D.Ast Cornell

DE-FG02-86ER45278

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DEFECT STUDIES IN THIN FILM III-V THIN FILM SEMICONDUCTORS

PROGRESS REPORT, SEPT 86 - MAY 87

A/86/87
DOE

Prepared by:

D.G.Ast

Materials Science and Engineering

Bard Hall

Cornell University

Ithaca N.Y. 14853

May 1987

**NOTICE FOR
HANDLING PROPOSALS**

"This proposal is to be used only for DOE evaluation purposes and this notice shall be affixed to any reproduction or abstract thereof. All Government and non-Government personnel handling this proposal shall exercise extreme care to insure that the information contained herein is not duplicated, used, or disclosed in whole or in part for any purpose other than to evaluate the proposal, without the written permission of the offeror (except that if a contract is awarded on the basis of this proposal, the terms of the contract shall control disclosure and use). This notice does not limit the Government's right to use information contained in the proposal if it is obtainable from another source without restriction. This is a Government notice, and shall not by itself be construed to impose any liability upon the Government or Government personnel for any disclosure or use of data contained in this proposal."

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

T3

A/86/87
m

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Table of Content

1) Synopsis of first year progress	
i) Instrumental	3
ii) Materials	3
iii) Ongoing Studies	4
iv) Results	5
v) Discussion	6
2) List of publications generated under contract	7
3) List of other federal funds	8
4) Status of Graduate Students	8
5) Objectives for second year	
a) Basic Interface work	9
b) Device Work	10
Small Signal Devices	
Solar Cells	
6) Appendix	11
Examples of work performed in first year	

1) Synopsis of First Year Progress: Sept 86/ May 87

i) Instrumental:

i) We added a nondispersive cathodoluminescence (CL) system to the MSC operated Jeol 35 SEM in Bard Hall, using funds (10K) which we won in a Cornell internal competition for PROSUS. (Prosus: Program for Submicron Structures).

(CL allows to generate CRT images on the SEM screen proportional to the intensity of recombination radiation emitted from the sample under e-beam scanning. The signal, therefore, maps out the spatial distribution of minority carrier recombination centers).

ii) In April 87, we added a spectrometer plus a S1 photomultiplier to the CL set up. Wavelength dispersive CL allows us to identify the chemical composition of individual layers in multilayered samples from measurements of the wavelength of the emitted light.

(Both modifications were carried out in such a way that the CL equipment could be removed after every experimental session as the SEM is an MSC operated general user instrument, where users are not permitted to make permanent modifications. This restriction made the design much more difficult than for conventional CL.)

iii) We investigated systematically the variation of etch rate with etch composition for two common III-V etches: phosphoric acid and sulfuric acid based. We therefore can remove tightly controlled amounts from single and multilayered samples (for examples of removal work, see Appendix).

iv) Using the Submicron facility at Cornell we went through all the processing steps necessary for III-V device fabrication (photolithography, ion etching, ion implantation, contact evaporation and sintering). As a proof, we made working GaAs FET's.

ii) Samples & Samples preparation:

i) A severe handicap is that our group does not own a facility to prepare III-V samples (nor is there one in the building). We continued our efforts to add a preparation facility, see below.

To get samples, we are cooperating with L. Eastman (EE, Cornell) who operates 2 MBE systems and J. Woodall & P. Kirchner (IBM Yorktown) who operate one MBE system. To get MOCVD samples, we started a NYS funded, joint program with CVD Equipment

Corporation. The IBM samples come with no strings attached. However, to get EE samples we have to carry out service type work such as CL intensity as function of gas ambient in RIBE etching or to help develop non alloying ohmic contacts to p type GaAs.

iii) Ongoing Studies:

a) MBE InGaAs/GaAs interfaces:

Using IBM supplied specimens, we are studying misfit effects in the system InGaAs(epilayer)/GaAs(substrate). The system is of great interest to IBM (and others) because InGaAs does not develop DX centers which appear in AlGaAs upon n-type doping. IBM has supplied us with samples in which individual layer thickness, In concentration and dislocation density of the substrate are systematically varied.

(InGaAs/GaAs can be grown without interface dislocations only in a rather thin layer; i.e. pseudomorphic growth. The critical thickness depends on the In concentration and is on the order of a few 1000 Angstrom. Critical thickness depends also on the size of the area covered by overgrowth.)

