2008**). It is interesting to note that the films of untreated, oleic acid stabilized PbS NCs were highly insulating possessing very poor photo-response. However, composite solids made of PbS/ PCBM in a 1:1 weight ratio exhibited $D^* \approx 2.5 \times 10^{10}$ Jones with a gain of 10^4. The spectral response followed the absorption spectrum of PbS NCs with cutoff wavelength in the near-IR. These results confirmed the basic concept of efficient electron transfer as described above.

In typical applications of IR-photodiodes, solution grown NC photo-detectors were integrated with amorphous Si active matrix back planes wherein the PbS NCs were used as infrared-sensitive component (Rauch, et al, **2009**). Near-IR photo-sensitivity appeared across the nanostructured inorganic-organic bulk hetero-junction operating in contrast to organic visible imagers on the concept of charge separation between PbS NCs based IR sensitizer and separate electron (PCBM) or hole (P3HT) accepting and transporting layers (Yu, et al, **1999**).

Graphene with very high room temperature electron mobility of 60,000 cm^2/Vs, along with better prospects of hybridization with other materials, offered conductance that was very sensitive to electrostatic perturbation by photo-generated carriers close to the surface. This kind of involved interactions with charge carriers projected graphene as a particularly promising material for high-gain photo-detection via photo-gating effect (Konstantatos, et al, **2012**). Graphene is an extremely thin, flexible and durable material that can be prepared on a large scale and can easily be transferred onto silicon wafer, allowing monolithic integration with standard integrated circuits. It is, thus, expected that photo-detection gain observed in graphene might become the basis for a number of applications including graphene-based integrated optoelectronic circuits, biomedical imaging devices, remote sensing systems, optical communications systems and quantum information technology based devices (Konstantatos, et al, **2012**). In this scheme of realizing a light-activated transistor, spectrally tunable and light absorbing NCs, the photo-generated charge carriers are transferred to graphene, while oppositely charged carriers remain trapped in the NC layer that provide photo-gating effect, where the presence of these charges changes the graphene sheet resistance through capacitive coupling. The main feature of this kind of device is its ultrahigh gain, which originates from the high carrier mobility of the graphene sheet and the recirculation of charge carriers during the lifetime of the carriers that remain trapped in the PbS NCs. The phenomena of photo-detection gain can be quantified (Konstantatos, et al, **2012**) by considering the typical lifetimes for electrons and holes. Photo-excited holes in the PbS NCs are transferred to the graphene layer and drift by means of a voltage bias V_{DS} to the drain, with a typical timescale of $t_{transit}$, which is inversely proportional to the carrier mobility. Electrons remain trapped with a typical timescale of $t_{lifetime}$ in the PbS NCs as a result of the built-in field at the NC/graphene interface as well as the electron traps in the PbS NCs. Charge conservation in the graphene channel leads to the replenishment of holes from the source as soon as a hole reaches the drain. Accordingly, multiple holes circulate in the graphene channel following a single electron–hole photo-generation, leading to photo conducting gain $G \sim t_{lifetime}/t_{transit}$, indicating the importance of long lifetime and high carrier mobility. The measured performance of these devices yielded – a lower threshold limit of noise-equivalent power of 10^{-17} W resulting in a specific detectivity $D^* = 7x10^{13}$ Jones with a gain of 10^8 @ 10 Hz bandwidth, which is as good as that of epitaxially grown III–V phototransistors (Konstantatos, et al, **2012**).

In a novel configuration of photoconducting detector employing a 50x60 nm^2 size CdSe/ZnS core-shell NCs based material was operated at room temperature by incorporating a NCs thin film across a lithographically defined metal nano-gap. The electron transport comprising of the field-induced ionization of the photo-generated excitons was proportional to the electron tunneling between neighboring NCs and the high electric field assisted current flow across the nano gap. E-beam lithography defined metal electrode gap with annealed assembly of NCs exhibited significant improvement in sensitivity and bandwidth (Hegg, et al, **2010**).

In a more recent refinement of single layer NC thin film based photodetector, NCs bridged the space between nanometer spaced electrodes, where the current transport involved individual NCs to tunnel current resulting in a gain of around 38 electrons per photon with a response time of 300 ns (Prins, et al, **2012**).

In another similar development, a PbS NCs based photo detector combined with FET was reported in which PbS NCs were blended with P3HT and PCBM, which extended the photosensitive spectrum of the blend into the near-IR region. A FET-based photodetector having ITO/PMMA (180 nm)/ P3HT: PCBM: PbS(110 nm)/Al configuration, in which PMMA acted as the dielectric layer and P3HT:PCBM:PbS the active layer, showed broad bandwidth, responsivity of 0.391 mA W^{-1} and a specific detectivity of 1.31×10^{11} Jones @V_{GS} = 1 V under 600 nm illumination with an intensity of 30 μWcm^{-2} (Yang, *et al.,* **2012**).

3.4 Photovoltaic Solar Cells

A photovoltaic solar cell (PVSC) converts solar radiation into electrical energy using a photosensitive material that absorbs photons when exposed to solar radiation creating photo-generated electron-hole pairs, which are subsequently separated and collected at the opposite contacts preferably before recombining. Most popular examples of solar cells including p-n junctions, donor-acceptor pairs, Schottky barriers and semiconductor-liquid interfaces have all been experimentally explored for implementing NC-based devices (Pearce, **2002**). For example, a device consisting of p and n-type conducting layers of NC solid sandwiched between transparent conducting oxide and metal electrodes are essentially equivalent of p-n junction configuration as mentioned above.

The first generation of mono and polycrystalline silicon PV devices are, till date, the market leaders while sharing only 15% of the world market with second generation devices of thin film SCs involving materials like cadmium telluride (CdTe), copper indium gallium selenide (CIGS) along with amorphous silicon (Zhou, et al, **2011**). Although, the third generation devices like organic photovoltaic (OPV) and dye sensitized solar cells (DSSCs) are emerging fast, the over all technology developments are expected to improve the performance of the first and second generation SC devices as well in the coming years (Zhou, et al, **2011**). The upcoming third generation devices are still under development and it will take some time to mature before they are compared with the devices of first two-generations in actual field of applications. Silicon SCs attained the best value power conversion efficiency (PCEs) of 25.0, 20.4 and 10.1 % for single crystal, polycrystalline and amorphous silicon devices, respectively, whereas, 20.3 and 16.7% efficiencies were reported for CIGS and CdTe thin film devices, respectively (Zhou, et al, **2011**). The best value PCEs for OPV and DSSC are 8.5 and 11.2 % respectively, whereas the modules involving single crystal, polycrystalline silicon; CIGS and CdTe thin films; DSSC and OPV devices performed with PCEs of 22.9, 17.55, 15.7, 10.9, 5.38 and 3.86 %, respectively (Zhou, et al, **2011**). The relative difference in PCE achieved in single cell and the respective module indicates the level of technology maturity. A narrow margin, in this context, indicates that the fabrication technologies of first two-generation PV devices are getting matured, whereas there is still scope of further improvement in case of third generation PVSC devices.

Keeping in view the possible objective of meeting the ever-growing global needs of renewable energies, the future development of PVSC devices would primarily be guided by how high efficiency would be realized at the lowest cost of production. In this context, semiconductor NCs are emerging prominently for such applications mainly due to their superior combination of tunable optical and electronic properties along with the proven technology of low cost solution-grown material synthesis and device fabrications. NC-PVSC devices, once developed sufficiently, would probably be the most desired kind that would make a significant technological impact in times to come.

Organic SCs using conjugated polymers or polymer-fullerene composites are currently being explored as low cost alternatives to conventional Si PVSCs, where the major fabrication involves printing techniques (Hoth, et al, **2007**) with the choice of using even flexible substrates (Yu, et al, 1**995**; Brabec, **2004**) as additional feature. These solar cells, with single active layer and tandem configuration with different band gaps, demonstrated efficiency of 5 and 7% respectively (Ma, et al, **2005**; Reyes-Reyes, et al, **2005**; Kim[1], et al, **2007**) with the outdoor cell life > 1 year (Hauch, et al, **2008**). The main factor that adversely affected the performance of such devices was chemical and photochemical stability of the polymers and contact layers besides poor electronic properties of organic materials involved. Typically the used polymers had the hole mobilities ~0.1 cm^2/Vs, while the electron mobilities were relatively much poorer $<10^{-4}$ cm^2 /Vs.

Organic-inorganic hybrid PVSC devices have also been explored using a simple configuration involving a photoactive layer sandwiched between two contact electrodes having work functions appropriate for efficient collection of photo generated electrons and holes. A high conductivity transparent indium tin oxide (ITO) under layer followed by thin films of Al, LiF/Al or Ca/Al on the top served as contact electrodes (Zhou, et al, **2011**). The photoactive films consisting of a conjugated polymer and semiconducting NCs in form of a bilayer or bulk hetero-junction configuration were also used. The bulk hetero-junction structures were prepared by blending the donor and acceptor materials together (Zhou, et al, **2011**). The photon absorption in organic semiconductors generated strongly bound excitons having 10-20 nm diffusion lengths in conjugated polymers (Zhou, et al, **2011**). For efficient collection of electrons and holes generated from the dissociations of these excitons, the donor-acceptor interface, where charge transfers took place should preferably be within the diffusion lengths as mentioned above. This is why the bulk-hetero-junction structure was so chosen that the donor and acceptor materials were intimately mixed together such that the interfacial area was enhanced while the excitons reached the interface much faster. Electrons and holes generated from the excitons travel via polymer and NCs in percolation pathways towards the respective electrodes. An inter-digitated donor-acceptor configuration was found as a better structure for efficient exciton dissociation and charge carrier transports (Zhou, et al, **2011**).

The conjugated polymers behave as electron donors and semiconducting NCs with different morphologies such as spherical quantum dots (QDs), nanorods (NRs) and tetrapods (TPs) as well as the C_{60} derivative PCBM as electron acceptor materials. Matching of the energy levels of donor and acceptor materials is necessary for efficient charge separation at the interface. A number of rigorous experimental methods were therefore employed to verify these energy levels matching for efficient separation of charge carriers.

It is well known that, in case, one electron-hole pair is created and separated before recombining for every photon absorbed, the ultimate ICPE is 100%. However, under practical conditions, the fate of photo-generated carriers is decided by the product of $\mu\tau$, where μ and τ are the carrier mobility and the lifetime, respectively, determined from the material and device structure used and this product has to be as large as possible to ensure carrier separation before their recombination. This underlying principle is employed in selecting the right kind of acceptor and donor materials for hybrid PV devices as mentioned above.

Considering the availability of 0.5 to 3.5 eV photons in the solar radiation, it is not necessary to bother about those with energies lower than the semiconductor band gap as they are not absorbed, while those with energies above the band gap create hot electrons and holes with kinetic energies equal to the difference between the photon energy and the band gap (Nozic, et al, **2010**). A major factor that limits the ideal conversion efficiency in single band gap cells to 31% is that the absorbed photon energy above the semiconductor band gap is consumed as heat through electron-phonon interactions while the carriers relax to their respective band edges - conduction band bottom for the electrons and valence top for the holes (Nozic, et al, **2010**). The simplest approach that is immediately conceived of for improving the efficiency is to use a stack of multiple p-n junctions, where the band gaps map the entire solar spectrum. This, in other words, means that the higher energy photons are absorbed in the higher band gap and the lower energy ones in the lower band gap semiconductors, thus reducing the overall heat loss due to carrier relaxation via phonon emissions. Ideally, in an infinite stack of band gaps perfectly matching to the entire solar spectrum, the ultimate conversion efficiency at one sun intensity would add up to about 66%.

It is, thus, quite logical to expect that the conversion efficiency of PVSCs would definitely improve by reducing the losses due to thermal relaxation of photo-generated hot electrons and holes by collecting them before they relax to the band edges via phonon emission (Miller, et al, **1995**). In this context, there are two approaches of employing photo-generated hot carriers in enhancing either photo-voltage or photocurrent for improving the photon conversion efficiency. For instance, for enhanced photo-voltage (V_{OC}), the photo-generated carriers must be extracted before they cool down by loosing their energies and for this to happen, the processes of photo-generated carrier separation, transport, and interfacial transfer across the metal semiconductor contacts must be faster as compared to the rate of carrier cooling. Whereas, for increased photocurrent (J_{SC}), the energetic hot carriers should produce a second or more electron-hole pairs through impact ionization. High-energy electrons and holes not only cool at different rates because of differing effective masses but also depend upon the density of the photo-generated hot carriers or in other words the absorbed light intensity.

Theoretically, it is known that in NCs the cooling via Auger process is faster than that due to phonon scatterings. Therefore a hot electron can give its excess kinetic energy to a thermalized hole via an Auger process and subsequently the hole can cool quickly because of its higher effective mass and more closely spaced energy states. However, in case the hole is removed from the QD core by a fast hole trap at the surface, the Auger process is blocked and the phonon bottleneck effect can occur, thus leading to slow electron cooling. This effect was first observed in CdSe QDs (Shim and Guyot-Sionnest, **2000**; Blackburn, et al, **2003**) followed by that in InP NCs, where a fast hole trapping species like Na biphenyl was found to slow the electron cooling to about 3-4 ps (Blackburn, et al, **2003**; Ellingson, et al, **2003**). This compared to the electron cooling time of 0.3 ps for passivated InP NCs without a hole-trap and the holes in the NC core underwent an Auger recombination with the electrons (Blackburn, et al, **2003**; Ellingson, et al, **2003**). The two pathways for enhancing the conversion efficiency, mentioned above, are possible to realize in three different NC based solar cell configurations. However, these potentially high-efficiency configurations are merely based on theoretical calculations and there are no experimental results yet that demonstrates actual enhanced power conversion efficiency in NC-SCs over present-day solar cells.

The simplest NC-configuration that is immediately available for its use in preparing PVSCs could be an ordered 3-D superlattice with sufficiently small inter-dot spacing such that strong electronic coupling is there to allow long-range electron transport. In case, monodisperse NCs are arranged in a superlattice, there may be a miniband formed therein. Such a moderately delocalized but still quantized states could be expected to produce multiple exciton generation. Also, the slower carrier cooling and delocalized electrons could permit the transport and collection of hot carriers to produce a higher photo-voltage in a photovoltaic or photo-electrochemical cell. Significant progress has been made, in recent past, in preparing arrays of both colloidal (Murray, et al, 2000) and epitaxial (Mukai, et al, **1999**) IV-VI, II-VI, and III-V NCs. The former two systems were fabricated using the process of evaporation, crystallization or self-assembly of colloidal NC solutions containing monodisperse NCs. Although the process can lead to close-packed NCs films, they also exhibit some degree of disorder. Concerning the III-V materials, arrays of epitaxial NCs have also been formed by successive deposition of epitaxial NC layers; after the first layer of epitaxial NCs is formed; successive layers tend to form with the NCs in each layer aligned on top of each other (Mukai, et al, **1999**; Nakata, et al, **1999**). Theoretical and experimental studies of the properties of NC arrays are currently under way. Major issues are the nature of the electronic states as a function of inter-dot distance, dispersions, orientation and shapes, surface states, surface structure, surface passivation and chemistry. Transport properties of charge carriers in NCs arrays are of critical importance, and they are currently under very active investigations.

CdSe based NCs were the first employed in PVSC devices, exhibiting the highest PCEs compared to the devices using NCs from other materials. These CdSe NCs absorb solar radiations from 300 to 650 nm and are good electron acceptors in association with the conjugated polymers besides having well established solution grown synthesis. Blending of about 90% by weight of CdSe NCs resulted in external quantum efficiencies (EQE) of 10%, clearly indicating efficient exciton dissociation at the interface. However, the low value of PCE ~ 0.1% was attributed to an inefficient electron transport between the individual nanocrystals (Zhou, et al, **2011**).

Semiconducting NCs are currently being examined as promising sensitizers as they allow the absorption of radiation to extend into the red and near-IR regions of solar radiation. Various combinations of NCs and conductive polymers are thus being evolved for bulk hetero-junction donor-acceptor PVSCs. This method uses thorough blending of p and n-type materials to achieve efficient charge separation at the interfaces, followed by charge transport through the percolation pathways. Since electron-hole pairs are generated in close proximity of the interfaces and are promptly separated into two groups, this scheme is especially applicable in case of the short diffusion length of excitons observed in organic semiconductors. A typical example of donor-acceptor combination of P3HT (Heeger, **2001**) and soluble fullerene derivative PCBM layers (Sariciftci, **1995**; Yu, et al, **1995**; Thompson and Jean, **2008**; Hwang, et al, **2008**) blended together. The existence of interpenetrating networks of columnar structures observed in efficient P3HT/PCBM devices (Ma, et al, **2005**; Moon, et al, **2009**) indicated the critical importance of nanoscale morphology control throughout the blend adequately. Improved photon absorption, well controlled solution grown synthesis of NCs and fine-tuning their electronic structures - all strongly motivate towards the integration of NCs into bulk heterojunctions PVSC devices. In hybrid solar cells, NCs are introduced as either p or n-type components (Guenes and Sariciftci, **2008**) derived from materials like Si, CdSe, $CuInSe_2$, ZnO, CdS, PbS, PbSe, and HgTe QDs in fabricating prototype SC structures (Talapin, et al, **2010**).

