Energy-loss-spectroscopy studies on the adsorption of hydrogen on cleaved Si(111)-(2×1) surfaces

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Localized vibrations of hydrogen adsorbed on Si(111)-(2×1) cleaved surfaces have been investigated by energy-loss spectroscopy (ELS). A new vibrational mode of $\hbar\omega = 100$ meV has been found after exposure to molecular hydrogen. Its intensity is dependent on the surface step density indicating that this mode is related to adsorption sites near or on step atoms. Models for this type of adsorption are proposed. Off-specular measurements and spectra taken after coadsorption of deuterium show evidence for the simultaneous existence of SiH, SiH$_2$, and SiH$_3$ configurations indicating an erosive action of hydrogen even at an early stage of adsorption.

INTRODUCTION

The adsorption of hydrogen on Si(111) surfaces has been the subject of numerous studies theoretically as well as experimentally with different methods. Most of the theoretical studies of the H-Si(111) system are based on band-structure-type models.[1-4] Appelbaum and Hamann[1] performed a self-consistent calculation of the electronic structure using a pseudopotential method. The density of states they obtained agrees well with the adsorbate-induced peaks observed by ultraviolet photoemission spectroscopy (UPS).[5,6] The hydrogen equilibrium position and the vibrational bond force constant perpendicular to the surface have been determined via the Hellmann-Feynman theorem and reasonable values are obtained. Similar results were obtained by Pandey[2] using a semiempirical tight-binding method for a semi-infinite substrate. Ho et al.[3] studied two different adsorption modes, the monohydride phase and the trihydride phase using again a self-consistent pseudopotential method. These calculations mainly supported the interpretation of the earlier ELS[5] and UPS[6] results with regard to the electronic structure and also helped to explain the extra adsorbate-induced structure in the experimental data in the submonolayer region.

Additional information was obtained by high-resolution ELS studies[7] where the Si-H stretching vibration has been observed which supports the assumption that upon adsorption of atomic hydrogen the reconstruction relaxes to a primitive 1×1 surface lattice[5] with the hydrogen positions on top of the silicon surface atoms saturating the dangling bonds. Results of corresponding cluster-model calculations by Hermann and Bagus[4] on the basis of

ab initio Hartree-Fock—LCAO (linear combination of atomic orbitals) theory were quite consistent with this assumption and the experimental data. The calculated and measured stretching vibrations differ only by about 10%. New information was added by recent high-resolution ELS results from the hydrogen adsorption on Si(111)-(7×7) surfaces observed by Wagner et al.,[8] who found evidence for a SiH$_2$ configuration and flash desorption studies carried out by Schulze et al.,[9] who could observe a distortion of the surface structure associated with silane production. These effects gave evidence for a chemical erosive action at the surface when it is exposed to atomic hydrogen by silane formation. Stimulated by these recent findings, new interest was attracted to restudy the room-temperature adsorption on Si(111)-(2×1) cleaved surfaces with high-resolution ELS with an improved sensitivity compared to the former experiment.[7] The results of these measurements will be reported in the following.

EXPERIMENTAL

The measurements were performed with a double-pass electrostatic cylindrical deflector spectrometer with an angular resolution of about 1.7°. The angular aperture at a beam energy of 5 eV is estimated to be of the order of 1°. All spectra were measured with a spectrometer resolution of 7 meV corresponding to a pass energy of about 0.5 eV. The samples were oriented so that the [$\bar{2}$11] direction always was perpendicular to the plane of incidence. The UHV system was pumped by an ion-getter pump supported by a liquid-nitrogen-cooled titanium sublimation pump (TSP). The pumping unit could be closed off by a separation valve. The ex-

periments were carried out at a pressure of 5×10^{-11} mbar or less. Clean Si(111) surfaces were produced from silicon bars cut from n-type single-crystal material ($\rho = 30$ Ω cm) using the common two-wedge method. The bars were previously oriented by the Laue x-ray technique. The targets could be heated resistively.

