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Growth Studies of CVD-MBE by In-situ Diagnostics

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Abstract

This is a progress report for the first year of the DARPA - URI program "Growth Studies of CVD-MBE by in-situ Diagnostics." The goals of the program are to develop non-invasive, real time epitaxial growth monitoring techniques and combine them to gain an understanding of processes that occur during MBE growth from gas sources. We are developing and adapting these techniques on a commercially designed system (Vacuum Generators Inc.) to facilitate technology transfer out of the laboratory into industrial environments. Experimental results, when combined with a Monte Carlo simulation, should give some insight into the growth mechanisms that occur.

Progress has been mostly in the construction of the in-situ diagnostic techniques and in modification of the gas source MBE. Several problems have been solved and we are now in a position to acquire data by three techniques; spectroscopic ellipsometry (SE), laser induced fluorescence (LIF) and RHEED. These developments are described below.

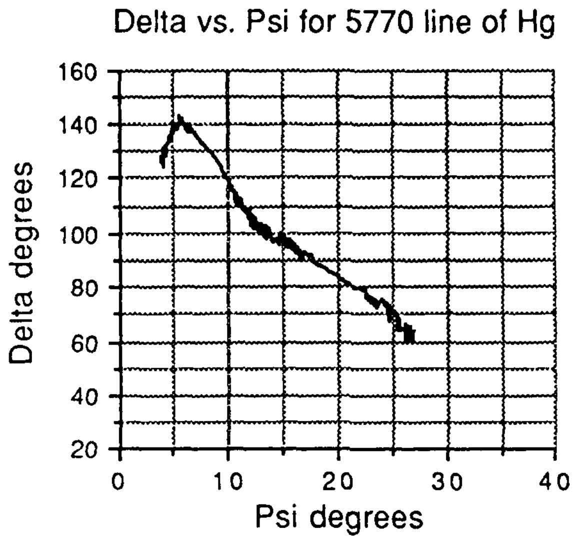
Plans for the next period of performance are to calibrate all of the measurements, take data versus substrate temperature and V/III ratio and compare with growth theories.

Optical measurements / spectroscopic ellipsometry)

A major impediment in the development of in-situ optical characterization techniques is the coating of optical surfaces by species that are being used for epitaxial growth. Arsenic and phosphorus dimers are especially reactive and coat all surfaces quickly, thus degrading window transparency and introducing polarization effects. The optical window coating problem was addressed by using gate valves and a separate pumping system for the optical ports. Bakeable windows having very low birefringence were purchased from Bomco Corp. We can thus, without breaking vacuum, remove the windows for cleaning, bake them and eliminate system down time for this exercise. The windows can also be baked into the external pumping system while they are still on the MBE by valving the chamber off. Relaxing the requirement of breaking vacuum for window service is compatible with a production environment where down time needs to be kept to a minimum.

We have entered into a collaboration with J.A. Woolam Company who is a manufacturer of ellipsometer systems. Several design iterations on an in-situ system for our MBE were performed and we have settled on a rotating polarizer, rotating analyzer spectroscopic system using a Hg lamp. The lamp is used to provide sufficient intensity to produce a detectable signal in the MBE environment which has high ambient light.

A four wavelength system was first tested. The system has the advantages of simplicity and speed. Data can be taken at four different wavelengths (577nm, 435nm, 365nm, and 313nm) in one second. In principle, this ability to monitor psi and delta at multiple wavelengths simultaneously is a great advantage when attempting real-time monitoring and analysis of growth. While this configuration has the capability of performing measurements at short time intervals, the noise introduced by the optical system is high enough to introduce uncertainties in the measurement of Ψ and Δ. Sample data taken on GaAs as a function of time between 300°C and 800°C is shown below.



Listed here are some of our test results with the four wavelength system.

