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O. Dippel, S. Wright, and E. Hasselbrink

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Photochemical routes to silicon epitaxy

O. Dippel, S. Wright, and E. Hasselbrink[a)]
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

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The photochemistry of Si_2H_6 adsorbed on a hydrogen terminated silicon surface and the subsequent reactions of the photolysis products were investigated using high resolution electron energy loss spectroscopy and by measuring time-of-flight distributions with a mass spectrometer. The cracking pattern of the products ejected directly into the gas phase without colliding with either the surface or other molecules indicates that the primary photolysis channels yield mostly fragments that contain one silicon atom. It is likely that silicon is added to the surface by insertion of SiH_2 radicals into Si–H bonds at the surface but there is little evidence for reactions that remove excess hydrogen from the surface at 110 K. © *1997 American Vacuum Society.* [S0734-2101(97)56903-X]

I. INTRODUCTION

Very few of the increasingly numerous and detailed investigations of surface photochemistry have considered highly reactive products and chemical modification of the surface itself, presumably because of the difficulties involved in understanding the elementary chemical and photochemical processes. In this article we describe preliminary studies of the photochemistry of Si_2H_6 adsorbed on Si(100) with an emphasis on the mechanisms of epitaxial growth. A disadvantage of using conventional chemical vapor deposition (CVD) techniques during the fabrication of electronic devices is that existing structures are degraded at the substrate temperatures required to achieve epitaxial or polycrystalline growth. Consequently, there has been considerable interest in the development and optimization of photochemical processes that lead to silicon growth at low substrate temperatures. It is undoubtedly because of this application that many aspects of the photochemical routes to silicon growth and the gas phase photolysis of Si_2H_6 have been reported in recent years. Most notably, there have been a number of studies[1–4] that has focused on such mesoscopic parameters as the rate of growth but there is little understanding of the elementary reaction mechanisms.

Dissociative adsorption of Si_2H_6 on Si(100) is facile even at 110 K but our interest is not particularly in the thermal reactions of Si_2H_6 with silicon surfaces since these have been studied in detail previously.[5,6] However, exposure of a clean Si(100) surface at a temperature of approximately 630 K to atomic hydrogen results in a saturated monohydride phase[7] that does not react further with a Si_2H_6 overlayer at 110 K.[8] It is likely that most of the surface dangling bonds will be passivated with hydrogen during a continuous photoinduced growth process at low temperatures. While some have chosen to photolyze gaseous Si_2H_6 in low pressure reactors and to characterize the growth of micrometer thick and often amorphous silicon layers,[4,9] we choose to study the photochemistry of Si_2H_6 adsorbed on a well characterized monohydride phase at 110 K in an ultrahigh vacuum (UHV) environment. The identities and kinetic energy distributions of the photolysis and reaction products that are ejected from the surface were determined by measuring time-of-flight (TOF) distributions with a quadrupole mass spectrometer. Reactions of the photolysis products which result in addition of silicon containing species to the surface itself have been investigated using high resolution electron energy loss spectroscopy (HREELS).

II. EXPERIMENT

The single crystal silicon samples ($13\times13\times0.5$ mm) were cut from a $(100)\pm0.5°$ oriented, lightly doped, p-type wafer (resistivity 7–14 Ω cm) and mounted in an UHV chamber with a base pressure of 1×10^{-10} mbar. A sharp 2×1 low-energy electron diffraction (LEED) pattern was obtained after removing the native oxide from the surface by slowly heating it to 1200 K at a pressure not exceeding 1×10^{-9} mbar. A saturated monodeuteride phase was prepared by exposing the clean surface to atomic deuterium at 630 K and covering it with an overlayer of Si_2H_6 at 110 K. The surface was then illuminated with pulsed 193 or 248 nm light from an excimer laser (Lambda Physik, EMG 150) at repetition rates between 5 and 25 Hz. Reactions of the Si_2H_6 photolysis products with the surface are easier to characterize if the dangling bonds are terminated with deuterium rather than hydrogen.

A simple HREEL spectrometer with a resolution of approximately 10 meV was housed in a μ-metal can and is described in detail elsewhere.[10] A bias voltage was applied to the crystal in order to compensate for the difference in work function between the spectrometer and the deuterium terminated Si(100) surface. After photolysis of adsorbed Si_2H_6, the crystal was heated to 273 K before recording a HREEL spectrum in order to desorb any excess Si_2H_6 or weakly bound products that might be left on the surface.

