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| TITLE OF PROPOSED PROJECT Silicon and Germanium Quantum Dot Films for Photovoltaics | | | | | | |
| REQUESTED AMOUNT \$ 367,000 | | PROPOSED DURATION (1-60 MONTHS) 36 months | | REQUESTED STARTING DATE 10/01/07 | | SHOW RELATED PRELIMINARY PROPOSAL NO. IF APPLICABLE |
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CERTIFICATION PAGE

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In addition, if the applicant institution employs more than fifty persons, the authorized official of the applicant institution is certifying that the institution has implemented a written and enforced conflict of interest policy that is consistent with the provisions of Grant Policy Manual Section 510; that to the best of his/her knowledge, all financial disclosures required by that conflict of interest policy have been made; and that all identified conflicts of interest will have been satisfactorily managed, reduced or eliminated prior to the institution's expenditure of any funds under the award, in accordance with the institution's conflict of interest policy. Conflicts which cannot be satisfactorily managed, reduced or eliminated must be disclosed to NSF.

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Silicon and Germanium Quantum Dot Films for Photovoltaics

The *vision* of this proposed project is to perform the basic research required to develop efficient, low-cost solar cells from silicon (Si) and germanium (Ge) quantum-confined nanocrystals (quantum dots). The proposed research ultimately aims at enabling the manufacture of multi-junction solar cells from conductive films of size-controlled, electrically doped Si and Ge quantum dots, in which different quantum dot layers will absorb different ranges of the solar spectrum, as determined by the quantum dot size. Among the potential advantages of Si and Ge as materials for solar cells are their non-toxicity, lack of environmental hazard, stability, and abundance. Hardly any other quantum dot material offers this range of desirable attributes.

The proposed research has four objectives: 1) The development of gas- and liquid-phase routes for the assembly of conductive films of Si and Ge quantum dots, and the determination of the mechanisms governing the films' electrical conduction; 2) the electrical doping of Si and Ge quantum dot films and the study of their electrical properties; 3) the detailed investigation of the basic optical absorption properties of systems of non-interacting and interacting quantum dots, which will be either doped or undoped; and 4) the evaluation of junctions formed from *p*- and *n*-doped films of Si and/or Ge quantum dots with respect to their photovoltaic capacity, and the detailed characterization of the physical properties of such *p-n* junction devices.

The Si and Ge quantum dot synthesis will rely on a high-yield nonthermal plasma synthesis approach previously developed in the principal investigator's laboratory, which is already being commercialized by an industrial partner. Liquid- and gas-phase approaches will be employed to functionalize the quantum dot surfaces. Subsequently, quantum dots will be assembled into unordered and ordered films and electrical characterization using field effect transistor test devices will reveal the films' electrical properties. Quantum dots will be doped by introducing impurity precursors during the plasma synthesis; electrical studies of films of doped quantum dots will elucidate whether the impurities have been incorporated and become active. Optical measurements on non-interacting quantum dots in dilute systems and on densely packed films, in which the quantum dots do interact, will characterize the quantum dots' absorption properties. Junctions of *p*- and *n*-doped Si and Ge quantum dot films will be fabricated and standard solar cell characterization methods will quantify their photovoltaic capacity. This set of studies is innovative in that none of these studies has been reported for Si and Ge quantum dot films.

The *intellectual merit* of this project lies in new methods to form conductive films from Si and Ge quantum dots that will be developed through the proposed research. This project will also elucidate how electrical doping of Si and Ge quantum dots can be achieved and how doping affects the electronic and optical properties of quantum dot films. Finally it will develop, for the first time, solar cells made exclusively from Si and/or Ge quantum dot films.

The *broader impacts* of this project are significant. The proposed research may ultimately enable a new approach to the manufacturing of low-cost multi-junction quantum dot solar cells, which may have the potential to become a disruptive new solar technology for more environmentally benign and sustainable energy production. Leverage provided by an NSF-IGERT for "Nanoparticle Science and Engineering" will enhance educational opportunities for graduate students supported by this project. The involvement of at least two graduate students and minority undergraduate students will foster the integration of research and training, and the participation of underrepresented groups. Outreach collaboration with the Science Museum of Minnesota will communicate results of this research to a broad public. A close collaboration with an industrial partner, Innovalight, Inc. will ensure rapid knowledge transfer to industry.

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I. Introduction

a) Perspective

Even by conservative estimates, the world need of primary energy is expected to roughly double by 2050, reaching a level of ~30 Terawatts (TW).^{1,2} As discussed by Hoffert *et al.*,¹ if this need is to be met while stabilizing the atmospheric carbon dioxide level at 550 ppm—twice the pre-industrial level—15 TW of carbon-free energy will be needed.

This daunting goal could be achieved either by installing 15,000 1-GW nuclear power plants by 2050, roughly one reactor every day for the next 43 years, or by installing 20 km² of 20%-efficient solar cells every day over the same period of time. If 20%-efficient solar cells could be manufactured based on a 1 μm thick layer of silicon or germanium quantum dots (Si QDs, Ge QDs), it would require ***QD production at a rate of 50 tons per day***. Even if these examples are unrealistic in that they consider the use of only a single carbon-free energy source, they clearly define the grand challenge for future photovoltaic (PV) devices. Future solar cells need to be based on materials that are:

- environmentally benign and non-toxic,
- stable over extended periods of time,
- inexpensive and abundant, and
- economically manufacturable.

b) Vision, Opportunity and Feasibility

Multi-junction solar cells, also called tandem cells, in which different portions of the solar spectrum are preferentially absorbed by a series of p-n junctions with different band gaps, are the most developed approach for achieving high-efficiency solar cells. While the theoretical efficiency limit for a single junction cell is ~30%,³ the limit for a quadruple junction cell is ~55%.⁴ Quantum dots are interesting materials for multi-junction solar cells, as their band gaps can be tailored via the QD diameter, with smaller particles having larger band gaps as a result of quantum confinement effects.^{5,6} Developing multi-junction cells based on close packed arrays of Si and Ge QDs, such as sketched in Fig. 1, would be highly attractive, since Si and Ge meet the above mentioned materials requirements.

Our vision is *to perform the enabling research to develop photovoltaic cells based on arrays of Si and Ge QDs, assembled from solution or the gas phase, which have high electrical conductivities and tunable band gaps from the near infrared (0.7 eV) into the visible range of the spectrum (>2 eV).*

While this vision is aggressive and possibly revolutionary, a number of key elements have been demonstrated that, when considered together, support the feasibility of this vision:

1. Green's group, which holds several "world records" for the highest efficiency crystalline Si solar cells,⁷ recently proposed the concept of all-Si multi-junction cells based on Si QD arrays.^{8,9} The group reported measurements of dark conductivities of Si QD arrays embedded in silicon dioxide (SiO₂) that matched those of high-quality amorphous Si,^{9,10} the current benchmark material for low-cost solar cells.
2. The use of QD arrays as high-quality "artificial semiconduc-

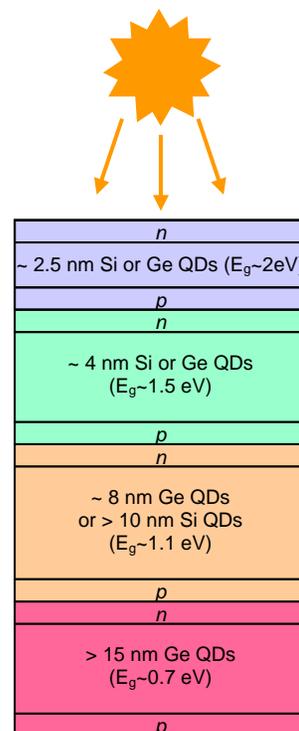


Figure 1. Schematic of a quadruple junction Si/Ge QD solar cell.

tors” has recently gained significant credibility with the demonstration of high conductivities and mobilities of solution-assembled lead selenide (PbSe) QD arrays by Talapin and Murray,¹¹ exceeding the properties of high-quality amorphous Si films.

3. Fujii and coworkers demonstrated that it is possible to dope Si QDs both *p*- and *n*-type and that the dopants become electrically active.¹²⁻¹⁴
4. Our group has recently developed a unique low-pressure plasma synthesis approach for efficient production of Si and Ge QDs.¹⁵ This approach has been licensed by the University of Minnesota to Innovalight, Inc., St. Clara, CA, a company that is working to commercialize this synthesis route to manufacture Si QD solar cells.
5. Our group has developed surface passivation techniques that allow one to prepare stable colloidal solutions of Si and Ge QDs. The excellent passivation of surface defect states is evidenced by our ability to achieve photoluminescence quantum yields > 60%.¹⁶

Given these recent exciting developments, we strongly believe that all the pieces necessary to realize our vision through targeted research are in place.

II. Scientific Questions and Objectives

The overall goal of the proposed research is to *perform the enabling research* necessary to develop Si and Ge QD films with good electrical properties and tunable absorption for low-cost *p-n*-junction-based multi-junction solar cells. To achieve this goal, **the objectives of the proposed work are to study and answer the following basic scientific questions:**

1. Can Si and Ge QDs be assembled to form *conductive QD films*? If so, which approach produces films with the best electrical properties? What are the conduction mechanisms in these films?
2. How will doping the Si and Ge QDs affect the electrical properties of QD films? Can QDs be doped using approaches consistent with low-cost manufacturing of solar cell materials?
3. What are the fundamental optical properties and, in particular, the absorption cross sections of Si and Ge QDs? How do these properties change in dilute and dense systems, and as a function of the QD doping?
4. Will charge carriers separate across junctions formed from *p*- and *n*-doped Si and Ge QD films? Will such junctions produce a photovoltaic effect?

While the emphasis of the proposed work will be on fundamental studies focusing on questions 1-3, we feel that testing Si and Ge QD films in an actual PV device to address question 4 will be a logical final step of the proposed research.

III. Results from Prior NSF-Support

IRG-Seed Grant from University of Minnesota Materials Research Science and Eng. Center, DMR-0212302: “Nanoparticle-based Materials,” PI: U. Kortshagen, with 6 co-P.I.s, Award: \$500,000, 01/01/2004-12/31/2006.

Under this MRSEC IRG-seed grant, Kortshagen’s group has focused on developing a technique that exploits the unique properties of nonthermal plasmas to synthesize controllably semiconductor nanocrystals, including Si and Ge QDs.¹⁵ This approach improves on some of the drawbacks of other synthesis methods that make them unsuitable for forming Si and Ge QD films for large-scale, low-cost solar cell manufacturing. In particular, liquid-phase approaches¹⁷⁻³⁰ are time-intensive and often have small mass yields; solid-phase methods³¹⁻³⁹ produce QDs embedded in solid-state matrices, which limits the flexibility in QD processing; and gas-phase

processes⁴⁰⁻⁵⁰ can offer high mass yields but are often affected by particle agglomeration, which may annihilate some of the desired size-dependent properties of QDs.⁴⁴

The plasma approach developed by Kortshagen's group differs from other aerosol processes in that the precursor gas is dissociated at low gas temperatures (~300-600 K) through the impact of very hot electrons (~30,000-50,000 K). This pronounced nonequilibrium environment provides two unique advantages for QD synthesis:

1. Due to the much higher mobility of electrons in the plasma compared to that of the ions, particles immersed in plasmas are usually unipolarly negatively charged, which charge **prevents or strongly reduces nanoparticle agglomeration.**^{51, 52}
2. As a result of highly exothermic reactions at particle surfaces and slow heat transfer at low pressures, particle temperatures in nonthermal plasmas often exceed the gas temperature by several hundred Kelvin. This allows for the **production of high-quality nanocrystals within a few milliseconds** of plasma exposure at gas temperatures close to room temperature.^{15, 53}

A schematic of our plasma reactor is shown in Fig. 2. A precursor gas such as silane (SiH₄) or germanium tetrachloride (GeCl₄) entrained in an argon or helium buffer enters a flow-through reactor. A plasma about 3-5 cm long is created in a 6-12 mm inner diameter quartz tube by applying ~20-80 W of radiofrequency power at 13.56 MHz to a ring electrode pair. The typical operating pressure is ~200-300 Pa. The gas flow in the system is adjusted such that the residence time of particles in the plasma zone is on the order of 2-20 ms. The residence time is the main parameter affecting the particle size, with longer residence times leading to larger particles. Fig. 3(a) shows Ge QDs synthesized with this plasma process and collected on a transmission electron microscope (TEM) grid. The particles are crystalline and their size distribution has a standard deviation of ~15-20% of the mean size (measured by TEM). The electrostatic repulsion among particles in the plasma enables operating this reactor at high mass loadings. In initial tests, we achieved mass yields of 50 mg/hr—to our knowledge the highest yield reported to date.

