UNIVERSITY OF ILLINOIS

.....May...1.1................., 198.9....

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ENTITLED..........Surface Studies of Semiconductors..

....

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF.........Bachelors of Science...

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Surface Studies of Semiconducting Surfaces

by

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Thesis

for the
Degree of Bachelor of Sciences
in
Chemical Engineering

College of Liberal Arts and Sciences
University of Illinois
Urbana, Illinois
1989

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SUMMARY

Two ultra high vacuum system were built, and the
phenomena of Temperature Programmed Desorption (TPD),
Photoreflectance, and Second Harmonic Generation (SHG) were
or will be investigated. Specifically, the desorption of
atomic hydrogen off of a substrate of gallium arsenide, the
photoreflectance properties of GaAs, and characterization
GaAs using SHG were the projects to be undertaken.

For TPD, the main pieces of equipment included a
Cryogenics cryopump, a Dycor mass spectrometer, an
ionization gauge, a sample mount apparatus, and a cubic
vacuum chamber. A small vacuum system was built to do
quick TPD, as opposed to detailed TPD which would have
involved the use of an Auger/LEED analyzer in addition to
the equipment already mentioned. Molecular hydrogen was
cracked to atomic hydrogen before it was adsorbed onto a
GaAs substrate. The desorption at 300 C was observed, and
was monitored with the mass spectrometer. A mechanism of
chemisorption is postulated.

The construction of a larger vacuum chamber took place
to permit the further characterization of GaAs using
photoreflectance and SHG. Some photoreflectance baseline
calibration curves have been generated, but the actual
investigation of different substrates is yet to be done.

INTRODUCTION

Gallium arsenide is a material of wide applications in future high technology industry, and is the primary focus of our study. It may very well be the replacement of silicon as the real estate on computer chips becomes increasingly scarce and the demand for computational speed increases. In addition, its ability to generate different frequencies of light promises to create as many applications as the mind can imagine.

A major obstacle in the use of GaAs in computer chips is the uniformity of the crystal and dielectric layer growth. Because GaAs involves a class III and VI compound, as opposed to silicon which is a class IV compound, uniform crystal growth is difficult. Currently, the procession of GaAs chips is being done without the knowledge of a growth mechanism. Consequently nonuniform, inefficient, and costly empirical processing of chips results. The high cost of this processing severely confines the use of GaAs chips to highly specific applications where computational speed is of utmost importance. If the growth mechanism, and surface characteristics of GaAs crystals could as well understood as that of silicon's, GaAs may very well replace silicon in the future multibillion dollar semiconductor industry.

Because much of the applicable chemistry in gallium arsenide happens at the surface of a crystal substrate, it is important to characterize its surface extensively. To do surface studies, we chose to use Auger electron spectroscopy, Low Electron Energy Diffraction (LEED), Second Harmonic Generation (SHG), Temperature Programmed Desorption (TPD), and Photoreflectance. Explanations of the applications of these techniques will be discussed as each is presented individually. To perform techniques such as this, we first need to house the crystal in a clean atmosphere, or more precisely, a vacuum. In addition, to do the optical experiments such as photoreflectance, a clean lab is essential to limit the scattering of laser light.

The lab consists of a smaller and a larger vacuum chamber. The smaller vacuum chamber, pictured in Figure 1, was meant to do quick TPD, while the larger vacuum chamber pictured in Figure 2, was meant for use with the bulk of the experiments in the Seebauer group. Most of the work done during the year involved getting the two vacuum systems functional, while data taking has been sporadic and frequently frustrating because of problems with the equipment.

