

Chapter 4. Chemical Reaction Dynamics at Surfaces

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4.1 Chemical Reaction Dynamics on Semiconductor Surfaces

Sponsor

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Project Staff

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The etching of semiconductor materials in halocarbon plasma environments is a complex chemical process. The plasma is used to produce species that are highly reactive with the semiconductor surface. Because many different reactive species, including radicals, ions, and highly excited neutral molecules are produced in a plasma, the mechanism of the etching reaction is difficult to probe in this environment. Our program is aimed at systematically examining the role of each of these species in the etching process with molecular beam reactive scattering techniques.

While investigating the role of translationally excited F_2 molecules in the etching of Si(100), we were surprised to find that, even with F_2 translational energies as low as 0.5 kcal/mole, F_2 reacts with a clean Si(100) with unit probability to form a fluorinated layer. However, its reactivity stops at fluorine coverages above approximately a half of a monolayer. The translational energy of the F_2 molecule must be raised by molecular beam techniques to achieve further fluorination of the surface to provide enough fluorine to

produce the etch product SiF_4 . Prior to this discovery, F_2 had never been observed to etch silicon. Therefore, we have shown that silicon can be efficiently etched by molecular beam techniques without using a high energy plasma. Unlike plasma techniques, the molecular beam techniques do not cause radiation damage or introduce defects into the silicon.

4.2 Collision Induced Dissociative Chemisorption: Chemistry with a Hammer

Sponsors

National Science Foundation
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Project Staff

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We have now completed thorough investigations of our newly discovered mechanism for dissociative chemisorption — collision induced dissociative chemisorption. In this process, the dissociation of CH_4 , molecularly adsorbed on a Ni(111) surface at 46 K, is induced by the impact of incident Ar atoms. The impact of the Ar atoms deforms the physisorbed CH_4 into the configuration for the transition state that leads to dissociation.

Detailed measurements have shown that the absolute cross section for collision induced dissociative chemisorption exhibits a compli-

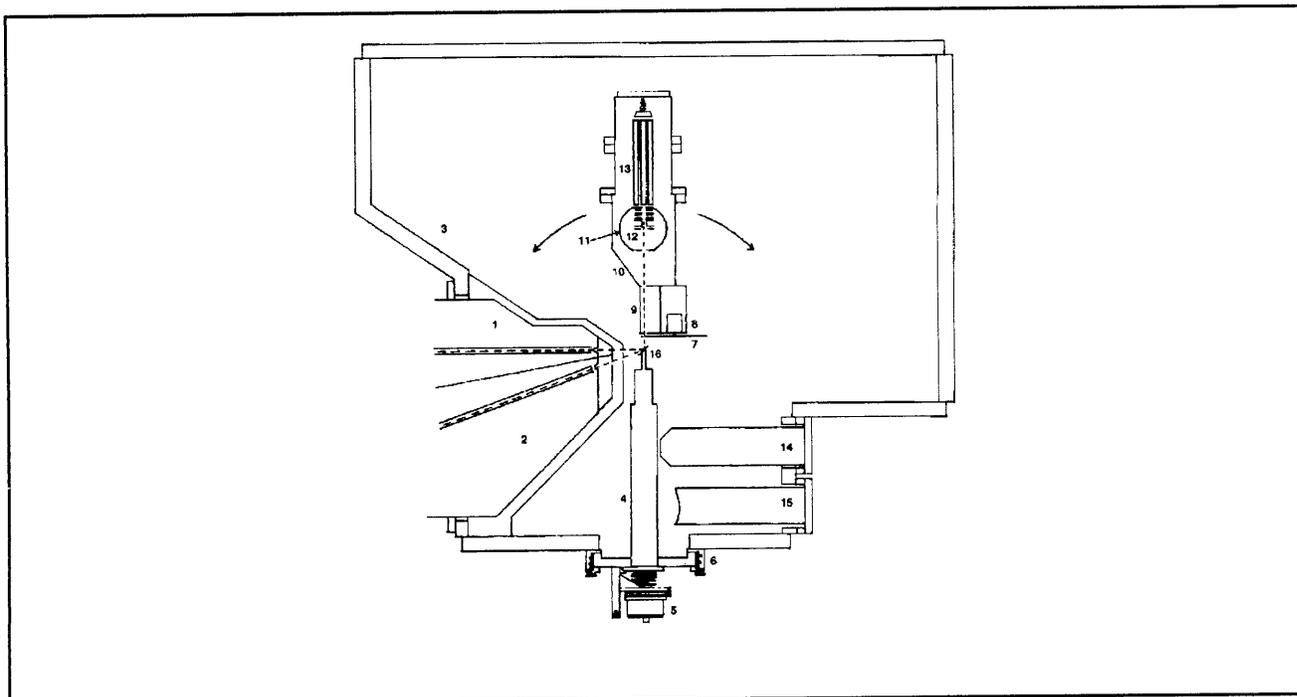
cated dependence on the normal component of the kinetic energy of the Ar atoms. The strict adherence to normal kinetic energy scaling observed in the case of translational activation of methane is not observed in collision induced activation. We have shown that the breakdown in normal energy scaling in the Ar kinetic energy is expected because of the range of impact parameters which contribute to the cross section for dissociation.

