

REPORT DOCUMENTATION PAGE		Form Approved OMB NO. 0704-0188	
Public Reporting Burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington DC 20503			
1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE:	
		3. REPORT TYPE AND DATES COVERED Final Report 1-Feb-2005 - 31-Oct-2005	
4. TITLE AND SUBTITLE Intersubband Photoconduction in CdTe/DcS and CdTe/CdSe Nanowires		5. FUNDING NUMBERS W911NF0510030	
6. AUTHORS David Crouse		8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES CUNY (City College of New York) 138 Street @ Convert Avenue 79 Fifth Ave. New York, NY 10031 -			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER 47586-EL-II.1	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The abstract is below since many authors do not follow the 200 word limit			
14. SUBJECT TERMS Quantum wires, infrared detectors, II-VI semiconductors, alumina, focal plane arrays		15. NUMBER OF PAGES Unknown due to possible attachments	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

Report Title

Intersubband Photoconductance in CdTe/CdSe and CdTe/CdS Nanowire Arrays

ABSTRACT

The aim of the project is the theoretical analysis of intersubband IR detection in semiconductor nanowires and the nonlithographic fabrication and the structural, optical and electrical characterization of II-VI semiconductor nanowires and II-VI/II-VI semiconductor nanowire heterostructures. Significant progress has been made on the theoretical analysis and fabrication portions of the project. The theory has used both analytical and finite difference algorithms and has shown that the method of fabricating the nanowires is capable of producing the necessary small diameters of the nanowires. CdSe/CdTe nanowires and CdSe/Zn_{1-x}Cd_xSe are shown to be possible and will be able to detect near, mid and long wavelength IR radiation. The electron subband states and the absorption in the IR spectral range due to intersubband transitions has been calculated. The surface optical and longitudinal optical phonon modes have been calculated and the proper quantization procedure has been developed. Electron-phonon scattering has been investigated and high temperature operation has been investigated. The development of the nanotemplate has been completed and thin films of II-VI semiconductors and II-VI nanowires has started and some optical and structural characterization has been performed.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

[1] David Crouse, Michael Crouse" Design and numerical modeling of normal oriented quantum wire infrared photodetector array " Infrared Physics and Technology, Available online 28 February 2006.

[2] David Crouse, "Phonon Modes and Electron-Phonon Interactions in Cylindrical Quantum Wires: Macroscopic and Microscopic Analyses and Device Applications", J. Appl. Phys. (in press).

Number of Papers published in peer-reviewed journals: 2.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Papers presented at meetings, but not published in conference proceedings (N/A for none)

Number of Papers not Published: 0.00

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

NAME	PERCENT SUPPORTED	
Ataul Ikram	0.50	No
FTE Equivalent:	0.50	
Total Number:	1	

Names of Post Doctorates

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Names of Faculty Supported

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Names of Under Graduate students supported

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Names of Personnel receiving masters degrees

NAME

Pavan Keshavareddy

No

Ravina Solomon

No

Total Number:

2

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

1. Forward

The aim of the project is the theoretical analysis of intersubband IR detection in semiconductor nanowires and the nonlithographic fabrication and the structural, optical and electrical characterization of II-VI semiconductor nanowires and II-VI/II-VI semiconductor nanowire heterostructures. Significant progress has been made on the theoretical analysis and fabrication portions of the project. The theory has used both analytical and finite difference algorithms and has shown that the method of fabricating the nanowires is capable of producing the necessary small diameters of the nanowires. CdSe/CdTe nanowires and CdSe/Zn_{1-x}Cd_xSe are shown to be possible and will be able to detect near, mid and long wavelength IR radiation. The electron subband states and the absorption in the IR spectral range due to intersubband transitions has been calculated. The surface optical and longitudinal optical phonon modes have been calculated and the proper quantization procedure has been developed. Electron-phonon scattering has been investigated and high temperature operation has been investigated. The development of the nanotemplate has been completed and thin films of II-VI semiconductors and II-VI nanowires has started and some optical and structural characterization has been performed.

