

UNIVERSITY of CALIFORNIA
SANTA CRUZ

**GERMANIUM QUANTUM DOTS IN
PHOTOVOLTAICS AND LIGAND EXCHANGE**

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In

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By

RILEY C. RUTAN

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The thesis of Riley C. Rutan is approved by:

Professor Sue Carter
Advisor

Professor David Belanger
Thesis Advisor

Professor Robert Johnson
Chair, Department of Physics

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Renee H. Sully.

Abstract

Quantum dots are crystals of semiconductors on the scale of a nanometer, and display many unique properties that differ from their bulk crystalline counterparts. Germanium quantum dots are subject of great interest in materials science research for use in high efficiency and low cost solar cells. In order to ensure stability and charge transport between Ge quantum dots, the preparation of methylammonium capped quantum dots was investigated. A partial replacement of original olelyamine surface ligands with methylammonium ligands was reported using FTIR spectroscopy.

Introduction

Since the industrial revolution, the ever-growing human population has been dependent on burning coal and fossil fuels to meet its energy requirements.

Humanity's traditional forms of energy production have caused an unprecedented spike in greenhouse gases in the atmosphere, and irreversibly damaged the earth's environment. From the melting of polar ice caps to more frequent and violent natural disasters, the need for low cost and sustainable energy production has never been more apparent. Solar cells provide a sustainable source of energy, and their efficiencies are rising.

A quantum dot (QD) is a particle of a semiconductor on the nanometer scale, and is of wide interest in a variety of fields. Due to the small structure of QDs, their physical properties such as electron transport are quite different from those of bulk materials. Thin films of germanium quantum dots show promise for use in photovoltaics.

Thin-Film solar cells are made by depositing layers of photovoltaic material on a substrate such as glass, metal or plastic. These solar cells contain heterojunctions, or interfaces of two different crystalline semiconductors, which determines the electron and hole transport of a device. This manipulation of charge transport properties through design of material interfaces in a thin-film solar cell is often referred to as bandgap engineering. Thin-films of quantum dots have potential as the active layer of low cost and high efficiency thin-film solar cells.

There is much work to be done until quantum dots of germanium are ready to be used in the solar cells of tomorrow. A quantum dot dispersion, or colloidal crystals on the scale of a nanometer, is not the most stable form of germanium. Capping molecules, or ligands, are introduced during the synthesis process to stabilize the structure of each quantum dot and to protect them of oxidization. These ligands are usually long, organic molecules such as olelyamine (OAM). While these ligands are essential to the synthesis of germanium quantum dots, they are electrically insulating, making quantum dots useless for use in photovoltaics. The ligands need to be exchanged with a shorter molecule, such as methylammonium to passivate the quantum dot surface and allow charge transport between dots.

Background

Nanoscale semiconductor materials tightly confine the motion of conduction electrons, valance holes, and excitons in three spatial directions. These materials are also often referred to as zero-dimensional nanomaterials or artificial atoms, which emphasizes that a QD is a single object with discrete electron bound states, like an atom.

Quantum confinement arises in nanomaterials. As a quantum dot approaches the size of the Bohr radius, the electron can be approximated to be in a three dimensional potential well. This method can predict the confined energy levels of nanostructures by solving Schrodinger's equation, assuming infinite confining potential:

$$E_{n_x, n_y, n_z} = \left[\frac{\pi^2 \hbar^2}{2m^*} \right] \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \quad (\text{Eq. 1})$$

where n are the integer quantum confinement numbers, m^* is the effective mass of the electron and L_x, L_y, L_z are the spatial restraints. This approximation of quantum dots as three-dimensional infinite potential wells displays the quantum dot size dependence on discrete energy levels. By varying the size of the quantum dot, the confinement energy of the exciton can be controlled. And because the Bohr radius of Germanium is large (24.3 nm) compared to silicon (4.9 nm) [1], quantum size effects become apparent at larger sizes of quantum dots in germanium QDs compared to silicon QDs.

The dependence of the energy band gap on quantum dot size is displayed in figure 1, which shows the fluorescence of varying sized of cadmium selenide quantum dots. Each solution of quantum dots illuminates as a different color, because when an incident photon excites an electron across the band gap, the electron recombines to the valence band and emits a photon of a precise wavelength corresponding to the size of the band gap. The tunable band gap of quantum dots makes them attractive for use in photovoltaics. Easily altering the size and band gap of quantum dots of the same material allows for them to be used in a variety of different devices.

