This report describes our efforts and results during the first year of our two-year program for fabrication and characterization of nonlinear optical properties of HgCdTe superlattices. We determined early on in the program that performing nonlinear optical experiments (i.e., optical phase conjugation and optical bistability) on such superlattices requires the fabrication of thick (2 μm) samples. The growth of thick superlattices with very thin individual layers, on the other hand, can best be accomplished by using an automated MBE system. We launched a major effort to automate our existing MBE system which is due for completion by the end of July 1985. This report also describes the automation design, software, and the computer-controlled hardware.
SUPERLATTICE OPTICAL BISTABILITY RESEARCH

FIRST ANNUAL REPORT

5 JULY 1984 THROUGH 30 JUNE 1985

AIRFORCE OFFICE OF SCIENTIFIC RESEARCH

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1.0 Introduction

Our major effort during the first year of the program has been the growth and fabrication of HgTe-CdTe superlattices. These superlattices are grown by molecular beam epitaxy in a MBE system specifically designed to handle mercury. MBE is an ultrahigh vacuum evaporative technique that achieves epitaxial growth on a substrate wafer through the reaction of multiple beams of atomic and molecular fluxes. Its versatility lies in its unprecedented control of layer thickness, composition and dopant concentration. One particularly useful characteristic of this technique is its low growth temperature. As a result interdiffusion at various interfaces during growth is much reduced, and abrupt interfaces can be produced for multilayer heterojunction and superlattice device applications.

2.0 Growth Studies

The MBE growth of mercury compound is still relatively new and novel, therefore the growth process is not as well understood as that of III-V semiconductor compounds. In HgTe-CdTe superlattices the CdTe deposition is relatively straightforward since Cd and Te evaporated congruently from a single effusion cell charges with small pieces of high purity polycrystalline CdTe. The growth of HgTe, however, was complicated by the high volatility of mercury. A large amount of mercury flux must be maintained to compensate the mercury reevaporation loss from the film. Under mercury deficient conditions, the unreacted tellurim would impede growth of HgTe and result in polycrystalline material, which could be easily detected by the reflection high-energy electron diffraction (RHEED) patterns. By monitoring the RHEED pattern of the growing films, one can then determine the minimum required Hg flux for growth of single phase HgTe. Figure (1) illustrates a plot of mercury flux versus the growth temperature in which the full circles represent stoichiometric HgTe films and the triangles represent conditions where mercury deficiency was found. The dotted line in the figure represents the mercury flux required to produce a
stoichiometric film at all temperatures. Its exponential dependence on temperature appeared in agreement with the observation that the sticking coefficient of mercury decreases when the substrate temperature is raised.

Such high mercury flux is expected to produce substantial beam scatter leading to non-uniformity in sample thickness. The effect can be estimated using a simple model involving hard sphere collisions. We found from the estimate that for pressure greater than $10^{-4}$ torr substantial attenuation of other beams would result. This was verified in our experiments. Therefore the equivalent of $10^{-4}$ torr is an upper limit of the mercury flux that should be employed. In a later section we shall also discuss the effect of interdiffusion between layers during the growth. These two considerations provide a narrow temperature and flux window where good superlattice crystals may be grown.

Since bandgap related properties of the superlattice is a sensitive function of individual layer thickness, the experimental parameters must be tightly controlled. We have spent substantial amount of effort toward achieving that goal by automating the deposition procedure. The substrate temperature is monitored by a close proximity thermal couple as well as by an IR pyrometer; they are calibrated in each run against suitable eutectics placed directly on the substrate block to obtain accurate temperature reading. The mercury flux in measured by two separate ion gauges and other fluxes are monitored by mass spectrometer and crystal thickness monitor. Experimental conditions are fed directly to a computer to facilitate real time control.