2. Program Objective

This final report will discuss the results of the Short Term Innovative Research Project on intersubband transitions in CdTe/CdS and CdTe/CdSe nanowires. This program objectives required the theoretical analysis of intersubband transitions in nanowires and the development of a practical approach to fabricate the nanowires. In particular, the following tasks were to be performed:

- Task 1. Develop numerical modeling techniques to model the IR detecting quantum wires.
- Task 2. Fabricate prototype nanotemplates and CdTe/CdS and CdTe/CdSe nanowire heterostructures.
- Task 3. Electrically and optically characterize the prototype nanotemplate, nanowires and photodetectors

As stated before, the above tasks were to be performed to analyze the intersubband transitions and also to show that these II-VI/II-VI semiconductor quantum wire heterostructures can be used for mid and long wavelength IR detection as quantum wire infrared detectors (QRIPs) with the following advantages over existing quantum well infrared photodetectors (QWIPs):

1. The ability to detect normally incidence light.
2. *Possibly higher temperature operation due to the inhibition of phonon scattering.*
3. The ability to detect multiple wavelengths of IR radiation
4. The ability to integrate the IR detecting devices on any desired substrate including Si.
5. Integration of photodetecting and electronic aspects of FPAs.

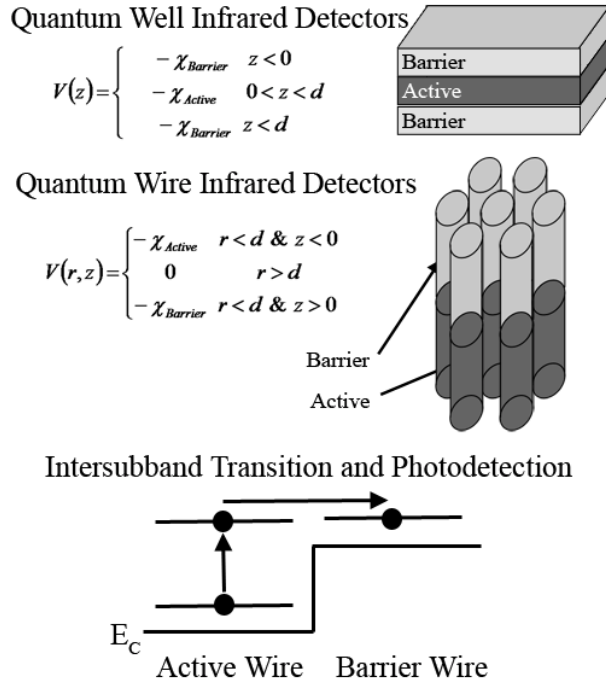


Figure 1: The structures of a QWIP and QRIP. If normal incident light falls on the detectors only the QRIP will produce an appreciable current because of the photon absorption selection rules. The concept of intersubband transitions is also shown along with the

6. The ability to fabricate the FPA using CMOS compatible fabrication processes.
7. To develop a fabrication mechanism that reduces the cost of FPA fabrication while producing superior performing devices.

3. Results

Quantized intersubband levels are produced in nanoscale structures, such as quantum wells, wires and dots where the conduction band and valence band subbands are “quantized”, or in other terms, the energy difference between subband levels becomes comparable to the energy of IR radiation (Fig. 1). The state of the art with intersubband detectors includes recently developed quantum well infrared photodetectors (QWIPs) that use GaAs/AlGaAs/GaAs quantum wells and a variety of other materials. However, QWIPs have several significant drawbacks that have limited their implementation in practical and widespread sensor systems. One major drawback is their inability to detect normal incident light as a result of the well known selection rules for photon absorption in these structures. This characteristic of QWIPs requires the use of grating couplers or other techniques to produce off-normal incidence. The second issue with QWIPs is that phonon scattering is not inhibited to the same degree as occurs in quantum wires (QR) and quantum dots (QD), disallowing the possibility of higher temperature operation.

