Field evaporation of silicon and field desorption of hydrogen from silicon surfaces

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The field evaporation of silicon in ultrahigh vacuum and in hydrogen has been studied with the use of the pulsed-laser atom probe. Measurements of the ion yields of various field-evaporated and field-desorbed species were made as a function of applied voltage, laser power, hydrogen background pressure, and laser pulse rate. The results indicate that, in ultrahigh vacuum and above cryogenic temperatures, field evaporation of silicon is qualitatively the same as for metals. In hydrogen, however, the field-evaporation process is quite different from that of metals, with the rate-limiting step being the field-enhanced formation of surface hydrides. Field-desorbed H^+ and $H_2{}^+$ ions are shown to arise from a field-adsorbed binding state, and the voltage range where $H_2{}^+$ dissociates to H^+ is used to calibrate the electric field strength. The low-temperature evaporation field of silicon is estimated from this calibration to be 3.3—3.6 V/Å, which is considerably higher than the currently accepted value of 2.0 V/Å. Field-desorbed $H_3{}^+$ ions are detected only when oxide contamination is present on the silicon surface. If we assume that the mechanism of $H_3{}^+$ formation is the same as that proposed for metals, this observation suggests that weakly bound, chemisorbed hydrogen atoms exist on silicon only in the presence of surface contamination.

I. INTRODUCTION

In an electric field of a few volts per angstrom, surface atoms desorb as positive ions. This process is known as field evaporation[1] if the desorbing species are substrate atoms or field desorption[1] if they are absorbates. Because of their importance in field-ion microscopy[1] and atom-probe mass spectroscopy,[2] the processes of field evaporation and field desorption have been extensively studied both experimentally and theoretically. Most of these studies, however, have been carried out on high-conductivity samples (i.e., metals and alloys). With recent developments in sample preparation procedures and instrumentation, it has become possible to examine semiconductors[3–13] and even insulators[14] with the field-ion microscope and atom probe. In the particular case of silicon, this possibility has led to atom-probe studies of technologically important processes such as surface-hydride formation,[7,15] oxygen adsorption,[16] and silicide formation.[17,18] With this increased activity in the application of high-field techniques to silicon, it becomes desirable to gain a better understanding of the field-evaporation process for silicon. In an attempt to gain such an understanding, we report here an experimental investigation of the field evaporation of silicon and the field desorption of hydrogen from silicon surfaces using the pulsed-laser atom probe.[11]

Experimental studies of silicon field evaporation were stimulated by the early work of Melmed and Stein,[3] who found that ordered field-ion images of silicon could be obtained by imaging in hydrogen. They also found that field evaporation of silicon in the presence of hydrogen was uniform and proceeded layer by layer as in metals. Later, Sakurai *et al.*[6] showed that the low-temperature field evaporation of silicon in ultrahigh vacuum was anomalous, i.e., the field-evaporation process was sporadic with surface atoms desorbing primarily as clusters. They also reported that the presence of hydrogen drastically reduced the electric field strength required for field evaporation. Sakata and Block[12] investigated the dependence of the silicon evaporation voltage on temperature and hydrogen background pressure and found that, unlike metals, the applied voltage required for evaporation of silicon in hydrogen increased with increasing temperature. Their explanation for this behavior was that adsorbed hydrogen, which reduces the evaporation voltage, was thermally desorbed at high temperatures. This explanation was subsequently confirmed by Kellogg,[19] who found that in ultrahigh vacuum the silicon field-evaporation voltage decreases with increasing temperature, the same as for metals. This same study also showed that the anomalous field evaporation observed at cryogenic temperatures disappeared at temperatures above 150 K.

The first atom-probe study of silicon was carried out by Sakurai *et al.*[7] using a magnetic sector atom probe which employs dc field evaporation. The study was carried out in the presence of H_2 and identified various hydride species desorbed during the field-evaporation process. The first time-of-flight atom-probe study of silicon was carried out by Kellogg and Tsong[11] using the pulsed-laser atom probe. This study was also carried out in the presence of H_2 and indicated that the abundance of SiH^+ compared to Si^+ was very dependent on the hydrogen background pressure. Pulsed field evaporation of silicon in ultrahigh vacuum was subsequently studied by Kellogg,[16,20] who found that in the absence of H_2, silicon field-evaporates exclusively as Si^{2+} above 2.5 V/Å and Si^+ and Si^{2+} between 1.5 and 2.5 V/Å. At temperatures above 1000 K and field strengths below 1.2 V/Å, cluster ions up to $Si_5{}^+$ were found to field-evaporate from the clean surface.

The drastic reduction in the silicon evaporation field due to the presence of hydrogen along with the increasing evaporation voltage with increasing temperature indicates that field evaporation of silicon in hydrogen is quite different from that in ultrahigh vacuum. In the study re-

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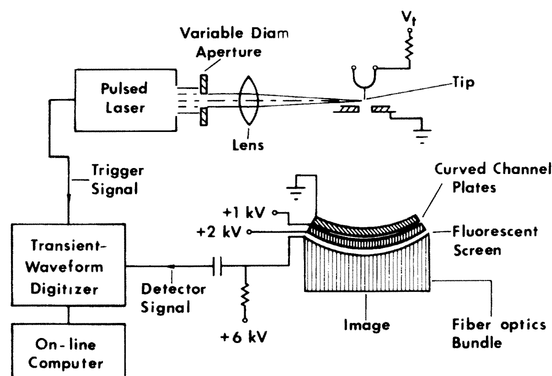


FIG. 1. Schematic drawing of the pulsed-laser atom-probe—field-ion microscope used in this study.

