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14. ABSTRACT A fully automated metalorganic vapor phase epitaxial (MOVPE) system to grow various II-VI semiconductor thin films was acquired and installed at Rensselaer Polytechnic Institute (RPI) during the year 2013. The design and construction of the system was completed in 2012 and the final installation and testing has been carried out during 2013. A set of growth experiments to deposit CdTe and ZnTe thin films on GaAs and Si substrates was carried out to test the system operation. For these test experiments, dimethyl cadmium, diisopropyl tellurium and diethylzinc were used as the Cd, Te and Zn precursors. The system was shown to operate as designed and the plan was to use					
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Report Title

Final Report: Metalorganic Vapor Phase Epitaxial Reactor for the Deposition of Infrared Detector Materials

ABSTRACT

A fully automated metalorganic vapor phase epitaxial (MOVPE) system to grow various II-VI semiconductor thin films was acquired and installed at Rensselaer Polytechnic Institute (RPI) during the year 2013. The design and construction of the system was completed in 2012 and the final installation and testing has been carried out during 2013. A set of growth experiments to deposit CdTe and ZnTe thin films on GaAs and Si substrates was carried out to test the system operation. For these test experiments, dimethyl cadmium, diisopropyl tellurium and diethylzinc were used as the Cd, Te and Zn precursors. The system was shown to operate as designed and the plan was to use the system for various thin film deposition. The installed system significantly enhanced the capability of RPI in the area of MOVPE of II-VI materials.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

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

Received

Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

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

Received

Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
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:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

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)

Scientific Progress

Accomplishments:

- A fully automated metalorganic vapor phase epitaxial (MOVPE) system was acquired and installed at RPI during the Spring of 2013. The design and construction of the system was completed in 2012 and the transport of the system to RPI was done during the November –December 2012. The fit up of the system and testing at RPI was completed during the Fall 2013.
- After the fit up, dimethyl cadmium, diisopropyl tellurium, diethylzinc, and the carrier gases were installed. 1% germane and 0.01% arsine gases were ordered and also installed. These were ordered using associated research contracts.
- The system is now operational and several CdTe and ZnTe films, doped and undoped were grown and characterized.
- We are currently using the system for several research in II-VI materials which will be detailed later in the report. See Attachment

Technology Transfer

1. Discussions with researchers from First Solar in depositing single crystal solar cell materials. A research contract worth over \$150K was awarded to RPI by First Solar based on the MOVPE research capability at RPI.
2. Discussions with James Pattison, Materials Engineering, RDRL-SEE-I, US Army Research Laboratory regarding low temperature deposition of CdTe for IR detector surface passivation.

**Metal-Organic Vapor Phase Epitaxial Reactor for the Deposition of Infrared
Detector Materials**

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Final Report
Contract No. W911NF-10-1-0191

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Table of Contents

1. Objective.....	3
2. Accomplishments:	3
3. Equipment Purchased.....	3
4. Instrument Location	4
5. System Operation	5
6. Ongoing Projects that benefit directly or indirectly from the system.....	8
Project 1:	8
Project 2:	8
Project 3	9
Project 4:	9
Project 5	10
Proposal submitted but not funded:	10
7. Training of Graduate and Undergraduate Students	11
8. Conclusion	11
9. Appendix A.....	12

1. Objective

The objective of this grant is the acquisition and installation of a fully automated metal organic vapor phase epitaxial (MOVPE) system for depositing II-VI semiconductor materials. The system is to have 4 bubbler lines and a gas line in the gas handling section and a glove box in the reaction chamber section.

2. Accomplishments:

- A fully automated metalorganic vapor phase epitaxial (MOVPE) system was acquired and installed at RPI during the Spring of 2013. The design and construction of the system was completed in 2012 and the transport of the system to RPI was done during the November –December 2012. The fit up of the system and testing at RPI was completed during the Fall 2013.
- After the fit up, dimethyl cadmium, diisopropyl tellurium, diethylzinc, and the carrier gases were installed. 1% germane and 0.01% arsine gases were ordered and also installed. These were ordered using associated research contracts.
- The system is now operational and several CdTe and ZnTe films, doped and undoped were grown and characterized.
- We are currently using the system for several research in II-VI materials which will be detailed later in the report.