These two issues are either solved or mitigated by using QRs and intersubband transitions QR heterostructures. First, the photon absorption rules can be avoided by structures that restrict electron or hole motion in directions parallel to the surface of the device, as is accomplished in QRs. Second, the one dimensionality of the QRs produces a strong optical-phonon (OP) scattering around the OP energy Δ that, if the QR is fabricated accordingly, can produce electron confinement to electron states below Δ [8]. This then should allow for IR photodetectors that are capable of operating at higher temperatures compared to state of the art QWIPs and the more conventional bulk HgCdTe-based IR photodetectors.

In this project, we have been modeling normal-oriented II-VI semiconductor quantum wire heterostructures and evaluating their use as QRIPs. These QRs use a solvent-based DC electrochemical growth of II-VI semiconductors quantum wires in an anodized aluminum (i.e., alumina) template. As shown in Figs. 2, the II-VI semiconductor QRs in the alumina structure are composed of a hexagonal array of normal

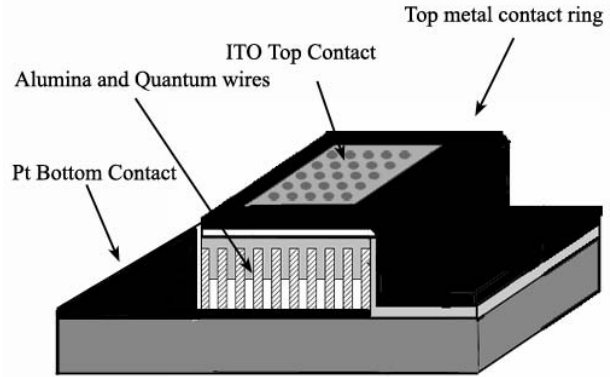


Figure 2: One design of a QRIP that uses the multilayer nanotemplate. This one pixel detector has a Si substrate with a Pt bottom electrode, a ITO Top contact and metal contact ring. The active wire (white) is next to the substrate and the barrier wire (gray) is above it and makes an electrical contact with the ITO.

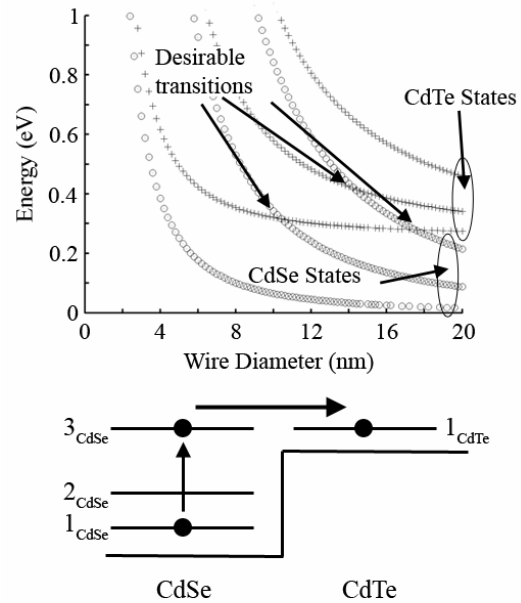


Fig. 3: Top: The electron subband levels in CdSe and CdTe. Bottom: A diagram of the $1_{\text{CdSe}} \rightarrow 3_{\text{CdSe}} \rightarrow 1_{\text{CdTe}}$ transition for a wire with diameter 17.4 nm allowing for $4.76 \mu\text{m}$ IR radiation to be detected.

oriented wires (i.e., normal with respect to the substrate surface). Each wire is composed of two parts, one part being the active wire where photons are absorbed and another part that serves as a barrier region where ideally, only photo-excited electrons are capable of traversing. In the proposed project, we investigated whether an alumina-based template would be feasible to fabricate the QRs and subsequently the FPA with the associated read-out integrated circuitry (ROIC).

Uniform Quantum Wires

In this part of the project, the electron states in the conduction band subbands of the quantum wires have been calculated using two methods. For uniform quantum wires composed of only one material, the states are calculated using the well known but simplified model of a finite cylindrical potential well. For the complete quantum wire composed of the active and barrier regions, a finite difference (FD) technique is used to allow for the accurate modeling of the states and the effects of the heterostructure and interface between the two portions of the wire, an applied bias, doping and surface effects. For a uniform quantum wire oriented with its axis parallel to the z-axis, with a wire radius R and electron affinity of the semiconductor as χ , the electron potential energy is $-\chi$ within the wire and zero outside the wire. The Hamiltonian is then solved for the wavefunctions and quantized energy levels.