The influence of non-spherical morphologies of NCs on conversion efficiency was also examined in detail after CdSe nanocrystals became available in various forms like rods and tetrapods. For example, PVSCs comprising of P3HT and CdSe NCs and NRs forming donor-acceptor hetero-junctions were developed while trying to improve carrier separation efficiency at P3HT-CdSe interface by partially stripping the original hydrocarbon ligands off the CdSe NC surface and replacing by pyridine molecules (Huynh, et al, **2003**). It was shown that using CdSe NRs achieved higher conversion efficiencies as compared to spherical CdSe QDs due to the smaller number of inter-particle hopping events necessary for electrons to reach the collecting electrode. Under standard simulated illumination, devices employing 7 × 60 nm CdSe rods showed PCE of ~1.7%. However, the inherent tendency of nanorods to align parallel to substrate was not found favorable for efficient collection of the photo-generated electrons. Subsequently, using high boiling point TCB in place of chloro-benzene as solvent for P3HT resulted in a fibrilar morphology that facilitated extended pathways for holes resulting in improved device efficiencies up to 2.6%. Alternately, using CdSe tetrapods (TPs) instead of NRs, suitably blended with poly(2-methoxy-5-(3″,7″-dimethyl-octyloxy)-p-phenylenevinylene) - OC_1C_{10}-PPV resulted in improved electron transport (Sun, et al, **2003**) showing conversion efficiency of 1.8%. The use of hyper-branched CdSe and CdTe NCs prevented the formation of phase-separated domains and aggregates, a well-known problem observed in hybrid solar cells. Furthermore, large hyper-branched NCs (Gur, et al, **2007**) could span the inter-electrode distance, eliminating the need for rigorous control of the blend morphology. This resulted in power conversion efficiencies of ~2.2% that was still lower than expected, presumably due to the limited penetration of polymer chains between densely packed branches of CdSe component. Devices based on pyridine treated CdSe TPs exhibited efficiencies up to 2.8%. Recently, by using the lower band gap polymer PCPDTBT, which can absorb a higher fraction of the solar emission, an efficiency of 3.19% was reported that was up to that time the highest efficiency for colloidal NCs based bulk-hetero-junction hybrid SCs (Zhou, et al, **2011**). The PCEs comparable to the CdSe/P3HT cells were also obtained using ZnO NCs along with P3HT @ $\eta \approx 0.9\%$ (Beek, et al, **2004**; **2006**) or with MDMO-PPV exhibiting $\eta \approx 1.4\%$ (Beek, et al, **2004**).

Narrow gap semiconductor nanocrystals have also been used in preparing hybrid PVSCs to harvest IR part of solar spectrum (Talapin, et al, **2010**). The hybrid PVSCs, reported so far, using HgTe, PbS, and PbSe QDs, showed power conversion efficiencies

<1%, presumably due to inappropriate surface chemistry resulting in traps, insulating surface ligands and partial phase separation of the blended components. The crucial role of surfaces in NC based SCs had to be properly addressed to in future studies. Also, a better understanding of the morphology of the NC-polymer blends and its control were required for affecting more improvements in performance (Soreni-Harari, et al, **2008**).

Relatively poor stability of conductive polymers arising due to oxidation and photo-degradation is not only the problem faced by polymer based PVSC devices but it is expected to affect the solar cells utilizing NC-polymer blends as well. Alternatively, fabricating all-inorganic PV cells using colloidal NCs avoiding unstable organic compounds while still retaining the advantages of solution-based device fabrication seems to be a better option. In this context, CdSe and CdTe NCs were used as donor-acceptor combination with a band alignment similar to the one present at CdSe/P3HT interface. A PVSC structure was fabricated by spin coating of pyridine coated CdTe and CdSe NRs wherein the photo generated electrons and holes transferred to CdSe and CdTe phases respectively (Gur, et al, **2005**). The difference in work functions of ITO and Al electrodes provided additional driving force for charge separation. Sintering of the NRs significantly improved the carrier mobility and the device performance resulting in PCE of 3% and impressive stability in air (Gur, et al, **2005**). In a similar device configuration, with Cu_2S NCs and CdS NRs, a PCE of 1.6% was reported (Wu, et al, **2008**). Unlike hybrid PVSCs, blending of CdTe and CdSe NRs into a single layer showed much inferior performance, presumably because of shortcuts and insufficient driving force for carrier separation.

Bulk chalcopyrite compounds, in general (Miller, et al, **1981**), and copper indium-gallium selenide (CIGS), in particular, are found to be efficient PV materials wherein CIGS thin film PV devices demonstrated PCE of □□□□ being useful for numerous commercial applications (Ramanathan, et al, **2003**; Repins, et al, **2008**). Additionally, CIGS devices are free of toxic elements. However, stoichiometric thin film deposition of CIGS material involves elaborate techniques for controlling the compositions of the quaternary phases involving evaporation of In, Cu and Ga layers followed by selenization using Se vapors or H_2Se gas that are very toxic in nature. In order to replace the deposition of conventional CIGS thin films by solution based synthesis, using hydrazine-based CIGS precursor demonstrated promising solar conversion efficiencies of 10.3% (Mitzi, et al, **2008**). Consequently, several attempts were made using colloidal synthesis of $CuInS_2$ (Czekelius, et al, **1999**; Castro, et al, **2003**; **2004**; Choi, et al, **2006**; Tang, et al, **2008**), $CuInSe_2$ (Castro, et al, **2003**; Guo, et al, **2008**; Tang[4], et al, **2008)** and CIGS NCs (Tang[4], et al, **2008**; Panthani, et al, **2008**; Allen, et al, **2008**) for fabricating prototype SCs having configuration of glass/Mo/(p-type I-III-VI_2 semiconductor)/ CdS/ZnO/ITO. PCEs in the range of 3% were reported in case of sintered $CuInSe_2$ NCs (Guo[1], et al, **2008**).

Schottky type PVSC devices, using solution deposited PbS and PbSe NCs thin films on ITO-coated glass followed by top metal contact of Mg, Al, Ca/Al, were also developed subsequently. In a layer-by-layer deposition of NCs films, it involved either cross-linking of each NC monolayer with short-chain dithiol molecules or spin-casting of the film followed by a dip into a solution of butyl-amine, ethanedithiol or benzenedithiol to exchange original bulky surface ligands with smaller molecules. PCE of PbSe-based SC was 1.1% (Koleilat, et al, **2008**) and 2.1% (Luther[2], et al, **2008** whereas PbS NCs based devices showed efficiencies of 1.8% (Johnston, et al, **2008**).

In a dye-sensitized solar cell (DSSC) (Grätzel, **2003**), there is a molecularly engineered light harvesting dye-sensitized photoanode along with counter electrode and electrolyte containing a redox couple. The photoanode is a porous nanocrystalline film consisting of a wide band gap metal oxide like TiO_2, ZnO_2 or SnO_2. The simplest electrolyte contains the iodide/triiodide redox couple in some organic solvents. The counter electrode is coated with Pt-catalyst on a conducting glass substrate that has indium tin oxide (ITO) or fluorine doped tin oxide (FTO). When the dye molecules absorb solar radiation, electrons are excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the dye molecules. The electrons from the excited state of the dye are injected into the photoanode, made of a nanoporous semiconductor and electrons from the redox couple of the electrolyte subsequently regenerate the oxidized dye molecules. The injected electrons diffuse through the nanoporous film before they arrive at the contact where they are released to the external circuit to finally return to the counter electrode (CE) where they are readily available for regenerating the oxidized redox species. In this way, the device generates electricity from light without any permanent chemical transformation.

Since the first successful implementation of DSSCs, reported in 1991, a number of significant improvements have been made. However, for last several years, the PCE of DSSCs has stuck somewhere around 11% (Bisquert, **2011**). Still, the DSSCs hold considerable promise for a low cost PVSC technology due to cost effective raw materials and simpler processing techniques appropriate for automated manufacturing (Bisquert, **2011**). In order to take care of the unavoidable additional losses incurred during scale-up of smaller area cells to larger size modules, higher levels of PCEs are necessary along with rugged device packaging to ensure a longer life cycle. Despite facing some sort of stagnation in PCEs of DSSCs, the recent investigations made while continuously searching for better alternatives, do indicate towards brighter prospects. In this context, it is rather useful to have a quick look into the salient points of these developments that are reported in connection with improving different components of DSSCs including hole transport layer, light sensitizer, photoanode and counter electrode.

Referring to the basic configuration of a conventional DSSC, it is natural to anticipate that for higher efficiency PVSC devices, faster electron injection and more efficient regeneration of dye and redox couple are essential. Taking the overall reaction kinetics into consideration, it is clearly noted that there is a competition between the forward processes including electron injection into the semiconductor, oxidized dye and redox couple regenerations and the backward process involving recombination of the photogenerated electrons. The recombination of photogenerated electrons also involve oxidized dye molecules or electron acceptors in the electrolyte present there in a DSSC while the photo injected electrons traverse through a relatively longer path involving TiO_2 layer surrounded by dye and electrolyte molecules. Though, these recombination processes are slower than the forward process mentioned above, but eventually, the competition between the forward and backward processes affects the overall efficiency of the device. For instance, careful considerations of these forward and backward processes in designing liquid electrolyte-based DSSCs could make these devices cross the efficiency over 11%.

The availability of an appropriate redox couple as HTL plays a crucial role in efficient functioning of a DSSC by facilitating the hole transfers from the dye molecules towards the counter electrode. In most of the devices, developed so far, an electrolyte containing the I^-/I_3^- redox couple has been quite frequently used. Devices using this electrolyte exhibited higher PCEs and improved reliability (Wang, et al, **2005**). Besides having numerous advantages like low cost raw materials, simple manufacturing process, lightweight and eco-friendly technology, the liquid electrolyte-based devices have not yet been able to gain the industrial acceptance due to the major concerns of solvent leakage and corrosion. There is yet another limitation that these redox couples possess a lower redox potential because of which the V_{OC} does not go above 0.7–0.8 V resulting in inefficient dye-regeneration as it involves formation of I_2^- intermediate radicals. In addition, Iodide-containing liquid electrolytes corrode metal thin films like Au, Ag and Cu and thus restricting their use in preparing interconnects for fabricating larger size modules besides being sensitive to certain part of solar radiation spectrum. In order to get rid of these limitations, the development of stable, noncorrosive redox couples with higher redox potentials than I^-/I_3^- redox is highly desirable.

In this context, a number of alternative redox couples were examined, including halogenides (Wang, et al, **2005**; Teng, et al, **2009**) or pseudo halogenides (Oskam, et al, **2001**; Wang^2, et al, **2004**), organic radicals (Zhang, et al, **2008**), thiols (Wang, et al, **2010**) and inorganic (O'Regan, et al, **2005**) as well as p-type organic conductors (Wang, et al, **2010**). However, all of these redox couples exhibited inferior PCEs compared to those with the I^-/I_3^- redox couple, especially under full sunlight illumination (Nusbaumer, et al, **2003**; Wang, et al, **2010**).

A redox couple comprising of cobalt (II)-bis [2,6-bis (1″-butylbenzimidazol-2″-yl) pyridine] demonstrated a significant promise (Nusbaumer, et al, **2001**) rivaling the performance of the tri-iodide/iodide couple that was exclusively used in DSSCs. Such polypyridine based Co-complexes were found suitable for replacing the I_3^-/I^- redox system because of their low visible light absorption, higher redox potentials and the reduced corrosiveness towards metallic conductors but otherwise exhibited lower PCEs possibly due to the slow mass transport and faster back reaction of photo-injected electrons with the oxidized redox species coupled with the slow regeneration of the Co (II) species at the cathode. However, the experimental realization of an improved PCE of 6.7% using a D-π-A organic sensitizer named D35 in conjunction with the cobalt (III/II) tris-bipyridyl complex, $[Co\ (III)\ (bpy)_3](PF_6)_3/\ [Co(II)(bpy)_3](PF_6)_2$ couple triggered a renewed interest in this direction (Yum, et al, **2012**). The tunable redox properties of Co-complexes by appropriate choice of donor/acceptor substituents offered attractive alternate to the traditional I_3^-/I^- redox shuttle used in DSSCs. V_{OC} in excess of 1V was observed in these Co-complex based DSSCs. However, D35 dye harvested sunlight only below 620 nm, limiting J_{SC} to ~ 10 mA/cm^2. The spectral response of D35 dye was subsequently extended into the red region by incorporating a CPDT bridging unit in the D-π-A structure. This novel dye Y123, exhibited a J_{SC} in excess of 15 mA/cm^2 under full sunlight with PCE of up to 9.6% with the $[CoII(bpy)](B(CN))/[CoIII\text{-}(bpy)_3](B(CN)_4)_3$ redox couple (Tsao, et al, **2011**). Later on, a complex with tridendate ligands $[Co(bpy\text{-}pz)_2]^{3+/2+}(PF_6)_{3/2}$ as redox mediator along with Y123, adsorbed on TiO_2, resulted in PCE of more than 10% at standard illumination. This result indicated that the molecularly engineered cobalt redox shuttle was a legitimate alternative to the commonly used I_3^-/I^- redox shuttle (Yum, et al, **2012**).

While conducting the detailed study of hole-transport in spiro-OMeTAD (Fabregat-Santiago, et al, **2009**) in a solid-state DSSC, it was noted that the electron transport in TiO_2 was almost identical in both types of devices namely - high-performance DSSCs with liquid electrolytes and ionic liquids (ILs) based devices. Precision measurements were carried out to estimate the transport and recombination parameters under different operating conditions in the dark, where recombination was found to be two orders of magnitude higher in spiro-OMeTAD based SC and this turned out to be the main cause of relatively lower PCEs (Fabregat-Santiago, et al, **2009**). The anticipated enhancement in V_{OC} due to a lower Fermi level of holes was offset by the excessive recombination losses. Under low potentials, the charge carrier transport was mainly due to the electron transport in the TiO_2, but at higher potentials spiro-OMeTAD transport related resistance took over in reducing the fill factor and PCE of the devices. Thus, the enhanced recombination was noted as the major cause of the lower efficiency of these SCs.

In this search for a suitable HTL, another organic conductor named P3HT was examined by comparing it with the performance of spiro-OMeTAD with two dyes namely: D35 and M3 used in fabricating similar devices (Yang, et al, **2012**).

Absorbed photon to current conversion efficiency close to unity was noted in case of spiro-OMeTAD based devices resulting in PCE of 4.7% and 4.9% with D35 and M3, respectively, whereas in case of P3HT rather poorer efficiencies of 3.2% and 0.5% were exhibited for the corresponding combinations. Photo-induced absorption measurements indicated incomplete regeneration of the dyes and the polymer infiltration in case of P3HT, while spiro-OMeTAD regenerated the dyes very efficiently. The dye hole conduction thus appeared important (Yang, et al, **2012**) in optimizing the energy conversion in such hybrid TiO_2/dye/polymer systems.

Solid state DSSCs utilizing conducting polymer (CP) hole transport layer may offer significant technological advantages over the commonly used I^-/I_3^- redox couple used in organic or ionic liquid electrolyte solutions (Mozer, et al, **2010**). The CP plays the important role of regenerating dye-cations produced by the injection of electrons from photo-excited dyes to TiO_2 and transporting the positive charge to the cathode. Therein, it was noted that the kinetics of dye regeneration in a 3% efficient solid state DSSCs using PEDOT was actually orders of magnitude slower than either the I^-/I_2^- redox couple or the frequently used spiro-OMeOTAD limiting J_{SC} of these devices, which possibly originated from the low dye to CP ratio.

In this context, more number of alternative redox couples were examined, including halogenides (Wang, et al, **2005**; Teng, et al, **2009**) or pseudo halogenides (Oskam, et al, **2001**; Wang, et al, **2004**), organic radicals (Zhang, et al, **2008**), thiols (Wang, et al, **2010**), and inorganic (O'Regan, et al, **2005**) as well as organic (Wang, et al, **2010**) p-type conductors. However, all of these redox couples exhibit relatively lower PCEs compared to the I^-/I_3^- redox couple, especially under full sunlight (Nusbaumer, et al, **2003**; Wang, et al, **2010**). A similar behavior of PCE lower than 5% was noted in case of cobalt polypyridine complexes, despite extensive investigations carried out in the last decade (Nusbaumer, et al, **2001**; Sapp, et al, **2002**; Nusbaumer, et al, **2003**; Cazzanti, et al, **2006**) until a donor-π-acceptor (D-π-A) sensitizer, coded D35, was introduced along with a cobalt (II/III) tris-bipyridyl redox couple (Feldt, et al, **2010**) that enhanced the PCE to 6.7%. However, the restricted spectral response of D35 below 620 nm was suitably modified by introducing CPDT bridging unit in the D-π-A structure, which enhanced the spectral response of the novel dye Y123, such that it enhanced J_{SC} over 40% above that in case of D35 (Li, et al, **2010**). This remarkable modification pushed J_{SC} to almost 15 mA/cm^2 under full sunlight resulting in PCE of 9.6%. The photo anode and CEs of these devices had a combination of 2μm thin nanoporous TiO_2 film covered by a 5μm thick light-scattering layer consisting of TiO particles and platinized FTO glass respectively. The TiO_2 film was immersed in Y123 dye solution in a tert-butanol/acetonitrile mixture. The Co-electrolyte contained 0.22M $[Co(II)\text{-}(bpy)_3](B(CN)_4)_2$, 0.05 M $[Co(III)(bpy)_3](B(CN)_4)_3$, 0.1 M $LiClO_4$, and 0.2 M tert-butylpyridine in acetonitrile.

