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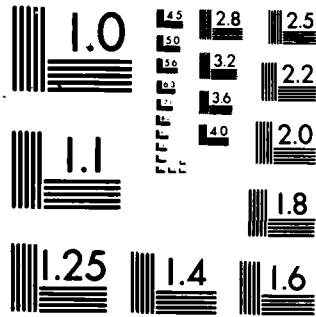
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Laser Driven Processes at GaAs Surfaces

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I. INTRODUCTION

The broad goal of this project was to learn about electronic and vibrational relaxation of molecules interacting with solid surfaces. A specific goal of the project was to use the available energy transfer information to develop photochemical techniques to aid in the processing of GaAs and other III-V semiconductor surfaces. During the period covered by this report we made significant progress toward the broad goal of understanding energy transfer in the general sense. As of this date, however, we have not been able to apply this general knowledge to the specific case of laser chemistry on GaAs.

Because the techniques we explored were not previously discussed in the scientific literature, much of our efforts have been aimed at defining the limits experimental sensitivity to laser induced effects on surfaces. Unfortunately, this process is very time consuming and the results are often disappointing. For instance, one phenomenon that is of great interest is the possibility of infrared laser induced photodesorption of molecules from surfaces. We chose to investigate this phenomenon for the system of CH_3F on GaAs. It turned out that the bond between the molecule and the surface was too strong for single-photon-induced desorption to be effective. These results will be discussed in Section III.

The biggest success of the project has been the demonstration that direct UV photochemistry can be observed for low coverage layers of $\text{Fe}(\text{CO})_5$ physisorbed onto Si(110) and Ag(111) surfaces. This result encourages us to pursue UV photochemistry as a means of producing high resolution images on semiconductor surfaces. Most studies aimed at demonstrating laser deposition of metal films have involved irradiating the metal carbonyl molecules in the gas phase near the surface to be coated. The resolution of the image is then limited by diffusion of the metal atoms before they reach the surface. Clearly, diffusion is much less of a problem if the molecules are already attached to a specific surface site before irradiation. Our experiments on this problem are described in Section IV.

Five technical reports which describe work funded by this contract are already published. Two further publications are in preparation. Although the goals stated in our original proposal turned out to be more ambitious than could be met in a three-year period, we have demonstrated that laser chemistry on molecules on surfaces does have a strong possibility to provide useful routes for low temperature deposition of refractory metal films. I hope to continue this effort in the future using real time pump-probe experiments to understand the mechanism of the metal carbonyl photochemistry. A proposal describing these planned efforts has already been submitted to the ONR.

II. SUMMARY OF PUBLISHED RESULTS

- A. Technical Report #1 "Direct Inelastic Scattering of Ar from Pt(111)"
J. Chem. Phys. 78, 1559 (1983).

This paper describes results which characterize the extent of energy transfer in single collisions of Ar atoms with a close packed platinum surface. It was found that, on average, the energy transfer could be described by energy accommodation relationships even though individual scattering events might appear to be quite different from the average event.

- B. Technical Report #2 "Direct Inelastic and Trapping Desorption Scattering of N₂ and CH₄ from Pt(111)" *Surface Science*, 130, 395 (1983).

This is an extension of the atomic scattering technique to molecular examples. It was surprising that energy transfer between the translational and rotational degree of freedom of the scattered molecule was quite limited. This effect is probably the cause of a low-striking coefficient for N₂ and CH₄ on nonreactive surfaces.

- C. Technical Report #3 "Photodesorption of Weakly Bound Molecules"
Surface Science, 141, 169 (1984).

This paper provides a theoretical basis for the experiments in which we attempted to observe infrared induced photodesorption from solid surfaces. The paper shows that given the correct set of physical parameters it should be possible to observe single photon-induced desorption. As discussed below, we have not yet reached this goal in the laboratory.

- D. Technical Report #4 "Trapping Desorption Scattering of Ar from Pt(111)"
J. Chem. Phys., 83, 1376 (1985).

This paper describes the very exciting result that when Ar atoms are thermally desorbed from a Pt surface, the Ar velocity distribution is not described by a Maxwell-Boltzmann velocity distribution at the surface temperature. This means that the desorption event is fast enough that equilibrium is not maintained in the vibrational degrees of freedom during the energy transfer from the surface to the adatom. These results provide hope that lasers can be used to induce reactions on surface that will be significantly different from the reaction that would be induced by simple heating.

- E. Technical Report #5 "Bakeout Controller for the use of Helium Closed-Cycle Refrigerators in UHV Applications" *J. Vac. Sci. Tech.*, A4, 1939 (1986).

One technological limitation on performing low-temperature experiments on semiconductor samples is that commercial refrigerators are constructed using some materials that cannot be baked out at high temperatures. This paper described a method to solve this problem.

- F. Technical Report #6 "UV Laser Induced Dissociation of $\text{Fe}(\text{CO})_5$ on Single Crystal Surfaces" in preparation.

