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Absolute total cross sections for electron-stimulated desorption of hydrogen and deuterium from silicon(111) measured by second harmonic generation

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Using second harmonic generation (SHG) as a sensitive measure of the amount of hydrogen or deuterium remaining on a silicon(111) surface, we have measured absolute total cross sections for electron stimulated desorption (ESD) over a range of incident energies from 50 to 300 eV. The measured cross sections for hydrogen are approximately a factor of 10 smaller than those found by Fuse [T. Fuse *et al.*, Surf. Sci. **420**, 81 (1999)] on the Si(100) surface and a factor of 10 greater than found for deuterium on the Si(111) surface by Matsunami [N. Matsunami *et al.*, Surf. Sci. **192**, 27 (1987)]. The measured cross sections for deuterium are consistent with the measurements of Matsunami *et al.* on the Si(111) surface. This indicates that while there is a significant isotope effect, the choice of surface also plays an important role. The details of the desorption spectrum are consistent with the multihole desorption model. Comparison to calculated ionization cross sections suggests that the $2s$ core hole excitation is more likely to lead to desorption than the $2p$ core hole excitation.

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I. INTRODUCTION

Hydrogen plays a critical role in silicon semiconductor technology. It mediates chemical vapor deposition (CVD) growth of silicon devices as well as passivating electrically active defects at Si/SiO_2 interfaces.[1–3] Electron stimulated desorption (ESD) of hydrogen from silicon surfaces helps elucidate the nature of the Si-H bond and direct bond breaking mechanisms. Also, an understanding of ESD is directly applicable to the emerging technology of electron beam patterning of silicon devices.[4,5]

There has been considerable effort to measure and understand thermal desorption.[6–8] ESD is less well studied due in part to the difficulty in measuring desorbed hydrogen. Measuring only those atoms that escape the surface in an ionized state, Madden *et al.*[9] found a desorption threshold at approximately 24 eV of incident energy. By analyzing Auger line shapes, they attributed the desorption to a shake up process, which leaves two holes in the Si-H bond. They noted that the interaction energy of two holes would be sufficient to push them out of the valence band so that the state would have a lifetime long enough to cause desorption. If this is indeed the case, then desorption should also proceed by the Knotek-Feibelman process,[10] where the two-hole state is produced by Auger decay of a silicon core hole. This process was only recently observed by Fuse *et al.*[11]

Recent studies of ESD have focused on desorption induced by scanning tunneling microscopy (STM). Lyding *et al.*[12] identified two paths for STM desorption. At energies below 6 eV, they attribute desorption to a serial vibrational excitation mechanism that is unique to the STM environment.[13] Above 6 eV desorption is attributed to a Menzel-Gomer-Redhead[14,15] (MGR) process, which is also heavily influenced by the proximity of the STM tip.

There have been only a few measurements of absolute total cross sections for electron-stimulated desorption of hydrogen or deuterium from silicon surfaces. Matsunami *et al.*[16] measured the amount of deuterium remaining on a silicon (111) surface during ESD by neutron activation and found extremely low cross sections for desorption (10^{-20} cm^2 at 200 eV). Recently, Fuse *et al.*[11] combined time of flight (TOF) and elastic recoil detection analysis (ERDA) to monitor the amount of hydrogen remaining on a Si(100) surface during electron bombardment. They found much larger cross sections (10^{-18} cm^2 at 200 eV) than Matsunami *et al.* and attributed the difference to an isotope effect without considering the influence of the differing crystal surfaces.

In this work, the technique of monitoring hydrogen coverage using second harmonic generation has been applied to electron-stimulated desorption. Using this approach we were able to measure the absolute total cross section for electron-stimulated desorption of hydrogen from the Si(111) surface over a range of incident energies from 50 to 300 eV. For comparison to the work of Matsunami *et al.*, we also measured deuterium desorption from the Si(111) surface. By performing the experiment on the same crystal surface as Matsunami *et al.* [Si(111)] we can separate the isotope effect from the effect of differing crystal surfaces. Our deuterium measurements are consistent with those of Matsunami *et al.* Our measured hydrogen cross sections are approximately 10 times greater than the deuterium measurements and can be attributed to an isotope effect. However, they are approximately 10 times less than the hydrogen measurements of Fuse *et al.*, indicating a dependence on crystal surface orientation. Our measurements are consistent with the two-hole desorption mechanism of Madden *et al.* Comparison to calculated silicon core ionization cross sections indicates that Knotek-Feibelman desorption proceeds more readily from a $2s$ core hole than from a $2p$ core hole.

