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14. ABSTRACT
The long-term objective of this research was to contribute towards the development of higher quality mercury-based materials intended for infrared photo-detectors. The samples studied were grown by molecular beam epitaxy (MBE) on alternative composite substrates, such as Si or GaAs, with (Cd,Zn)(Se,Te) intermediary buffer layers, and the work was carried out in collaboration with colleagues in government laboratories who were responsible for the materials growth. Advanced transmission electron microscopy (TEM) and associated analytical methods were

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Report Title

Final Report: Materials Science, Advanced Microscopy and Analytical Studies for Hg-based Infrared Detector Materials and Substrates

ABSTRACT

The long-term objective of this research was to contribute towards the development of higher quality mercury-based materials intended for infrared photo-detectors. The samples studied were grown by molecular beam epitaxy (MBE) on alternative composite substrates, such as Si or GaAs, with (Cd,Zn)(Se,Te) intermediary buffer layers, and the work was carried out in collaboration with colleagues in government laboratories who were responsible for the materials growth. Advanced transmission electron microscopy (TEM) and associated analytical methods were used for achieving an improved knowledge and understanding of the structural defects present in various HgCdTe-based materials and device structures. Cross sections of samples prepared by focused-ion-beam milling were used to study surface etch pits of different shapes and to identify the nature of the underlying threading defects via conventional Burgers' circuit analysis with two-beam bright-field imaging conditions. Alternative strategies for defect reduction, including thermal-cycle annealing and mesa-structured materials, were also investigated. Etchants suitable for defect identification in HgCdSe films were briefly studied.

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
02/27/2017	1	Majid Vaghayebegar, Randolph N. Jacobs, J.D. Benson, A.J. Stolz, L.A. Almeida, and David J. Smith. Correlation of Etch Pits and Dislocations in As-grown and Thermal-Cycle-Annealed HgCdTe(211) Films, Journal of Electronic Materials, ( ): . doi:

TOTAL: **1**

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
02/27/2017	4 Majid Vaghayenegar, R.N. Jacobs, J.D. Benson, A.J. Stolz, L.A. Almeida, and David J. Smith. Correlation of Etch Pits and Dislocations in As-grown and Thermal-Cycle-Annealed HgCdTe(211) Films, Microscopy and Microanalysis 2017. 07-AUG-17, St. Louis, MO. : ,
02/27/2017	2 Majid Vaghayenegar, B.L. VanMil, S. Simagalam, Y.P. Chen, and David J. Smith. Microstructural and Chemical Analysis of HgCdTe/CdTe/ZnTe/Si (211) for Infrared Detectors, Microscopy and Microanalysis 2015. 03-AUG-15, Portland, OR. : ,
02/27/2017	3 M. Vaghayenegar, S. Simingalam, Y.P. Chen, and David J. Smith. Dislocation Analysis of Thermal-Cycle-Annealed Mesa-Structured HgCdTe/HgTe/CdTe/ZnTe/Si (211), Microscopy and Microanalysis 2016. 26-JUL-16, Columbus, OH. : ,

TOTAL: **3**

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

David J. Smith: Elected Fellow, Microscopy Society of America, 2013
David J. Smith: Distinguished Physical Scientist Award, Microscopy Society of America, 2014
David J. Smith: Helmholtz International Fellowship Award, 2014

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Majid Vaghayenegar	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
David J. Smith	0.05	
FTE Equivalent:	**0.05**	
Total Number:	**1**	

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

See Attachment

Technology Transfer

Final Report: Proposal 63749EL

Title: (Materials Science) Advanced Microscopy and Analytical Studies for Hg-based Infrared Detector Materials and Substrates

Principal Investigator: David J. Smith (Arizona State University)

Summary

The long-term objective of this research was to contribute towards the development of higher quality mercury-based materials intended for infrared photo-detectors. The samples studied were grown by molecular beam epitaxy (MBE) on alternative composite substrates, such as Si or GaAs, with (Cd,Zn)(Se,Te) intermediary buffer layers, and the work was carried out in collaboration with colleagues in government laboratories who were responsible for the materials growth. Advanced transmission electron microscopy (TEM) and associated analytical methods were used for achieving an improved knowledge and understanding of the structural defects present in various HgCdTe-based materials and device structures. Cross sections of samples prepared by focused-ion-beam milling were used to study surface etch pits of different shapes and to identify the nature of the underlying threading defects via conventional Burgers' circuit analysis with two-beam bright-field imaging conditions. Alternative strategies for defect reduction, including thermal-cycle annealing and mesa-structured materials, were also investigated. Etchants suitable for defect identification in HgCdSe films were briefly studied.

