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PHOTOGENERATED CARRIER-INDUCED
REACTION ON SEMICONDUCTOR SURFACES

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Photogenerated Carrier-Induced Reaction on Semiconductor Surfaces

Abstract

We have begun studying the effect of illumination on the chemical interaction of molecular chlorine with a well-defined GaAs(110) surface under ultra-high vacuum (UHV) conditions. We have found that chlorine adsorbs dissociatively at temperatures as low as 85 K. Illumination of molecular chlorine-covered surface at 85 K with 193-nm radiation led to desorption of Cl-atoms accompanied by Cl₂ molecules, as well as formation of AsCl₂/AsCl₃, which desorbed at 180 K. Illumination with 351-nm excimer-laser radiation caused exclusively Cl-atoms ejection, at a lower rate. It also resulted in smaller amounts of arsenic chloride formed on the surface. No new species were observed when the surface was irradiated with a 535-nm laser. We suggest that the surface reaction is initiated by dissociation of adsorbed molecular chlorine, which we believe, is mediated by photoemission of electrons from the substrate upon 193-nm irradiation. Finally, we have nearly completed the construction of a second UHV system for the study of laser-induced dissociation of metal alkyls on GaAs surfaces. This system will incorporate total-internal-reflection Fourier-transform IR spectroscopy to follow reaction intermediates, a time of flight mass spectrometer, low electron energy diffraction and Auger electron spectroscopy.

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Introduction

Most of the first year has been devoted to the construction of an experimental ultrahigh vacuum (UHV) system for studying the effect of UV and visible light on the chlorine interaction with GaAs(110) sample. The combination of low cryogenic temperatures and a corrosive gas made the apparatus construction and operation particularly difficult. Despite this, we have been able to obtain results which can be correlated with a closely related system of O₂ on GaAs, previously studied by us. In addition, we have nearly completed construction of a second UHV system which will be devoted to studying effects of light on metal alkyls adsorbed on GaAs.

Interaction of Cl₂ with GaAs(110) with and without laser irradiation

We have studied an interaction of a well-defined GaAs surface with Cl₂ both in the dark and under laser irradiation. We have chosen this system as a model for an investigation of effects of photogenerated carriers on semiconductor surface reactions. Since photocarrier effects have been observed during reactions of GaAs surfaces with O₂ [1,2] and since Cl₂ is a strong electronegative species, adsorption of Cl₂ on the surface is expected to be dependent on the presence of carriers. For example, it has been shown that chlorine adsorption on GaAs indeed leads to similar band bending effect close to the surface [3].

Most of the first year has been dedicated to completely rebuilding the existing equipment. This experimental system consists of an ultrahigh vacuum (UHV) chamber with a base pressure of 2×10^{-10}

Torr, equipped with low energy electron diffraction (LEED) and an Auger electron spectrometer (AES). A differentially pumped ($P < 1 \times 10^{-10}$ Torr) quadrupole mass spectrometer (QMS) serves to obtain temperature-programmed desorption (TPD) spectra and to measure time-of-flight (TOF) distributions of molecules leaving the surface upon illumination with an excimer laser pulse.

Experiments were performed on semi-insulating and *n*-type ($2 \times 10^{17} \text{ cm}^{-3}$) GaAs(110) samples. Samples were mounted on a liquid nitrogen-cooled / radiatively-heatable rotatable sample manipulator. This setup allows the temperatures to be controlled from 80 K and up, with an accuracy of 1° in the 80 - 200 K region.

We have chosen to work with the (110) surface of GaAs because of its stability and ease of preparation. Surface reconstruction is minimal and independent of temperature and the relaxed surface contains both Ga and As atoms [4].

Before loading into the vacuum chamber, we degreased the sample and then rinsed it with $\text{NH}_4\text{OH}(30\%):\text{H}_2\text{O}::1:1$ to remove any native oxide. Further cleaning was achieved by Ar^+ ion sputtering followed by annealing at 850 K. For *n*-type samples, the above procedure yielded a sharp (1x1) LEED pattern with a dark background. We could not obtain a LEED pattern for semi-insulating samples due to charging effects. Therefore, although we observed the same phenomena on both sample types, we concentrated on *n*-type GaAs.