II. EXPERIMENT

A 1 cm×2 cm sample was cut from a Si(111) wafer at an azimuthal orientation that maximizes the amount of second

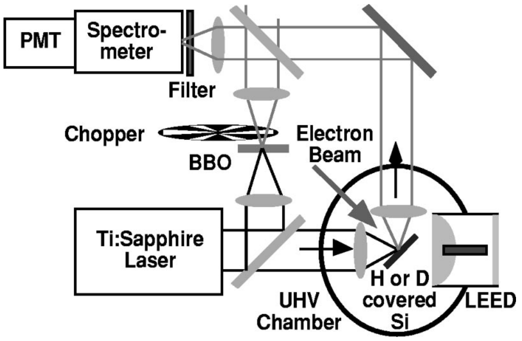

FIG. 1. Experimental arrangement.

harmonic light produced in the experimental apparatus.[14] After cleaning the sample by a standard RCA process, it was inserted into an ultrahigh vacuum (UHV) chamber that was evacuated to a base pressure of 2×10^{-10} Torr. The sample holder allowed direct resistive heating, and the sample temperature was determined by a pyrometer. Once vacuum was achieved, the surface was prepared by flash heating to 1500 K for 30 s. Reducing the temperature to 1000 K the sample was then exposed to 3 Torr of H_2 for 10 min. This method has been shown to produce a surface superior to surfaces produced by the more common hot filament dissociation technique. The experiments of Mao *et al.* suggest that the monohydride terminated Si(111) surface produced by this technique is similar in quality to the nearly ideal surface produced by the standard wet etch process.[17] In this experiment, the surface quality was verified by low energy electron diffraction (LEED). After dosing, the surface exhibited a sharp bright unreconstructed (111) LEED pattern. On several occasions during the course of these experiments the quality of the surface produced by this procedure was further verified by thermally desorbing the hydrogen at lower temperature and observing the LEED pattern from the bare surface. A sharp, bright 7×7 reconstructed (111) LEED pattern was observed.

The experimental apparatus is shown in Fig. 1. A mode-locked Ti:sapphire laser provides the intense light necessary for second harmonic generation. Second harmonic light is separated from the fundamental light by filters and a grating monochromator. A photomultiplier tube detects the second harmonic light. A Faraday cup on the sample holder provides a measure of the electron beam flux, and a mirrored aperture plate on the Faraday cup insures alignment of the electron beam with the laser.

To remove any long term fluctuations in the laser intensity or the detection electronics, the signal is normalized to second harmonic light produced in a BBO crystal. Using a chopping scheme, the same detection electronics are used for both signals. For simplicity, only one chopping wheel is used, so the detected signal is either the sample signal alone, or the sample signal plus the BBO signal. Due to the pulse structure of the laser, the combined beams do not overlap temporally and the resulting signal is a simple sum. The properly normalized signal is algebraically constructed from these.

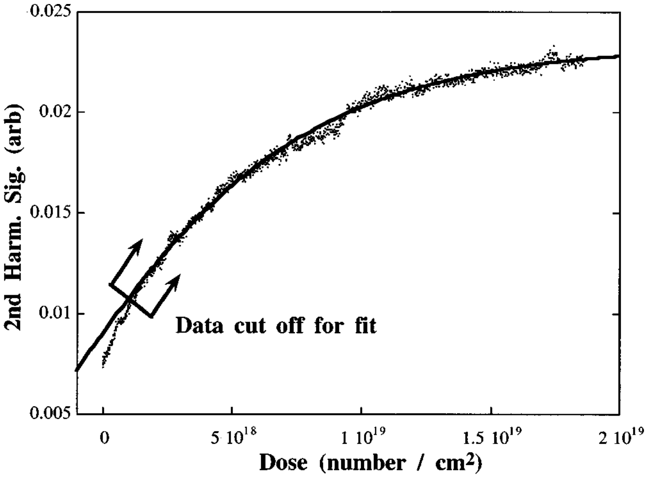

FIG. 2. Data for 300 eV. The function is fit only to that data in the range of validity above the indicated cutoff.

