LASER VAPORIZATION/FTMS AS A PROBE OF SILICON SURFACE REACTIVITY

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Received 18 November 1987; accepted for publication 24 February 1988

Exposure of a silicon surface to several reagent gases followed by laser vaporization produces unusual ions in addition to the silicon cluster ion (Si_n^+) distribution typical for clean silicon surfaces. The appearance of these ions is correlated to silicon surface reactions. Laser vaporization of silicon following exposure to the gases NH₃, XeF₂, CF₃I, O₂, NO, CH₃OH, H₂O, C₂H₄, D₂, and CH₄ has been studied. Changes in the relative intensities of product ions as a function of exposure are measured for some of the reagent gases. The results from laser vaporization/Fourier transform mass spectrometry (FTMS) are compared to studies of silicon surface reactions using other experimental techniques and to some secondary ion mass spectrometry (SIMS) results.

1. Introduction

Laser vaporization or laser desorption using a pulsed laser to produce gas-phase ions can be used in conjunction with mass spectrometry to study a variety of systems. The technique is useful in analytical mass spectrometry to desorb species from surfaces [1-3], either to study the surface or the gas-phase vaporized ions or neutrals. It is especially useful in conjunction with Fourier transform ion cyclotron resonance mass spectrometry (FTMS) [3-8], due to the pulsed nature of both techniques and to the high vacuum requirements of this type of mass spectrometry. Laser vaporization has been used as a cluster ion source in FTMS to produce a variety of cluster ions, including silicon (Si⁺_n), in order to study their reactivity [4-8]. One goal of this type of study is the comparison of the silicon cluster ion chemistry to reactions on silicon surfaces [5,7,8].

In this paper, we show that laser vaporization/FTMS can provide a probe of the chemistry of silicon surfaces. Following exposure of a silicon surface to a reagent gas, laser vaporization produces unique ions in addition to the usual silicon cation cluster distribution Si_n^+ , n = 1-6, which is observed from a clean

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0039-6028/88/\$03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) silicon surface. These product ions may be correlated to known surface reactions of silicon. The relative abundance of the product ions compared to the Si_n^+ species increases as a function of exposure of the gas to the surface, which provides a probe of the kinetics of the surface reaction. To our knowledge, this type of measurement of silicon surface reactivity has not been previously reported, although it is similar to laser desorption/FTMS studies of neutrals from platinum surfaces as a probe of surface reactions [3].

Secondary ion mass spectrometry (SIMS) has been used to sputter ions from silicon and other surfaces which are related to surface reaction products [9-14]. The secondary ions can be used to study the exposure dependence and depth dependence of surface reactions. Laser vaporization differs from SIMS in several respects. The Q-switched laser pulse has a length of 10-20 ns, in contrast to a SIMS ion or neutral beam which generally operates continuously, although pulsed beams with narrow pulse widths are used in time-of-flight (TOF) mass spectrometry due to the pulsed nature of the technique. The pulsed nature of the laser and the FTMS facilitate the measurement of time, or exposure dependence, for the production of these ions. The laser can be easily focused to small spot sizes, as in the laser microprobe technique (LAMMA) [2], allowing high spatial resolution. Since the mechanisms of desorption and ionization for SIMS and laser vaporization are quite different, with that of laser vaporization being much more complex and not as well characterized as SIMS, one might expect different distributions of ions to be produced for some systems. Laser vaporization is generally the desirable technique for FTMS, since the FTMS cell must be located in a strong magnetic field, which puts geometrical constraints on the ion source. More detailed experimental considerations will be discussed in the next section.

We have used laser vaporization/FTMS to study the effects of exposure of a silicon surface to the gases NH_3 , XeF_2 , CF_3I , O_2 , NO, CH_3OH , C_2H_4 , D_2 , and CH_4 . Most of these reactions are of technical interest in semiconductor device processing applications, and have been studied extensively with other experimental techniques. The observed vaporized ions are reported, and exposure dependences of some of the reactions are discussed. These results are compared to studies of the surface reactions by other analytical techniques.

2. Experimental

The experimental apparatus has been described in previous publications [4,5,15]. The laser vaporization is performed with the output of a frequency doubled Quanta-Ray DCR-2 Nd: YAG laser (532 nm, 5–10 mJ/pulse, 20 Hz repetition rate) focused to a 0.5 mm spot size (100–200 MW cm⁻²) on the sample with a 1 m lens. The sample is a piece of single crystal silicon (p-type, 0.2 Ω cm) and is mounted even with the bottom (excitation) plate of a 2.5 cm

cubic ion cyclotron resonance cell. The cell is situated in a vacuum chamber between the pole caps of a 1.0 T electromagnet which have a clearance of 5 cm. The cell trapping plates are parallel to the pole caps. In a previous paper we have discussed the advantages and disadvantages of using this experimental geometry [16]. In brief, the spatial constraints and the strong magnetic field perpendicular to the pole caps make it difficult to install other instruments to prepare and characterize the surface (e.g. an ion gun, accurate temperature controllers, or XPS or Auger instruments). Therefore, all reactions are studied at 300 K, and the laser is used both for surface cleaning and as a reaction probe, as discussed later.

