

ARMY RESEARCH LABORATORY



**Development of 6.1 A Materials for IR Applications
(Second-year Report)**

by Gregory Brill and Yuanping Chen

ARL-TR-5855

December 2011

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory

Adelphi, MD 20783-1197

ARL-TR-5855

December 2011

Development of 6.1 A Materials for IR Applications (Second-year Report)

Gregory Brill and Yuanping Chen
Sensors and Electron Devices Directorate, ARL

REPORT DOCUMENTATION PAGEForm 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 information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) December 2011		2. REPORT TYPE DRI		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Development of 6.1 A Materials for IR Applications (Second-year Report)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Gregory Brill and Yuanping Chen				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: RDRL-SE 2800 Powder Mill Road Adelphi, MD 20783-1197				8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-5855	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The development of mercury cadmium selenide (HgCdSe) material for infrared (IR) applications was initiated in fiscal year 2010 (FY10) at the U.S. Army Research Laboratory (ARL) under a Director's Research Initiative (DRI) program. Material growth conditions using molecular beam epitaxy (MBE) were identified to achieve reasonably good material quality in terms of surface morphology, defect density, and crystallinity as measured by x-ray diffraction. Additionally, it was determined that the bandgap of HgCdSe could be tuned by controlling the selenium (Se) to cadmium (Cd) flux ratio during growth. This research has continued in fiscal year 2011 (FY11) with an emphasis placed on developing composite substrate technology (zinc telluride [ZnTe]/silicon [Si] and Zn(Se)Te/gallium antimonide [GaSb]) for HgCdSe as well as understanding the electrical properties of HgCdSe material. An etching process was developed to identify dislocations in HgCdSe. Finally, the continued study of MBE growth parameters and their impact on material properties was conducted.					
15. SUBJECT TERMS HgCdSe, ZnTe, MBE, IR, GaSb					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 26	19a. NAME OF RESPONSIBLE PERSON Gregory Brill
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) (301) 394-0192

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Contents

List of Figures	iv
Acknowledgments	v
1. Objective	1
2. Background	1
3. Approach	2
3.1 Teaming.....	2
3.2 Research Plan	3
4. Results	3
4.1. Development of Composite Substrates for HgCdSe	3
4.1.1 MBE Growth of ZnTe/Si.....	3
4.1.2 MBE Growth of Zn(Se)Te/GaSb	6
4.2 Etch Pit Density (EPD) Measurements of HgCdSe	6
4.3 HgCdSe Structural Characterization	8
4.4 HgCdSe Electrical Characterization.....	10
5. References	13
6. Transitions	14
List of Symbols, Abbreviations, Acronyms	15
Distribution List	17

List of Figures

Figure 1. Energy Gap vs. lattice parameter for several semiconductor material systems.	2
Figure 2. X-ray FWHM (right axis) and EPD measurements (left axis) of ZnTe/Si(211) films under different Zn/Te fluxes.	5
Figure 3. Surface morphology of ZnTe/Si(211) films under different Zn/Te fluxes.....	5
Figure 4. HgCdSe surface before (left) and after (right) etching in a solution designed to reveal the presence of dislocations.	7
Figure 5. Etch rate of the EPD etch for HgCdSe material being developed at ARL.	8
Figure 6. Surface images from two HgCdSe layers. Each was grown under identical conditions except for an increase in Hg flux.	9
Figure 7. TEM images and optical microscopy images of HgCdSe grown on ZnTe/Si substrates under various growth temperature and flux ratios.	10

Acknowledgments

We wish to acknowledge the efforts of Mr. Kevin Doyle and Prof. Thomas Myers from Texas State University for assistance with HgCdSe growth and electrical characterization. Additionally, we would like to thank Dr. Sudhir Trivedi of Brimrose Corporation for his assistance with etchant chemistry research.

INTENTIONALLY LEFT BLANK.

1. Objective

This project is a continuation of research that began in fiscal year 2010 (FY10) on the development of mercury cadmium selenide (HgCdSe) material for infrared (IR) applications. At the time, virtually no information existed regarding HgCdSe material growth on nearly lattice-matched zinc telluride (ZnTe)/silicon (Si) or gallium antimonide (GaSb) substrates using molecular beam epitaxy (MBE). Reasonably good material quality in terms of surface morphology, defect density, and crystallinity as measured by x-ray diffraction was obtained during the first year of this program. Additionally, it was determined that the bandgap of HgCdSe could be tuned by controlling the selenium (Se) to cadmium (Cd) flux ratio during growth (1). Based on these promising initial results, further studies were warranted and carried out.

2. Background

Currently, mercury cadmium telluride (HgCdTe) is the material used in the majority of fielded Army IR systems and much effort has been expended to push the technology to both large-format and low-cost systems while still maintaining superior performance. However, this technology has been limited in its application due to the size and cost constraints related to its substrate, bulk grown cadmium zinc telluride (CdZnTe). One potential solution is to use large area Si substrates for the growth of HgCdTe. However, due to the huge lattice mismatch between Si and HgCdTe (19%) and the associated strain energy, misfit dislocations need to be generated somewhere in the thin-film stack to alleviate this energy, which ultimately propagates into the IR absorbing layer. Generally, a two orders of magnitude higher dislocation density is present in scalable HgCdTe/Si material with respect to non-scalable HgCdTe/CdZnTe. It has been demonstrated that this higher dislocation level results in lower device performance (2).