The maximum power flux from the electron gun during any of these experiments was 0.015 W/cm^2. Considering the conductivity of silicon and the conductivity of the electrical leads connected to the sample, this power load is not expected to change the surface temperature by more than 1 °C. The expected thermal desorption is negligible. To determine if the laser induces a significant amount of desorption, the signal from a hydrogenated surface was monitored without the electron gun. Over a period of 3 h no detectable desorption was observed.

Data from a typical experiment is shown in Fig. 2. The second harmonic signal is monitored during electron bombardment. Electron flux measurements before and after the experiment are used to convert time to dose and the normalized signal is plotted as a function of electron dose.

Silicon surfaces are known to be extremely robust under low-energy electron bombardment, but that may not be remain true for a hydrogenated surface. It is important to note that the signal very nearly returns to the level observed on the clean unbombarded surface, and the post bombardment LEED pattern shows little degradation. Some surface damage may have occurred, but at a level small enough to only slightly influence the signal level and therefore the desorption measurement.

The dependence of second harmonic signal on hydrogen coverage was investigated by Höfer,[18] who found that for 0% to 40% of a monolayer of coverage, the dependence of the second harmonic signal on the fractional coverage θ is well modeled by the simple relation

$$\text{SHG signal}=S_0(1-1.3\theta)^2, \tag{1}$$

where S_0 is the signal at zero coverage. Note that 40% coverage corresponds to a signal level about 25% of maximum. Assuming first order kinetics, the dependence of coverage on electron dose can be modeled as a simple exponential,

$$\theta=\theta_0 e^{-\sigma D}, \tag{2}$$

where D is the electron dose and σ is the cross section. Combining this with Eq. (1) gives the expected dependence of second harmonic signal on electron dose:

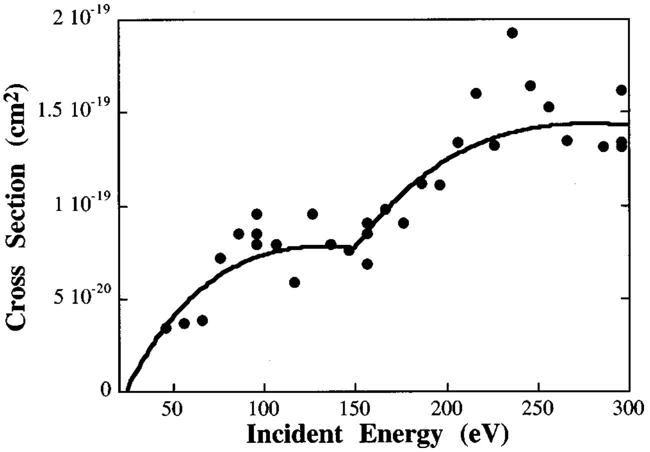

FIG. 3. Absolute total cross sections for electron-stimulated desorption of hydrogen from Si(111). The fit function is described in the text.

$$\text{SHG signal} = S_0(1-1.3\theta_0 e^{-\sigma D})^2. \tag{3}$$

The curve plotted in Fig. 2 is a fit of this function (plus a measured background term) to the experimental data. From this fit, the cross section is determined.

Due to the small size of the cross sections, it was not always practical to measure for long enough periods to establish the asymptote of the exponential. To circumvent this problem, we modified the experiment. At the beginning of the experiment we bombarded at high energy long enough to drive the coverage up to the range of validity for the fit function. Then we bombarded for a few hours at the desired energy to establish the slope. Finally, we thermally desorbed the remaining hydrogen and measured the bare surface for a several minutes to establish the asymptote. The asymptote data were manually inserted into the previous data at a very large dose value and then the data were fitted as indicated above.