The group is mainly using the five techniques above to characterize semiconductor surfaces, and in particular, gallium arsenide. I personally have been involved in all
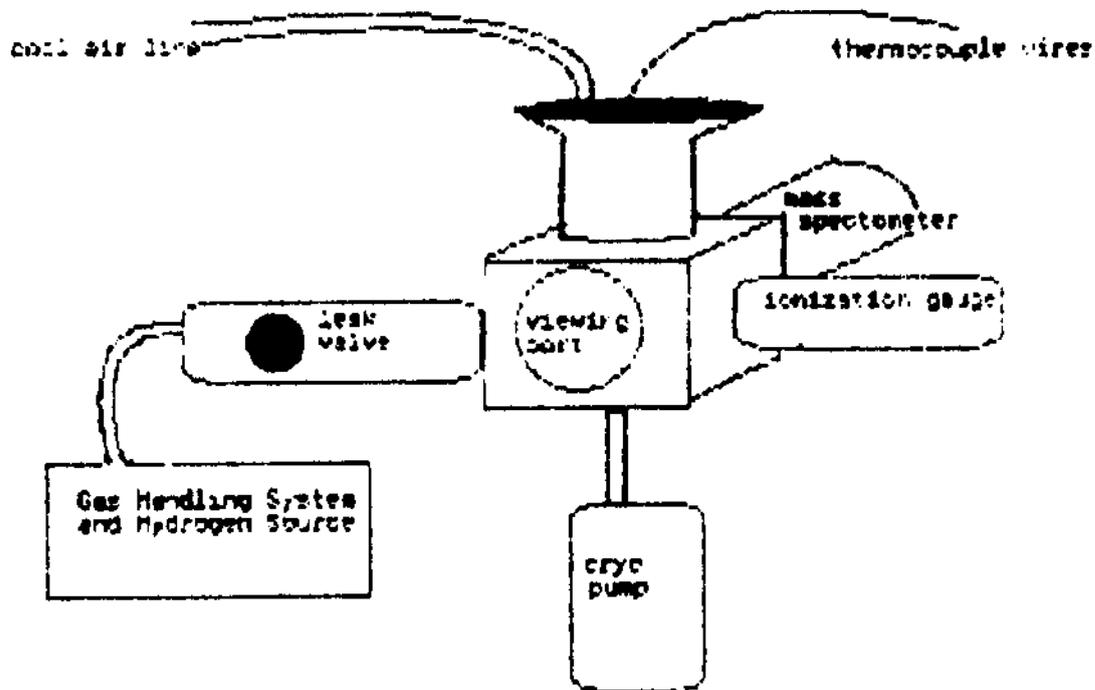
cool air line
thermocouple wires

mass spectometer

leak valve

viewing port

ionization gauge

Gas Handling System and Hydrogen Source

cryo pump

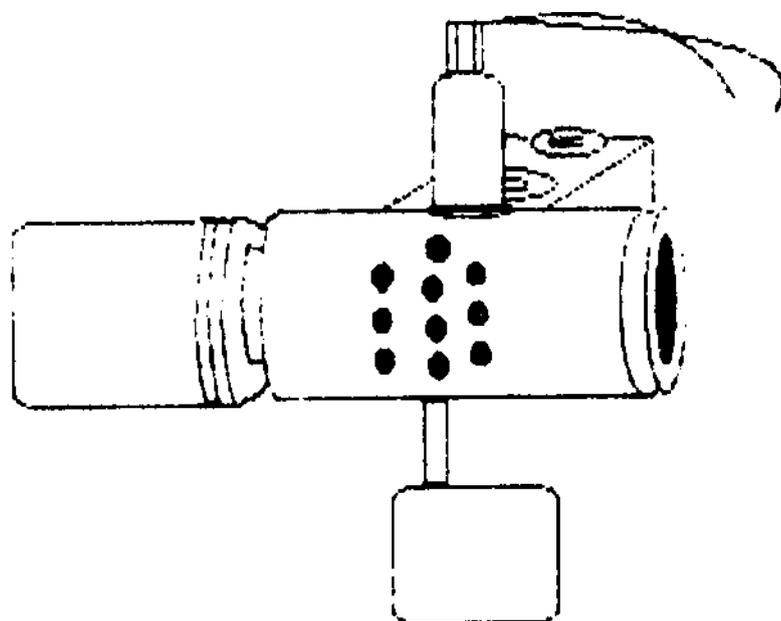**Figure 1: The Small Vacuum System**

Figure 2: Large Vacuum System

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five, to a lesser or greater degree, so to begin, it would be favorable to discuss TPD first for two reasons. First, the process of doing a TPD experiment exemplifies most of the work done during the year for both vacuum systems, and second, we were able to get some data and run an experiment using TPD before the chamber that housed the process was dismantled. Other characterization processes and their applications will be discussed with less emphasis because they did not constitute a majority of the time involved.

TEMPERATURE PROGRAMMED DESORPTION

Information about the binding of substances to GaAs substrates is important in the production of semiconducting devices. Many substances including oxygen, nitride, gold, titanium, etc., are diffused onto GaAs during device production. For example, diffusion of oxygen to the substrate to form a dielectric layer depends on the chemisorption of atomic oxygen. Analogously, atomic hydrogen was chemisorbed onto a GaAs substrate in our TPD experiments. Another example is in high temperature anneals. High temperature anneals are a problem in GaAs chip production because GaAs will tend to dissociate at high temperatures. If there was a way to cover the surface with a substance that could be absorbed and desorbed, the anneal would take place, and dissociation of the substrate would not.