TEST RESULTS

1. A full system alignment can be achieved in a short period of time (less than 45 minutes).
2. Continuous sample rotation did not introduce any more scatter to data than was present with the sample stationary.
3. Mechanical stability of the sample manipulator was found not to be a problem.
4. The signal strength from the light source was sufficient, even with the high ambient light present at elevated substrate temperatures.
5. Ambient light from the effusion cells or room did not constitute a problem for the detection system.
6. Data taken with both Si and GaAs substrates is in good agreement with previously published results and data acquired on independent non-commercial systems.
7. Time dependent optical data on GaAs substrates heated to the point of surface decomposition correlates extremely well to independent measurements. To view the surface decomposition, no external arsenic flux was used.
8. Optical data taken versus time as a Si wafer was being heated showed temperature dependent effects on the SiO_2/ Si system. This optical data was later used to measure the substrate temperature with a reproducibility of $\approx \pm 5°C$ at temperatures of approximately 500°C.
9. The software has full analysis capability and can fit data as it is being acquired.

Future plans

Based on the results of testing the prototype, another system has been developed and will be tested in late July. This is a dispersive, full spectroscopic system in the wavelength range $0.4\ \mu m < \lambda < 1\ \mu m$. We plan to use the four wavelength mode to study time dependent processes while the spectroscopic system will be used for the measurement of thickness and index of refraction in multilayer films.

A useful characteristic is that the ellipsometer assembly can be removed from the MBE chamber and mounted onto a tabletop goniometer for ex-situ comparison of grown films. This has not been implemented yet because of lack of funds to purchase a goniometer. We are exploring possible donations.

Measurements of the desorption of GaAs has been performed using the time dependent measurement system. An oxide desorption stage is first observed, followed by a decrease in reflectivity as the As desorbs and leaves the surface Ga rich. Finally as the Ga surface coverage approaches unity, all phase information is lost.

Substantial progress has been made toward reaching our goal of in-situ detection of gas phase transient compounds by laser spectroscopic techniques.