Exposures to atomic hydrogen were carried out by moving the target surface opposite to a tungsten filament heated up to 2100 °C. Molecular hydrogen was applied with the target placed in the scattering chamber of the spectrometer. Care was taken to avoid coadsorption of hydrocarbons, water, and oxygen by carefully flushing the system with hydrogen and cooling the titanium sublimation pump as well as the stainless-steel reservoir of the gas inlet system with liquid nitrogen throughout the whole measurements. All gas exposures were carried out with the ion pump and the TSP almost closed by a separation valve. This was found to be absolutely necessary to minimize exchange reactions in the ion pump and to avoid backstreaming of contaminants out of the pump unit. In addition when dosing with molecular hydrogen all filaments were turned off except for one remote low-temperature ion gauge. Control measurements of the mass spectra during hydrogen inlets did not show any increase of gases other than hydrogen. After cooling the TSP trap with liquid nitrogen, the analysis of the residual gas in the chamber showed that mainly hydrogen contributed to the base pressure. This condition enabled us to take measurements for many hours without any coadsorption of hydrocarbons, water, or oxygen which would be indicated by the appearance of extra peaks at around 360 and 130 meV.[10-12]

RESULTS AND DISCUSSION

Figure 1 shows loss spectra taken from clean Si(111) cleaved surfaces. The spectrum drawn in full line is that of a freshly cleaved surface with 2×1 superstructure and the dashed line spectrum is that of an annealed target with a 7×7 superstructure. The quite intensive loss peak at 57 meV of the 2×1 spectrum has been interpreted[13] as the excitation of a surface phonon, correspondingly the gain peak of -57 meV is due to its deexcitation. The small loss at 114 meV is due to the excitation of the first overtone of the phonon. As there was no experimental indication of the existence of a similar excitation on the 7×7 surface (see dashed drawn spectrum) the existence and intensity of the 57-meV loss may be used as a definite indicator for the presence of the 2×1 superstructure. For a freshly cleaved sample the relative intensity of that peak with regard to the elastically reflected intensity was
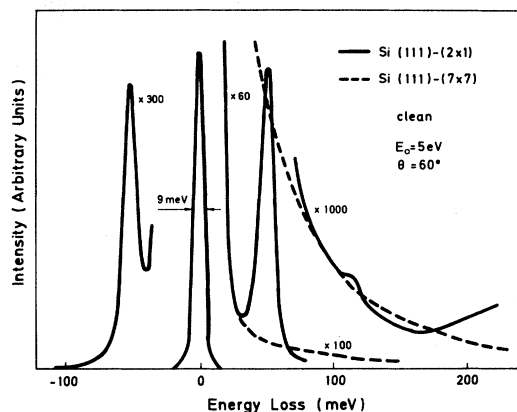

FIG. 1. Loss spectra of a clean Si(111) surface. The spectrum drawn in full line is that of a freshly cleaved surface which has a 2×1 superstructure. The small structure visible at 114 meV is the overtone of the longitudinal surface phonon which exists only on the Si(111)-(2×1) surface. The dashed curves reveal the spectrum of Si(111)-(7×7) surface.
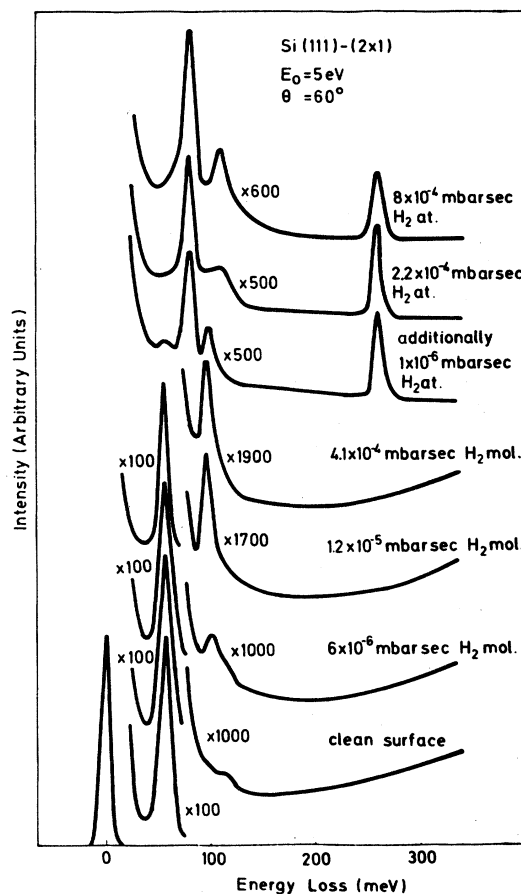