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APPARATUS

The systems consist of various parts, because TPD was performed in the small system, its major parts, the cryopump, the chamber, the sample holder, the ionization gauge, and the mass spectrometer will be discussed separately. Although other important parts exist in the small system, they will be mentioned in conjunction with the major parts listed above.

The cryopump is the key piece of equipment used in achieving the low pressures (10^{-9} to 10^{-10} torr) we desire. The pump works on the principle that gas particles will solidify on a cold surface (15K, and activated charcoal is used), thereby decreasing the pressure in the chamber. A problem can occur when the cryopump becomes choked with solid gas and the pump can pump no more. Consequently, the pump goes from a warm to cold stage when pumping down, and vice versa when going to atmosphere. Because we can choke the cryopump if too much gas solidifies on it, we must pump down to a low pressure using a roughing pump. The roughing pump system is shown in Figure 3. We can use this pump to pump down to pressures of 10^{-6} torr before turning on the cryopump. The cold trap's purpose is to condense all the oil vapor that could feasibly get into the vacuum chamber. To do this, we use a piece of flexible tubing packed with a molecular sieve to absorb any oil passing through. This

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tubing is U-bent as shown, into a large dewar where it is
covered with dry ice (solid CO_2). This is an efficient
mechanism for pulling vacuum while simultaneously trapping
oil. A common mistake is to hook up the vacuum line up to
the exhaust of the roughing pump. The result can be the
ruin of the flexible tubing, molecular sieve, or even the
vacuum chamber itself. We also monitored the roughing
pump pressures with 1 torr and 1 millitorr beratrons and
voltmeters. Once the pressure reaches 10^{-6} torr in the
chamber, the Cryogenics cryopump and its cooling water is
turned on to get to 10^{-9} torr. The cryopump pumpdown takes
about 10 hours, and is usually done overnight.

After we have achieved ultra high vacuum, the next
step is to 'bake out' the system. This involves wrapping a
fiberglass resistive heating tape around all exposed metal
surfaces of the chamber. The objective is to bake off the
water that has adhered to the inside chamber walls. If
this is not done, outgassing can occur the system may have
a difficult time achieving the needed pressures. A
variable power source sends current through the tape to
heat it to 400 to 500 C. This must be done overnight to
insure that the chamber walls are as clean as possible.
Thermocouples are placed at various places outside the
chamber, and under the heating tape. A direct correlation
between the voltage generated from the thermocouple (via

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the heat), and the temperature, allows us to monitor the temperature rise.

The vacuum chamber itself, its flanges and other parts exposed to vacuum are made of stainless steel. It was built in the metal shop in Roger Adams Lab, and had to be specially treated. The cube design has 6 open faces, which connects the cryopump, ionization gauge, sample holder, mass spectrometer, leak valve and gas handling system, and quartz viewing window.

Much work had to be done to make the chamber suitable for ultra high vacuum. The chamber itself had to be cleaned thoroughly with soap, water, and Brillo pads initially to clean off the welds as well as possible. The chamber was then dipped in Diversey (Acid that etches metal; mostly composed of HCl) for about 20 minutes. This gave us a clean inner surface because a few layers of metal were etched when placed in Diversey. All flanges and vacuum exposed metals are likewise etched in diversey prior to use for precisely the same reason. Care was taken to thoroughly rinse off the acid with water, because the acid is a hazardous material.

The system had to be checked for leaks also. To do this we first had to use blank flanges to cover up the open portholes. Then a nitrogen line was snugly fit into the system, and nitrogen was blown into the chamber, while the exterior, especially the welds, were coated with a leak

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detector called 'Snoop'. Snoop is basically expensive soap water used to detect larger leaks. The exterior surface was then checked for bubbling from the nitrogen on the inside. Any leaks would make it necessary to return the chamber to the metal shop for rewelding.

Once the preliminary leak check proved satisfactory, a more precise leak check was performed. To do this, the mass spectrometer (whose operational theory will be discussed later) was hooked up to one opening, the cryopump to another, and the rest were blanked off. The exterior was then selectively coated with acetone, while observing the acetone peak on the mass spectrometer. Any microscopic leaks were evident when a large rise of an acetone presence was observed on the mass spectrometer.