By combining measurement data with physical controls in a central computer, we are able to coordinate the deposition parameters repeatably and comprehensively. A Hewlett Packard Model 216 personal computer has been chosen as the central computer, and HP3497A Data Acquisition and Control Unit performs the key Task of interfacing between the computer and the electronic instruments. The convenience of this equipment and our experience in programming for laboratory automation has been proven in other systems.
Because the procedure for depositing superlattices is quite different than the procedure for a uniform MBE grown thin films, similar but independent software programs are necessary. The initial plan for implementation for computer control of the MBE systems is to deposit a superlattice using timed shutter control and automatic control of the substrate temperature. The intent of this first program is to increase the number and improve the quality and uniformity of the superlattice layers deposited. The number of layers will no longer be limited by operator fatigue because of automatic shutter control. The quality and uniformity will be improved because the timing of the shutter control will be precise within one second and the operator will be able to concentrate his efforts on maintaining uniform deposition rates.

The software for this plan is complete and is illustrated in Figure (2). It begins by requesting operator inputs for the number of superlattice periods. Then the time periods and substrate temperatures for the anneal, buffer, and superlattice stages of the program must be inputted. After the inputs are printed and verified by the operator, the program takes control of the setpoint of the substrate temperature controller which has been carefully preset using a eutectic. At the end of the anneal period, the substrate temperature automatically makes a transition to the buffer layer temperature. After stabilization, the shutters are opened for the CdTe buffer layer. This program requires the technician to manually prepare and control the source fluxes. If necessary he may pause the program at any point. When the buffer layer is finished the substrate temperature makes another transition to the superlattice deposition temperature. At this point the program must pause so that the technician may establish a steady mercury flux using the digital ionization gauge. The other source fluxes must also be set using the crystal monitor. When the program is continued the alternating superlattice layers are deposited through a timed sequence of shutter movements until the specified number of layers has been deposited. Finally, the substrate heater is turned off and a constant flux of mercury prevents depletion of the substrate as it cools.
3.0 Characterization

Experimentally one suspects that interdiffusion in the layers may cause deviation from ideal SL structure which assumes atomically abrupt interfaces. Quality of a SL, therefore, depends also on the extent of interdiffusion that may have occurred at the growth temperature. The diffusion width for mercury, W, can be approximately defined as \( W = 3.8 \ D(T) \tau \ \text{cm} \), where \( D(T) \) is the temperature-dependent diffusion coefficient and \( \tau \) is the diffusion time. For a typical growth time of one hour, this becomes \( W = 2.28 \times 10^6 \ D(T) \ \text{um} \). Figure 3 shows data from two previous studies which, when extrapolated to lower temperature range, disagree with each other by more than two orders of magnitude. Prior optical and Auger profiling results carried out at Honeywell seemed to indicate that interdiffusion at interfaces would be less than 10A, in somewhat agreement with the lower curve in Figure 3. Interdiffusion on such small scale is very difficult to detect. A very significant experiment was carried out recently. Temperature dependent study of x-ray diffraction pattern has been performed. X-ray diffraction was taken on a superlattice sample consisting of 12 layers of 60A each of CdTe and HgTe. Because of the additional periodicity introduced by the alternating layers in the superlattice one observes satellite diffraction peaks in addition to the main Bragg diffraction peak. As shown in Figure (4), several high order satellite peaks are clearly identified indicating the high structural quality of the superlattice. The sample was then heated to 185\(^\circ\)C for several hours before their x-ray diffraction patterns were measured again. After each heating cycle the intensity of these peaks decreased until after a total of ten hours of heating the satellite peaks totally disappeared, indicating interdiffusion had completed. This experimental investigation is very significant in that it practically set an upper limit of the growth temperature for HgTe-CdTe superlattices. We have also taken x-ray measurements on superlattice samples grown at 195\(^\circ\)C where satellite peaks were not observed. The latter result also collaborated the temperature dependent x-ray study that growth temperature should be limited to below about 190\(^\circ\)C.
Photoluminescence measurements on the superlattices have also been performed. Previously we have reported optical transmission data on superlattices. Absorption coefficients were then extracted to obtain bandgap information. Unlike HgCdTe alloys, however, the optical data on HgTe-CdTe superlattices have proved to be difficult to interpret because of thinness of the samples and uncertainties in theoretical understanding. The infrared photoluminescence technique, on the other hand, could in principle give a more definitive value of the bandgap. The technique is simply the optical excitation of a sample to create electron-hole pairs. The lifetime of their decay depend on various energy states of the materials, and the highest energy signal could be near the bandgap. The work was carried out in collaboration with Professor T.C. McGill and S.R. Hetzler of Caltech and J.P. Baukus and A.T. Hunter at Hughes Research Laboratories, Malibu. Figure (5) shows the resulting bandgap information as a function of temperature, of a sample consisting of 150 layers of 50Å each of HgTe and CdTe. These values agreed very well with theoretical models. Unlike optical transmission data they also showed a clear temperature dependence. This represents the first time that photoluminescence has been observed on HgTe-CdTe superlattices. Since it is a difficult technique for infrared wavelength region, and the intensity depends strongly on material quality, the observation of it demonstrated very high quality of the HgTe-CdTe superlattices fabricated at Honeywell.