3. Equipment Purchased

- A turn-key MOVPE system was purchased with the following features and the complete price list is included in Appendix A. All the items listed in the Appendix A was purchased, and in addition to the items, a spare heater and the reaction chamber was also purchased using associated funds from other research contracts.
- The system is able to handle 3” diameter substrates with temperature of operation as high as 750°C.
- The system has a glove box and load lock so that the reaction chamber will not be exposed to atmosphere during sample loading and unloading. This is critical to get reproducible results.
- The complete system is computer controlled.

- The gas handling system has a fast switching manifold so that abrupt interfaces between two different layers can be obtained.

The system was delivered to RPI by CVD equipment Corp. and the fit up installation cost was paid for by RPI cost share.

4. Instrument Location

The MOVPE instrument is located in room 7218 in Johnson Engineering Center. The room currently had an old home-built MOVPE system that has not been in use for many years, and the new system was installed in its place as shown in [Figure 1](#). Even though the lab has the exhaust system in place, additional fit up was required since the newer system has many new features that were not there in the home-built system. Also, many gas handling required updates due to newer safety regulations and some of these required updates are shown in [Figure 2](#).



Figure 1 Photo of MOCVD reactor installed at RPI Johnson Engineering Center room 7218 during Spring of 2013.



Figure 2 (a) Installation of exhaust system to the reactor and the rest of the fit up equipment (b) Installation of dedicated nitrogen for glove box and reactor purging (c) Installation of toxic gas cabinet for gases such as germane and 500ppm arsine in hydrogen.

5. System Operation

Most of the work this year was focused on learning the system construction and operation and learning the system software. After several dummy runs, a few growth runs to deposit CdTe and ZnTe, both doped and undoped, were grown on 3-inch diameter Si substrates or part of GaAs substrates. The results were compared to our home-built existing MOVPE system. The growth experiments are more reproducible in the new system and the uniformity of the growth is also significantly improved.



Figure 3 A wafer of p-GaAs is being loaded to the system for growing ZnTe. The wafer is being used to fabricate single crystal CdTe solar cells (funded by First Solar)

For the FirstSolar-funded project on solar cells, a p-type CdTe layer was grown on p-GaAs substrate with arsenic-doped ZnTe buffer layer using the installed system (see Figure 3. P-type ZnTe was first grown on p-GaAs(100) substrate as the template for CdTe growth (NS05). Arsenic doped CdTe was then grown on ZnTe/GaAs (NS08). The ZnTe buffer layer was ~ 50 nm. The CdTe growth rate was ~ 700 nm/hr and the total CdTe

thickness was 1.8 μm . Initially several trial experiments were conducted to get these required growth characteristics. [Figure 4](#) shows the XRD θ -2 θ scan of CdTe grown on GaAs(100) substrate with a thin ZnTe buffer layer. Only CdTe (200) and CdTe (400) peaks were observed indicating the epitaxial growth on GaAs substrate. [Figure 5](#) shows the XRD rocking curve of CdTe (400) peak. The full width at half maximum was ~ 662 arcsec ([Figure 5](#)) indicating good crystal quality for the thin layer, considering that not much efforts have gone into optimizing the structural properties at this stage.

A dopant source, 500ppm arsine in hydrogen, was installed for p-type doping of CdTe and ZnTe. A 0.7 μm thick ZnTe grown on GaAs with 10sccm of arsine source (500ppm arsine in H_2) had hole concentration of $1.3 \times 10^{18} \text{cm}^{-3}$, mobility of $10.6 \text{cm}^2/\text{Vs}$ and resistivity of 0.45 ohm-cm (NS04). As grown arsine doped CdTe had p-type carrier concentration of mid 10^{16}cm^{-3} . These results are very encouraging and we are currently working with Colorado State University, First Solar and others in developing these films for use as copper-free contact layers in solar cells.

As part of another project funded by Arizona State University/DOE, subcontract from Bay Area Photovoltaic Consortium, we are currently using the system to grow undoped and p-type doped ZnTe on silicon. These films are used as a heterojunction passivation layer as well as p-type lateral conduction layer. Our simulation shows higher efficiency solar cells in silicon without the use of high temperature processing steps, thus potentially reducing cost. Excellent surface passivation is demonstrated as shown in [Table 1](#). As shown bare silicon has lifetime of 1.25 μs whereas ZnTe passivated silicon has lifetime in excess of 10 μs . [Figure 6](#) shows cross sectional view and top view of 350nm thick ZnTe grown on Si(211) as part of passivation studies of silicon for use in HIT-type solar cells.