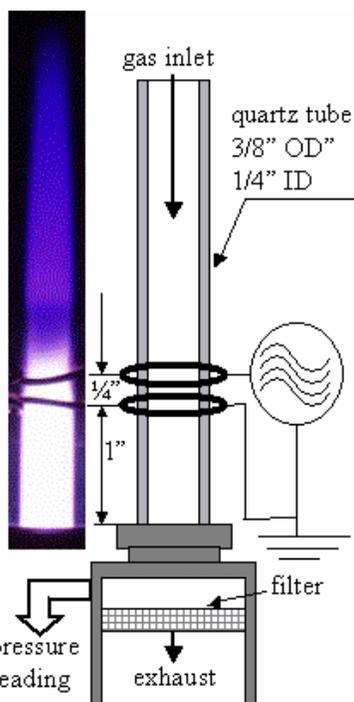


Figure 2: Schematic of experimental apparatus with digital picture of the argon-silane discharge during operation.

Our plasma process was licensed by Innovalight, Inc., which after preliminary scale-up efforts, routinely produces Si QDs at rates of g/hr with bench-top-scale reactors.

The tunable band gap of Si and Ge QDs is crucial for their use in multi-junction solar cells. Si QDs produced with our approach have demonstrated size-tunable band gaps that range from the bulk band gap of 1.1 eV up to about 2.1 eV, as evidenced by photoluminescence spectra with emission wavelengths as short as 600 nm.¹⁶ Similarly, Fig. 3(b) demonstrates the tunable band gap of Ge QDs. While observing a shift of the absorption edge in the infrared is not always easy, Fig. 3(b) shows the blueshift of an absorption feature at 260-280 nm, which was assigned by Wilcoxon *et al.* to a direct transition at the *X* point of the Ge band structure.²⁵ In bulk Ge, this feature would occur at 290 nm. Reducing the Ge QD size to 7 nm and 5 nm shifts this feature to 280 nm and 260 nm, respectively, which indicates the widening of the Ge QD band gap through enhanced quantum confinement.

In addition to the synthesis of Si and Ge nanocrystals our group has developed a suite of surface functionalization techniques for QDs.¹⁶ In a liquid-phase reaction scheme known as hydrosilylation (hydrogermylation),⁵⁴ organic

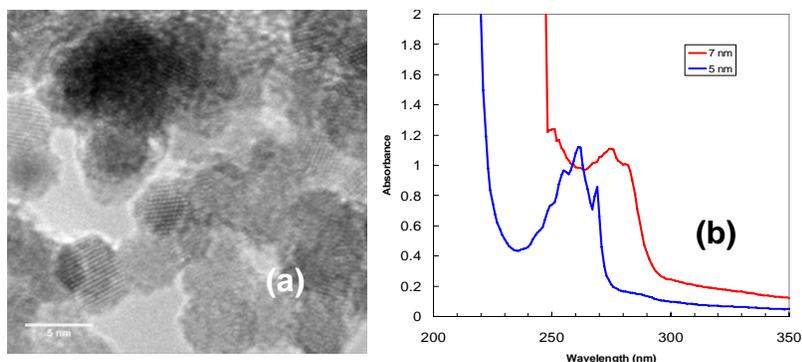


Figure 3: Ge QDs synthesized with the nonthermal plasma approach. (a) TEM image showing a relatively monodisperse distribution of small crystallites. (b) Blueshift of absorption features with the shrinking of the nanocrystals, indicative of a widening band gap.

“QD ink.” A stable colloidal dispersion of Ge crystals is shown in Fig. 4(a). It is interesting to note that Ge nanocrystals drop-cast from a colloidal suspension have a strong tendency to form self-assembled glassy (i.e., long-range disordered) films. Fig. 4(b) shows a self-assembled monolayer of ~ 8 nm Ge QDs that were surface functionalized with 1-dodecene and drop-cast from a toluene solution onto a TEM grid. Fig. 4(c) shows that the ~ 8 nm QDs are separated by spaces of ~ 2 nm, which corresponds to the thickness of about two layers of the passivating 1-dodecene molecules. We have now successfully demonstrated these reactions with various alkenes, alcohols, amines, and organic acids.

We still need to assess the electrical properties of the self-assembled monolayers produced from solution. However, in other preliminary work, we have studied the conductivities of gas-phase-assembled networks of Ge nanocrystals. Fig. 5 shows a schematic of the electrical analysis of gas-phase deposited Ge QD networks. Two aluminum (Al) contacts, 100 nm in thickness and separated by a 0.1 mm gap, were evaporated onto high electrical resistivity Corning 1737 glass. Ge QDs were deposited onto these substrates from the gas phase for several minutes up to an hour. A low-density, “fluffy” network of Ge QDs is formed through agglomeration of individual QDs during deposition, which is stabilized by spinning on styrene and polymerizing it at above 80°C . This styrene encapsulated network of Ge QDs (Fig. 5b) can be up to $1\ \mu\text{m}$ thick. Current-voltage characteristics of such a device and a control device with a pure polystyrene film are shown in Fig. 5(c), both under simulated Air-Mass 1.5 solar irradiation and in the dark. The conductivities obtained from these low-density networks of QDs are photosensitive and surprisingly high. For the sample shown in Fig. 5(c) the conductivity was $\sim 10^{-5}\ \text{S cm}^{-1}$, ap-

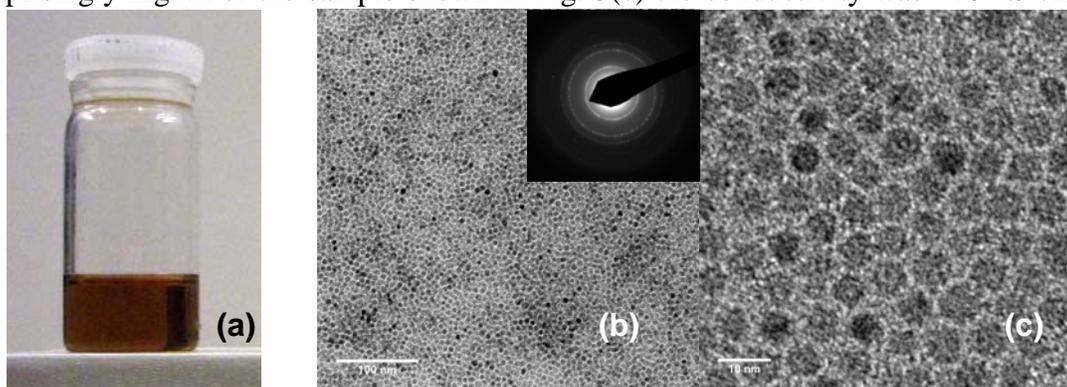


Figure 4. (a) Colloidal 1-dodecene-capped Ge QDs in toluene. (b) and (c) A self-assembled monolayer of ~ 8 nm Ge QDs. The nanocrystals were passivated with 1-dodecene, dispersed in toluene, and drop-cast on a TEM grid.

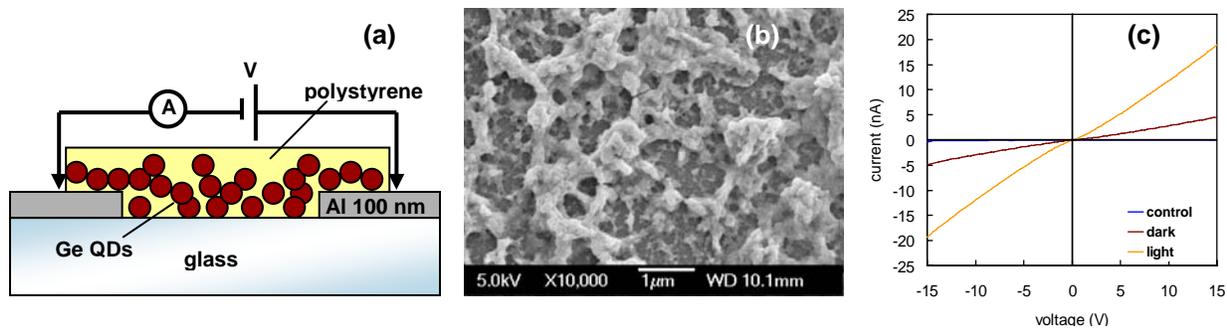


Figure 5. (a) A device for conductivity measurements of Ge QD networks. (b) Morphology of gas-phase-deposited Ge QD film after spin-coating of polystyrene. (c) Current voltage characteristics. Note that the control sample (without particles) is so resistive that the instrument baseline is tested. The currents with Ge particles are reproducible between different samples.

proaching the light conductivity of high-quality amorphous Si—the “gold standard” for low-cost electronic films—of $\sim 10^{-4} \text{ S cm}^{-1}$. Our preliminary results are thus very encouraging, particularly since the low QD density of the films was not accounted for in our conductivity calculations.

Support from Kortshagen’s portion of this IRG-seed grant has resulted in seven journal publications,^{15, 16, 55-59} two patent applications, four invited lectures at conferences, and more than ten conference contributions. Three graduate students, among them one female student and one minority student, were in part supported by this grant.

IV. Proposed Research

a) Conductive Si and Ge QD Films

Background: Assembly of QD films with high electrical conductivities, as would be required for solar cells, has proven to be far from trivial. According to Collier *et al.*,⁶⁰ the electrical properties of QD lattices are determined by three characteristics: the QD charging energy, the QD-QD interaction, and the spatial order within the QD lattice. These characteristics are primarily determined by the QD material and size, the interparticle spacing, and the chemical nature of the shell surrounding the QDs.

While achieving highly conductive QD films has been a challenge until recently, a host of conduction mechanisms has been identified in QD arrays. Tunneling conduction may be the dominant mechanism at low temperatures or for small interparticle spacings.⁶⁰ At higher temperatures, some sort of activated hopping conduction may occur. The idea of hopping conduction by thermal excitation of an electron from an occupied state below the Fermi energy level to a nearby state was first introduced by Miller and Anderson.⁶¹ Mott pointed out that hopping will not usually occur to the closest available site, but to the site that provides the best compromise between the required hopping energy and tunneling probability (variable range hopping, VRH).⁶² A model of VRH shows that the electrical conductivity σ depends on the temperature as $\sigma \propto \exp(-(T_0/T)^\nu)$, with T_0 a materials constant and $\nu = 1/4$ for a three-dimensional system. Efros and Shklovskii later pointed out that it was essential to consider the Coulomb interaction between electrons, which led them to find a similar dependence $\sigma \propto \exp(-(T_0/T)^\nu)$ with $\nu = 1/2$ for a three-dimensional system (Efros-Shklovskii VRH, or ES-VRH).⁶³ Another conduction model, which is cited in the QD films literature, was derived for percolation transport in granular metal-insulator films.^{64, 65} This model assumes thermally activated tunneling between metal particles embedded in an insulating matrix and yields the same temperature dependence as ES-VRH ($\nu = 1/2$); however, the value of T_0 is often very different.