Using EE samples (Eastman), we study influence of interface dislocations on HBT performance. The HBT's generally incorporate both AlGaAs/GaAs and GaAs/InGaAs interfaces. InGaAs is used in the base to generate band offsets relative to the emitter and also to set up drift fields (graded) to accelerate e- transport across the base. In a joint effort with a visiting scientist from Toshiba (in Eastman's group) we are constructing special large HTBs (gate area about 1 cm^2) which will allow us to carry out both CL and EBIC on one device as a function of operating conditions (Varying V_{SD} , V_G).

b) OMCVD Samples:

Jointly with CVD Equipment Corporation, we won a small contract (Cornell share 36 K) from the New State Office for Technology Development to fabricate large GaAs solar cells by OMCVD. CVD Equipment Co responsibility is to grow the layers and our responsibility is materials analysis and processing, i.e. design and fabrication of front contact and back contact metallization. In addition, we assist in OMCVD reactor modeling studies.

Our main reason for competing for this contract was that as part of this contract we will have access to one OMCVD system located at CVD Equipment Corporation in Long Island. We plan to have one student on and off at the location to grow InGaAs/GaAs sample

structures.

c) Efforts to obtain funds a specimen preparation facility:

A substantial amount of the PI's time was spend on writing a proposal to the DOE Equipment Program for an MBE system. The proposal contained contributions from faculty members from the the EE, Physics and Applied Physics Departments (Tang, Silcox, Sievers, Silsbee, Lee, Wolga) which, in turn, required the coordination of many conflicting individual interests. NY State committed 75 K to the project, Cornell 65 K and Varian (after some negotiations) gave us a 300 K contribution. If funded, the MBE machine would go into the Submicron Facility at Cornell and would be connected to an ion beam writing machine. This would allow fabrication of 3-D heterojunction devices.

iv) Results :

InGaAs work:

The main research objective was to understand the defect formation at the InGaAs/GaAs interface as a function of the misfit parameter (i.e. In content), layer thickness and starting substrate dislocation density. (There are very little data in the semiconductor literature on misfit dislocations in high misfit systems and their influence on the electronic properties.) A secondary objective was to study epitaxial growth on very small islands to verify theoretical predictions of critical layer thickness as function of area.

By combining high voltage transmission electron microscopy, Cl, and Normarski the following results were obtained:

1) No 1:1 correlation exists between darkline defects and misfit dislocations at the InGaAs/GaAs interface. The latter are spaced about a factor ten denser then the former.

(This is a new result: common assumption in the literature is that darkline spacing and misfit dislocation spacing are identical.)

2) Darkline defects consist of tight bundles of dislocations.

3) Recombination along darkline defects is variable.

4) As the misfit parameter increases, misfit dislocations are less and less confined to the interface. Partial dislocations are expelled from the interface, resulting in small stacking fault loops protruding in the InGaAs layer as well as the buffer layer. (New result for III-V, but documented in the 80'th for high misfit metallic epistystems.)

5) Surface ridges on the specimen correlate with darkline defects.

The overgrowth studies have progressed to the point where we can etch well defined very small mesa structures into GaAs. (An example of a micron sized mesa is shown in the appendix. It took considerable experimentation with various dry etching methods to get to this stage). We are now waiting for MBE growth.

The HBT studies, which were carried out with EE, had the objective to understand the effects of misfit dislocations at the emitter/base interface on emitter efficiency. (The results have been published in J.Appl.Phys.). As the In concentration of the base is increased beyond 2%, dense misfit dislocation networks develop. Amazingly, the influence of these dislocations on emitter efficiency is quite weak.

The objective of the contact research was to develop a non alloying contact to p type GaAs with a resistance of less than 10^{-8} . This was achieved using Mg implants and a Pd overlayer.

To get acquainted with all the GaAs processing steps we made a series of GaAs FETs with gates as small 1.25 microns. Even these very small devices worked even though the devices were made with a non self aligned process. Electrically, the devices are not the best, but we feel that we have mastered all GaAs processing steps sufficiently to make useful devices for analytical purposes.

v) Discussion:

The analytical part of the III-V research appears to be off to a good start. We built up a nice CL facility considering the difficult circumstance that we have no control over the SEM and must remove, after every session, whatever we put on the instrument.

Using the CL in combination with high voltage TEM (which we carry out using the 1.2 MeV Instrument operated by NYS at Albany) has proven to be a powerful technique to study misfit dislocations.

HVTEM is well matched to CL in that CL specimen need to be of a thickness which is at least equal to the generation volume diameter. This diameter varies with the 1.75 th power of the voltage and is on the order of a micron at the lower end of useful SEM operation.

Such specimens are too thick for conventional microscopy, but micron thick specimen are transparent to 1 MEV electrons. Thus, we can correlate CL and TEM (i.e recombination properties and structure) on one and the same specimen. Our group seems to be the only one that does this kind of work, presumably because few

groups use HVTEM.