Results

a) Si (211)B substrates for next generation of HgCdTe IR detectors
(Collaboration with Y. Chen, S. Simingalam, ARL)

Due to its smaller wafer size (7×7 cm^2) and higher cost (\$220/cm^2), CdZnTe cannot fulfill the current and projected needs of advanced HgCdTe technology. Thus, the search for alternative substrates, including Si, Ge, GaAs, and GaSb has been ongoing. Among these alternatives, Si has unique advantages. Its lower cost (< \$0.5/cm^2), larger wafer size (6 in. diameter), and similar thermal-expansion coefficient to the read-out circuitry in a focal-plane-array structure, make it attractive for HgCdTe growth. However, the large lattice mismatch with HgCdTe (19%) requires the growth of buffer layers to accommodate the misfit strain. Representative samples of HgCdTe/ HgTe/ CdTe/ ZnTe/ Si(211)B, long-wave infrared (LWIR) and short-wave infrared (SWIR) materials have been examined. The microstructure of the CdTe/ ZnTe/ Si(211)B was found to be quite similar in all samples examined. Micrographs taken at low-magnification showed high densities of defects at the CdTe/Si interfaces,

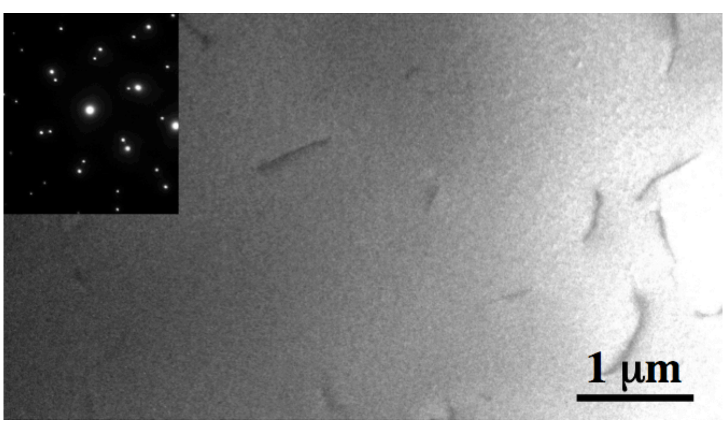

Fig. 1. Cross-sectional electron micrograph showing isolated threading defects in the upper regions of CdTe(211)B epilayer grown on ZnTe(211)/ Si(211), together with corresponding SAED pattern showing 3.76° rotation between CdTe/Si lattices.

but many of the defects were entangled and did not extend to the CdTe/HgCdTe interface, as shown in Fig. 1. The SAED patterns showed 3.7° tilt between the CdTe and Si crystal lattices. High-resolution TEM images, such as Fig. 2, revealed the formation of many {111}-type stacking faults at the ZnTe/Si interface, while HAADF images and EDS line profiles showed considerable Cd and Zn interdiffusion occuring at the CdTe/ZnTe interface.

Another aspect of this project was to establish whether introduction of an HgTe buffer layer between CdTe and HgCdTe could block propagation of dislocations into HgCdTe. Low-magnification TEM micrographs showed that films without the HgTe layer were highly defective with some dislocations threading all the way to the top surface. The overall quality of HgCdTe in samples with thin HgTe layers was clearly improved. However, the HgTe buffer layer did not appear to successfully block all of the threading dislocations.

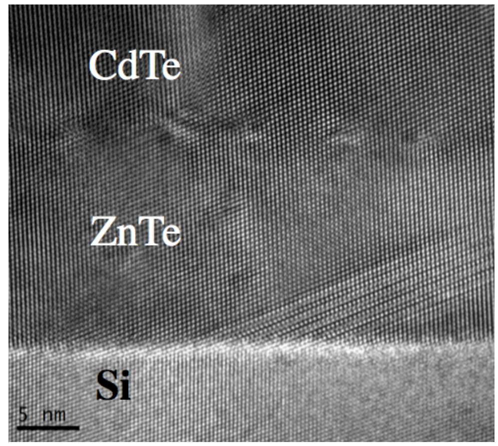

Fig. 2. Enlargement showing atomic level structure close to ZnTe/ Si(211) interface.

b) Understanding defect propagation in thick HgCdTe epilayers (Collaboration with R.N.Jacobs, and colleagues at NVESD)