Figure 1 shows the lattice constant and bandgap of various semiconductor systems. As shown in the figure, numerous materials have lattice constants at or near 0.61 nm, including mercury selenide (HgSe) (a semimetal) and cadmium selenide (CdSe) (a wide bandgap semiconductor). By forming an alloy of $\text{Hg}_{1-x}\text{Cd}_x\text{Se}$, the bandgap of the material can be tuned to absorb any wavelength of IR light, resulting in an ideal material to cover the entire IR spectral range. This system is completely analogous to mercury telluride (HgTe) and cadmium telluride (CdTe) binary semiconductors with the significant advantage being that two III-V binary semiconductors are available to use as substrates for HgCdSe, specifically indium arsenide (InAs) and GaSb. These substrates are scalable and readily available from commercial suppliers within the United States, in stark contrast to CdZnTe substrates. By using III-V bulk substrates, a starting template

for HgCdSe growth with large areas and very low dislocation density is available. Presently, GaSb is quoted as having a dislocation density of less than 10^3 cm^{-2} (data from Galaxy Corporation and Wafer Technology).

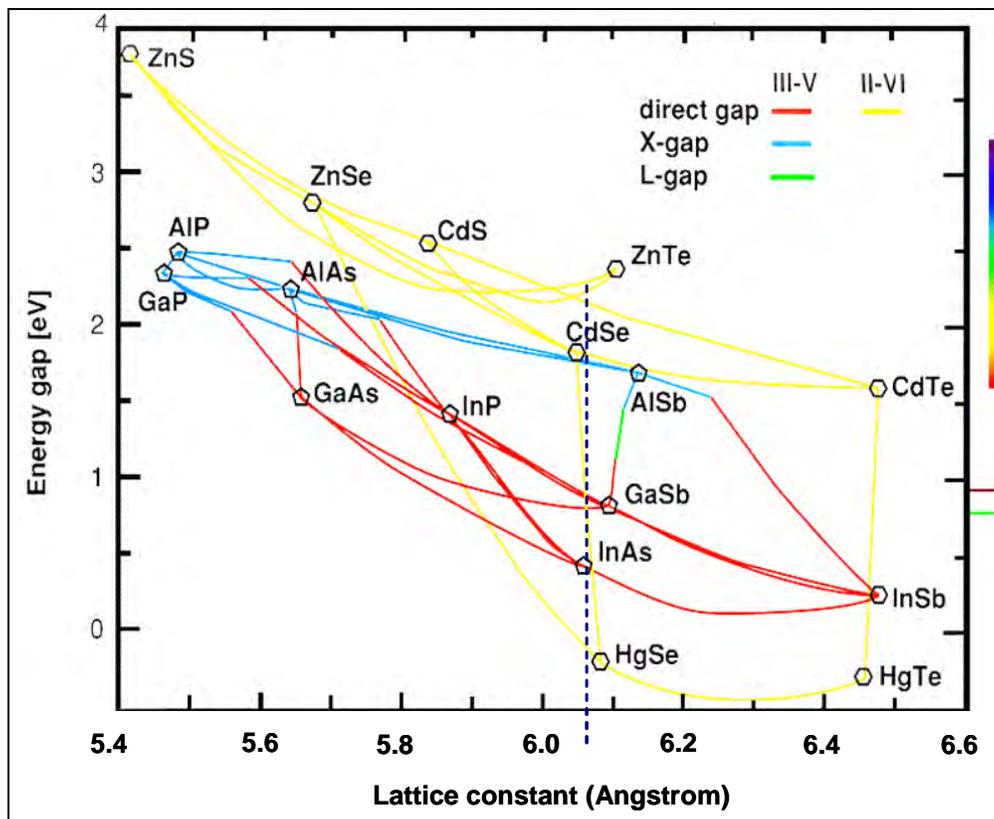


Figure 1. Energy Gap vs. lattice parameter for several semiconductor material systems.

3. Approach

3.1 Teaming

For the second year of this program, the U.S. Army Research Laboratory (ARL) has teamed with Texas State University to further study material and electrical properties of HgCdSe. HgCdSe MBE growth is carried out at ARL with initial layer characterization (structural and electrical) also conducted at ARL. Specific layers were then transferred to Texas State University for more detailed and advanced electrical measurements. Texas State also conducted MBE growth and characterization of Zn(Se)Te/GaSb in order to develop a substrate with exact lattice matching to HgCdSe material.

Additionally, ARL leveraged ongoing HgCdTe research being conducted at Arizona State University to use transmission electron microscopy (TEM) to study HgCdSe growth interfaces

on different substrates as well as investigate material quality due to changes in growth temperature. This work was conducted under an Army Research Office (ARO)-funded program titled “Advanced Microstructural Characterization for Development of Improved HgCdTe.”

3.2 Research Plan

Three distinct areas of research were conducted related to this technology and are discussed in this report.

Initially, minimal research time was devoted to the growth or preparation of the substrate materials as the goal was to study the growth parameters and material characteristics related to HgCdSe material. However, with the success achieved in the first year of the program, it was determined that significant effort was warranted on developing composite substrate technology specifically for HgCdSe. To this end, ARL conducted a systematic study of ZnTe/Si growth with the goal of achieving smoother surface morphology material, with minimal defects and the highest crystallinity, as determined by x-ray diffraction and etch pit studies of dislocation density. As a corollary project, research was conducted on growing Zn(Se)Te on GaSb substrates at Texas State University by MBE. By incorporating Se into the ZnTe matrix, exact lattice matching between HgCdSe and the bulk grown GaSb substrate could be achieved.

The second area of research focused on the continued study of MBE growth parameters on the structural quality of HgCdSe material. Constituent fluxes were varied as well as changes in the growth temperature. Additionally, a significant effort was placed on developing a dislocation revealing etch to ascertain the quality of material grown both on ZnTe/Si substrates as well as on GaSb substrates. This was necessary as no etch existed that could reveal dislocations within HgCdSe(211) material, a key metric for determining quality of material. Also, TEM studies were carried out at Arizona State University under an existing ARO program with the goal of understanding substrate preparation processes and epilayer nucleation processes.