The laser pulse results in vaporization of both ions and neutrals from the sample. The ions are trapped in the cell and detected by the technique of Fourier transform mass spectrometry (FTMS), which has been discussed in detail previously [17–19]. To summarize, ions are trapped for up to several seconds in the cell by parallel magnetic (1.0 T) and electric (2.0 V) fields. Ions are detected by first exciting them to larger coherent cyclotron orbits using a swept radio frequency excitation pulse. The coherent motion of the ions induces a transient image current on the cell detection plates, which is digitized and stored. Up to several thousand experimental cycles can be summed for signal averaging, after which the signal is Fourier transformed to obtain the frequency spectrum of all the ions in the cell. The frequency spectrum is converted to a mass spectrum using the known magnetic field. A Nicolet FTMS/1000 data system was used in these experiments for data collection and manipulation.

The vacuum system has a typical base pressure of $< 5 \times 10^{-9}$ Torr. To study reactions, the reagent gas is maintained in the cell at a constant pressure of $(1-5) \times 10^{-7}$ Torr. Exposure of the surface to the gas is controlled by varying the laser repetition rate from 20 to < 0.1 Hz. The longer times between laser pulses allow the surface to react with the reagent gas at a constant pressure. Alternately, the exposure can be varied by keeping the laser repetition rate constant and changing the pressure of the reagent gas in the vacuum chamber from 5×10^{-8} to 5×10^{-6} Torr. For the studies reported here, variation of the laser repetition rate is used to control the exposure due to the better resolution obtainable in changing the time delay rather than the pressure. However, this requires manual adjustment of the laser to maintain constant power as the repetition rate is changed. The FTMS experimental cycle time period is varied by changing the length of the quench pulse which is applied to the cell trapping plates to eject the ions. Ions are detected as soon as possible (the minimum time necessary to perform ion excitation, etc., is approximately 3 ms) after formation to minimize gas-phase ion/molecule reactions with the reagent gas.

The sample was not pretreated, e.g. by cleaving, annealing, or ion sputtering, before introduction into the vacuum chamber. Laser vaporization removes foreign material from the surface at the vaporization site. When the laser focus is repositioned to irradiate a new location, only a few laser shots are required to remove all contaminants from the surface and produce only Si_n^+ species in



Fig. 1. Laser vaporization mass spectrum of silicon sample with one laser pulse, (a) before, and (b) after exposure of the sample to 5 L NH₃. The Si⁺ ion (m/z = 28) is ejected from the cell, but is 10 to 20 times as intense as Si⁺₂ in (a) and Si₂N⁺ in (b).

the mass spectrum. In addition, after pumping out the reagent gas, only one or two laser shots are required to eliminate all surface product ions and restore the Si_n^+ distribution. Therefore, qualitatively, one laser pulse removes enough material from the surface to expose a silicon surface which is void of major contaminants. This observation is consistent with cratering studies at comparable laser powers, for which it is reported that 10 to 1000 monolayers of material are removed per laser pulse [1]. It is also consistent with studies of laser desorption of neutrals from metal surfaces [3], for which one laser pulse is sufficient to remove adsorbates from the surfaces.

A more quantitative measurement of the surface cleaning efficiency of the laser pulses was performed by monitoring the reaction of the surface with NH₃. This is a practical reaction to study since a large abundance of the Si_2N^+ ion is produced. Fig. 1a shows the Si_n^+ distribution before exposure to NH₃. The Si⁺ atomic ion is ejected from the cell in all the experiments by resonant frequency ejection of m/z = 28 during ion formation, because the Si^+ signal is 10 to 20 times more intense than that of Si_2^+ . The peaks from ²⁹Si⁺ and ³⁰Si⁺ isotopes were not ejected and are still present in the mass spectrum. After exposure to 5 L (1 Langmuir = 10^{-6} Torr s) of NH₃, the spectrum in fig. 1b is observed. The Si_2N^+ ion is the predominant peak, and a small amount of $SiNH_2^+$ is observed, while the Si_n^+ species are much lower in relative intensity. The mass spectrum in fig. 1b was obtained with one laser pulse, and is effectively identical to those obtained by signal averaging several experimental cycles. This demonstrates that surface heating or effects due to multiple laser pulses during signal averaging do not alter or contribute to the observed signal.

Fig. 2 shows the exposure dependence of the relative intensity of Si_2N^+ compared to the total ion signal. The exposure was varied by changing the laser repetition rate at a constant pressure. It is clear that the amount of



Exposure (L)

Fig. 2. Exposure dependence of the ratio of the relative intensity of Si_2N^+ to the total ion signal. The pressure in the cell is 1.5×10^{-7} Torr, measured with an uncorrected ionization gauge.

 Si_2N^+ produced approaches zero at zero exposure, within the approximately 10% scatter of the data, even when the reagent gas is present at a constant pressure in the cell. This result, which is observed for the other reactions as well, provides convincing evidence that each laser pulse removes ~ 90% of the reactants and reaction products on the surface to expose a clean silicon surface layer. This result is very convenient experimentally, since it allows the laser pulse to be used both to detect products and to clean the surface for the next reaction cycle. This allows fast repetitions of the measurements, and avoids slow and laborious surface cleaning procedures which can be time consuming for kinetics measurements. The only long term deleterious effect observed in these experiments is a gradual decrease in the total ion intensity over several hours as a hole is formed in the sample. The signal is restored by relocating manually the laser focus, and using several laser pulses to clean the new location.