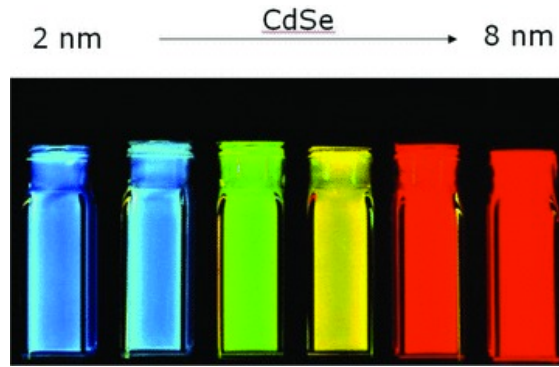


Figure 1: Energy band gap dependence on the size of cadmium selenide quantum dots (image sourced from [2]).

Germanium has high absorption coefficient for a wide range of incident wavelengths, compared to other semiconductors as seen in figure 2. A high absorption coefficient means that a photon will travel less distance into a material before being absorbed and generating an exciton. Germanium's superior absorption coefficient over a spectrum of wavelengths allows for very thin films to still absorb photons and generate excitons with high efficiency.

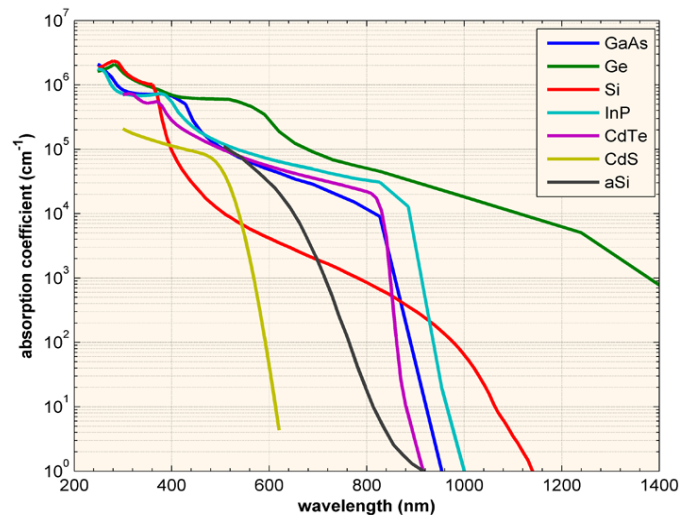


Figure 2: The absorption coefficients (cm^{-1}) versus wavelength of incident light (nm) of several semiconductors (image sourced from [3]).

In a conventional solar cell, the absorption of a single photon leads to the excitation of one electron from the valence band to the conduction band. This electron is coupled with the positively charged electron hole it left behind through the electrostatic Coulomb force. This electron and hole pair is known as an exciton, an electrically neutral quasi-particle that can transport energy without transporting net electric charge. When a photon of energy greater than the band gap is absorbed, a single exciton is produced and the excess energy dissipated as heat, a process known as thermalizing.

In a thin-film quantum dot solar cell, the absorption of a high-energy photon can create multiple excitons, a phenomenon called multiple exciton generation (MEG). An excited carrier may use some of its excess energy to excite another electron across the band gap, instead of thermalizing. The capability of MEG allows a quantum dot photovoltaic device to make use of a broader energy range of incident photons. By generating an average of more than one exciton for each optical excitation, quantum dot solar cells also have the potential of greatly increased energy production efficiencies. Germanium QD devices should theoretically achieve MEG at a high rate due to its low band gap of 0.66 eV. Multiple exciton generation should be possible over a wider range of incident photon energies.

The low band gap of Germanium is also useful for the bottom layer of high efficiency high efficiency solar cells. Multi-junction solar cells use several different semiconductors to convert light with a broad range of wavelengths into electrical current. Multi-junction cells boast efficiencies as high as 46% under concentrated

sunlight [4], while single junction silicon solar cells peaked at an efficiency of 25% in 2012 [5]. As seen in figures 3 and 4, germanium can be used as the bottom layer of a multi-junction solar cell to absorb longer wavelength and lower energy of the electromagnetic spectrum. With the understanding to produce thin-film of Ge QDs as a superior photovoltaic material to bulk germanium, the efficiencies of multi-junction cells could be improved even further.