Finally, the electrical properties of HgCdSe were investigated using Hall measurements at both ARL and Texas State University.

4. Results

4.1. Development of Composite Substrates for HgCdSe

4.1.1 MBE Growth of ZnTe/Si

As shown in figure 1, ZnTe is nearly lattice matched to HgCdSe and was chosen as a substrate for this program. This was done so that a baseline HgCdSe growth process could quickly be achieved since ARL has extensive expertise in cleaning, preparing, and nucleating mercury (Hg)-based compounds on II-VI based composite substrates. However, ZnTe material is generally

only grown as a buffer layer for CdTe/Si, and hence, little focus has ever been given to growing thick ZnTe material as a substrate. As the need for high quality ZnTe/Si material became more desirable, a systematic study on ZnTe nucleation and growth on Si(211) substrates was conducted. The (211) orientation was chosen as this is the preferred orientation for the HgCdSe material we have been developing (1). Besides, its potential use for HgCdSe material, high quality ZnTe/Si can also be used for Type II superlattice materials, which are comprised of GaSb and InAs, both with lattice parameters at or very near 0.61 nm (see figure 1).

To initiate ZnTe growth, migration enhanced epitaxy (MEE) was used after proper thermal cleaning and passivation of the Si substrate was completed (4). The MEE process entails opening the Te source for 10 s, followed by a null period of 10 s during which no material flux is allowed to reach the substrate surface. Then the Zn source is opened for 10 s, again followed by a null period of 10 s. This process is then repeated 66 times followed by a high temperature annealing process under appropriate fluxes. Ultimately, the MEE process nucleates an approximately 5-nm-thick ZnTe layer, which is of good crystal quality. This is the standard process used for CdTe/Si composite substrate technology, an ARL-developed process used for HgCdTe IR material growth. However, for HgCdSe, ZnTe/Si itself is the desired composite substrate; hence, much thicker material is required.

For MBE growth, it is well established that growth temperature is one of the key parameters that dictates the quality and morphology of the epilayer. Since ZnTe was grown using a two-step process, both the nucleation temperature and growth temperature were optimized independently. Additionally, the Zn/Te flux ratio used during growth was also a parameter of study. Multiple ZnTe/Si layers were grown and analyzed using x-ray diffraction to measure overall crystallinity, etch pit density (EPD) measurements of dislocation density using the Benson etch (3), and optical microscopy observations of the surface morphology.

Results indicate that a temperature of 300 °C is optimal for both the nucleation of ZnTe using MEE as well as the final growth temperature used when non-MEE (i.e., congruent deposition of Zn and Te simultaneously) ZnTe is deposited. A significant increase in EPD was observed for a higher nucleation temperature (340 °C) as well as a slight increase in the x-ray diffraction peak full width at half maximum (FWHM), which indicates a more disordered/defective crystal structure. Similar results were obtained when the growth temperature was decreased (260 °C) as both the EPD values and x-ray FWHM values increased. Overall though, there is about a 20 °C nucleation and growth temperature window in which high quality ZnTe/Si can be grown.

In this investigation, we also studied the influence of the Zn/Te flux ratio on surface morphology and crystalline quality of ZnTe(211)/Si(211). All ZnTe layers were nucleated and grown at 300 °C using the abovementioned growth procedures in three consecutive runs under three different II/VI flux ratios of 0.5, 1, and 2, respectively. The x-ray FWHM (right axis) and dislocation density (left axis) as well as surface morphologies of these three ZnTe(211)/Si layers are shown in figures 2 and 3. The results indicate that ZnTe/Si(211) layers of much higher

quality were obtained when grown under either Te-rich or equal Te and Zn fluxes. ZnTe(211) layers grown under a Zn-rich environment, exhibit, without exception, a very hazy surface morphology visible, even to the unaided eye, and a very broad x-ray FWHM, a factor of four higher than that of the layers grown under Te-rich conditions.

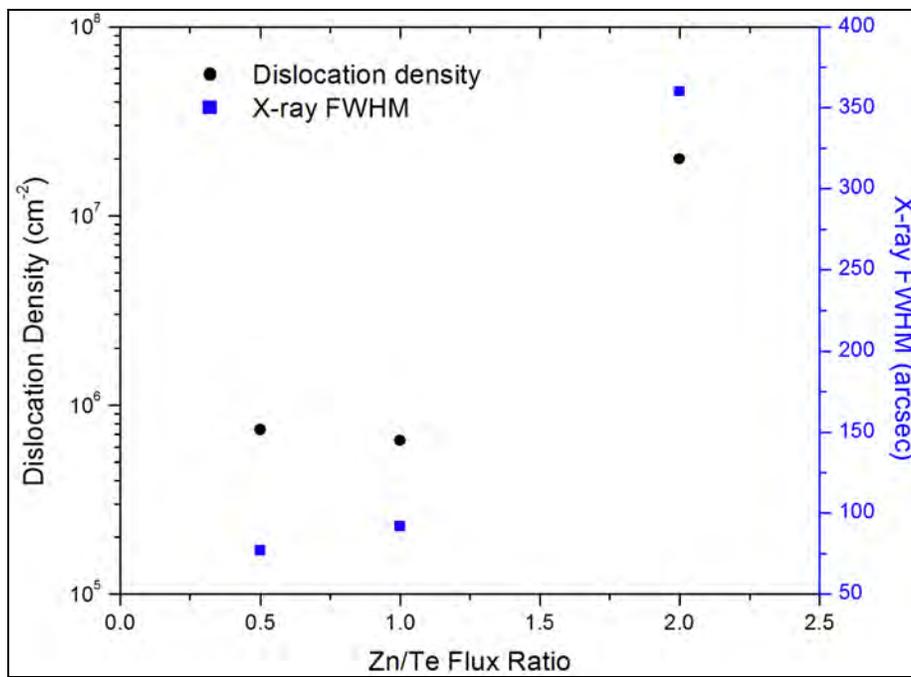


Figure 2. X-ray FWHM (right axis) and EPD measurements (left axis) of ZnTe/Si(211) films under different Zn/Te fluxes.