Replacing the existing redox couple electrolyte with a nonvolatile ionic demonstrated power conversion efficiency of 7%. Using eutectic imidazolium salts as another replacement improved the efficiency to 8.2%. Search for better replacement of liquid redox junction and TiO_2 light harvester is still on by considering a number of emerging promising materials.

It is clear from the above description that a right kind of dye sensitizer is essential for absorbing sufficient solar radiation in DSSCs followed by its conversion into photocurrent. The primary role of a sensitizer is not only to harvest light but also inject photo-generated electrons into the semiconductor. Ideally a dye sensitizer should have a number of characteristic features for its successful use in DSSCs. First of all, it should cover a wide range of the solar spectrum for high photocurrent. Secondly, it must have attached radicals like carboxylate or phosphonate to graft itself easily on the TiO_2 surface and to inject electrons from the excited dye to the TiO_2 conduction band. In addition, a dye with high molar extinction coefficient is advantageous to absorb more light with a thinner TiO_2 film, particularly in the solid state DSSC device. Finally, it should sustain its photoactive property for at least 20 years of operation under illumination.

The dye sensitizers that have already been explored can be divided into inorganic and organic categories. Ruthenium and osmium-complex dyes are the representative inorganic dyes that have been investigated and improved considerably. Recently, NCs have also been examined as light absorbers in DSSCs because of their unique opto-electronic properties. A large number of purely organic dyes with good PV performance were reported as they were synthesized easily with tunable properties and were low cost compared to the ruthenium-based sensitizers.

A higher extinction coefficient dye is more relevant in case of solid state DSSC as it can enhance J_{SC} leading to higher overall efficiency with small amount of dye. Metal-free organic dyes have major advantages over Ru-based sensitizers especially in terms of their higher molar extinction coefficients that are attractive for thin film and solid-state DSSC applications; containing no precious metal such as Ru to reduce the overall cost of device production and the ease in design with tunable features. For these reasons, organic dyes are being considered as viable alternatives to the conventional Ru-based sensitizers in DSSCs.

Most of the organic dyes possess a donor-π-bridge-acceptor (D-π-A) structure, which is easy to design for extending the absorption spectra, adjusting HOMO and LUMO levels to complete the intra molecular charge separation. Coumarin, indoline, and triarylamine moieties, which are electron-rich arylamines, are representatively employed to the donor groups. The most popular moieties for *π-bridge* typically contain thiophene-based radicals like oligothiophene, thienothiophene and EDOT because of their excellent charge separation properties. For the acceptor group, a cyanonacrylic acid containing carboxylic acid is most often used and it plays a role as an anchoring group.

Among the diverse number of donor groups, a large number of triarylamine dyes were designed showing good power conversion efficiencies in DSSCs because of their prominent electron donating and hole-transport properties. To improve dye performance, a number of research groups have substituted triarylamine donor groups like dimethylfluorenylamino electron donor, dendronized triarylamine and methoxy triphenylamnine. The tailored triarylamine electron donor can increase electron density of the donor moiety as well as enhance stability of DSSCs. Another way to increase efficiency in the D-π-A structure is by expanding the *π-conjugation* of the bridge between the donor and acceptor by introducing more conjugation units such as thienothiophene6, bithiophene, EDOT7 and carbon-carbon double bonds, which increase molar extinction coefficient and a bathochromic shift in the absorption spectra.

The high molar extinction coefficients, exhibited by D-π-A dyes, are especially desirable for thin TiO_2 films in solid state DSSCs. For instance, an indoline dye D1028 yields over 90 % absorption over a broad spectral range when sensitizing merely 1.4 μm TiO_2 films as compared 10 μm TiO_2 required in case of ruthenium. Therefore, sensitizers with high extinction coefficient are essential to enhance photovoltaic performance of the solid state DSC device.

Although organic dyes have many advantages as sensitizers in DSSCs, the efficiency of devices prepared with them has been limited mainly due to two factors: first, increasing the size of the conjugated system chain in organic dyes causes dye aggregation or $\pi - \pi$ stacking on the TiO_2 surface due to their planar structures. Dye aggregation results in an unwanted back electron transfer causing reduction in cell performance. Second, the sensitizers, reported so far, to result in higher efficiencies mostly have absorption bands below 550nm, indicating that photons in the longer wavelength region are not absorbed efficiently. They should, however, harvest incident light in a broad spectral range to obtain higher J_{SC}. Some organic dyes show panchromatic response, but the obtained J_{SC} and efficiency are not as high as expected due to their low LUMOs, which reduces injection efficiency. New highly absorbing near infrared dyes need to be designed to improve device performance.

Carbazole dyes named as TC301 and TC306 along with Br^-/Br_3^- redox couple in dried CH_3CN solution demonstrated V_{OC} and PCE combination of 1.56V/3.68% and 0.939V/5.22%, respectively (Teng, et al, **2009**). These dyes, having more positive HOMO than Br^-/Br_3^- redox couple regenerated more efficiently. DSSC devices fabricated using I^-/I_3^- redox couples demonstrated a combination of 0.696V/2.36% and 0.621V/4.1%, which compared very well with the corresponding combinations mentioned above.

A solvent free ionic liquid (IL) electrolyte comprising of $SeCN^-/(SeCN)_3^-$ redox couple was noted to outperform the well-known I^-/I_3^- system with the associated PCE in the range of 7.5-8.3% under standard illumination (Wang^2, et al, **2004**).

Semiconductor NCs are also being examined as substitute for Ru-dyes in DSSCs, where low cost, solution processing, and size-tunable energy levels make them very attractive sensitizer besides other advantages including sharp absorption onset, large absorption coefficients and robustness of inorganic materials. In NC-sensitized solar cells (NC-SSC), their role is to absorb light and inject photo-generated electrons into nanostructured TiO_2, while the holes are scavenged and transported to the opposite electrode by the redox couple. Such electron transfer is quite efficient and fast at the TiO_2/CdSe interface. Various semiconductor NCs including CdS, InP, InAs, PbS, and Bi_2S_3 were examined as sensitizers and most of them were grown directly at the surface of TiO_2 electrode with poor control over the materials properties and surface chemistry. NC-SSCs gave relatively low efficiencies: for example, some of the best SCs sensitized by CdSe NCs combined with $Co^{(II)}/Co^{(III)}$ redox system demonstrated efficiency around ~1% only. However, it is anticipated that using well-engineered colloidal NCs of CdTe, $CuInSe_2$, PbS, PbSe or InAs would improve the performance as well as its commercial prospects.

It is worth having a look at the developments taking place in the area of using semiconducting NCs and their combinations with other nanostructured materials for improving the conversion efficiency of PVSCs while offering the roles of light harvesting and charge carrier collecting layers. From the recent results reported in the published literature it is clear that there are enough possibilities to improve the efficiency of future PVSCs in a significant manner.

Using a layer-by-layer deposition technique, PbS NCs /TiO_2 hetero-junction solar cells were fabricated by depositing NCs on a 500 nm thick TiO_2 film wherein these PbS NCs acted as photosensitizer as well as hole conducting layer and demonstrated an efficiency of 3.5% (Etgar, et al, **2012**). High-performance PVSCs based on P3HT : CdSe NC blends were prepared through post-deposition ligand exchange by *n*-butanethiol (*n*-BT) showing high PCE of 3.09% (Fu, et al, **2012**).

The concerted efforts made over a period of time in the area of improving the PCEs of all solid state DSSCs has started showing the results now including Sb_2S_3 sensitized mesoscopic TiO_2 films based cells having PCE of 6.3% (Chang, et al, **2010**) while the dye sensitized solid state heterojunctions demonstrated 7.2% (Burschka, et al, **2011**). V_{OC}=1.02 V was measured in organic dye-TiO_2 film along with spiro-MeOTAD (Jang, et al, **2011**). PCE=8.5% was reported for devices employing combination of N719 dye with the p-type semiconductor $CsSnI_3$ (Chung, et al, **2012**). $(CH_3NH_3)PbI_3$ NCs when used with iodide/tri-iodide redox electrolyte pushed PEC up to 6.54% (Kojima, et al, **2009**; Im, et al, **2011**). Because the $(CH_3NH_3)PbI_3$ NCs exhibited an order of magnitude higher absorption coefficient than the conventional N719 dye, much thinner TiO_2 layers were required compared to that in liquid junction devices. In another very recent report (Kim, et al, **2012**), using $(CH_3NH_3)PbI_3$ NCs as a light absorber and spiro-MeOTAD as a hole-transporting layer, a conversion efficiency of 9.7% was obtained along with excellent long term stability.

In this context, attempts were also made to explore using nanostructured species of different morphologies in improving the performance of light harvesting for PVSC applications as highlighted below.

While comparing the light harvesting efficacies of different morphologies of nanostructured species, CdSe NRs were deposited by electrophoresis onto mesoporous TiO_2 electrodes and compared with NCs (Salant, et al, **2012**). A rather high efficiency of 2.7% was observed in case NR sensitized solar cell, being a case of ex-situ synthesized NC sensitizers. The NR based PVSCs exhibited a red shift of the electron injection onset and charge recombination was significantly suppressed compared to NC based sensitizers. The improved performance was assigned to the elongated shape that allowed the build-up of a dipole moment along the rod leading to a downward shift of the TiO_2 energy bands relative to the NRs causing improved charge injection (Salant, et al, **2012**).

Graphene films have been explored to fortify light harvesting by studying the processes of electron and energy transfers from photo-excited NCs to graphene oxide and reduced graphene oxide and the excited state lifetimes were estimated as a function of degree of oxidation and charging. Incorporating more of graphene oxide in colloidal CdSe NC films deposited on conducting glass electrodes enhanced the charge separation and electron conduction through the NC film, thus demonstrating three-dimensional sensitization (Lightcap and Kamat, **2012**).

The phenomena of carrier multiplication or multiple exciton generation (MEG) in solar cell, involving generation of multiple electron-hole pairs from the absorption of a single photon (Nozic, **2008**; Sukhovatkin, et al, **2009**) has been known since early 1950s but only with very low efficiency (Zhang, et al, **2012**). High efficiency MEG could be demonstrated in semiconductor NCs for the first time in 2004 (Schaller and Klimo, **2004**). Thereafter, the continued efforts were made to investigate about the occurrence of MEGs in a number of semiconductor NCs including PbSe, PbS (Ellingson, et al, **2005**), PbTe (Murphy, et al, **2006**), CdS, CdSe (Schaller, et al, **2006**), InAs (Pijpers, et al, **2007**), and InP along with the confirmation of strong presence of carrier multiplication in Si NCs (Beard, et al, **2007**) in the range of 0.5-3.5 eV of solar spectrum.

It is common in most of the semiconducting materials that an energetic photon having energy in excess of its band gap generates only a single exciton while the excess energy is lost in generating phonons. In case, under special circumstances a high-energy photon is somehow made to generate multiple excitons, the energy conversion efficiency of nanocrystal based solar cells would certainly be improved significantly though harvesting the energy would still be poor because of the short lifetimes of the multiple-excitons (Nozic, **2002**). The quantum mechanical origin of MEG is still not properly resolved suggesting the most plausible explanations to be the impact ionization (Timmerman, et al, **2008**).

Contrary to a standard solar cell, where it is ensured that the photo-generated carriers are collected well before they recombine, a hot carrier SC must collect them before these carriers cool and this is possible in case these carriers either traverse the cell very quickly or their cooling is alternatively slowed down considerably. For the hot carriers to be effective, they must be collected from the absorber over a very narrow energy range by using some special contacts (Conibeer, et al, **2008**). The limiting efficiency of this approach can reach 86.8% - the same as an infinite tandem cell stack. However, in order to achieve this limiting efficiency, carrier cooling must be reduced sufficiently or radiative recombination be accelerated significantly, the latter being faster than the former (Green, **2002**).

Despite showing efficiency benefits clearly on the basis of theoretical considerations, no practical device has been developed so far (Zhang, et al, **2012**), partly because of the difficulty of a suitable absorber material (Hirst, et al, **2011**). Developing a hot carrier absorber material, which exhibits sufficiently slow carrier cooling to maintain a hot carrier population under realistic levels of solar concentration, is a key challenge (Zhang, et al, **2012**). In this context, a NC-superlattice may be explored for their possible application (Patterson, et al, **2010**). For example, In-GaAs/GaAsP was proposed as a suitable absorber material and the GaAs surface buffer layer was reduced in thickness to maximize photon absorption in the well region. An enhanced hot carrier effect was observed in the optimized structures (Hirst, et al, **2012**). Besides, the hot carrier solar cell with indium nitride (InN) absorber layer, gave highest efficiency of 37.1%, taking into account the realistic transport properties of energy selective contacts (Feng, et al, **2012**). The efficiency of the hot carrier solar cell, with GaSb-based heterostructures as absorber material, was improved significantly compared to a fully thermalized single p-n junction of similar band gap (Le Bris, et al, **2012**).

In a p-i-n type NC-array based PVSCs, the miniband states are expected to slow the carrier relaxation and permit the transport and collection of hot carriers at the respective p and n-contacts to produce a higher photo-potential (Nozic, **2002**; Brown and Wu, **2009**). Due to extremely thin grain boundaries, inter-dot coupling in uniform and ordered silicon NCs thin films were controlled easily. Researchers at Solar Energy Research Institute, Shanghai Jiao-tong University, not only observed two Gaussian-type photocurrent peaks attributed to transitions from a tail band in the nc-Si:H/c-Si heterostructure, but also revealed the unique electronic states of the miniband in the nc-Si:H thin film (Zhang[1], et al, **2007**).

The preliminary results reported in case of hot carrier solar cells show clearly that there are number of issues which are required to be resolved before some useful device structures would be available for verifying the related concepts.

3.5 FETs

During the past two decades, R&D activities into the applications of organic semiconductors have been intensified considerably for their applications in active electronic devices. Despite having electron mobility much lower than that of typical inorganic semiconductors, because of hole mobilities being quite comparable to that of amorphous silicon, organic semiconductors still show considerable promise in low-cost, flexible, lightweight, and environmentally friendly applications.

A variety of organic field effect transistors (OFETs) configurations have been developed with impressive performance improvements while attempting to produce low cost replacement of silicon devices and circuits especially for their non-demanding applications. However, the status of the current development of these devices is practically getting saturated because of two major limitations: including low carrier mobilities at the best in the range of few cm^2/Vs even in case of the optimized structures and the limited success in producing ambipolar organic FETs (Horowitz, **1999**; Zaumseil and Sirringhaus, **2007**). It has also been noted that most of the studied organic materials are reasonably good for p-channel devices but the search for suitable materials for n-type FETs is still continuing for realizing CMOS circuits using solution grown organic and/or inorganic components. In addition, there are other classes of materials for solution grown FETs such as molecular precursors for inorganic semiconductors, carbon nanotubes, nanowires and hybrid organic-inorganic films but none of these materials has been found to exhibit a performance comparable to that of the conventional inorganic semiconductors (Boudjouk, et al, **1994**; Li, et al, **1999**; Kagan, et al, **1999**; Snow, et al, **2003**; Zhou, et al, **2004**; Bekyarova, et al, **2005**; Talapin, et al, **2007**).

The poor control of electronic conduction in organic semiconductors, despite synthesizing them in very high quality materials and developing very good methods of doping them based on the process of oxidation or reduction, is the main cause of lower carrier mobilities observed experimentally till date. The situation does not appear to change much before some newer class of materials is found out with still better control of charge carrier conduction. At this stage, it seems quite natural to think of replacing the polymeric molecules by NCs solids, where enough latitude is there to manipulate the electronic conduction besides retaining the low cost of production aspects involving solution grown materials synthesis followed by spin coating and printing for device production on a mass scale. Therefore, various research groups are anticipating better performance using semiconducting NCs in the near future.

However, here as well, a number of problems are there to sort out before NC solids are put to use in FETs and related integrated electronic circuits. Performance of NC FETs depends on the strength of the electronic coupling between individual NCs that needs to be maximized by proper design of NCs and ligands. NCs capped with bulky organic ligands are not appropriate for charge carrier transport due to weak inter dot exchange coupling (Ginger and Greenham, **2000**; Morgan, et al, **2002**). To improve conductivity of the NC solids, larger capping ligands should preferably be replaced with smaller molecules and/or should be stripped off by thermal or chemical treatments while exercising care to minimize the effect of nonzero charging energies and carrier traps at the NC surface, both affecting the carrier transport adversely in NC solids (Talapin and Murray, **2005**; Kim[1], et al, **2006**; Law, et al, **2008**; Luther[1], et al, **2008**).

In principle, NC FETs consist of a solution grown NCs assembled conducting channel along with source and drain contacts directly attached to the transistor channel by using lithographic patterns on SiO_2 dielectric layer prior to NC deposition. The gate electrode is formed such that it is insulated from the transistor channel through a thin film of 1 - 300 nm layer of "gate dielectric" generally prepared from wide band gap oxides such as SiO_2, Al_2O_3 or HfO_2 along with some polymers like PMMA dielectric layers. In a typical prototype FET structure, thermally grown SiO_2 coated heavily doped silicon substrate is used for physical vapor and atomic layer depositions of gate and the dielectric layers, respectively, on the top of QDs layer. Though top-gated FETs structures have successfully been operated at lower voltages but in case of some demanding applications, both bottom and top gates can be electrically biased for better control of the transistor channel properties. Depending on the initial type and concentration of carriers in the channel, the additional charges either deplete the channel thereby increasing its resistance, or cause accumulation enhancing the source-drain current due to the influence of bias on the gate electrode. By controlling the gate voltage, the current through the semiconductor channel can be easily switched 'on' and 'off' enabling signal amplification and logic operations.