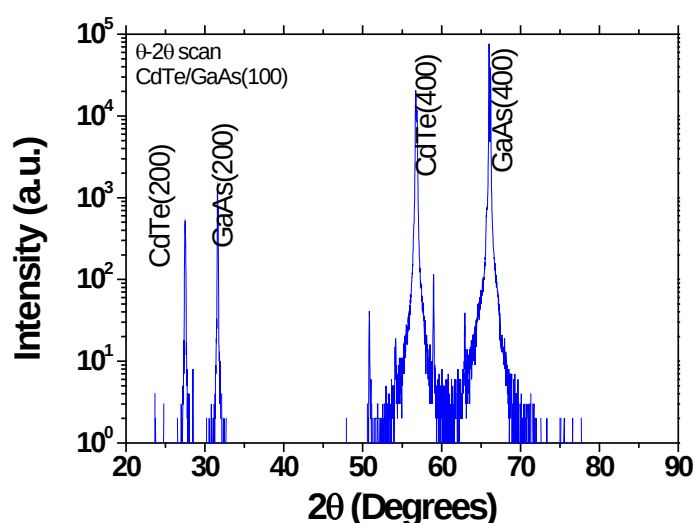


Figure 4 XRD θ -2 θ scan of CdTe grown on GaAs(100) substrate with a thin ZnTe buffer layer.

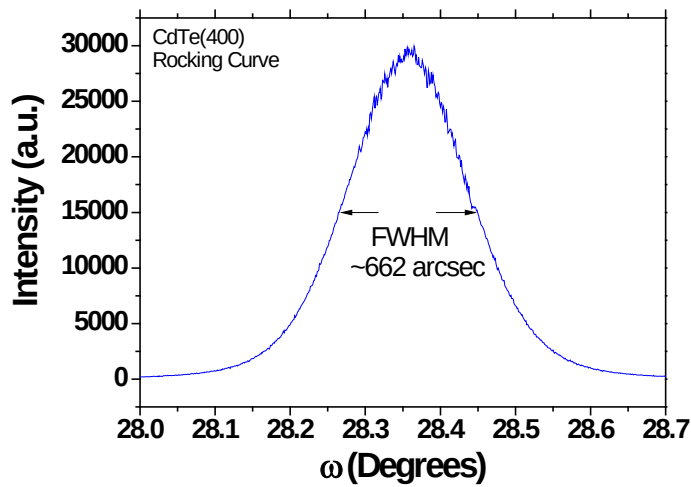


Figure 5 XRD rocking curve of CdTe grown on GaAs(100) substrate with a thin ZnTe buffer layer.

Sample No.	Layer Structure	Sample Description	Measured Lifetime (μ s)
	Si(211)	Si (211) substrate	1.25
NS09	ZnTe/Si(211)	Without As passivation	12.1
NS10	ZnTe/Si(211)	As passivation at 550°C for 5 mins	10
NS09	ZnTe/Si(211)	Annealed sample without As passivation	5
NS10	ZnTe/Si(211)	Annealed sample with As passivation at 550°C for 5 mins	3.33

Table 1 List of samples grown using the new MOVPE system for use in passivation of Si wafers using p-type ZnTe. The samples are being used to make HIT-type solar cells in silicon using a new type of structures, funded by ASU/DOE as part of Bay Area Photovoltaic Consortium (BAPVC)