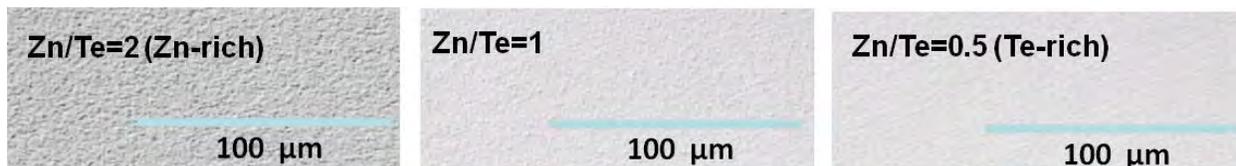


Figure 3. Surface morphology of ZnTe/Si(211) films under different Zn/Te fluxes.

This is an important result for developing high quality ZnTe/Si material for HgCdSe growth. It also differs from our experience in growing CdTe/Si(211) and was not implemented during the initial phase of this study (1). In the case of ZnTe, which is comprised of elements from row 3 (Zn) and row 4 (Te) of the Periodic Table, increased imbalance in the thermodynamic properties of Zn and Te probably leads to increased sensitivity of surface morphology and crystalline quality to the Zn/Te flux ratio. In contrast, for CdTe, both elements reside on row 4 of the Periodic Table and have more similar thermodynamic properties. Hence, for CdTe, a 1:1 flux ratio is easily obtained and is sufficient for high quality growth.

4.1.2 MBE Growth of Zn(Se)Te/GaSb

As ARL focused its efforts on improving ZnTe/Si as a composite substrate for HgCdSe, our partners at Texas State University focused growing II-VI materials on GaSb substrates. Texas State University has expertise with H cleaning of GaSb substrates, which makes for a more reproducible cleaning process (5) as well as facilities that include a II-VI MBE growth chamber interconnected through ultra high vacuum (UHV) to a III-V MBE growth chamber. Therefore, they can properly clean large-area GaSb substrates, re-grow a GaSb buffer layer if so desired, and then deposit a Zn(Se)Te thin film that is lattice matched to HgCdSe all without exposing the sample to atmosphere. This is a capability ARL does not have as our II-VI and III-V MBE growth chambers are isolated systems.

Recently, Texas State has demonstrated pseudomorphic growth of ZnTe on GaSb with a critical thickness determined to be 350 nm. For ZnTe films kept below this thickness, very high quality material was grown as determined by low temperature photoluminescence (PL) imaging, which can indicate the presence of defect centers associated with dislocations. From these measurements, ZnTe/GaSb material with a dislocation density estimated with an upper limit of $\sim 1 \times 10^5 \text{ cm}^{-2}$ was obtained (6). This result is very encouraging for this program as it indicates that strained, defect-free ZnTe material can be deposited on large-area GaSb substrates. This is the ideal substrate for subsequent HgCdSe growth. Furthermore, x-ray measurements have confirmed that if Se is added to the ZnTe matrix, exact lattice matching to HgCdSe can be achieved. With these two new developments, extremely low dislocation density HgCdSe grown on large-area GaSb should be able to be achieved as the very small lattice mismatch between HgCdSe and GaSb will be now accounted for, which otherwise could have led to an increase in HgCdSe dislocation density.

4.2 Etch Pit Density (EPD) Measurements of HgCdSe

The key motivation for studying and developing HgCdSe materials is the desire to develop a tunable IR material on a large-area scalable substrate with low dislocation density. For HgCdTe, an industry etch has been in place for over 20 years that reveals dislocation within the material in order to ascertain this important material quality characteristic. Recently, Benson et al. (3) developed a new etch that improves the dislocation etching process and works equally well on HgCdTe(211) and CdTe(211). However, when these etches were applied to HgCdSe(211) no discernible etch pits were formed and the surface was more or less unaffected. By replacing Te atoms with Se atoms, the chemistry of the etching process has been significantly altered. Under this program, we have been developing the appropriate chemistry that can etch HgCdSe and reveal the presence of dislocations.

Several possible etchants were selected by studying the literature related to ZnSe, CdSe, and HgSe. Unfortunately, even in these binary semiconductor systems, no standard dislocation revealing etchant exists. Through literature search, trial and error, and extensive discussions with Dr. Sudhir Trivedi, a visiting scientist at ARL from Brimrose Corp with extensive

knowledge of chemistry related to materials science, we have come across a promising solution that reveals etch pits that by all indications appear to be related to dislocations in HgCdSe. Currently, no direct TEM evidence between an etch pit and an atomic dislocation has been obtained, but this type of study is a focus of our ongoing work. Nonetheless, a pit revealing etch is a first for this material system.

Figure 4 shows the as-grown HgCdSe surface and the surface after undergoing a 20-s etch in a solution of nitric acid (HNO₃):hydrochloric acid (HCl) (2:1) followed by a 20-s etch in sulfuric acid (H₂SO₄) followed by a water rinse. The active EPD etching solution is the HNO₃:HCl solution, whereas the H₂SO₄ is used to remove and residual Se that remains and roughens the surface making identification of the pits difficult.