FIG. 2. Sequence of loss spectra taken after several dosages of molecular hydrogen (lower part) and atomic hydrogen (upper part).
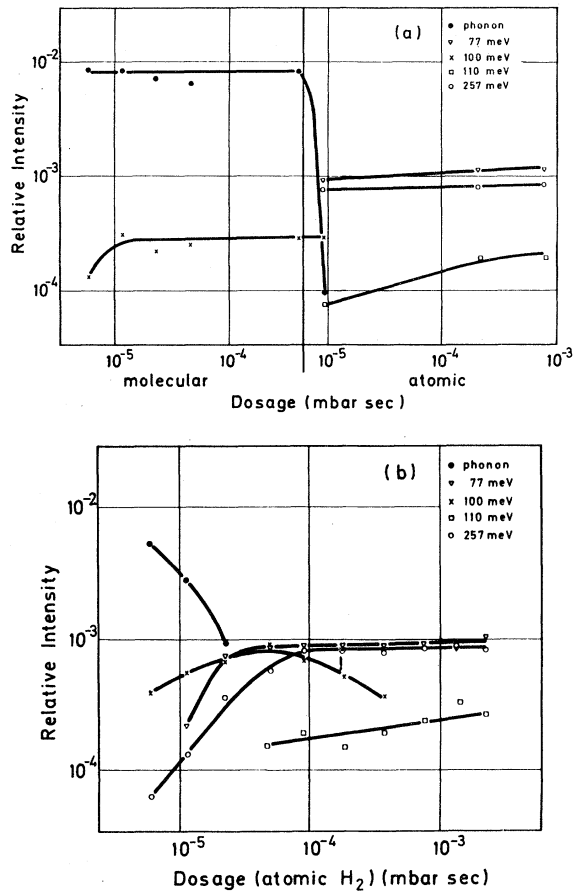
FIG. 3. (a) Relative intensities of the dominant losses versus dosage of molecular hydrogen and additional dosage of atomic hydrogen. (b) Behavior of the structure when atomic hydrogen is applied directly.

always approximately 1%. Another quite sensitive indicator for the quality of a 2×1 superstructure is the increase of the background with increasing loss energy ($\hbar\omega > 150$ meV). Spectra taken up to loss energies of 700 meV show a maximum of this increase at about 500 meV. This suggests that the increase is due to the direct electron interband transition between critical points of the dangling-bond surface states. This transition has already (in the following called interband transition) been observed in several other experiments.[13–14] Upon annealing to about 400 °C both excitations disappear indicating the transition from a 2×1 into a 7×7 superstructure. In contrast to the spectra taken at the 2×1 surfaces no such structure can be observed in the 7×7 spectrum. No extra broadening of the peak of the elastically reflected electrons or any significant increase of its loss sidetail[15] could be observed in our measurements. Regardless of superstructure but very dependent on the quality (step density) of the

cleavage we observed an increase of the full width half maximum (FWHM) and base width by about 40% with regard to the spectrometer widths, measured directly without a target. This broadening, especially that of the base width, could be partially reduced by readjusting the spectrometer optics. This clearly indicates that the observed broadening is not an inelastic process at the crystal surface, but is rather due to the second-order angular aberration of the deflectors.[16]