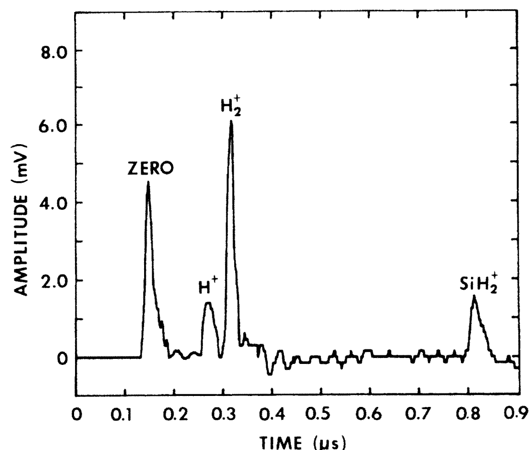


FIG. 2. Example of a pulsed-laser atom-probe mass spectrum taken from a silicon sample in the presence of hydrogen.

ported here, we have examined this difference in more detail using pulsed-laser-stimulated field evaporation. Measurements of the relative field-evaporation rate of silicon as a function of applied voltage in ultrahigh vacuum and in hydrogen have been carried out. We have also investigated the change in field-evaporation rate as a function of applied laser power (i.e., the surface temperature during desorption), hydrogen background pressure, and laser pulse rate. From these results we will present a qualitative picture of silicon field evaporation and how it changes when hydrogen is present. We have also investigated the field desorption of hydrogen from clean silicon surfaces and surfaces contaminated with oxides. The results from the clean surface are compared to previous studies of hydrogen field desorption from metals and discussed in relation to calibration of the electric field strength at a silicon surface. The results from the contaminated surface are discussed in relation to the formation of H_3^+ ions and the influence such contamination has on the presence of weakly bound, chemisorbed hydrogen.

II. EXPERIMENTAL

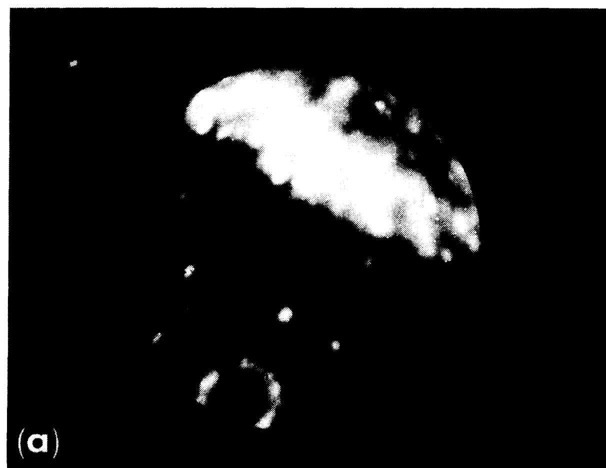
A. Apparatus

The pulsed-laser atom-probe—field-ion microscope used in this investigation is shown schematically in Fig. 1. A field emitter "tip" is placed in a vacuum chamber opposite to a curved-channel-plate—fluorescent-screen assembly.[21] Conventional field-ion microscropy[1] is carried out by admitting an imaging gas (H_2 is used for Si) to the vacuum chamber and applying a positive voltage (3—15 kV) to the tip. The intensified image is viewed on the fluorescent screen through a fiber-optics bundle. Atom-probe mass spectroscopy is carried out the same as in the earlier imaging atom probe,[21] except that here the field desorption of surface species is initiated with a short-duration laser pulse and a dc applied voltage rather than a high-voltage electrical pulse. The applied laser power is varied by adjusting a variable-diameter aperture located in the path of the laser beam. The thermal stimulation provided by the laser pulse in combination with the high electric field at the surface causes surface atoms to desorb as positive ions. The mass-to-charge ratios of the field-desorbed ions are determined by measuring their flight time from the tip to the channel-plate ion detector. The flight time is measured from the sweep of a fast, transient-waveform digitizer triggered by the laser pulse. Figure 2 shows an example of such a digitizer trace taken from a silicon sample in the presence of hydrogen. The first peak in the trace corresponds to the firing of the laser, and subsequent peaks correspond to the arrival of various species at the detector. Since the channel plates are operated well below saturation, the peak amplitudes are directly proportional to the relative abundances of the field-desorbed species. Plots of these peak amplitudes as a function of several experimental parameters are presented later in the paper.

B. Procedure

The silicon samples used in this study were prepared from whiskers[22] grown by the reduction of $SiCl_4$. Sample resistivities were of the order of 200 Ω cm (Ref. 16). The tips were sharpened by dipping the whiskers in a 50%-50% mixture of nitric and hydrofluoric acids[3] and mounted on a platinum wire loop using silver paint. The silver paint was subsequently cured by heating the loop to 700 K in vacuum for a period of several hours.

Field-ion images of freshly prepared silicon samples were relatively low in contrast and exhibited no atomic structure. These images resulted from the native oxide layer formed during the etching process and air exposure. This oxide layer could be removed by field evaporation in the presence of hydrogen.[3] Figure 3(a) shows a field-ion image of a silicon surface with part of the oxide layer removed. The upper portion of the image corresponds to the oxide layer and the lower portion to the silicon substrate with the (111) plane partially visible. Note that the boundary betweeen the oxide and the substrate is very distinct. As the field-evaporation process was continued, this boundary retreated exposing more of the silicon substrate [see Fig. 3(b)]. Eventually, the oxide layer was completely removed from the imaged portion of the tip. However, under certain conditions of field strength and temperature the oxide layer would migrate back to the imaged region. As we will show later, the presence of oxide contamination