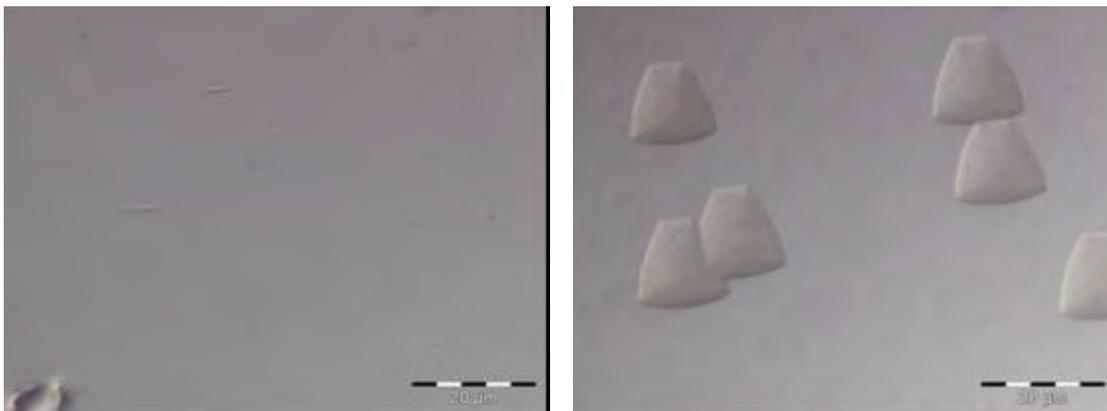


Figure 4. HgCdSe surface before (left) and after (right) etching in a solution designed to reveal the presence of dislocations.

The pits formed are trapezoidal in shape and are generally well defined. Figure 5 shows the etch rate for this solution. Ideally, the etch rate would be much slower so that a more precise control of the dislocation density as a function of depth could be obtained. Additionally, a slower etch rate will limit the size of the pits. Otherwise, pits will overlap easily making an accurate dislocation count difficult. Currently, different ratios of the etching solution are still under experimentation including the use of a buffering agent to reduce the etch rate.

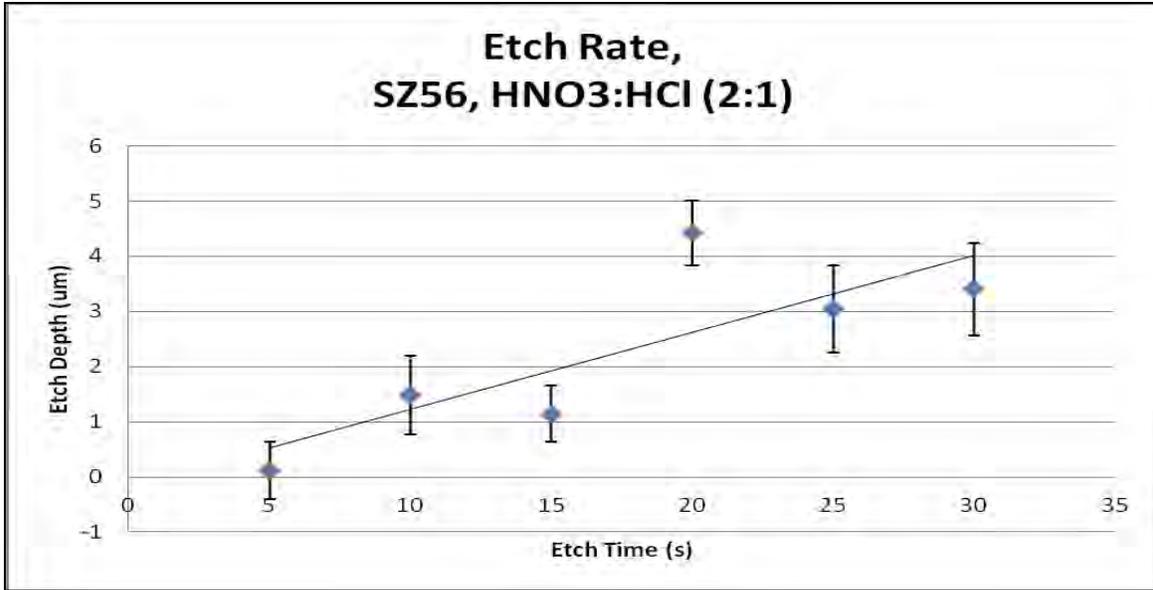


Figure 5. Etch rate of the EPD etch for HgCdSe material being developed at ARL.

With the HgCdSe EPD etchant preliminary developed, we have made some initial measurements of the dislocation density with values generally ranging between 1×10^6 to $6 \times 10^6 \text{ cm}^{-2}$ for HgCdSe grown on ZnTe/Si. Since the focus has been primarily on developing the etch chemistry, layer statistics are lacking but the data are very encouraging nonetheless. Previously, we measured the EPD of ZnTe/Si using the standard Benson etch (section 4.1.1) to determine optimal growth conditions. Generally, EPD of good quality ZnTe/Si measured between 2×10^6 to $6 \times 10^6 \text{ cm}^{-2}$. This indicates that during nucleation and growth of HgCdSe on ZnTe/Si we are nucleating no or very few new dislocations. This is expected as the lattice-mismatch strain is minimal as these materials are very nearly lattice matched. To date, we have not measured EPD on HgCdSe grown on GaSb substrates as we need to determine the effect of the GaSb material may have on the etching chemistry (in contrast, Si is inert to the etching chemistry). However, these results are extremely exciting, indicating that very low dislocation density HgCdSe material can be obtained on bulk-grown and scalable GaSb.

Future work is ongoing in this area to optimize the EPD etching chemistry and etching procedures. Additionally, scanning electron microscopy (SEM) and atomic force microscopy (AFM) analysis of etched layers is underway to determine pit size and shape relative to crystal orientation. TEM will also be used to correlate pits revealed with the new EPD solution to dislocations within the material.