Some of the initial work on conductive nanoparticle films was conducted with colloidal metal particles, in particular silver (Ag). Achieving high conductivities in such films soon turned

out to be a challenge. Several groups reported that the interparticle spacing,⁶⁶ the dispersion of the size distribution,⁶⁷ and the long-range order of the films are important factors controlling the electrical properties.⁶⁸ Studies of electrical conduction in arrays of semiconductor nanocrystals have mainly focused on chalcogenide semiconductors such as CdSe and PbSe. Close-packed three-dimensional arrays of CdSe QDs passivated with various ligands were studied by Bawendi's group.⁶⁹ The authors observed photoconductivity in these arrays, and showed that annealing of the QD films led to a significant increase in their dark conductivity,⁷⁰ which they attributed to a transformation of the organic cap and a shrinking of the interparticle distance.

Breakthrough electrical conductivities of up to $0.6 \times 10^{-2} \text{ S cm}^{-1}$ and mobilities of up to $0.8 \times 10^{-2} \text{ cm}^2/\text{Vs}$ were first achieved in CdSe arrays by the group of Guyot-Sionnest using a method known as cross-linking.^{71, 72} The authors cross-linked CdSe QDs with conjugated molecules (1,7-heptanediamine, or 1,4-phenylenediamine) and added electrons to the QDs by doping them with potassium or immersing them in an electrolyte.

More recently, Talapin and Murray reported a method to turn initially poorly conducting PbSe QD arrays into highly conductive materials with very high mobilities.¹¹ They assembled highly ordered arrays of oleic-acid-capped 8-nm PbSe QDs with initial conductivities of $\sim 1 \times 10^{-11} \text{ S cm}^{-1}$. Subsequent hydrazine treatment led to a removal of the surfactants and a shrinking of the interparticle distance, causing the electrical conductivity to increase by *ten orders of magnitude* up to $\sigma \sim 1 \times 10^{-1} \text{ S cm}^{-1}$ with electron and hole mobilities of 0.9 and 0.2 cm^2/Vs , respectively. The electrical properties of these PbSe QD films far exceed those of amorphous Si ($\sigma \sim 10^{-4} \text{ S cm}^{-1}$, mobilities $\sim 1 \text{ cm}^2/\text{Vs}$), and are likely favored by the excellent properties of bulk PbSe ($\sigma \sim 10^2 \text{ S cm}^{-1}$, mobilities $\sim 10^3 \text{ cm}^2/\text{Vs}$).⁷³ The hydrazine treatment also led to an apparent *n*-doping of the PbSe QDs, which could be transformed to ambipolar and then to *p*-doping through vacuum-heating removal of the hydrazine. High conductivities in oleic-acid-capped PbSe films were also observed by Romero and Drndic after annealing of the films at 523 K.⁷⁴

A few studies have investigated electrical conduction in Si and Ge QD arrays prepared by pulsed laser ablation,⁷⁵ co-sputtering,^{76, 77} plasma synthesis,^{78, 79} or derived from porous Si.⁸⁰ A common theme among these studies was that they focused on Si and Ge QDs that either were formed in a silicon oxide (SiO_x) matrix^{76, 77} or were terminated with a SiO_x shell by other means.^{75, 78, 79} Due to the large band gap of SiO_2 , an oxide shell presents a large tunneling barrier for charge carriers. Correspondingly, conductivities found in all these studies were low, generally, below $< 10^{-6} \text{ S cm}^{-1}$, suggesting Si and Ge QDs embedded in or capped with SiO_2 are unsuitable for forming highly conductive QD films. Green's recent studies, which suggest that inorganic matrix materials with a smaller band gap than SiO_2 —such as SiC or SiN_x —might be more suitable,⁸¹ support this conclusion.

Talapin and Murray¹¹ observed that a slight loss of quantum confinement accompanies the increase in conductivity which results from decreasing interparticle distance and increasing QD-QD coupling. Thus, it may be expected that any approach to achieve highly conductive QD films will have to balance film conductivity and QD quantum confinement, so that the tunability of the band gap is not lost. While our crude first attempts at forming Ge QD films yielded promising conductivities as high as $\sim 10^{-5} \text{ S cm}^{-1}$, the Ge QDs were in direct contact, likely causing an almost complete loss of quantum confinement. In this context, Van Buuren and coworkers reported that quantum confinement in densely packed layers of Ge QDs can be completely restored by grafting very short ligands such as methanol (CH_3OH) onto the Ge QD surfaces.⁸² Talapin and Murray argued that the high conductivity of their PbSe films was a consequence of the small interparticle spacing achieved with hydrazine (N_2H_4) treatment combined with the large Bohr exciton radius of PbSe ($\sim 23 \text{ nm}$), which they assumed caused a strong overlap of the QD wave-

functions.¹¹ While the Bohr exciton radius in Si QDs is rather small (~5 nm),⁸³ Ge QDs have a larger Bohr radius of ~24 nm.⁸⁴ Hence, Ge QDs functionalized with short ligands may exhibit electrical properties similar to those of the PbSe QD films of Talapin and Murray.¹¹

Hypothesis: Our working hypothesis is that *dense, solution- or gas-phase-assembled films of Si and Ge QDs, whose surfaces are functionalized with short organic ligands, may exhibit high electrical conductivities and charge carrier mobilities, and that the charge carrier transport mechanisms may depend on the QD size distribution and the ordering of QDs in the films.*

Proposed Research: One advantage of our synthesis approach is that it produces freestanding Si and Ge QDs in the gas phase which opens up a wide spectrum of options for surface functionalization and assembly of the QDs. QDs can be used with bare surfaces, or be functionalized with organic or inorganic shells in the gas or liquid phases. QD films can be formed by direct gas-phase deposition or liquid-phase assembly.

Our research approach is outlined in Fig. 6. QDs will be synthesized using our plasma process and will either be collected for surface passivation in the liquid phase, with which we have significant experience,^{16, 55, 56} or fed into a second low-pressure plasma reactor for gas-phase functionalization. While liquid-phase surface functionalization leads to an excellent surface coverage with organic ligands, as indicated by the excellent optical properties found with this approach,¹⁶ the grafting of very short ligands may be a challenge,⁸⁵ since it is difficult to overcome the van der Waals forces between agglomerated particles with short molecules. However, as the requirements for the surface coating with ligands to remove potential surface states are currently unknown, a study of films of liquid-phase functionalized QDs is essential. A range of ligands with different lengths will be investigated to determine the influence of interparticle spacing in QD films on both conductivity and quantum confinement.

Plasma-assisted surface functionalization may be able to overcome the problem of attaching short ligands to QDs, since the surface reactions proceed in the gas-phase where QDs are still isolated (not agglomerated). In initial trials with plasma grafting of organic ligands onto Si nanocrystals, we have successfully functionalized Si QDs with dodecane, 1-dodecene, hexene, and acrylic acid.⁸⁶ Si QDs were injected from the synthesis plasma into a second plasma in which the organic precursor was introduced as a vapor in an argon stream. Radicals of the ligand molecules are formed by electron impact activation which react with the Si QD surfaces. Si QDs

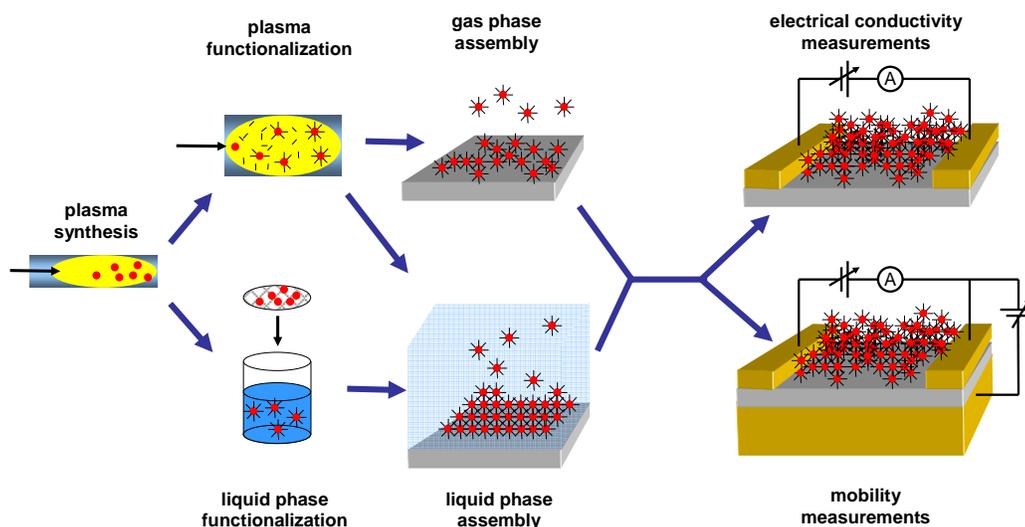


Figure 6. Schematic of the QD film assembly and characterization process.

collected in powder form become readily soluble in nonpolar solvents (or polar methanol in the case of acrylic acid). As seen in Fig. 7, Si QDs are nonsoluble without plasma surface functionalization, but they form a clear solution after plasma grafting of 1-dodecene.

The functionalized Si and Ge QDs will then be assembled either from the gas phase or the liquid phase. Gas-phase assembly is an option following gas-phase functionalization of QDs and will involve depositing QDs on suitably prepared substrates. While we have noticed that gas-phase deposition leads to low-density QD networks, we have also noticed that the QD films become significantly more compacted when a solvent is either dropped or spun onto the sample and allowed to evaporate. Agglomerates are likely compacted by the surface tension of the evaporating surrounding liquid. We will study whether further densification can be achieved through multiple solvent-compaction cycles, multiple deposition-compaction cycles, or possibly ultrasonication in a solvent. The fact that respectable conductivities were already achieved with our first crude trials makes us hopeful that significant improvements are still possible. Embedding QDs in inert polymer matrices such as polystyrene will also be an essential part of our QD film fabrication process, particularly for the less dense gas-phase-deposited films. We expect that for Si and Ge QDs, which quickly form a large band gap surface oxide when exposed to air, a polystyrene film may stifle oxidation that would otherwise hinder QD-to-QD charge transport.