A quadrupole mass spectrometer (QMS) with an off-axis secondary electron multiplier detector was mounted on flexible bellows so that the distance from the sample to the ionizer could be set between 90 and 190 mm. An advantage of being able to change the distance is that the drift times of ions in the QMS, which are not negligible, can easily be measured. In Fig. 1, the total modal TOF (the peak maxi-

[a)]Electronic mail: Hasselbrink@FHI-Berlin.mpg.de

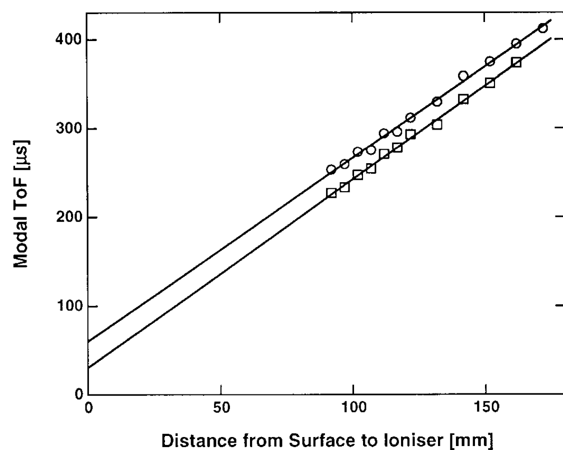

FIG. 1. Plots of the modal TOF of photodesorbed Si_2H_6 vs the distance from the surface to the ionizer for $m/e=30$ (□) and $m/e=60$ (○). The drift time of each ion is equal to the intercept of the y axis at zero distance.

mum) of Si_2H_6 desorbed from the surface using 248 nm light is plotted against distance from the ionizer to the surface for both $m/e=30$ and $m/e=60$. The drift times of these cracking products in the QMS are obtained by extrapolating the plots to zero distance.

III. RESULTS

The reactions of the photolysis products with the Si–D and Si–Si bonds on the surface are revealed and characterized by HREEL spectroscopy. Typical spectra of the monodeuteride phase prior to reaction and of the surface after photolysis of adsorbed Si_2H_6 at 193 nm are given in Figs. 2(a) and 2(b), respectively. The loss peaks at 57 and 188 meV were reported previously[11] and were assigned to the Si–D bending modes (losses at 52 and 62 meV can be distinguished at higher resolution) and stretching modes, respectively. In a similar study by Isobe *et al.*,[12] it was found that hydrogen containing temperature programmed desorption (TPD) products could be detected if a continuous flux of Si_2H_6 was supplied to a deuterium passivated surface during photolysis, but no reaction was observed when a multilayer coverage of Si_2H_6 was prepared before photolysis. Not only do we detect H_2 and HD during TPD after photolysis of an overlayer of Si_2H_6, but the new loss peaks identified at 83, 105, and 262 meV are also clearly the result of reaction. It is possible that silicon atoms bonded to one H atom (SiH), two H atoms (SiH_2), three H atoms (SiH_3), one H atom and one D atom (SiHD) or two H atoms and one D atom (SiH_2D) might be present after reaction of the photolysis products with the D terminated surface. The loss peaks at 83 and 262 meV are characteristic of hydrogen adsorbed on silicon surfaces[13,14] and can be assigned to the bending and stretching vibrations of the Si–H bonds in any of these species. The broad feature centered at 105 meV might envelope the scissor vibrations of SiHD and SiH_2, which are found at 100 and 113 meV, respectively,[13–15] but is also probably consistent with the umbrella vibrations of SiH_3 and SiH_2D.