4.3 HgCdSe Structural Characterization

Previously, we reported that the main type of defect observed on HgCdSe material was a needle defect, which appeared whether nucleation occurred on a ZnTe/Si or GaSb substrate (1). Initially, the onset and density of needle defects was determined to be a function of growth

temperature. In this study, we also investigated the role of Hg flux on the formation of needle defects. Figure 6 shows images from two layers grown at identical temperatures, Se flux, and Cd flux, but with a doubling of Hg flux. The layer grown with the higher Hg flux exhibits an overall smoother surface as well a significant mitigation of needle defect formation. This fits well with the observation that needle density increases with temperature. Growth at higher temperature generally means less Hg adsorption/migration on the surface due to the very low Hg sticking coefficient. By adding more Hg this effect is mitigated. It should also be noted that the composition of the layers did not appreciably change with the addition of extra Hg, implying that the excess Hg only modifies the growth front and does not become incorporated into the bulk of the layer.

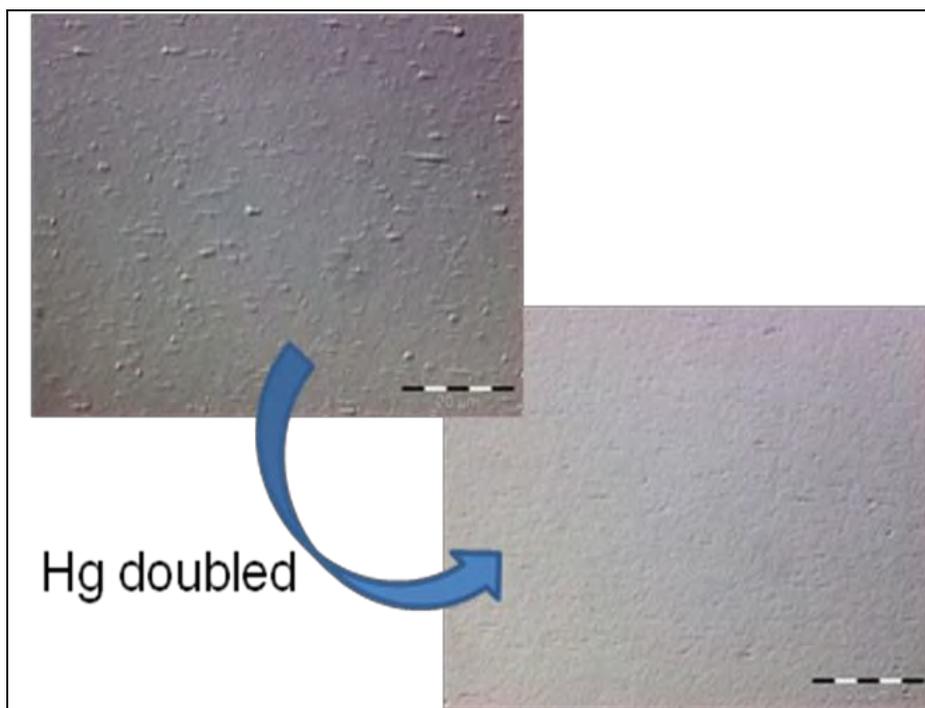


Figure 6. Surface images from two HgCdSe layers. Each was grown under identical conditions except for an increase in Hg flux.

Further structural studies of HgCdSe layers were conducted using TEM. Analysis revealed that growth at higher temperatures results in poorer crystal quality material given a set of flux conditions. This is seen in figure 7 which shows TEM images from two layers grown at 100 °C and 140 °C under identical material fluxes (figures 7a and 7c, respectively). Figures 7b and 7d show the corresponding optical microscopy images of the surface. Growth at lower temperatures resulted in very few structural defects as observed in cross-sectional TEM. In contrast, {111}-type stacking defects were visible near the HgCdSe/ZnTe interface, as shown arrowed in figure 7c indicative of a much poorer nucleation process. When the Se/Hg flux ratio was increased for the same growth temperature (140 °C) very high dislocation densities were

observed in the HgCdSe epilayer, as shown in figure 7e, and the surface displayed an odd type of defect structure, which has not yet been identified, as shown in figure 7f.