Once we were satisfied with the integrity of the system with respect to leaks, we could then hook up the mass spectrometer and ionization gauge The principles of the mass spectrometer and ionization gauge are similar with the exception of the fact that the ionization gauge measures total pressure in the chamber, whereas the mass spectrometer does not.

The ionization gauge is the more general of the two pieces of equipment and will be discussed first. Figure 4 shows the general schematic of the ionization gauge design. It mainly consists of a collector, grid, and filament. The hot filament produces electrons which are then attracted to
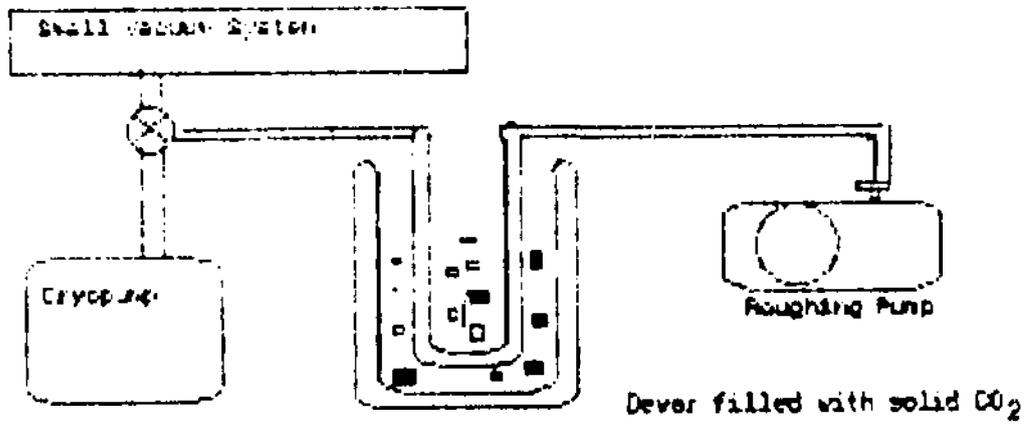
Devar filled with solid CO_2
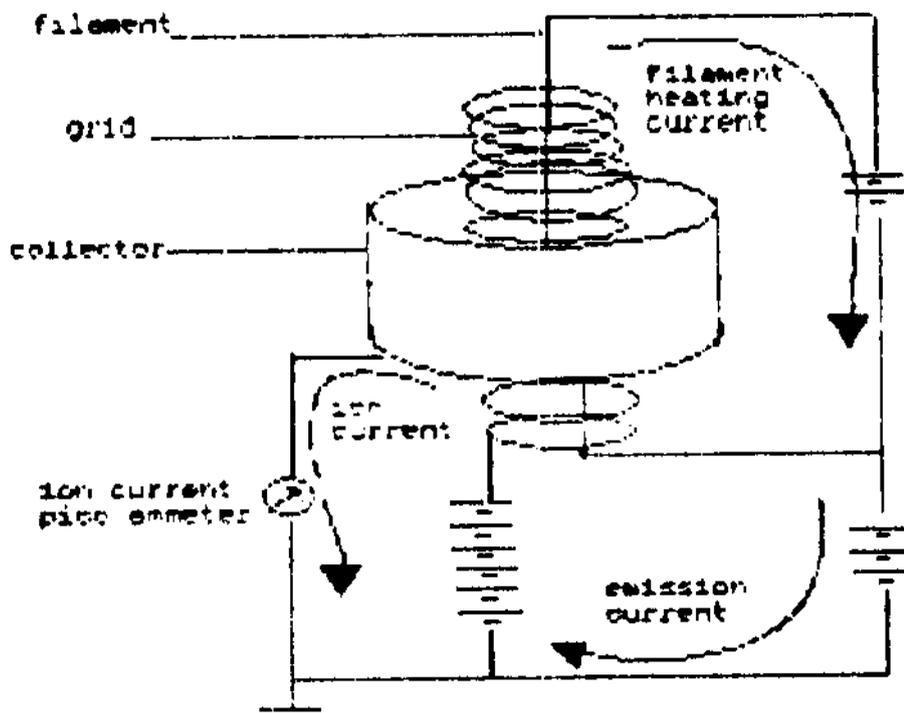
Figure 3: Rough Pumping System

Figure 4: Ionization gauge and simplified circuit

the grid. Hence, a potential is set up between the grid, and filament, and any gas molecules in between have the probability of being ionized and sent to the collector. The ion current produced is then characteristic of the chamber pressure.