This research has already shown that some common held assumptions (darkline defect spacing equal to misfit dislocation spacing; interface dislocations restricted to interface) are invalid in the InGaAs/GaAs system and quite likely in other high misfit systems as well.

The weak point of the program continues to be that we have no control over specimen preparation and have to live off hand outs from other groups. The program would be much stronger if specimen preparation would be a part of it, but there is simply not enough capital to implement it.

As a result of this, we tend to study what is of interest to the groups controlling specimen preparation, rather than fundamental aspects. We try to get out of this loop by trading service work on EE devices for the fabrication of MBE structures which are of interest to us. For example, to get the island program along (the purpose of which is to confirm study the relationship between critical thickness, dislocation nucleation at the critical thickness and island size) we have to do CL analysis on processing problems in Eastmans group until we have accumulated enough good will that they will carry out a dedicated MBE run for us.

Related to this aspect is that the program involves more device and processing work than in most analytical groups. This is simply a measure of self defense relative to our specimen supplier. We already depend on them for MBE runs. If we would also depend on them on processing and device fabrication they would totally control the direction of our research.

2) List of publications generated under the contract:

i) Published during period, but generated under preceding contract:

"The Microstructure of Lase Material"
S.Q.Feng, T.D. Sullivan and D.G.Ast
Solar Cells, 17 (1986) 275-283

"Oxygen Measurements in Thin Ribbon Silicon"
S.L. Hyland, D.G. Ast and A. Baghdadi
J. of Crystal Growth 82 (1987) 193-196

ii) Work under this contract:

"Cathodoluminescence of InGaAs-GaAs Single Heterostructures"
E.A.Fitzgerald, K.L.Kavanagh, D.G.Ast, P.Kirchner, G.D.Pettit
and J.M. Woodall. Proc. Materia. Res. Soc. Meet, Boston Mass (1986)
(North Holland)

"Lattice Strained Heterojunction inGaAs/GaAs Bipolar Structures:
Recombination Properties and Device Performance"
L.P.Ramberg, P.M.Enquist, Y-K Chen, F.E.Najjar, L.F. Eastman,
E.A. Fitzgerald, K.L.Kavanagh,
J.Appl.Phys. 61 (3) (1987) 1234

3) List of other federal funds:

ONR "Interfaces in Composites" 45 K

4) Status of Graduate Students:

a) Sandra Hyland (Ph.D. candidate)

Background: RPI (EE), Maryland (MS&E), 5 year stint at JPL.

Carry over from old Si program (DOE; DOE-JPL). Topic:
high temperature deformation of WEB silicon bicrystals.

When the JPL program was terminated, an IBM fellowship picked up
S.H. for the 86/87 academic year. This fellowship expires 5/31/87.

Recently, S.H. won a DAAD fellowship. She will join Prof. Peter
Haasen's group at Goettingen University for 3 to 4 month,
starting in August of 1987 and then return to Cornell.

Tentative graduation date: Dec 1988

b) George Perreault (Ph.D)

Background: Georgia Tech (Chem.Eng); two year stint at IBM Fishkill

Works on simultaneous EBIC/STEM imaging in the Jeol 200 CX. Very
difficult project as specimens thin enough for TEM are very
small and present difficult contacting problems. Present
specimens are Si but if the technique works out, the application
will be switched to GaAs.

Tentative graduation date: Spring 1989

c) Gene Fitzgerald

Background: MIT (MS&E)

Very good student, physics oriented. Works on CL/HVTEM analysis of interfaces in InGaAs.

Tentative graduation date: To early to tell

d) Roberto Proano

Background U. of Missouri (Metalurgy).

Very good student, process oriented, does all GaAs processing. Works together with G.F. on MBE island growth studies.

Presently on NSF minority fellowship.

5) Objectives for Second year:

a) Interface studies in III-V

The objectives for the second year are those outlined in the original proposal.

As a new instrumental development, we plan to modify the SEM such that we can apply voltages to two and three terminal devices while doing CL and EBIC. (CL and EBIC as a function of voltage allow quantitative conclusions on band bending and determination of punch through voltage. Bell Labs has done some work on this, but there seems to be no follow up, perhaps because Petroff recently joined UCSB.)

Our main objective continues to be a better understanding of the structure as well as the electronic properties of dislocations at interfaces and the relationship between the two. In 78/88 we plan to further investigate the InGaAs/GaAs system. Our next goals in this system is to understand the relationship between surface ridges and darkline defects and the relationship between critical thickness and island size.

In order to understand the surface ridges we must understand the factors that lead to a periodic bunching of misfit dislocations.

