

Dual atom beam studies of etching and related surface chemistries

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Abstract - Most surface science studies relating to plasma-assisted etching processes have been carried out using model systems in which clean surfaces in ultrahigh vacuum environments are subjected to controlled fluxes of reactive neutral species and energetic ions chosen so as to be representative of a plasma-assisted etching environment. This approach allows both control over the particle fluxes and in-situ surface characterization which are not easily achieved in a reactive gas plasma environment. Most of these studies have involved stable reactive molecules such as XeF_2 or Cl_2 . However in a plasma process the key species are believed to be atomic or molecular radicals, often involving more than one halogen, halogen-hydrogen or other gas mixtures. Whereas there have been some studies in which atom beams are directed onto surfaces, very little work has been reported involving two separate beams of reactive species. Recently studies have been carried out in which various binary combinations of fluorine, chlorine and hydrogen atoms and/or molecules have been directed onto Si(111) and other surfaces with and without energetic ion bombardment. The gaseous species evolved from or reflected from the surface under study are monitored with modulated beam mass spectrometry. Some interesting synergistic effects are observed on Si(111) and some catalytic reactions have been noted on other surfaces.

INTRODUCTION

The surface science associated with plasma-assisted etching processes encompasses several virtually unexplored areas. For example, the influence of energetic ion bombardment on the kinetics of simultaneously occurring gas-surface interactions has only recently been studied in detail, little is known about atom and molecular radical reactions with surfaces with or without ion bombardment, and reactions of more than one beam of reactive species with surfaces have received little basic research interest. Yet all these phenomena are involved in present-day plasma-assisted etching technology. This paper will briefly summarize some preliminary studies of ion-assisted etching of Si(111) at room temperature using various binary combinations of fluorine, chlorine and hydrogen atoms and molecules. Also an interesting Pd-catalysed reaction of hydrogen molecules with both fluorine and chlorine molecules will be described.

EXPERIMENTAL

A top view of the ultrahigh vacuum system (ref. 1) used for this work is shown schematically in Fig. 1. The atom fluxes are generated by two 2.45 GHz microwave discharges (labelled E in Fig.1). The ion gun is not shown in Fig. 1 but is mounted above the axis of the product detection system on the left side of the figure. 2 keV Ar^+ ions are used in this work and they are incident on the sample surface (S) at an angle of 26 degrees from the surface normal. Etch products, recombination products or reflected incident species are detected by the modulated beam mass spectrometric detection system on the left side of Fig. 1. There are four stages of differential pumping between the sample and the Balzers 420 mass spectrometer. The neutral species passing through the axis of the detection system are ionized by 60 eV electrons in the magnetically enhanced ionization chamber

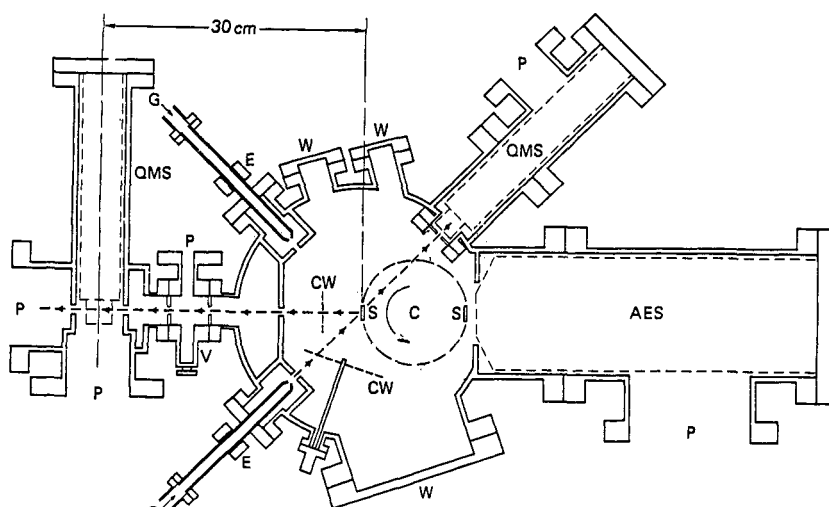


Figure 1. Top cross-section view of dual atom beam apparatus. The meaning of the symbols is as follows: AES = Auger electron spectrometer; P = turbopumps; QMS = quadrupole mass spectrometers; S = sample (Si); C = carousel; CW = chopper wheel; W = viewport; E = Evenson microwave cavity; G = gas supply; V = gate valve (from Ref. 1).

of the mass spectrometer. Most of the ionization is dissociative and no attempt will be made in this discussion to identify the parent neutral molecules from the observed ion spectra. A UTI 100C quadrupole (upper right of Fig. 1) is used to characterize the species emanating from the discharge source at the bottom of Fig. 1. Surface conditions are periodically monitored by the Auger electron spectrometer on the right of Fig. 1.