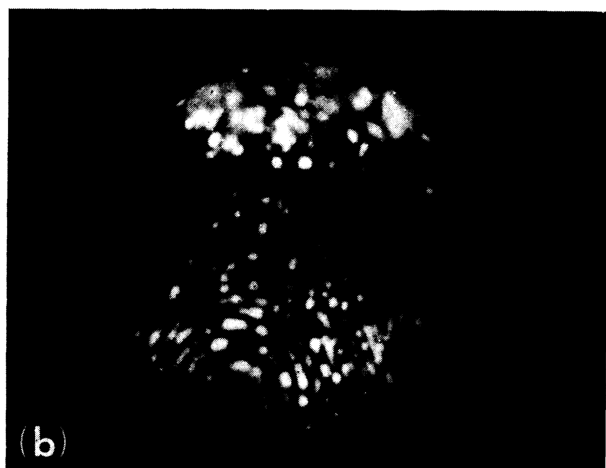
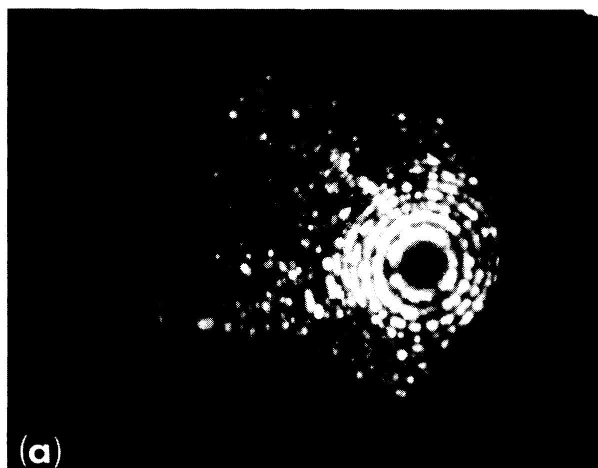


FIG. 3. Field-ion images of silicon showing the removal of the native oxide layer. Both images were recorded in 2×10^{-5} Torr H_2. (a) $V=3.52$ kV, (b) $V=4.50$ kV.



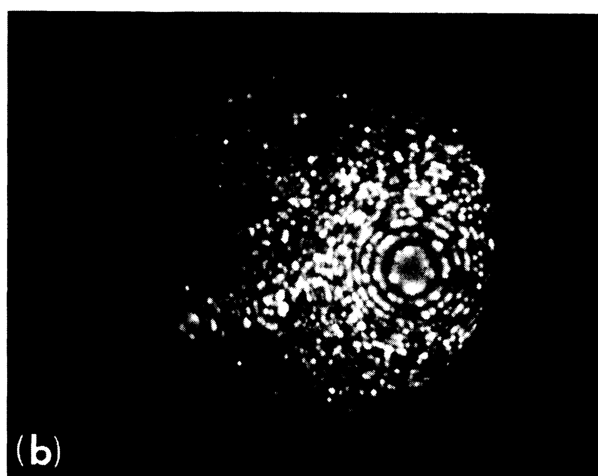


FIG. 4. Field-ion images of the silicon surface used in the study of field evaporation and field desorption from the clean surface. Both images were recorded in 3×10^{-6} Torr H_2. (a) $V=5.9$ kV, (b) $V=8.4$ kV.

on the surface strongly influenced the type of hydrogen species desorbed from the surface, making it necessary to monitor the field-ion images to ensure that no oxide species were present. The ability to easily distinguish the oxide from the ordered silicon surface was therefore quite useful.

In the following section pulsed-laser atom-probe mass spectra taken from both clean and oxide-contaminated silicon surfaces will be presented. The experimental procedure consisted of recording mass scans such as the one shown in Fig. 2 and monitoring the peak heights of the various species as a function of applied voltage, laser power, laser pulse rate, and hydrogen background pressure. For each measurement 32 individual mass scans were averaged to give a more statistically significant indication of the relative species abundances. Since the peak heights are a measure of the relative abundances of the desorbed species in a fixed time interval (i.e., the laser pulse duration), changes in the peak heights directly reflect changes in evaporation rate. Thus increases in a species peak height will often be referred to as an increase in its field-evaporation or field-desorption rate.

In those measurements where the applied voltage was varied, the results are plotted as a function of applied voltage and not field strength, even though the field strength is the more appropriate parameter when discussing the field-evaporation process. The conversion from applied voltage to electric field strength was not made because of the ambiguity concerning the value of the low-temperature evaporation field (see Sec. IV) which is used in the conversion. Therefore, when comparing figures involving applied voltages, it is important to note the value of V_0 (vacuum evaporation voltage at $\sim$50 K), since the tip radius was not the same for all the measurements.

III. RESULTS

A. Clean surface

Figure 4 shows field-ion images of the surface used in the study of clean (oxide-free) silicon. The two images correspond to the surface near the beginning and the end

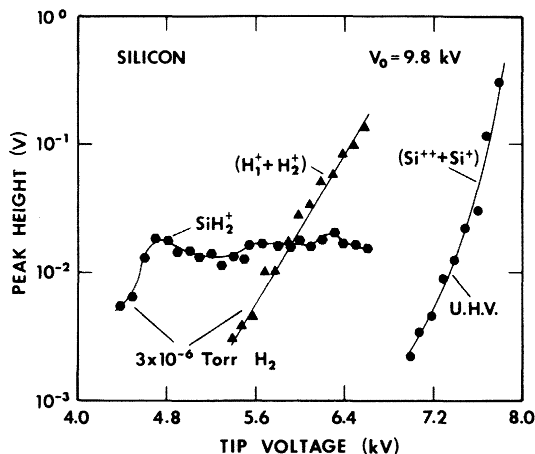


FIG. 5. Peak heights of various signals as a function of applied voltage at fixed laser power and pulse rate. The laser-induced temperature rise is estimated to be ~300 K. In ultrahigh vacuum (UHV) the silicon signal increases very rapidly with applied voltage, whereas in 3×10^{-6} Torr H_2 the silicon signal is relatively constant.