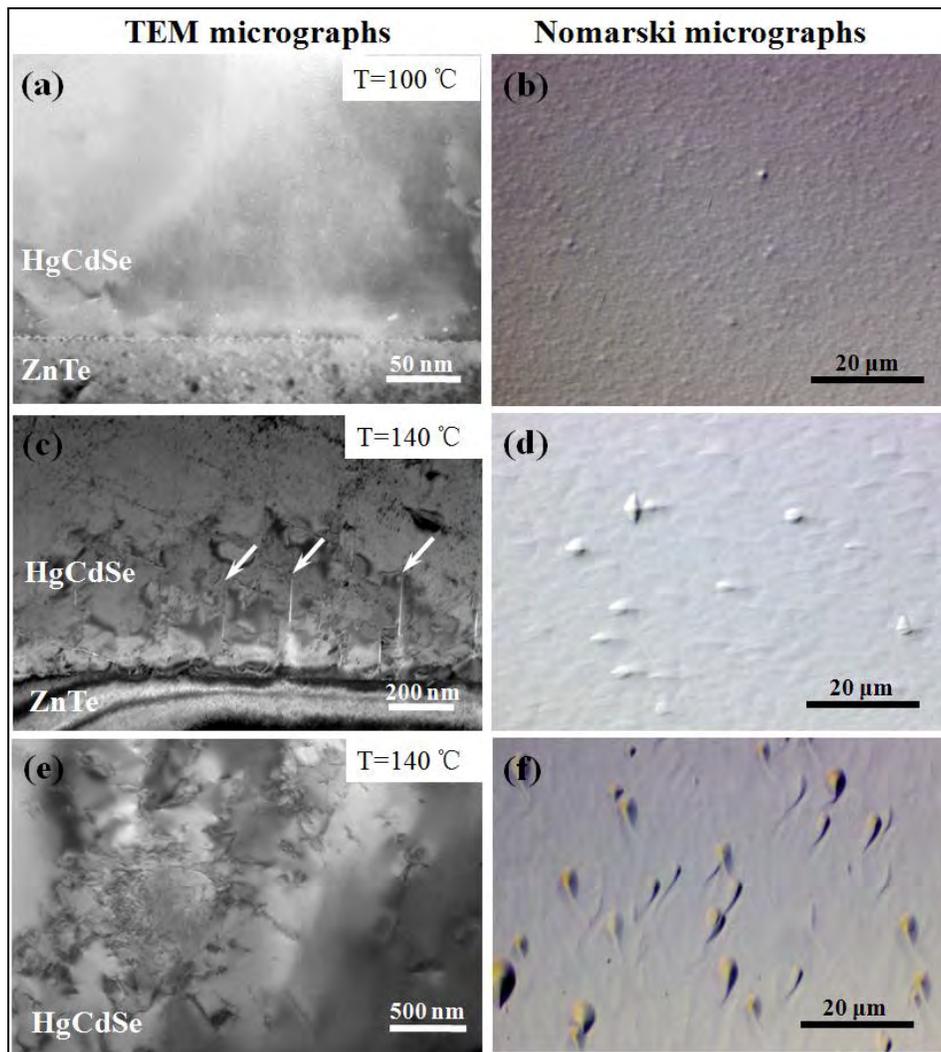


Figure 7. TEM images and optical microscopy images of HgCdSe grown on ZnTe/Si substrates under various growth temperature and flux ratios.

4.4 HgCdSe Electrical Characterization

Much has been learned about the relationship between growth and nucleation conditions of HgCdSe by MBE and the overall structural quality of the material. To date, ARL has grown the best HgCdSe on either ZnTe/Si(211) or GaSb(211) substrates. Although, much progress has been made to date, there are still numerous parameters to study to further optimize the growth with respect to x-ray diffraction, surface morphology, defect formation, and EPD measurements. However, the quality of HgCdSe material with respect to structural properties as it stands now is suitable for device fabrication and testing. To this end, an investigation of the electrical properties of HgCdSe material was undertaken.

Simple Van der Pauw Hall measurements (300 and 77 K) were conducted at ARL while Texas State performed quantitative mobility spectrum analysis (QMSA) on selected samples using variable magnetic fields over a wide range of temperatures (300 to 4 K). Additionally, several annealing experiments were carried out to study the overall electrical performance of the material.

Results at ARL indicated high intrinsic n-type doping (carrier concentrations measuring $1 \times 10^{17} \text{ cm}^{-3}$ or greater) of as-grown material if grown intentionally undoped. This result differs considerably from intentionally undoped HgCdTe material in which as-grown material can be p-type due to the presence of Hg vacancies. As this high value of n-type intrinsic carrier concentration is not desirable for devices, several annealing experiments were conducted. Annealing under either a vacuum environment or a Se environment at 250 °C for 24 h did not significantly alter the intrinsic carrier concentration. However, the mobility of the material did generally improve after such anneals by approximately a factor two. In contrast, annealing under a Hg environment lead to an order of magnitude increase in carrier concentration. Initially, this effect was attributed to Hg interstitials being formed within the crystal, which can act as double ionized donors (7). However, this result was only temporary. If the same sample was measured months later, the carrier concentration would be back to the as-grown levels. At this time, it is uncertain if annealing under Hg creates a temporary surface state, which alters the electrical activity, or if some other factor is involved.

Further Hall studies were conducted at Texas State University, which has the capability to cool the samples to 4 K as well as measure Hall under various magnetic fields. QMSA analysis indicated the presence of at least two n-type carries in most samples. At this time, it is unclear as to the origin of each carrier type, although it is assumed that the interface may be contributing as well as the bulk of the material. Also, one of the carrier types displayed a broad mobility spectrum indicative of the nonhomogeneity of the sample. Neither of these results is particularly surprising as the samples studied were grown prior to optimization of the ZnTe/Si substrate material or the nucleation process. More important was the finding that the carrier concentration of intentionally undoped HgCdSe material remained relatively flat from 4 to 300 K. This indicates that the behavior observed is most likely intrinsic to the material and a function of growth conditions. With this information, we are revisiting our growth process. Specifically, we were growing HgCdSe using a standard Se source, which is known to produce Se_6 molecules. It is speculated that the Se_6 is hard to incorporate into the growing film, especially given the low growth temperatures needed to obtain good material quality (100 °C). This is also different to HgCdTe film growth in which a standard MBE Te source produces Te_2 . If Se_6 is not being fully incorporated, we are in essence growing HgCdSe with a high number of Se vacancies, which can act as n-type dopants. To test this hypothesis, we will start “cracking” Se using a Se cracker source during MBE growth so that we can vary the species of Se between Se, Se_2 , and Se_6 . It is expected that HgCdSe growth using Se_2 will act very similarly to HgCdTe grown using Te_2 and

low intrinsic carrier concentration material will be grown suitable for device fabrication. This will be a focus of this program in the upcoming year.