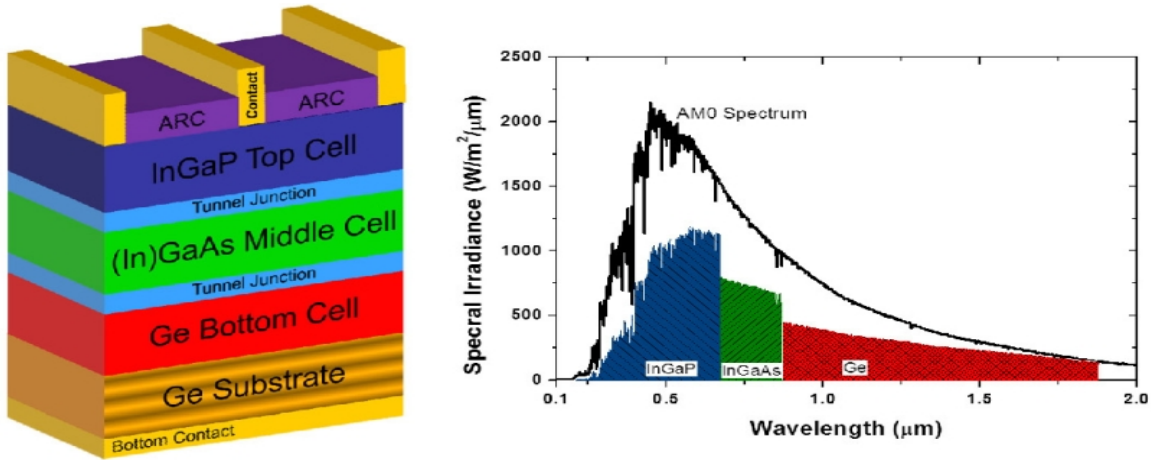


Figure 3: Schematic diagram of a multijunction solar cell using germanium as bottom layer (left).
Figure 4: Spectral Irradiance ($\text{W/m}^2/\mu\text{m}$) versus wavelength of incident light (right) (image sourced from [6])

The germanium quantum dots were synthesis by our collaborators, the Kauzlarich group at University of California, Davis. Germanium iodide (GeI_2 and GeI_4) precursors and oleylamine (OAM) were heated to 210°C for 60 minutes. The ratio of these two precursors controls the size of the QDs. The OAM molecules attach to the surface of the QD's and stabilize them in solution, protect them from oxidization, and passive the germanium. The long hydrocarbon chains in

oleylamine (OAM) ligands, as seen in figure 5, are useful for storing and transporting QD solutions.

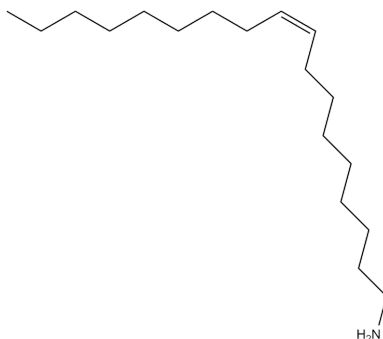


Figure 5: Molecular structure of Oleylamine ligand(image sourced from [7]).

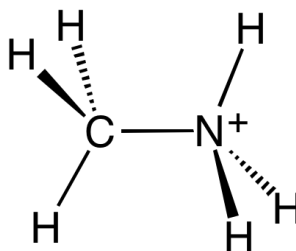


Figure 6: Molecular structure of Methylammonium ligand (image sourced from [8]).

While essential to the production of the QDs, the long oleylamine ligands prevent the quantum dots from electrically coupling to their neighbors and insulate the movement of charge carriers; which is depicted in figure 7.

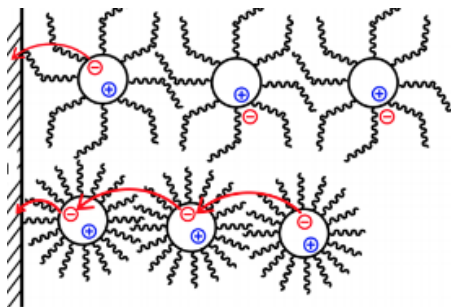


Figure 7: Schematic diagram of charge transport properties of OAM capped (top) and methylammonium capped (bottom) Ge QDs (image sourced from [9]).

The much shorter methylammonium ligands, as seen in figure 6, allow for the quantum dots to be closer together when spun into a thin film. To enable the transport of charge carriers necessary for use in a photovoltaic device, the OAM ligands on the quantum dots must be exchanged with methylammonium.