Figures 2 and 3 show the development of the loss spectra with increasing dosages of molecular and atomic hydrogen. The most interesting feature which can be observed in the two figures is that, except for a small region at around 6×10^{-6} mbar sec, the spectra reveal only two dominant loss peaks in the range of molecular and three in the range of atomic exposure, respectively. It can clearly be seen that besides the practically unchanged phonon loss and an unchanged slope of the background intensity, a second loss at $\hbar\omega = 100$ meV appears with a saturation dosage of 1.2×10^{-5} mbar sec. This structure dominates the spectra until the target is exposed to atomic hydrogen, which causes the phonon intensity, the interband transition, and the 100-meV loss
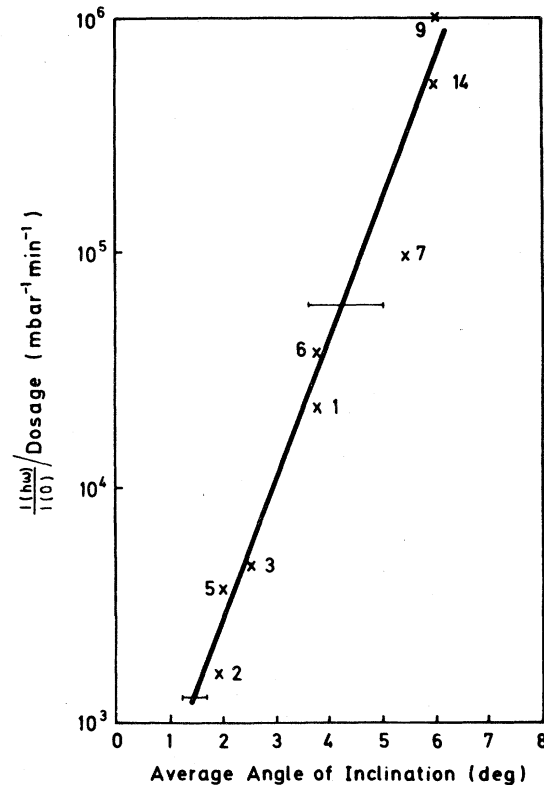

FIG. 4. Initial slopes of loss intensities of the 100-meV loss versus dosages as a function of the mean step density. The numbers indicate the corresponding samples.

to disappear while three new losses appear at 257, 110, and 77 meV dominating the spectra up to very high dosages. A similar behavior can be observed when the target is exposed to atomic hydrogen only [Fig. 3(b)]. In this case the 100-meV loss appears simultaneously with the 77-, the 110-, and the 257-meV loss while the phonon loss and the background decrease. With increasing dosage the 100-meV loss intensity goes through a maximum and then decreases until only the three losses at 77, 110, and 257 meV dominate the spectra again. The simultaneous appearance of all four losses can be explained by the fact that exposure to atomic hydrogen is always associated with an exposure to molecular hydrogen. From the intensities of the 100-meV loss observed, a dipole moment effective charge of $q_\perp \simeq 3e_0$ can be derived assuming a linear dependence between the number of step atoms occupied by hydrogen and the corresponding loss intensity.

It should be noted that there were decisive variations in the intensities of the low-energy losses ($\hbar\omega \leq 120$ meV) from sample to sample, certainly dependent on the quality of the cleavage. Such a dependence is demonstrated in Fig. 4. It shows intensities of the 100-meV loss related to the corresponding intensity of the elastically reflected electrons and the corresponding dosage versus the step density. For each sample selected for representation the data are derived from the first spectrum which exhibits a 100-meV loss well developed above the limit of detection [$I(\hbar\omega)/J_{el} \geq 10^{-4}$] with regard to the dosage.

Thus for samples with a high step density the values are calculated from the adsorption of the residual gas at a pressure below 5×10^{-11} mbar, assuming about the same partial pressure of H_2. The step density has been determined by the macroscopic angular deviation from the [111] direction.[17] These measurements allowed to estimate a value of the sticking coefficient for molecular hydrogen which is close to one.