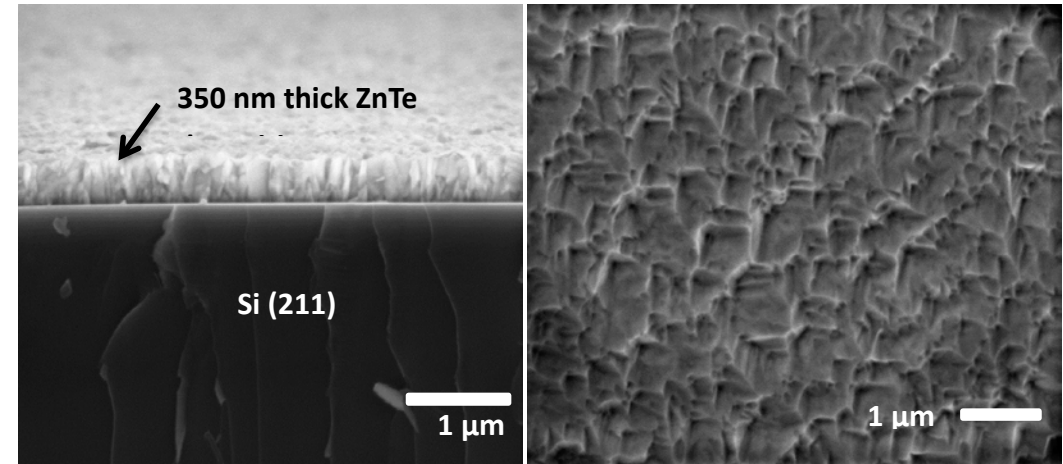


Figure 6 Cross sectional view and top view of 350nm thick ZnTe grown on Si(211) as part of passivation studies of silicon for use in HIT-type solar cells.

6. Ongoing Projects that benefit directly or indirectly from the system

The following ongoing projects in which Prof. Bhat is a PI or Co-PI, greatly benefit from the acquired equipment. These are in addition to the projects mentioned in the original proposal. For example, the acquisition of the equipment generated some additional research contracts that would not have happened without the grant.

Project 1:

- Title of Project: Synergistic experimental and theoretical studies of the growth and characterization of near-single crystal semiconductors on glass
- Source of Funding: NSF
- Duration: 9/15/2011 – 6/30/2014

Abstract: This project aims at the fundamental study of the growth of near-single crystal Ge on non-crystalline substrates such as glass. A glass substrate does not have a well ordered atomic lattice and therefore cannot induce the growth of epitaxial semiconductors. A key challenge is whether it is possible to grow a single crystal film on glass at all. In this project it is proposed to use a biaxial CaF_2 buffer layer on glass to induce an epitaxial growth of near-single crystal Ge films. If successful, similar CdTe films can also be grown that will have significant impact on poly-CdTe solar cell efficiency.

Several CdTe layers have been grown on glass substrates with and without the CaF_2 buffer layers for use in this project.

Project 2:

- Title of Project: Epitaxial Single Crystal CdTe Solar Cells
- Source of Funding: First Solar Inc.
- Duration of Funding: 5/1/2012 – 5/30/2015

Abstract: The objective of the proposed work is to investigate the electrical and optical properties of single crystal doped CdTe epitaxial films grown by MOCVD, and to study the electrical properties of CdTe p-n homojunctions and heterojunctions. A variety of device structures will be grown and characterized and some selected layers will be processed to make solar cells and further characterized both at RPI and at First Solar.

The substrates will be small area (1 cm^2) CdTe bulk wafers supplied by First Solar as well as silicon and GaAs wafers.

The system is used to deposit CdTe and ZnTe on Si and GaAs substrates for use in this project. Some layers have been processed to make solar cells.

Project 3

- Title of Project: Atomic Layer Deposition of CdTe for IR Detector Passivation
- Source of Funding: EPIR (US Army Prime) and Raytheon Vision System
- Duration of Funding: 3/1/2013 –

Abstract: Atomic Layer Deposition (ALD) of CdTe at low temperature ($<100\text{ }^{\circ}\text{C}$) will be developed using a novel hot-wall configuration and using metalorganic sources. The thin films of CdTe will be deposited on HgCdTe IR detector devices for surface passivation. The surface passivation efficacy will be determined using lifetime measurements, variable temperature Hall measurements and measuring IR detector I-V testing with and without passivation.

Even though another system is being used for this work, the installed equipment frees up time in the other systems for use in the project.

Project 4:

- Title of Project: Si/II-VI double heterostructure solar cells
- Source of Funding: Arizona State University (DOE Prime)
- Duration of funding: 1/1/2013 – 12/31/2015

Abstract: This proposal offers a novel approach to boost the efficiency and reduce the thickness of Si solar cells. As the demand of Si wafers has been continuously increasing, the use of novel structures to reduce the usage of Si and improve the efficiency has become more and more important. Recently, the heterojunction with intrinsic thin-layer (HIT) structure has demonstrated an efficiency of 22.8% and a 50% reduction of Si wafer thicknesses. This proposal offers a novel alternative approach using double-heterostructure II-VI semiconductor layers to further improve the performance of Si solar cells with comparable thickness to HIT structures.

We use the installed system to deposit ZnTe films, doped and undoped, for passivation of Si substrates and to improve the solar cell efficiency.