4.0 Summary and Conclusion

Here the fabrication and some important characterization of the HgTe-CdTe superlattices are reported. They have led to increased understanding of this interesting material system. High material quality has been demonstrated, and prospect for growing thick samples is very good because of the implementation of system automation. Future work will concentrate on improved experimental parameter control and doping behavior of the superlattice.
As of June 16, 1985, $89,100 through price has been spent.
Figure (1)  HgTe GROWTH PARAMETERS

$J_{\text{mercury flux atoms sec}^{-1} \text{cm}^{-2}}$

GROWTH TEMPERATURE

- $\Delta$ NON STOICHIOMETRIC
- $\bullet$ STOICHIOMETRIC
OPERATOR INPUTS:
A) # SUPERLATTICE PERIODS
B) TEMPERATURES
C) TIME PERIODS

PRINT INPUTS

NO

INPUTS OK?

YES

OUTPUT ANNEAL SUBSTRATE TEMPERATURE SETPOINT

WAIT FOR ANNEAL PERIOD

OUTPUT BUFFER LAYER SUBSTRATE TEMPERATURE SETPOINT

WAIT 10 SEC.

IS ACTUAL SUBSTRATE TEMPERATURE = SETPOINT?

NO

WAIT 5 MIN. TO STABILIZE

OPEN CdTe AND SUBSTRATE SHUTTERS

WAIT BUFFER LAYER DEPOSITION PERIOD

CLOSE SHUTTERS
OUTPUT DISPOSITION
SUBSTRATE TEMPERATURE
SETPOINT

WAIT 10. SEC.

NO

IS

NO

ACTUAL SUB-
STRATE TEMP =
SETPOINT?

YES

WAIT 5 MIN. TO STABILIZE

NO

ARE

Hg, CdTe, & Te
FLUXES AT DESIRED
LEVELS?

YES

OPEN Hg, Te, AND
SUBSTRATE SHUTTERS

WAIT HgTe PERIOD

CLOSE SHUTTERS

WAIT A SHORT DELAY
PERIOD

OPEN CdTe AND SUB-
STRATE SHUTTERS

WAIT CdTe PERIOD

CLOSE SHUTTERS

N = N + 1

NO

IS

N = TOTAL #
PERIODS

YES
Is CdTe THE FINAL LAYER

NO

OPEN Hg, Te, AND SUBSTRATE SHUTTERS

WAIT HgTe PERIOD

CLOSE Te AND SUBSTRATE SHUTTERS

TURN SUBSTRATE HEATER OFF

WAIT 20 SECONDS

OPEN SUBSTRATE SHUTTER

END

YES

OPEN Hg SHUTTER
Figure 3

Mercury Diffusion
Width vs Temperature

- $X = 0.2$ into CdTe, Te rich

- LPE
- CSVPE
- MOCVD (VPE)
- SPUTTER
- MBE (LABA)

- Almasi and Smith
  J.A.P. 39, 233 (1968)

$\Delta W$ (µm)

$10^3/T\ (°K^{-1})$

550 500 450 400 350 300 200 100

5 7 9 11

1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6

Honeywell
Figure 4

- X-ray Diffraction Peaks of HgTe-CdTe Superlattice

Honeywell

# COUNTS

0 100 200 300 400 500

20.00 21.75 23.50 25.25 27.00

SL #8503

SATELLITE PEAKS FROM SUPERLATTICE PERIODICITY

85-EGS-644
Figure 5: Temperature Dependence of SL Photoluminescence

- Hg$_{.50}$Cd$_{.50}$Te Band Gap
- IRPL from Sample 2

Energy (meV) vs Temperature (K)