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Time-of-flight study on the thermal etching of AI with Cl₂

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A pseudorandom cross-correlation technique has been used to study the thermal etching of aluminum with molecular chlorine. Time-of-flight (TOF) distributions of particles desorbing from the substrate are measured by modulating the ejected product beam. Modulation is achieved by a rotating chopping disk with slots in a pseudorandom sequence on its periphery. TOF distributions and temperature-dependent reaction product yields are measured for the products desorbing from the chlorinated aluminum substrate in the temperature range from 300 to 900 K. A reaction mechanism will be discussed in some detail.

Many questions concerning the fundamental chemical and physical mechanisms underlying plasma etching are still unanswered. Investigations on this subject are often hampered by the complexity of the problem. Plasma etching is therefore frequently studied by separately investigating the various processes that are of importance.1 To understand at least part of the reaction mechanisms in these isolated processes, the measurements of mass, velocity, and angular distributions of reaction products under "ideal" conditions, i.e., in ultrahigh vacuum, using well-defined surfaces and well-defined molecular and ion beams are helpful.¹ Measurements of mass distribution will give information on the chemistry and measurements of velocity and angular distributions on the kinetics of the reaction mechanism. As will be shown later energy distributions can also provide information about the type of desorbing molecules.

One of the processes taking place in plasma etching, which has been studied extensively, is ion beam assisted chemical etching.¹⁻³ Another important process in plasma etching, taking place in ion beam assisted chemical etching as well, is thermal etching, i.e., etching of a surface in the absence of energetic radiation. Here we describe a measuring technique that is used to study thermal etching by obtaining time-of-flight distributions of (neutral) reaction products. As an example, some results on the thermal etching of Al with Cl_2 will be given.

The usual way of obtaining neutral particle energy distributions is to measure the time that those particles need to travel a path of a known length, i.e., obtaining a time-offlight (TOF) distribution. The experiments of our interest are often hampered by the low signal-to-noise ratios involved, which lead to relatively long measuring times. One important cause of the low signal-to-noise ratio is the actual measuring technique itself that is used. In the conventional TOF technique the particle beam is transmitted during a very short gate time. A factor that affects the signal-to-noise ratio in this case is the ratio of the gate time to the time between successive gate openings: the transmission. Together with the channel width of the analyzer, the gate time determines to a large extent the time resolution of the TOF distribution. High resolution requires a short gate time. On the other hand, the time between successive gate openings has to be long to prevent interference between slow and fast particles that have passed the gate during different gate openings. These two requirements lead to a low transmission (less than 1% in most cases) and therefore a low signal-tonoise ratio and long measuring times.

A TOF technique that does not have the disadvantage of a low transmission is the pseudorandom cross-correlation chopping technique.⁴⁻⁷ In this technique the outcoming or incoming particle beam is transmitted according to a pseudorandom sequence, while the times between successive gate openings are of the same order as the gate time. The timedependent signal obtained is deconvoluted according to the pseudorandom sequence used, giving the actual TOF distribution. This technique leads to a considerable increase of the transmission (up to 50%) without loss in resolution. It has been shown that the gain in measuring time to achieve equal statistical accuracy using the pseudorandom technique depends on the signal-to-noise ratio.⁴ The gain is larger than unity if the mean signal is smaller than approximately twice the noise. If the signal-to-noise ratio is much smaller than unity, the (maximum) gain $\simeq (1/4)N$, where N is the number of pseudorandom sequence elements (in our case N = 63).

The experimental setup is given schematically in Fig. 1. In an ultrahigh vacuum (UHV) environment a sample is exposed to a beam of reactive gas molecules. The sample can be heated from the rear by a small oven. A thermocouple is used to measure the substrate temperature. The beam of reaction products, which are formed at the sample surface and subsequently desorb, is modulated by a UHV compatible chopper disk. Slots are situated at the periphery of the disk, in two pseudorandom sequences of 63 elements long. The



FIG. 1. Schematic drawing of the experimental setup.

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disk is driven by a motor of which the rotor is magnetically suspended. Because of the low friction of the magnetic suspension, a constant and smooth rotation of the disk with a frequency up to 400 Hz can safely be achieved, giving a minimum channel width of $\sim 20 \,\mu s$. After traveling a flight path of 290 mm the particles are detected time dependently in a quadrupole mass spectrometer (Extranuclear QMS). To allow angle-dependent measurements, the QMS can be rotated inside the vacuum chamber. The particle counts are fed into the channels of a multichannel analyzer. To synchronize the rotation of the chopper disk and the advance of the channels of the multichannel analyzer, the drive and advance frequencies are directly coupled. The time-dependent signal obtained is deconvoluted using an HP 9820 computer. Since the efficiency of the ionizer of the QMS is inversely proportional to the velocity of the particles, a correction for this effect is applied in the computation of the spectrum.