This paper will give a complete description of the work summarized in Section IV.

- G. Technical Report #7 "I. IR Photodissociation Spectroscopy of Large van der Waals Clusters. II. UV Laser-Induced Photochemistry of $\text{Fe}(\text{CO})_5$ on Single Crystal Surfaces" Ph.D. Thesis, Francis G. Celii, CalTech, 1985.

This thesis presents work that is (or will be) published in the open literature in technical reports #5 and #6.

III. INFRARED PHOTODESORPTION

One goal of this project was to observe single photon induced infrared photodesorption from surfaces. As outlined in Technical Report #3, rate laws for photodesorption and quenching have to be within certain boundaries for this effect to be observed. There are two fundamental difficulties. First the laser intensity has to be kept low enough that the surface does not measurably heat up. Thermal desorption is a commonly studied process and is not a mechanism of interest to us. Second, surfaces are known to be fast quenchers of vibrationally excited molecules so an example of photodesorption must be found for which the photodesorption rate is very fast. Although these two constraints severely limit the range of photodesorption events which might be observed, the rewards of finding an example of the phenomenon make the search worthwhile. If infrared photodesorption can be observed this would give us a tool for direct rate measurements of energy transfer rates that the surface. Although there is extensive theoretical work on this subject, there is very little data available to serve as a guide to the theory.

We first attempted to observe infrared photodissociation for molecules physisorbed onto GaAs surfaces. The motivation for this choice was that once we started to observe infrared induced chemistry, GaAs would be a desirable surface for photochemical modification studies. The problems involved in preparing GaAs surfaces with the desired stoichiometry and surface order are well known. In addition to these problems, we want to be able to cool the surface to 25K in order to physisorb small molecules. The required cooling capability was achieved with imperfect GaAs samples and infrared induced desorption was observed. Since the result was obtained with laser intensities as low as 20 mW/cm^2 , too low to significantly heat the surface, we initially thought that a true photodesorption event was observed. Subsequent experiments showed that the event we observed would be better described as resonant heating of a thin surface film. This conclusion rests on the coverage dependence of the observed signal and the molecule-surface bond energies that were obtained, *vide infra*. So far, a true infrared photodesorption event has yet to be observed, in spite of significant efforts in at least six laboratories in the United States and Europe.

In the course of attempting to observe infrared photodesorption we made approximate measurements of several molecular adsorption energies on GaAs. The method used was temperature programmed desorption. These are given in Table I. These results indicate that GaAs turned out to be a poor choice for observing single photon desorption. The laser we used in these studies is a line tunable CO₂ laser which produces photons at 10 microns. This wavelength corresponds to a photon energy of just under 3 kcal/mol. As shown in Table I, most of the molecules we had chosen to study had bond energies stronger than this photon energy so there was no way that one photon could break the bond. These bond energies are stronger than we expected and probably indicate that the surface is very poor. Unfortunately, there are very few molecules that might be expected to have a weaker bond energy to the surface and still have a vibrational mode that can be excited with the CO₂ laser.

Table I. Approximate Bond Energies of Molecules to GaAs Surfaces

Molecule	Estimated Bond Energy (kcal/mole)	
	Low Coverage	High Coverage
CH ₄	2.5	
CO ₂	3.5	
C ₂ H ₂	3.5	
C ₂ H ₄	3.5	1.2
CH ₃ F	4.0	1.5
H ₂ O		8.4

Since it was found that the CO₂ laser would be ineffective for observing desired event, we tried to use an f-center laser to excite the C-H stretching mode of C₂H₂. This 3000 cm⁻¹ vibration corresponds to 8 kcal/mole, enough energy per photon to overcome the problem encountered in the CO₂ laser experiments. Unfortunately, photodesorption could not be observed in these experiments either, even for the case of multilayer coverage of the C₂H₂ molecules. There are several possible explanations for this failure. 1) Perhaps physisorption of C₂H₂ shifts the infrared transition out of the range of our laser. I consider this possibility to be unlikely. 2) Perhaps the C-H stretching mode couples extremely slowly to the weak bonds that must be broken for desorption to occur. There is evidence in the gas phase that this may be the case. 3) Perhaps a 3000 cm⁻¹ excitation is getting close enough to the bandgap of the GaAs that impurity states would provide a fast quenching mechanism for the excitation.

Although these efforts have not been productive to date, I feel that the phenomenon is important enough that eventually I would like to make another effort to observe it. To solve several of the problems that may have affected the acetylene experiment it would be desirable to first obtain spectroscopic results on the transition frequencies before trying to observe the dynamics. One possible way to do this would be to coadsorb methane and Ne. The f-center laser would be tuned through the methane transitions while a mass spectrometer was set to observe any Neon that evaporates as a result of the deposition of energy into the film. If the Neon evaporation rate can be observed to depend on

the laser frequency, then this method could be used to measure the methane absorption spectrum. Considerable extra effort would be necessary to try this experiment. The mass spectrometer would need to be differentially pumped to be specifically sensitive to Neon desorbing from the surface. The surface would have to be cooled to about 10 K to obtain a stable Ne overlayer. Because of the time involved to make these improvements to the apparatus, we are postponing these studies to a later date.