Both gas-phase- and liquid-phase-functionalized QDs will also be assembled in the liquid phase. Again, initial trials shown in Fig. 4 have revealed the tendency of surface-functionalized Ge QDs to self-assemble. There are well-documented procedures in the literature to achieve close-packed three-dimensional assemblies of QDs.^{69, 87, 88} We may find, as others have in the past,⁶⁷ that the electronic properties of an ordered (crystalline) assembly may be superior to an unordered (glassy) film. The QD size distribution, which will be characterized by TEM and atomic force microscopy (AFM), may have a significant influence on the ordering of the QD films during liquid-phase assembly. If our QD size distribution proves too polydisperse to achieve ordered assemblies, we will use some of the well-documented colloidal methods such as size-selective precipitation to narrow the distribution.⁸⁹ The ordered character of our assemblies will be analyzed with small angle X-ray scattering (SAXS), which will also provide information about the size distribution and the interparticle spacing.⁸⁸

Electrical characterization of the QD films will focus on measuring the films' electrical conductivity and charge carrier mobility. The conductivity will be determined by depositing QD films onto substrates with pre-deposited electrodes (Fig. 5). We currently utilize microfabricated substrates with 100 nm thick electrodes separated by gaps of 5-100 μm . Mobility measurements will be performed by using samples in which a highly doped Si substrate acts as a gate electrode, which is separated from the two electrodes (source and drain) by a thermally grown oxide insulating layer. By depositing QD films between the electrodes, field-effect transistors will be formed. The charge carrier mobility can be deduced from analyzing the transistor characteristics, as described in detail in the supporting information of ref.¹¹ Electrical measurements will be performed in a cryostat at temperatures ranging from room temperature to cryogenic temperatures. By studying the films' conductivity as a function of the temperature, we will be able to identify the conduction mechanism, as discussed above. Simultaneous studies of the conduction mechanism and structural properties (film order, interparticle spacing, size distribution)

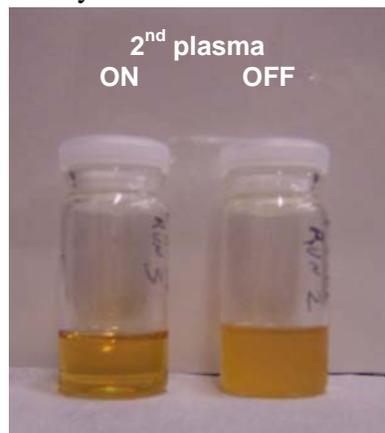


Figure 7. Effect of plasma-grafting of 1-dodecene onto Si QDs.

will help us correlate the electrical properties with the structural characteristics of the QD films.

An important goal of our studies will be to find the optimal compromise between high film electrical conductivities and strong QD quantum confinement, which determines the QD band gap. Hence, in addition to characterizing the electrical properties of the fabricated QD films, it will be crucial to characterize their optical properties. These studies are described in more detail in Section IV.c.

b) Doping of Si and Ge QDs

Background: The solar cells we are envisioning here will likely rely on the principle of a *p-n* junction. Doping with donors and acceptors is crucial to the functioning of such cells. Impurities from group III such as boron (B), aluminum (Al), gallium (Ga), and indium (In) are acceptors in Si and Ge. Impurities from group V such as phosphorous (P), arsenic (As), and antimony (Sb) act as donors in Si and Ge. While doping of bulk Si is well understood,⁹⁰ understanding of doping of Si and Ge QDs is just beginning to emerge.

In a series of elegant papers, Fujii and coworkers reported experimental studies in which Si QDs embedded in silicon oxide were doped with P,^{12,91} B,^{14,92} and In.⁹³ The impurities were introduced by co-sputtering of the dopants, Si, and SiO₂. In the resulting doped, Si-rich SiO_x films, Si QDs were formed by annealing. Through infrared absorption studies, the authors showed that the dopants were indeed incorporated into the Si QDs and became electrically active. In ref.⁹⁴, the authors showed that the introduction of P into the Si QDs led to a new absorption feature in the infrared range at wavelengths > 1.1 μm, i.e., at energies lower than the bulk Si band gap. The authors found that this infrared absorption spectrum was well fit by a $\lambda^{1.7}$ -dependence (with λ the wavelength), which they interpreted as free-electron absorption assisted by scattering on acoustic phonons. The presence of free-electron absorption in the infrared absorption spectrum of Si QDs and its clear dependence on the P concentration provided convincing evidence for activation of the P donors. In a later experiment, the authors demonstrated the electrical activity of B in a similar way.⁹⁵ By progressively increasing the B concentration in previously P-doped samples, the authors showed that the P-related infrared absorption features decreased due to the compensation of P donors with B acceptors, as seen in Fig. 8. A further increase of the B concentration led to a reappearance of the infrared absorption continuum, likely due to intra-valence band transitions (free-hole absorption). Using electron spin resonance (ESR) measurements,¹² the authors concluded that for the highest P concentration, most Si QDs actually contained two P donors. The appearance of a photoluminescence signature at 0.9 eV in co-doping experiments provided additional evidence for the electrical activity of B and P donors. The authors attributed this peak to donor-to-acceptor transitions.^{95,96}

Detailed theoretical studies of doped Si and Ge QDs have started to emerge recently. Melnikov and Chelikowsky⁹⁷ were able to reproduce some of the ESR hyperfine splitting observed in P-doped Si QDs by Fujii.¹² They also found a significant modification of the ionization energy of P-doped QDs from the energy of undoped QDs. Zhou *et al.* demonstrated that the binding energy of donors and acceptors is significantly enhanced in Si QDs compared to bulk Si.⁹⁸ This is due to the reduced screening of the Coulomb interaction in the

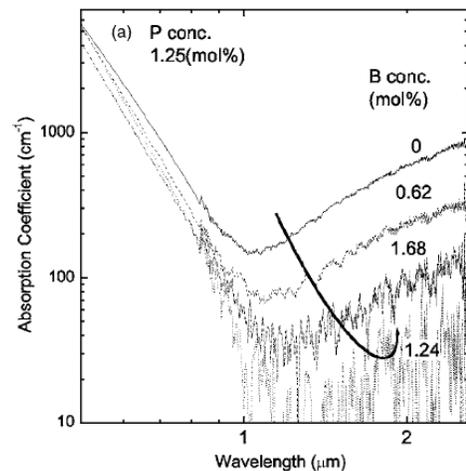


Figure 8. Infrared absorption of P- and P/B-doped Si QDs. Reproduced from ref. 101.

small crystal. Detailed studies of the formation and binding energies of doped Si QDs found that it becomes increasingly difficult to incorporate dopants into QDs as their size shrinks.^{99, 100} However, these studies also suggest a strong influence of the position of the dopant atom in that it becomes significantly easier to incorporate dopants close to the surface than at the center of Si QDs.¹⁰⁰ Not surprisingly, the computations also imply that the formation energy of co-doped, compensated clusters is much smaller than those of *p*- or *n*-doped clusters.

In summary, there seems to be convincing evidence that Si QDs can be successfully doped with donors and acceptors, and that these become electrically active. However, important open questions remain, such as how doping will affect the electrical and optical properties of QD films. No studies have been performed for Si and Ge QD films, but the studies on doped PbSe¹¹ and CdSe¹⁰¹ QD films¹⁰¹ suggest that doping will significantly enhance the electrical conductivity of the films. It is also important to mention that the doping experiments on Si QDs performed so far either require high temperature annealing or ion implantation, which may not be compatible with our overall vision of high-volume, low-cost manufacturability of Si and Ge QD films. It is thus important to study whether doping can also be achieved directly during gas-phase synthesis of QDs, as pursued in this project.

Hypothesis: Our hypothesis is that *p*- and *n*-doped Si and Ge QDs can be synthesized in a single-step gas-phase plasma process. We also hypothesize that *p*- and *n*-doping will increase the electrical conductivity of the QD films.

Proposed Research: In this proposed project, we will study doping during plasma synthesis of Si and Ge QDs by adding dopant precursors into the plasma during the synthesis process. As discussed above, our synthesis method relies on plasma decomposition of gaseous precursors such as SiH₄ and GeCl₄.^{15, 16} Doped Si and Ge films are routinely deposited by introducing dopant gases during plasma-enhanced chemical vapor deposition (PECVD).¹⁰² For example, B and P doping of Si and Ge can be achieved by introducing diborane (B₂H₆) and phosphine (PH₃). We anticipate that the dopant diffusion times are significantly longer than the growth times of Si and Ge QDs in our plasma process, which are of the order of a few ms. Consequently, we expect homogeneous dopant incorporation into the QD cores.¹⁰³ We also expect that the doping level—the number of impurities per QD—may be reliably controlled by adjusting the flow rate of the dopant gas.

Following synthesis and doping, the properties of doped Si and Ge QDs will be studied both for noninteracting QDs (dilute QD solutions or low-volume fractions of QDs embedded in polymers) and interacting QDs in densely packed QD films. The study of noninteracting QDs will rely on optical methods, and will be discussed in Section IV.c, while electrical characterization will be performed on densely packed QD films. QDs will be functionalized and assembled into films with the best methods we will have developed for undoped QDs (discussed in Section IV.a). The electrical conductivity and mobility of doped QD films will be measured as discussed above, which will yield information about the carrier density in the QDs and thus information about the activity of the dopant atoms. Electrical measurements will be correlated with the films' optical properties, which are discussed in Section IV.c.

We will also try to capitalize on the fact that the surfaces of our freestanding QDs are easily accessible, in contrast to QDs produced with many other synthesis approaches. Some surface modifications have been shown to help activate dopants that are not readily active, such as the activation of B in porous Si by the adsorption of nitrogen dioxide (NO₂) gas.¹⁰⁴ As discussed above, when doped QDs are used in device structures, it may be desirable or necessary to embed them into a matrix material. This provides an opportunity to find a matrix material that increases

the carrier mobility of doped QD assemblies. For instance, in ref.¹⁰⁵ the conductivity of B-doped porous Si increased by an order of magnitude when the sample was embedded in a liquid with a high dielectric constant. In addition, the activation energy of the B impurity was lowered. We will perform similar experiments with matrices of different dielectric constants, and study their effect on the conductivity, mobility, and optical properties of doped QD films.

The doping experiments require handling of highly toxic dopant precursor gases. For these experiments, we will use an experimental setup that currently is located in the University of Minnesota Nanofabrication Center (NFC). The NFC provides the safety infrastructure and staff support needed to run such experiments with full account for the safety of the student researchers. Gas cylinders are kept in vented gas cabinets equipped with gas sensors and automatic safety shutoffs, and gas lines are double-walled, gas-monitored stainless steel lines. The experimental setup is housed in a walk-in fume hood that is kept under negative pressure when experiments are operated. Exhaust gases are scrubbed in a burn box. All critical maintenance work is performed by the highly trained full-time NFC staff. Students and post-docs have to undergo extensive safety training before they are allowed to use the equipment.

c) Optical Properties of Si and Ge QDs and QD Films

Background: The ability of nanocrystals to absorb radiation can be described by their optical absorption cross section σ_{abs} , which is related to the optical absorption coefficient α via $\alpha = N \sigma_{abs}$, with N the QD density (or concentration). The absorption cross section strongly depends on the QD energy-band structure (and therefore QD size, surface passivation, and defect density), as well as the energy of the incident radiation. Knowledge of σ_{abs} and its dependencies on important QD parameters is required in order to understand and predict absorption in QD films.

In spite of the importance of σ_{abs} and the fact that the optical properties of Si QDs have been studied intensely by many groups for the past 15 years, there are surprisingly few experimental studies of σ_{abs} for Si QDs, and only one for Ge QDs. The difficulties in determining σ_{abs} are often based on the fact that in many systems the QD density and size distribution are poorly characterized, so that the dependence of σ_{abs} on QD size cannot be determined. Insightful optical measurements on colloidal Si²¹ and Ge²⁵ QDs synthesized in inverse micelles with good size control were reported by Wilcoxon and coworkers. Unfortunately, since the authors were unable to determine the QD concentration in their suspension, they were unable to report absolute values of σ_{abs} . Absolute data for σ_{abs} of Si QDs has been reported by only two groups.^{35, 106} Kovalev and coworkers, using the Auger-recombination-related saturation of the photoluminescence (PL) intensity with increasing optical pump power to extract σ_{abs} of Si QDs in porous Si, found a strong dependence of σ_{abs} on the excitation photon energy $\hbar\omega_{ex}$. They found σ_{abs} ranging from $\sim 10^{-19}$ cm² at $\hbar\omega_{ex} = 1.48$ eV to $\sim 10^{-14}$ cm² at $\hbar\omega_{ex} = 3.53$ eV. Garcia *et al.*^{35, 107} used a similar PL technique to find σ_{abs} for Si QDs embedded in SiO_x. Both groups had to cope with a relatively broad size distribution of Si QDs, leading to a strong dependence of their results on the used detection energy $\hbar\omega_{det}$, which was inconsistent between both studies. The interpretation of PL-based methods is also complicated by the fact that a large, usually unknown, fraction of Si QDs can be “dark,” i.e. absorbing but not emitting radiation.¹⁰⁸

Theoretical studies provide insight into the absorption properties of Si and Ge QDs as well. Several studies suggest that the optical properties of Si QDs are strongly affected by the ligand coverage,¹⁰⁹ surface reconstruction,¹¹⁰ and the QD shape.¹¹¹ Computational studies of the absorption features of Si and Ge QDs show that σ_{abs} should indeed have a number of distinct features which result from strong transitions.¹¹²⁻¹¹⁶ However, it is likely that such features can be detected only for sufficiently monodisperse QDs. These studies also confirm that Ge QDs

should have significantly stronger absorption than Si QDs at photon energies in the visible and near infrared range of the solar spectrum, i.e. at energies less than ~ 3 eV. Other studies of the optical properties of doped Si QDs suggest that impurities significantly affect their optical absorption,⁹⁸ consistent with Fujii's experiment.