Mass spectrometric measurements on thermal etch reactions are often hampered by the fact that the type of reaction products cannot be accurately determined because of the cracking by the ionizer of the mass spectrometer before detection. We will show that the TOF technique provides a method to determine the parent molecules of the detected ions. In our experiments the measured TOF distributions could all be simulated with Maxwell-Boltzmann (MB) distributions or compositions of MB distributions. If the temperature T of particles desorbing from the surface is assumed to be equal to the (measured) temperature of the substrate, only one parameter (mass m) is left, and fitting of the experimental data becomes relatively simple. By measuring TOF distributions it is possible to distinguish signals originating from different parent molecules. Since reaction products have energy distributions that can be characterized by the same T_{r} , reaction products with a different mass will give rise to shifted flight-time distributions. A TOF distribution measured for a specific m/e value can therefore consist of several contributions, each corresponding to a MB distribution at a different mass. It is possible to fit measured spectra with composed distributions consisting of more MB distributions at different masses. This enables us to determine the relative contributions of parent molecules to the yield of the detected ionized particles.

The thermal etching of aluminum with chlorine has been studied by several investigators.⁸⁻¹³ It was found that Cl₂ etches Al spontaneously at a high rate, even at room temperature.9,11,12 Chlorine is adsorbed on the Al surface in a physisorbed and a chemisorbed layer.⁸ Al₂Cl₆ and AlCl₃ are formed as the major reaction products at low temperature (300 K) and high temperature (480 K), respectively.¹¹ We have investigated the thermal etching of Al with Cl₂ in the surface temperature range from 300 to 900 K and at a Cl_2 flux of 7×10^{16} molecules cm⁻² s⁻¹ by measuring TOF distributions and the temperature dependence of the AICl⁺, $AlCl_2^+$, and $AlCl_3^+$ ion signals. The Cl_2 flux used gives a background pressure of 1×10^{-6} mbar. At the time of these experiments the mass spectrometer configuration that was used did not allow detection of particles with m/e > 140. The reported reaction product Al_2Cl_6 (m = 268) and its fragment $Al_2Cl_5^+$ (m = 233) could therefore not be observed

directly in the present experiments. TOF distributions of Cl₂, reflected or desorbed from the surface, were measured at three surface temperatures, T = 440, 720, and 800 K. The mass spectrometer and the target were positioned in such a way that the specular reflected beam was not seen. It appears that the TOF spectra obtained are for the major part (90-95%) MB distributions at the measured temperature of the surface and the mass of $Cl_2(m = 70)$ and for the remaining part at the temperature of the original Cl_2 beam (290 K) and m = 70. This indicates that chlorine easily physisorbs on the Al surface and/or a chlorine-covered Al substrate and has a sufficiently long residence time to acquire the temperature of the surface. The temperature of the sample was measured at a position in between the sample and the oven. The Cl₂ desorption measurements show that the temperature derived from the thermocouple signal corresponds to the surface temperature very accurately.

The reaction products that we find from measured ion signals and TOF distributions in the etch reaction of Al with Cl₂ are Al₂Cl₆, AlCl₃, and AlCl. TOF measurements of the AlCl⁺ signal at three temperatures are displayed in Fig. 2. At T = 410 K, the measured TOF distribution can be simulated with a MB distribution at mass m = 268 (Al₂Cl₆), at T = 625 K with mass m = 134 (AlCl₃), and at T = 870 K with mass m = 62 (AlCl). (Note that only the most probable mass of the isotopic manifold is indicated.) These measurements clearly show that the method applied here enables us to determine the parent molecules of the detected ion very well. In Fig. 3 temperature dependences of the reaction product yields are presented. The variations of the Al₂Cl₆ and AlCl yields with temperature are derived from the $AICl^+$ ion signal and that of the $AICl_3$ yield from the $AICl_2^+$ signal. Al₂Cl₆ is the major reaction product at temperatures below ~450 K and AlCl₃ between ~500 and 650 K. At temperatures above ~700 K AlCl becomes the main reaction product and above ~800 K the etch reaction yields exclusively AICl. In the temperature range between 375 and 500 K it is shown that the AlCl₃ signal increases and the Al₂Cl₆ signal decreases with increasing temperature. This



FIG. 2. Time-of-flight distributions and the best fits of the AlCl⁺ ion (m/e = 62) at three temperatures T = 410, 625, and 870 K. The spectra can be simulated with Maxwell-Boltzmann distributions at mass m = 268 (Al₂Cl₆), m = 134 (AlCl₃), and m = 62 (AlCl), respectively.