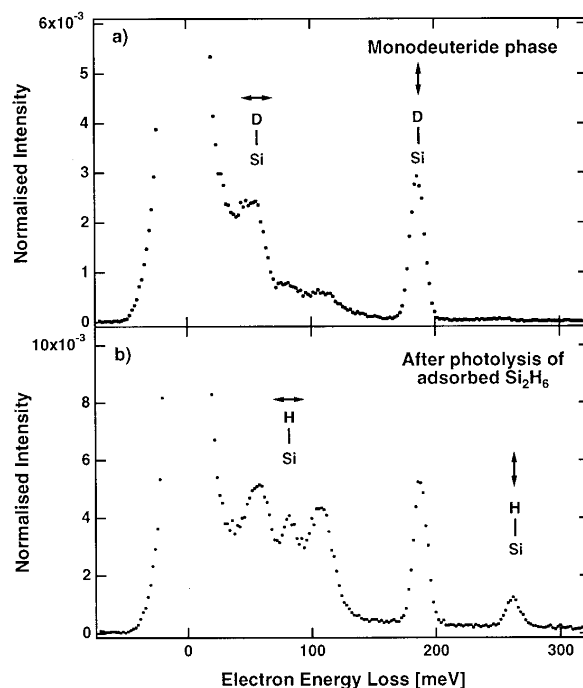

FIG. 2. (a) A typical HREEL spectrum of a saturated monodeuteride phase. The two losses identified at 57 and 188 meV are assigned to the Si–D bending and stretching vibrations, respectively. The spectrum in (b) was recorded after photolysis of adsorbed Si_2H_6 at 193 nm. The new losses at 83, 105, and 262 meV are assigned to the vibrations of hydrogen containing species adsorbed on the surface.

A complication with this and any other mass spectrometric study that uses electron impact ionization is cracking of Si_2H_6, SiH_4, and presumably all the other silicon containing products, whatever they might be. However, we find that the signal recorded for any ion from $m/e=56$ to $m/e=63$ can be attributed to cracking of photodesorbed Si_2H_6 without interference from any photolysis or reaction product. It is also fortunate that the signal for any ion from $m/e=28$ to $m/e=33$, which we attribute to photolysis and reaction products containing one silicon atom, is considerably in excess of that arising from Si_2H_6 cracking.

Some typical TOF distributions for the photolysis, reaction, and photodesorption products escaping into the gas phase are shown in Fig. 3. The bimodal TOF distribution recorded at $m/e=30$ is representative of all data recorded at $m/e=28$ to $m/e=33$. In common with other analyses of TOF distributions,[16] we use a least-mean-squares procedure to fit the slow component to a flux-weighted Maxwell–Boltzmann distribution,

$$f(v) \propto v^3 \exp(-mv^2/2k_BT), \quad (1)$$

and the fast component to a shifted velocity distribution of the form

$$f(v) \propto v^3 \exp\{[-(v-v_0)/\alpha]^2\}, \quad (2)$$

where v is the velocity, v_0 is a ''stream'' velocity, and α is a measure of the width of the distribution. The velocity distribution of the fast component can be characterized by a

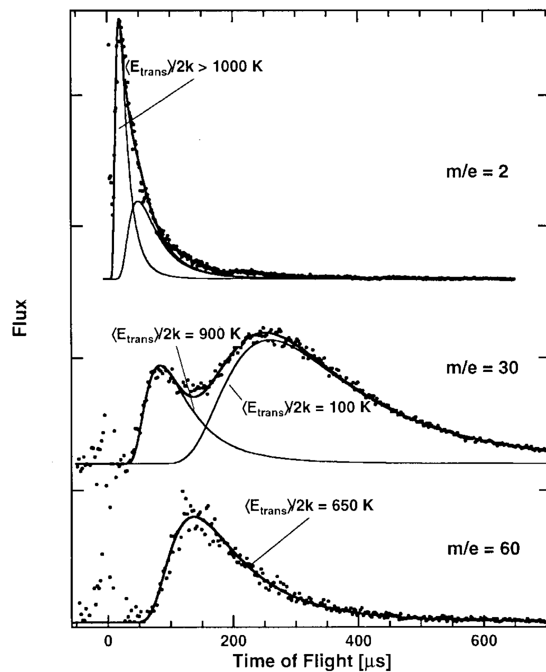

FIG. 3. Typical TOF distributions for the reaction, photolysis, and photodesorption products escaping into the gas phase. The bimodal TOF distribution recorded at $m/e=30$ is attributed to photolysis and reaction products containing one silicon atom. The fast channel corresponds to photolysis products that are ejected directly into the gas phase whereas the slow channel represents products that have become accommodated to the surface temperature as a result of collisions and reactions.