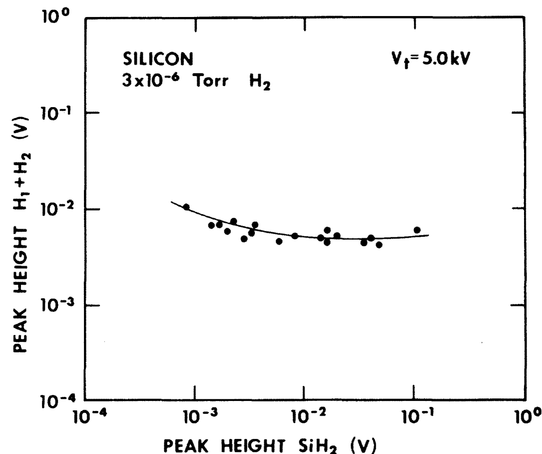


FIG. 7. Change in the $H^+ + H_2^+$ signal intensity compared to the change in the SiH_2^+ signal intensity produced by increasing the laser power. Increasing the laser power caused the SiH_2^+ signal to increase by more than 2 orders of magnitude, while having little effect on the $H^+ + H_2^+$ signal.

of the experiments, respectively. The field image was monitored throughout the experiment to make sure no oxide species diffused on to the surface from the shank.

As in the case of dc field evaporation, pulsed-laser-stimulated field evaporation of silicon in the presence of hydrogen was found to be quite different than that observed in ultrahigh vacuum. This is illustrated in Fig. 5, which shows plots of the intensity of various field-desorption products as a function of applied voltage. The measurements were recorded at a fixed laser power and fixed laser pulse rate. In ultrahigh vacuum (3×10^{-10} Torr) the silicon field-evaporation rate was found to increase very rapidly with increasing applied voltage. This increase is shown at the far right of Fig. 5 where the intensity of the silicon signal (predominantly Si^{2+}) is seen to grow by more than 2 orders of magnitude for an increase in applied voltage of 800 V. In contrast, the onset voltage for the appearance of silicon-containing ions in 3×10^{-6} Torr H_2 was reduced by 63%, and the signal intensity remained relatively constant over a voltage range of 2.2 kV. This behavior is also shown in Fig. 5. The measured mass-to-charge ratio of the predominant silicon peak in the presence of H_2 was $m/z=30$, indicating that the desorbing species was SiH_2^+. This identification was subsequently confirmed by replacing the hydrogen with deuterium and noting that the peak shifted from $m/z=30$ to 32. These observations suggest that the rate-limiting step in the field evaporation of silicon in H_2 is the formation of SiH_2, and not the field-induced ionization of surface atoms. This point will be discussed further in the next section.

Between applied voltages of 4.4 and 5.4 kV only SiH_2^+ was detected in the mass scans. At 5.4 kV hydrogen signals (H^+ and H_2^+) began to appear. The sum of the peak heights ($H^+ + H_2^+$) is plotted on Fig. 5. Unlike the SiH_2^+ signal, the H^+ and H_2^+ signals were found to increase very rapidly with applied voltage. It is interesting to note that the fraction of H_2^+ ions compared to H^+ ions did not change with increasing applied voltage, but remained relatively constant (~0.8) in the voltage range from 5.6 to 6.6 kV. However, a significant change in the $[H_2^+]/[H^+]$ ratio was detected when the hydrogen pressure was reduced to 5×10^{-7} Torr (to reduce the dc evaporation of silicon) and the applied voltage further increased. This result is shown in Fig. 6, in which the intensity of the two signals along with the fraction of H_2^+ ions is plotted as a function of applied voltage. In comparing Fig. 6 to Fig. 5 it should be noted that the tip radius is slightly larger in Fig. 6, and the value of V_0 has increased to 10.9 kV. The decomposition of H_2^+ to H^+ is clearly evident in Fig. 6. In the next section this field-induced decomposition will be discussed in relation to the calibration of field strength above a silicon surface.

Figure 7 shows the effect of varying the laser power on the relative intensities of the SiH_2^+ and $H^+ + H_2^+$ signals. Since neither the laser power intercepting the tip nor the

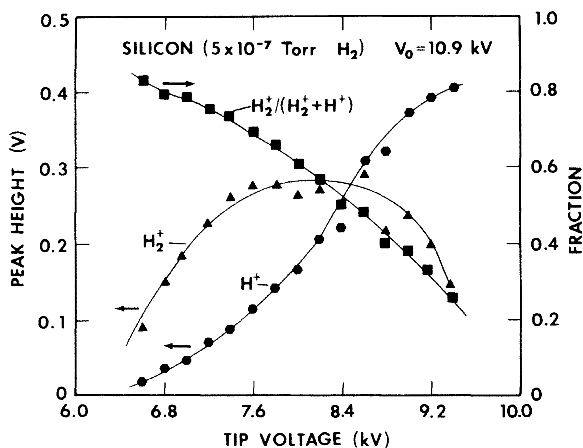


FIG. 6. Change in relative signal intensities of field-desorbed H^+ and H_2^+ as a function of applied voltage. The decomposition of H_2 can be used to calibrate the field strength as discussed in the text.

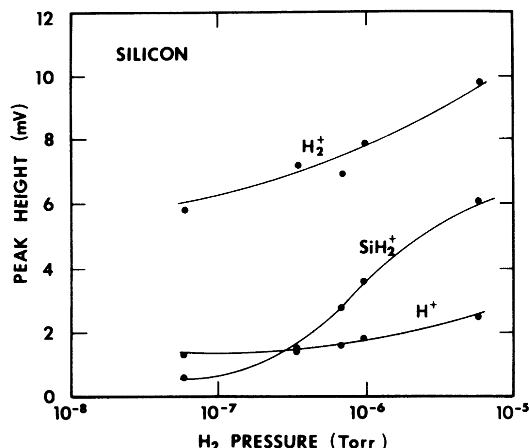


FIG. 8. Change in H^+, H_2^+, and SiH_2^+ signal intensities as a function of hydrogen background pressure. Tip voltage is 5.0 kV, $V_0 \approx 8$ kV.