IV. UV PHOTOCHEMISTRY

Several laboratories have studied the photodeposition of metal films onto semiconductor surfaces by the technique of UV photodissociation of organometallic molecules just above the substrate surface. In order to obtain the maximum possible spacial definition of the film, it might be preferable to irradiate a physisorbed layer of the organometallic molecule instead of a vapor. This would eliminate the step in which a gas phase metal atom diffuses to the surface. There is no information in the literature, however, to suggest whether or not surface photochemistry is competitive with electronic quenching of the laser excitation.

To provide an initial feasibility test for observing surface photochemistry of organometallic compounds, we have studied the photodecomposition of $\text{Fe}(\text{CO})_5$ on Al_2O_3 , Si(111) and Ag(100) surfaces. The $\text{Fe}(\text{CO})_5$ was deposited onto a surface at 100 K and irradiated with the unfocused output of an N_2 laser ($h\nu = 3.7$ eV, $50 \mu\text{J}/\text{cm}^2$ pulses). On all three surfaces, photodecomposition was found to be competitive with electronic quenching with the surface. This conclusion is based on the observation of product CO by a mass spectrometer positioned above the surface. The implication of this result is that even for metal surfaces, which should be the most efficient quenchers of excited states, photochemistry is a viable technique for metal deposition.

$\text{Fe}(\text{CO})_5$ was chosen as the prototype molecule for study because it is known to undergo dissociation on the picosecond time scale in the gas phase. This made the odds very favorable, but not certain, that the dissociation would compete with quenching even on the metal surface. The next step in the project will be to perform the same test for other molecules until we find an example for which quenching dominates dissociation. This will allow us to determine the quenching rate absolutely, something which has not yet been performed for any molecule deposited on a clean, well-characterized surface.

The three-surfaces we studied were chosen to provide a range of expected quenching rates. The sapphire surface would not directly quench electronic excitations at all and serve as a standard for comparison of quantum yield measurements. Silicon serves as an intermediate example for which electronic quenching is quite likely to be favorable since the excitation energy of $\text{Fe}(\text{CO})_5$ is well above the Si bandgap. Si was chosen instead of GaAs for the feasibility experiment because we thought it would be advantageous to start with a well-characterized surface for which there would be no question about the surface morphology. Silver is expected to be the most efficient quencher since classical theories predict a $1/r^3$ dependence of quenching rate on distance from a metal surface to an excited chromophore. Taking the classical results literary would, of course, predict instantaneous quenching as r goes to zero, so it was not obvious that even the dissociation of $\text{Fe}(\text{CO})_5$ would be competitive with

quenching. In fact we found that the quantum yield is only reduced by twenty percent in going from sapphire to silver. This is very exciting both in terms of the technological possibility of using photochemistry for metal deposition and of the scientific possibility of determining the real time quenching rate on a smooth metal or semiconductor surface.

For each surface the study was performed by using UHV surface preparation and characterization techniques to ensure that the observed phenomena were not due to an artifact associated with ill defined surfaces. LEED was used to ensure that the surfaces were flat and well ordered. Temperature programmed desorption was used to ensure that the $\text{Fe}(\text{CO})_5$ undergoes no thermal reactions that could be mistaken for photochemistry. In each case, the molecule was found to desorb at 200 K without undergoing decomposition.

So far, we have been doing low laser power, low surface coverage experiments. This has meant that we never created an observable metal film on the surface. For this purpose the iron on silicon example is probably not favorable as iron has been found to migrate into the silicon solid. Work in the future will involve several different questions. 1) Can we observe a case for which quenching and photochemistry occur at approximately the same rate to allow us to measure branching ratios, infer lifetimes and observe the surface dependence of the dynamics? 2) Can we find a favorable example of film formation for which conventional methods are not favorable? We will investigate the refractory metals (e.g. tungsten, iridium, and rhodium) and less robust surface (e.g. GaAs) to see if the technique is capable of forming interfaces that have not been extensively studied in the past. 3) We will seek to determine in some detail how the surface affects the photochemical dynamics of an adsorbed molecule.

The results of the UV photochemistry studies are currently being prepared for publication.

V. SUMMARY

In this project we have examined a number of examples of photodynamics of molecules on surfaces. Unlike gas phase studies where the observation of fast dynamics is becoming ever more commonplace, surface dynamics studies are difficult and time consuming. To date, no example of single infrared photon induced dynamics on a surface has been observed. Our work has shown the feasibility of observing direct ultraviolet photochemistry on semiconductor and metal surfaces, however, and we are anxious to explore the range of phenomena that can be observed.

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