Such an understanding starts with a Burgers vector analysis, which is very difficult in densely bunched systems of dislocations. The surface ridges may be related through stress effects on the nucleation rate.

There are no studies of critical thicknesses as a function of island size and few studies on the basic aspects of misfitted

MBE or MOCVD growth on mesa surfaces. Our plan for 77/78 is to study t as a function of island size and shape. We hope that we will^c be able to learn something about growth on mesa structures. Depending on the results, the island program may expand to a more basic program of the atomistic nature of MBE and OMCVD growth of non lattice matched systems on non planar surfaces. (If the program were to develop in this direction, it would be a new direction relative to the original proposal).

Finally, we would like to augment the CL/EBIC/HVTEM interface program with a study which conducts DLTS on InGaAs/GaAs interfaces grown close enough to a surface such that the interfaces lie in the depletion layer of Schottky diode.

The PI will continue to write proposals for a specimen preparation facility. This is extremely tough. Not only are MBE and or OMCVD systems very expensive but they are (and this is known to most reviewers) already present at Cornell in the EE department. It is difficult to convince outside reviewers that this facility does not and does not want to operate as a source for materials for other groups in need of III-V specimens.

b) Device Work:

i) Small signal devices.

Work will continue with the L. Eastman group on HTBs with InGaAs interlayers. Large HBTs (gate area one cm^2) will be used to study band bending effects on CL intensity. A better understanding of these effects will benefit our interface studies since interfaces generally introduce band bending.

ii) Solar cells

As discussed in the sample & sample preparation section, we will process 40 OMCVD wafers grown by CVD Equipment Corporation into finished solar cells. About 10 of these cells will be send to SERI for efficiency measurements. (New, part of NSY program).

Acknowledgements.

We would like DOE and NYS ERDA for support of this program.

Appendix

InGaAs/GaAs Experiment:

Picture 677:

CL image of $1\mu\text{m In}_{.12}\text{Ga}_{.88}\text{As}$ on a $1\mu\text{m GaAs}$ buffer layer (9800 dis./ cm^2 EPD substrate). All layers doped with Si at 10^{18} cm^{-3} . The area shown has $4000\text{\AA}$ removed from the surface. The corresponding spectra shows mostly InGaAs emission from the $6000\text{\AA}$ layer- most GaAs photons are absorbed in the InGaAs layer and re-emitted as InGaAs photons.

Picture 683:

CL image of same sample in which the interface region has been removed. The image shows that the defects which propagate into the buffer layer act as high recombination centers. The CL spectra shows only GaAs emission, indicative of interface removal. EDX spectra also showed no indium.

Pictures 648 & 649:

CL image (648) and SEM image (649) of the correlation between surface ridges and the dark line defects. The surface ridges are sensitive to growth conditions. This correlation suggest that the defects responsible for the dark line defects are preferred areas of nucleation due to stress and steps near the defects.

Cross-sectional TEM:

Cross-sectional TEM micrograph of an $\text{In}_{.13}\text{Ga}_{.87}\text{As}$ layer with $t=8000\text{\AA}$. Notice:

- A. Propagation of looping dislocations into buffer layer
- B. Open arrow shows a loop with striations, possibly a stacking fault; leading dislocation is

therefore a $(1/6)a\langle 112 \rangle$ partial edge dislocation (proved in next figures)

C. The closed arrow shows a loop in which the beam conditions are causing the fault to be lighter than the rest of the buffer layer

Partial Array:

On the same page as the cross section is the Burger's vector analysis of the loops which propagate away from the interface. All micrographs are of the same planar area of a sample in which the interface region has been removed. Dislocations disappear when g is along the dislocation $\langle 110 \rangle$ line; therefore, the Burger's vector b is perpendicular to $\langle 110 \rangle$. The stable edge dislocation which can glide in this system is $(1/6)a\langle 112 \rangle$. Misfit dislocations at the interface dissociate, and the partial edge dislocation can glide away from the interface due to the presence of many defects (repulsion forces):

$$(1/2)a[0\ 1\ 1] \Rightarrow (1/6)a[-1\ 1\ 2] + (1/6)a[1\ 2\ 1]$$

We are fortunate to be investigating a material where the stress is intermediate and we are able to observe the formation of stacking faults; the same mechanism is probably how stacking faults form in the higher misfit systems, such as GaAs on Si.

CL/TEM Correlation:

First compare the CL composite with the g_{220} 1 MeV TEM composite. Note that the CL picture has a resolution approximately at the diffusion length limit of the carriers. This is because the CL system is very efficient, even at 15KeV, and therefore the excitation volume for CL signal is not much greater than $\approx 1\mu m$. m is the marker used to correlate the two composites. A&B mark the DLD's in the CL micrograph and the corresponding defects under g_{220} excitation. Notice defects A&B are strongly excited under this excitation, and that the bend contour shifts when it

passes across the defects. The defects are best seen just off the bend contour.

