Chemical Physics of Digital Etching

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We have investigated the chemisorption of halogens on semiconductor surfaces in order to develop a better understanding of passivation and etching of these surfaces. We have shown that halogen chemisorption occurs onto both Si(111) and GaAs(100) via both dissociative chemisorption and abstraction. In abstractive chemisorption of a diatomic molecular halogen, one halogen atom sticks to the surface while the other is ejected back into the gas phase. The abstraction process can be chemically selective for one of the two atoms in an interhalogen such as ICl. Furthermore, both abstraction and dissociation can be chemically selective for the Ga atoms on the GaAs(100) surface. The chemisorption of halogens can passivate the surface both chemically and electronically. Passivation occurs when a stable homogeneous monolayer of surface monohalide is formed. For GaAs(100), passivation can unpin the Fermi level; this is a critical step in developing a CMOS technology of GaAs. We are now studying the deposition of insulators on GaAs for use in high speed low power wireless communication and satellite technology with support from DOD.
(a) Cl₂, Br₂, and I₂ Chemisorption on Si(100) 2x1

The two most common forms of dissociative chemisorption on metal surfaces are direct and precursor mediated. We have performed a series of experiments that show that these two mechanisms also can describe the chemisorption of halogens on semiconductors. In direct chemisorption, a molecule dissociates during the gas-surface collision to form adatoms; this process may have an activation barrier. In precursor mediated chemisorption, the molecule first adsorbs/traps into a molecular precursor state prior to dissociation. This precursor state can be a physisorbate or a charged molecular state. Our experiments have shown that for the heavy diatomic halogens (Cl₂, Br₂, and I₂) at incident translational energies greater than 0.1 eV, the sticking probability is independent of the surface temperature and increases with incident translation energy. This indicates that the heavy halogens chemisorb via direct activated chemisorption at high incident translational energy. At low incident energies, the initial sticking probability, S₀, decreases with increasing surface temperature, and the sticking probability decreases with increasing incident energies between 0.02 eV and 0.06 eV. Therefore, all three heavy diatomic halogens can adsorb via precursor-mediated chemisorption at low incident translational energy. We have also done a series of experiments upon the chemisorption mechanisms of Cl₂ on the Ga-rich GaAs(100) c(8x2), As-rich GaAs(100) c(2x8), and stoichiometric GaAs(100) (1x1) surfaces. In addition, we have examined the competition between etching and passivation on these GaAs surfaces by Cl₂ at 300 K. Further experiments were done on F₂ and O₂ Chemisorption Mechanisms on Si(100) 2x1 and Si(111) 7x7.

(b) STM of Local Adsorbate Structure for Precursor-mediated Versus Direct Chemisorption

As far as we know, we are the only group to have studied the effect of translational energy upon local adsorbate structure using STM. We have developed a unique machine to dose a crystal surface in ultra-high vacuum with a mono-energetic molecular beam and then examine the adsorbate structure with STM. Using this technique, we have identified the role of the chemisorption mechanism in the formation of adsorbate structures for F₂, Cl₂, Br₂, ICl, IBr, I₂Cl, and O₂ upon Si(111)-7x7 surfaces at 300 K. When Si(111)-7x7 is dosed with 0.05 eV Cl₂ (precursor-mediated chemisorption), the dominant adsorbate structure is SiCl islands. The SiCl islands are hundreds of Angströms apart at low coverage and nucleate at missing adatom defects. Conversely, for 0.44 eV Cl₂ dosing (direct-activated chemisorption), island formation is not observed, and only single site center-adatom preferred chemisorption is present. It is proposed that island formation results from Cl₂ adsorption via a mobile molecular physisorption state that dissociates at the edges of SiCl islands while the center-adatom preferred reaction results from instantaneous direct-activated chemisorption. When the Cl-Si(111) 7x7 surface is heated to 600 °C and partial desorption occurs, the adsorbate structure is independent of adsorption mechanisms because the SiCl forms a 2-D lattice gas prior to second order recombinative desorption as SiCl₂. These island formation studies are important in understanding defect formation in stimulated etching.

(c) STM of Local Adsorbate Structure for Abstractive Versus Dissociative Chemisorption

Molecular dynamics simulations by Carter et al. have shown that the reaction of F₂ with the Si(100)-(2x1) surface always proceeds in a stepwise fashion; the first step is the chemisorption of one F atom followed by the cleavage of the F-F bond. The escape or adsorption of the second F atom is the difference between abstractive and dissociative chemisorption. We have recorded atomic-resolution STM images of the Si(111)-(7x7) surface after chemisorption of F₂, Cl₂, Br₂, or I₂ molecules with low and high translational energies. These images allow direct observation of how the probability for abstraction varies with incident translational energy in the limit of zero coverage. For low F₂ incident translational energies, nearly all chemisorption sites are Si-F monomers, isolated single sites. These monomer sites are formed through abstractive chemisorption. We also show that for higher F₂ incident translation energy, many more chemisorption sites are dimers, two nearest neighbor Si-F sites. These dimer sites are formed through dissociative chemisorption. This trend of increased dissociative chemisorption at high energy is also observed for Cl₂ and Br₂ and is in agreement with theoretical models.
The chemically selective dissociation of interhalogens on Si(111)-7x7 has been investigated using supersonic molecular beams, scanning tunneling microscopy (STM), Auger electron spectroscopy (AES), and thermal desorption spectrometry (TDS). Empty-state STM topographic images show two chemisorption channels: 85% abstractive and 15% dissociative chemisorption. The abstractive chemisorption probability for ICl is considerably higher than Br₂ at similar translational energies even though they have very similar bond strengths and lengths. AES measurements of ICl chemisorption on Si(111)-7x7 show that the absolute ratio of iodine to chlorine is 3:1 at low coverage. This was verified by mass-resolved TDS experiments. Despite the much larger exothermicity for the formation of silicon monochloride (Si-Cl) than silicon monoxide (Si-O), the chlorine atom in an ICl molecule is preferentially ejected from the surface and the iodine atom remains on the substrate in a single abstractive chemisorption event. The high sticking probability and the selective abstraction of iodine suggest that the interaction between the asymmetric p* antibonding highest occupied molecular orbital (HOMO) on ICl and the silicon dangling bonds on the Si(111)-7x7 orients the ICl molecules into an Si-I-Cl conformation during abstraction. Experiments on I₂Cl₆ and IBr chemisorption confirm the role of the asymmetric antibonding orbitals in chemical selectivity in abstractive dissociation on Si(111)-7x7.