As the mean step density of surfaces produced by cleavage cannot be controlled, statistical values of kinetic factors would only be obtained from a much larger number of samples. Because of the obviously high sticking coefficient and the strong dependence of the 100-meV loss intensity on the step density, this loss is attributed to hydrogen adsorption onto step edges or on sites in the vicinity of steps.

The interband transition disappears as soon as atomic hydrogen has adsorbed, indicated by the simultaneous appearance of the 257-meV loss. No change in slope is observed for molecular hydrogen exposure. This supports the former interpretation that atomic hydrogen saturates the dangling-bond surface states whereby the 2×1 superstructure con-
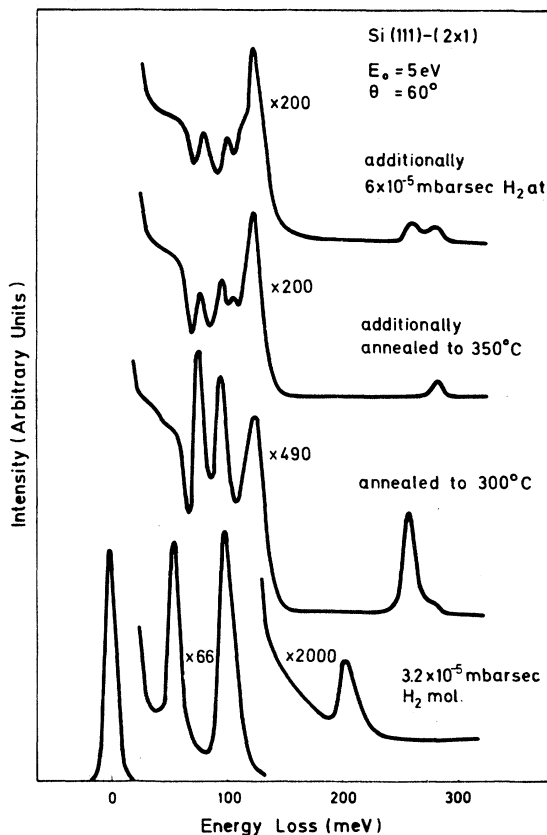

FIG. 5. Development of the loss structure upon annealing. The uppermost spectrum indicates the change with coadsorption of atomic hydrogen.

verts to the 1×1 surface. This can also be seen by the disappearance of the phonon intensity and from low-energy electron-diffraction (LEED) observations. There is no change observable of the 2×1 pattern upon exposure to molecular hydrogen.

Since coadsorption of atomic hydrogen causes the 100-meV loss intensity to decrease, the question arises as to whether this decrease is due to a transformation from a metastable state, characterized by the 100-meV loss, into a stable state characterized by the losses at 77 and 257 meV. To test this a target presaturated with molecular hydrogen was heated. This was based on the premise that a heat treatment might have a similar activation effect as coadsorption of atomic hydrogen.

Figure 5 shows sequential spectra taken after several heating cycles as indicated. As can be seen from the spectrum taken after annealing to 300 °C, the phonon loss as well as the 100-meV are reduced. The losses at 77 and 257 meV plus an extra loss at 120 meV and a shoulder at the high-energy side of the 257-meV loss appear. With further annealing to 350 °C the losses at 77 and 257 meV virtually disap-

pear and the spectrum consists only of two dominant losses at 120 and 280 meV. An increase in pressure during this anneal from 7 to 10×10^{-11} mbar could indicate that hydrogen was desorbed. However, it could not be determined whether this increase was due to desorption from the target holder or the target itself. Dosing the target with molecular hydrogen at this stage did not change the spectrum at all, indicating that the sites occupied after molecular hydrogen adsorption were still occupied or inactive. Only atomic hydrogen was accepted by the surface, indicated by an increase of the 77- and the 257-meV loss. These results suggest that the adsorption of molecular and atomic hydrogen occur as independent processes whereby the adsorption of molecular hydrogen is related to step positions and the adsorption of atomic hydrogen predominately occurs on the terraces. However, it is not quite clear whether a certain amount of steps or other surface imperfections as activation centers is necessary to initiate the adsorption of hydrogen at all. This is suggested by the fact that several samples did not accept hydrogen at all either in molecular or in atomic form. Scheithauer[18] made the same observation with cleaved Si(111) surfaces.