III. RESULTS

Figure 3 shows the measured cross section for electron stimulated desorption of hydrogen from the Si(111) surface as a function of the kinetic energy of the incident electrons. Multiple measurements were performed at 300, 160, and 100 eV. The spread in these data is indicative of the experimental error. The measured cross sections are approximately one tenth of the values measured by Fuse *et al.*[11] for electron-stimulated desorption of hydrogen from the Si(100) surface, indicating a strong dependence of ESD on surface structure. There is an inflection at approximately 150 eV that can be explained as the onset of a Knotek-Feibelman process. The curve passing through the data is a fit function described in detail below.

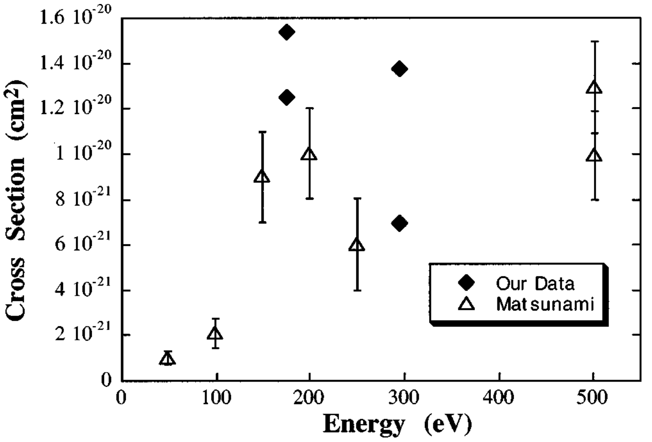

FIG. 4. Absolute total cross sections for electron-stimulated desorption of deuterium from Si(111) as measured in this experiment (black diamonds) and as measured by Matsunami *et al.* (Ref. 16) (open triangles).

Figure 4 shows the measured cross sections for electron stimulated desorption of deuterium from the Si(111) surface as a function of the kinetic energy of the incident electrons. Also plotted are the data of Matsunami *et al.*[16] for the same process. Two points were measured at both 300 eV and 180 eV. The spread of these data is indicative of the error in the measurement. Although the error is quite large and the values tend to be slightly larger, these data are comparable to the measurements of Matsunami *et al.* The values for deuterium are a factor of 10 lower than the hydrogen cross sections measured at the same energy on the same surface, indicating a strong isotope effect. For comparison, Fig. 5 shows all available total ESD cross section data together on a log plot. Note that the cross section for electron-stimulated desorption of hydrogen from Si(111) is about 10 times larger than that for deuterium from the same surface and 10 times smaller than for hydrogen from the Si(100) surface.

IV. DISCUSSION

In our data for hydrogen, an inflection can be discerned at approximately 150 eV. This happens to be the energy required for liberating a 2*s* electron from silicon, suggesting the onset of a Knotek-Feibelman process. If this is the case,

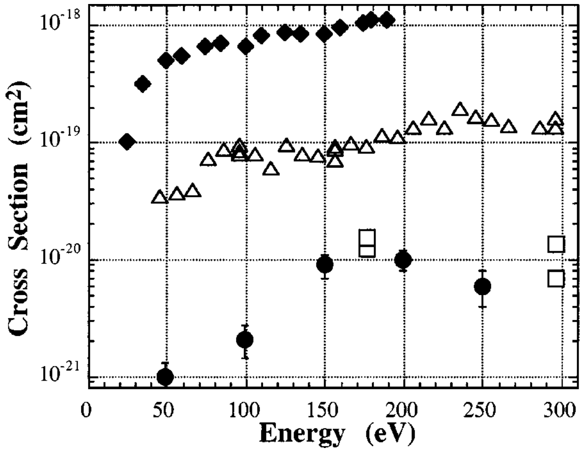

FIG. 5. Absolute total cross sections for electron stimulated desorption. Black diamonds are hydrogen on Si(100) from Fuse *et al.* (Ref. 11), open triangles are hydrogen on Si(111) from this work, black circles are deuterium on Si(111) from Matsunami *et al.* (Ref. 16), and open boxes are deuterium on Si(111) from this work.