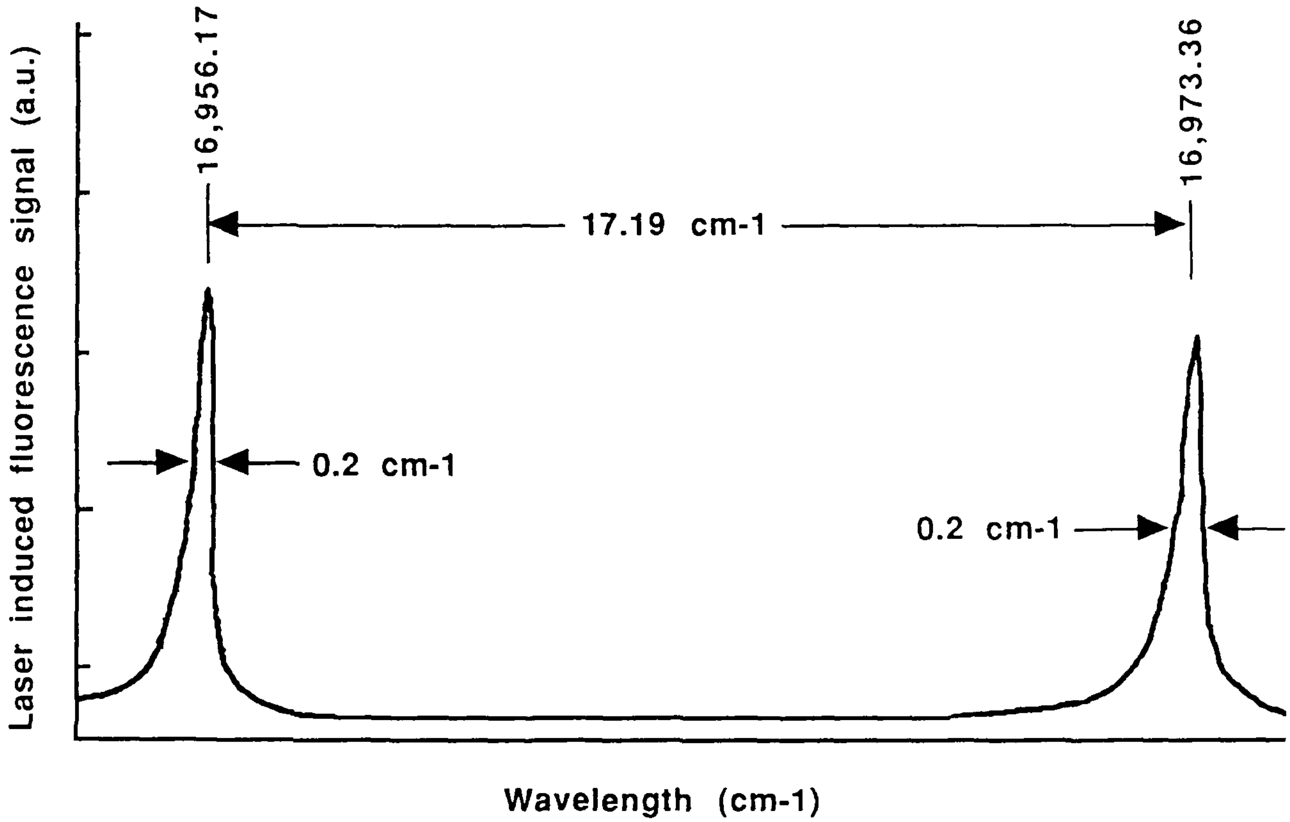
The pulsed dye laser system has been brought on line and a small reactor cell assembled. The initial project has been to generate As_2, As_4 and GaAs in this prototype reactor and detect their laser induced fluorescence spectra. This exercise serves as a means of establishing the optimum set of experimental parameters for detection of these compounds in the growth chamber. The parameters that need to be optimized include laser wavelength for excitation, wavelength for the detection of the LIF and time delay from the excitation pulse to the detection. Tunable pulsed radiation is derived from an excimer pumped dye laser system (Lumonics Hyperdye - 300) which operates in the 370 - 850 nm spectral range at a repetition rate of up to 100 Hz. The majority of the radiation is directed into the prototype reactor cell, with a small portion directed toward a I_2 LIF cell used for wavelength calibration. The LIF signals are processed with a boxcar integrator. A microcomputer stores the output of the boxcar and controls the scan of the laser.

We have focussed on the detection of As_2 produced from the Knudsen evaporation of GaAs. The published vapor pressure information [Foxon, 1974] for GaAs indicates that at the maximum temperature obtainable in our prototype reactor (1200 K) we can obtain approximately 0.3 mTorr. This concentration should be sufficient for LIF detection if an appropriate strong optical transition can be pumped with the pulsed laser system. The spectroscopy of As_2 is fairly well characterized [Huber, 1979]. A band system assigned to the $X^1\Sigma_g^+$ - $c^3\Sigma\hat{u}$ (T_{00}= 14,400 cm^{-1}) transition has been seen by matrix isolation techniques and was selected for this study. Although this is a spin forbidden transition, it was expected that the large spin-orbit mixing of this heavy molecule would give the transition substantial oscillator strength. After carefully searching, no trace of the LIF signal for this band system was detected, even though it had been readily detected in the matrix. A possible explanation is that there is a substantial change in the excitation wavelength transition strength in going from the matrix to the gas phase.

Our observations were confirmed by the recently published results of Smilgys and Leone [Smigly, 1990]. They used a commercial As_4 oven-cracker to produce beams of As_2 which were monitored by pulsed LIF. Their attempts to detect the $X^1\Sigma_g^+$ - $c^3\Sigma\hat{u}$ (T_{00}= 14,400 cm^{-1}) transition failed but excellent S/N LIF spectra could be recorded in the $A^1\Sigma_u^+$ - $X^1\Sigma_g^+$ (T_{50} = 42,080 cm^{-1}) transition. We are now in the process of modifying our measurement system to study this band system.

Shown in the figure is system calibration data for our LIF system. One observes that the measured laser line width is less than 0.2 cm^{-1}which is sufficient to study the rotational resolved spectra in the MBE system.