In summary, the basic optical properties of Si and Ge QDs are still largely unexplored; the few existing studies have produced incomplete and sometimes contradictory results. All of the above mentioned studies focused on non-interacting, free QDs. We are not aware of any studies addressing the effect of QD-QD coupling for Si or Ge. However, studies on CdSe⁷⁰ and PbSe¹¹ suggest that increased QD-QD interactions, which result from small interparticle spacings, lead to a strong modification of the optical absorption, which is usually signaled by a redshift of absorption features due to reduced quantum confinement.

Hypothesis: Our hypothesis is that *our unique ability to prepare monodisperse colloidal solutions of Si and Ge QDs will enable us to perform accurate optical measurements of σ_{abs} .* We also hypothesize that *the optical absorption of Si and Ge QDs will strongly depend on size, doping, surface passivation, and QD-QD interactions in densely packed QD arrays.*

Proposed Research: For many fluorescent nanoparticle systems, such as colloidal CdSe QDs or Si QDs synthesized in inverse micelles,²¹ each particle is coated with an unknown number of surfactant molecules during synthesis, making mass measurements of the semiconductor QD core problematic. Our ability to synthesize bare, size-controlled Si and Ge QDs will enable us to estimate the number of QDs produced from mass measurements before the surface functionalization is performed. This will allow us to produce Si QD colloids with known QD concentration that will be used to study the QD optical absorption properties and, in particular, to perform absolute measurements of σ_{abs} . Errors in this method mainly result from the particle size distribution. If desirable, the particle size distribution of the as synthesized particles (~ 15 - 20%) can be further narrowed to <5 - 8% standard deviation through aerosol instruments such as a differential mobility analyzer¹¹⁷ (DMA). (A DMA is available in the PI's lab.) After the mass measurements, samples will be coated with ligands using our standard liquid-phase-passivation approach. Since the material loss during this processing is low, we expect to be able to arrive at colloidal suspensions in which the concentration of Si and Ge QDs is known to within 50% accuracy.

The above procedure of preparing Si and Ge colloids with well-characterized QD concentrations and sizes will be applied to intrinsic, doped, and compensated co-doped QDs. The absorption cross section as a function of the excitation wavelength can then be determined from standard absorption measurements. A suitable light source, absorption setup, and spectrometer with visible and infrared detectors are available on campus.

After performing studies on dilute (and thus non-interacting) colloidal QDs, similar studies will be performed on films of interacting QDs. Films of intrinsic, *p*- and *n*-doped, and co-doped QDs will be prepared with the methods developed under Section IV.a. The QD density in the films will be estimated by studying the aerial density of QDs in films with high-resolution TEM and by measuring the film thickness with profilometry and scanning electron microscopy. The structural properties of the films will be assessed through TEM and SAXS. Absorption measurements performed on the thin films samples will be used to determine σ_{abs} for interacting QD films. The absorption cross section will be studied as a function of the interparticle distance, which will be adjusted by attaching ligands of different lengths to the QDs' surfaces. Other studies will focus on the effect of the order (glassy, crystalline) of the films. The results of these optical studies will be correlated with the results of the electrical studies described in Section IV.b.

d) *p-n* Junction Cell from Si and Ge QD Films

Background: While recent discoveries such as the high conductivities found in QD superlattices,^{11,72} and the observation of efficient generation of multiple electron-hole pairs upon absorption of a single photon¹¹⁸⁻¹²² have created significant excitement for QD-based solar cells, the field is still in its infancy. Nozik first proposed that QDs could enable higher efficiency solar cells¹²³ by minimizing the energy loss of “hot carriers”, electrons and holes that are excited far beyond their respective band edges when absorbing energetic photons. Hot carrier relaxation leads to wasteful heating of a solar cell. Nozik suggested that superlattices of very monodisperse QDs could form minibands, that would limit the hot carrier energy loss. In practice, to our knowledge, such minibands have not been realized to date.

Initial attempts at fabricating QD solar cells tried to emulate the highly successful dye sensitized solar cells,¹²⁴⁻¹²⁶ in which an exciton (an electrostatically bound electron-hole pair) is created by photon absorption in dye molecules that are adsorbed to the surface of a mesoporous network of titanium oxide (TiO₂) nanocrystals. In such an “excitonic” solar cell,¹²⁷ the heterojunction between the energy levels of the dye and the TiO₂ particles leads to exciton dissociation, followed by injection of the electron into the TiO₂, where it diffuses to the electrode. The hole is removed from the dye molecule by an electrolyte which conducts the hole to the other electrode. Initial work on QD solar cells focused on replacing the organic dye with more stable inorganic QDs.¹²⁸⁻¹³¹ In recent efforts to improve the performance of dye sensitized solar cells, the groups of Aydil and Yang used zinc oxide (ZnO) nanowires¹³²⁻¹³⁴ as electron transport medium with the goal of enhancing the transport by eliminating the need for electrons to cross many grain boundaries before reaching the terminal. The groups of Aydil, Norris, and Kortshagen also recently reported a successful embodiment of QD solar cells based on colloidal CdSe QDs and ZnO nanowires.¹³⁵

In a recent effort to improve on the stability of QD solar cells, Alivisatos’s group reported an all inorganic cell based on colloidal CdSe and CdTe nanorods.¹³⁶ This cell relies on exciton dissociation at the heterojunction created at the interface between the CdSe and CdTe phase. The solar cells proved to be long-term stable, where the best performance was achieved when cells were annealed, likely leading to a partial sintering of the nanorods.

The cell structure proposed here is different from all the QD devices discussed above in that it relies on a QD *p-n* junction. In contrast to excitonic cells, which rely on diffusion of charge carriers to the terminals, the carrier transport in *p-n* junction cells is driven by the intrinsic voltage that results from the close contact of *p*- and *n*-type doped semiconductors. To our knowledge, a *p-n* junction cell based on Si or Ge QD superlattices, such as the one proposed here, has not been reported to date.

Hypothesis: Our hypothesis is that *charge carriers will separate across junctions formed by conductive films of p- and n-doped Si or Ge QDs, and that the absorption of such p-n junction PV devices may be tuned through the band gap of the quantum-confined nanocrystals.*

Proposed Research: Using our knowledge gained from the research described above, it is our goal to build *p-n* junction solar cell devices to test the above hypothesis. As we are aiming here only at a proof-of-concept and due to the expected complexity of building multi-junction cells, we will here only study single-junction cells with tunable absorption, such as the one shown in Fig. 9. This device will be fabricated from the top layer down, starting with a commercially available glass substrate coated with a layer of a transparent conductive oxide (TCO), such as indium tin oxide (ITO). A *p*-doped layer of Ge or Si QDs will be deposited onto the ITO, followed by an *n*-doped layer. Finally, a suitable metal such as Al will be evaporated onto this

structure to form the back contact. The thickness of the QD layers will depend on the material (Si or Ge) and the target wavelength range to which the solar cell is to be tuned. Layer thickness will be determined based on the results of the studies described in Section IV.c.

A variety of solar cell structures will be tested, including cells that use an intrinsic (undoped) layer to form *p-i-n* structures. Also, different metals will be tested for the back contact to find a material whose work-function optimally matches the band structure of the QD films.

The solar cells will be subjected to a variety of standard solar cell characterization methods, which are available on campus.¹³⁷ In particular, current-voltage characteristics under simulated Air Mass 1.5 solar radiation will be used to calculate the open-circuit voltage, short circuit current, fill factor, and overall cell efficiency.¹³⁷ The fill factor is the ratio of the maximum power produced by the cell at the optimal working point to the power provided by a hypothetical cell that operates with the short circuit current at the open circuit voltage, and is therefore a measure of the power output of the cell under a load. Two other quantities of interest are the light harvesting efficiency (LHE) and the internal photon-to-current conversion efficiency (IPCE). The LHE will be determined through optical absorption measurements and will provide information about the efficiency with which different wavelengths of the solar spectrum are absorbed by the cell. The LHE will strongly depend on the QD material, film thickness, and QD size. Altering the size (and therefore the degree of quantum confinement) of the QDs in a solar cell should alter the absorption spectrum of the cell, and thus its LHE. The IPCE is a measure of a cell's ability to convert absorbed photons into actual current. It will be determined by measuring the short-circuit current of the cell as a function of the incident radiation wavelength. The IPCE will provide important information about the cell's electronic quality, including, for instance, losses of charge carriers through trapping at interface or defect states. All measurements will be performed with freshly produced solar cells, and cells that have been "light-soaked" in order to understand the stability of these cells after prolonged exposure to solar radiation. All diagnostics described here are readily available on campus.

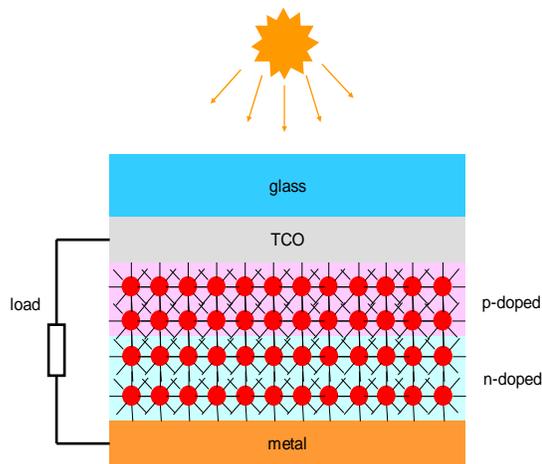


Figure 9. Schematic of a *p-n* junction QD solar cell.

V. Broader Impact

To ensure the broadest possible impact of this project, we will make use of the infrastructure provided by the NSF-IGERT for "Nanoparticle Science and Engineering" at the University of Minnesota (<http://www.nanoigert.umn.edu>, P.I.: Kortshagen) that was designed to supplement and support research projects such as the one proposed here.

Integration of teaching, training and research: This project will involve at least two graduate students and, through the IGERT summer research program (see below), several undergraduate students. Under previous NSF support, Kortshagen involved a high school physics teacher through a 3-month RET (Research Experience for Teachers), and four high school students in his nanoparticle research. This approach was extremely successful in that Kortshagen recruited two of these students to study in Mechanical Engineering at the University of Minnesota and to continue research in his lab. We will continue this successful outreach through the relationship to science teachers at Roseville Area High School.

Participation of underrepresented groups: The IGERT maintains an undergraduate summer research program that targets students from several Historically Black Colleges and Universities. Undergraduate students perform REU-like summer research stays at the University of Minnesota, and Kortshagen will continue to offer these opportunities. Over the past three years, three minority undergraduate students and one minority junior faculty member from Jackson State University have worked in Kortshagen’s group over the summer. Out of these REU experiences, several minority students were recruited for graduate studies at the University of Minnesota, two of them currently work in Kortshagen’s group (co-advised by other faculty members).