There are several disadvantages to the technique, however. There is considerable shot-to-shot variation in the relative amounts of ions formed, as is evident in fig. 2. Every point in the figure is from a mass spectrum obtained by averaging 100 experimental cycles. The variation in signal may have several sources. There is some shot-to-shot variation in the laser power, which affects the amount of vaporization. However, variation in the number of ions produced per pulse cannot be accounted for using only the laser power fluctuations. There may also be some contribution from residual surface products which are not removed by each laser pulse. In addition, the mechanism of ionization by laser vaporization is not well understood, and may depend on small variations in the laser and surface characteristics.

Since the vaporization is very energetic, and occurs at temperatures on the order of 10^4 K [1], the nature of the surface may vary somewhat from pulse to pulse. Several groups [20,21] have studied the nature of the laser-heated silicon surface, although more work is necessary for a detailed understanding of the surface chemistry. Since the vaporization process may alter the surface structure, it is difficult to study the kinetics of well-ordered crystalline faces. It is also difficult to determine directly the surface species which give rise to the observed ions. The observed ions may be formed for kinetic or energetic reasons in the laser plasma, rather than being structurally identical to surface species. This problem is also common in SIMS studies [10–14]. However, comparisons to past studies using other surface techniques can provide insight into the surface reactions.

With the present apparatus, it is difficult to analyze the observed kinetics. The dependence of the vaporized product ions on exposure has a reproducible time dependence. Since the laser only cleans a small area of the surface, there may be contributions from surface diffusion as well as from gas-surface collisions. Multiple layers of chemisorbed and physisorbed gas can accumulate on the rest of the surface. so molecules may diffuse to the clean (irradiated)

area to contribute to the observed product ion signal. There are indications that this is a large effect at pressures higher than approximately 5×10^{-6} Torr. More detailed diagnostic experiments, such as temperature programmed desorption or pulsed dosing of the surface, in conjunction with laser vaporization, can be used to understand the contributions to the kinetics.

3. Results and discussion

Table 1 shows a list of the reagent gases which were studied, and the corresponding vaporized ions which were observed in addition to the Si_n^+ ions. In the following sections, each reaction is compared to representative studies from the literature using other experimental techniques, although no attempt is made to exhaustively review the literature. In general, a correspondence is observed between previously observed surface reactions and the laser vaporized ions, although there are a few unexpected exceptions.

3.1. NH₃

Table 1

As shown in fig. 1, the predominant ion observed following exposure of the sample to NH_3 is Si_2N^+ , with a smaller amount of $SiNH_2^+$. These ions are different from the products from gas-phase ion/molecule reactions of Si_n^+ at 300 K, in which $SiNH_2^+$ is the major product ion from the reaction of Si^+ and Si_2^+ with NH_3 [5]. The Si_2N^+ ion is only one of several minor products of the reaction of Si_3^+ with NH_3 [5]. Since the predominant ion formed by laser vaporization is Si^+ , gas-phase reactions would be expected to yield primarily $SiNH_2^+$. In addition, the exposure dependence shown in fig. 2 is not consistent with gas-phase reactions since the background gas pressure and trapping time of the ions were constant for these measurements. Therefore, gas-phase reactions, either at 300 K or at elevated temperatures, do not significantly contribute to the observed product ions.

Reagent gas	Ions (in addition to Si_n^+)	
NH ₃	Si_2N^+ , $SiNH_2^+$	
XeF ₂	SiF ⁺	
CF ₁ Ī	SiF ⁺ , SiI ⁺	
O ₂	Si ₂ O ⁺	
NO	$\tilde{Si_2N^+}$, Si_2O^+	
CH ₂ OH	SiOCH ⁺	
H ₂ O	SiOH ⁺ , Si ₂ O ⁺	
C_2H_4 , C_2H_4 , C_2H_2	$Si_nC_2H_x^+, n = 1,2,3; x = 1,2$	
D_2, CH_4	None	

Ions observed by laser vaporization after exposure of the silicon sample to the reagent gas

The Si_2N^+ ion has been observed from several systems using SIMS. This ion was observed from a silicon surface exposed to NH₃ and sputtered with a fast-atom beam in a ZAB-2F sector mass spectrometer [22]. It was also observed as an intense ion from SIMS of silicon Libride [11], and from silicon reacted with N atoms [12]. Laser vaporization of a mixture of silicon powder and boron nitride also produces a large abundance of Si_2N^+ [16,23]. Therefore, Si_2N^+ is probably very stable energetically, since it is easily formed from either sputtering or in a laser-generated plasma from surfaces containing silicon and nitrogen.