The Dycor mass spectrometer operates on the same basic principle, with the variation that there is a quadrapole filter that intercepts ionized gas molecules before they enter the ion collector. The special quadrapole filter separates ions of different mass by causing ions with different charge to mass ratios in an electric field to follow different trajectories. The quadrapole, or alternating electric field, then provides the mass selective action to analyze the gases present. A problem with the mass spectrometer is that it can only give an instantaneous analysis of the chamber gases. That is, all atomic masses must be scanned, and the longer the scan, the more accurate the reading. So if one would like to scan multiple amu's quickly, one would forfeit accuracy and vise versa.

On the side of the chamber, we also have a leak valve, and connection to a gas handling system. This is simply a system used to input the donor gas at a controlled rate. The leakvalve is special because it can be used to leak gas at the slow rates need for TPD. A gas handling system is then connected to the leakvalve to provide selective dosing

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of the donor gases. There are two lines for gases, one for nitrogen, and one for air. It is constructed of inexpensive tubing, swadgelocks and valves. In our case, a canister of hydrogen was hooked up to the gas handling system.

Finally, we have the sample mount. This piece fits on top of the system, and is composed of different sustances.. The mount is made of a stainless steel backing, while two strips of tanalum foil are spotwelded in a way that can hold the gallium arsenide sample in place. The sample itself has current passing through it, and is grounded. Resistive heating is used to heat the sample, and two thermocouple wires are used to monitor the temperature of it.

In the top, we have air blowing in to cool the sample mount and the wires leading to it. We therefore have only the sample at the temperature desired, which is what we are trying to achieve, because we want to study TPD at different temperatures.

PROCEDURE

We began by pumping down the vacuum system. As described above, we first used a roughing pump and proceeded to approximately 10^{-6} torr. At this point, we

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turned on the cryopump and let it pump down overnight where
we achieved pressures of 10^{-9} torr the next morning.

We then proceeded to dose the sample with the
appropriate amount of gas. Using the relationship

$$1 \text{ Langmuir} = 10^{-6} \text{ torr*sec}$$

we dosed the sample with 500, 1000, and 10,000 L. Using
the leak valve, we leaked in hydrogen from the hydrogen
canister via the gas handling system. Simultaneously
leaking, and monitoring the total pressure on the ion
gauge, we leaked in the desired pressure for a set amount
of time to get the correct Langmuirs of dosing. After
dosing, the leak valve was shut, and the excess hydrogen
was allowed to go to the cryopump. Once we were back to
our pressure of about 2×10^{-9}, we then proceeded to
resistively heat the sample. Then we monitored the
temperature rise in the sample with the thermocouple and a
voltmeter. We turned up the sample to 14 amps, which
corresponded to about 400 C and observed the desorption of
hydrogen off of gallium arsenide on the mass spectrometer
terminal.

Later on we proceeded to do more experiments. Except
that this time, we had not taken into account a change in
sample mount design we that had recently been made. This
new design was built to heat the sample more efficiently.

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We then started to dose, and then heat the sample. The current was turned up to 15 amps, and the tanalum consequently vaporized all over the inside of the chamber. After that, the chamber was dismantled, and cleaned. Diversey proved effective in taking much of the tanalum off of the walls of the chamber, but the damage was done. Once the system was put back together, our large vacuum system arrived from the metal shop. We then directed our efforts to that system, and because the group owns only one mass spectrometer, we were not able to continue to do TPD on the smaller vacuum system.

RESULTS

The data presented in Figure 6 shows what kind of desorption profile we obtained for 10,000 L. After doing the first two scans at 100 and 500 L and using the mass spectrometer, monitoring molecular hydrogen with a scan speed of 1/sec, no noticeable adsorption was observed. However, when dosing at 10,000 L (specifically $P = 10^{-5}$ torr; time = 16.7 min; temp = 25 C), with the same scan speed, and the sample at 400 C, we were able to observe desorption.