This simple analysis can served as a starting point to evaluate potential combinations of II-VI semiconductors that can be used in QRIPs. Figure 3 shows a plot of the energies of the electron states in uniform CdTe and CdSe quantum wires as a function of wire diameter. It is necessary that the energies of the electron states match to a large degree in the two halves of the wire to allow for the electrons in the excited state in the active wire to easily drift to the barrier wire. It is seen that the first excited state in the CdSe (denoted as 2_{CdSe}) QR matches the ground state in the CdTe (denoted as 1_{CdTe}) QR when the wire diameter is 10.4 nm, 3_{CdSe} matches 2_{CdTe} when the wire diameter is 14.2 nm, and 3_{CdSe} matches 1_{CdTe} when the wire diameter is 17.4 nm. These diameters (D) are achievable with the anodized alumina template and allow the flowing transitions:

Possible Transitions

$D=10.4\text{nm}$: $1_{\text{CdSe}} \rightarrow 2_{\text{CdSe}} \rightarrow 1_{\text{CdTe}}$ allowing $4.83\mu\text{m}$ IR detection

$D=14.2\text{nm}$: $1_{\text{CdSe}} \rightarrow 3_{\text{CdSe}} \rightarrow 2_{\text{CdTe}}$ allowing $3.17\mu\text{m}$ IR detection, $2_{\text{CdSe}} \rightarrow 3_{\text{CdSe}} \rightarrow 2_{\text{CdTe}}$ allowing $4.95\mu\text{m}$ IR detection

$D=17.4\text{nm}$: $1_{\text{CdSe}} \rightarrow 3_{\text{CdSe}} \rightarrow 1_{\text{CdTe}}$ allowing $4.76\mu\text{m}$ IR detection, $2_{\text{CdSe}} \rightarrow 3_{\text{CdSe}} \rightarrow 1_{\text{CdTe}}$ allowing $7.40\mu\text{m}$ IR detection

An important thing with the CdSe/CdTe system is that the detection wavelengths can be increased by alloying the CdTe with Se producing $\text{CdTe}_{1-x}\text{Se}_x$. This alloying procedure will reduce the conduction band

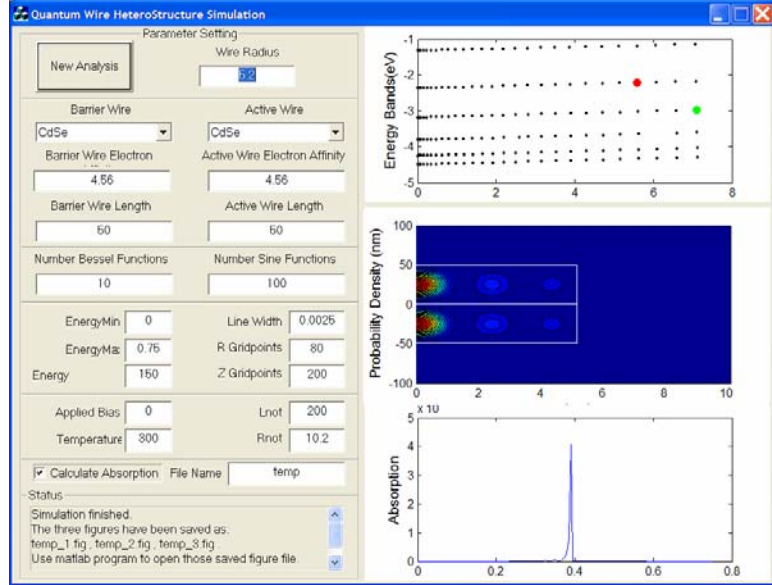


Fig. 4 The GUI for the FD algorithm to model QRIPs. This program was developed in this project and will allow for more sophisticated modeling of the QRIPs. It is being copyrighted and licensing opportunities are being explored.

discontinuity and the differences in energy of the quantum states in the two portions of the wire. This procedure of alloying the CdTe with Se is important because it will allow for detectors to be developed that can operate from the near IR to the mid and long wavelength IR spectral ranges as desired in this project. To progress any further in the analysis, a flexible FD technique was developed and will be used for the remainder of the project.