The reaction of NH₃ on Si(100) and Si(111) has been studied previously using other surface techniques [24-29]. Bozso and coworkers [24,25] suggest that Si(100) reacts rapidly with NH₃ at temperatures as low as 70 K, and that the NH₃ molecules are completely dehydrogenated so that the H atoms occupy Si dangling bonds. Studies by Kubler and coworkers [26,27] suggest that on Si(100) and Si(111) the N atoms are not completely dehydrogenated, so species of the type NH_x, for x = 1 or 2, exist on the surface. In either case, NH₃ hapidly chemisorbs on the surface at 300 K at low pressure. A study by Kilday et al. [28], however, suggests that no reaction occurs at 300 K.

These observations taken together suggest that in the present experiments NH_3 chemisorbs on the surface and accumulates during the exposure. The laser pulse then vaporizes the products from the surface reactions, which results in the formation of Si_2N^+ as the most stable gas-phase ion. Since this ion may not necessarily be identical to the surface species, it is not possible at this time to determine whether the NH_3 is completely dehydrogenated on the surface. It is also uncertain how the surface structure formed following laser vaporization compares to the crystal structures that have been studied previously.

3.2. XeF₂

Laser vaporization following exposure to XeF_2 produces only SiF⁺. This is a major product of the gas-phase reactions of Si⁺_n with XeF₂ [8], although other product ions in addition to SiF⁺ are observed.

This reagent gas is used extensively in semiconductor device etching, although the reaction conditions are typically very different from those in the present FTMS studies. Several studies have been done on the low-pressure, low-temperature reactions of XeF₂ with silicon [30–35]. It has been shown that prolonged reaction of silicon with XeF₂ produces several surface layers of mono-, di-, and tri-fluorinated silicon species [31,35]. Therefore, an effort was made to observe the vaporized ions SiF₂⁺ and SiF₃⁺, which could be indicative of these layers. However, after exposing the surface to approximately 7×10^3 L XeF₂ at 1×10^{-6} Torr total pressure, no fluorine containing ions other than SiF⁺ were observed. The partial pressure of XeF₂ in the cell was difficult to

determine accurately, due to the partial decomposition which occurs in the inlet and vacuum chamber. The XeF_2 pressure may have been as little as 10% of the measured pressure, making the actual exposure less by a factor of 10. The amount of etching estimated using the steady state etch rate [34] for this exposure is approximately 6 nm of the silicon surface.

The $\operatorname{SiF}_{x}^{+}$ (x = 1-4) ions were observed in the FTMS, however, using electron impact to ionize the gas-phase species in the cell, but without the use of the vaporization laser. This observation indicates that neutral SiF₄ is formed by etching of the silicon surface with XeF₂. Therefore, multiply fluorinated silicon species may exist on the surface as suggested by the previous studies [31,35]. Laser vaporization of these surface species does not form the corresponding multiply fluorinated ions, however, possibly due to dissociation of larger species in the laser plasma to form only SiF⁺.

3.3. CF₃I

Vaporization following exposure to CF_3I produces SiF^+ and SiI^+ ions, with similar relative abundances. Exposure measurements show that the maximum amounts of SiF^+ and SiI^+ , compared to the total ion signal, are formed with an exposure of greater than 1 L. The ratio of the sum of the relative intensities of both ions compared to the total ion signal is 0.6–0.8. The exposure dependence is similar to that of the NH_3 reaction and has the same zero intercept at zero exposure.

Several halomethanes, including CF_3I , are used in etching as sources of F atoms or CF_3 radicals in plasmas or by photolysis. The molecules themselves, however, are very inert and have small sticking coefficients at 300 K [33,36–38]. Therefore, it is surprising that vaporized product ions are observed for this reagent gas, since chemisorption of CF_3I on the surface at a rapid rate is not expected, in contrast to the behavior of NH_3 and XeF_2 .

Some possible explanations for the observations can be proposed. One possibility is that the laser pulse photolyzes physisorbed molecules, and that the fragments react with the surface or with vaporized silicon species. This mechanism is unlikely for several reasons. First, the sticking coefficient of CF₃I is estimated from other halomethanes to be 10^{-6} to 10^{-7} for physisorption [33,38]. Therefore, after 1 L of exposure there should be on the order of 10^{-6} monolayer of CF₃I present on the surface at the time of the laser pulse. For a laser spot size of 0.5 mm, approximately 10^{6} molecules of CF₃I are available on the surface for reaction. Since the laser vaporization ionization efficiency is typically 10^{-4} – 10^{-5} , there would be on the order of 10^{2} ions produced which contain F or I atoms. The ions could not be detected, since the minimum sensitivity of the FTMS instrument used in this study is ~ 10^{3} ions. In addition, the exposure dependence and relative intensities of the SiF⁺

and SiI⁺ compared to Si⁺_n are not consistent with a small number of ions being formed by a slow physisorption process. In the gas-phase, the thermal ion/molecule reactions of Si⁺_n with CF₃I yield primarily CF₂I⁺ and some SiI⁺, but no SiF⁺ is produced at 300 K. Therefore, gas-phase reactions of Si⁺_n ions with CF₃I which may be desorbed by the laser cannot account for the observed ions. It is possible that more complex high temperature or plasma reactions are involved, although this seems unlikely.