Most of the gas on the surface of the GaAs crystal should have an atomic hydrogen, cracked to atomic hydrogen by the filament. Because we were monitoring
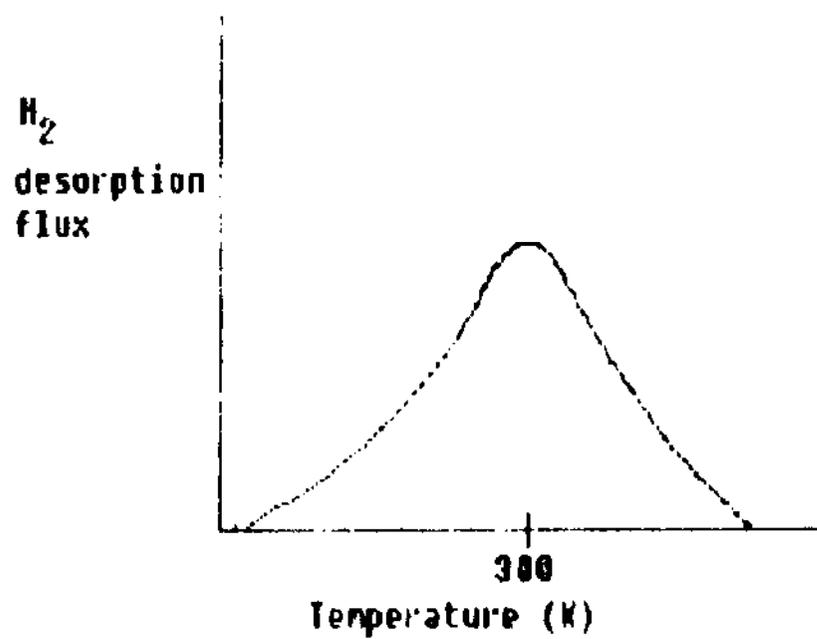
Figure 5: Hydrogen desorption off GaAs

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molecular hydrogen in the chamber, we cannot conclude anything about the surface adsorption mechanism. The atomic hydrogen recombines either on the surface of the crystal, or in the gas phase to form molecular hydrogen. Which, we don't know.

What we can estimate, is the activation energy of adsorbed hydrogen. With the Arrhenius equation, and with the aid of a few assumptions, we can estimate the energy of activation. The derivation of a suitable equation and calculations of the energy are presented in the appendix. From the appendix, we can see that we have obtained an activation energy: E_a = -119 kJ/mole. Physisorbed species generally have activation energies between -25 and -40 kJ/mole, while chemisorbed species have activation energies greater than -40 kJ/mole. Because we are well above the latter range, we are confident that atomic hydrogen is chemisorbed onto GaAs.

To do more quantitative and through TPD, we would need to use an Auger LEED analyzer to know the structure and composition o' the GaAs. Knowledge of the structure is important because, hydrogen will adsorb differently on different surfaces. For example, hydrogen will stick better to a highly defected surface as opposed to a smooth surface. In addition, the surface we were desorbing off of may have been laced with impurities such as fingerprints, thereby distorting the data and conclusions.

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PHOTOREFLECTANCE

Cleaner ways of characterizing the surfaces of
semiconducting compounds are needed now, and in the future.
Traditional characterization methods such as Raman
spectroscopy, and electroreflectance (ER) have not proved
to be the most effective techniques. For instance, Raman
measurements are almost always performed at low
temperatures, and ER involves special surface preparation.
Photoreflectance is attractive because it incorporates
neither of these problems, and is contactless and can be
performed at room temperature.

The reflectivity of a semiconducting surface changes
as a HeNe laser injects photons into crystal substrates.
Electron hole pairs develop, thereby causing a change in
the electric field at the surface which causes a change in
the reflectivity of the surface. This change in
photoreflectivity is measured by simultaneously reflecting
monochromatic light off the same surface, and measuring the
energy of the reflected light with a photodiode and lock in
amplifier.

APPARATUS AND PROCEDURE

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At the beginning of the year, we attempted to do photoreflectance in air to first demonstrate its feasibility. A setup such as the one shown in figure 6 was used. We first used a HeNe laser to induce the electron holes in the sample, varying its intensity using a chopper. Simultaneously, light from a xenon lamp was fed through a monochrometer and was relected off the same spot. The reflected light from the monochrometer was detected with a photodiode and a lock in amplifier. The lock-in amplifier and voltmeter were used to measure the change in reflectivity DR/R. Using the monochrometer, the energies of the visible light spectrum were varied, and the change in reflectivity was measured. A typical photoreflectance spectra is presented in figure 7.

The first attempt to obtain a signal and spectra was successful, and the reflectivity and plot were all calculated by hand. Later, experiments were performed in the vacuum chamber, and the data was automatically directed to a computer database.

