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ABSTRACT

The objective for this experimental work was to examine the reaction mechanisms, half-collision dynamics, and other optically induced chemical effects, that are operable on a well characterized single-crystal semiconductor surface. Of particular interest were reactions induced by charge transfer from the semiconductor surface including hot carrier and thermalized carrier processes. The primary technique to measure the desorbed fragment translational energies was time-of-flight mass-spectroscopy, used in conjunction with a pulsed tunable laser source. The work was carried out in ultrahigh vacuum, thus other surface spectroscopies such as temperature-programmed desorption, (TPD), (LEED), etc. were used as needed.

In the project, the photoreactions of several halogen-containing molecules on GaAs(110) surfaces have been investigated. The studies have made the first observations of several new photochemical processes on UHV prepared surfaces including intermolecular charge transfer; desorption by thermal-carrier-induced reactions (including the measurement of coverage-dependent changes in the translational energies of the desorbed products); interferometric oscillation of photoinduced reactions; and self-quenching of thermal carrier reactions on surfaces.

Papers Published Under DOE Sponsorship^{1*}

1. Z. Lu, M.T. Schmidt, D.V. Podlesnik, C.F. Yu and R.M. Osgood Jr., "Ultraviolet-Light-Induced Oxide Formation on GaAs Surfaces," J. Chem. Phys. 93, 7951 (1990).
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9. W.N. Schwarz, Q.Y. Yang, and R.M. Osgood, Jr., (invited), "Surface Photochemistry on GaAs(110)," paper to be published in LAMP'92 Proceedings, Niigata, Nagaoka, Japan, (June 7-12, 1992).
10. Q.Y. Yang, W.N. Schwarz and R.M. Osgood, Jr., "Thermal-Carrier Mediated Dissociative Electron Attachment of Admolecules on GaAs(110)," submitted to Phys. Rev. Lett. (1992).

Papers in Final Stages of Preparation

1. Q.Y. Yang, W.N. Schwarz and R.M. Osgood, Jr., "Self-Quenching of CH₃Br on GaAs(110) Induced by Thermalized Photogenerated Carriers," to be submitted to J. Chem. Phys. by July, 1992.

^{1*} Abstracts and extended abstracts are listed on the following two pages.

**Professional Talks on Research
Sponsored by DOE**

1. IBM, East Fishkill, NY, March 6, 1990
"Studies of Light Induced Surface Chemistry on Semiconductors," R.M. Osgood, Jr.
2. MATERIALS RESEARCH SOCIETY SYMPOSIUM, Boston, MA, November 26-
December 1, 1990, Surface Chemistry and Beam-Solid Interactions,
"Laser Induced Interaction of Cl_2 with GaAs(110)," Vladimir Liberman
3. MICROPHYSICS OF SURFACES CONFERENCE, Sante Fe, NM, February 11, 1991
"UV Laser-induced Interaction of Cl_2 with GaAs(110)," Gaddi Haase
4. GORDON RESEARCH CONFERENCE, Andover, NH, August 5-9, 1991
Dynamics of Gas-Surface Interactions,
"Effect of Optical Interference on Photodissociation of Methyl Bromide on GaAs(110) by
Standing Waves," Qingyun Yang
5. AMERICAN VACUUM SOCIETY, Seattle, WA, November 11-15, 1991
"The Dynamics of Photodissociation of Methyl Bromide on GaAs(110)," Qingyun Yang
6. MATERIALS RESEARCH SOCIETY SYMPOSIUM, Boston, MA, December 2 - 6, 1991
Photons and Low Energy Particles in Surface Processing,
"Ultraviolet Laser-Induced Reaction of CCl_4 with GaAs (110)," Richard M. Osgood, Jr.
7. MATERIALS RESEARCH SOCIETY SYMPOSIUM, Boston, MA, December 2 - 6, 1991
Photons and Low Energy Particles in Surface Processing,
"Laser Photodissociation of CH_3Br on GaAs(110)," Wolfgang Schwarz
8. 5th INT'L. WORKSHOP ON DESORPTION INDUCED ELECTRONIC TRANSITIONS,
Taos, New Mexico, April 1-4, 1992
"A Dynamical Study of Photodissociation of CH_3Br on GaAs(110)," Qingyun Yang
(extended abstract)
9. AMERICAN CHEMICAL SOCIETY, San Francisco, CA, April 5-10, 1992
Surface Photochemistry Symposium Program,
"Photoinduced Reactions of Electronegative Molecules on GaAs(110) Surfaces,"
Richard M. Osgood, Jr. (invited)
10. LASER ADVANCED MATERIALS PROCESSING CONFERENCE, Nagaoka, Niigata,
Japan, June 7-12, 1992,
"Surface Photochemistry on GaAs(110)," Richard M. Osgood, Jr. (invited)