A more plausible explanation for the observations is that the laser vaporization produces a very reactive Si surface structure which is characterized by many defects and dangling bonds. This structure may be reactive enough to attack even the inert CF_3I molecule. The molecules can then dissociatively chemisorb on the surface, so that they rapidly accumulate and are vaporized by the laser pulse. This suggests that the surface is much more reactive than crystal faces such as Si(100) or Si(111) which are typically studied. It may be informative to study this reaction in conjunction with other surface techniques.

3.4. O₂

After exposure of the sample to O_2 , Si_2O^+ was observed following laser vaporization of the surface. This ion was produced much more erratically than the product ions for the previous reagent gases studied, and thus no reasonable time dependence could be measured. The formation of Si_2O^+ qualitatively appeared to be much slower than the other exposure dependences.

The oxidation of several crystal surfaces of silicon has been studied extensively [11–14,39–45]. The surface readily oxidizes, but the rate depends on the surface structure. It is generally agreed that oxygen dissociates at least partially on the silicon surface, forming a layer of Si-O bonded species, until eventually a layer approximating a SiO₂ structure is produced. Since Si-O bonds are much stronger than Si-Si bonds, it is probably more difficult to vaporize the oxidized surface than the clean silicon surface. This is consistent with the observation that Si_2O^+ is formed erratically. The oxidized surface may be even more sensitive than the clean surface to variations which affect the formation of vaporized ions. Higher laser power can be used to break the Si-O bonds, but this tends to produce more atomic ions such as Si⁺, rather than the molecular or cluster ions which are characteristic of surface products. Higher energy (shorter wavelength) radiation can also be more effective for vaporization than the 532 nm used in the present experiments. For example, quadrupled (266 nm) Nd : YAG laser radiation has been used to laser vaporize silicon dioxide [46]. Another example of this type of dependence of laser vaporization ion yield on surface exposure and wavelength is observed for the reaction with NO.

3.5. NO

The ions Si_2N^+ and Si_2O^+ are observed sporadically following exposure to NO. When they are observed, these ions have a low relative abundance compared to Si_2^+ or the ²⁹Si⁺ and ³⁰Si⁺ isotopes of Si⁺, although the Si₂N⁺ ion is approximately two to three times as abundant as Si₂O⁺. Following exposure of the surface to greater than 1 L of NO, the number of ions vaporized by 532 nm radiation, including Si⁺_n, decreases dramatically, especially for n > 3. Ions were more reproducibly observed if frequency tripled Nd: YAG (355 nm) laser radiation was used, suggesting that strongly bound species are present on the surface.

In the NH_3 reaction, Si_2N^+ is the predominant ion in both the laser vaporization and SIMS mass spectra, which suggested that the ion was easily formed under laser vaporization conditions. This ion is observed by vaporization of a surface exposed to NO, but with only small abundances and the total amount of ionization is suppressed.

Results from previous studies of the reaction of silicon surfaces with NO [25,47] are consistent with these observations. These studies suggest that NO dissociatively chemisorbs on the silicon surface. At high temperatures, the surface rearranges to form a silicon nitride structure. Avouris et al. [25] observed that at low temperatures and exposures, the O atoms remain on the surface, and the N atoms occupy subsurface sites. The laser vaporization behavior can be interpreted in terms of the surface structure. Since NO dissociatively chemisorbs, strong Si-N and Si-O bonds form at the surface which may replace the Si-Si bonds. These strong bonds make it more difficult to vaporize species, as was the case with vaporization of the surface after oxidation by O_2 . Higher laser power produces more atomic ions rather than molecular ions, so that even a species that should be stable, like Si_2N^+ , is not observed in a reproducible manner. Therefore, this result illustrates that laser vaporization is sensitive to the nature of the surface structure, both in the types and amounts of ions produced. This is analogous to SIMS studies which show that ionization efficiency can depend on the nature of the surface [12,13].

3.6. CH₃OH

The most abundant product ion formed following exposure to CH_3OH and laser vaporization has a mass to charge ratio of 59, which corresponds to the formula SiOCH₃⁺. The exposure dependence observed with methanol is similar to that of NH₃. Previous studies of this reaction [48–50] have shown that methanol undergoes rapid dissociative chemisorption on the surface, forming methoxy groups and hydrogen atoms bound to the surface. The surface reaction product observed is analogous to the ion/molecule reaction observed for the gas-phase cluster ion Si_6^+ which reacts with methanol to form $Si_6OCH_3^+$ [5].

It is possible that the observed ion of m/z = 59 arises from vaporization of intact units of SiOCH₃ groups which are formed on the surface. The mechanism of ion formation is probably more complicated than this, however, since laser vaporization is such a high temperature process. It is unlikely that the entire SiOCH₃ group is removed intact from the surface in the high temperature laser-generated plasma. The structure of the m/z = 59 ion cannot be determined unequivocally, thus the ion may be a different, more stable isomer of SiOCH₃⁺ (e.g. HOSiCH₂⁺, OSiCH₃⁺ etc.). In addition, the formation of an ion of this mass in the gas-phase Si_n^+ reactions with CH₃OH for all n suggests that it is a very stable ion. Therefore, it is possible that the ion is formed due to its enhanced stability rather than because it is structurally related to the surface reaction product. However, as with the NH_3 reaction, the observation of the m/z = 59 ions, with similar exposure dependence to the NH₃ reaction, is reasonable evidence that the methanol rapidly chemisorbs and accumulates on the surface prior to laser vaporization. This is in reasonable agreement with previous studies [48-50].