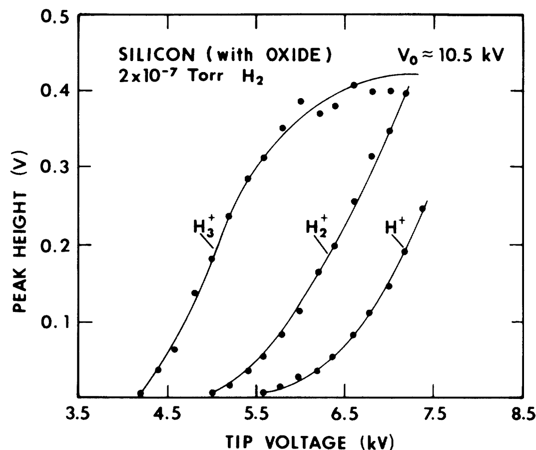


FIG. 10. Change in H^+, H_2^+, and H_3^+ signal intensities as a function of applied voltage from an oxide-contaminated silicon surface. The laser power was relatively high, but the temperature rise was not determined.

laser-induced temperature rise could be accurately determined, we have plotted the $H^+ + H_2^+$ intensity as a function of the SiH_2^+ intensity. Note that both scales are logarithmic. Increasing the laser power was found to cause a large increase in the SiH_2^+ signal (over 2 orders of magnitude), while having very little influence on the intensity of the hydrogen signals (a small decrease was actually detected). Figures 8 and 9 show plots of the H^+, H_2^+, and SiH_2^+ signal intensities as a function of hydrogen pressure and laser pulse rate, respectively. Increasing the hydrogen background pressure caused all three signals to increase, but had a much more pronounced effect on the SiH_2^+ intensity. Varying the laser pulse rate had no effect on the SiH_2^+ and only a minor effect on the H_2^+ and H^+ intensities. Interpretations of these various trends are discussed in more detail in Sec. IV.

B. Oxide-contaminated surface

As long as the silicon surface remained free of oxide contamination, the only species detected at the low-mass end of the scale were H^+ and H_2^+ over the entire voltage range probed. Mass spectra recorded from surfaces where oxides were present, however, contained significant quantities of H_3^+. Even if only a small portion of the field-ion image exhibited the characteristic fuzzy image associated with the oxide, the H_3^+ signal was found to be comparable to the H^+ and H_2^+ signal. The onset voltage for the H_3^+ signal was typically lower than the onset voltage for the H_2^+ and H^+ signal, and the relative abundance of the H_3^+ signal in comparison to the other two depended on the laser power. Figures 10 and 11 show the intensities of the three hydrogen signals as a function of applied voltage for conditions of high and low laser power, respectively. Using relatively high laser powers, the H_3^+ signal appeared at voltages ~ 1 kV below the appearance of H_2^+ and dominated the mass spectrum for a voltage increase of 2–3 kV (Fig. 10). At reduced laser powers, the intensities of all three signals were significantly lower, and the voltage dependences were more complicated (Fig. 11). The H_3^+ signal appeared first but did not become significant until after the appearance of H_2^+. All three signals were found to decay at higher voltage strengths when lower laser powers were employed. Qualitative interpretations of

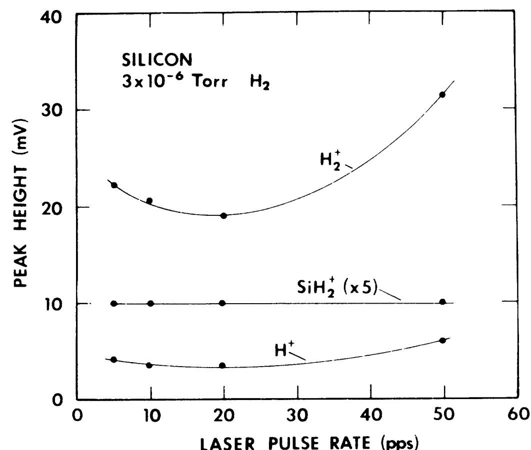


FIG. 9. Change in H^+, H_2^+, and SiH_2^+ signal as a function of laser pulse rate. Tip voltage is 5.0 kV, $V_0 \approx 8$ kV.

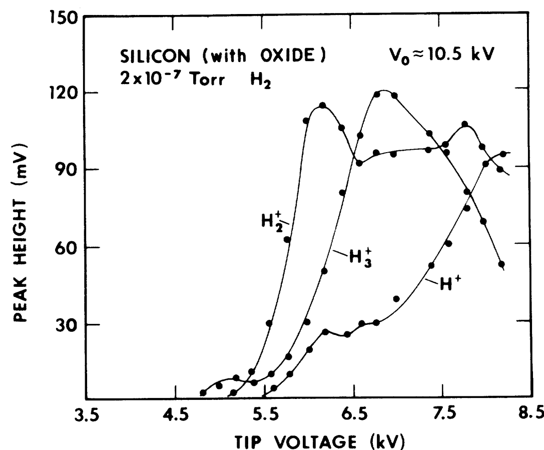


FIG. 11. Change in H^+, H_2^+, and H_3^+ signal intensities as a function of applied voltage from an oxide-contaminated silicon surface. The laser power was considerably lower than that used in Fig. 10.

the data shown in Figs. 10 and 11 are given later in the paper.