(d) HALOGEN PASSIVATION GaAs(100)

One of the more important technological challenges of GaAs device fabrications is deposition of a nearly defect-free insulator on GaAs that can be used as a gate in a transistor. Unfortunately, unlike silicon, when GaAs is oxidized, Ga₂O₃ is formed along with metallic As. In general, when insulators are deposited from the gas phase, they react with the GaAs to create interfacial defects which prevent the fabrication of a useful device. We are studying how the GaAs(100) surface can be passivated with molecular halogens so that molecular insulators can be deposited without formation of interfacial defects that pin the Fermi level. When the Ga-rich GaAs(100)-(c8x2) surface is dosed with molecular halogens, a 1x1 LEED pattern is formed. We have found that this overlayer is chemically passive: it greatly inhibits the absorption of O₂ or H₂O. Therefore, it has the required chemical properties for deposition of insulators onto GaAs. The second requirement for the interface is electrical passivation. The GaAs(100) surface is pinned midgap. Reactions with halogens remove the dangling bonds and may even remove the dimer row reconstruction. We have tested this hypothesis by measuring the current versus voltage for electron tunneling at the halogen passivated surface with scanning tunneling microscopy. Our initial results look promising, but we need to repeat the experiments with lower defect density samples. The project also includes depositing molecular insulators onto passivated GaAs surfaces and studying the electronic properties in collaboration with Motorola. Motorola is developing gate technology on GaAs for use in their cellular phones and pagers. A low leakage gate technology on GaAs would enable both the logic and microwave devices to be integrated on a single chip that should lower power consumption and increase the bandwidth of wireless communication devices.

Recently, we have continued our investigation of halogen chemistry on GaAs(100) with funding from the NSF-Division of Materials research. We have focused upon chemical selectivity in the chemisorption of halogens on GaAs(100). The As-rich GaAs(001)-(2x4) surface consists of a top layer of As dimers and a second layer of Ga atoms. When high translational energy Br₂ chemisorbs on this surface at low coverage, there is complete, near perfect, chemical selectivity for the second layer substrate atoms compared to the top layer atoms. Our STM images show that Br₂ molecules react exclusively with the second layer Ga atoms instead of the first layer As atoms. A simple molecular orbital model shows that the Ga atoms are more reactive than the As atoms because the Ga atoms have empty dangling bonds while the As atoms have filled dangling bonds. The bonding of the halogens to the second layer Ga atoms weakens the As-Ga back bonds and depletes the As dangling bonds. Thus, for high exposure to Br₂, the arsenic atoms react to form AsBr₂ adsorbates. The Ga-rich GaAs(001)-(c8x2) surface has a top layer of Ga dimers and a second layer of Ga atoms. Our STM studies have shown that on this surface there is near perfect selectivity for halogen reaction with the Ga atoms. Again, a simple molecular orbital model predicts that the Ga atoms should be the only reactive sites since only the Ga atoms have empty dangling bonds.

(e) DIGITAL ETCHING

We have done a series of experiments upon digital etching of both GaAs(100) and Si(100). Digital etching of GaAs(100) can be implemented with thermal desorption. When the Ga-rich surface GaAs(100)-(c8x2) is dosed with Cl₂, the adsorption is self limiting and a monolayer of Ga-Cl is formed. Heating the surface removes the GaCl layer and the surface reconstructs to the As-rich GaAs(100)-(c2x8) surface. If this As-rich surface is heated, the surface monolayer of As is desorbed and the Ga-rich surface GaAs(100)-(c8x2) is formed. By repeating this process an
integral number of layers can be etched from the surface, digital etching. We have invested thermal digital etching as well as laser induced and ion stimulated digital etching. However, as explained to us by our industrial collaborators, the application of halogen-GaAs(100) chemistry to passivation and gate deposition is much more important technologically than digital etching. Therefore, we have refocused our halogen surface chemistry applied research upon chemical and electronic passivation for the deposition of gate insulators on GaAs(100). This research is described in a previous paragraph.
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14. K. A. Pettus, T. Ahmadi, E. Lanzendorf, and A. C. Kummel "Comparison of Chemical Selectivity and Kinetic Energy Release in Si(s) + ICl(g) and H(g) + ICl(g)" submitted to J. Chem. Phys.
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