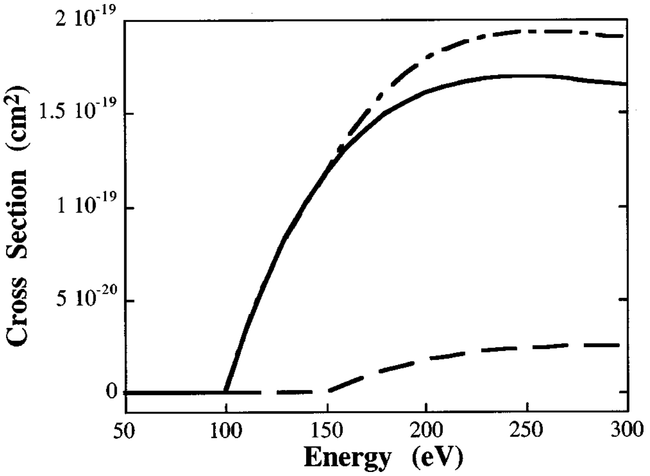

FIG. 6. Calculated cross sections for silicon core ionizations under electron bombardment from Matsunami *et al.* (Ref. 16). The solid line is the cross section for liberating a silicon 2*p* core electron. The long-dashed line is for a silicon 2*s* electron, and the long-short dashed line is the sum of the two.

then the shape of the extra desorption probability should be proportional to the 2*s* ionization cross section. Using a simple two-body approximation, ionization cross sections for core electrons can be calculated.[19] Although the absolute value of the cross section obtained from such a simple calculation can be off by a factor of 2 or more, the shape of the probability as a function of incident energy and the relative sizes of different core ionizations have been found to be in good agreement with experiment. In the work by Matsunami *et al.*, cross sections were calculated for 2*s* and 2*p* core ionizations in silicon. These are plotted in Fig. 6 along with their sum.

The shapes of these ionization cross sections are similar and typical of electron-electron ionization processes in this energy range. If the remaining desorption probability is due to the double ionization of the H-Si bond as indicated by the work of Madden *et al.*, it would be reasonable to assume that that component of the desorption probability also has a similar shape. For the purpose of this analysis, we used the calculated shape of the 2*s* ionization shifted so that the threshold is at 24 eV as an ad hoc functional form for the remaining desorption probability. Using this ad hoc functional form multiplied by a scaling factor for the underlying desorption probability plus the calculated ionization cross sections multiplied by another scaling factor, we performed a two-parameter fit to our data. Since there is no great inflection at 150 eV in the ionization cross sections, this did not fit our data very well. However, if we leave out the 2*p* ionization probability we get a much more reasonable fit. These fits are shown in Fig. 7. This suggests that a 2*p* core ionization does not lead to desorption as readily as a 2*s* ionization.

Based on this observation, we applied the same analysis to the data of Fuse *et al.* and obtained the same result. These fits are shown in Fig. 8. Although they have one data point that might indicate 2*p* core holes can result in desorption, there seems to be little doubt that desorption via a 2*p* ionization is largely suppressed.

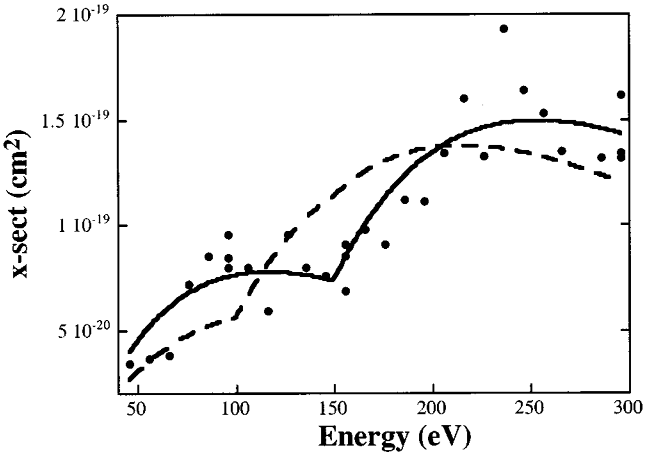

FIG. 7. Two fits to our data. The dashed line includes 2*p* core ionizations. The solid line excludes 2*p* core ionizations.