3.7. H₂O

Vaporization following exposure to H_2O produces the ions SiOH⁺ and Si₂O⁺. The exposure dependences of these ions are shown in fig. 3. The ions have similar exposure dependences, and are also similar to that of the NH₃



Fig. 3. Exposure dependence of the ratio of the relative intensity of (a) SiOH⁺, and (b) Si₂O⁺ to the total ion signal. The pressure in the cell is 5.4×10^{-7} Torr, measured with an uncorrected ionization gauge.

reaction (fig. 2). At coverage of more than 1 L, the relative intensity of both vaporized ions is less than 15% of the total ion signal.

The reaction of H_2O with silicon has been studied in detail for several crystal structures [51,52]. These studies suggest that H_2O dissociatively chemisorbs onto Si(111) [51] and Si(100) [52]. When the surface is heated to > 700 K, the adsorbed species change from Si-OH and Si-H to a Si-O-Si structure similar to that formed from reaction with O_2 .

It is interesting that Si_2O^+ is observed in the laser vaporization of the H_2O reaction as well as the O_2 reaction. The similar exposure dependence of SiOH⁺ and Si₂O⁺, shown in fig. 3, suggests that both ions are produced from promptly-formed surface species. It is possible that the surface is so reactive that the Si-O-Si structure is formed at low exposures at 300 K, although the Si₂O⁺ could also be formed from vaporization of Si-OH species. Other surface techniques may be able to clarify this question.

3.8. C_2H_4 , C_3H_6 , C_2H_2

After exposure to the unsaturated hydrocarbons C_2H_4 , C_3H_6 , and C_2H_2 , laser vaporization produced ions of the type $Si_nC_2H_x^+$, for n = 1 to 3 and x = 1, 2, and 3. The most abundant ion observed corresponded to n = 1 and x = 1 for all the hydrocarbons. All of the ions had low relative abundances of less than 10-20% of the corresponding Si_{n+1}^+ signal. Therefore, these ions were difficult to observe for n > 3. The value of x depends somewhat on the hydrocarbon, for example only x = 1 and 2 are observed for C_2H_2 . The ons observed are quite similar to gas-phase ion/molecule reaction products of Si_n^+ with C_2H_2 [5].

Some studies of the surface reactions of C_2H_4 [53] and C_3H_6 [54] have reported that rapid chemisorption occurs, with partial dissociation of the hydrocarbon. Bozack et al. [54] find that a disordered surface caused by Ar⁺ bombardment is more reactive with C_3H_6 than an ordered surface. This is consistent with our previous discussion of the reaction of CF₃I. However, due to the small amounts of product ions observed for the hydrocarbon reactions, it is difficult to form any conclusions about the nature of the reactions.

3.9. D_2 , CH_4

No vaporized ions other than silicon cation clusters (Si_n^+) were observed after exposure to at least 10 L of either D₂ or CH₄. This is consistent with the unreactive nature of these gases with silicon surfaces [33,55], and therefore no chemisorbed surface products are formed before vaporization. This result may not be conclusive, however, because vaporized ions of the type Si_nH_x⁺ are not observed in any of the reactions in this study, even though several of the reactions involve dehydrogenation to form H atoms on the silicon surface. It is possible that this type of ion is difficult to make by laser vaporization of silicon, or that it dissociates in the laser plasma. If CH_4 reacts with the surface, however, one would expect to observe $Si_nCH_x^+$ ions, in analogy to the observations for the previous hydrocarbon reactions. The fact that these ions are not observed supports the conclusion that no surface reactions occur for D_2 and CH_4 .

4. Conclusions

This study has demonstrated that laser vaporization of silicon surfaces which are exposed to several reagent gases produces ions that are correlated to surface reactions. For reactions of NH₃, XeF₂, O₂, NO, CH₃OH, H₂O, and some unsaturated hydrocarbons, ions are vaporized which correspond to previously reported surface reactions. The actual ions which are observed, however, may depend on the stability of the ions in the laser generated plasma, rather than the structure of the surface species. The reactions of NO and O₂ demonstrate that the type and amount of vaporized ions may depend on the surface structure. This type of effect may be helpful in characterizing reacted silicon surfaces. The absence of vaporized product ions for exposures with the reagent gases D_2 and CH_4 is consistent with the expected unreactivity of these gases. In contrast, vaporized ions observed after exposure to CF₃I suggest that dissociative chemisorption occurs for this reagent gas, even though this reaction is not observed with other experimental techniques on crystal surfaces. This observation suggests that the surface structure produced by laser vaporization is more reactive than a well-ordered crystal structure. This is consistent with previous observations that particle bombardment of a silicon surface enhances the reactivity [54]. Therefore, the detailed structure and reactivity of the surface may be quite different from that of crystalline structures that are usually studied. Comparison of the types of structures may provide a better understanding of the nature of irregular or defect-covered surfaces.