For example, the Ar atom can collide with the adsorbed methane molecule with an impact parameter as large as the hard sphere collision diameter or as small as zero in a head-on collision. The effectiveness of the collision of the Ar atom with the methane in transferring energy and thereby promoting deformation that leads to dissociation depends on the type of collision or impact parameter. A head-on collision transfers much more energy than a glancing collision. Once the collision has occurred, the Ar atom is reflected from the surface, and the rest of the CH_4 -surface collision is the same as in the case of translational activation. The methane molecule with its newly acquired energy is accelerated into the surface, deforms and dissociates. The important

point is that only the energy of the Ar atom that is actually transferred in the normal direction to the methane molecule leads to overcoming the barrier. It is the dependence of the energy transfer on impact parameter that results in the breakdown in normal energy scaling in the Ar kinetic energy.

This picture has been shown to be correct by comparing the experimental cross section for dissociation with that calculated from the probability for dissociation integrated over the impact parameter. The dissociation probability at the energy acquired by the methane molecule after its collision with the Ar atom is obtained from the translational activation results. The energy transferred in the normal direction to CH_4 by collision with Ar is calculated from a hard sphere collision model. The cross section calculated from this procedure yields the observed dependence on the normal component of the Ar atom energy.

Therefore, dissociation of methane after translational activation, and after collision induced activation are completely consistent with each other. They are simply different methods for providing the energy to deform the molecule, but the mechanism for dissociation of the methane is the same.



Schematic of the molecular beam-surface scattering apparatus showing two beams aimed at a Si-surface and the triply differentially pumped, rotatable quadrupole mass spectrometer as a detector of the scattered reaction product.

4.3 Collision Induced Desorption

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In competition with dissociation induced by the impact of the Ar atom, collision induced desorption also occurs. That is, once the Ar atom transfers energy to the methane, the methane molecule collides with the surface and can rebound into the gas phase if the site on which it is physisorbed or if its orientation are not energetically favorable for dissociation. Desorption induced by collisions is roughly an order of magnitude more probable than collision induced dissociation.

The dynamics of collision induced desorption are studied by measuring the desorption cross section as a function of the energy and incident angle of the Ar atoms. The absolute magnitudes of the cross sections are about an order of magnitude smaller than the hard sphere, gas kinetic cross section for collision between Ar and CH₄. The magnitudes of the desorption cross sections measured in the isolated CH₄ molecule limit are identical to those measured at a saturated CH₄ monolayer coverage. These two observations imply that only direct, small impact parameter collisions of the Ar atom with the physisorbed methane are responsible for the desorption event.

The desorption cross section at an incident energy of 51.8 kcal mol⁻¹ is observed to approximately double as the incident angle is increased from 0 degrees to 70 degrees. However, the magnitude of the increase in the cross section is dependent on and is largest for high total energies of the incident Ar atom. This is the result of two competing effects. As the incident angle is increased, the normal component of the kinetic energy,

which is the component responsible for desorption, decreases. This should lead to a decrease in the desorption cross section as the incident angle is increased because there is less energy in the normal direction to push the molecule away from the surface. However, as the incident angle increases, the collision or geometrical cross section of an incoming Ar atom with the adsorbed molecule increases, thereby countering the decrease in the energy in the normal direction. The complicated dependencies of the desorption cross section on energy and incident angle are the result of these competing factors. We have carried out classical trajectory calculations to confirm this picture.

Perhaps more important than the physics behind these processes is the fact that they have been observed and what the knowledge of their existence means for understanding the complex environment of high pressure heterogeneous catalysis. Collision induced chemistry and desorption probably play important roles in high pressure catalytic reactions because, under these conditions, a catalyst is covered with adsorbate and the adsorbate covered catalyst is continually bombarded by gas phase molecules.

With the observation of these processes, no mechanism for a high pressure reaction can now be considered complete without an assessment of the role of collision induced chemistry and desorption as potential major steps. These observations are now cause for reexamination of the mechanisms of catalytic reactions in which inert gas effects on reaction rates have been noted. Collision induced chemistry and desorption are additional contributors to the pressure gap in the reactivity of heterogeneous catalysis. They are additional reasons why surface chemistry at high pressures is often very different from surface chemistry at low pressures.

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