IV. DISCUSSION

A. Field evaporation of silicon

According to existing theoretical models,[1] field evaporation above cryogenic temperatures is a thermally activated process governed by an Arrhenius rate equation of the form

$$k = k_0 e^{-Q(F)/k_B T}, \qquad (1)$$

where k is the evaporation rate, k_0 is the evaporation rate at zero activation energy, k_B is Boltzmann's constant, T is the temperature, and $Q(F)$ is the field-dependent activation energy of desorption. Although the different models of field evaporation give different analytical expressions for $Q(F)$, all models predict a rapid increase in the rate of evaporation with increasing field strength. This behavior has been experimentally observed for many metals.[1] In ultrahigh vacuum (UHV) the silicon field-evaporation rate is also found to increase very rapidly with applied voltage (see Fig. 5), in agreement with the theoretical predictons and the experimental results for metals. Moreover, previous studies of silicon field evaporation in UHV have shown that the shift in the field-evaporation charge state from doubly to singly charged with decreasing field strength is consistent with the post-ionization model of field evaporation,[20] and that the reduction in the evaporation field with increasing temperature is nearly the same as that measured for metals.[9] These similarities lead us to conclude that above ~ 150 K the field evaporation of silicon in ultrahigh vacuum is qualitatively the same as metals and is governed by the rate equation given above.

In the presence of hydrogen, however, the field-evaporation process for silicon changes dramatically. Although "hydrogen promotion" of field evaporation (the reduction in evaporation field due to the presence of hydrogen) has been reported for metals,[23] the effect is relatively minor compared to silicon. As reported earlier[6] and illustrated again in Fig. 5, the presence of hydrogen at pressures $\sim 10^{-6}$ Torr causes the evaporation field of silicon to drop by more than 60%. Furthermore, large increases in the applied voltage have little effect on the silicon evaporation rate (Fig. 5), whereas increases in the applied laser power (Fig. 7) and hydrogen background pressure (Fig. 8) cause the rate to change considerably. These results suggest that the field evaporation of Si in hydrogen involves the formation of surface hydrides, which in the presence of a high electric field are more weakly bound than the silicon atoms themselves. The relative independence of the evaporation rate on the applied voltage above a threshold field strength (Fig. 5) indicates that the ionization-desorption process is more rapid than the formation of surface hydrides, i.e., surface-hydride formation is the rate-limiting step. Assuming that laser-induced photoeffects are not involved in surface-hydride formation, the increase in the field-evaporation rate with increasing laser power (Fig. 7) indicates that either the hydride formation is a thermally activated process, or the supply of hydrogen to the sites where hydrides are formed is enhanced by pulsed-laser-stimulated surface diffusion. The increase in evaporation rate caused by higher hydrogen pressures (Fig. 8) can be attributed to an increased supply of hydrogen.

In previous studies of the dc field evaporation of Si in hydrogen[6] the formation of surface hydrides was also proposed as an explanation of the observed reduction in evaporation-field strength. In those studies, however, the predominant species detected was SiH^+, whereas in the pulsed-laser study reported here the predominant species was $SiH_2{}^+$. This probably can be attributed to the difference in evaporation rates; however, it may imply that the formation of $SiH_2{}^+$ requires the additional thermal activation supplied by laser heating. The fact that the formation of either SiH or SiH_2 causes a considerable reduction in the silicon evaporation field implies that the binding strengths of both species in a high electric field are significantly less than the silicon atoms on the hydrogen-free surface.

B. Field desorption of H_2

In a previous pulsed-laser atom-probe study of H_2 field desorption from molybdenum,[24] it was shown that the hydrogen detected in the mass scans as H^+ and $H_2{}^+$ originated from a field-adsorbed binding state at temperatures below 150 K. Field adsorption is a surface binding caused by a field-induced dipole–image-dipole interaction,[25,26] and the binding strength of field-adsorbed species are typically of the order of several tenths of an electron volt (in the electric field range of interest). Field-adsorbed hydrogen is also known to be present on silicon surfaces at cryogenic temperatures.[12] The large abundance of field-desorbed hydrogen species along with the similarity between the H_2 field-desorption data shown in Figs. 5 and 6 for silicon and the previous data for molybdenum suggest that the H^+ and $H_2{}^+$ signals detected in this study also come from a field-adsorbed binding state. The rapid increase in the $H^+ + H_2{}^+$ signal intensity with increasing applied voltage shown in Fig. 5 is consistent with higher field-ionization probabilities at higher field strengths, and the observation that the $SiH_2{}^+$ signal intensity does not change in the voltage range where the $H^+ + H_2{}^+$ signal becomes very large is evidence that the H^+ and $H_2{}^+$ do not come from the decomposition of SiH_2. The shift from $H_2{}^+$ to H^+ with increasing voltage shown in Fig. 6 is very similar to previous results on metals,[11,24,27] where the decomposition was shown[24] to be a field-induced process occurring at a distance of several angstroms away from the surface. The slight decrease of the $H^+ + H_2{}^+$ signal intensity with increasing laser power (Fig. 7) is different from the results on molybdenum,[24] where the total hydrogen yield was found to increase with increasing laser power. There are two possible explanations for this difference: (1) under the present conditions of field strength and hydrogen pressure all of the field-adsorbed hydrogen is thermally desorbed with each laser pulse even at the lowest laser powers (keeping the total hydrogen yield constant), or (2) at higher laser powers hydrogen on silicon is not desorbed as H^+ and $H_2{}^+$ but decomposes and interacts with the surface to form the hydride species detected as $SiH_2{}^+$. Neither of these explanations is inconsistent

with the conclusion that the hydrogen detected as H^+ and H_2^+ arises from a field-adsorbed state.

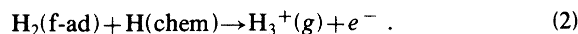
C. Field-strength calibration

The electric field required to field-evaporate silicon at cryogenic temperatures in 1.2×10^{-4} Torr hydrogen has been reported[6] to be 1.1 V/Å. This value was obtained from a field-calibration method using the energy distribution of field-ionized gases.[28] Since the field strength required for field evaporation of silicon in hydrogen was reported in the same study[6] to be 58% lower than in vacuum, the vacuum evaporation field for silicon should be 2.0 V/Å. This value is in general agreement with a more recent determination[12] based on the increase in the silicon field-evaporation voltage with temperature (in the presence of H_2). However, a comparison of the measured shift in the field-evaporation charge states of silicon ions as a function of applied voltage[20] to calculations based on the post-ionization model of field evaporation[29] has indicated that the vacuum evaporation field of Si is much higher, approximately 3.5 V/Å. Here we discuss a calibration procedure based on the field-induced decomposition of H_2 which suggests that the higher field strength is the appropriate value.