Broad dissemination of results: Through the IGERT, Kortshagen has initiated a collaboration with the Science Museum of Minnesota (SMM), which annually attracts ~1.2M visitors. As part of this collaboration, Kortshagen and other IGERT faculty and students advise SMM staff on exhibits around nanotechnology. Currently, one of Kortshagen’s students, Ghidewon Arefe, meets with SMM staff once a week to discuss his Ph.D. project on using Si QDs for cancer diagnostics. Ghidewon and his work were recently prominently featured on the SMM website under the “Science Buzz,” which involved a section where the public could post questions that were answered by Ghidewon (see Fig. 10). This collaboration with SMM is ongoing and will involve more students from Kortshagen’s group, and likely students working on this propose project.



Figure 10. Ghidewon Arefe at the Science Museum of Minnesota website.

On the more formal professional side, the PI and students on this project will routinely visit a wide spectrum of scientific conferences. In addition, results of this research will be disseminated through a project website. Kortshagen is also actively involved in teaching graduate courses in the University of Minnesota Freestanding Minor for Nanoparticle Science and Engineering, for which he serves as Director of Graduate Studies. Results of this research will be used as teaching material in the course NPSE 8001 “Introduction to Nanoparticle Science and Engineering,” which every fall semester attracts more than 30 students.

Our close relation with Innovalight, Inc., as well as our frequent consultations with other companies will also provide for fast dissemination of our results to industry. For instance, Kortshagen is the group leader for the “Nanoparticle Technology” group of IPRIME, an industrial consortium with ~40 member companies that supports pre-commercial materials research at the University of Minnesota.

Benefits to society: Developing alternative sources of carbon-free energy will be of crucial importance to enable global economic development while limiting the effects of global climate change through greenhouse gas emissions. This proposed research, if successful, may ultimately lead to a new paradigm for the manufacturing of low-cost, efficient, multi-junction solar cells based on quantum dot materials that are non-toxic, environmentally benign, long-term stable and abundant. We realize that the proposed project entails high risks and that success is anything but certain. However, the tremendous potential payoff definitely justifies the investment of dedicated efforts, and hopefully also that of financial support.

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Uwe R. Kortshagen, Ph.D.

Professor

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Professional Preparation:

Ruhr-Universität Bochum, Germany, Physics, Diploma, Jun. 1988

Ruhr-Universität Bochum, Germany, Physics, Ph.D., Jan. 1991

Ruhr-Universität Bochum, Germany, Physics, Habilitation, Nov. 1995

Appointments:

08/06- : Director of Graduate Studies, Mechanical Engineering, U. of Minnesota

08/03- : Professor, Mechanical Engineering, University of Minnesota

08/99-08/03: Associate Professor, Mechanical Engineering, University of Minnesota.

07/96-08/99: Assistant Professor, Mechanical Engineering, University of Minnesota.

06/96-07/96: Privatdozent, Faculty of Physics, Ruhr-Universität, Bochum, Germany

03/95-03/96: Visiting Scholar, University of Wisconsin-Madison, Dept. of Physics

01/92-07/96: "Wissenschaftlicher Assistent," Ruhr-Universität Bochum.

Five publications most closely related to proposed project:

1. "High-Yield Synthesis of Luminescent Silicon Nanocrystals," L. Mangolini, E. Thimsen, U. Kortshagen, NanoLetters **5**(4) 655-659, 2005, available online: DOI: [10.1021/nl050066y](https://doi.org/10.1021/nl050066y).
2. "Silicon nanocrystals with ensemble quantum yields exceeding 60%," David Jurbergs, Elena Rogojina, Lorenzo Mangolini and Uwe Kortshagen, Appl. Phys. Lett. **88**, 233116 (2006).
3. "Plasma synthesis and liquid-phase surface passivation of brightly luminescent Si nanocrystals," L. Mangolini, D. Jurbergs, E. Rogojina, and U. Kortshagen, J. Luminescence **121**, 327-334 (2006).
4. "Room-temperature atmospheric oxidation of Si nanocrystals after HF etching," X. D. Pi, L. Mangolini, S. A. Campbell, U. Kortshagen, Phys. Rev. B **75**, 085423 (2007).
5. "Synthesis of highly oriented, single-crystal silicon nanoparticles in a low-pressure, inductively coupled plasma," Ameya Bapat, Christopher R. Perrey, Stephen A. Campbell, C. Barry Carter, and Uwe Kortshagen, J. Appl. Phys. **94**, 1969 (2003).

Five other significant publications:

1. "Plasma synthesis of single crystal silicon nanoparticles for novel electronic device applications," Ameya Bapat, Curtis Anderson, Christopher R. Perrey, C. Barry Carter, Stephen A. Campbell, and Uwe Kortshagen, Plasma Physics and Controlled Fusion **46**, B97-B109 (2004).
2. "Modeling gas-phase nucleation in inductively-coupled silane-oxygen plasmas," S.-M. Suh, S. L. Girshick, U. R. Kortshagen and M. R. Zachariah, Journal of Vacuum Science and Technology **A 21**, 251-264 (2003).
3. "Numerical study of the effect of gas temperature on the time for onset of particle nucleation in argon-silane low-pressure plasmas," Upendra Bhandarkar, Uwe Kortshagen and Steven L Girshick, J. Phys. D: Appl. Phys. **36**, 1399-1408 (2003).

4. “Modeling of particulate coagulation in low pressure plasmas,” U. Kortshagen and U. Bhandarkar, Phys. Rev. E **60**, 887 (1999).
5. “Modeling of silicon hydride clustering in low-pressure silane plasma,” U. V. Bhandarkar, M. T. Swihart, S. L. Girshick, and U. R. Kortshagen, J. Phys. D: Appl. Phys. **33**, 2731 (2000).

Synergistic Activities:

- Board of Directors, International Plasma Chemistry Society, 2003-2007. Vice President, International Plasma Chemistry Society, 2006-2007.
- Director, NSF-IGERT project for “Nanoparticle Science and Engineering” involving 23 faculty members and 34 graduate students from five science and engineering departments at the University of Minnesota. Director of Graduate Studies for Mechanical Engineering and the the Minor program in “Nanoparticle Science and Engineering”
- Member of Editorial Board for Plasma Sources Science and Technology and Advisory Board for Contributions to Plasma Physics.
- Program Leader, “Nanoparticle-based materials” initiative of the University of Minnesota Materials Research Science and Engineering Center; Program Leader, Nanoparticle Technology Program, Industrial Partnership for Research in Interfacial and Materials Engineering (IPRIME, <http://www.iprime.umn.edu>).
- Executive committee (2001-2003) and Organizer of 55th Annual Gaseous Electronics Conference of the American Physical Society held in Minneapolis, MN, Oct. 2002.

Research Collaborators: (other than students and above listed as co-author)

Stephen Campbell, Electrical and Computer Engineering, University of Minnesota; John H. Ingold, Brathel Physics, Cleveland, OH; David Jurbergs, InnovaLight, Inc.; James Kakalios, Physics, University of Minnesota; Peter McMurry, Mechanical Engineering, University of Minnesota; J. Darryl Michael, GE Research, Schenectady, NY.

Graduate Advisor: Hans Schlüter, Dept. of Physics, University Bochum, Germany
Undergraduate Advisors: Alexander Piel, Dept. of Physics, University Kiel, Germany
 Hans Schlüter, Dept. of Physics, University Bochum, Germany

Post-doctoral, Graduate, and Undergraduate Advisees:

total advised: 11 post-doc, 25 graduate students, and 13 undergraduate students.

Post-docs:

Dr. Upendra Bhandarkar, Dr. Christoph Eggs, Dr. Min Hur, Dr. Feng Liao, Dr. Tomohiro Nozaki, Dr. Konstantin Orlov, Dr. Xiaodong Pi, Dr. Jason Schmidt, Dr. Vitaly Schweigert, Dr. Eli Stoykova, Dr. Dirk Uhrlandt.

Graduate Students:

Curtis Anderson, Rebekah Anthony, Ghidewon Arefe, Upendra Bhandarkar, Toni Borders, Gurprit S. Chandhoke, Patrizio Cernetti, Federico Galli, Marco Gatti, Gianluca Gregori, Thomas Hatch, Chengbin He, Michael Hebert, Brian G. Heil, Zak Holman, Vamshi K. Krishna, Chin-Yi Liu, Antonio Maresca, Lorenzo Mangolini, Paul Schwendinger, Zhe Shen, Svetoslav Stoykov, Giovanni Visentin, Siri Suzanne Thompson, Peng Zhang.

SUMMARY PROPOSAL BUDGET YEAR 1

| ORGANIZATION University of Minnesota-Twin Cities | | | | FOR NSF USE ONLY | | | |
|---|---|--------------|--------------------|---------------------------------|------------------------------|-----------------------------|-------------------------------------|
| | | | | PROPOSAL NO. | DURATION (months) | | |
| PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR Uwe Kortshagen | | | | AWARD NO. | Proposed | Granted | |
| A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets) | | | | NSF Funded Person-months | | Funds Requested By proposer | Funds granted by NSF (if different) |
| | | CAL | ACAD | SUMR | | | |
| 1. | Uwe R Kortshagen - Prof. | 0.50 | 0.00 | 0.00 | █ | \$ | |
| 2. | | | | | | | |
| 3. | | | | | | | |
| 4. | | | | | | | |
| 5. | | | | | | | |
| 6. | (0) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE) | 0.00 | 0.00 | 0.00 | 0 | | |
| 7. | (1) TOTAL SENIOR PERSONNEL (1 - 6) | 0.50 | 0.00 | 0.00 | █ | | |
| B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS) | | | | | | | |
| 1. | (0) POST DOCTORAL ASSOCIATES | 0.00 | 0.00 | 0.00 | 0 | | |
| 2. | (0) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.) | 0.00 | 0.00 | 0.00 | 0 | | |
| 3. | (2) GRADUATE STUDENTS | | | | 34,043 | | |
| 4. | (0) UNDERGRADUATE STUDENTS | | | | 0 | | |
| 5. | (0) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY) | | | | 0 | | |
| 6. | (0) OTHER | | | | 0 | | |
| TOTAL SALARIES AND WAGES (A + B) | | | | | 41,259 | | |
| C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) | | | | | 25,496 | | |
| TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C) | | | | | 66,755 | | |
| D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING \$5,000.) | | | | | | | |
| TOTAL EQUIPMENT | | | | | 0 | | |
| E. TRAVEL | | | | | 2,500 | | |
| 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS) | | | | | | | |
| 2. FOREIGN | | | | | 2,500 | | |
| F. PARTICIPANT SUPPORT COSTS | | | | | | | |
| 1. | STIPENDS \$ _____ | 0 | | | | | |
| 2. | TRAVEL _____ | 0 | | | | | |
| 3. | SUBSISTENCE _____ | 0 | | | | | |
| 4. | OTHER _____ | 0 | | | | | |
| TOTAL NUMBER OF PARTICIPANTS (0) | | | | TOTAL PARTICIPANT COSTS | 0 | | |
| G. OTHER DIRECT COSTS | | | | | | | |
| 1. MATERIALS AND SUPPLIES | | | | | 8,464 | | |
| 2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION | | | | | 0 | | |
| 3. CONSULTANT SERVICES | | | | | 0 | | |
| 4. COMPUTER SERVICES | | | | | 0 | | |
| 5. SUBAWARDS | | | | | 0 | | |
| 6. OTHER | | | | | 8,000 | | |
| TOTAL OTHER DIRECT COSTS | | | | | 16,464 | | |
| H. TOTAL DIRECT COSTS (A THROUGH G) | | | | | 88,219 | | |
| I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) | | | | | | | |
| TDC-grad fringe (Rate: 49.5000, Base: 64205) | | | | | | | |
| TOTAL INDIRECT COSTS (F&A) | | | | | 31,781 | | |
| J. TOTAL DIRECT AND INDIRECT COSTS (H + I) | | | | | 120,000 | | |
| K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPG II.C.6.j.) | | | | | 0 | | |
| L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K) | | | | | \$ 120,000 | \$ | |
| M. COST SHARING PROPOSED LEVEL \$ | | | | 0 | AGREED LEVEL IF DIFFERENT \$ | | |
| PI/PD NAME Uwe Kortshagen | | | | FOR NSF USE ONLY | | | |
| ORG. REP. NAME* Kevin mckoskey | | | | INDIRECT COST RATE VERIFICATION | | | |
| | | Date Checked | Date Of Rate Sheet | Initials - ORG | | | |