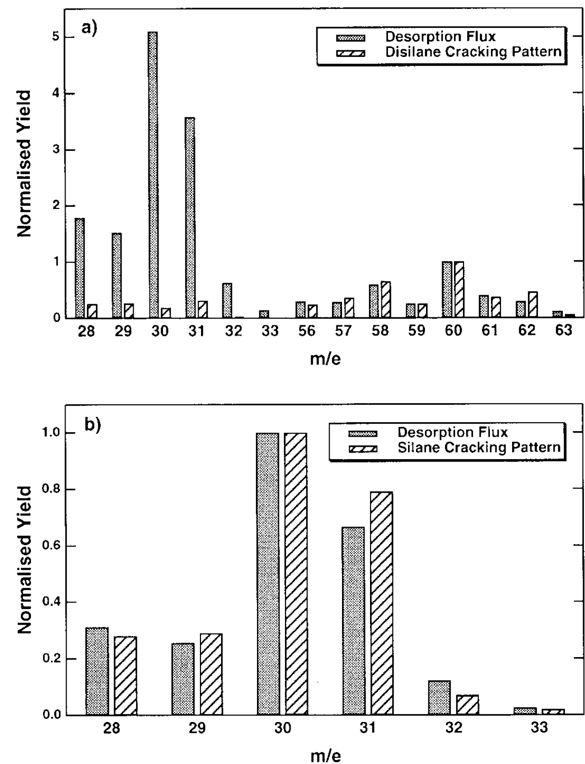

FIG. 4. The total integrated ion yields of the photolysis and photodesorption products escaping into the gas phase are compared with the (a) cracking pattern of gaseous Si_2H_6 measured using our QMS and (b) the reported cracking pattern of gaseous SiH_4. The distribution of ions containing two silicon atoms ($m/e=56$ to $m/e=63$) is consistent with cracking of photodesorbed Si_2H_6 only. The yields for ions containing one silicon atom ($m/e=28$ to $m/e=33$) are much greater than expected for the cracking of Si_2H_6 and the distribution is similar to that for SiH_4. Note that the Si_2H_6 cracking products were subtracted from the measured ion yields plotted in (b).

temperature of 900 K, which is far greater than the surface temperature. We obtain this by dividing the average kinetic energy by $2k_B$, although this is only strictly correct and meaningful for a Maxwell–Boltzmann distribution. In contrast, the thermal velocity distribution of the slow component is characterized by a temperature of 100 K and, hence, the translational energy of these molecules is accommodated to the surface temperature. A fast and a slow component were also resolved in the TOF distribution of H_2 but the fits to the data were less satisfactory and were not very consistent from one set of data to another. Nevertheless, we can conclude that the fast component is characterized by a translational energy in excess of 1000 K. The TOF distribution of photodesorbed Si_2H_6 presented in Fig. 3 was recorded at $m/e=60$ and is representative of all data recorded at $m/e=56$ through to $m/e=63$. It is too wide to be fitted convincingly with a Maxwell–Boltzmann distribution but is well fitted with the shifted velocity distribution given by Eq. (2). While the photolysis and reaction products could only be detected in the gas phase when the surface was illuminated with 193 nm light, photodesorbed Si_2H_6 was also easily detected when the surface was illuminated with 248 nm light.

Each TOF distribution can be integrated to give an ion yield and these are plotted in Fig. 4(a) together with the cracking pattern obtained for gaseous Si_2H_6 using our mass spectrometer. There is very good correspondence between the ion yields and the Si_2H_6 cracking pattern from $m/e=56$ to $m/e=63$ and hence we identify these ions with the cracking of photodesorbed Si_2H_6 only. It is clear from Fig. 4(a) that the ion yields measured at $m/e=28-33$ are far in excess of what is expected for Si_2H_6 cracking. Although a mixture of photolysis and reaction products might be expected to escape into the gas phase, Fig. 4(b) shows that there is a very convincing correlation between the ion yield distribution and the reported[17] cracking pattern for SiH_4 (we have not recorded this with our QMS). One of the reasons for using a deuterium passivated surface was to identify reactions of the photolysis products that remove deuterium from the surface. However, the ion yield distributions resulting from the photolysis of Si_2H_6 adsorbed on a hydrogen passivated surface and on a deuterium passivated surface were very similar so we find little evidence of deuterium abstraction from the surface.