As an experimental method for ionizing surface species, laser vaporization is quite different from SIMS techniques. Laser vaporization is a high temperature process, which makes it less suitable for producing large, complicated molecular ions. However, it is a convenient technique in a confined space such as an FTMS cell. The method also facilitates the study of time dependent phenomena such as the changes in product ion abundance as a function of exposure.

Laser vaporization as a probe of surface reactions can be combined with other surface techniques to increase its versatility. Temperature-programmed desorption in conjunction with laser vaporization may provide more detailed kinetic information about the surface reactions and the nature of the products. Studies of both reacted and nonreacted surface structures produced from laser vaporization, using other surface techniques, will indicate the relationship of these surfaces to the crystal structures that are typically studied. A better understanding of the surface structure, including the number of defects, would be helpful in interpreting the chemistry. Use of other types of mass spectrometry with greater dynamic range can be used to measure the dependence of the vaporized ion abundances on exposure, which would be interesting in studying the O_2 and NO reactions. Finally, detailed studies of the nature of the laser ionization process will be helpful in understanding the relationship of the observed ions to surface species, and in using the technique for analytical applications such as laser microprobe studies.

Acknowledgments

The authors thank A. O'Keefe for helpful suggestions, and M.M. Ross and J.H. Callahan for their fast atom beam analysis of the silicon surface reaction with NH_3 . They also acknowledge useful discussions by H.H. Nelson and J.R. McDonald, and thank R.J. Colton for a critical analysis of the manuscript.

References

- [1] R.J. Conzemius and J.M. Capellen, Intern. J. Mass Spectrom. Ion Phys. 34 (1980) 197.
- [2] Z.A. Wilk and D.M. Hercules, Anal. Chem. 59 (1987) 1819;
 D.E. Mattern, F. Lin, and D.M. Hercules, Anal. Chem. 56 (1984) 2762;
 F.P. Novak, K. Balasanmugam, K. Viswanadham, C.D. Parker, Z.A. Wilk, D. Mattern and D.M. Hercules, Intern. J. Mass Spectrom. Ion Phys. 53 (1983) 135;
 P. Feigl, B. Schueler and F. Hillenkamp, Intern. J. Mass Spectrom. Ion Phys. 47 (1983) 15;
 C.L. Wilkins, D.A. Weil, C.L.C. Yang and C.F. Ijames, Anal. Chem. 57 (1985) 520;
 M.J. Southon, M.C. Witt, H. Harris, E.R. Wallach and J. Myatt, Vacuum 34 (1984) 903.
- [3] M.G. Sherman, D.P. Land, J.C. Hemminger and R.T. McIver, Jr., Chem. Phys. Letters 137 (1987) 298.
- [4] S.W. McElvany, W.R. Creasy and A. O'Keefe, J. Chem. Phys. 85 (1986) 632;
 S.W. McElvany, B.I. Dunlap and A. O'Keefe, J. Chem. Phys. 86 (1987) 715.
- [5] W.R. Creasy, A. O'Keefe and J.R. McDonald, J. Fhys. Chem. 91 (1987) 2848.
- [6] W.D. Reents, Jr. and V.E. Bondybey, Chem. Phys. Letters 125 (1986) 324.
- [7] M.L. Mandich, W.D. Reents, Jr. and V.E. Bondybey, J. Phys. Chem. 90 (1986) 2315;
 M.L. Mandich, V.E. Bondybey and W.D. Reents, Jr., J. Chem. Phys. 86 (1987) 4245;
 W.D. Reents, Jr., M.L. Mandich and V.E. Bondybey, Chem. Phys. Letters 131 (1986) 1.
- [8] W.D. Reents, Jr., A.M. Mujsce, V.E. Bondybey and M.L. Mandich, J. Chem. Phys. 86 (1987) 5568.
- [9] M.P. Kaminsky, N. Winograd and G.L. Geoffroy, J. Am. Chem. Soc. 108 (1986) 1315.
- [10] N.H. Turner and R.J. Colton, Anal. Chem. 54 (1982) 293;
- N.H. Turner, B.I. Dunlap and R.J. Colton, Anal. Chem. 56 (1984) 373R.
- [11] A. Benninghoven, W. Sichtermann and S. Storp, Thin Solid Films 28 (1975) 59.
- [12] K. Mann and M.L. Yu, Phys. Rev. B 35 (1987) 6043.
- [13] P. Sander, U. Kaiser, R. Jede, D. Lipinsky, O. Ganschow and A. Benninghoven, J. Vacuum Sci. Technol. A 3 (1985) 1946.
- [14] A. Benninghoven, Surface Sci. 53 (1975) 596.