Defect propagation and defect reduction in thick HgCdTe (MCT) epilayers continues to be a highly active area of investigation. Post-growth thermal cycle annealing (TCA) is being investigated as a possible strategy for reducing defect densities. Surface decoration pits are formed by dislocation etching and these are being used a reference markers for subsequent cross-sectioning lift-out using focused-ion-beam milling. The morphology of these pits in as-grown MCT has been classified by their shapes as Triangular, Skew or Fish-eye, as shown in Fig. 3. After thermal-cycle annealing (TCA), further observations showed that the Fish-eye shapes were absent whereas Triangular and Skew pits were still visible. Identifying the nature of the dislocations corresponding to each type of pit using two-beam diffraction-contrast imaging and standard Burgers vector determination has been the primary activity of this particular study. Triangular pits had a mixture of Frank partials and Perfect dislocations, while fish-eye shape were associated with perfect dislocations. The nature of dislocation beneath the skew pits is not yet settled but they seem to be associated with a mixture of Shockley and perfect dislocations. Dislocation analysis of the TCA sample showed that the majority of the dislocations were perfect dislocation and the rest were Shockley partials. The absence of

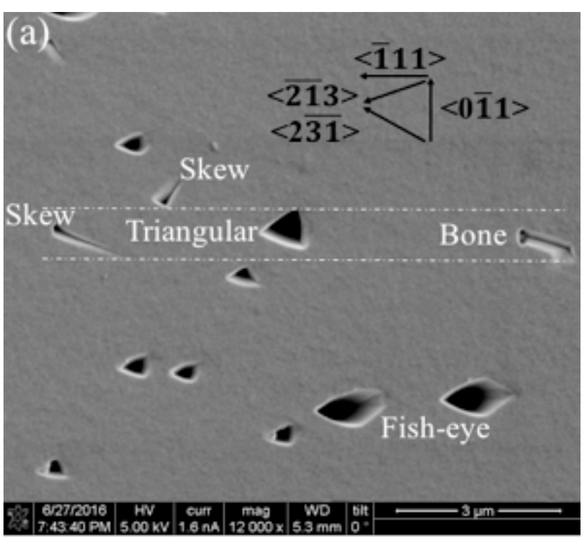

Fig. 3. SEM micrograph showing classification of different etch-pit shapes in as-grown MCT sample.

fish-eye shape pits suggested the likelihood that they were associated with mobile dislocations that had reacted with other dislocations to lower the etch-pit density. The end results of these studies are contributing towards a better understanding of how TCA reduces dislocation densities in MCT. The major results have just been submitted for publication.

c) Development of an etchant for threading defects in HgCdSe
(Collaboration with K. J. Doyle, S. Trivedi, and P. Wijewarnasuriya, ARL)

Although HgCdTe has been the dominant material for infrared detection, its approximately 100 times higher dislocation density, when grown on Si substrates, degrades the performance of next generation infrared focal-plane arrays. HgCdSe (MCS) is an alternative material anticipated to have similar performance as HgCdTe especially for long-wave infrared photodetectors. Two major advantages of HgCdSe over HgCdTe are i) smaller changes in lattice constant with changing concentration, which should make growth of LWIR layers on MWIR layers easier; and ii) the possibility of growth on large-size GaSb wafers with good lattice-matching, which promises lower defect density. While well-known etchants for revealing dislocations and measuring their density have been developed for HgCdTe, no suitable etchant has yet been developed for reliable defect delineation and etch pit density measurements of HgCdSe. Currently, attempts to optimize etchant concentration (HNO_3 : HCl : Lactic acid) and etching time for producing pits that correspond to threading dislocation are ongoing.

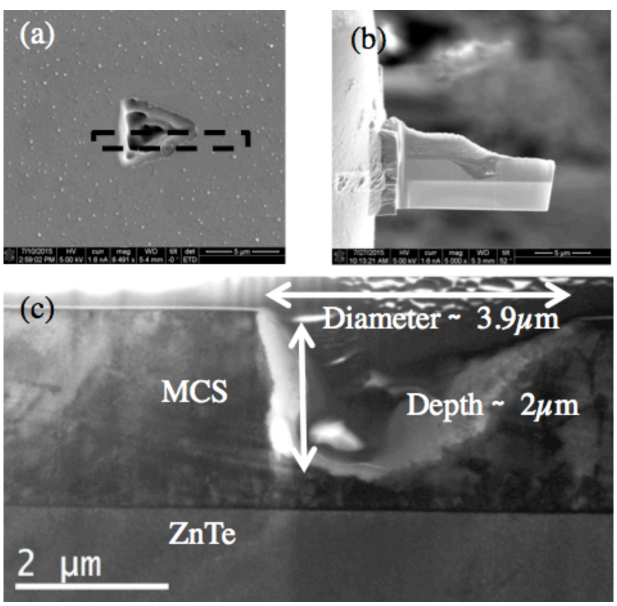

Fig. 4. (a) SEM image showing MCS surface etch pit and FIB lift-out region; (b) FIB lift-out ready for XTEM; (c) XTEM image showing cross section of pit.