Now compare to the 1MeV g_{-220} composite diagram. Note that defects can still be observed in A&B. Thus, the DLD's are not solely composed of $(1/6)a\langle 112 \rangle$ edge partials, since $\langle 112 \rangle$ type defects disappear under the other $\langle 220 \rangle$ excitation. The other defects may be 60° type dislocations or $\langle 121 \rangle$ type 30° partials left in the interface after the edge partial has glided away from the interface. The g_{-220} micrographs also show another area, E, where defects are non-vanishing under excitation, and this also correlates with a dark line defect in CL. C&D defects are also pointed out, and they correlate with the DLD's as indicated.

HBT Project:

Pictures 851 & 852:

CL images of the uniform composition base structure of the AlGaAs emitter, $In_{.05}Ga_{.95}As$ base, and GaAs emitter HBT. Notice the large asymmetry of the defect structure.

Picture 853 & 854:

CL images of the same structure as above except the $In_xGa_{1-x}As$ base is graded from $x=0$ at the emitter-base interface to $x=.05$ at the base-collector interface. As can be seen in the image, there are fewer defects at the interfaces in this structure. This is expected since the overall In concentration in the base is less. The dots are most likely threading dislocations, and the lines are the beginnings of misfit dislocation formation. Since dislocations cannot end in a crystal, the defects are either loops reaching the interface from the surface, or threading dislocations which

have glided partially along the interface. The lower magnification picture also shows an oval defect.

Compare the CL spectra from the two layers (graded vs. abrupt):

A. The smaller peak is the AlGaAs peak, and the shift indicates a slight difference in Al composition.

B. The uniform base structure has a lower GaAs emission. Two reasons for this are the greater absorption of GaAs photons as they pass through the uniform base, which has more In; and the number of defects are greater in the uniform base structure, so more non-radiative events are possible.

C. The height of the GaAs peak in the graded base sample is reduced in the full page CL spectra graph, so that the shape of the spectra can be compared. There is InGaAs emission in the uniform base structure (blue curve, InGaAs is to the right of the larger GaAs peak), but none in the graded base structure (red curve). Therefore the built in E-field separates the carriers, decreasing the radiative recombination. This indicates better base transport.

Picture 856:

CL image of an HBT structure with a graded $\text{In}_x\text{Ga}_{1-x}\text{As}$ from $x=0$ to $x=.1$. Even though there is grading, a full array of defects are present at the interface. The total In concentration is equal to the amount in the uniform $x=.05$ base, so the total stress is the same and the defect structure is expected to be similar.

Pictures 891 & 892

These are CL images of an inverted HBT structure, i.e. GaAs emitter, InGaAs base, and AlGaAs collector. Note the light lines, the dark lines (especially near corners), and dots. The

difference in apparent recombination strength may be because the dislocations are at different interfaces, or they may be a different type of defect. The dots are likely threading dislocations.

Left: CL images and CL spectra of 6000 Å InGaAs on GaAs. Right: After removal of InGaAs. Note interface defects propagating into InGaAs layer.

Correlation between darkline defects (CL image, top) and surface ridges (SEM image, bottom). For more details, see text.

Upper left corner: Cross sectional TEM of InGaAs/GaAs interface. Arrow indicates expelled partial. Other images are plan view, taken with different reflections. For more details, see text.

Cl image of InGaAs interface. The two following pictures are 1 MeV images of the same area, taken at same magnification and at two different operating reflections. For details of comparison, see text.

1 MeV TEM image of area depicted in CL image on previous page. For details of comparison, see text.

1 MeV image, same area as previous image, but at g_{220} . For more details, see text.

CL image and spectra of HBT, non-graded In(5 at%)GaAs base. For more details, see text.

CL image of HBT, graded InGaAs base. Average In concentration 2.5 at%. For more details, see text.

CL spectra of HBT's with graded (red, narrow main peak) and non graded (blue, wider main peak) InGaAs base regions. Main peak: GaAs. 700 nm peak: InGaAs. Spectra are normalized on GaAs peak. For more

Top: Graded base HBT, average In concentration 5 at%. Bottom: Cl images, inverted HBT, average In concentration 2.5 at %

B) Island and FET work

Mask layout for island growth experiment

Example of 2 um size, etched island, ready for MBE.

I-V I_{SD} vs V_{SD} at various V_G for 5 μm GaAsFET
fabricated on semi-insulating GaAs by ion implantation