The pulsed-laser atom-probe study of hydrogen on molybdenum[24] mentioned above along with similar studies on rhodium[11] and tungsten[27] has identified the field range where molecular hydrogen is field dissociated to atomic hydrogen. The dissociation occurs between 2.0 and 3.5 V/Å in all cases, and the field strength at which the H_2 intensity equals the H^+ signal is 2.8, 2.6, and 2.6 V/Å for Rh, Mo, and W, respectively. The equivalence of these fields strengths is further evidence that the field-dissociation process is insensitive to the surface material. Assuming that the hydrogen detected in this study does, in fact, come from the same field-adsorbed binding state as the hydrogen detected in the studies on metals (and noting that the work function of silicon is about the same as Rh, Mo, and W), we can use the data from this study to obtain a rough field-strength calibration by comparing the applied voltage where the H_2^+ signal equals the H^+ signal in Fig. 6 to the field strengths given above. From Fig. 6 this applied voltage is $0.78V_0$, where V_0 is the low-temperature dc vacuum field-evaporation voltage. Comparison to the field strengths above yields an evaporation-field strength of 3.3–3.6 V/Å, in good agreement with the value predicted from the post-ionization measurements, but much higher than the earlier calibrations. The reason for the discrepancy between this value and the 2.0 V/Å determined previously is not clear, particularly since the details of the earlier calibration have never been published.

D. Field desorption of H_3^+

The occurrence of H_3^+ ions in field ionization was first reported by Clements and Müller[30] in 1962 and has been subsequently observed by a number of investigators.[31–34] Detailed investigations of the relative abundance of H_3^+ ions as a function of field strength and temperature have led Ernst and co-workers[35–37] to conclude that the formation of H_3^+ is a field-induced surface process involving a reaction between field-adsorbed hydrogen molecules, H(f-ad), and chemisorbed hydrogen atoms, H(chem), i.e.,



$$H_2(\text{f-ad})+H(\text{chem})\rightarrow H_3^+(g)+e^- . \quad (2)$$

Unlike the formation of H_2^+ and H^+ ions, which occurs at or beyond the critical distance of field ionization, according to this model the H_3^+ ion is formed at the surface and therefore contains information on the hydrogen substrate interaction. Ernst *et al.*[35] have suggested that measurements of the appearance energies of H_3^+ can be used to calculate the binding strength of chemisorbed hydrogen atoms.

One of the more interesting findings of this study is that H_3^+ ions are not detected desorbing from silicon surfaces unless oxide contamination is present. Since we have indicated that field-adsorbed H_2 molecules are present on silicon surfaces, the absence of H_3^+ ions in the mass scans implies that any chemisorbed hydrogen atoms which may be present on contamination-free surfaces are so strongly bound to the surface that the creation and desorption of H_3^+ is energetically unfavorable. Considering the strength of the Si—H bond (3.3 eV) compared to typical hydrogen chemisorption energies on metals ($\sim$1 eV), this is an intuitively reasonable explanation. The observation that even small amounts of oxide contamination cause a strong H_3^+ signal to appear is evidence that weakly bound hydrogen atoms exist only when oxide contamination is present on the surface. This conclusion contracdicts recent photoemission studies[38] of H_2 on the Si(111) surface where it has been proposed that weakly bound, chemisorbed hydrogen atoms are present on the contamination-free surface.

Detailed interpretations of the data presented in Figs. 10 and 11 are difficult because the uncertainty in the laser-induced temperature rises. The laser power setting used to obtain the data in Fig. 10 was significantly higher than that used in Fig. 11, but temperature calibration procedures have not been developed for silicon to determine the magnitude of the difference in the corresponding temperature rises. There is also some uncertainty in the value of V_0, which was estimated from the evaporation voltage in H_2. Nevertheless, there are obvious differences in the data recorded at high (Fig. 10) and low (Fig. 11) laser powers, which are quite interesting and lend themselves to qualitative interpretations. First we note that in Fig. 10 the H_3^+ signal begins to saturate when the H_2^+ and H^+ signals become more intense. This could mean that either the H_2^+ and H^+ signals arise from the field-induced dissociation of H_3^+, or that the H_2 required to produce H_3^+ is desorbed at higher fields as H_2^+ before having a chance to form H_3. The data shown in Fig. 11 suggest the latter. Here the lower laser-induced temperature rise inhibits the formation of H_3^+ at lower fields (see below). The H_2^+ signal, however, still appears at the same applied voltage as in Fig. 10, and there is a clear reduction in the H_2^+ signal in the voltage range where H_3^+ grows to its maximum value. These observations are a strong indication that the same hydrogen species responsible for the H_2^+ signal (field-adsorbed H_2 molecules) are involved in the formation of H_3^+. The reason for the reduced H_3^+ signal at lower laser powers can be attributed to reduced mobility of the species which go into the formation of H_3^+, i.e., the

hydrogen species are inhibited from diffusing to the sites where H_3^+ is formed. This explanation is consistent with Ernst's[37] recent interpretations of H_3^+ formation on metals, in which H atoms must migrate to the reaction sites on the surface. Thus the same mechanism used by Ernst to describe the H_3^+ formation process on metals appears to be applicable to oxide-contaminated silicon surfaces. The origin of H^+ species in Figs. 10 and 11 cannot yet be unambiguously identified; however, there is nothing in the data that is inconsistent with a simple field-induced dissociation of the H_2 molecules as proposed for the uncontaminated surface.