Finally, it should be noted that Hall experiments were not conducted on HgCdSe grown on GaSb substrates due to the highly conducting nature of GaSb, which would ultimately bury any signal due solely to the HgCdSe material. All of the data gathered was on HgCdSe/ZnTe/Si. However, we will be working with a group at Kenyon College (Gambier, OH) to use spectroscopic ellipsometry (SE) to optically probe the material. From careful analysis of the optical data obtained, information about the carrier concentration will be able to be obtained, further expanding our electrical database of HgCdSe

5. References

1. Brill, G.; Chen, Y. *New Material System for 3rd Generation IR Applications*; ARL-TR-5418; U.S. Army Research Laboratory: Adelphi, MD, December 2010.
2. Johnson, S. M.; Rhiger, D. R.; Rosbeck, J. P.; Petersen, J. M.; Taylor, S. M.; Boyd, M. E. *J. Vac. Sci. Tech. B* **1992**, *10*, 1499.
3. Benson, J. D.; Smith, P. J.; Jacobs, R. N.; Markunas, J. K.; Jaime-Vasquez, M.; Almeida, L. A.; Stoltz, A. J.; Bubulac, L. O.; Groenert, M.; Wijewarnasuriya, P. S.; Brill, G.; Chen, Y.; Lee, U. *J. Electron. Mater.* **2009**, *38*, 1771.
4. Chen, Y.; Simingalam, S.; Brill, G.; Wijewarnasuriya, P.; Dhar, N.; Kim, J. J.; Smith, D. J. *J. Electron Mater.* in press, 2011.
5. Weiss, E.; Klin, O.; Grossman, S.; Greenberg, S.; Klipstein, P. C.; Akhvlediani, R.; Tessler, R.; Edrei, R.; Hoffman, A. *J. Vac. Sci. Technol. A* **2007**, *25* (4), 736.
6. Chai, J. H.; Dinan, J. H.; Myers, T. H. *J. Electron Mater.* in press, 2011.
7. Whitsett, C. R.; Broerman, J. G.; Summers, C. J. *Semiconductors and Semimetals* **1981**, *16*, 53–117.

6. Transitions

Through the progress made under this Director's Research Initiative (DRI) program, we have gained outside funding for continued work in developing HgCdSe material for IR applications. The Air Force Office of Scientific Research (AFOSR) is funding a five-year collaboration between ARL and Arizona State University titled, "Optically biased monolithically integrated multicolor photodetectors." This program is designed to develop materials, including HgCdSe, for multiband (ultraviolet [UV] to IR) sensor capabilities within a single pixel. This program started in July 2010 and ARL is receiving \$125K/year.

ARO is also funding Texas State University to study HgCdSe material for IR applications. Texas State is receiving \$50K/year in funding and a graduate student is dedicated to this research. This program began in July 2010 and is being monitored closely by the principal investigator (PI) of this DRI program to ensure the best use of resources and highly coordinated effort is undertaken between ARL and Texas State University.

During the 2011 U.S. Workshop on the Physics and Chemistry of II-VI Materials an entire session was devoted to HgCdSe material with the PI of this program a co-author on four papers for his contributions with both expertise and HgCdSe material used for analysis. This was the first time that HgCdSe has been featured at this conference and indicates the great interest generated in this topic within the community as a result of the work done at ARL under the DRI program.

List of Symbols, Abbreviations, Acronyms

AFM	atomic force microscopy
AFOSR	Air Force Office of Scientific Research
ARL	Army Research Laboratory
ARO	Army Research Office
Cd	cadmium
CdSe	cadmium selenide
CdTe	cadmium telluride
CdZnTe	cadmium zinc telluride
DRI	Director's Research Initiative
EPD	etch pit density
FWHM	full width at half maximum
FY10	fiscal year 2010
FY11	fiscal year 2011
GaSb	gallium antimonide
H ₂ SO ₄	sulfuric acid
HCl	hydrochloric acid
Hg	mercury
HgCdSe	mercury cadmium selenide
HgCdTe	mercury cadmium telluride
HgSe	mercury selenide
HgTe	mercury telluride
HNO ₃	nitric acid
InAs	indium arsenide
IR	infrared

MBE	molecular beam epitaxy
MEE	migration enhanced epitaxy
PI	principal investigator
PL	photoluminescence
QMSA	quantitative mobility spectrum analysis
Se	selenium
SE	spectroscopic ellipsometry
SEM	scanning electron microscopy
Si	silicon
Te	Tellurium
TEM	transmission electron microscopy
UHV	ultra high vacuum
UV	ultraviolet
Zn	zinc
ZnTe	zinc telluride
ZnSeTe	zinc selenide telluride

NO OF. COPIES	ORGANIZATION
1 ELEC	ADMNSTR DEFNS TECHL INFO CTR ATTN DTIC OCP 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218
1	DARPA MTO ATTN N DHAR 3701 NORTH FAIRFAX DR ARLINGTON VA 22203-1714
1 CD	OFC OF THE SECY OF DEFNS ATTN ODDRE (R&AT) THE PENTAGON WASHINGTON DC 20301-3080
5	CECOM NVESD ATTN AMSEL RD NV A STOLTZ ATTN AMSEL RD NV D BENSON ATTN AMSEL RD NV J PELLEGRINO ATTN AMSEL RD NV L ALMEIDA ATTN AMSEL RD NV R JACOBS 10221 BURBECK RD STE 430 FT BELVOIR VA 22060-5806
1	DIRECTOR US ARMY RSRCH LAB ATTN RDRL ROE L W CLARK PO BOX 12211 RESEARCH TRIANGLE PARK NC 27709
20	US ARMY RSRCH LAB ATTN IMNE ALC HRR MAIL & RECORDS MGMT ATTN RDRL CI J PELLEGRINO ATTN RDRL CIO LL TECHL LIB ATTN RDRL CIO MT TECHL PUB ATTN RDRL SE J RATCHES ATTN RDRL SEE G WOOD ATTN RDRL SEE I G BRILL (5 HCS) ATTN RDRL SEE I H HIER ATTN RDRL SEE I P UPPAL ATTN RDRL SEE I P WIJEWARNASURIYA ATTN RDRL SEE I S FARRELL ATTN RDRL SEE I S SVENSON ATTN RDRL SEE I W SARNEY ATTN RDRL SEE I Y CHEN ATTN RDRL SEE L BLISS ATTN RDRL SEE P GILLESPIE ADELPHI MD 20783-1197

TOTAL: 29 (1 ELEC, 27 HCS, 1 CD)

INTENTIONALLY LEFT BLANK.