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Report #1

IN-SITU ELECTRON AND OPTICAL SPECTROSCOPIES OF TRANSLATIONAL
AND VIBRATIONAL ACTIVATED BOND BREAKING AND FORMATION ON
SEMICONDUCTORS

Grant No. F49620-92-J-0309
Project-Task 2303/BS, 2305/ES

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IN-SITU ELECTRON AND OPTICAL SPECTROSCOPIES
OF TRANSLATIONAL AND VIBRATIONAL ACTIVATED
BOND BREAKING AND FORMATION ON SEMICONDUCTORS

Objective:

The main objective of this project is to understand the nature of bond breaking and formation on semiconductors relevant to materials growth and processing of group IV elements: C, Si, and Ge.

Approach:

The interactions of molecules with clean and modified Si surfaces are investigated by seeding the molecules in a supersonic jet and employing in-situ probes of the surface. Potential precursors for chemical vapor deposition of Ge and C on Si are screened.

Systems Investigated:

The dissociative sticking of CO_2 , $\text{CH}_x\text{F}_{4-x}$ ($x=0-4$), and CH_3Cl on $\text{Si}(100)2\times 1$ is observed. In contrast, H_2 and CO do not dissociate. For the $\text{CH}_x\text{F}_{4-x}$ ($x=0-4$) series, dramatic differences in the reactivity are observed on $\text{Si}(111)7\times 7$.

Summary of Research:

The experiments on translational and vibrational activated dissociative and nondissociative sticking of molecules on semiconductor surfaces were performed in a custom ultra-high vacuum chamber equipped with time resolved electron energy loss spectroscopy (TREELS), Auger electron spectroscopy (AES), temperature programmed desorption (TPD) and a three-stage molecular beam doser. With differential pumping of the spectrometer, sticking measurements were made with TREELS which could be carried out while dosing the sample at normal incidence.

We have used absolute sticking coefficient measurements to determine the reactivity of the fluoromethane series $\text{CH}_x\text{F}_{4-x}$, $x=0-4$. We observe near unity probability dissociative adsorption on $\text{Si}(100)2\times 1$ at 90 K with only one of the five molecules while the remaining had undetectable reactivity (maximum sticking coefficient $< 10^{-4}$) even with very high translation and vibrational energies obtained from a supersonic molecular beam doser with heated alumina and ruby nozzle. Seeding 5% of each of these molecules in hydrogen enabled us to achieve translational energies ranging from 1.6 eV for CH_4 to 4.2 eV for CF_4 . The reactive species, CH_3F , reacts even at room temperature energies. We suspect that it is more prone to sticking due to the fact that the highly electronegative fluorine atom is more charged than when there are additional fluorine atoms in the molecule. While it is not surprising that the more spherical molecules, CH_4 and

CF_4 , were unreactive it is compelling that two intermediate gases, CH_2F_2 and CHF_3 , resisted adsorption since a previous experiment done with our apparatus found that CHF_3 reacted readily with the $\text{Si}(111)7\times7$ surface.

Similar studies established that CH_3Cl is as reactive as CH_3F . This makes it an interesting candidate for chemical vapor deposition (CVD) growth of diamond films. Typically the hydrogen content is high in CVD chambers. In an attempt to elucidate the role of hydrogen we repeated our reactivity study of CH_3Cl on a di-hydride saturated, monohydride saturated, and partially hydrogen covered $\text{Si}(100)$ surface. H coverages were prepared by heating a filament in a hydrogen ambient. Both H saturated surfaces were inert to CH_3Cl with nozzle temperatures up to 1000 K and translational energies up to 1.25 eV. Dosing the partially hydrogenated surface resulted in coadsorption of preadsorbed H and the dissociated products: CH_3 and Cl.

The adsorption of molecular CO_2 was found to be activated as the CO_2 incident translational energy is increased from 0.1 eV (neat gas) to 1 eV (5% seeding in He) for nozzle temperatures of 300 K and 1000 K, respectively. Desorption of CO_2 occurs at 110 K. A new state of CO with desorption temperature of about 400 K was observed in addition to the 160 K peak for CO adsorbed alone on the surface. This new state is populated by increasing the incident translational energy of the CO_2 .

On the Si(100)2x1 surface at 70 K, the adsorption of CO was found to be nonactivated. The adsorbed CO gives rise to a desorption peak at around 160 K. With increasing coverage, a second peak appears at around 100 K. However, no dissociation of CO was observed for kinetic energies less than 1 eV.

Molecular hydrogen did not dissociate upon acceleration from the supersonic expansion. This implies that in order to obtain atomic hydrogen either a hot filament or a plasma discharge can be used.

Publications:

We are currently preparing two manuscripts: one on the reactivity of fluoromethane series and the other on the CO₂ sticking.

Conference Presentation:

1. K.A. Brown, R.A. Machonkin, and W.Ho, "Reactivity of CH_xF_{4-x} and CH₃Cl with Si(100)2x1", 53rd Annual Conference on Physical Electronics, June 21-23, 1993, Rensselaer Polytechnic Institute, Troy, NY.

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