- [15] A. O'Keefe and J.R. McDonald, Chem. Phys. 103 (1986) 425;
 A. O'Keefe, S.W. McElvany and J.R. McDonald, Chem. Phys. 111 (1987) 327.
- [16] S.W. McElvany, H.H. Nelson, A.P. Baronavski, C.H. Watson and J.R. Eyler, Chem. Phys. Letters 134 (1987) 214.
- [17] J. Beauchamp, Ann. Rev. Phys. Chem. 22 (1971) 527.
- [18] M.B. Comisarow and A.G. Marshall, J. Chem. Phys. 62 (1975) 293.
- [19] E.B. Ledford, Jr., S. Ghaderi, C.L. Wilkins and M.L. Gross, Advan. Mass Spectrom. B 8 (1980) 1707.
- [20] R.J. Phaneuf and E.D. Williams, Phys. Rev. B 35 (1987) 4155.
- [21] B.C. Larson, J.Z. Tischler and D.M. Mills, J. Mater. Res. 1 (1986) 144; D.H. Lowndes, S.J. Pennycook, G.E. Jellison, S.P. Withrow and D.N. Mashburn, J. Mater. Res. 2 (1987) 648.
- [22] M.M. Ross and J.H. Callahan, private communication.
- [23] S.W. McElvany, unpublished results.
- [24] F. Bozso and Ph. Avouris, Phys. Rev. Letters 57 (1986) 1185.
- [25] Ph. Avouris, F. Bozso and R.J. Hamers, Phys. Rev. B, in press.
- [26] E.K. Hill, L. Kubler, J.L. Bischoff and D. Bolmont, Phys. Rev. B 35 (1987) 5913.
- [27] L. Kubler, E.K. Hill, D. Bolmont and G. Gewinner, Surface Sci. 183 (1987) 503.
- [28] D.G. Kilday, G. Margaritondo, D.J. Frankel, J. Anderson and G.J. Lapeyre, Phys. Rev. B 35 (1987) 9364.
- [29] A. Glachant and D. Saidi, J. Vacuum Sci. Technol. B 3 (1985) 985.
- [30] F.A. Houle, J. Chem. Phys. 87 (1987) 1866.
- [31] F.A. Houle, J. Appl. Phys. 60 (1986) 3018.
- [32] H.F. Winters and F.A. Houle, J. Appl. Phys. 54 (1983) 1218.
- [33] Y.-Y. Tu, T.J. Chuang and H.F. Winters, Phys. Rev. B 23 (1981) 823.
- [34] H.F. Winters and J.W. Coburn, Appl. Phys. Letters 34 (1979) 70.
- [35] B. Roop, S. Joyce, J.C. Schultz and J.I. Steinfeld, Surface Sci. 173 (1986) 455.
- [36] N. Selamoglu, M.J. Rossi and D.M. Golden, J. Chem. Phys. 84 (1986) 2400.
- [37] J.H. Brannon, J. Phys. Chem. 90 (1986) 1784.
- [38] H.F. Winters, J. Appl. Phys. 49 (1978) 5165.
- [39] H. Ibach, K. Horn, R. Dorn and H. Luth, Surface Sci. 38 (1973) 433.
- [40] K. Edamoto, Y. Kubota, H. Kobayashi, M. Onchi and M. Nishijima, J. Chem. Phys. 83 (1985) 428.
- [41] C.M. Garner, I. Lindau, C.Y. Su, P. Pianetta and W.E. Spicer, Phys. Rev. B 19 (1979) 3944.
- [42] R.H. Brockman and G.J. Russell, J. Phys. C 15 (1982) 6677.
- [43] M.L. Knotek and J.E. Houston, J. Vacuum Sci. Technol. 20 (1982) 544.
- [44] M.C. Munoz, V. Martinez, J.A. Tagle and J.L. Sacedon, Phys. Rev. Letters 44 (1980) 814.
- [45] C.-E. Richter and M. Trapp, Intern. J. Mass Spectrom. Ion Phys. 38 (1981) 21.
- [46] C. Michiels, A. Celis and R. Gijbels, Intern. J. Mass Spectrom. Ion Phys. 47 (1983) 23.
- [47] M. Nishijima, H. Kobayashi, K. Edamoto and M. Onchi, Surface Sci. 137 (1984) 473.
- [48] J.A. Stroscio, S.R. Bare and W. Ho, Surface Sci. 154 (1985) 35.
- [49] K. Edamoto, Y. Kubota, M. Onchi and M. Nishijima, Surface Sci. 146 (1984) L533.
- [50] J.A. Schultz, Y.S. Jo, S. Tachi and J.W. Rabalais, Nucl. Instr. Methods B 15 (1986) 134.
- [51] M. Nishijima, K. Edamoto, Y. Kubota, S. Tanaka and M. Onchi, J. Chem. Phys. 84 (1986) 6458.
- [52] J.A. Schaefer, F. Stucki, D.J. Frankel, W. Gopel and G.J. Lapeyre, J. Vacuum Sci. Technol. B 2 (1984) 359.
- [53] M.N. Piancastelli, M.K. Kelly, D.G. Killary, G. Margaritondo, D.J. Frankel and G.J. Lapeyre, Phys. Rev. B 35 (1987) 1461.
- [54] M.J. Bozack, W.J. Choyke, L. Muehlhoff and J.T. Yates, Jr., Surface Sci. 176 (1986) 547.
- [55] H. Kobayashi, K. Edamoto. M. Onchi and M. Nishijima, J. Chem. Phys. 78 (1983) 7429, and references therein.