11. 52nd PHYSICAL ELECTRONICS CONFERENCE, University of California at Irvine, June 22-24, 1992
"Self-Quenching of Thermalized-Carrier-Induced Surface Chemistry on a Semiconductor Surface," Qingyun Yang (extended abstract)
12. AMERICAN VACUUM SOCIETY, Chicago, IL, November, 1992
"Self-Quenching of Thermalized-Carrier-Induced Surface Chemistry on GaAs(110)," Qingyun Yang (extended abstract)
13. AMERICAN CHEMICAL SOCIETY, Washington, DC, August 23-28, 1992
Surface Chemistry from Reaction Dynamics through Materials Growth
"Adsorbate Photochemistry on Semiconductor Surfaces: from Submonolayer to Submicrometer Films," Richard M. Osgood, Jr. (invited)

Introduction

The research on this DOE program has been focused on understanding the fundamental physics of adsorbate photochemistry on semiconductor surfaces and, in particular, on determining the role of charge-carriers in the first stages of these photoreactions. The research can thus be viewed in the same context as earlier studies on gas-phase photochemistry, or, from another viewpoint, as photon-stimulated desorption at low photon energies.

The specific thrust of our current DOE program has been to use time-of-flight spectroscopy (in concert with other more conventional surface tools) to obtain a molecular-level understanding of the dynamics and mechanisms of surface photodissociation on semiconductor surfaces. Such time-of-flight techniques have also been used, for example, by Cowin and co-workers^{1,2} to study photodissociation on metal surfaces.

Halogenated molecules on single-crystal GaAs make a useful, initial family of adsorbate systems for studying the effects of charge carriers on photoreactions. Since carrier densities are known to be important in the adsorption of electronegative molecules on semiconductors, and since many halogenated molecules are strongly electronegative species, the chemisorption of this class of molecules on surfaces is expected to be dependent on the presence of carriers.³ For example, it has been shown that the abstraction of electrons from the bulk during chlorine adsorption on GaAs leads to bending of the bands at the surface;^{3,4} that is, during adsorption a dipole layer is formed, which in turn sets up an electric field in the bulk to retard further charge flow to the surface. In addition, at the start of this program, there had been prior work in our laboratory indicating that both thermalized^{5,6} and hot carriers⁶ were important in oxide growth during UV illumination on a GaAs surface.

Design and Fabrication of Time-of-Flight Instrumentation

In the present program, we first devoted considerable time to the design and construction of two custom-designed ultrahigh vacuum (UHV) systems for studying the effect of UV and visible light on the interaction of halogen-containing molecules with GaAs samples; a sketch of the second of these instruments is given in Fig. 1.

With these two systems, we have investigated the photochemistry of three adsorbate systems: CCl_4 ,⁷ CH_3Br ⁸ and Cl_2 ⁹ adsorbed on bare GaAs (110) under UHV conditions. As a result of these experimental studies, we have made the first observations of several new surface phenomena. These are listed in Table 1.

Each of our two UHV machines has a time-of-flight system as its central tool for studying photofragmentation, which is used after irradiation of the surface with a line tunable excimer or a continuously tunable dye-laser pulse. The first of these instruments has excellent time resolution for resolving flight times, and is the somewhat simpler design of the two; we were able to use it for our initial work to achieve a good overall view of the key chemical mechanism and optical physics. The second was of much more complex design which, in addition to TOF capability, had provision for *in situ* optical fluorescence from the semiconductor substrate, using both cw visible and ultraviolet laser excitation, as well as for infrared total internal reflection spectroscopy of the GaAs sample surface. Both the TOF energy resolution and the sensitivity of the second apparatus were excellent.