SUMMARY PROPOSAL BUDGET YEAR 2

| ORGANIZATION University of Minnesota-Twin Cities | | | | FOR NSF USE ONLY | | | |
|---|------|--------------|--------------------|---------------------------------|-------------------|-----------------------------|-------------------------------------|
| | | | | PROPOSAL NO. | DURATION (months) | | |
| PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR Uwe Kortshagen | | | | AWARD NO. | Proposed | Granted | |
| A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets) | | | | NSF Funded Person-months | | Funds Requested By proposer | Funds granted by NSF (if different) |
| | CAL | ACAD | SUMR | | | | |
| 1. Uwe R Kortshagen - Prof. | 0.50 | 0.00 | 0.00 | | | \$ | |
| 2. | | | | | | | |
| 3. | | | | | | | |
| 4. | | | | | | | |
| 5. | | | | | | | |
| 6. (0) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE) | 0.00 | 0.00 | 0.00 | | 0 | | |
| 7. (1) TOTAL SENIOR PERSONNEL (1 - 6) | 0.50 | 0.00 | 0.00 | | | | |
| B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS) | | | | | | | |
| 1. (0) POST DOCTORAL ASSOCIATES | 0.00 | 0.00 | 0.00 | | 0 | | |
| 2. (0) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.) | 0.00 | 0.00 | 0.00 | | 0 | | |
| 3. (2) GRADUATE STUDENTS | | | | | 35,065 | | |
| 4. (0) UNDERGRADUATE STUDENTS | | | | | 0 | | |
| 5. (0) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY) | | | | | 0 | | |
| 6. (0) OTHER | | | | | 0 | | |
| TOTAL SALARIES AND WAGES (A + B) | | | | | 42,570 | | |
| C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) | | | | | 26,276 | | |
| TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C) | | | | | 68,846 | | |
| D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING \$5,000.) | | | | | | | |
| TOTAL EQUIPMENT | | | | | 0 | | |
| E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS) | | | | | 2,500 | | |
| 2. FOREIGN | | | | | 2,500 | | |
| F. PARTICIPANT SUPPORT COSTS | | | | | | | |
| 1. STIPENDS \$ _____ | | | 0 | | | | |
| 2. TRAVEL _____ | | | 0 | | | | |
| 3. SUBSISTENCE _____ | | | 0 | | | | |
| 4. OTHER _____ | | | 0 | | | | |
| TOTAL NUMBER OF PARTICIPANTS (0) TOTAL PARTICIPANT COSTS | | | | | 0 | | |
| G. OTHER DIRECT COSTS | | | | | | | |
| 1. MATERIALS AND SUPPLIES | | | | | 7,949 | | |
| 2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION | | | | | 0 | | |
| 3. CONSULTANT SERVICES | | | | | 0 | | |
| 4. COMPUTER SERVICES | | | | | 0 | | |
| 5. SUBAWARDS | | | | | 0 | | |
| 6. OTHER | | | | | 8,000 | | |
| TOTAL OTHER DIRECT COSTS | | | | | 15,949 | | |
| H. TOTAL DIRECT COSTS (A THROUGH G) | | | | | 89,795 | | |
| I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) TDC-grad fringe (Rate: 49.5000, Base: 65060) | | | | | | | |
| TOTAL INDIRECT COSTS (F&A) | | | | | 32,205 | | |
| J. TOTAL DIRECT AND INDIRECT COSTS (H + I) | | | | | 122,000 | | |
| K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPG II.C.6.j.) | | | | | 0 | | |
| L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K) | | | | | \$ 122,000 | \$ | |
| M. COST SHARING PROPOSED LEVEL \$ 0 | | | | AGREED LEVEL IF DIFFERENT \$ | | | |
| PI/PD NAME Uwe Kortshagen | | | | FOR NSF USE ONLY | | | |
| ORG. REP. NAME* Kevin mckoskey | | | | INDIRECT COST RATE VERIFICATION | | | |
| | | Date Checked | Date Of Rate Sheet | Initials - ORG | | | |

SUMMARY PROPOSAL BUDGET YEAR 3

| ORGANIZATION University of Minnesota-Twin Cities | | | | FOR NSF USE ONLY | | | |
|---|--|--------------|--------------------|---|-------------------|---------|---------------|
| | | | | PROPOSAL NO. | DURATION (months) | | |
| PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR Uwe Kortshagen | | | | AWARD NO. | Proposed | Granted | |
| | | | | A. SENIOR PERSONNEL: PI/PI, Co-PI's, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets) | | | |
| | | | | CAL | ACAD | SUMR | |
| 1. Uwe R Kortshagen - Prof. | | | | 0.50 | 0.00 | 0.00 | \$ |
| 2. | | | | | | | |
| 3. | | | | | | | |
| 4. | | | | | | | |
| 5. | | | | | | | |
| 6. (0) OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE) | | | | 0.00 | 0.00 | 0.00 | 0 |
| 7. (1) TOTAL SENIOR PERSONNEL (1 - 6) | | | | 0.50 | 0.00 | 0.00 | \$ |
| B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS) | | | | | | | |
| 1. (0) POST DOCTORAL ASSOCIATES | | | | 0.00 | 0.00 | 0.00 | 0 |
| 2. (0) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.) | | | | 0.00 | 0.00 | 0.00 | 0 |
| 3. (2) GRADUATE STUDENTS | | | | | | | 36,118 |
| 4. (0) UNDERGRADUATE STUDENTS | | | | | | | 0 |
| 5. (0) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY) | | | | | | | 0 |
| 6. (0) OTHER | | | | | | | 0 |
| TOTAL SALARIES AND WAGES (A + B) | | | | | | | 43,923 |
| C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) | | | | | | | 27,081 |
| TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C) | | | | | | | 71,004 |
| D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING \$5,000.) | | | | | | | |
| TOTAL EQUIPMENT | | | | | | | 0 |
| E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS) | | | | | | | 2,500 |
| 2. FOREIGN | | | | | | | 2,500 |
| F. PARTICIPANT SUPPORT COSTS | | | | | | | |
| 1. STIPENDS \$ _____ | | | | 0 | | | |
| 2. TRAVEL _____ | | | | 0 | | | |
| 3. SUBSISTENCE _____ | | | | 0 | | | |
| 4. OTHER _____ | | | | 0 | | | |
| TOTAL NUMBER OF PARTICIPANTS (0) TOTAL PARTICIPANT COSTS | | | | | | | 0 |
| G. OTHER DIRECT COSTS | | | | | | | |
| 1. MATERIALS AND SUPPLIES | | | | | | | 8,044 |
| 2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION | | | | | | | 0 |
| 3. CONSULTANT SERVICES | | | | | | | 0 |
| 4. COMPUTER SERVICES | | | | | | | 0 |
| 5. SUBAWARDS | | | | | | | 0 |
| 6. OTHER | | | | | | | 8,000 |
| TOTAL OTHER DIRECT COSTS | | | | | | | 16,044 |
| H. TOTAL DIRECT COSTS (A THROUGH G) | | | | | | | 92,048 |
| I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) TDC-grad fringe (Rate: 49.5000, Base: 66570) | | | | | | | |
| TOTAL INDIRECT COSTS (F&A) | | | | | | | 32,952 |
| J. TOTAL DIRECT AND INDIRECT COSTS (H + I) | | | | | | | 125,000 |
| K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPG II.C.6.j.) | | | | | | | 0 |
| L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K) | | | | | | | \$ 125,000 \$ |
| M. COST SHARING PROPOSED LEVEL \$ 0 | | | | AGREED LEVEL IF DIFFERENT \$ | | | |
| PI/PI NAME Uwe Kortshagen | | | | FOR NSF USE ONLY | | | |
| ORG. REP. NAME* Kevin mckoskey | | | | INDIRECT COST RATE VERIFICATION | | | |
| | | Date Checked | Date Of Rate Sheet | Initials - ORG | | | |

SUMMARY PROPOSAL BUDGET Cumulative

| ORGANIZATION University of Minnesota-Twin Cities | | | | FOR NSF USE ONLY | | | |
|---|--|--------------|--|---------------------------------|-------------------|-----------------------------|-------------------------------------|
| | | | | PROPOSAL NO. | DURATION (months) | | |
| PRINCIPAL INVESTIGATOR / PROJECT DIRECTOR Uwe Kortshagen | | | | AWARD NO. | | | |
| | | | | Proposed | Granted | | |
| A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets) | | | | NSF Funded Person-months | | Funds Requested By proposer | Funds granted by NSF (if different) |
| | | | | CAL | ACAD | SUMR | |
| 1. Uwe R Kortshagen - Prof. | | | | 1.50 | 0.00 | 0.00 | \$ |
| 2. | | | | | | | |
| 3. | | | | | | | |
| 4. | | | | | | | |
| 5. | | | | | | | |
| 6. () OTHERS (LIST INDIVIDUALLY ON BUDGET JUSTIFICATION PAGE) | | | | 0.00 | 0.00 | 0.00 | 0 |
| 7. (1) TOTAL SENIOR PERSONNEL (1 - 6) | | | | 1.50 | 0.00 | 0.00 | \$ |
| B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS) | | | | | | | |
| 1. (0) POST DOCTORAL ASSOCIATES | | | | 0.00 | 0.00 | 0.00 | 0 |
| 2. (0) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.) | | | | 0.00 | 0.00 | 0.00 | 0 |
| 3. (6) GRADUATE STUDENTS | | | | | | | 105,226 |
| 4. (0) UNDERGRADUATE STUDENTS | | | | | | | 0 |
| 5. (0) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY) | | | | | | | 0 |
| 6. (0) OTHER | | | | | | | 0 |
| TOTAL SALARIES AND WAGES (A + B) | | | | | | | 127,752 |
| C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) | | | | | | | 78,853 |
| TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C) | | | | | | | 206,605 |
| D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING \$5,000.) | | | | | | | |
| TOTAL EQUIPMENT | | | | | | | 0 |
| E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS) | | | | | | | 7,500 |
| 2. FOREIGN | | | | | | | 7,500 |
| F. PARTICIPANT SUPPORT COSTS | | | | | | | |
| 1. STIPENDS \$ _____ | | | | 0 | | | |
| 2. TRAVEL _____ | | | | 0 | | | |
| 3. SUBSISTENCE _____ | | | | 0 | | | |
| 4. OTHER _____ | | | | 0 | | | |
| TOTAL NUMBER OF PARTICIPANTS (0) TOTAL PARTICIPANT COSTS | | | | | | | 0 |
| G. OTHER DIRECT COSTS | | | | | | | |
| 1. MATERIALS AND SUPPLIES | | | | | | | 24,457 |
| 2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION | | | | | | | 0 |
| 3. CONSULTANT SERVICES | | | | | | | 0 |
| 4. COMPUTER SERVICES | | | | | | | 0 |
| 5. SUBAWARDS | | | | | | | 0 |
| 6. OTHER | | | | | | | 24,000 |
| TOTAL OTHER DIRECT COSTS | | | | | | | 48,457 |
| H. TOTAL DIRECT COSTS (A THROUGH G) | | | | | | | 270,062 |
| I. INDIRECT COSTS (F&A)(SPECIFY RATE AND BASE) | | | | | | | |
| TOTAL INDIRECT COSTS (F&A) | | | | | | | 96,938 |
| J. TOTAL DIRECT AND INDIRECT COSTS (H + I) | | | | | | | 367,000 |
| K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPG II.C.6.j.) | | | | | | | 0 |
| L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K) | | | | | | | \$ 367,000 \$ |
| M. COST SHARING PROPOSED LEVEL \$ 0 | | | | AGREED LEVEL IF DIFFERENT \$ | | | |
| PI/PD NAME Uwe Kortshagen | | | | FOR NSF USE ONLY | | | |
| ORG. REP. NAME* Kevin mckoskey | | | | INDIRECT COST RATE VERIFICATION | | | |
| | | Date Checked | | Date Of Rate Sheet | | Initials - ORG | |