Finite Difference Calculation of QRIPs

After the simple analytic technique was used to approximate the necessary diameters of the quantum wire, a FD technique was then developed to calculate all other aspects of the optical and electronic behavior of the wire. The FD method used in this work is based on the stabilization method. With the FD method, any electron potential $V(r,z)$ can be used including the effects of the heterostructure, doping, applied bias and surface effects. In this project, the electron states in a QRIP with zero applied bias was calculated first followed by the calculation of the states when a bias is applied. The potential that is used to for the CdSe/CdTe QRIP with zero applied bias is:

$$V(r,z) = \begin{cases} -\chi_{CdSe} & \text{for } r \leq R \text{ and } z < 0 \\ -\chi_{CdTe} & \text{for } r \leq R \text{ and } z > 0 \\ 0 & \text{otherwise} \end{cases} \quad (1)$$

The quantum states are expressed as a linear combination of basis functions:

$$\Psi = \sum_{m,n} a_{m,n} \varphi_{m,n} \quad \text{with} \quad \varphi_{m,n} = \sqrt{\frac{2}{\pi L_o R_o^2 J_1^2(s_m R_o)}} J_0(s_m r) \sin(k_n z) \quad (2)$$

where $s_m R_o$ are the zeros of $J_0(x)$ and $k_n = 2\pi n / L_o$. The Hamiltonian, with $V(r,z)$ given by Eq. (1) is then diagonalized using the above basis functions. A fast C++ code with an easy to use graphical user interface (GUI), shown in Fig. 4, was developed to allow for fast analysis and design of QRs and QRIPs. The FD method reproduced the same results as the analytic method for the uniform CdSe quantum wire indicating that the method is accurate as well as having the flexibility to model the effects of the heterostructure in a QRIP and an applied bias.

Absorption

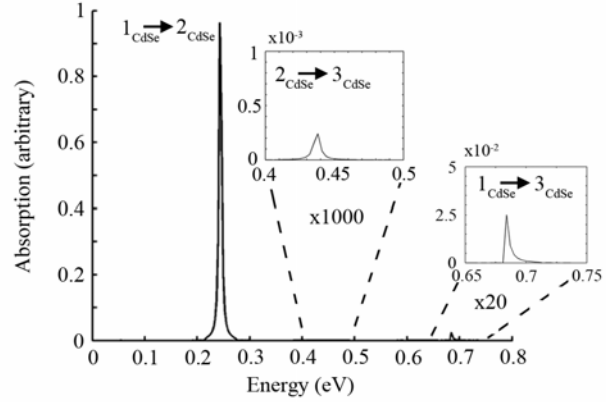
Once all of the electron quantum states were calculated in the CdSe/CdTe QRIP, the absorption $\alpha(\omega)$ was calculated using first order perturbation theory and Fermi's golden rule. In this case, the temperature is taken to be 300K, the CdSe is n-type, the CdTe is nonintentionally doped. Thus the absorption is produced almost entirely by the CdSe portion of the quantum wire. As a first approximation, the electron distribution is assumed to obey Fermi-Dirac distribution function denoted as $F(E)$. This assumption is used only as a starting point since it has previously been discussed that the true distribution of electrons in quantum wires and quantum dots experience can be significantly modified due to modified phonon scattering, but the complete description of the phonon scattering is outside the scope of this paper. The absorption in this case can be written as:

$$\alpha(\hbar\omega) = \frac{2\pi e^2}{n_{wire} c \epsilon_o m_o^2 \omega V_{wire}} \sum_{f,i} |\hat{e} \cdot \mathbf{p}_{fi}|^2 L(\Gamma, E_f - E_i - \hbar\omega) (F(E_i) - F(E_f)) \quad (3)$$

where n_{wire} and V_{wire} are the index of refraction and volume of the wire, $\hat{e}$ is the polarization of the incident light and $L(\Gamma, E_f - E_i - \hbar\omega)$ is a Lorentzian function with linewidth Γ :

$$L(\Gamma, E_f - E_i - \hbar\omega) = \frac{\Gamma/2\pi}{(E_f - E_i - \hbar\omega)^2 - (\Gamma/2)^2} \quad (4)$$