In contrast to metal surfaces the sample preparation required for reproducible surface chemistry, a semiconductor sample such as GaAs, places very difficult design criteria on the manipulator (shown also in Fig. 1) and the crystal preparation techniques are very tedious to

TABLE 1
Accomplishments in our Current DOE Program

- Construction and operation of two time-of-flight systems for studying semiconductor surface photochemistry
- First observations of intra-adsorbate charge transfer for surface-phase photochemistry
ex: $\text{Cl}_2 + \text{Cl}_2 + h\nu \rightarrow \text{Cl}_2^- + \text{Cl}_2^+ \rightarrow \text{Cl} + \text{Cl}_2^+ + \text{Cl}^-$
- First observation of interference effects on surface photodissociation and discussion of its use for the determination of the molecular structure of physisorbed films
- First observation on a semiconductor surface of surface dissociation by dissociative electron attachment, and its energetics using UV excitation,
ex: $e_{\text{thermal}} + \text{CH}_3\text{Br} \rightarrow \text{CH}_3\text{Br}^- \rightarrow \text{CH}_3 + \text{Br}^-$
- First observation of self-quenched, carrier-mediated, photochemical reactions on semiconductor surfaces.

Upper Chamber For Measurements

Schematic sketch of the upper UHV chamber used for TOF and TPD data acquisition.

Lower Chamber For Sample Preparation

Schematic sketch of the lower UHV chamber used for sample preparation.

Sample manipulator.

Figure 1: Two level (two chamber) UHV system with coolable/heatable sample manipulator; this was the second UHV chamber built on this DOE program.

develop. The (110) surface (see Fig. 2) was selected for this study because it can be reproducibly formed in a stoichiometric, fully reconstructed form; in contrast, for example, reconstruction on GaAs(100) is extraordinarily complex and irreproducible.

In the current program we have focused exclusively on physisorbed molecular systems. This was a useful initial approach because the direct photochemistry of weakly bound molecules should to some extent be analogous to that of the free molecule. In particular, for physisorbed molecules we expect the electronic structure of an isolated ad molecule to be only slightly perturbed.^{2*,10} For this case, the chief effects of the surface are to open up new excitation channels and to alter the dynamics of the departing fragments. Further, for physisorbed systems the properties of the initial surface are well known and characterized since the surface bonding is not disrupted during the formation of the adlayer.

Photochemistry of Physisorbed CCl_2 on GaAs(110): Intermolecular Charge Transfer

For our first study, we selected Cl_2 ,⁹ since as mentioned earlier, it is known to dissociatively chemisorb by capture of a bulk electron. In its free molecular form Cl_2 can be directly dissociated over a broad range of ultraviolet wavelengths to yield ground state or spin-orbit excited Cl atoms.¹¹ In study, we investigated physisorbed- Cl_2 on GaAs(110) at 85 K. Despite this low-temperature, a slow thermal reaction resulted in the formation of ~ 0.8 ML of chemisorbed Cl on Ga sites during the dosing process. Surface chlorination was determined

^{2*} Note, however, as will be shown below, for Cl_2 , at high coverage, important changes in the excited state structure even occur for physisorbed molecules.

For (110), Stable (1x1)
Reconstruction to $\sim 700^\circ\text{K}$

For(100), As-Dependent
Reconstruction

(Side View)

Figure 2:

We have used the GaAs(110) surface throughout in this project because it has a robust, (1x1) reconstructed surface which can be readily prepared using sputter-annealing. Our *in situ* photoluminescence work, mentioned later, helped us further optimize the preparation. In contrast, for example, the technologically important (100) surface has a complex, unstable surface which could not be used in or experimental setup.