In the future, different samples will be characterized using this method, but must include data from the Auger/LEED analyzer. For the same reason as TPD, the surface composition must be known before any conclusions about photoreflectance data can be drawn.

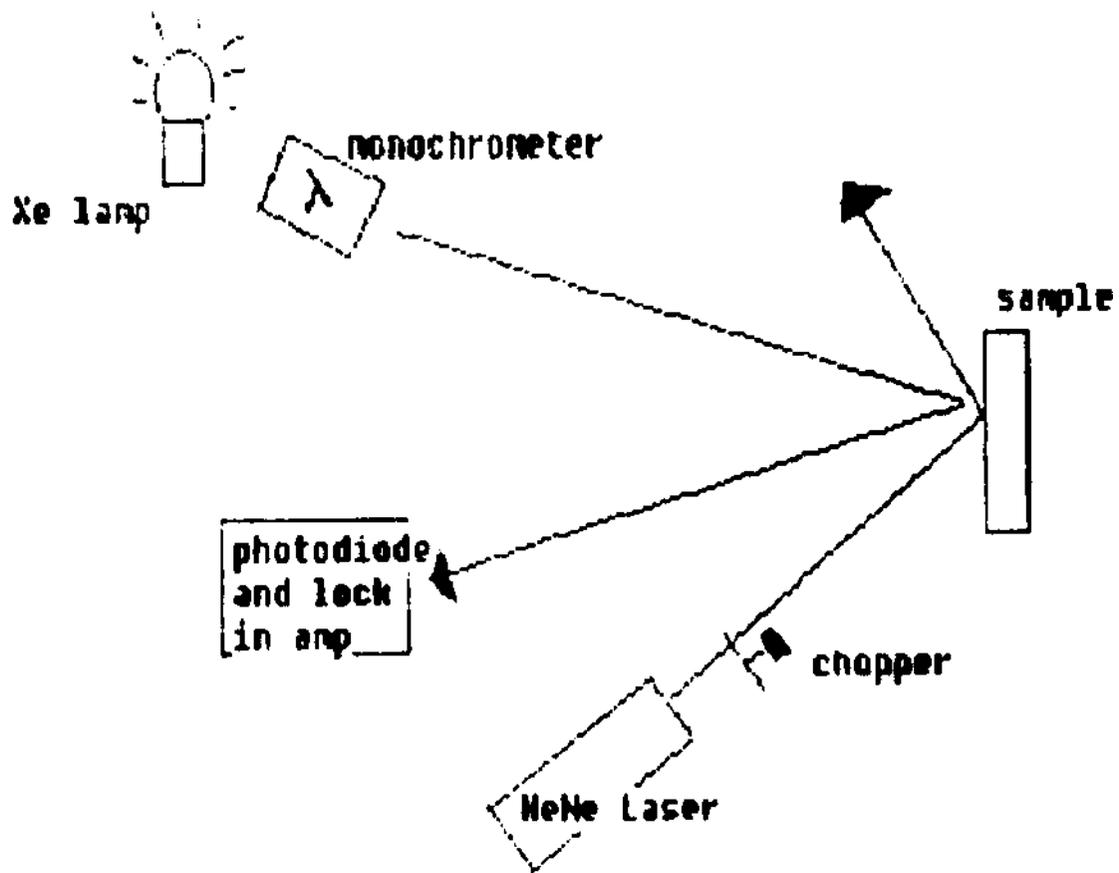A pictorial of the SHG process at the surface is shown in figure 8.
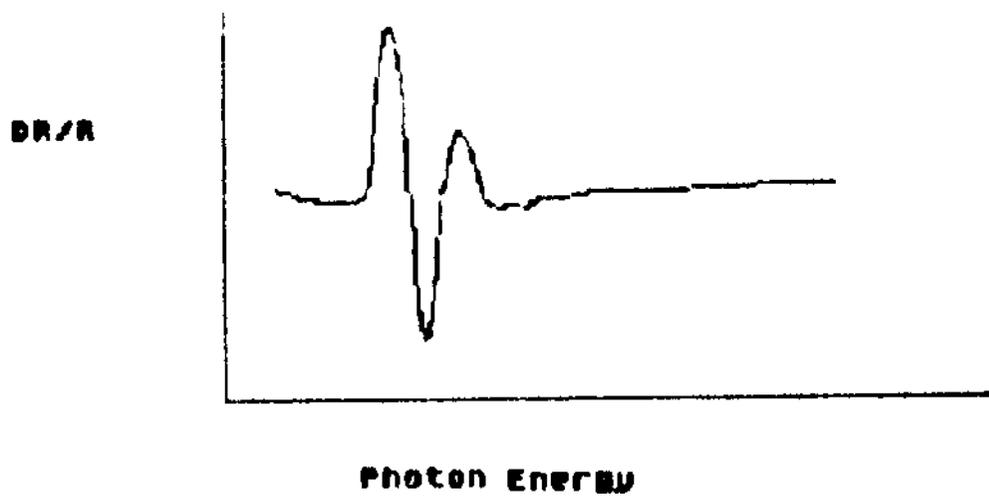
Figure 6: Diagram for photoreflectance