Laser induced fluorescence of sodium D line (system calibration)



Progress on LIF

The excimer pumped dye laser system was purchased and delivered three months late. It was installed and made operational early this Spring.

The laser was calibrated (linewidth ~ 0.1 cm^{-1} , P ~ 100 mJ) using iodine gas in a small test vacuum chamber.

The optical detection system was constructed and successfully tested.

A fluorescence spectrum of copper oxide formed by plasma discharge was obtained as a reference. Good agreement with cataloged data was obtained.

A spectrum of the thermal decomposition of GaAs was obtained in attempts to measure the amount of Ga and As desorption from the surface. This measurement will be repeated in the specially designed MBE chamber.

Reflection high energy electron diffraction (RHEED)

Reflection high energy electron diffraction (RHEED) imaging will be used to obtain the structural properties of the growth surface as the epitaxial layer grows. Data obtained from the real-time imaging will complement the chemical and optical properties measurements discussed earlier.

The computer controlled system is operational and work is in progress to develop better software for RHEED analysis. Images can be stored to disk at the rate of approximately five frames per second for future analysis. Real time analysis requires greater computational power than we presently have available. Time dependent intensity oscillations (RHEED oscillations) are routinely used to calibrate growth rates.

Progress

Computer controlled RHEED imaging system is operational

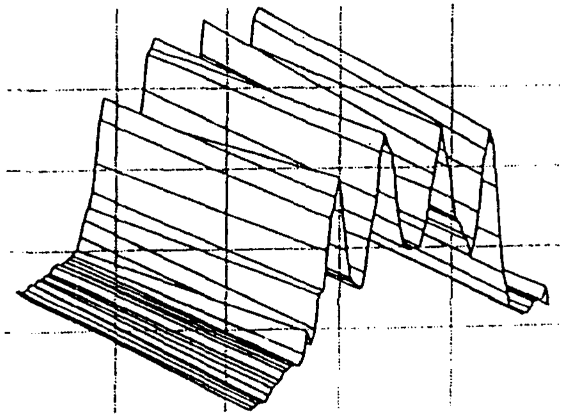
Three dimensional intensity contours can be obtained to analyze the RHEED patterns.

One dimensional intensity cross sections are also generated to measure parameters such as lattice constant or atomic step distribution.

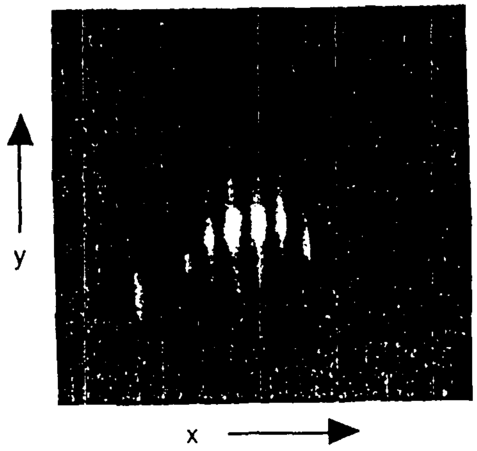
Work is in progress to upgrade image analysis software.

RHEED Imaging Data

3D representation of RHEED pattern

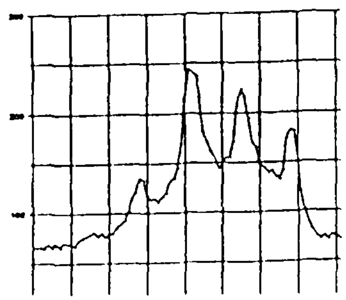


Digitized RHEED image



RHEED streak profile (260)

Intensity across RHEED pattern



Growth modeling

A Monte Carlo model written by Singh and Bajaj will be used to model the growth of III-Vs initially using solid group III and gaseous group V sources. While the simulation has already generated results in the past, experimental data of parameters such as sticking coefficients are required for inclusion into the model. As these parameters become available, they will be incorporated into the model.

This year attempts have been made to make the code operational on the ASU mainframe computers.