by temperature programmed desorption (TPD).^{3*} Irradiation at 193, 248, and 351 nm of physisorbed Cl₂ molecules on this partially chlorinated surface led to the desorption of ~ 0.1 - 0.2 eV Cl atoms as well as to further surface chlorination. Since the ratio of the cross section for photofragmentation at 193 nm versus 248 nm was markedly different from that of the free chlorine molecule and since other studies have indicated that the free molecule spectra is not strongly perturbed for physisorbed systems, we could conclude that direct photodissociation is an unlikely source of band cleavage in this case. A second possible route to dissociation is photoemission of electrons from the GaAs followed by some form of electron-mediated dissociation. This hot-electron process has been reported by Cowin et al.,¹² White et al.,¹² the group at NIST,¹² etc., as well as for our work on O₂ photoreactions on GaAs.⁶ However, since the Cl atoms' time-of-flight distributions as desorbed from GaAs and other transparent substrates, such as Al₂O₃ and quartz were virtually identical, we concluded that the photoinduced reactions were not initiated by surface photoemission. Instead, we concluded that for the case of Cl₂, intra-adsorbate charge transfer between adjacent Cl₂ molecules gives Cl₂⁻, which then dissociated by dissociative electron attachment,

The wavelength dependence of the first step in this process, i.e. intermolecular charge transfer, has been measured in the form of the adsorption spectrum of condensed Cl₂ by Cousins and Leone.¹³ Their spectra match our measured wavelength reaction rate for Cl₂ on GaAs very closely.

^{3*} Note that TPD can indicate chlorination of surfaces unambiguously; however, its use does not provide unambiguous identification of specific surface-adsorbed reaction products.

Our experiments provide the first observations which show that intermolecular charge transfer followed by dissociation is an important surface photochemical mechanism at mid-UV wavelengths in surfaceadsorbed molecules.

Finally, we note that for this system the reaction of the surface with Cl_2 , even at the 85°K temperature used in our experiment, apparently prevented observation of substrate-mediated carrier reactions. Thus, irradiation of the surface with longer wavelength visible light (photon energy $> E_g$), that is, light whose only possible chemical effect would be to create electron hole pairs, did not cause further chlorination of the surface.

Photochemistry of CCl_4 on GaAs(110): Photogenerated Carrier Chemistry Plus Direct Dissociation

In our second system we used CCl_4 ,⁷ which, in contrast to chlorine, does not thermally react with GaAs(110). In this case, charge-transfer photochemistry was observed. We found using lamp illumination with various filters, that surface photochemistry in the first monolayer, and specifically chlorination could readily be promoted by illuminating the GaAs crystal with above-bandgap radiation. The wavelength dependence of this chlorination process, shown in Fig. 3, made it clear that the reaction was driven by transfer of carriers from the crystal to the surface adsorbate. In this case, the reaction was undoubtedly a result of the dissociative attachment of an electron onto CCl_4 yielding

Again, surface chlorination was detected by TPD of the chemisorbed product, GaCl. For coverages $< 1\text{ML}$, it was not possible to detect either of what, we believe are, the nascent products by Cl^- and CCl_3 by TOF, probably because the one ejected product, CCl_3 , has too low

Using Calibration Curve of GaCl v.s. Photons (obtained from XeCl Irradiation)

Find $N_{645}:N_{715}:N_{850} = 7.3:4:1$

Figure 3: Surface chlorination rate as obtained by lamp illumination of CCl_4 on GaAs, using lamps with various cutoff filters. The rate measure by TPD of GaCl.

a KE to be sensitively detected in our system and the Cl⁻ remained chemisorbed on the surface.

For $\theta > 1\text{ML}$, the use of TOF techniques with the same adsorbate system showed that direct photodecomposition, similar to that seen in gas-phase molecules, did occur for 193 nm illumination, yielding Cl as the desorbed fragment. This direct fragmentation reaction appeared to overwhelm, in terms of total yield, any reaction based on "hot" electron emission into the adlayer, since the fragmentation pattern followed the gas-phase wavelength-dependent absorption curve and appeared only at 193 nm. The direct process is strongly quenched at low coverage on GaAs apparently due to energy transfer to excitation of valence-band electrons of the substrate.¹⁴ For a sapphire substrate, the much larger band gap eliminates this quenching mechanism and direct photochemistry is seen even at $\theta < 1\text{ML}$, by the desorption of atomic Cl. In addition, at higher coverage, the other product of the dissociation, CCl₃, becomes manifest through the formation of the dimer C₂Cl₆,

This secondary product is detected by post-irradiation TPD of the physisorbed film. Note that as shown in Fig. 4, the amount of C₂Cl₆ formed saturates for CCl₄ coverages greater than 3-4 ML. This result is attributable to the fact that the recombination reaction

is more important deep in the film where Cl desorption does not occur.