ETCHING OF Si(III) WITH FLUORINE AND CHLORINE

It is well established that both F atoms and H atoms etch Si effectively at room temperature without ion bombardment. Cl_2 on the other hand, does not etch Si under these conditions. Previously it was observed that when a flux of Cl_2 molecules was superimposed upon a flux of H atoms etching Si, the etching stopped (ref. 1). A similar experiment was carried out using F atoms instead of H atoms and the quartz crystal microbalance data is shown in Fig. 2. Note that the addition of Cl_2 molecules at $t = 175$ sec almost tripled the etch rate. This result is similar to that obtained by Suto et al. (ref. 2). The same experiment was carried out using a Si(111) crystal instead of the poly-Si used for the quartz crystal microbalance data of Fig. 2. The product ion signals SiF^+ , SiF_2^+ , SiF_3^+ and Si_2F_5^+ all increase by about the same amount as the etch rate shown in Fig. 2. The SiF_4^+ peak remained approximately constant but the measurement was complicated by the facts that this peak has a low intensity and there is a mass spectral interference with the ^{29}Si isotope in the SiF_2Cl^+ ion signal. SiF_4^+ is unique in this group of ionic signals in that it is less likely to be formed from a chlorine-containing parent molecule. For example SiF_3^+ could be formed from either SiF_4 or SiF_3Cl parent molecules. It is clear however, that the addition of the Cl_2 molecules increases the reaction probability for the F atoms. Much more fluorine is observed in the etch products and the reflected F atom signal decreases when the chlorine is added.

The product mass spectra are quite complex with F atoms and Cl_2 molecules incident on the Si surface. Many species of the form $\text{SiF}_x\text{Cl}_y^+$ are observed but the products are dominated by fluorine as expected. The F/Cl ratio in the etch product ion signals (ie. after electron impact ionization) is about 8. When the Cl microwave was turned on to generate Cl atoms, the situation did not change much- the etch products were still dominated by fluorine, the etch rate increased slightly. Ion bombardment increased the etch rate substantially (about a factor of 2) and the intensity of the signals for the etch products increased, but the dominance of fluorine continued. Fig. 3 is an example of a spectrum observed with both atom sources on and with 2 keV argon ion bombardment. The reflected

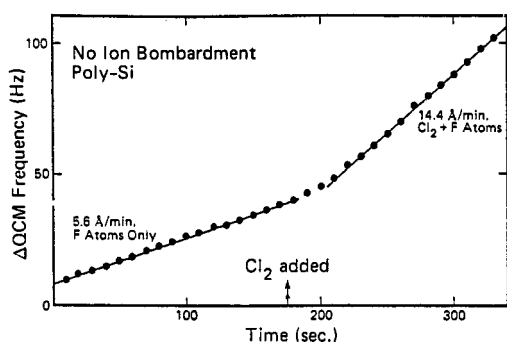


Figure 2. Etch rate of poly-Si, as measured by a quartz crystal microbalance, as a flux of molecular chlorine is added to a flux of atomic fluorine. The flux of both F and Cl_2 is in the range 10^{14} to 10^{15} per cm^2/sec . The Si is at room temperature.

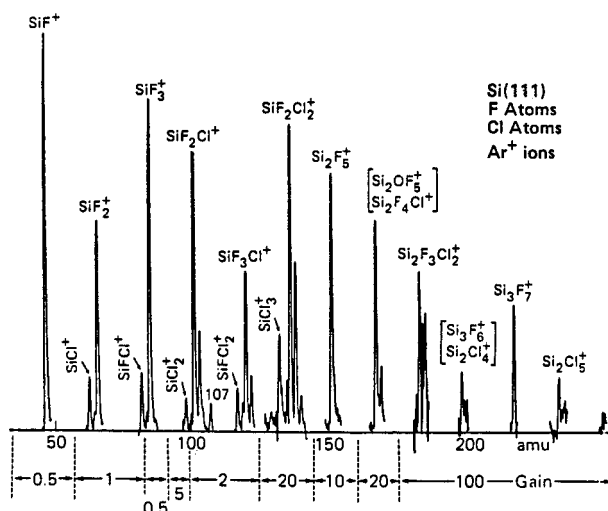


Figure 3. The products observed with the modulated beam mass spectrometer during the 2 keV Ar^+ -assisted etching of Si(111) with F and Cl atoms. Ionizing electron energy = 60 eV. Total chlorine flux is approximately 10^{15} molecules/ cm^2/sec with about 30% dissociation. Total fluorine flux is about 1.5×10^{15} molecules/ cm^2/sec with about 90% dissociation. Ar^+ flux is 8×10^{12} ions/ cm^2/sec .

chlorine and fluorine were not recorded in this spectrum. The only contaminants which have been observed are a small peak at mass 107 which is attributed to an F atom reaction with a ultrahigh vacuum compatible epoxy used in the source construction and a small CF_3^+ peak (not shown in Fig. 3). No evidence has been found which indicates that this contamination from the F atom source in any way contaminates the surfaces.