The surface chemistry of a quantum dot, which greatly affects its charge transport properties, can be studied through FTIR analysis. A Fourier-transform infrared spectroscopy (FTIR) machine shines a beam of infrared light generated by a broadband source through a sample. The intensity of light transmitted through the sample is recorded, and decomposed into a wide spectrum of wavelengths using a Fourier transform. The absorption of a certain wavelength of light, or corresponding wavenumber, will be displayed as a drop in transmittance on the FTIR output. Absorption of a certain wavelength corresponds to a resonant frequency of a sample, which occurs when the frequency of the incident photon matches the vibrational frequency of the sample. These resonant frequencies directly depend on molecular structure. Therefore, the wavelength (or wavenumber) that is absorbed displays the molecular composition of a sample. The peaks in absorbance that correspond to molecular structures and atomic bonds are displayed in figure 8.

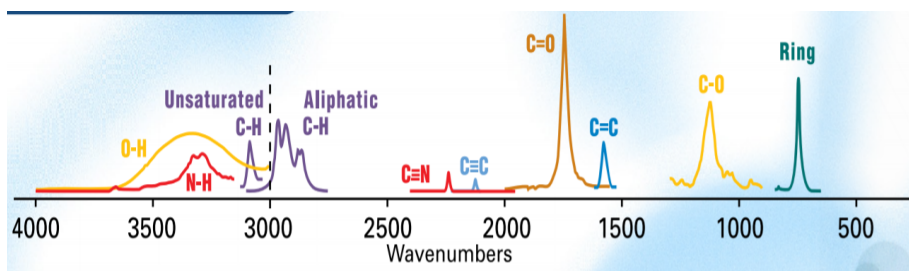


Figure 8: Typical absorbance peaks and corresponding molecular structures and bonds (image sourced from [10]).

A Fourier transform infrared spectroscopy machine was used to probe the surface chemistry of the germanium quantum dots, and the success of each ligand exchange. The two or three sharp absorbance peaks at wavenumbers around 2900 cm^{-1} shows the presence of the long hydrocarbon (C-H) chains in olelyamine ligands. These peaks OAM peaks should only be present in pre-exchange measurements. A broader peak in wavenumbers in the low three thousands indicate the presence of the hydrogen-nitrogen (N-H) bonds present in the methylammonium ligands. Infrared spectroscopy data of quantum dots with this broad peak without the presence of the sharp C-H peaks would suggest a complete and successful ligand exchange.

Procedure

For use in thin-film optoelectronics, solutions of germanium quantum dots were stripped of their oleylamine ligands, which were replaced with shorter methylenonium molecules. To avoid the oxidization of the Ge quantum dots, all procedures were done in a nitrogen environment glove box. The dispersion of 160 μL of germanium quantum dots, 0.16 grams of methylenammonium iodide (MAI), 1 mL of dimethyl formaldehyde (DMF), 50 μL of toluene and a stir bar were placed in a 7 mL glass vial. The DMF was included to act as a solvent, and the toluene was added to help remove the OAM for the system. The solution was stirred at 80° C for 48 hours. After this step, the ligand exchange should be complete, but there is still oleylamine in the solution that needs to be removed. To wash the quantum dots, the contents of the vial were then centrifuged for about 10 minutes to isolate the QDs, and the colorless supernatant was discarded. Next, 1 mL of DMF and 40 μL of toluene were added to the centrifuge tube and sonicated for 10 minutes. The washing process was then repeated two more times. After the third wash and centrifuge, a single drop of the quantum dot dispersion was removed from the centrifuge tube and placed on a KBr pellet for FTIR analysis. The quantum dots were placed back into a glass vial, and the entire process was repeated two more times, with samples taken for FTIR analysis after each exchange and wash.