The sample was dosed at a temperature of 85 K with chlorine gas from a multichannel capillary array glass doser. The dosage was clearly proportional to exposure time, although absolute magnitudes could not be calibrated. All TPD experiments ended at a temperature

of 850 K. After a chlorine exposure - TPD cycle, a sharp (1x1) LEED pattern with no background was observed and no traces of chlorine on the sample could be detected with AES.

The laser experiments were done using an ArF (193 nm) and XeF (351 nm) excimer laser or visible excimer-pumped dye laser with fluences in the range of 0.5 - 5 mJ/cm². The laser beam was at a normal incidence when irradiating the surface prior to TPD experiments and at 43° to the surface normal for TOF experiments. The short laser pulse (~20 ns) made TOF measurements possible.

Many difficulties were encountered due to corrosive nature of chlorine gas. Leaks evolving from etching of cold metal parts, on which chlorine condensed, led to several unplanned delays. Nevertheless, we have already begun to collect data. The following results start to elucidate the nature of light-induced reaction of Cl₂ on GaAs(110) surface.

Thermal reactions

In the first series of experiments a GaAs(110) surface at 85 K was exposed to varying dosages of chlorine and TPD spectra were recorded. Following low exposures, a TPD peak at a temperature of 650 K was detected at the GaCl mass (104 amu). The GaCl uptake, based on the area underneath this peak, rose with increasing dosage and saturated at a relatively low exposure (~30 s). In addition, As₄ and As₂ (or doubly ionized As₄) were seen desorbing from the surface at temperatures above 700 K. These arsenic signals were not observed without exposing a sample to chlorine.

A molecular chlorine (mass 70 amu) TPD peak appeared after ~30 s dosing time. The exact value was somewhat sample dependent, corresponding approximately to the dosing time required to achieve the saturation of the GaCl uptake. Initially, the molecular chlorine desorption peaked at 125 K. The origin of this peak may be either from molecules adsorbed by surface defects or chemisorbed chlorine sites. Further exposure to chlorine resulted in a rapid growth of a second molecular chlorine peak. Its center temperature shifted with increasing coverage from 105 K to 93 K. We attribute this shift to a reduction in the molecule-to-surface binding energy, possibly due to repulsion between adsorbed molecules. After 55 ± 5 s dosing, the peak shifted back to 98 K. We define one monolayer (ML) as the coverage achieved after 55 ± 5 s dosing, corresponding to the first step on the uptake curve as a function of dosage and the shift of the desorption peak to 98 K. This shift may be a result of some reorientation of molecules on the surface upon completion of the first monolayer. Successive layers desorbed at the same temperature.

Note that at all coverages, the LEED measurements showed a (1x1) pattern on a diffuse background, the intensity of which increased with increasing exposure. Care was taken to reduce the electron beam exposure, to minimize stimulation of surface reactions and desorption.

The presence of GaCl TPD peak after a low chlorine dosage at 85 K, before any molecular chlorine adsorption has taken place, indicates that dissociative chemisorption occurs at this low temperature. This observation suggests a very low activation energy for chlorine

dissociation and formation of a bond to the substrate, similar to other cases of charge transfer reactions.

Margaritondo [5] and Schnell [6] presented evidence for chlorine adsorption on arsenic sites of the (110) surface. These results indicate that GaCl, which is the only chlorine containing species that we observe (besides Cl₂), must be formed by rearrangement of the surface chlorine prior to desorption.

Laser-induced reactions

In the following experiments, a sample at 85 K, covered with several chlorine layers, was illuminated with a UV excimer laser. TPD spectra, run after the illumination, revealed formation of AsCl₂ and AsCl₃ species which desorbed at 180 K. At the fluences used, 1-1.5 mJ/cm², the transient temperature rise, based on the temperature-dependent material properties of bulk GaAs, was calculated not to exceed 7°C. Our most unexpected observation was that significantly higher rate of arsenic chloride formation was measured after 193 nm irradiation than after 351 nm.