The general requirement of a channel allowing sufficient flow of source-drain current during operation puts some design constraints for practical NC-FETs. The first and foremost condition to meet is the coupling energy between individual NCs that should be high enough to allow easy passage of charge carriers through the NC solid. Second condition is that source and drain electrodes should form ohmic contacts to the NC solid.

The response of the current flowing through the FET to the applied gate voltage depends on the type of majority carriers in the transistor channel. In case NC solid layer is n-type conducting, a negative gate bias depletes electrons in the channel causing the device to switch 'off'. FETs switch from conducting to insulating state when the bias applied to the gate approaches the value called threshold voltage (V_T) that depends on the parameters of the semiconductor channel having initial doping level, presence of deep trap states are filled before gate induced charges flow and on the properties of the gate dielectric. The performance of an FET can be evaluated in terms of parameters like the carrier mobilities; the current modulation ratio - I_{on}/I_{off}, where I_{on} and I_{off} are the source-drain currents when the device is in 'on' and 'off' states, respectively; and the sub-threshold slope defined as $S = dV_G/d(\log I_D)$.

Historically, the first batch of inorganic NC-FETs was reported in 1999 (Ridley, et al, **1999**), employing pyridine-capped CdSe NC film as active channel material. The annealing of NC solid layer above 250□□□ practically sintered the CdSe NCs into a polycrystalline thin film. Therefore, the devices mentioned above were not strictly NC solid based structures. The prolonged annealing over a period of one hour @ 350 □□□ resulted in the following device parameters: mobility $\mu_{lin} = 1$ cm^2/V·s, $I_{on}/I_{off} = 3.1 \times 10^4$, and $V_T = 6.7$ V. It is worth noting that carrier mobility in inorganic FETs is significantly larger than those achieved in case of printed organic FETs.

The first batch of NC-FETs, in real sense, was subsequently prepared (Talapin and Murray, **2005**) from the oleic acid capped PbSe NCs embedded in close-packed thin films by spin coating or drop-casting. These NC films were insulating with a conductivity of $\sigma \approx 10^{-10}$ Scm^{-1} and did not show any gate effect. Replacing oleic acid with hydrazine molecules for capping reduced the inter-particle spacing from ~1.2 to ~0.4 nm and increased the conductivity of PbSe NC films by ~10 orders of magnitude wherein the size as well as the morphology of NC films, did not change after hydrazine treatment. I_{on}/I_{off} improved to ~2.5 × 10^3 for a PbSe NC n-FET. In the 'on' state, the low-field specific conductance of PbSe NC film was ~0.82 Scm^{-2}, and the saturation current density approached 2.7×10^4 A/cm^2. Field-effect electron mobilities extracted from a series of devices were: $\mu_{lin} \approx 0.4$ cm^2/Vs and $\mu_{sat} \approx 0.7$cm^2/Vs, in the linear and saturation regime respectively (Talapin and Murray, **2005**). Since then, considerable improvements in processing were made resulting in electron mobility: $\mu_{sat} \approx 2.5$ cm^2/Vs for 8 nm PbSe NC FETs, keeping the I_{on}/I_{off} above 10^3 (Beard, et al, **2009**; Talapin, et al, **2010**). It is important to note that all of these results belong to the devices prepared at room temperature without any further heat treatment retaining the NC structures intact.

In various studies, it was observed that PbSe NC solids behave as n-type material after treatment with N_2H_4. However, the removal of hydrazine in vacuum switched its conductivity from n-type to ambipolar and finally to p-type after complete desorption of hydrazine. This kind of p-type FETs showed stable operation with room temperature hole mobilities μ_{sat}= 0.12-0.18 cm^2/Vs and I_{on}/I_{off} ~10^2 which increased to ~1.6 × 10^4 @ 120 K while the hole mobility reduced to μ_{sat} ~0.09 cm^2/Vs independent of the gate voltage. The hydrazine treatment was necessary for realizing reversible switching between electron and hole based conduction. Annealing hydrazine-treated PbSe NC films at ~200□□□and again treating with hydrazine solution converted them into degenerately doped films with a metallic conductivity $\sigma \approx 8.5$ Scm^{-1}. This kind of semiconductor to metal transition was reversible, as the partial removal of hydrazine resulted in n-type films with rather high electron mobility $\mu_{lin} \approx 2.5$ cm^2/Vs. This study demonstrated the possibility of tailoring the electron coupling and the doping density that led to controllable switching between insulating, semiconducting and metallic states in N_2H_4-treated PbSe nanocrystal films.

Another research group reported FETs realized from PbSe NC films treated with different ligands including hydrazine, methylamine, pyridine and ethanedithiol (Murray, et al, **1993**; Luther^2, et al, **2008**). SEM/TEM analyses clarified that though these treatments did not alter nanocrystal shape and size, but markedly reduced the inter-particle spacing, which is critically important for charge conduction. For example, PbSe NC films treated with 1 M N_2H_4 in ethanol resulted in n-type FETs with high conductivity but poor current modulation.

Treatment of the nanocrystal films with methylamine or pyridine in ethanol resulted in significant conductivity increase, while the films were p-type. The films treated with 1,2-ethanedithiol showed ambipolar behavior in the dark, but converted to p-FETs with 30-60 times higher conductance after exposure to 300mW/cm^2 broadband illumination. These observations point to the complexity of the processes involved in the chemical treatments of PbSe NC films and the important role of surface ligands. Simple removal of the surface ligands and their replacement with small molecules is the only one of several processes necessary to achieve good performance of NC FETs. Proper surface treatment simultaneously affects the exchange coupling energy, charging energy, trap density, and the doping. For instance, hydrazine treatment saturates the dangling bonds at the nanocrystal surface by donating a lone pair of electrons besides preventing oxidation of the bare nanocrystals surface and "repairing" them with oxidized surface sites. This is an important step because oxidation of surface atoms can introduce carrier trapping mid-gap states. Replacement of oleic acid with N_2H_4 molecules reduces the charging energy, which in association with enhanced coupling behave as charge-transfer dopants in PbSe nanocrystal solids.

Hydrazine treatment of other nanocrystal solids including PbSe (Talapin and Murray, **2005**; Law, et al, **2008**; Mentzel, et al, **2008**; Luther^2, et al, **2008**), PbS (Lee, et al, **2008**), PbTe (Urban, et al, **2006**; **2007**) and SnTe (Kovalenko, et al, **2007**) was investigated in detail by several groups where it was shown that hydrazine solution in acetonitrile treated PbTe nanocrystals films showed ~10 orders of magnitude improvement in conductivity and n-channel behavior with electron and hole mobilities in the linear region as ~0.95 and 0.15 cm^2/Vs, respectively (Urban, et al, **2006**). The mobility of hydrazine treated PbS NC n-FET was ~0.08 cm^2 /Vs in the linear region and 0.12 cm^2/Vs in the saturation regime (Luther^2, et al, **2008**). PbS NC FETs were noted to be more stable than PbSe and PbTe based devices.

Further optimization of nanocrystal exchange coupling, doping, and improvements in film morphology could significantly increase carrier mobility. For example, bottom and top gated FETs with p-channels of sintered HgTe nanocrystal demonstrated the possibility of achieving high field-effect mobility at low gate voltages for solution-processed inorganic FETs by employing high-k dielectric materials as the gate insulators.

The gate insulator materials were found to significantly influence the carrier mobility in semiconductor channel due to the formation of surface states at the semiconductor–dielectric interface. The advantage of top-gated FETs in using them for print electronic circuits on virtually any substrate was demonstrated in case of p-type HgTe NC-FETs fabricated on glass and plastic substrates. On glass, the hole mobility was: μ_{sat} =1.06 cm^2/Vs and μ_{lin} = 0.55 cm^2/Vs. The I_{on}/I_{of}f and V_T were ~10^3 and 0.2 V, respectively. HgTe NC FETs, fabricated on flexible polyethersulfone substrates, demonstrated for holes - μ_{lin} = 1.2 cm^2/Vs, I_{on}/I_{off}=10^3 and V_T = -3 V (Kim^2, et al, **2006**).

Solution grown ZnO NCs represent another very interesting class of materials for FET devices that have specific advantages of their nontoxic nature, low cost, chemical stability and being transparent in the visible region, which seems to be very promising candidate for thin-film transistors in applications like liquid-crystal flat-panel displays. NC films, prepared from butylamine capped ZnO and spin-cast on Si wafers with a 300 nm layer of SiO_2 gate dielectric and pre-patterned Cr/Au electrodes, annealed at 230 □□□under N_2/H_2 atmosphere for 30 min demonstrated significantly increased carrier concentration and mobility leading to μ_{lin} =2.4×10^{-4} cm^{2}V^{-1}s^{-1} and μ_{sat} =4.6×10^{-4} cm^{2}V^{-1}s^{-1}, and the I_{on}/I_{off} = 5 × 10^3. Replacement of nanocrystal NCs by nanorods significantly improved the performance of ZnO FETs as 65 nm-long 10 nm-diameter nanorods showed almost 2 orders of magnitude higher mobility as compared to the devices made from 6 nm spherical nanocrystals. Nanorod-based devices exhibited an I_{on}/I_{off} = 1.1 × 10^5, μ_{sat} = 0.023 cm^{2}V^{-1}s^{-1} and μ_{lin} =

0.013 $cm^2V^{-1}s^{-1}$. The approximately 10-fold larger size of the nanorod particles as compared to the nanospheres reduced the number of inter-particle hopping events that an electron has to undergo when moving from source to drain electrode. By using octylamine surface ligands for ZnO, partial assembly of monodisperse ZnO nanorods in the transistor channel turned into superstructures with nematic liquid crystalline ordering. This kind of nanorods alignment resulted in improved performance as the devices with octylamine-capped ZnO nanorods after annealing exhibited μ_{sat} = 0.1- 0.12 $cm^2V^{-1}s^{-1}$ and I_{on}/I_{off} = 10^5-10^6. This mobility value was 5-6 times higher than that of butylamine-capped ZnO FETs and the improvement in mobility with ligand length was fully consistent with the changes in film morphology and showed that a high degree of in-plane nanorods alignment is beneficial for transport in the nanorod films.

The performance of ZnO nanorods FETs was further improved by the post-deposition hydrothermal growth of a thin layer of ZnO chemically deposited into the voids between ZnO nanorods and after such a treatment followed by H_2 annealing, the devices demonstrated improved mobility of 1.2-1.4cm^2/Vs and an I_{on}/I_{off} of 10^6-10^7 (Sun and Sirringhaus, **2006**). These mobility values, combined with optical transparency and solution-based fabrication, offer a good opportunity for producing ZnO nanocrystal FETs for their large-scale commercial applications.

NC-FET channels, fabricated using spin coating of 3.6 nm ZnO colloids followed by annealing @ 600 ^{0}C to remove capping molecules and increasing the inter-dot couplings were completely defect free and transparent and especially useful for bottom-gate configuration (Joo-Seob Ahn, *et al*, **2010**). A small quantity of Sn doping into the NC channel layer further improved the electrical characteristics and exhibited a higher mobility of 0.282 cm^2/Vs that was more than 4 times that of un-doped ones (Joo-Seob Ahn, *et al*, **2010**). Subsequently, fully transparent Sn-doped QD-based device were successfully fabricated using sputter deposition of Ga-doped ZnO as source-drain transparent electrodes (Joo-Seob Ahn, *et al*, **2010**).

In further development of NC-FETs, efforts were made to combine multiple functionalities of engineered NCs as the building blocks for fabricating transistor channels. For example, co-integration of materials with different functionalities in form of core-shell, dumbbell, and other nanostructures provided exotic possibilities of realizing NC-FETs. In 2008, NC-FETs comprising of multifunctional core-shell structures consisting of plasmonic Au core and semiconducting PbS shell (Lee, et al, **2008**) were fabricated wherein intra-particle charge transfer between Au core and PbS shell formed the charge-transfer complex resulting in p-type doping of the FET channel. In subsequent developments, FETs combining semiconductor and magnetic functionalities were demonstrated using core-shell and dumbbell nanostructures combining FePt and PbS along with PbSe as magnetic and semiconducting components, respectively, resulting in good device performance, with n-type operation and μ_{sat} = 0.01 cm^2/Vs and I_{on}/I_{off} ~10^2 (Talapin, et al, **2010**). The FET behavior was complemented by superparamagnetic response of FePt core directly integrated in the transistor channel. The examples of FETs assembled from Au/PbS ad FePt/PbS multicomponent nanostructures offer completely new directions for developing devices suitable for newer electronics applications. The progress in synthetic chemistry will further expand the list of material combinations; developments in the ligand designs should enable strong electronic coupling between the components and development in electronic structure calculations of nanostructures will provide deeper understanding of interactions between the components both at intra and inter-particle levels. Having acquired competence in all these areas mentioned above, bright prospects are anticipated for multi-component nanostructures in various electronic device applications.

While preparing larger size NC-thin-films for device applications, it was invariably noted that the films contained cracks and lumps, which impaired the carrier conduction to a large extent. In a recent attempt (Mentzel, et al, **2012**), it was demonstrated that the films prepared with the reported technique were free from this problem showing ~ 200 times better conductivity as compared to the conventional films of the same composition. The e-beam lithography and lift-off techniques were found equally applicable to a number of other materials like PbS, PbSe, CdSe NCs and $Zn_{0.5}Cd_{0.5}Se$-$Zn_{0.5}Cd_{0.5}S$ core-shell NCs for their applications in device fabrication.

3.6 Memory Devices

Before starting discussion on NC-memory devices, it is useful to refresh the terminologies used in this context (Semiconductor Memory). For example, RAM refers to a nonvolatile memory with both 'Read and Write' capabilities whereas ROM is a read only type having no on-line write capability and is nonvolatile. SRAM holds data as long as power is applied whereas DRAM loses data unless refreshed periodically. PROM is a nonvolatile, user programmable, and read only memory. EPROM uses UV light to reset all bits whereas EEPROM is electrically erasable PROM, slow and complex to write, not good for fast cache, best choice for nonvolatile program memory. DRAM is high-density cheap data cache though slower than SRAM, which is the fastest, low density, more expensive, generally used in small volumes. Register contains flip-flops very similar to SRAM but less dense reserved for only data manipulations. Flash memory is a solid-state EEPROM that maintains stored data without external power and is commonly used in portable electronics as a removable storage device replacing the computer hard drives. Though, regular EEPROM erases content byte-by-byte; most flash memories erase data in whole blocks, making it suitable for use with applications where larger amounts of data require frequent updates.

USB flash drives, introduced recently, contain memory with controller in a small package offering high capacity, fast transfer rate, flexibility and convenience while storing more data and provide easy file transfer between most devices with a USB interface. Memory cards, initially developed as CompactFlash cards in 1994, went through postage-stamp-size Secure Digital cards to the latest mini-SD and micro-SD cards, with higher capacities and faster transfer speeds. These solid-state-drives replace computer's hard drives having no moving parts, so mechanical failure is almost zero. Solid-state drives are quieter and smaller than hard drives, and they provide faster response, access and boot-up times consuming much less power and running cool. Traditional hard drives currently offer greater capacity and a lower price, but likely to change in near future.

There are three prominent memory technologies such as DRAM, magnetic hard-disk drives (MHDDs) and flash memory that are currently in vogue besides few others like magnetic random-access memory (MRAM), ferroelectric random access memory (Park, et al, **1999**; Sheikholeslami and Gulak, **2000**), phase-change memory (Pirovano, et al, 2004; Wuttig and Yamada, 2007) and resistive memories employing switching characteristics of inorganic and organic materials (Scott and Bozano, **2007**).

The DRAM cell requires one transistor compared to about six in a typical SRAM memory cell and therefore cost less than SRAM, and provides much higher memory density. Recently developed SDRAMs, the improved version of DRAM, offer better levels of speed and density appropriate for modern computing technology.

MHDDs contain few rotating discs coated with magnetic material to retain data even when power is off is another kind of storage device with magnetic heads arranged on a moving actuator arm to 'read' and 'write' data from/to the disc surfaces. The MHDD's performance is quantified by the time to move the heads to a file plus the time it takes for the file to move under its head, which is a function of the physical rotational speed and the speed at which the file is transmitted. The most common MHDDs are available today in 3.5 inch for desktop computers and 2.5-inch for laptops. The primary competing technology for MHDD is flash memory. Though MHDDs are there as dominant secondary storage medium for the foreseeable future due to advantages in recording capacity and price per unit of storage but flash memories are fast replacing MHDDs especially in portable electronics where speed, physical size, and durability are the major considerations than cost and capacity.

A flash memory cell contains a MOSFET with two gates where the one at the top is the control gate (CG) below which is situated an oxide insulated floating gate (FG). The electrons put on the FG are strongly attached such that under normal conditions do not discharge even after many years. The electrons, put on the FG, partly screen the influence of the CG by modifying the threshold voltage. The current flow through the MOSFET channel is the signature of the binary code of the stored data. In a multi-level cell device, which stores more than one bit per cell, the amount of current flow is sensed rather than simply sensing its presence or absence, in order to determine more precisely the level of charge on the FG. The major advantage of a flash memory is its non-volatility, which comes at the cost of low write-erase speed and limited number of rewrite cycles.