When both atom sources are turned off and molecular fluorine and molecular chlorine are incident on the Si with energetic ion bombardment, the etch product spectra are dominated by chlorine as shown in Fig. 4. The etch rate is lower by about an order of magnitude compared to the etch rate observed with atom fluxes (ie. conditions pertaining to Fig. 3). The F/Cl ratio of the etch product signals in Fig. 4 is about 0.2 compared to a value of about 6 for Fig. 3.

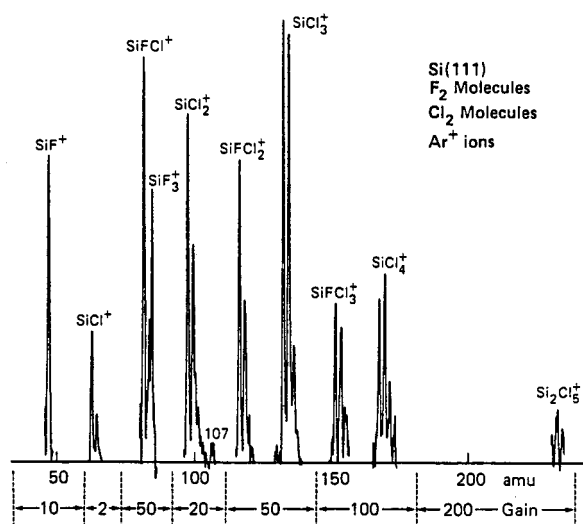


Figure 4. The products observed with the modulated beam mass spectrometer during the 2 keV Ar^+ -assisted etching of Si(111) with F_2 and Cl_2 molecules. Conditions as in Fig. 3 except the microwave discharges are off (no dissociation).

ETCHING OF Si(111) IN FLUORINE AND HYDROGEN

The dominant effect of hydrogen additions to fluorine-containing etching plasmas is to decrease the F atom concentration by forming HF molecules. In this study, gas phase processes are not present and only the surface chemistry is involved. Both H atoms and F atoms etch Si at room temperature in the absence of ion bombardment and with comparable efficiencies. Ion bombardment increases the efficiency of F atom etching dramatically whereas the effect of ion bombardment on H atom etching appears to be small. H₂ alone does not react with Si and its presence during energetic ion bombardment causes no observable effect on the sputter etch rate. F₂ does etch Si at room temperature without ion bombardment but at such a slow rate that no etching can be observed with the fluxes used in this experiment (10¹⁵ molecules/cm²-sec). However, ion-assisted etching of Si with F₂ is easily observed.

The results obtained with both hydrogen and fluorine can be summarized as follows. Whenever F atoms are present, hydrogen (atoms or molecules) has no observable effect on the Si etching with or without ion bombardment. This suggests that the formation of HF on the Si surface is not limiting the etch rate. The situation is more complex with F₂ molecules. In this case, not unexpectedly, H₂ remains essentially inert with respect to the etching process. However with H atoms and F₂ molecules, there is an interaction. When F₂ is added to the H atom etching of Si(111) in the absence of ion bombardment, the etch rate decreases (about a factor of 2 in our conditions) and the products change from SiH_x, Si₂H_x and Si₃H_x to the product spectrum shown in Fig. 5 which is dominated by fluorine chemistry. Recall that F₂ alone does not etch Si under our conditions. It is suspected that the reaction $H + F_2 \Rightarrow HF + F$ on the Si surface is responsible for the increased reaction probability of the F₂ molecules.