In addition to the TPD spectra, we also obtained TOF distributions of species desorbing from an 85 K *n*-GaAs(110) sample following exposure to chlorine. Laser fluences of <1.1 mJ/cm² were used to eliminate a possibility of thermal desorption of chlorine. Only chlorine molecules and atoms were seen leaving the surface upon irradiation with the 193 nm excimer laser (1 mJ/cm²) at this sample temperature. The Cl atom to Cl₂ molecule signal ratio was >3, although the velocity distributions of the two species (after proper correction for the residence time in the mass spectrometer and the dissociation in the

ionizer) were comparable. The velocity distributions were fitted to a peak temperature of ≈ 180 K with a stream energy of ≈ 0.04 eV. On the other hand, irradiation with 351-nm laser pulses resulted in more than an order of magnitude smaller mass 35 signal, and produced no mass 70 signal at all. Cl atoms were observed leaving the surface with a velocity distribution similar to the species desorbed by 193-nm radiation.

It is possible to rule out several mechanisms for the laser-induced surface reaction based on additional experiments. First, irradiation of the chlorine covered surface with visible dye laser light ($\lambda = 535$ nm) produced no new species on the surface in the fluence range of 6 to 80 mJ/cm², regardless of molecular chlorine coverages. Moreover, no species were detected leaving the surface in the TOF measurements. Since the photon energy used was 0.9 eV above the GaAs direct band gap energy, these results exclude the possibility of reactions induced by thermal electron-hole pairs. Second, the calculated temperature rise in the UV laser experiments was low enough to assure that no thermal reaction had taken place. The very different behavior seen at 351 nm and 193 nm, despite the similar temperature rise induced by the two wavelengths for the same laser fluences, also suggests an absence of a thermal process.

Two important candidates for alternative mechanisms would include reactions initiated by direct photon absorption of adsorbed molecular chlorine or reactions mediated by hot carriers [1,7]. Notice that one could expect both mechanisms to be initiated by reactions with atomic chlorine. Evidence for a formation of arsenic chlorides from atomic chlorine is observed by Freedman *et al* [8]. Thus, a

mechanism that includes dissociation of chlorine molecules as a first step is conceivable.

UV absorption spectrum of gas-phase Cl_2 [9,10] is characterized by a wide absorption band centered around 330 nm and a weaker absorption continuum in the far UV extending to about 180 nm. Absorption within both of these bands is known to lead to dissociation. Based on our UV spectrophotometer measurements of gas-phase chlorine absorption, the ratio of the gas-phase cross section at 351 nm to that at 200 nm (the lowest wavelength limit of our instrument) is >26 . Assuming that absorption spectrum of physically adsorbed molecular species is not significantly perturbed from the gas-phase spectrum [11], we conclude that 351-nm radiation would be expected to have a considerably higher cross section than 193 nm for the direct photodissociation of adsorbed chlorine species. The higher signals observed at 193 nm suggest that direct photodissociation of adsorbed chlorine species is not the dominant mechanism.

A second possible mechanism, which is based on hot carrier formation, may be that of electron photoemission from a GaAs surface into a condensed Cl_2 layer, leading to chlorine dissociation. The Cl atoms (or ions) thus formed serve as reactive species that interact with a substrate to form volatile arsenic chlorides. Evidence of such a mechanism was presented by Cowin *et al* for excimer-laser irradiation of methyl halides [12,13] and others [14].

Troost *et. al.* reports an increase of ionization energy of up to 1.4 eV for chlorinated GaAs(110) surfaces [15], which when added to the ionization energy of a clean surface, 5.5 eV, results in 6.9 eV. However, the onset of photoemission into a condensed phase may be

lower due to polarizability of the medium, allowing low energy electrons to be emitted when irradiating with 193 nm ($h\nu = 6.4$ eV) radiation. Also the laser fluence used at 193 nm, where the absorption depth is $<100\text{\AA}$, produces enough electron-hole pairs to flatten the bands and cause photoemission from the conduction band, resulting in a higher free electron kinetic energy. The rate of electron attachment to gaseous Cl_2 exhibits a strong maximum at electron energies below 0.3 eV, followed by smaller maxima at 2.5 and 5.6 eV [16,17,18]. However, the resonance at <0.3 eV may not exist for condensed chlorine [19] yet electrons with kinetic energy above 2 eV may still be ejected from the substrate. A 351 nm ($h\nu = 3.5$ eV) photon, on the other hand, has much less energy, making the photoemission-induced chlorine dissociation unfeasible.