V. SUMMARY

The results of this and previous studies indicate that the field evaporation of silicon in ultrahigh vacuum is qualitatively the same as that for metals if the substrate temperature is above 150 K during desorption. The rate of evaporation rapidly increases with applied voltage, and the evaporation voltage decreases with increasing temperature consistent with similar experiments on metals. The shift in the charge state from doubly to singly charged is in agreement with calculations based on the post-ionization model of field evaporation if the low-temperature evaporation field of silicon is assumed to be 3.5 V/Å.

In the presence of hydrogen the evaporation field of silicon is significantly reduced due to the formation of surface hydrides. The observation that in hydrogen the evaporation rate of silicon does not increase with increasing field strength indicates that the formation of these hydrides is the rate-limiting step. Measurements of the change in field-evaporation rate with laser power and hydrogen background pressure support this conclusion.

Pulsed-laser-stimulated field-desorbed hydrogen species (H^+ and H_2^+) arise from a field-adsorbed binding state. The field-induced decomposition of H_2^+ occurs over a voltage range consistent with a vacuum evaporation-field strength of 3.3–3.6 V/Å, in agreement with the post-ionization calculations, but considerably higher than the currently accepted value of 2.0 V/Å. Field desorption of H_3^+ is not detected unless oxide contamination is present. Measurements of the voltage dependence of the H^+, H_2^+, and H_3^+ at high and low laser powers give results which are consistent with the mechanism of H_3^+ formation proposed for metals; i.e., the field-induced reaction between a chemisorbed hydrogen atom and a field-adsorbed hydrogen molecule. The fact that H_3^+ is observed only when contamination is present suggests that weakly bound chemisorbed hydrogen on silicon is associated with surface contamination.

ACKNOWLEDGMENT

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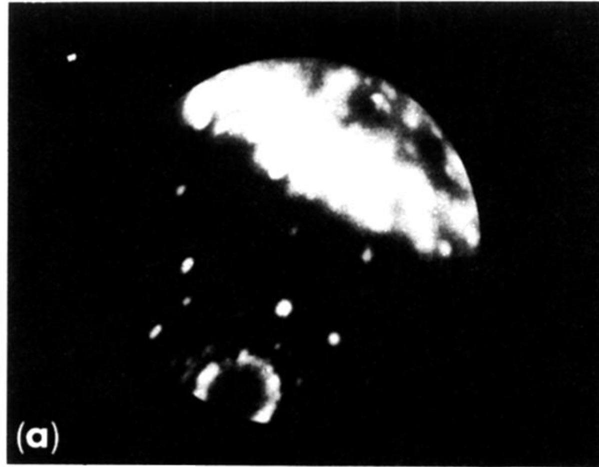


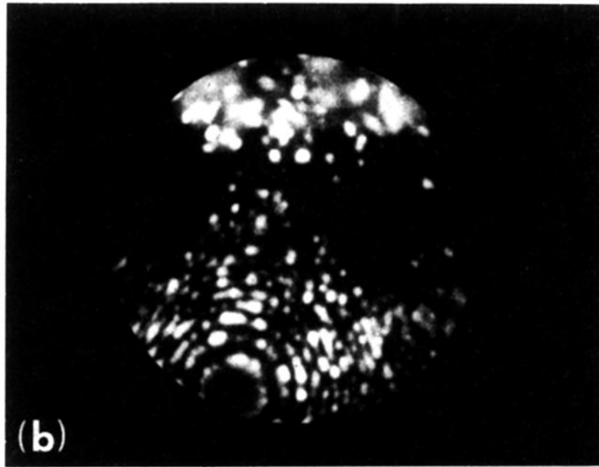
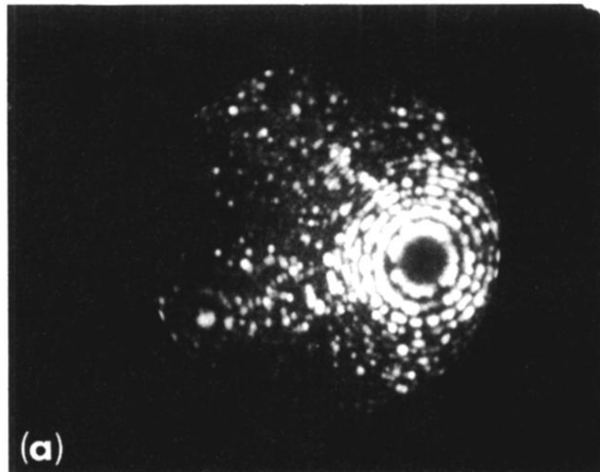


FIG. 3. Field-ion images of silicon showing the removal of the native oxide layer. Both images were recorded in 2×10^{-5} Torr H_2. (a) $V=3.52$ kV, (b) $V=4.50$ kV.



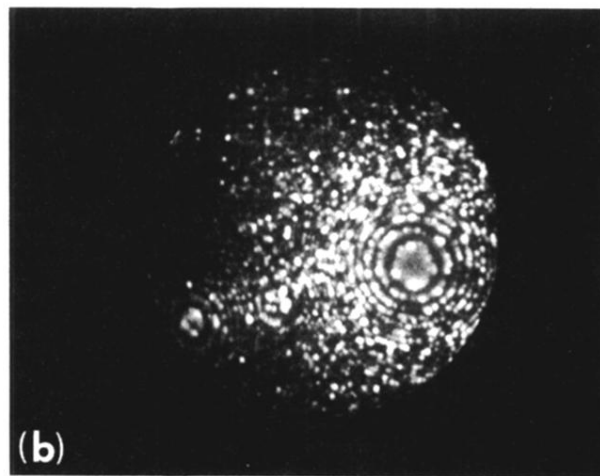


FIG. 4. Field-ion images of the silicon surface used in the study of field evaporation and field desorption from the clean surface. Both images were recorded in 3×10^{-6} Torr H_2. (a) $V=5.9$ kV, (b) $V=8.4$ kV.