Figure 5 shows the absorption for a uniform CdSe quantum wire and a CdSe/CdTe heterostructure quantum wire at 300K. The linewidth is chosen as 5 meV for all CdSe and CdTe transitions. As has been purposely chosen, most of the absorption in the CdSe/CdTe quantum wire is due to the CdSe. The absorption of the alumina in the IR is minimal with only a broad band



Multilayer Alumina Nanotemplate

To fabricate the quantum wires described in this project, a nanoporous alumina template was used as a mold to electrochemically grow various II-VI semiconductors. We have developed a practical method of integrating the porous alumina with any desired substrate with the ability of having a Pt film at the base of the pores. This method does not involve any complicated film transfer techniques and minimizes the number of chemical procedures necessary for the fabrication. A schematic of the multilayer template and the alumina structure are shown in Fig. 6. To fabricate this template, the following metal layers are initially deposited on the desired substrate:

1. A thin (~ 30 -50 nm) Pt layer that serves as an electrode for the DC electrodeposition of metals or semiconductors within the pores of the alumina. Too thick of a Pt layer may produce undesirable roughness and too thin of a Pt layer may result in a discontinuous film and high resistivity.
2. A thin (~ 5 -8 nm) Ti layer that serves to inhibit Si/Pt intermetallics and to isolate the Pt layer from the electrolyte used to fabricate the porous alumina. This layer will be transformed into TiO_2 during the anodization of the aluminum.
3. A thick aluminum layer that will be anodized into alumina. The thickness can be as thin as approximately 150 – 200 nm and can be at least as thick as $2\mu\text{m}$ without any problems of stress-induced delamination of the metal layers.

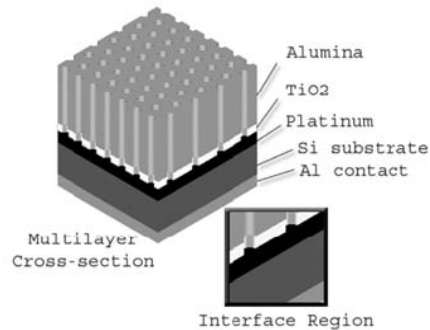
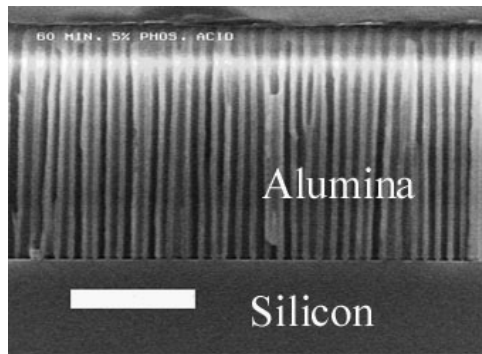


Figure 6: Left: Cross-section view of the alumina pores. The white bar is 1 micron.¹⁷ Right: A schematic of the multilayer nanotemplate after anodization and voltage ramping to remove the TiO_2 layer at the base of the pores. Once the template fabrication is complete, the pores terminate at the Pt.

After the above metal layers are deposited, the structure was anodized in 0.5M H_2SO_4 at a temperature of 10°C . The pore spacing and diameter are dependent on the anodization voltage and roughly obeys the relation *Pore Spacing (in nm) = $2.5 \times \text{Applied Voltage}$* , therefore the voltage that is chosen for the anodization will depend on the pore spacing and diameter desired. Once the anodization of the alumina is done at the chosen constant voltage, the voltage is then ramped to produce anodic breakdown and dissolution of the TiO_2 at the base of the pores and subsequently exposing the Pt. Once the TiO_2 is eliminated at the base of the pores, the pores are cleaned and widened by the H_3PO_4 etch and the template is ready for quantum wire deposition.