The characteristic properties of the memory elements, in vogue, include parameters like: data density, writing and erasing speeds, data retention time, number of erase-rewrite cycles, power consumption and cost per bit of stored information. In reality, there is no ‘ideal memory’; rather different kinds of devices have their strong and weak points and therefore target different application niches. For example, DRAM is relatively expensive and needs refresh every few milliseconds consuming power in each cycle. On the other hand, MHDDs can achieve very high data density at rather low cost and allow many write-erase cycles, but are slow to access, consume significant power to be in readiness and prone to the head crashes. The major advantage of flash memory is its non-volatility, which, however, comes at the expense of low write-erase speed and limited number of rewrite cycles.

Use of various types of NCs in memories is currently being explored as possible solutions to overcome number of issues in the development of nonvolatile memories (Tiwari[1,2], et al, **1996**; Sun and Murray, **1999**; Kapetanakis, et al, **2000**; Takahashi, et al, **2000**; King, et al, **2001**; Kanoun, et al, **2004**; Duguay, et al, **2005**; Lee and Kwong, **2005**; Zhao[1], et al, **2006**) and HDDs (Zhang, et al, **1999**; Grochowski and Halem, **2003**). The NCs especially possess the characteristics of precisely controlled electronic and magnetic properties of materials by tuning their sizes and shapes besides employing low cost device fabrication technology of solution-based synthesis resulting in significant cost reductions, especially important for the products such as wireless identification tags and smart cards where the prime criterion is cost rather than their outstanding performances.

In a conventional flash memory, tunnel oxide quality is critical for it’s successful operation. For instance, the ‘writing’ and ‘erase’ speeds strongly depend on the thickness of tunnel oxide, which should not exceed a few nanometers (Tiwari[1,2], et al, **1996**). However, thinner oxides, in general, cause breakdown voltage reduction besides influencing the leakage and tunneling currents through defects (Yi, et al, **1998**). The emergence of even one weak spot in the tunneling oxide is sufficient to create a discharge path damaging the entire element. A better way to get rid of such possibilities would be to store charges not on a continuous polysilicon FG, but on a layer consisting of discrete and isolated nanocrystals, while still preserving the basic operation of the flash memory. Individually, each nanocrystal will store only few electrons; while the charges stored on the nanocrystals as aggregate would effectively control the threshold voltage of the FET. The concept of distributed charge storage is more fault-tolerant because minor damages in the tunnel oxide layer would not be detrimental to the memory operation. Under these conditions, using thinner oxides would be advantageous in achieving lower operating voltages and/or increasing the operating speed.

In addition, continuous memory programming is also found to degrade the quality of tunnel oxide layer in terms of data retention time. Although, stability may be improved by increasing oxide thickness; however, the thicker oxide layers reduce the tunneling current besides demanding higher operating voltages for write/erase, and putting restrictions on miniaturizing the dimensions. Keeping in view the inversely proportional relationship between the retention time and operating speed, several techniques were developed for acquiring fast programming speed and the long retention time of memory simultaneously (Yi, et al, **1998**; Garrido, et al, **2003**; Lu[1,2], et al, **2005**) and consequently current focus is on improving the data retention time without decreasing the programing speed at low voltages (Park, et al, **2007**, Chan, et al, **2008**, Yun-Shan, et al, **2008**). For this, it was contemplated to replace the conventional SiO_2 layer with a high-k gate dielectric for the control and tunnel oxide layers. High-k dielectric materials with lower conduction band offsets with Si provide lower tunneling barriers across the dielectric and channel interface.

The idea of NC-based flash memory was proposed way back in 1996 (Tiwari[1,2], et al, **1996**) and since then, different metallic and semiconducting nanocrystals were employed as FGs (Hasler and Lande, **2001**; Liu, et al, **2002**; Tsoukalas, et al, **2005**). Incorporating 5 nm Si nanocrystals into the gate oxide was noted to strongly influence the transfer characteristics of the MOSFET by significantly shifting the threshold voltage (Prakaipetch, et al, **2006**). Of course, NCs based flash memories depend strongly on the accurate control of monodispersity and density in a thin oxide layer (Hasler and Lande, **2001**; De Blauwe, **2002**; Lombardo, et al, **2004**; Tsoukalas, et al, **2005**).

Encouraged by the promising performance, Si nanocrystals-based flash memory is currently picking up as one of the promising candidates for the next generation of nonvolatile memory devices (Tiwari[1,2], et al, **1996**; Kapetanakis, et al, **2000**; Takahashi, et al, **2000**; Han, et al, **2001**; Ammendola, et al, **2002**; Muller, et al, **2002**; Ohba, et al, **2002**; Garrido, et al, **2003**; Li, et al, **2003**; Rao, et al, **2004**; Bonafos, et al, **2004**; Feng, et al, **2005**; Talapin, et al, **2010**). The very first Si nanocrystals-based memory device used FG embedded in a SiO_2 layer and operated on tunneling and storage of electrons in the nanocrystals, where the electron were injected through direct tunneling from an inversion layer created by the appropriate gate voltage. Such devices demonstrated <100s of nano-second per ‘write-erase’ cycle speed, smaller dimensions and long operation times in excess of 10^9 cycles (Tiwari[1,2], et al, **1996**).

Further studies of Si nanocrystals-based FG devices (Punchaipetch, et al, **2006**) confirmed that 10 nm SiO_2 tunnel oxide gave the most stable performance as compared to the thinner oxide layers and the threshold voltage degradation was not observed even after 10^8 cycles. It was further observed that with increase in nanocrystals density, operational speed got enhanced considerably (Lu, et al, **2006**).

Interestingly, Ge nanocrystals based memory devices were found to operate at lower voltages and higher speeds (King, et al, **2001**) as compared to Si devices. In another report, memory devices employing Ge nanocrystals embedded in $LaAlO_3$ high-k dielectric (Lu[2], et al, **2005**) showed very high stored charge density of $2 \times 10^{13}/cm^2$. Excellent charge retention time with only 8% decay in memory capacitance after 10^4s of stress under a flat band voltage was observed in Ge devices. Extending the search for still better nanocrystals, SiGe were embedded in HfO_2 layer (Kim, et al, **2003**) resulting in a still faster charge carrier trapping and de-trapping at low voltages even when the oxide thickness was slightly thicker than that for SiO_2 tunneling oxide memory.

Comparative search for still better nanocrystals for FG application indicated that using metallic nanocrystals could be superior to the devices utilizing semiconductor nanocrystals (Sun and Murray, **1999**; Lee and Kwong, **2005**; Lee, et al, **2005**; Zhao, et al, **2006**; Liu[2], et al, **2006**; Park, et al, **2007**; Shahrjerdi, et al, **2007**; Chen, et al, **2007**; Chan, et al, **2008**; Yun-Shan, et al, **2008**). The advantages of metallic NCs for FG applications include: higher density of states near the Fermi level, stronger electrostatic coupling to the conducting channel, tunable work function and small energy perturbations due to carrier confinement. The work function is possible to tune by using different metals and metal alloys offering an opportunity to optimize the trade-off between 'write-erase' speed and charge retention because the work function of the NC FGs controls not only the depth of the potential well at the storage node but also the density of states available for carrier tunneling. Numerous attempts were, thus, made to develop nonvolatile memory devices using metallic NCs including Au, Pt, Ni, Co and Ag (Liu, et al, **2002**; Tsoukalas, et al, **2005**) out of which Au was the most successful materials because of its chemically stability and a large work function. Isolated Au NCs form a deep quantum well between the control and tunnel oxides, desirable for the FG application. For instance, memory characteristics of Au NCs embedded in the amorphous HfAlO tunnel layer (Chan, et al, **2008**) showed a significant threshold voltage shift due to charge trapping on Au NCs with a memory window and stored charge density as ~10 V and ~1 × 10^{14}/cm^2, respectively. Smaller diameter Au NCs showed a higher tunneling coefficient and a larger memory window. Au nanocrystals were also used along with a multi-stacked layer of $Al_2O_3/HfO_2/SiO_2$ (Yun-Shan, et al, **2008**) showing high efficiency charge injection and de trapping with long retention times (Liu, et al, **2002**; Tsoukalas, et al, **2005**; Hou, et al, **2006**; Pavel, et al, **2008**).

It is interesting to note that the results included in these descriptions mentioned above belonged to CVD based nanocrystals processes having a number of limitations. On the contrary, solution grown synthesis of NCs could provide better solutions for a number of problems faced in gas phase synthesis. It includes synthesis of monodisperse NCs of different materials with precisely tunable size along with integration into the memory devices using low temperature processing. Recently, a number of memory devices using solution grown NCs as charge-trapping elements were reported (Mohanta, et al, **2006**; Park[1,2], et al, **2006**; Das, et al, **2007**; Lee, et al, **2007**; Li[2], et al, **2007**; Li[1,2], et al,**2008**; Son, et al, **2008**). For example, in one case atomic layer deposition was employed to embed Au between thermally grown SiO_2 tunnel oxide and Al_2O_3 control oxide (Park[1], et al, **2006**). The estimated number of charge carriers stored in the Au NCs was about 3 × 10^{11} cm^{-2} when the voltage was swept in the range of 7 V. The device also showed relatively good retention time, after losing ~18% of initial charge during the first 500 s, remaining charge stabilized with ~2% additional decay after 10^4 s.

In another study, a Pt NC monolayer was deposited onto a SiO_2 substrate with poly (4-vinylpyridine) as a surface modifier (Choi, et al, **2008**). The devices realized on these structures exhibited a relatively large memory window of 5.8 V under 7 V for 'write-erase' voltage. A binary mixture of NCs with different electron affinities (Co and Au) (Lee, et al, **2009**) demonstrated to tune the properties of charge-trapping layer. All these results indicate that solution grown metallic NCs can be successfully integrated into nonvolatile flash memory devices with advantages as compared to the classical devices.

Integrating solution grown NCs into a matrix of organic insulator could be put to use for charge-trapping in a memory device as shown in form of *C-V* hysteresis curves measured for a metal-insulator-semiconductor (MIS) capacitor with the insulating layer composed of polyelectrolyte/Au NC multilayer films (Lee, et al, **2007**) prepared by the layer-by-layer deposition process. The optimum performance with a memory window of ~1.8 V was observed for a device with three polyelectrolyte/Au-NC bilayers and a 1.4 nm thick HfO_2 tunneling oxide layer. Similarly, charge trapping leading to *C-V hysteresis* curves and electrical bistability was reported in case of CdSe/ZnS core-shell nanocrystals embedded in MEH-PPV617 or C_{60} fullerene matrices (Li[1], et al, **2007**; Li[1,2], et al, **2008**).

Improving the syntheses of various configurations of core-shell or core-multiple shells type NCs might accelerate further progress in this context in near future. For instance, a thin uniform layer of SiO_2 or TiO_2 grown over Au NCs (Garcia-Santamaria, et al, **2002**; Liz-Marzan and Mulvaney, **2003**) provided perfect configuration for FG memory applications because they include both FG and tunnel oxide co-integrated together in the form of solution processed units with precisely tunable size of Au core and thickness of SiO_2 shell.

Devices incorporating switchable resistive materials are generically classified as resistive random access memory (RRAM). The appeal of RRAM is that each element is a two-terminal device: switching between high and low resistance is achieved by means of an appropriate electrical pulse, and the read-out process requires applying a lower voltage to probe the state of the resistance. This type of element can be incorporated into cross-point arrays provided that it exhibits sufficient rectification or other nonlinear response (Lee and Chen, **2012**). Many inorganic and organic materials exhibit electrical switching behavior and, potentially, can be considered for resistive memory applications. In the recent years, hybrid inorganic-organic composites containing metal or semiconductor NCs are considered among the most promising materials for this type of memory. Several hybrid memory devices combine inorganic NCs blended into an organic host. For example, resistive switching was demonstrated in a system containing 2.8 nm Au NCs capped by dodecanethiol ligands, an inert polymer such as polystyrene (PS) or poly(methyl methacrylate) and conjugated organic compound such as Alq3, 8-hydroxyquinoline (8HQ) or 9,10-dimethylanthracence (DMA) (Yang, et al, **2006**). The electrical transition from the 'off' state to the 'on' state took place @ 6.1 V with an abrupt current increase from 10^{-10} to 10^{-6} A with good stability in high conductivity state during the subsequent voltage scan. The 'high' conductivity state was able to return to the 'low' conductivity state by applying negative bias where the current suddenly dropped to 10^{-10} A @ -2.9 V and this switching behavior could be repeated numerous times and be driven by short voltage pulses as well. The transition time from the 'off' state to the 'on' state was less than 25 ns. The electrical behavior of the device was strongly dependent on the nature of the metallic NCs and the conjugated small organic compound. An electric-field-induced charge transfer between the Au NCs and DMA of 8HQ through the layer of dodecanethiol ligands was proposed for the switching mechanism (Yang, et al, **2006**). The insulator coating on the Au NC prevented recombination of the positive charges on the 8HQ and Au NCs. The use of metallic NCs with specially designed surface ligands such as Au NCs capped with naphthalenethiol (Ouyang, et al, **2005**) and incorporating them with inert polymer allowed one to obtain write-once-read-many times (WORM) electronic memory elements (Lai, et al, **2014**). WORM devices were characterized by a rapid increase in conductivity when applied voltage exceeded the threshold voltage. Once switched to the high-conductivity state, neither a low nor high voltage bias of either polarity was able to cause the device to revert to the low-conductivity state. There are numerous examples of bi-stable switching behaviors observed in NCs-organic hybrid systems (Li[1], et al, **2007**; Das, et al, **2007**; Son, et al, **2008**; Das and Pal, **2008**; Lai and Chen, **2008**). Au NCs/poly-(N-vinylcarbazole) memory devices were prepared resulting in electrical bistability for a broad range of nanocrystals-to-poly-(N-vinylcarbazole) weight ratios (Lai and Chen, **2008**). In another example of resistive memory included Pt NCs deposited onto the surface of tobacco mosaic viruses and blended as NWs into poly (vinylalcohol) (Tseng, et al, **2006**). Semiconducting NCs have also been blended into organics, including wide band gap inorganic oxides (ZnO) in polystyrene (Verbakel, et al, **2006**), and copper-phthalocyanine in Alq3 (Bozano, et al, **2005**). Electric-field-induced transfer of electrons from organic molecules to NCs appears to be the most common explanation of the switching from insulating to conducting states in hybrid devices containing metallic or semiconducting NCs and conducting organic polymer or small molecules. Formation of the charge-transfer complex increases the number of mobile charge carriers (holes) in the organic component. The shell of insulating ligands at the surface of NCs is assumed to act as a barrier to recombination (Ouyang, et al, **2004**; Yang, et al, **2006**; Prakash, et al, **2006**).

Electrical bistability and resistive switching was also observed in semiconducting NCs (Fischbein and Drndic, **2005**; Li[1,2], et al, **2007**; Das, et al, **2007**; Son, et al, **2008**; Li, et al, **2008**). Low and high-conductivity states and switching behavior in semiconducting NC thin films separated by poly (allylaminohydrochloride) PAH or poly (methylmetacrylate) PMMA molecules were reported. Different semiconducting NCs showed similar switching behavior pointing to general character of electrical bistability in these semiconducting NCs (Das, et al, **2007**). To date, switching and memory effects were observed in systems containing CdSe/ZnS (Li[1,2], et al, **2007**; Son, et al, **2008**; Li, et al, **2008**), CdSe/PbS (Ghosh, et al, **2008**), CdSe/Ag_2S (Ghosh, et al, **2008**), CdS (Das and Pal, **2008**), CdSe (Mohanta, et al, **2006**; Das, et al, **2007**), PbS (Das and Pal, **2008**)' and PbSe (Das and Pal, **2008**) NCs blended with different organic matrices. Design of the NC structure is possible to use in tailoring the switching behavior. Recently reported CdS/PbS core-shell NCs showed significantly enhanced on/off ratio as compared to individual CdS or PbS NCs (Ghosh, et al, **2008**), where memory characteristics are controlled by tuning the shell thickness. Similarly, CdS/Ag_2S core-shell NCs showed reproducible electrical bistability with the on/off ratios approaching 10^4 (Ghosh, et al, **2008**). Close-packed arrays of CdSe NCs capped with trioctylphosphine oxide ligands were reported to show memory effects in electronic transport (Fischbein and Drndic, **2005**). Many reports have mentioned that switching of the conductivity in semiconducting NCs is possible to control by voltage pulses and is quite stable over many on/off cycles (Das, et al, **2007**; Das and Pal, **2008**; Ghosh, et al, **2008**). Though, there is no model for switching behavior in semiconducting NCs, it is only speculated that redox processes involving oxidation or reduction of chalcogen atoms at the NC surface may lead to conductivity switching. It is also known that shallow mid gap states often form in II-VI and IV-VI semiconductor upon oxidation or reduction of surface sites and can behave as dopants for semiconductor NCs (Mentzel, et al, **2008**).