IV. DISCUSSION

The lowest energy band in the ultraviolet spectrum of gaseous Si_2H_6 has a threshold for absorption at approximately 220 nm,[18] which explains why no photolysis or reaction products were observed after illumination with 248 nm light. Single photon excitation can be conveniently achieved

with 193 nm light from an ArF excimer laser and this is a popular choice for studies of both gas phase and surface photochemistry. In principle, it would be desirable to know the identity and concentrations of the species that might react with the surface. Unfortunately, it is fair to say that the photolysis of Si_2H_6 and the subsequent reactions of the products are not well characterized. If attention is confined to single photon excitation, then 20 fragmentation channels are energetically feasible at this wavelength.[19] The only primary products that survive in gas phase experiments are H_2 and SiH_4 but the other products of these 20 channels also include H, SiH, SiH_2, SiH_3, H_3SiSiH, H_3SiSiH_2, H_2SiSi, H_2SiSiH, Si, and Si_2 in addition to the closed shell species H_2SiSiH_2 and $Si(H_2)Si$. These must all eventually react to give mostly H_2, SiH_4, and Si_2H_6 with some higher silanes including solid compounds (from oligomerization reactions) since these are the only products that remain after photolysis.[20,21]

The importance of multiphoton excitation and multiple photolysis is not clear, but optical emission has been observed[4,22] from the $^2\Delta$ excited electronic state of SiH, which is not a product of any of the single photon fragmentation channels. Although both the $^2\Pi$ ground state and the $^2\Delta$ excited state were detected readily, there is some evidence[22] to suggest that most of the ground state population comes from decay of the excited state. Typically, laser fluences between 50 and 200 mJ cm^{-2} are used for gas phase photolysis[4,21–23] whereas fluences of no more than 30 mJ cm^{-2} were used in the present experiments. It may well be then that the concentrations of SiH and other products of multiphoton processes are negligible in our and other similar experiments.[1–3,9]

We have obtained the somewhat surprising result that some of the photolysis and reaction products escaping into the gas phase have a nonthermal velocity distribution and a characteristic temperature of 900 K whereas the translational energy of the rest is accommodated to the surface temperature. After considering the photolysis of Si_2H_6 and the likely fate of the products, we conclude that the fast component is the consequence of photolysis and ejection of the products directly without any collisions. If, however, the photolysis and reaction products scatter from either the surface or other molecules, they eventually become accommodated to the surface temperature. This phenomenon might well be observed whenever highly energetic products are produced by photolysis of condensed phases. Indeed, the velocity distribution of CO resulting from the photolysis of condensed Cl_2CO is also bimodal.[24] Since CO is a primary photolysis product and does not react further with Cl_2CO, the slow component was simply attributed to photolysis in the second and in deeper layers while the fast component was attributed to photolysis in the top layer only.

Given the many products that might be produced by photolysis, it is curious that the photolysis and reaction products escaping into the gas phase seem to be mainly SiH_4 and H_2. Having identified the fast component with photolysis products only, we have the opportunity to remark on which of the 20 single photon fragmentation channels are likely to be important. If the photolysis products contain a significant amount of H_2SiSiH_2, H_3SiSiH, $Si(H_2)Si$, H_2SiSi, H_3SiSiH_2, and H_2SiSiH, which all contain two silicon atoms, then some evidence for these should be found in the ion yield distribution from $m/e=56$ to $m/e=63$. However, the ion yield distribution closely matches the cracking pattern of Si_2H_6, which suggests that very little, if any, of the photolysis products are radical and closed shell species containing two silicon atoms. It is conceded that there is the possibility that these species could crack in the ionizer and give mostly fragments that contain one silicon atom and a cracking pattern that fortuitously resembles that of SiH_4. It would appear that the most important primary photolysis pathways yield SiH_4 rather than radical and closed shell species containing two silicon atoms. If this is the case, then either SiH_2 or Si and H_2 must be produced at the same time as SiH_4, according to the 20 possible fragmentation channels listed by Stafast.[19] As there is a fast component in the H_2 TOF distribution and we have evidence for the addition of hydrogen to the surface, both of these pathways are likely. The channel leading to SiH and H can be dismissed on the grounds that it is one of the least exothermic channels and all spectroscopic studies seem to agree that SiH is mostly the product of a multiphoton process.[22,25]

While comparisons between gas phase and surface photochemistry are useful to some extent, it would be unreasonable to expect the primary photolysis product yields to be the same. Electronic excitations which would yield dissociation products in gas phase experiments are likely to be efficiently quenched when Si_2H_6 is in close proximity to a silicon surface. Consequently, the relative and absolute yield of products will depend on the lifetime of the excited state or states and the ground state potentials for possible dissociation pathways.