Of all the approaches of depositing semiconductor material into the pores of the anodic multilayer template, the electrochemical synthetic approach is the most favorable. This is particularly the case for II-VI semiconductors that, due to their particular ionic states and related electronic affinities, are well suited to single potential deposition techniques. An important additional consideration is the existence of a planar Pt electrode at the base of the pores that allows for a constant current reaction system (voltage floats as necessary) to be setup in the pore, creating a directed crystal growth system from the bottom of the pore towards the top at a defined nucleation rate. The synthesis uses a constant current to insure a constant nucleation rate, an aspect known to be important for high quality single crystalline type growth. The synthesis is carried out by dissolving CdCl_2 in a nonaqueous, polar, aprotic solvent, typically Dimethyl Sulfoxide (DMSO). This technique is favored for two reasons. Firstly, the deposition is known to give a dense, polycrystalline CdS when deposited as a thin film with comparatively low impurity levels at $100\text{-}160^\circ\text{C}$. Secondly, the nonaqueous nature of the synthesis eliminates deleterious side reactions with the porous alumina template such as the water hydrolysis reaction and the dissolution of the alumina. The concentration of the CdCl_2 in the DMSO solvent was set to 0.055 M and the concentration of sulfur was set at the saturation point for DMSO at 140°C . Figure 7 shows our preliminary results for using the multilayer nanotemplate to deposit CdS. The growth of CdSe, CdTe, ZnSe and associated ternary semiconductors is now being done, as well as the optical characterization of these materials and structures.

Figure 2 in the introduction shows one potential design of a one-pixel QRIP that uses the multilayer nanotemplate. In such a design, several aspects need to be considered including the top and bottom electrical contacts and the design of the read-out integrated circuitry (ROIC). All of these additional aspects are being investigated including the electrical contacts, the packaging techniques, cooling techniques and other aspects.

Phonon Modes

The phonon modes have been investigated in nanowires. Surface optical and longitudinal optical modes have been calculated. The quantization procedure for these phonon modes have been developed. At the conclusion of this project, we have just started on the analysis of the electron-phonon scattering.

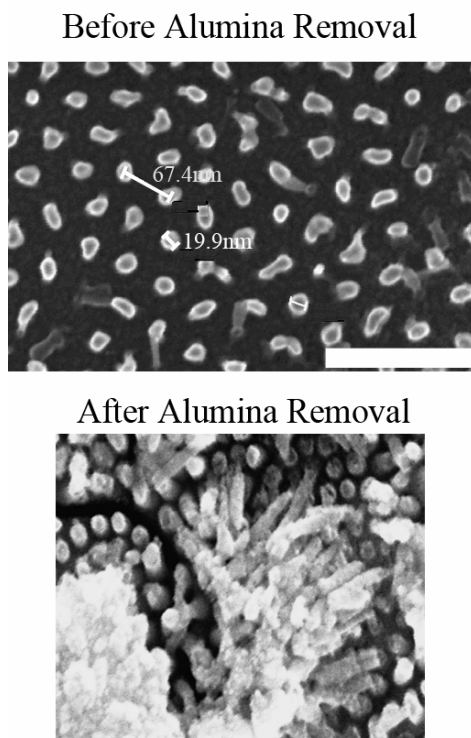


Fig. 7. Top: A top view of alumina template after the CdS QR growth has been performed and before the alumina is removed. The white bar is 200nm. Bottom: The same structure after the alumina is removed by the H_3PO_4 etch. The CdS nanowires are clearly evident.

Conclusion of Technical Results

The results of this project has been significant. Many theoretical tasks have been performed including the calculation of the electron subband states, the IR absorption due to intersubband transitions, the calculation and quantization of phonon modes and the analysis of electron-phonon interactions. The fabrication has advanced but significant issues remain in the high quality grown of quantum wires.