Results and Analysis

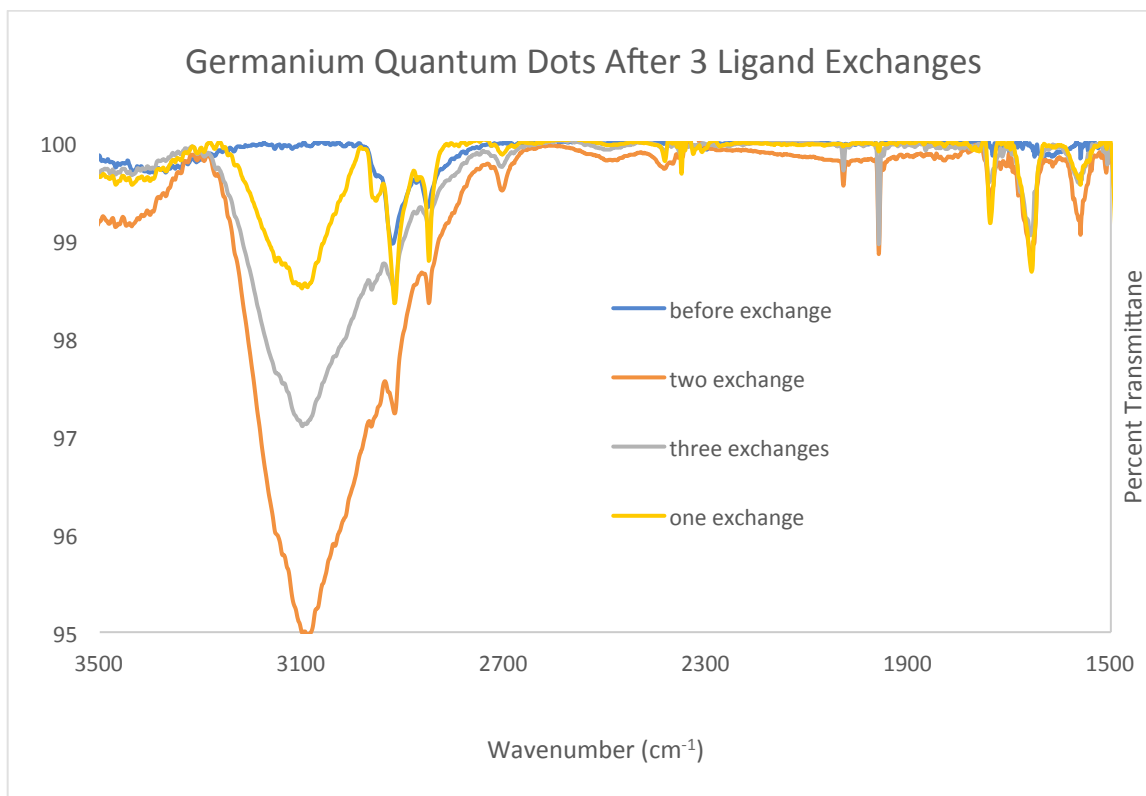


Figure 9: FTIR results of Ge QD's before and after multiple exchanges, plotting wavenumber (cm⁻¹) versus percent transmittance.

The results of FTIR analysis of the germanium quantum dots after three ligand exchanges are displayed in figure 9. The data set before exchange in blue displays only the peaks corresponding to aliphatic hydrocarbon chains in the OAM ligands. After one exchange, displayed in yellow, the FTIR analysis displays the broad NH, suggesting the attachment of the methylammonium ligands, but still shows a strong signal for the hydrocarbon chains of the olelyamine ligands. The data taken after two and three ligand exchanges, displayed in orange and grey, suggests that the multiple exchanges allowed for the methylammonium molecules

to attach to the surface of the quantum dots. But, even after two and three exchanges the presence of OAM molecules is still detected with small peaks at wavenumbers around 2900 cm^{-1} . The only OAM molecules introduced to the system were attached to the quantum dots pre-exchange. After three exchanges, and nine total washing procedures, it is highly unlikely that any of the OAM molecules detected in the FTIR had been stripped the QD and still present in the QD dispersion. Therefore, the presence of absorbance peaks of both olelyamine and methlyammonium ligands suggests an incomplete ligand exchange. It seems some, but not all of the original OAM molecules were stripped from the surface of the QD and replaced with methylammonium molecules. It is unclear how this incomplete exchange would affect the charge carrying properties of the quantum dot film, that is the ratio of desirable methalyammonium to insulating OAM ligands may be great enough to allow electronic coupling of quantum dots.

Conclusion

Thin films of germanium quantum dots have peaked the interest of material scientists for a variety of reasons. While using little material, quantum dot solar cells have the capability of high-energy efficiencies through multiple exciton generation. Their physical properties are highly tunable and depend on size, which makes them versatile for use in a variety of different optoelectronic devices. The superior absorption coefficient of germanium allows for thinner, more lightweight and material efficient devices. And the low energy band gap of germanium allows

for use as a bottom layer of multi-junction solar cells that report the highest power output efficiencies. The charge transport properties of QDs are greatly dependent on their surface chemistry, and the manipulation of the molecules attached to their surface is essential for this novel material to be used in photovoltaic devices. A partial ligand exchange of germanium quantum dots was observed using FTIR spectroscopy. Most, but not all of the long and insulating oleylamine ligands were stripped from the quantum dots and replaced with shorter electronically activating methylammonium ligands.

With more samples of germanium quantum dots coming from our collaborators at UC Davis, a procedure for a complete and total ligand exchange can soon be achieved. Photothermal detection spectroscopy (PDS) can be used to determine the energy band gaps of quantum dot thin films, and how they are affected by different ligands. Next, a thin-film solar cell device can be fabricated using Ge QDs as an active layer.

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