We are currently completing more detailed measurements using our TOF system. A report of the initial results on this system is being prepared for submission to Chem. Phys. Lett.

Laser-induced dissociation of organometallic molecules on GaAs

As a second example of a molecular system in which photogenerated carriers may play a role in semiconductor surface chemistry, we will study photoinduced processes in metal alkyls in bare semiconductors. Unlike the case of chlorine, this process does not result in removal of surface atoms. In this study we will utilize total-internal-reflection-Fourier-transform Infrared (TIRFTIR) spectroscopy to identify and follow intermediates on the surface. The same technique, though not under UHV conditions, was used by our

group previously to study metal dimethyl UV photodissociation processes on SiO_2/Si surfaces [20].

In order to perform these experiments, a new UHV system has been designed and constructed. The system, currently being completed, consists of a load-lock mechanism, which allows a sample, mounted on a coolable/heatable manipulator, to be transferred between 3 zones. One zone will be designated for AES, LEED, TPD and laser-desorption analysis, and will be kept clean of the organometallic compounds. The second zone is equipped with ZnSe windows for the TIRFTIR spectroscopy. The third zone will allow exposures of samples to higher pressures (up to one atmosphere) of organometallic molecules without contaminating the rest of the apparatus.

Future program

- In our next series of experiments on the Cl_2/GaAs system we will measure the rate of $\text{AsCl}_2/\text{AsCl}_3$ formation as a function of a UV laser wavelength. This experiment can be done either by adding two more measurements at 248 and 308 nm excimer laser or by utilizing a frequency-doubled excimer pumped dye laser as a tunable source. Although the Fermi level at a chlorinated $\text{GaAs}(110)$ is expected to be pinned at the surface [3,15] at saturation coverages, we wish to see if the wavelength-dependence of the cross section for this reaction changes with sample doping and type. An effort will be directed to increase resolution of the TOF measurement in order to distinguish between laser induced desorption caused by direct photon absorption by the adsorbed molecule and photoemitted electron-induced Cl_2 dissociation.

As mentioned earlier, chemisorbed chlorine was observed to desorb as GaCl from the GaAs(110) surface. TPD measurements revealed a coverage dependence of the GaCl desorption temperature. We would like to estimate a repulsive energy between the chlorinated species on the surface from the coverage-dependent TPD spectra for different sample dopings. Combined with photoreflectance experiments, we wish to study a role of charge transfer in the interaction of the first dissociatively adsorbed chlorine layer with the surface.

At the next phase of our work, we would like to probe other chlorine-containing molecules for laser-induced charge transfer reactions that lead to chlorination of the GaAs substrate. An example is phosgene (Cl_2CO) that has been shown by White *et al* [21] to photodissociate on Ag(111) surfaces when irradiated with UV light. Possible mechanisms as dissociation by capture of photoemitted electrons or hot carrier-reactions will be studied.

- In the organometallic system we will start by probing thermal reactions of trimethylgallium with GaAs(100). We will use TIRFTIR to identify species that exist on the surface upon adsorption and follow their coverage. The next organometallic molecule will be dimethyl cadmium whose gas-phase photophysics is well known.

Papers and presentations prepared with DOE funding

- "Ultraviolet-Light-Induced Oxide Formation on GaAs Surfaces", Z.Lu, M.T. Schmidt, D.V. Podlesnik, C.F. Yu and R.M. Osgood, Jr., *accepted for publication in J. Chem. Phys.* (1990).

- "Interaction of Cl₂ with GaAs(110) with and without laser irradiation", V. Liberman, G. Haase and R.M. Osgood, Jr., *in preparation, to be submitted to Chem. Phys. Lett.*

We are scheduled for a presentation at the American Vacuum Society meeting in October, 1990 and have submitted a second manuscript for the Material Research Symposium in November 1990.

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