A Model System for Surface Photochemistry CH₃Br on GaAs(110)

More recently, we have begun a careful time-of-flight study of carrier-mediated chemistry using the model system of CH₃Br on GaAs(110) with our more sensitive TOF system.^{8,15,16}

Figure 4: Time-integrated mass-164 ($C_2Cl_4^+$) TPD spectra obtained after irradiation of CCl_4 -covered GaAs(110) surface with 600 pulses of 0.15 mJ/cm^2 193nm radiation, as a function of CCl_4 coverage.

We selected this molecule because its direct photochemistry and dissociative electron attachment process have been carefully studied in the gas phase. Further, its methyl ligand is ejected with energies much greater than the thermal energy, thus giving a clear TOF signature in our system. *Our interest in this experiment was to use a well known model system to obtain a clear and precise understanding of surface photochemistry. Our results have, in fact, uncovered several major new phenomena, which although not previously observed are key to understanding photochemistry on UHV surfaces.*

A. Interferometric Surface Photochemistry: A New Method for Determining the Properties of Adsorbate Layers

Our initial experiments examined the photochemistry with multilayer coverage. This experiment enabled us first to examine carefully the translational energies of the methyl fragment, as formed by direct dissociation in the top 1-2 layers of the adsorbed layer, and to show that these values corresponded quite accurately with gas-phase values, if allowance for internal vibrational excitation and fragment surface collisions was taken into account. In addition, this experiment enabled us to make the first observation of the influence of the optical interference of standing UV waves on the surface photodissociation process, a process which is observed by mass detecting the yield of the desorbed fragment, CH_3 , as a function of the adlayer thickness.¹⁵ As shown in Fig. 5, oscillation or "fringes" are seen in the desorbed CH_3 as CH_3Br coverage is increased. This observation is interesting, not only because it represents a previously unreported optical phenomena which must be considered in interpreting surface photochemistry, but, more important, because it can be used as a new technique for measuring the optical properties and the structure of adsorbed layers. In particular, using this technique

the adlayer optical properties can first be obtained by fitting the observed fringes, which are observed using s-polarized UV light, with a theoretical model of wave propagation in the layered medium: vacuum, adlayer, and GaAs (see solid curve in Fig. 4). Note that in order to develop this model it is necessary to treat the boundary conditions for the optical field as it crosses from outside to inside the outermost molecular monolayer and to consider fragments originating only from this outermost layer. If, on the other hand, p-polarized light is used, it is possible to determine the structure, i.e. the molecular orientation, of the film, since, in this case, both the amplitude and the direction of the optical electric field vary with film thickness; Fig. 6a shows the data for p-polarized radiation. Our fitted results for the structure are in agreement with that measured by Kawaguchi using x-ray techniques, see Fig. 6b.¹⁷

B. TOF Studies of Dissociative Electron Attachment (DEA) and Self-Quenched Surface Reactions

Our findings, using this same model system for $\theta < 1\text{ML}$, have also given us insight into the importance and energetics of dissociative electron attachment as a surface photochemical mechanism. In particular, by paying particular attention to the initial photochemistry on a carefully prepared (1x1) GaAs(110) substrate, we have unequivocally shown that thermalized photogenerated carriers and photoemitted electrons do indeed play an important role in dissociating the first 1-3ML of adsorbed molecules. In contrast, photochemistry by direct photodissociation does not occur below 1ML because of quenching of adsorbate electronic excitation by substrate electrons prior to fragment separation, a process recently described by Cowin et al.¹⁴ Concerning the process based on transfer of thermalized electrons, this process provides the exclusive pathway to molecular dissociation for molecules in the first monolayer

Interference Pattern; S-Polarization

Figure 5: TOF signature of desorbed CH₃, formed direct photodissociation of CH₃Br on GaAs(110), versus the thickness of the CH₃Br adlayer (calibrated in L) Top: 193nm, Bottom: 248nm.

on a clean reconstructed surface. Once electrons are transferred, both the wavelength dependence of the reaction rate and the invariance of the fragment energy with wavelength show that bond-cleavage proceeds by dissociative electron attachment (DEA) of thermal electrons. These effects are shown in Fig. 7, which show the CH_3 TOF signature versus velocity for several visible and UV irradiation wavelengths, and the total yield versus wavelength, respectively. As indicated in Fig. 8, which shows schematic PES's for CH_3Br , both gas and adsorbed-phase, the energetics of this process are influenced by both solvation and image potential effects. Since both affect the position of the ionic PES.^{18,19} Thus, as shown in Fig. 6, we find experimentally that the translational energy of the CH_3 fragment changes with CH_3Br coverage going from 0.6 eV at 1ML to 0.25 eV at 2ML.