Although we have no first principles description of the expected shape for the low-energy desorption probability, the success in fitting an ad hoc function derived from ionization cross sections is consistent with the double ionization process described by Madden *et al.* We therefore conclude that desorption in the measured energy range proceeds primarily through the doubly ionized state, which is either produced directly or above 150 eV via Auger decay of a 2*s* core hole.

We may also speculate on the reasons for the differences between hydrogen and deuterium. The probability for desorption can be broken into two parts: the probability of producing the desorbing state, and the probability of that excitation producing desorption. We expect that an isotopic change should have little effect on the electronic excitation. Also, if the lifetime of the two-hole repulsive state is long compared to the time for the adatom to move away from the surface, desorption would occur for both species. However, if the lifetime of the excited state is comparable to the desorption time, we would expect an isotopic effect. In a fixed amount of time in the repulsive state, the lighter species will

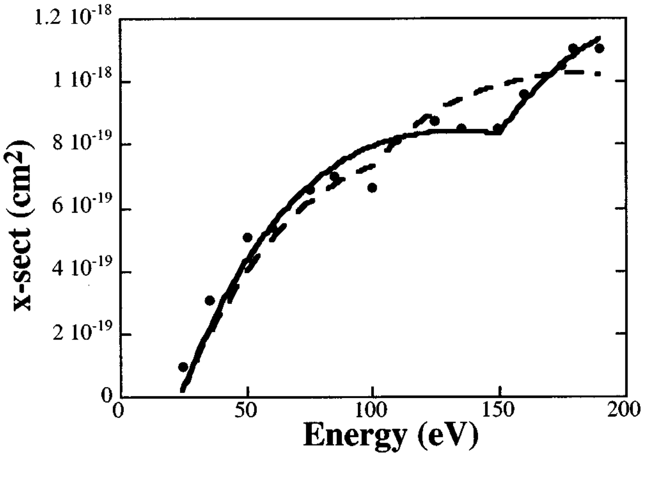

FIG. 8. Two fits to the data of Fuse *et al.* (Ref. 11). The dashed line includes 2*p* core ionizations. The solid line excludes 2*p* core ionizations.

move further from the surface than the heavier species and will also acquire more kinetic energy. Therefore the lighter species will be more likely to escape the surface. This may be the origin of the observed isotopic effect.

The reason for the difference between surfaces is less clear. It is possible that the excited state is longer lived on the (100) surface, increasing the likelihood of desorption, but it is also possible that the excited state is more easily produced perhaps due to some more advantageous symmetry. Bond angles and bond lengths differ significantly among the (100) dihydride, the (100) 2×1 reconstructed monohydride, and the (111) monohydride surfaces. This could affect the probability of producing the excited state as well as the probability of the excited state leading to desorption. Sensitivity of the surface structure to hydrogen coverage may also account for the observed differences.

V. CONCLUSION

Using second harmonic generation as a sensitive monitor of the amount of adsorbate remaining on the surface, we have measured absolute total cross sections for electron-stimulated desorption of hydrogen and deuterium from a silicon (111) surface over a range from 50 to 300 eV of incident electron kinetic energy.

In the work by Fuse *et al.*,[11] the factor of 100 increase in cross section over the work of Matsunami *et al.*[16] was attributed to an isotope effect without considering the difference in the surface structure. In this work, we have found that, while there does appear to be an isotope effect, there is also a difference due to the different surface structure. We find that the cross sections for desorption from the (111) surface are a factor of 10 lower than those from the (100) surface. Furthermore, on the (111) surface hydrogen desorbs approximately 10 times more readily than deuterium.

Our measurements are consistent with the primary desorption mechanism in this energy range, being double ionization of the silicon-hydrogen bond either directly, or, given sufficient energy, by an Auger transition to a $2s$ core hole in the silicon. We also find that a similar transition to a $2p$ silicon core hole is suppressed.

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