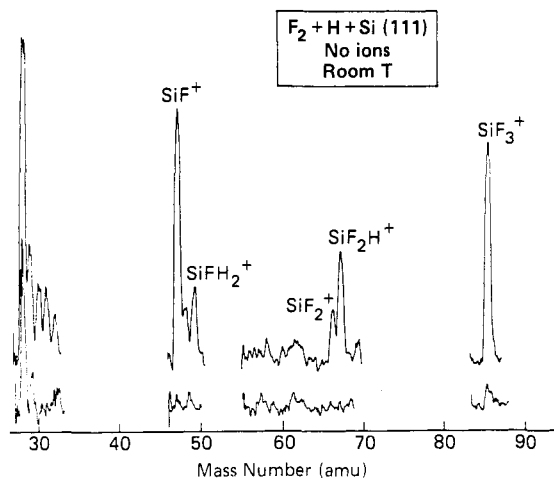


Figure 5. The products observed with the modulated beam mass spectrometer with fluxes of F₂ molecules and H atoms (upper trace) and H₂ molecules (lower trace) incident on Si(111) at room temperature without ion bombardment. The fluorine flux is about 2 x 10¹⁵ molecules/cm²sec and the hydrogen flux is about 8 x 10¹⁵ molecules/cm²sec. The hydrogen dissociation with the microwave discharge on (upper trace) is about 20%. The peak at mass 28 is partly due to an impurity in the injected gases.

Pd-CATALYSED REACTIONS OF HYDROGEN WITH FLUORINE AND CHLORINE

In the course of these studies, efforts have been made to search for non-etching reactions on surfaces other than silicon. It is possible that reactions occurring on the reactor walls or on metal masks (ref. 3) are influencing the concentrations of species in the gas phase in actual plasma processing environments. In this context, a polycrystalline Pd surface was found to catalyse very efficiently the reaction $H_2 + F_2 \Rightarrow 2HF$ at room temperature. The production of HF on the Pd surface was at least two orders of magnitude larger than on other surfaces in the system which included Ni, W, Ti, Cu, stainless steel and Si. The reaction is self-poisoning requiring excess hydrogen. If the reaction is poisoned by excess halogen, the reaction does not usually restart when the excess hydrogen flow is restored. The reaction can be reinitiated either by briefly shutting off the fluorine or by ion bombarding the surface for a few seconds. The reaction probability for the F₂ molecules (with excess H₂) is close to unity.

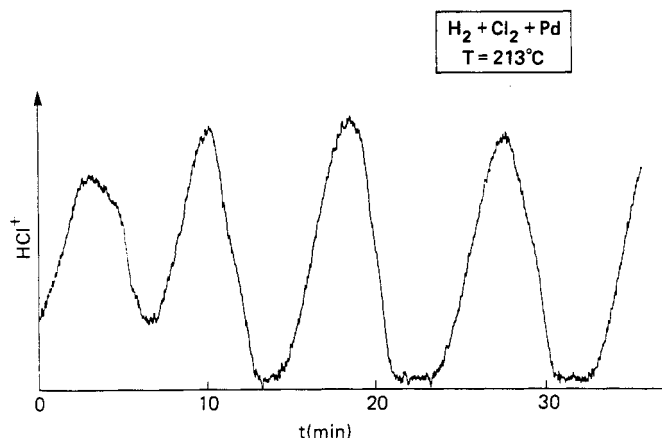


Figure 6. The oscillatory behavior of the HCl evolved from a polycrystalline Pd surface exposed to constant fluxes of H_2 ($\approx 1.6 \times 10^{15}$ molecules/cm²sec) and Cl_2 ($\approx 1.9 \times 10^{14}$ molecules/cm²sec). The Pd temperature is 213°C and there is no ion bombardment of the Pd surface.

A similar reaction between H_2 and Cl_2 has been observed but not at room temperature. The Pd surface must be heated to above about 160°C before the reaction will take place with high efficiency. In this system, when the hydrogen flux is decreased to near self-poisoning conditions, the rate of formation of HCl oscillates with a change in amplitude of about a factor of 20 and a period of the order of 10 minutes as shown in Fig. 6. No such oscillation has been found yet for the hydrogen-fluorine reaction. The detailed mechanism responsible for this oscillatory chemical reaction is not yet known but the participation of hydrogen absorbed in the bulk Pd is believed to be important. The elegant spatiotemporal concentration patterns responsible for the oscillatory oxidation of CO on Pt(110) reported by Ertl and coworkers (ref. 4) may also be playing a role in this system but facilities to observe such intriguing phenomena are not available in our apparatus.

SUMMARY

The proliferation of multicomponent etch gas mixtures currently used in plasma-assisted etching has created a need for a better understanding of the surface science issues associated with these processes. The use of two independently controllable sources of atoms/molecules as well as an energetic ion beam in an ultrahigh vacuum environment offers great opportunities for investigating a virtually unexplored but very complex area of surface science. The phenomena which are summarized in this paper are: 1) A Cl_2 -enhanced reaction of F atoms with Si(111); 2) A H atom-enhanced reaction of F_2 with Si(111); and 3) A Pd-catalysed reaction of H_2 with both F_2 and Cl_2 and the oscillatory behavior of the latter reaction.

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