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FIG. 3. Temperature dependences of the reaction products AI_2CI_6 (dotteddashed line and O), $AICI_3$ (dashed line and Δ), and AICI (solid line and \times). The signals have been corrected for the velocity dependence of the ionization efficiency of the mass spectrometer.

indicates that the desorption of Al2Cl6 is terminated in favor of the ejection of AlCl₃. The decrease of the AlCl₃ signal and the large increase of the AlCl signal both start at about the same temperature: \sim 700 K. This suggests that the decrease of the AlCl, formation is actually due to the onset of AlCl evaporation. At high temperatures (>725 K), we clearly see that the AlCl desorption increases drastically, while at temperatures below 700 K, where AlCl is not observed yet, the AlCl₃ signal increases slightly. It should be noted that Fig. 3 does not give much information about the relative yields of reaction products with respect to each other, because the ionization probabilities and cracking patterns of AlCl, AlCl₃, and Al₂Cl₆ in our mass spectrometer are not known. The signals are presented in the same ratio as they are actually detected. Neither measurements of Cl₂ reflecting from the surface nor mass spectral measurements of the detected AlCl⁺, AlCl₂⁺, and AlCl₃⁺ ions, however, show a largely varying etch rate for temperatures below 700 K. We do not therefore expect large deviations from the presented yields.

On the basis of our experimental results, we tentatively propose the following model for AlCl₃ and Al₂Cl₆ formation. When Cl₂ interacts with the Al surface, it can reflect, physisorb, or chemisorb by direct impact. From the physisorbed layer the chlorine can either desorb or chemisorb, forming a chlorinated aluminum layer.¹¹ After chemisorption reaction products like, e.g., AlCl can be formed on the surface. This Al-Cl complex seems to have a high binding energy with the substrate.⁸ As shown here for $T \leq 650$ K, AICl cannot desorb. If chlorine diffuses into the substrate, AlCl₃ is formed. It is likely that Al_2Cl_6 is formed in the chlorinated surface layer from two AlCl, molecules. If desorption of AICl₃ is relatively slow, two AICl₃ molecules on the surface will combine to form the energetically more favorable Al₂Cl₆ dimer. If Al₂Cl₆ desorption is slow as well, an equilibrium in the AICl₃ and Al₂Cl₆ surface concentrations will develop, viz., $2AlCl_3 = Al_2Cl_6$. From this state AlCl₃ and Al₂Cl₆ can desorb. According to the temperature dependence of the AlCl₃ and Al₂Cl₆ yields, the equilibrium position is temperature dependent. Below ~ 400 K, the equilibrium is to the right, while above 500 K, AlCl₃ is the only detected species. In this case the desorption rates are not of importance. If Al₂Cl₆ desorption is a very fast process, we cannot speak of an equilibrium. The temperature dependence of the AlCl₃ and Al₂Cl₆ formation is then explained by assuming that two competing pathways are involved in the reaction mechanism: direct desorption of AlCl₃ and desorption of Al₂Cl₆ after dimer formation from AlCl₃ molecules. Below 400 K only desorption of Al₂Cl₆ takes place. Above 500 K, surface residence times of AlCl₃ molecules have become too short to allow Al₂Cl₆ formation. The fast increase of the AICl signal above 700 K can be explained in two ways. First, direct desorption of AlCl from the surface can occur. The indiffusion of chlorine decreases and hence less AlCl₃ is formed. Second, the entire process can be described by the reaction $AlCl_3 = AlCl + Cl_2$. For T > 800 K the equilibrium is to the right.

We can conclude that the pseudorandom cross-correlation technique using mechanical chopping by a chopper disk is very well suited for measuring time-of-flight distributions. This type of measurement enables us to determine the type of products formed in a reaction if the temperature of the ejected particles is known. Using this technique we investigated the thermal etching of aluminum with molecular chlorine. TOF distributions and temperature-dependent reaction product yields were measured. The main reaction products are Al₂Cl₆ at low temperature (<450 K), AlCl₃ at medium temperature (between 500 and 650 K), and AlCl at high temperature (>700 K). A large part of the chlorine incident on the Al surface initially physisorbs and subsequently desorbs with a MB distribution at the substrate temperature.

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