Many materials including organic polymers and small molecules, inorganic solids, nanoparticle films, and hybrid organic-inorganic blends exhibit electrically bistable behavior necessary for RRAM operation. In one of the detailed studies carried out by the IBM Research Division, nine parameters of a memory device were identified for their detailed examination before the corresponding devices go for manufacturing (Scott and Bozano, **2007**). This included parameters like - the on-off resistance ratio, read time, 'write-erase' time, cycling endurance, retention time, power consumption, rectification, ruggedness and cost, for which acceptable limits for each of these parameters were estimated to decide their commercial viability.

Magnetic hard disk drives (MHDD), first introduced by IBM in 1956, with a recording density of 2 kb/inch^2 has already gone through different stages of development such that today an areal density of more than 700 Gb/inch^2 is commercially available and is expected soon to reach a level of 1Tb/inch^2 (Chokprasombat, **2011**). The conventional magnetic recording media contain thin granular films of Co, Cr and Pt, with additional elements such as B or Ta, deposited on a glass or NiP-coated Al substrate, where each ~10 nm grain, segregated by a nonmagnetic coat, behaves as a single-domain particle consisting of magnetic nanoparticles (Chokprasombat, **2011**). It takes almost few hundred such grains to form a bit of information, which can be read with good signal-to-noise ratio (SNR). Though, it is simple to increase recording density by decreasing the grain size but not without raising additional problems. For example, very small size grains face major problem of signal loss due to spontaneous magnetization reversal caused by thermal energy. Though it is possible to get away with this problem by using materials with higher magnetic anisotropy to prevent the thermal effects but then one does need higher magnetic field for the write head (Chokprasombat, **2011**).

Considering the situation that is conducive for aligning the electron spins parallel to each other inside magnetic NCs, and applying external magnetic field could also maneuver the orientation, it seems quite plausible to employ ferromagnetic NCs to store information encoded in magnetic moment. Based on these considerations, a proposal came in 2000, to use solution grown NCs for magnetic data storage applications (Sun, et al, **2000**) considering it as an optimal approach where magnetic NCs are assembled in a long-range ordered array and each NC element is used for storing information. Such an advanced magnetic media could possibly reach enormous magnetic recording densities up to 1 Tb/inch^2. However, technical realization of this great idea required addressing to several difficult problems. For instance, the magnetization direction in a material under consideration for magnetic storage medium should be very stable and not reversed by thermal fluctuations meaning thereby, the NCs should have high magnetic coercivity. It was found that the coercivity of a magnetic particle strongly depends on its size. In case, NCs contain only one magnetic domain, reducing particle size decreases the number of exchange coupled spins (Klabunde, **2001**; Murray, et al, **2001**) that causes coercivity to fall due to the progressively increasing role of the thermal fluctuations leading to super-paramagnetism. It is also known that coercivity of a superparamagnetic particle is zero because thermal fluctuations prevent the existence of a stable magnetization. Superparamagnetic NCs cannot therefore be used for data storage. To beat the superparamagnetic limit, magnetic materials with very large magnetocrystalline anisotropy have to be evolved and used in this context.

The family of FePt alloys (Sun, et al, **2000**) is the most studied magnetic nanocrystals that, as synthesized, possess superparamagnetic properties in chemically disordered face-centered cubic (FCC) phase of at room temperature not appropriate for magnetic recording. However, these FePt nanoparticles can be annealed under inert atmosphere making iron and platinum atoms to rearrange and convert them into chemically ordered face-centered tetragonal (FCT) phase and transforms them into nanoscale ferro-magnets with the room temperature coercivity high enough to use the arrays of these nanocrystals in a data storage device (Teng and Yang, **2003**; Nguyen, et al, **2005**; Sun, **2006**). The annealed FePt nanocrystals array can support stable magnetization reversal transitions at room temperature (Sun, et al, **2000**). Depending on Fe_xPt_{1-x} stoichiometry and nanocrystal size, the transition temperature could be somewhere in the range of 500-700 °C (Sun, **2006**), while for the bulk material the reported value was 1300°C (Hansen, **1958**). To reduce the phase transition temperature further, silver atoms were introduced into the lattice of FePt NCs during their synthesis suggesting that Ag atoms promote creating lattice vacancies at < 400°C which enhanced the mobility of Fe and Pt atoms, accelerating the phase transformation.

In the past decades, several protocols were developed to fabricate nanometer scale magnetic dot arrays using electron beam lithography, extreme UV lithography, X-ray lithography, nano-imprint lithography and self-assembly of magnetic nanocrystals on a suitable substrate. Among these methods, self-assembly of magnetic nanocrystals appeared most suited possessing highest areal density, low cost and long-range order

(Chokprasombat, **2011**). However, there are still issues that need to be resolved before this method is commercially implemented. The tunable morphology and composition of the particles, the aggregation of the particles due to high temperature annealing, the orientation of the easy axis and the controlling of the self-assembly of nanoparticles into regular arrays are the areas that need special attention in the nearest future (Chokprasombat, **2011**).

FePt nanoparticles (Chokprasombat, **2011**) with large uniaxial magnetocrystalline anisotropy and good chemical stability were found suitable for magnetic recording applications. For good ferromagnetic properties, a near-equal atomic percentage of Fe and Pt should be there in a face-centered tetragonal (FCT) phase in which the Fe and Pt atoms are arranged in alternate layers along the [001] direction, whereas in face-centered cubic (FCC) phase they are randomly situated causing superparamagnetic characteristics and therefore not appropriate for magnetic recording purposes (Chokprasombat, **2011**).

In an attempt to prepare magnetic nanocrystals for recording media, high quality monodisperse FePt nanoparticles were solution grown using decomposition of iron pentacarbonyl $Fe(CO)_5$ and the reduction of platinum acetylacetonate $Pt(acac)_2$ by 1,2 hexadecanediol in dioctyl/benzyl ether with oleic acid and oleylamine as surfactant. In this process, immediately after the reduction, a small group of Fe and Pt atoms combined to form clusters that acted as nuclei and then the crystal growth process was initiated leading to the formation of FePt nanocrystals. The surfactants helped in passivating the nanocrystals surfaces giving adequate stability. In another alternate approach, Pt/Fe_2O_3 core-shell type nanocrystals were synthesized using $Fe(CO)_5$ and $Pt(acac)_2$ as precursors and were deposited in a monolayer form on a substrate using a Langmuir-Blodgett technique (Teng, et al, **2003**). Annealing over a prolonged duration under a gas flow of $Ar(95\%)/H_2(5\%)$ in a tube furnace converted these Pt/Fe_2O_3 core-shell nanocrystals into simple FePt nanocrystals. Lesser toxic precursors like $Fe(acac)_2$ and $Fe(acac)_3$ were also utilized in preparing monodisperse FePt nanocrystals (Elkins, et al, **2003**; Liu, et al, **2004**; Nandwana, et al, **2005**; **2007**) wherein co-reduction of $Fe(acac)_3$ or $Fe(acac)_2$ and $Pt(acac)_2$ with 1,2 hexadecanediol produced monodisperse 2-3 nm diameter FePt nanocrystals. Despite considerable efforts, already made in past like the ones mentioned here, the effective method to control size, shape and composition of FePt nanocrystals by implementing the low toxic precursors remains a challenge (Chokprasombat, **2011**).

Keeping in view the parameters involved in preparing hierarchically ordered samples, it seems more appropriate to using inherent tendency of self-assembly of nanocrystals (Cheng, et al, **2004**; Jung and Ross, **2007**; Ruiz, et al, **2008**; Park, et al, **2009**; Zhao, et al, **2009**; Grzelczak, et al, **2010**; Jung, et al, **2010**). In this context, three major self-assembly methods namely: template growth, block co-polymer assembly and self-assembled nanocrystals were used in preparing patterned media. Despite considerable work already done in this area, a common problem that is still encountered in all these methods is poor long-range order (Yao, **2006**) as in most of the cases ordering takes place well over micrometer scale regions besides most particle arrays do not have a circular structure required for a hard disk geometry. Because of these unavoidable difficulties associated with self-assembly techniques, lithography-assisted self-assembled patterning seems a better choice where a pre-patterned substrate is lithographically prepared as a template for assembly of nanoparticles by self-assembly of block copolymers. Nevertheless, perfect ordering over large areas and circumferential geometry has not yet been achieved. In a recent report, without using lithography, only heating could modify the faceted surface of commercially available sapphire wafers to guide the self-assembly of block copolymers into oriented arrays with a long range order over arbitrarily large wafer surfaces. Areal density in excess of 10 $Tb/inch^2$ was obtained as a result (Park, et al, 2009). However, this is not yet the most promising route due to the need for high temperature annealing @ 1,300-1,500 ^0C

for 24 hours. Furthermore, for successful assembly of magnetic nanocrystals into such arrays, it needs further more detailed investigations. Block copolymers are very expensive and require capping ligand modifications to make the nanocrystals compatible with a specific side of the copolymers, which can be synthetically challenging (Zhao, et al, **2009**). Therefore, a controllable, simple, and low cost method to assemble the nanoparticles into regular arrays is still a need of the future.

The LB method is powerful yet simple to prepare high-density nanocrystals monolayer and multilayer films with controlled layer number and thickness (Aleksandrovic, et al, **2008**). Theoretically, hydrophobic nanocrystals are assembled at the air-water interface of the LB trough (Talham, et al, **2008**) and the barriers compress the particle layer until the desired surface pressure is achieved. The monolayer is thereafter transferred to the substrate by dipping into the densely packed film. Very recently, many nanocrystals monolayers and multilayers were prepared by the LB technique including Au (Chen, et al, **2000**; Chen, **2001**), Ag (Tao, et al, **2007**), and Fe_3O_4 (Lee[1], et al, **2007**; Wang, et al, **2007**; Mammeri, et al, **2009**; Patel, et al, **2009**; Heitsch, et al, **2010**). While attempting to transfer monolayers of 4 nm FePt nanocrystals on a glass substrate using the LB technique, it was observed that the transfer was very efficient for the first few layers (Wang, et al, **2007**). In another experiment (Patel, et al, **2009**), FePt nanoparticles were water dispersed in the LB trough and having acquired sufficient surface pressure, a polydimethylsiloxane (PDMS) stamp was brought into contact horizontally with the water resulting in the pattern transfer to the Si substrate and this way, micron-size circles, lines and square patterned monolayers and multilayers of FePt nanoparticles were successfully fabricated. Another study (Heitsch, et al, **2010**) of an ordered hexagonal monolayer of FePt nanocrystals was reported using LB, Langmuir-Schäfer and spin coating resulting in the most ordered superlattice films.

In a number of 'write-read' experiments it was noted that 4 nm FePt ferromagnetic nanocrystals assembly supported magnetization reversal transitions at moderate densities that could be read back nondestructively. However, achieving much higher recording densities, not only size and magnetic properties of individual nanocrystals are to be controlled, but also orientations of individual nanocrystals in the array are to be pinned to provide unidirectional alignment of easy axes of magnetization for individual nanocrystals. This is really a challenging problem, especially when we take into account that such alignment has to be achieved throughout the entire hard disk area by using high-throughput fabrication process. Depositing magnetic nanocrystals aided by a magnetic field or designing nanocrystals with anisotropic shape were proposed to have control over the individual nanocrystals orientation (Chen, et al, **2006**). Future perspectives of colloidal nanocrystals for magnetic data storage will strongly depend on the development of novel methods of synthesizing materials with very high magnetic anisotropy like Co_5Sm and methods for fast and reliable assembly of chemically synthesized nanocrystals into uniform, ideally, long-range ordered two-dimensional arrays.

3.7 Thermoelectric Devices

While studying the transport properties of the electrons and holes for determining the current-voltage characteristics in several kinds of semiconductor electronic devices, the influence of phonons due to lattice vibrations is included in the expression for the carrier mobility and the drift velocity versus electric field characteristics (Ahmad, **1998**). It is, however, different in case of the thermoelectric (TE) materials and devices, where the phonon interactions (Minnich, et al, **2009**; Vineis, et al, **2010**) need more involved considerations as their contribution in thermal conductivity arises from a multitude of structural changes in numerous ways met in actual materials. For example, lattice excitations interact with practically all kinds of defects creating a deviation from the periodicity of the lattice; grain boundaries; distributions of a wide variety of impurities and phase nonuniformity; structural inhomogeneity representing variations right from crystalline perfection to polycrystalline and then up to amorphous states, nanoparticles and segregation of different phases resulting in scattering arising due to effective mass difference. Moreover, the expression for the thermal conductivity has contributions from electrons as well as phonons. The electronic contribution to the thermal conductivity is related to the electronic conductivity via Wiedemann-Franze's relationship. In case of the nanostructured species, it is quite likely to get free from the Wiedemann-Franze's relationship and reduce the thermal conductivity still further by looking into the optimization of various components involved.

The thermoelectric materials convert thermal energy directly into electrical energy based on the Seebeck effect, wherein T. J. Seebeck, in 1821, noted a compass needle to deflect when a temperature gradient was created on two different metals connected in a closed circuit (Minnich, et al, **2009**). This phenomenon of generating an electrical current induced by a temperature gradient was termed as thermo-electricity. The phenomena of Seebeck effect is currently explained by considering the movement of the charge carriers from the hot side of the material to the cold side due to their higher thermal energies, causing diffusion from the hot to the cold side resulting in an inhomogeneous charge distribution that gives rise to an electric field to opposes the carrier diffusion necessary for establishing equilibrium condition (Minnich, et al, **2009**). Under open circuit condition, it reaches equilibrium, as soon as the rate due to diffusion led carrier movement equals that due to drift caused by the electric field established and an electrochemical potential appears in response to the existing temperature gradient (Minnich, et al, **2009**). This electrochemical potential difference per unit temperature gradient is known as the Seebeck coefficient. Once connected to a circuit, the electrochemical potential drives electrical current leading to thermoelectric power generation (Minnich, et al, **2009**).

The efficacy of converting thermal energy into electrical energy is represented by the figure of merit of thermoelectric (TE) materials (Vineis, et al, **2010**) defined as $ZT = \sigma S^2 T/\kappa$, where σ, S, κ, and T are: electrical conductivity, thermoelectric power, thermal conductivity of the material and absolute temperature, respectively.

For improving the thermoelectric performance of a material under consideration, either σS^2 should be enhanced or κ be reduced. In order to have highest value of ZT for a TE material, it should ideally be a phonon glass as well as an electronic crystal - meaning the material should have the lowest thermal conductivity of a glass and highest electrical conductivity of an electronic crystals (Slack, **1995**). Based on these considerations, an appropriate TE material should be a heavily doped semiconductor as a compromise between the two extremes as the insulators have poor electrical conductivity and metals have low Seebeck coefficient. Moreover, in a semiconductor, the thermal conductivity comprises of the contributions from electrons (κ_e) as well as phonons (κ_p), where phonons contribute more than electrons.

Much before the discovery of the impact of nanostructured materials on TE effect, the process of alloying, introduced in the later part of 1950s and known for reducing the thermal conductivity because of scattering due to mass difference in an alloy, was explored in detail for improving the performance of bulk TE materials (Ioffe, **1957**). Even in case of the currently available state-of-the-art TE devices, the material compositions are primarily in alloy form. For instance, a p-type bismuth and antimony telluride alloys of composition - $Bi_{0.5}Sb_{1.5}Te_3$ and n-type bismuth telluride and selenide alloy of composition - $Bi_2Te_{2.7}Se_{0.3}$ exhibit room temperature ZT ~ 1 (Goldsmid, **1964**). Although, each component of *ZT* namely - *S,* σ, and κ has individually been varied over several orders of magnitude; their inter-dependence, however, does not allow the overall *ZT to improve* much beyond 1 despite considerable efforts made in last five decades. Though, the target of *ZT* ≥ 3 is considered sufficient (Vineis, et al, **2010**) to make these solid-state TE systems competitive with traditional mechanical energy conversion systems, but the progress has been stuck for about half a Century like that.