Finally, in the course of studying the photoreaction of CH_3Br in the first adsorbed layer, we observed that the reaction would terminate after a very limited amount (< 0.05 ML) dissociated fragments formed on the clean GaAs surface,¹⁶ see Fig. 9. We have recently used *in situ* photoluminescence to observe directly the carrier lifetime before and during exposure to surface reactions. In this technique, infrared light from the recombination of photogenerated carriers is used to probe the instantaneous non-equilibrium density as well as the carrier lifetime. Our results show that, in this case, the chemisorbed Br forms surface states in the gap which reduce the carrier lifetime.²⁰ Since carriers at the surface may branch into either of two processes, transfer to the adsorbate or carrier loss by recombination, increasing the recombination rate reduces the reaction efficiency. Our results provide the first observation of the phenomena of self-quenching of a carrier-mediated surface photochemical reaction. Self quenching is expected to be quite general in semiconductor surface photochemistry, since many

Figure 7(a): TOF intensity of CH₃ vs velocity of 1ML of CH₃Br on GaAs, at multiple irradiation wavelengths.

Figure 7(b): Integrated yield of CH₃ vs illumination wavelength from data such as shown in Fig. 7(a).

Figure 8: Schematic neutral and ion curves for CH_3Br in the gas phase (solid) and on a metal surface (dotted).

Figure 9: Yield vs velocity curve for CH_3 , desorbed by DEA and showing limited exposure for which the thermal electron DEA process occurs. The wavelength is 193nm and $\theta = 1\text{ML}$.

other important chemisorbed species, e.g. O, which are products of surface bond cleavage, are known to form gap states. Note, for example, that our results explain an earlier observation that the rate of dissociation in the CCl₄ system changes drastically with irradiation time. n the CCl₄ system changes drastically with irradiation time.

Coordination with Other DOE Efforts

In the course of work we have spent considerable time interacting with other groups active in DOE-related research. In particular, we have benefitted greatly both in an intellectual and material sense by interactions with Professors Flynn, Bersohn, and Turro at Columbia. Bersohn and Flynn have loaned the dye laser and quadropole mass spectrometer used in our second TOF setup. All three have made important contributions to our discussions of the new effects seen in our experiments.

In addition, Jim Cowin and John LaFemina at Battelle Northwest were very helpful to our project in terms of the physics and instrumentation of our TOF system and in terms of discussing tight-binding-calculations on GaAs, respectively. In addition, I have had semiannual discussions with the Chemical and Laser Sciences Division at LANL on their programs. Finally, we have arranged seminars with Mike White (Texas) and Dwayne Miller (Rochester) at Columbia to hear of their related programs in surface photochemical reaction and energy transfer, respectively, and an earlier visit to Nate Lewis' lab was useful in helping orient us as to his work in determining transfer rates in liquid photoelectrochemical systems.

Conclusion

In this report we have summarized our research on understanding the operable photochemical mechanisms for physisorbed halogenated molecules on UHV prepared semiconductor surfaces. Our work shows that at high coverage, "gas-phase-" like direct photodissociation does occur, albeit with the half-collision dynamics altered by the substrate surface. This direct photodissociation process is also modified by the liquid-like density of the adsorbate (through intermolecular charge transfer) and by modification of the optical field due to interference within the adsorbed film. This latter effect may be used to obtain structural information on the film. For low coverage, $\Theta < 1\text{ML}$, direct photochemistry is quenched, but DEA by transfer of thermalized photogenerated electrons into the adlayer is important in bond cleavage. This process may be self-quenched by increased recombination of the electron hole pairs on sites containing chemisorbed product atoms. Each of the above two experiments were carried out on two new TOF systems built during the first year of the program.

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