Any SiH_4 produced by photolysis that does not have a direct trajectory into the gas phase will lose approximately 90% of its translational energy by one collision with an almost stationary Si_2H_6 molecule and will be fully accommodated to the surface temperature after very few collisions. Despite the complex chemistry of the reactive photolysis products in the Si_2H_6 overlayer, the final products, which again will be accommodated to the surface temperature after a few collisions, must be H_2, SiH_4, Si_2H_6, and higher silanes. Both H_2 and SiH_4 will desorb into the gas phase while Si_2H_6 and higher salines will remain adsorbed on the surface.

In the gas phase, the rate of insertion of SiH and SiH_2 into the Si–H bonds of SiH_4 is gas kinetic (the collision rate calculated using the kinetic theory of gases)[22,23] but there is no observable reaction[21] of SiH_3 with SiD_4 or Si_2H_6. Surprisingly, the surface loss probabilities (the sum of the sticking and reaction probabilities) for SiH, SiH_2, and SiH_3 impinging on hydrogenated amorphous silicon surfaces are reported as 0.94,[26] 0.15,[27] and 0.05–0.3,[28–30] respectively. Apparently, much of the SiH_2 is reflected from the surface without reaction, while the surface loss probability of SiH_3 may be higher than expected. Clearly, there are aspects of the reactions of silicon radical species with hydrogen terminated sili-

con surfaces that remain to be explored. Regardless of the detailed surface reaction dynamics, it is likely that insertion of a silicon containing radical, whether it be SiH_2 or some other species, leads to addition of silicon to the surface.

A specific requirement of epitaxial growth using Si_2H_6, whether by photochemical routes or by conventional CVD, is that there is some mechanism by which the excess hydrogen is removed from the surface. The rate limiting step in conventional CVD at low temperatures is found to be the thermal desorption of H_2 whereas a possible route after photolysis of Si_2H_6 is abstraction by radical species. It is easy to see how insertion reactions will lead to addition of silicon to the surface but there seems to be little scope for abstraction reactions. Hydrogen atoms are well known to abstract hydrogen adsorbed on silicon surfaces but there is a small activation energy of approximately 4–8 kJ mol^{-1} (Refs. 31 and 32) associated with the surface rather than the kinetic energy of the incident hydrogen atoms. The efficiency of abstraction by hydrogen atoms will, therefore, be rather small at 100 K and this might also be the case for other radical species. In the absence of an efficient mechanism for the removal of excess hydrogen, it is inevitable that silicon films grown at 110 K will be amorphous. Nevertheless, in addition to more efficient abstraction reactions, there is also the possibility of an alternative photochemical route to efficient hydrogen loss at moderate temperatures. If, as we suggest, there is a significant population of trihydride groups on the surface as a result of SiH_2 insertion, then these can react with adjacent adsorbed hydrogen to give gaseous SiH_4.[33,34] Thus the reaction of SiH_2 with surface Si–H bonds eventually leads to a net loss of two hydrogen atoms from the surface.

V. CONCLUSIONS

Some aspects of Si_2H_6 photochemistry relevant to silicon growth were explored. The morphology and rate of growth will be partly determined by the fate of the fragmentation products. A fraction of these products is ejected directly from the surface with a mean translational temperature far in excess of the surface temperature. The cracking pattern of all products escaping into the gas phase shows no evidence of primary photolysis products containing two silicon atoms. Reactive species that are not ejected directly are consumed by reaction with adsorbed Si_2H_6 and with the surface. Reaction of the photolysis products with the surface was revealed by HREEL spectroscopy but it was not possible to deduce the chemical identities of these strongly bound surface reaction products. We suggest, however, that an important reaction is insertion of SiH_2 radicals into Si–D bonds. While abstraction does not seem to be efficient at 110 K, it is possible that excess hydrogen can be lost from the surface at somewhat higher temperatures.

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