C *ELECTRONIC SIGNATURES REQUIRED FOR REVISED BUDGET

BUDGET JUSTIFICATION

Year 1:

- Line A1: Half a month of summer salary is requested for the P.I. for his participation in the research, supervision of graduate students, and coordination of the research effort.
- Line B3: In year 1 we request support for 2 graduate students. The support requested is for 1.5 research assistant positions. We expect that we will be able to supplement the funds for the remaining 0.5 RA position from fellowships or teaching assistantships. One student will focus on liquid phase processes for QD films formation, the other student will focus on gas phase processes.
- Line D: Permanent Equipment:
No permanent equipment is requested from NSF.
- Line E1: Domestic travel: We request funds for the students and the P.I. to present results at domestically held conferences such as the Materials Research Society Conference.
- Line E2: International travel: We request funds for the students and the P.I. to attend one international conference such as the International Conference on Photovoltaic Science and Engineering.
- Line G1: We request funds for general laboratory supplies such as gases, vacuum parts, etc.
- Line G6: Funds are requested for materials characterization work in the University of Minnesota Materials Characterization Facility, and for device fabrication work in the University of Minnesota Nanofabrication Center.
- Line I: Indirect cost is 49.5% of the total direct cost less graduate RA fringe and permanent equipment.

Year 2 & 3:

The same line items as in year 1 are requested for years 2 and 3. Personnel cost are adjusted for cost of living increases.

CURRENT AND PENDING SUPPORT: UWE KORTSHAGEN

Current Support:

- Title: "IGERT: Nanoparticle Science and Engineering"**
PI: U. Kortshagen Co-PI: J. R. Chelikowsky, J. T. Roberts
Source: National Science Foundation Location: University of Minnesota
Award: \$3,330,226 1.0 mo. sum period: 10/01/2001-09/30/2007
- Title: "NIRT: Single Nanoparticle Devices, A New Technique for Bottom-Up Manufacturing"**
PI: S.A. Campbell Co-PI: C. B. Carter, H. Jacobs, U. Kortshagen
Source: National Science Foundation Location: University of Minnesota
Award \$1,100,000 0.5 mo. acad. period: 08/15/2003-08/14/2007
- Title: "Nucleation and Dynamics of Nanometer-sized Particles in Silane Plasmas"**
PI: U. Kortshagen Co-PI: S. L. Girshick
Source: Dept. of Energy Location: University of Minnesota
Award: \$405,000 1.0 mo. sum period: 08/15/2003-08/14/2007
- Title: Collaborative Research: GOALI: Nanocrystal Formation and Morphology in Nonthermal Plasmas**
PI: U. Kortshagen, Co-PI: D.C. Jurbergs
Source: National Science Foundation Location: University of Minnesota
Award \$360,000 1.0 mo. sum. period: 08/15/2005-08/14/2008
- Title: NIRT: Photovoltaic devices based on semiconductor nanoparticles and nanowires**
PI: E. Aydil Co-PI: U. Kortshagen, D. Norris, X. Y. Zhu
Source: National Science Foundation Location: University of Minnesota
Award \$1,000,000 0.5 mo. acad. period: 08/15/2005-08/14/2009

Relation to this proposal: This project focuses on studying excitonic solar cells based on heterojunctions between quantum dots and wide-band-gap nanowires. The physical principle behind these cells is quite different from the p-n-junction approach proposed here. The project has significant synergy with the proposed project, but no overlapping work.
- Title: Solar cells based on semiconductor nanoparticles and nanowires**
PI: E. Aydil Co-PI: U. Kortshagen, D. Norris, X. Y. Zhu
Source: IREE-Initiative for Renewable Energy and the Environment
Location: University of Minnesota
Award \$200,000 0.0 mo. acad. period: 08/15/2005-08/14/2007

Relation to this proposal: This is a matching grant to grant no. 5. It also focuses on studying excitonic solar cells based on heterojunctions between quantum dots and wide-band-gap nanowires. The project has significant synergy with the proposed project, but no overlapping work.
- Scaleable High-Yield Plasma Production of Functionalized Semiconductor Nanocrystals**
PI: U. Kortshagen Co-PI: J. T. Roberts
Source: National Science Foundation Location: University of Minnesota
Award \$330,000 1.0 mo. acad. period: 04/01/2006-03/31/2008

8. **Separation Control using Plasma Actuators on Low Pressure Turbine Airfoils with Passing Wakes: Experiments and Modeling**

PI: T. Simon co-PI: D. Ernie, U. Kortshagen
Source: NASA Location: University of Minnesota
Award \$750,000 0.5 mo. acad. period: 01/01/2007-12/31/2009

Pending Support:

9. **Dual-Plasma Co-Deposition of Mixed Phase Thin Film Materials**

PI: J. Kakalios co-PI: U. Kortshagen
Source: National Science Foundation Location: University of Minnesota
Award \$419,769 0.5 mo. acad. period: 07/01/2007-06/30/2010

10. **Silicon and Germanium Quantum Dots Arrays as Materials for Efficient, Low-Cost Solar Cells**

PI: U. Kortshagen co-PI: D. Norris
Source: Dept. of Energy Location: University of Minnesota
Award \$750,000 0.75 mo. acad. period: 07/01/2007-06/30/2010

11. **NIRT: High brightness electroluminescent nanoparticle devices and systems**

PI: S. A. Campbell co-PI: U. Kortshagen, R. Holmes
Source: NSF Location: University of Minnesota
Award \$1,400,000 0.5 mo. acad. period: 07/01/2007-06/30/2011

12. **Nanodusty plasmas: Fundamental studies of particle charging and particle-plasma interactions**

PI: U. Kortshagen co-PI: S. L. Girshick
Source: NSF Location: University of Minnesota
Award \$562,366 1.0 mo. sum. period: 07/01/2007-06/30/2011

13. **this proposal: Silicon and Germanium Quantum Dot Films for Photovoltaics**

PI: U. Kortshagen
Source: National Science Foundation Location: University of Minnesota
Award \$367,000 0.5 mo. acad. period: 10/01/2007-09/30/2010

Facilities and Equipment

The experimental work on Si and Ge QD synthesis will be performed in Kortshagen's laboratory, which is part of the High Temperature and Plasma Laboratory (HTPL), in the Department of Mechanical Engineering at the University of Minnesota. The HTPL is one of the best equipped plasma technology laboratories in the world. The proposed research will be located in the new facilities that are part of the new Mechanical Engineering Building, which opened in 2001. This laboratory includes eight custom-built plasma reactors with the corresponding radiofrequency and microwave power supplies. A dedicated reactor will be available for the nanoparticle synthesis in this project. The reactor will be upgraded by adding a second plasma functionalization stage.

The laboratory is equipped with several spectrometers, continuum light sources, and integrating spheres. In addition numerous plasma diagnostics for investigating the plasma and the gas phase are available. Electrical testing will be done on existing systems including an HP 4156 Parameter Analyzer, and an HP 4194 Impedance Analyzer. A cryostat for low-temperature electrical measurements is available.

The PI is part of a group of about ten faculty involved in photovoltaics research at the University of Minnesota. Solar cell characterization will be performed on equipment jointly used with other faculty in this group. The instruments include several spectrometers for the UV-VIS-IR range, and a solar simulator which simulates AM1.5 radiation. For chemical functionalization work, the lab is equipped with two fume hoods, a controlled atmosphere glove box and two Schlenk lines for performing air-sensitive chemistry.

User Facilities on Campus

Device development will rely on the facilities provided by the Nanofabrication Center (NFC). The NFC is one node of the National Nanotechnology Infrastructure Network. With an annual budget of 1.6 M\$ and approximately 15 full time staff members, NFC operates a 7000 square foot facility, including 3000 square feet of class 10 clean room. The Lab contains all of the major pieces of processing equipment needed to build the desired structures for this proposal. This list includes dc and rf sputtering, conventional and rapid thermal processing systems, furnace oxidation systems, plasma and low pressure thermal chemical vapor deposition for a variety of semiconductors and insulators including high permittivity films, optical photolithography, reactive ion etching, high density plasma etching, ion milling, a direct write e-beam system, and a focused ion beam system.

In addition, the PIs have access to a large number of shared instruments and user facilities at the University of Minnesota, including a small angle X-ray scattering facility, and an electron microscopy center (part of the Materials Characterization Facility, "CharFac," <http://www.charfac.umn.edu/>). The equipment is too extensive to list here but some of the relevant characterization facilities include JEOL JEM-1210, Tecnai G2 F30 and FEI Tecnai T12 TEMs and STEM; JEOL 6500 and JEOL 6700 SEMs; and two small angle X-ray scattering lines. Several electronics, machine, and glass shops are also available at the University of Minnesota.



September 28, 2006

Dr. Kevin W. Lyons
Program Manager - Nanomanufacturing
National Science Foundation
4201 Wilson Blvd
Arlington, VA 22230

Dear Dr. Lyons:

I am writing to express Innovalight's support for the proposal entitled:

“Manufacturing Group IV Quantum Dot Solar Cells”

which is submitted by Prof. Uwe Kortshagen of the University of Minnesota. Innovalight is a venture-funded company focused on developing low-cost photovoltaic devices from silicon nanocrystals.

Innovalight has closely collaborated with Prof. Kortshagen's group since 2003. Parts of the synthesis of quality silicon nanocrystals devised by Prof. Kortshagen is at the core of Innovalight's technology development. In 2004, after a comparative evaluation of this approach against many other published nanocrystal synthesis schemes, Innovalight acquired an exclusive license from the University of Minnesota for this synthesis technique.

While Innovalight pursues its own proprietary technology to integrate the silicon quantum dots into functional photovoltaic devices, we maintain a continuing strong collaboration with Prof. Kortshagen. Innovalight's Director of Research and Development, Dr. David Jurbergs, is a co-P.I. on a GOALI grant to study the formation of nanocrystals with Prof. Kortshagen as P.I. Innovalight researchers have now published three joint publications with Prof. Kortshagen's group. This collaboration has been in the true spirit of mutual benefit.

Since the proposed research is closely aligned with Innovalight's business interests, the company has a most vital interest in the proposed research and will continue to closely monitor developments from Prof. Kortshagen's group. Innovalight's scientific staff continues regular exchange of ideas with Prof. Kortshagen and his students and will be happy to support Prof. Kortshagen in any way possible.

Sincerely,

Conrad Burke
President & CEO