Focused-ion-beam milling was again used to prepare samples for TEM observation, as illustrated in Fig. 4. For all observed samples, high densities of misfit dislocations were observed, with some threading all the way from the HgCdSe/ ZnTe interface. Short stacking faults (SF) were present at the MCS/ZnTe interface, at both ~19° and ~90º angles. Some of these SFs were also visible at the top HgCdSe surface. Although most defects entangled at the ZnTe/Si interface, some reached as far as the HgCdSe /ZnTe interface. In some samples, selected-area electron diffraction patterns showed a 2.5° rotation tilt at ZnTe/Si interface. The SFs were also decorating the ZnTe/Si interface, mostly oriented at 19° orientation with respect to the Si surface plane. This work is in the process of being written up for publication.

d) Alternative substrates for defect reduction in HgCdTe (Collaboration with Y.-P. Chen and P. S. Wijewarnasuriya, ARL)

Alternate substrates continue to be of much interest for advancing HgCdTe technology, but high defect densities represent a serious limitation on device performance. Representative samples of annealed ZnTe(211)B/ Si(211) composite substrates have been examined using both imaging and analytical techniques. Attention has focused on comparing the microstructure of the ZnTe layers as a function of nucleation and especially growth temperature. Initial observations showed high densities of short {111}-type stacking faults close to the As-passivated Si surfaces, with a marked drop-off in dislocation density in the epilayer moving away from the substrate, as shown in Fig. 5. An investigation of the geometrical uniformity and chemical composition of the top surface is ongoing.

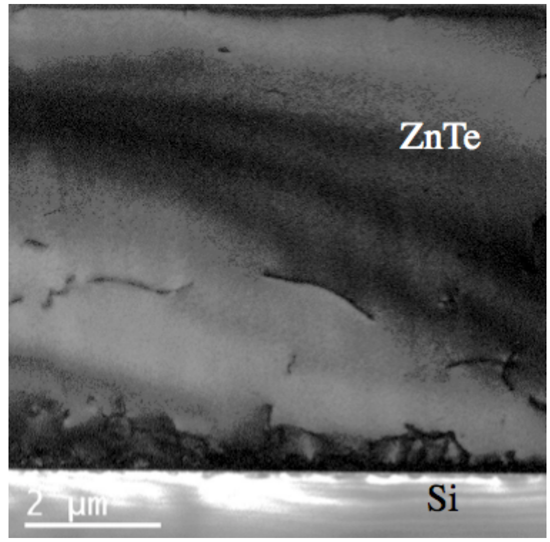

Fig. 5. Cross-sectional electron micrograph showing thick ZnTe(211) epilayer grown on Si(211) substrate. Rapid drop-off in defect density moving away from the substrate.

e) HgTe/CdTe Type-III superlattices for very-long-wavelength IR detectors
(Collaboration with P. Man and S. Sivananthan, University of Chicago-Illinois)

HgTe/CdTe superlattices with Type-III band alignment potentially offer the prospect of achieving very-long-wavelength infrared detectors. However, control over layer thickness as well as ensuring compositional uniformity are essential to achieving good quality device material. Initial and ongoing observations have focused on 'qualifying' the growth conditions since small changes in substrate temperature are found to have a marked impact on the overall material quality. Future work should be directed towards measuring interface abruptness and the extent of Hg diffusion into the CdTe layers.

f) Understanding the nature of dislocation reduction in fabricated mesa structures on HgCdTe
(Collaboration with S. Simingalam and Y. Chen, ARL)

Another strategy to reduce the detrimental effect of defects in HgCdTe induced by large lattice mismatch on alternate substrate is to create novel reticulated surfaces or mesa structures with near vertical sidewalls using plasma processing. Glide of defects to stress-free surfaces of these structures should reduce the number of dislocations in HgCdTe on alternate substrates. Work was initiated on two samples with mesa structure in order to determine where and how the dislocations interact: i.e., is the root of this dislocation density reduction due to dislocation-dislocation interaction or due to image forces moving the dislocation to the sidewall? Another unanswered question is whether the combination of thermal cycle / anneal treatment on mesa structures will produce higher quality HgCdTe on alternate substrates. More recent observations of long mesa bars along <111> showed that the dislocations were mostly Shockley partials with 1/6 <112> Burgers vector. Similar studies on mesa bars elongated along <110> should provide additional information on how different mesa orientations can getter different dislocation types.