In order to improve further upon the precision and control of varying compositions in alloy like microstructures of TE materials, thin film superlattices were examined in place of alloys for their TE applications. In this context, various compositions like - Bi_2Te_3/Sb_2Te_3, $PbTe/PbSe_xTe_{1-x}$, $Si/Si_{1-x-y}Ge_xC_y$, $GaAs/Al_xGa_{1-x}$ As, $In_xGa_{1-x}As/Al_yIn_zGa_{1-y-z}As$ and layered structures of WSe_2 were studied in detail (Capinski and Maris, **1996**; Koga, et al, **1998;** Venkatasubramanian, et al, **2001**; Fan[1,2], et al, **2001**; Caylor, et al, **2005;** Zide, et al, **2006;** Chiritescu, et al, **2007**; Vashaee, and Shakouri, **2007**; Vineis, et al, **2010**). In these structures, it was theoretically anticipated that quantum confinement of in-plane carriers would substantially enhance the power factor over that of homogeneous materials, leading to almost an order of magnitude improvement in *ZT.* Such enhancement was partly due to delta-function like electronic density of states of the quantum-confined carriers enabling a dopant tunable increase. Superlattice periods of < 3 nm were estimated to affect the *ZT* enhancements (Vineis, et al, **2010***).* A few reports did follow with the claim of QW-enhanced in-plane Seebeck coefficients in SLs involving PbTe/Te, PbTe/PbSe and $PbTe/Pb_{0.93}Eu_{0.07}Te$, but these results were later on found to be in error. In another example of $SrTiO_3/SrTi_{0.8}Nb_{0.2}O_3$ superlattice, a giant Seebeck coefficient and TE power factor due to two-dimensional electron gas was predicted (Vineis, et al, **2010***),* but this also needed several basic assumptions to be ascertained properly (Vineis, et al, **2010***).* In a more recent paper, the possibility of attaining large TE power factors in extremely small QWs were carefully re-examined and concluded that actual improvement in the TE power factor could be only 12-40% (Vineis, et al, **2010***).* In another comprehensive paper, it was suggested that the power factor would be a relatively weak function of QW width due to increased charge carrier scatterings in thinner QWs (Vineis, et al, **2010***).* Additionally, in multi-valley semiconductors, the lifting of degeneracy in a SL structure would perhaps reduce the power factor compared to a homogeneous material (Vineis, et al, **2010***).* These SL based devices operate in an in-plane mode where the heat would flow through both the well and the barrier materials while charge carriers would flow exclusively through the well and such a situation would degrade the performance significantly. Thin barriers are not of much use, as it would eventually result in tunneling between adjacent QWs, which would lead to energy level broadening and reduce any power factor improvement (Vineis, et al, **2010***).*

In early '90s came a conceptual breakthrough when quantum confinement of electrons and holes in low-dimensional materials (Hicks and Dresselhaus, **1993**) was predicted to enhance *ZT* well beyond 1. In this context, low-dimensional systems comprising of QDs, QWs and SLs were being seriously considered for their TE applications. The enhanced performance were predicted in comparison to their counterpart bulk materials, due to both delta-function like density of states and increased phonon scattering leading to reduced lattice thermal conductivity (Lin and Dresselhaus, **2003**). Since the TE performance is predicted to improve with decreasing dimensionality, QD should be the best out of the three configurations of QD, QW and SL. However, unlike QW or SL, where no confinement in one/two dimensions provides path for electronic conduction, QDs do not possess this property. However, inter-dot tunneling is one way to realize carrier conduction and consequently QD-SLs or SL-NWs emerge as appropriate candidates for TE applications. PbTeSe-based QD-SLs demonstrated *ZT* ~ 2 @ 300 K as compared to *ZT* ~1 for conventional bulk materials. This enhanced performance was ascribed to the emergence of miniband formation in a coupled 3D QDs arrays. The other configuration of SL-NWs consisting of a series of interlaced nano-dots of two different materials in which the electronic transport along the wire axis occurs due to tunneling between adjacent QDs. The uniqueness of each QD and its characteristics are maintained by the energy difference of the conduction or valence bands between different materials wherein the band offset provides quantum confinement besides creating a periodic potential for the carriers moving along the wire axis, which may result in a further sharper density of electronic states than the one in a conventional quantum wire. This new structure is especially attractive for TE applications, because the interfaces between neighboring nano-dots can reduce the lattice thermal conductivity by blocking the phonon conduction along the wire axis, while electronic conduction may be sustained and benefitted from the unusual electronic band structures due to the periodic potential perturbations (Lin and Dresselhaus, **2003**).

While this speculation of improved TE performance due to reduced dimensionality led to intensive search for appropriate materials for the purpose, still the exact role of low dimensionality in improving *ZT* is yet to be confirmed experimentally. In this context, several groups (Vineis, et al, **2010***)* did claim the improvement but the basic cause turned out to be the reduced thermal conductivity whereas the quantum confinement of the charge carriers did not contribute much. Moreover, since some of the results were not yet independently confirmed/reproduced, till date, the primary impact of reduced dimensionality in improving the performance of TE materials has possibly been due to the thermal effects and not the electronic.

Though alloys, containing atomic scale defects, promote significant phonon scatterings that reduce the thermal conductivities of mono and polycrystalline bulk thermoelectric materials, it is difficult to reduce beyond this “alloy limit” of thermal conductivity in the bulk. But in SLs thermal conductivity values not only went well below the alloy limit, occasionally even reached the value of the amorphous phase. For example, cross-plane value of 0.22 W/mK was reported in case of Bi_2Te_3/Sb_2Te_3 compared to a $Bi_{0.5}Sb_{1.5}Te_3$ alloy resulting in *ZT* of 2.4 (Vineis, et al, **2010**). Other examples of significant reductions in thermal conductivity values included: 0.5 W/mK for a $PbTe/PbTe_{0.75}Se_{0.25}$ SL, which was half of the alloy value; 3 W/mK for a dislocation-free 3-nm-period Si/Ge SL, which was 60% of the $Si_{0.8}Ge_{0.2}$ alloy value; and 3.1 W/mK for a short-period AlAs/GaAs SL that was 75% of $Al_{0.5}Ga_{0.5}As$ alloy value (Vineis, et al, **2010**).

The cause of thermal conductivity reductions in SLs may be attributed to the phonon spectrum modification with zone folding, band gap formations and phonon localizations, diffuse or specular interface scattering of phonons due to acoustic mismatch and scattering of phonons at dislocation defects (Vineis, et al, **2010**). But this could be put to advantage only in case the reduction in electronic conductivity is contained to a lesser degree. For minimizing the cross-plane carrier mobility degradation, several approaches were adapted, including pairs of materials with small or no band offsets like Bi_2Te_3/Sb_2Te_3 combination, as well as materials with large relative static permittivity like PbTe with a value of 400 at 300 K that effectively screens out scattering on crystal defects possibly present at lattice-mismatched material interfaces (Vineis, et al, **2010**).

In order to use charge carriers of different energy in current transport in TE materials, the approach of carrier energy filtering was proposed for enhancing performance further through two-dimensional nano-structuring, where carriers travel in cross-plane direction experiencing the lowest thermal conductivity (Vineis, et al, **2010**). Here, tall potential barriers are introduced in conduction or valence band of n and p-type materials, which transmit only high-energy carriers leaving out the rest of the lower-energy ones causing substantially increased Seebeck coefficient (Vineis, et al, **2010**). This kind of detailed study clarified the contributions of higher energy electrons to the electrical conductivity of bulk, QW, and quantum wire structures. Calculated power factors for bulk;

QW, and QWs of 4nm InSb are 0.007, 0.020 and 0.045 $Wm^{-1}K^{-2}$, respectively (Vineis, et al, **2010**). With hot electron filtering in InSb layers, the estimated power factor could reach a value of 0.058 W/mK. Energy filtering induced Seebeck enhancement was experimentally shown in $In_xGa_{1-x}As/Al_yIn_zGa_{1-y-z}As$ system (Vineis, et al, **2010**) and this enhancement was finally expected to offset, to some extent, by a reduction in the electrical conductivity since fewer carriers participate in conduction and the extent of this reduction depends critically on whether energy or momentum filtering occurs. Thus, the overall impact on the power factor from this approach would also be dependent on the specific material system used, but it was an exciting area worth looking into especially since it provided a possible method to enhanced power factors (Vineis, et al, **2010**).

A thermal diode approach for enhancing Seebeck coefficient involved an *n-p* diode that resulted in a combination of electron injection and blockage of the ohmic return current under a thermal gradient (Vineis, et al, **2010**). Systems involving InSb and HgCdTe demonstrated some improvements, while reflecting little or no reduction of electrical conductivity but causing substantial enhancement in power factor. However, the physics of this operation is still not well understood, and therefore needs further investigations (Vineis, et al, **2010**).

Based on the performance of QDs in improving upon the performance of TE materials, the solution-based synthesis of monodisperse nanocrystals would certainly offer a better option for low-cost production for their widespread applications in energy generations. Unlike the two extremes of mechanical ball milling or molecular beam epitaxy, solution based synthesis of nanocrystals provides a finer tuning of NC size in few nm diameter range opening better possibility of optimizing the TE properties of strongly quantum-confined materials. Strong confinement of charge carriers in NCs not only modifies the band structure but also introduces sharply changing electronic density of states, which is predicted to be the best possible electronic structure for a TE material (Mahan and Sofo, **1996**). It is also anticipated that these materials will have better thermal properties because the nanocrystal diameters are much smaller than the phonon mean free path (Chen, **2005**; Kim^2, et al, **2007**), causing a strong suppression of thermal conductivity due to phonon scattering at the nanocrystal boundaries (Wang, et al, **2006**; Prasher, **2006**).

Realizing higher electronic conductivity in NCs solids is perhaps one of the basic challenges for employing NCs in TE applications. For such applications, the conductivity of a NC-solid should be as good as that of degenerately doped bulk semiconductor. For example, the state-of-the-art $(Bi,Sb)_2Te_3$ TE materials exhibit $\sigma > 1000$ Scm^{-1}, it is not easy to achieve these levels of conductivity in NC-solids with organic ligands. However, recent developments in preparing surface ligands based on conducting inorganic molecules show better charge carrier transport through metal and semiconductor NCs arrays. For example, 5 nm diameter Au nanocrystals, capped with Sn_2S_{64}-Zintl ions demonstrated $\sigma \approx 200$ S/cm and $\sigma \approx 250$ S/cm in solution-processed $(Bi,Sb)_2Te_3$ nano-composite films formed from solution grown NCs (Kovalenko, et al, **2009**). The development of electronically transparent surface ligands may lead to high-mobility Bloch transport through three-dimensional minibands (Kovalenko, et al, **2009**). In addition, temperature dependence of electronic conductivity - σ for a nanocrystal solid has opposite trend as compared to the bulk phase, resulting in increasing conductivity with temperature facilitated by enhanced inter-particle coupling, typical for granular electronic transport systems (Beloborodov, et al, **2007**).

While improvements in ZT for nanostructured materials have generally been attributed to reductions in thermal conductivity, the unique electronic structure of low dimensional semiconductors can also have a strong impact on thermo-power and charge transport (Hicks and Dresselhaus, **1993**). The impact of strong quantum confinement on thermo-power of nanocrystal solids was recently studied (Wang, et al, **2008**). When a temperature gradient was created across such a nanocrystals film, an open circuit voltage proportional to the temperature gradient was observed. With decreasing nanocrystal diameters from 8.6 to 4.8 nm, the thermo-power increased from 700 to 1150 μV/K. The positive sign of thermo-power indicates that transport in these films was p-type. Despite theoretical predictions of enhanced ZT and power factor in quantum mires of low effective mass materials like InSb, there are no experimental results to confirm such speculations. In some recent publications, rough silicon nanowires possessed ZT of 0.6 at room temperature and it increased to 1 with the lowering of the temperature. This kind of 60 - 100 fold increase in ZT from 0.01 in case of bulk silicon was really a significant observation and possibly this increase was assigned to reduction in thermal conductivity due to boundary scatterings. In another work, a large enhancement in ZT at low temperatures of 150 K was shown due to phonon drag effects.

Numerous systems were studied for their thermoelectric applications including PbTe/PbSe QD SLs, $AgPb_mSbTe_{2+m}$(LAST-m: lead-antimony-silver-telluride), $NaPb_m Sb Te_{2+m}$ (SALT-m), ErAs:InGaAs, Pb(Sn)Te-PbS, PbTe:Sb, and Si/Ge. In these QDs-solids, the occurrence of enhanced TE performance was attributed to a strong reduction in lattice thermal conductivity, rather than an increase in the electrical power factor. Specifically, the lattice thermal conductivity values at room temperature were reported to be as low as 0.33 W/mK for PbTe/PbSe QD-SLs, which compared well with 2-2.5 W/mK for PbTe; 0.5-0.8 W/mK for LAST-m and other variants such as SALT-m; 3 W/mK for ErAs:$In_{0.53}Ga_{0.47}As$, which was a factor of two lower than the $In_{0.53}Ga_{0.47}As$ alloy; 0.4 W/mK for $(Pb_{0.95}Sn_{0.05}Te)_{0.92}(PbS)_{0.08}$; and 8 W/mK for Ge QDs embedded in Si. In almost all these cases, the lattice thermal conductivity values were well below the alloy limit, illustrating the power of nanostructuring to modify the material properties.

Another interesting NC system that actually exhibits three scales of inhomogeneity simultaneously is that of PbTe-PbS. The system $(PbTe)_{1-x}(PbS)_x$ does not form a solid solution but rather phase separates into PbTe-rich and PbS-rich regions to produce coherent nanoscale heterogeneities. For $x > 0.03$ the materials were ordered on three sub-micron length scales. The coherent nano inclusions in a close variant $(Pb_{0.95}Sn_{0.05}Te)_{1-x}(PbS)_x$, did not result in excessive electron scattering and a high electron mobility of >100 cm^2/Vs was observed at 700 K. At $x \sim 0.08$ the material achieved a very low room temperature thermal conductivity which was ~30% of that of PbTe and a $ZT \sim 1.5$ at 650 K was estimated.

While studying the lattice thermal conductivity of five PbTe-based materials systems plus pure PbTe (Vineis, et al, **2010**), it was observed that the solid-solution point defect scattering alone lowered κ_{latt} of PbTe by ~30-40%, nanostructuring added further totaling to an overall 75% reduction. Similar reductions were observed in PbTe samples containing <3% Sb NPs, whereas similar fractions of Bi or Pb NPs had no influence. InGaAs (ErAs) is another example where 2-4 nm ErAs NPs were distributed in the InGaAs-matrix causing thermal conductivity to reduce to 1/3 of the bulk alloy value due to atomic scale defects, differences in mass or strain fields present in the alloy. Study of phonon transport in InGaAs (ErAs) concluded that though shorter wavelength phonons were effectively scattered in alloys, but the mid-to-long wavelength phonons scattered from the multi-dispersed NPs causing further significant reduction in lattice thermal conductivity. Similar improvement was noted in case of skutterudites and half-Heusler alloys, where nano inclusion resulted in thermal conductivity reduction (Vineis, et al, **2010**).

In a recent attempt (Vineis, et al, **2010**), hot sintering of nano powders was found to introduce nanostructuring involving grain sizes in the range of 5 nm–10 μm in polycrystalline samples. Here, the TE material was prepared using nano powders, which were hot pressed to form extensive interfaces between the compacted NPs that can significantly lower the thermal conductivity. Though, compacting nanocrystalline samples was certainly a low-cost and high volume production method for wider uses in TE technology, it had a major flaw that the complete removal of any binder used in the grinding, milling and wet processing for having almost 100% of the theoretical density after compaction was not possible practically and this in turn reduced the carrier mobility by orders of magnitude for just a few percent deviation in density resulting in significant lowering of *ZT*. Nonetheless, some interesting results were recently reported about *ZT* of 1.2 in case of bismuth telluride *n-type* materials prepared from pressed NPs. Similarly, a *ZT* of 1.2 was observed at room temperature and 1.4 at 100 °C from a ball-milled and hot-pressed *p-type* BiSbTe alloy. The ZT values were about 20 and 40% higher, respectively, than the comparable state-of-the-art ingot based BiSbTe-alloy (Vineis, et al, **2010**). Interestingly, the electrical conductivity of the nanostructured material was higher than the ingot material over the entire temperature range of 25-250 °C, while the Seebeck coefficient was higher above ~160 °C, yielding a slightly enhanced power factor for the nanostructured material above ~75°C. The large improvement in *ZT,* though, was primarily due to a greatly reduced thermal conductivity (Vineis, et al, **2010**), particularly at elevated temperatures. Similarly, boron-doped Si/Ge nano-composites, formed by ball milling and hot pressing, were also reported to exhibit significantly reduced thermal conductivities compared to bulk SiGe alloys (Vineis, et al, **2010**). In addition, the nano-composite materials had increased Seebeck coefficients and only slightly reduced electrical conductivities, resulting in somewhat higher power factors over the temperature range of 300–1000 K. The increased power factor for the nano-composite was similar to what was observed for the BiSbTe-alloy above and predicted based on electron filtering effects at the grain boundaries (Vineis, et al, **2010**). Primarily driven by reduced thermal conductivity, the nano-composite materials exhibited an enhanced peak in *ZT* at 0.72 at 1000 K compared to 0.6 for the bulk SiGe alloy. Polycrystalline $Ag_{0.8}Pb_{18+x}SbTe_{20}$ formed by mechanical alloying of elemental powders followed by densification through spark plasma sintering produced a material with ~20-nm-sized precipitates. With a compacted density of ~95% of the theoretical value, the *ZT* of 1.5 was measured at 673 K and it was only 10% lower than the value reported for the related material grown from the melt. The high *ZT* of the mechanically alloyed material is believed to result from the same nano-precipitate related lattice thermal conductivity reduction as the similar materials prepared from the melt (Vineis, et al, **2010**).

Thermal conductivities of nanowires and thin film superlattices are reduced to 0.25 W/mK ensuring *ZT* of ~2 at 700-800 K without needing any further increase in current power factors. Based on experimental and theoretical results as of date, it would appear ~0.25 W/mK is the lowest we might expect to achieve while still retaining a high power factor (Vineis, et al, **2010**).

Taking the thermal conductivity as a product of specific heat, velocity of sound and 1/3rd of average phonon mean free path, the thermal conductivity is lowest in an amorphous material, where phonon mean free path is of the order of the lattice constant. For a material with a low Debye temperature, the sound velocity is ~ 2000–4000 m/s and the specific heat is $\sim 2 \times 10^6$ $Jm^{-3}K^{-1}$. The lowest thermal conductivity is thus estimated to be ~ 0.25 -1 W/mK, which is confirmed by more sophisticated theories. Therefore, unless new physical concept is introduced, it is unlikely that one can lower the thermal conductivity much lower than this value (Vineis, et al, **2010**).