Figure 7: Characteristic photoreflectance spectra

SECOND HARMONIC GENERATION

A third way in which we may charcterize the surface of GaAs substrates is by a technique called second harmonic generation (SHG). By pulsing an intense beam of laser light at a GaAs substrate, the substrate will demonstrate non-linear effects. That is, harmonics, or multiples of the incident light frequency are generated. As the harmonic increases, the intensity of that harmonic decreases. Therefore, the second harmonic would be the most useful in characterizing substrates, because it delivers the strongest signal. Because the second harmonic energy is weak compared to the incident beam energy, a high powered laser is needed. In our case, a YAG 660B-10 laser was used. Manufactured by Quantel, the powerful laser has the undesirable quality of being dangerous. Eye protection should be worn at all times when working with the laser, because even a partially relected beam off of a shiny surface an cause irreparable eye damage.

The laser will eventually be used in conjunction with the large vacuum system. Currently photoreflectance experiments are being done with the chamber, and at this time, the laser is being checked for operability. This includes checking the energy and quality of the laser light in a dust free environment.
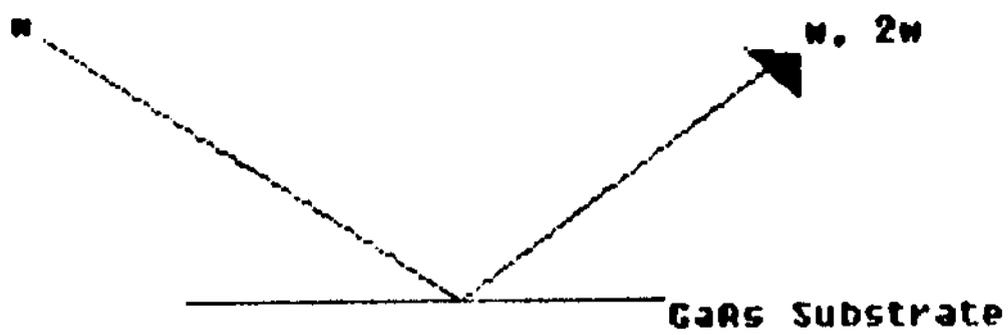
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Figure 8: Second Harmonic Generation

APPENDIX

Suppose for simplicity, the desorption is first order in H, and c = the surface concentration of H on GaAs.

$$-dc/dt = kc = (A\exp(-E_a/RT))c$$

If the temperature is increased linearly from some initial temperature (T = 25 C) so the $T = T_i + Bt$, the temperature T^* at which the desorption flux is at a maximum is:

$$d(-dc/dt)/dt = 0$$

Taking the derivative of the linear temperature function:

$$dT = Bdt$$

and

$$d(-dc/dt)/dT = d(kc)/dT = k(dc/dt)(dt/dT) + c(dk/dT)$$

$$-(A^2/B)c\exp(-2E_a/RT) + (E_ac/RT^2)\exp(-E_a/RT) = 0$$

$$(A/B)\exp(-E_a/RT) = E_a/RT^{*2} \quad [1]$$

A is the pre-exponential factor, and is assumed to be 10^{13} for a first order reaction. B is a linear temperature constant, and is found by using:

$$T = T_i + Bt$$

For T = 300 C, T_i = 25 C and t = 50 sec, B = 5.5 K/s.

With the aid of equation [1] above, by a trial and error solution, E_a = 119 KJ/mole.

ACKNOWLEDGMENTS

I deeply appreciate the guidance given, and patience exhibited by Dr. Seebauer, Dr. Masel, Mr. K. Schulz, and Ms. Theresa Shu.

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