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The chemisorption mechanisms of Cl2, Br2, and I2 on Si(100) 2x1 are very similar while those of F2 and O2 are very distinct. For the heavy diatomic halogens (Cl2, Br2, and I2), the sticking probability increases with incident translation energies above 0.1 eV, and the largest initial sticking probabilities are obtained at the highest incident energies, with So equal to 95-100% for I2 and br2, and 80-85% for Cl2. At low incident energies the initial sticking propability, So decreases with increasing surface temperature while at high incident energies the sticking probability is independent of surface temperature. In addition, for Cl2 very low energy molecular beams can be prepared, and the sticking probability is observed to decrease 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 and via direct - activated chemisorption activated chemisorption at high incident translational energy 1,2.

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(a) F_2, O_2 Chemisorption on Si(110) 2x1

The chemisorption mechanisms of Cl_2, Br_2, and I_2 on Si(100) 2x1 are very similar while those of F_2 and O_2 are very distinct. For the heavy diatomic halogens (Cl_2, Br_2, and I_2), the sticking probability increases with incident translation energies above 0.1 eV, and the largest initial sticking probabilities are obtained at the highest incident energies, with S_0 equal to 95 - 100% for I_2 and Br_2, and 80 - 85% for Cl_2. At low incident energies the initial sticking probability, S_o, decreases with increasing surface temperature while at high incident energies the sticking probability is independent of surface temperature. In addition, for Cl_2 very low energy molecular beams can be prepared, and the sticking probability is observed to decrease 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 and via direct - activated chemisorption activated chemisorption at high incident translational energy[1,2].

We just finished our studies of the chemisorption mechanism for F_2 and O_2 on both Si(100) 2x1 and Si(111) 7x7. Both F_2 and O_2 have chemisorption probabilities that increase with incident translational energy indicating that they have the usual activated chemisorption mechanism at high translational energy. In addition, both exhibit the inverse temperature effect: at high translational energy, the sticking probability increases with increasing surface temperature. This has been seen before for O_2/Si(100) by Engel and was ascribed to thermally assisted activated chemisorption; however, our results on F_2/Si(100) & Si(111) show the mechanism is more intricate. For F_2 and O_2 sticking on silicon, the activation barrier is sufficiently small that we can increase the translational energy so high that the sticking probability at 300 K goes to 100% and thus the inverse temperature effect disappears. Therefore, at high translational energy the molecules can directly dissociate without passing through the thermally assisted molecular chemisorption channel or there is more than one activated molecular chemisorption channel. At low translational energy, the F_2 sticking is large and nearly independent of translation energy; this low energy chemisorption was investigated further using STM and is a result of abstraction: when F_2 collides with a clean silicon surface, one atoms chemisorbs while the other is ejected into the gas phase[3]. We have also recorded the temperature programmed desorption (TPD) spectra of SiF_2 and SiF_4 from F_2/Si(100) and F_2/Si(111) and observed that the maximum coverages and SiF_4 TPD peaks increase with increasing incident F_2 translational energy. This indicates that the barrier to forming SiF_3 and SiF_4 species is greater than the barrier to forming SiF adsorbates and explains why only atomic F and XeF_2 are able to spontaneously etch silicon at 300 K. Therefore, although F and XeF_2 are preferable etchants for continuous etching of silicon because they form multilayer SiF_x adsorbates, for digital etching thermal F_2 is the preferred etchant since its absorption is limited to only a monolayer of SiF and SiF_2[4].

(b) STM of Local Adsorbate Structure as a Function of Chemisorption Mechanism

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 F_2, Cl_2, Br_2 and O_2 upon Si(111)-7x7 surfaces at 300 K. We are neither the first group to use STM to study the adsorption of halogens on semiconductors nor the first group to use STM to study etching of semiconductors by halogens, but we are the first group to use STM to study chemisorption as a function of adsorbate incident energy and thus chemisorption mechanism.

When Si(111)-7x7 is dosed with 0.05 eV Cl_2 (precursor-mediated chemisorption), the dominant adsorbate structure is SiCl islands. The SiCl islands are hundreds of Angstroms apart at low coverage and nucleate at missing adatom defects. Conversely, for 0.44 eV Cl_2 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 Cl_2 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[5,6]. When the Cl-Si(111)

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7x7 surface is heated to 600 $^\circ$C and partial desorption occurs, the adsorbates structure is independent of adsorption mechanisms because the SiCl forms a 2-D lattice gas prior to 2nd-order recombinative desorption as $SiCl_2$[7].

For F_2 chemisorption on Si(111) 7x7, there is no intrinsic physisorption state, and therefore no island formation is observed at low incident translational energy. Instead, at low translational energy, we observe that the dominant adsorption sites are single reacted adatoms, while at high translational energy, pairs of adjacent reacted adatoms are commonly observed. At low translational energy, the F_2 adsorbs via abstraction whereby when a F_2 collides with the surface, one F atom chemisorbs while the other is ejected into the gas phase. The abstraction mechanism was first identified theoretically by Carter et al[8] and experimentally by Li et al[9]. Our STM results show that this abstraction mechanism accounts for nearly all the chemisorption at low energy because nearly all the adsorption sites are single reacted adatoms. At high translational energy F_2 adsorbs primarily by dissociative chemisorption, and thus we observe adjacent pairs of reacted adatoms. The dominant type of reacted silicon pair is center adatoms from adjacent unit cells; this is most easily seen in the high translational energy Cl_2/Si(111) 7x7 or Br_2/Si(111) 7x7 where dissociative chemisorption is almost the exclusive adsorption mechanism. The preference for center adatoms from adjacent units cells is due to the center adatoms being more reactive as well as center atoms from adjacent unit cells being the most closely spaced adatom pairs on the surface along with center-center adatom pairs[10]. The preference for most closely spaced pairs in dissociative chemisorption can be understood from the theoretical work of Carter[11]: chemisorption of F_2 is a two-step process in which, upon collision with the surface, the F_2 forms a transient Si-F_2 species. At high translational energy, the initial momentum of the terminal F atom is so large that it is propelled onto the surface and forms a chemisorption bond at a nearby 1/2 filled dangling bond site. We have done a similar translational energy-STM study on O_2/Si(111) 7x7[12].

(c) Practical Digital Etching

Our digital etching chamber has been constructed and delivered. When will have it assembled and operational by the end of 1994. We will first investigate digital etching of GaAs(100) and Si(100) using Cl_2 and laser induced desorption even though better etch spatial anisotropies can be achieved with electron and ion induced desorption. We have initiated two collaborations to do digital etching with electron and ion induced desorption since these will be of greater interest to industry. We hope our collaborators will provide us with the funding for a plasma source as well as one additional person to perform the experiments. We have set up a collaboration with Intel for work upon digital etching of silicon (Dr. John Carruthers, Intel, Santa Clara). Intel has offered to provide us with substrates and metrology. We hope to expand this collaboration and have applied to Intel for funding for development of practical digital etching. We hope to set up a collaboration with Veeco Instruments (Jim Weldon, Veeco Instruments Inc, Milpitas, CA) for converting a commercial RF ion source into a pulsed ion and electron source for digital etching. We have a collaboration set up with Thermionics Inc (Michael Ricks, Thermionics Inc, Hayward, CA) to develop digital etching chambers for research scale investigations. We have already produced one chamber and after it has been tested, the product will appear in the next Thermionics Catalogue.

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