Recent reports of SLs prepared out of WSe_2/W layers, however, were quite intriguing as they suggested cross-plane lattice thermal conductivity values as low as 0.02 W/mK. While the mechanism is not yet fully understood (Vineis, et al, **2010**), it is quite likely that the layering created larger asymmetry in the directional phonon density of states and low coupling between phonons in different directions. It is unclear, though, whether this approach could be exploited while simultaneously achieving a high power factor for $ZT \geq 3$.

To reach *ZT* values of 3 or greater, it seems that further reduction in the thermal conductivity is though necessary but it will as such be insufficient; as some substantial improvement in the power factor are also required. Barring the welcome discovery of some new and unexpected single phase material with a *ZT* in this target range (Vineis, et al, **2010**), what is needed is to explore newer physical concepts on how to enhance the power factor by 2–4 fold in the existing leading materials. It addition, such increases must come mainly from enhancements in the thermo-power, as opposed to increases in the electrical conductivity (Vineis, et al, **2010**). With regards to thermal conductivity, any further reduction below the amorphous limit can only occur in case one could actively change the group velocity or reduce the number of phonon modes that propagate. This could result from coherent or correlated scattering effects, but so far this has remained elusive for phonons and thermal conductivity reduction through such mechanisms has never been conclusively demonstrated (Vineis, et al, **2010**). These observations indicate towards an exciting field of study by posing challenges to the researchers to come up with new scattering mechanisms and concepts that would help achieve very large increases in the power factor and simultaneous decreases in thermal conductivity (Vineis, et al, **2010**).

The prediction that the in-plane power factor could be substantially enhanced over that of homogeneous materials is yet to be realized. However, it is apparent that quantum confinement and nanostructure effects in thermoelectricity are not yet fully understood and they could still play a significant role in enhancing the power factor in case the proper conceptual framework is built. For example, it may be possible to use hot electron filtering in a bulk material with embedded NPs. The NP separation should preferably be less than the electron mean free path and with an appropriate potential barrier profile, the power factor could be enhanced without the need for a periodic structure or a uniform nanoparticle size distribution.

Recently, the concept of reversible diffusive electron transport in nanostructured TE materials was introduced (Vineis, et al, **2010**) as one of the means to improve the TE figure of merit. This approach aimed to minimize the irreversible effects in TE materials that limited their efficiency. The proposal included a fundamental thermodynamic argument for why the optimum density of states in a thermoelectric material was a delta function and how one could achieve energy-specific equilibrium between two reservoirs at different temperatures. This could be achieved via inhomogeneous doping or segmentation along the TE material. The electronic efficiency for thermoelectric cooling or power generation could thus approach the Carnot limit in case the electron transport between the hot and the cold reservoirs occurred in a narrow energy band under a finite temperature gradient and a finite external voltage. This was due to a decrease in electronic thermal conductivity by a significant reduction in the Lorenz number that relates thermal and electrical conductivities (Vineis, et al, **2010**).

One should finally note that as nanostructured materials in thermoelectric applications work under high temperatures and temperature gradients, it is important to study and optimize long-term stability, inter-diffusion and coarsening of nanostructures. This is still an open but significantly important consideration for useful TE device applications requiring thorough investigations of many of the nanostructured systems.

Two recent reports raised the hopes that significant increase in the power factor of PbTe might be forthcoming. Researchers have observed that large increase in the TE power factor at high temperatures was possible when PbTe was co-nanostructured with Pb and Sb. When Pb and Sb inclusions were present simultaneously throughout the matrix of PbTe, the mobility attained high values at temperatures ~700 K. This enhanced the power factors by as much as 80–90% over a similarly doped but not nanostructured PbTe sample. Why the mobility at high temperatures was higher in nanostructured PbTe when both Pb and Sb were simultaneously present but not when each of them was present alone, is still not clear and the mechanism of this behavior requires further study in detail. Another report confirmed that the incorporation of 2% Tl atoms in the Pb sub lattice of PbTe caused a distortion in the valence band density of states via a resonance state, which appeared to increase Seebeck coefficient and the power factor leading to $ZT \sim 1.5$ at 700 K. This was in agreement with theoretical predictions and also provided an impetus to move ahead (Vineis, et al, **2010**).

The recent decade has witnessed various significant advances in the field of TEs since 1950 as the barrier of ZT~1 has been scaled, and new materials, new concepts and enhanced understanding of the basic phenomenon involved have been explored to push the field forward in near future. The recent advances have raised the possibility of TE power generation and refrigeration for wider industrial usage instead of just small niche markets.

4. Discussions

Having gone through the brief description of device development activities primarily supported by NCs based solids prepared by chemical synthesis of the basic building blocks terminated by suitable ligands and further modified by linker molecules to ensure the desired inter-dot spacing in the ensuing superlattice structures, certain points clearly emerge as mentioned below in brief (Koppes, **2012**).

The capability of preparing monodisperse metallic, semiconducting and insulating NCs with reasonable control of size and shapes has been established in last two decades (Talapin, et al, **2010**; Koppes, **2012**). Preparing NCs with more than one constituent species as well as core-shell and/or core-multiple shells configurations is certain to add newer dimensions to the availability of a wide variety of building blocks needed in synthesizing more novel classes of materials in future (Koppes, **2012**). In addition, chemical conjugations of inorganic, organic, polymeric, phytochemical, and biomolecular species, demonstrated in recent past, is currently forcing the distinction to diminish between the synthetic molecules and natural species. This kind of chemical equivalence, once established under favorable conditions, would not only be explored for developing more green processes and products but also could be anticipated to provide some kind of genetic routes to modify the material properties as and when required in the long run. In this form the current dream of developing intelligent materials will be fulfilled practically. Further, it would be possible to get rid of the scare of using NCs in different configurations in medical applications would turn out to be more and more benign because of using natural molecules derived from plants as surface capping and linker species. Another significant advantage that will emerge from this kind of approach would be the better-targeted deliveries of various molecular species in form of conjugated NCs without causing undue concern for the associated toxicity as it is generally anticipated today (de Jong and Borm, **2008**).

In the domain of material synthesis, unlike what we witnessed in the 20th Century in acquiring spectacular capability of precisely handling the placement of single atoms at a time; the solution-grown technology of preparing and maneuvering a large class of nanocrystals introduced successfully has especially brought down the over all cost of the associated infrastructure and operating conditions involved therein (Talapin, et, **2010**; Koppes, **2012**). Employing fairly known chemical reaction kinetics based development of various synthesis protocols was initially not very successful practically in controlling the product quality but, later on with growing experience, especially relying more on the features like molecular recognition based site specific self-assembly and other related properties of the nanostructured entities are getting explored for their frequent uses in achieving the target specifications. The time is not very far off when autonomous control of chemical synthesis will be possible using intelligent features of the nanosize building blocks comprising of inorganic-organic-biomolecular species that will be available in near future.

Another important issue, which is slowly getting resolved with the further progresses made in studying the nanostructured species in more details, is that nanosize material species are not distinctly different from the micron size species due to mere difference in their sizes. Rather, quantum confinement of electrons and phonons provides altogether different energy states for modifying their responses to the externally applied electric, magnetic and electromagnetic fields. In the microworld of yesterday, the delocalized electrons and phonons supported in periodic lattice structures were put to use in realizing a whole host of discrete and integrated devices, circuits and systems and extensive use of scaling was employed for accommodating more and more number of components and devices per unit area of real state space on the substrate (Parviz, et al, **2003**). Currently, though, the fabrication technology has been advanced to successfully produce sub-10 nm devices but these devices still behave like a normal bulk device structure with well-defined classical features (Haron, et al, **2009**). Continued scaling of CMOS devices have been producing relatively smaller, faster, denser, and functionality richer electronic devices at lower cost throughout. However, the process of further scaling has entered a phase where physical gate length of these devices is already in the sub-10 nanometer scale invoking predominant quantum mechanical effects (ITRS-**2007**). In addition, the manufacturing of these extremely small size devices is not only becoming more cost intensive but also raising the problem of very high power dissipation and thus pushing the CMOS device scaling to its end in very near future (ITRS-**2007**; Iwai, **2004**; Chen, **2006**). Moreover, a mere reduction of size to nanometer level is not the real strength of nanomaterials. Rather, access to precisely controlled quantum confinement generated features of electrons and phonons in nanostructure species as well as their related hierarchical assemblies spanning from nm to cm scale will be more useful to explore in the domain of nanomaterials of tomorrow.

It could very well be noted from the discussions of the thermo-electric materials that certain features characteristics of nanostructuring were already present in the earlier studied alloys, solid solutions and superlattices resulting in improved performance in terms of reduced thermal conductivities but such features were practically vey difficult to realize reproducibly. Intentionally incorporating these features in nanostructured species is a more fruitful way to explore them in form of useful devices to be developed in future.

It has also been clearly noted in the previous discussions that the phenomena of quantum confinement of charge carriers superimposes certain restrictions in terms of allowed energy states that are added on top of the continuum states already present there due to the nature of the crystalline material used for preparing the QD (Talapin, et al, **2010**; Koppes, **2012**). These discrete energy states are not only appropriate for optical transitions resulting in size dependent optical properties but also the electrons occupying such states behave as if they are trapped. This means such electrons are not very good for conventional electronic conduction involving diffusion and drift phenomena in a classical sense. In case of bulk semiconductors, the impact of lattice symmetry causes energy band formation representing the collective behavior of electrons and phonons in a bulk sample. In this process, materials like silicon having indirect band gap are not appropriate for optical interactions, as the law of momentum conservation is not obeyed. In case of a direct band gap material, optical transitions are favored making the use of compound semiconductors popular in the area of optoelectronic devices (Ahmad, **1998**). In spite of having continuum states in direct band gap bulk semiconductors only certain energy states following the momentum conservation law allow the transitions due to optical radiations. But one distinction is there that such carriers are also available for drift/diffusion based transport in classical sense whereas in NCs the states responsible for optical transitions are hardly available for quasi-free charge carrier like behavior. Nevertheless, there is a way to introduce charge carrier transport through tunneling by introducing electrically transparent barriers in form of surface capping (Talapin, et al, **2010**). So, by controlling the inter-dot separation precisely, it is possible to control the electronic conductivity similar to the conducting polymers, which were found adequate for device applications. However, the charge carrier transport across surface capping ligands and linker molecules are certainly different from that of a homogeneous semiconductor that is already known. There are additional possibilities in NCs, for example, electrons and holes introduced can be separated from each other by providing band offsets at the interfaces of core-shell configurations. However, based on these discussions, it should not be presumed that the electrons present there in a NC do not respond to optical radiation in a collective mode. Surface Plasmon resonance is a distinct feature of metallic NCs, which has size dependent optical response over a wide range of spectrum. Plasmonic NC coatings applied on a solar cell have already been explored for enhancing the optical radiation harvesting resulting in improved power conversion efficiency.

In most of the current chemical syntheses in use, the reaction kinetics is predominantly influenced by a large variety of catalysts involving generally rare earth and noble metals, which are derived from a limited reserve and the rate at which modern chemical industries are using these catalysts, it is not going to last for long. Keeping this situation in mind, it is rather inevitable to look for better alternatives and in that context using biomolecular species, as catalysts, will be more attractive and economical proposition. Using a large variety of enzymes as catalyst will be a self-sustainable situation as compared to fast depleting reserve of rare earth and noble metals currently in use (Nestl, et al, **2014**). These possibilities are foreseen while observing the ligand specific interaction of NCs due to chemical affinities built in into the nature of certain species, which needs to be examined and catalogued for their use in form of a library. A combinatorial approach will be useful in this direction.

After understanding the basic differences between electron behavior in the bulk materials (Ahmad, **1998**) and the NCs (Talapin, et al, **2010**) made out of metallic, semiconducting and insulating materials, it is natural not to expect the similar performances on comparative basis from the devices realized from NC solids as can be seen from the results presented in brief in this review. Certain performances observed in NC-based devices are not possible in bulk-based devices and vice versa. Therefore, while exploring for the future applications, it has to be kept in view that these NC based devices would be useful for certain special niche applications.

With the availability of monodisperse NCs, the next step will be to assemble them into hierarchically ordered crystalline structures where the constituent nanocrystals play the role of artificial atoms. While some progress has been made along these lines in the field of NCs in the past, additional levels of control are expected in the coming decades (Hersam and Weiss, **2010**). Through the processes of self-assembly and directed assembly of nano-constituents of distinct properties, the next-generation nano-composite materials will have the unique and powerful attributes of independent tunability of previously coupled material parameters. For example, high conductivity bulk materials typically possess higher thermal conductivity. These properties are certainly being examined for their independent control in the next-generation nanocomposites. This specific example has applications in TE devices that convert waste heat into useful electricity (Hersam and Weiss, **2010**). The decoupling of electrical conductivity and optical reflectivity will, similarly, result into a new class of transparent conductors, which would serve as the basis of photovoltaic and display technologies of future (Hersam and Weiss, **2010**).

Biological systems possess a number of unique and more complex features that are not currently possible to realize to that extent in most of the engineered nanomaterials. This includes features like hierarchical, non-equilibrium, self-healing, reconfigurable, and defect-tolerant configurations with optimized interactions between organic and inorganic media. It is anticipated that in the coming decades it will be fruitfully possible to emulate various combinations of these features in nano-composite materials (Hersam and Weiss, **2010**).

In order to broaden the scope of nanocomposites, a whole host of superlattices comprising of a variety of semiconducting, metallic, magnetic, ferroelectric, dielectric and other species of NCs would possibly be combined in a variety of ways to realize smart and intelligent meta-materials in future. For instance, magnetic and semiconducting NCs based superlattices show promise for magneto-optic data storage and spintronic devices. Similarly, employing two different semiconductor NCs in a superlattice, a number of useful material combinations can be prepared for a new generation of solar PV and TE devices. Binary superlattices are currently emerging as useful candidates for designing novel and efficient catalysts having precise catalytic centers (Murray). This approach of binary superlattices is currently being extended to have hierarchical structures with multiple varieties of NCs for their future applications. The list of most often studied metallic and semiconducting NCs include - Au, Ag, Pd, and Pt; ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgSe, PbS, PbSe, and PbTe, respectively. The monodisperse NCs of Co, Ni, Fe, FePt, CoPt, $CoPt_3$, Co/Ni, Fe_2O_3, Fe_30_4, $MnFe_2O_4$ and $ZnFe_2O_4$ are magnetic species while CoO, NiO and Cr nanocrystals are antiferromagnetic in nature. Ferroelectric and high dielectric nanocrystals involving $BaTiO_3$ and $SrTiO_3$ have also been studied in this context (Talapin, et al, **2010**).

The future challenge primarily lies in understanding the chemical reactivity of the precursors for their applications in self-limiting growth of a monolayer shell of atoms at a time. Having acquired this precision, it will be possible to synthesize real artificial atoms for designing synthetic materials of tomorrow. It is further anticipated that when electro-active, optically active or biologically active ligands are employed in modifying the NC surfaces, completely newer avenues will be opened with immense applications (Murray).

For the development of devices already included in the discussion in this review as well as many such applications such as those emerging in the area of foldable electronic displays the technological aspects of related properties should also be developed simultaneously. The basic characteristic features of a large variety of NCs should be examined in detail before selecting the appropriate species and then the application of the chosen ones should be made using the features of biomimetic processes, which are at times very helpful in rendering the processes green and economical. It is true that in the microelectronics development of the last Century, first of all, the sources of impurities, inhomogeneity and process introduced variations were minimized to start with. Thereafter, precisely controlled amount of impurities were reintroduced along with some appropriate structural modifications using very high precision processes and mostly using high and ultrahigh vacuum environment once again to restrict the interactions of the unwanted species from the environment (Ahmad, **1998**). In contrast, while synthesizing and manipulating NCs, the medium of synthesis being some liquid eliminates the influence of the external environment in a very effective way besides the size of the NCs does not allow most of the impurities to stay therein. This is the prime reason that conventional doping of impurities in NCs has not been that successful as compared to that in the bulk materials. Now, understanding the basic process of nucleation and growth and chemical conjugations arising due to extremely active surfaces of the nanocrystals under consideration it is becoming possible to grow real artificial atom like NCs for synthesizing much more complex hierarchically ordered structures for their further applications in diverse fields. So, the current Century development of nanomaterials is going to evolve around liquid media high precision material growth and structural syntheses in contrast to that of single crystals of 20th Century that led to microelectronics revolution. A number of spectacularly novel developments are awaited from the ongoing developments in the area of nanoscience and technology synergized from the conceptual developments of other areas like molecular biology and biotechnology.

5. Conclusions

Solvent based synthesis of metallic, semiconducting and insulating nanocrystals has reached to level where nanocrystals based thin films and solids are showing promising results in the domain of electronic, optical, optoelectronic and memory devices. More refinement through better control of purity and processes are expected to give still better performing devices with more impressive device behavior. The current level of success attained in synthesizing band-structure-engineered nanocrystals has generated enough confidence among the research community to extend this attempt towards integrating nanocrystals based devices with those belonging to the mainstreams of the microelectronics and microsystems in fairly advanced states.

While examining the possible emergence of another revolution in large-scale displays and flexible electronics, where solution synthesized nanocrystals based band-structure-engineered nanomaterials find better acceptance, it is rather too early to comment as many outstanding problems like material instabilities due to environmental interactions and poor quality of charge carrier transport need proper solutions.

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