Project 5

- Title of Project: Heteroepitaxy of near single crystal semiconductors on flexible cube textured Ni sheet using CaF₂ buffer layer
- Source of Funding: NSF
- Duration of Funding: 8/15/2013 – 8/14/2015

Abstract: We deposit near-single crystal Ge(111) films on top of the CaF₂(111)/Ni(001) substrate. Electronic and electrical properties such as deep level trap density, carrier concentration, mobility, diffusion length and carrier life time in the grown Ge films are measured. We also use metal organic chemical vapor deposition technique to grow near-single crystal CdTe family of epitaxial films on selective Ge(111)/CaF₂(111)/Ni(001) substrates. Computational modeling using atomistic methods (including quantum-mechanical density function theory) is being employed to assist the experimental optimization of the growth parameters, to understand the structural and electronic properties of the domain boundaries, defects at the domain boundaries and their passivation, and to develop practical means to mitigate undesirable effects of defects in order to increase the quality of Ge films.

We use the system to deposit CdTe films on large area GaAs substrate as a nucleation layer and then use the wafer for further studies of CdTe and ZnTe growth, both doped and undoped, and for fabrication of solar cells.

Proposal submitted but not funded:

- Title: Model Thin Film Epitaxial CdTe Solar Cells by State-of-the-Art MOCVD and Advances for Manufacturing
- Source of Funding: Colorado State University (Prime DOE)
- Duration of Funding: 9/1/2013 – 8/31/2016

This was a large research contract totaled \$1.24M for RPI.

Mr. James Pattison and Mr. Nicholas Strnad of Army Research Lab, Adelphi, MD visited RPI on March 5, 2014 to discuss possible projects on CdTe surface passivation for HgCdTe devices. A new proposal idea is being discussed as a collaboration with RPI and ARL researchers to use the system. The new system will be useful for this study.

7. Training of Graduate and Undergraduate Students

Two graduate students (Ms. Sneha Banerjee and Mr. Peng Yu Su) were trained on the use of the new MOVPE system. A post doctoral researcher, Dr. Rajendra Dahal also can use the system. Two undergraduate students (Mr. Seth Lowenstern and Mr. Blake Powell) interacted with the graduate students during its operation but did not run the system independently. Nevertheless, the undergraduate students did learn a great deal on MOVPE of epitaxial films in general.

8. Conclusion

In summary, a new MOVPE system has been purchased and installed at RPI using the DURIP funds with cost share from RPI as well as from other sources (mainly industrial support). The total cost of the equipment is over \$350K out of which approximately \$225K was provided by the DURIP source. The equipment is being used regularly for growing high quality epitaxial layers of II-VI semiconductors and supported by several ongoing projects. Some of these projects originated due to the availability of the acquired state of the art equipment.

9. Appendix A

A complete list of actual equipment bought under this contract is included in the appendix. A detailed list is available as the full quote but a summary quote with the price list is included here for brevity.



CVD Quotation 6144F prepared for:
Dr. Ishwara Bhat, Rensselaer Polytechnic Institute

Proposed Solution

QTY	PART NO.	DESCRIPTION	PRICE
1	MOCVD Chemical Vapor Deposition System	MOCVD Chemical Vapor Deposition System per Technical Specification No. 6144F including: ▪ Complete set of process quartzware and susceptor ▪ Microprocessor control system ▪ Mass flow controlled gas system ▪ Integrated low pressure control system ▪ Process temperature – up to 750° Celsius ▪ Multi-Zone Infrared Heating System ▪ Safety system ▪ Onsite installation and training ▪ FOB Rensselaer Polytechnic Institute; Troy, NY – includes freight and insurance	\$224,750
		OPTIONS	
1	ET-MFC	Additional Mass Flow Controlled Gas Lines	\$11,850
1	Liquid Source Bubbler	Liquid Source #1 Bubbler and Push Line	\$23,000
1	Liquid Source Bubbler	Liquid Source #2 Bubbler and Push Line	\$23,000
1	Liquid Source Bubbler	Liquid Source #3 Bubbler and Push Line	\$23,000
1	Liquid Source Bubbler	Liquid Source #4 Bubbler and Push Line	\$23,000

Price Certification: The prices offered by CVD Equipment are equal to or lower than those offered to any government agency or private institution of both like items/services and quantities.