Loss spectra taken up to 700-meV loss energy did not show any structure due to the H_2 stretching vibration which could be expected at around 500 meV.[19] This indicates that the adsorption is either dissociative, or if molecular, the perpendicular component of the dynamic dipole moment giving rise to such a loss is too small. In the case of a dissociative adsorption the 100-meV loss has to be associated to a vibration of the hydrogen atom against the substrate. In comparison with the 257-meV stretching vibration of the silane-type configuration a vibrational energy of 100 meV is very small. When one assumes about the same total binding energy it can only be explained by the hydrogen atom being bonded in a wide straddled bridgelike configuration between two silicon step edge atoms.

This structure is quite similar to the nonconventional bond of hydrogen on Si(100) which is proposed by Appelbaum and Hamann[20] and found in boron hydrides. Such a model in the case of hydrogen adsorption at cleavage steps is strongly supported by the fact that cleavage step edge atoms provide also two dangling bonds. When one assumes such a nonconventional covalent multicentered bond which has in addition a reduced binding energy, a vibrational perpendicular mode with $\hbar\omega = 100$ meV is understandable. The observed effect of heating could then cause the hydrogen to change into a conventionally bonded mode. Similar observations have been made already on Si(110) surfaces by Sakurai and Hagstrum.[21] It should also be mentioned that

off-specular measurements up to $\Delta\Theta = 20°$ did not show any other loss than the one at 100 meV. This favors the assumption of a dissociative adsorption. Despite this straightforward interpretation it should be noticed that there is no absolute experimental evidence to exclude a molecular adsorption, and for reasons of completeness also this configuration should be discussed here with regard to our experimental findings. In this case the intermolecular binding energy has to be assumed to be large compared with the binding energy to the substrate.[22] As the lattice constant of Si is very large compared with the internuclear distance of H_2, which might not be changed very much upon adsorption, it could be assumed that the H_2 molecules are absorbed directly on the Si step atoms with the H—H bond direction parallel to the step edge. Under these conditions two vibrational modes of the observed frequency could be possible. One mode could be a bending vibration of the whole molecule about the step edge and the other possible mode could be a vibration of the whole molecule against the substrate. A H-H stretching vibration would not be observable since the perpendicular component of its dipole moment would be too small because of the ratio between the adsorption energy and molecular binding energy of the H_2 molecule.[23] The effect of heating could be explained by dissociation of the H_2 molecule whereby each hydrogen atom will be bonded to one dangling bond and thus forming a SiH_2 complex at the edge atom. The observed modes at 120 and 280 meV could then be explained as a bending and a stretching mode, respectively.

Inspection of Fig. 2 reveals that after disappearance of the 100-meV loss upon coadsorption of atomic hydrogen there is a structure at 120 and 280
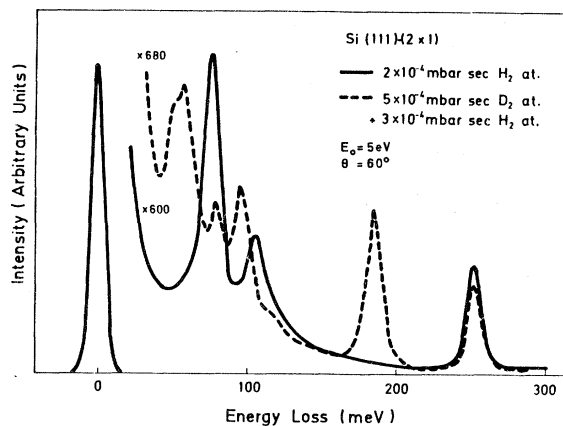

FIG. 6. Loss spectrum of a surface, saturated with atomic deuterium and hydrogen (dashed curve). For comparison a spectrum after adsorption of hydrogen is shown (solid curve).
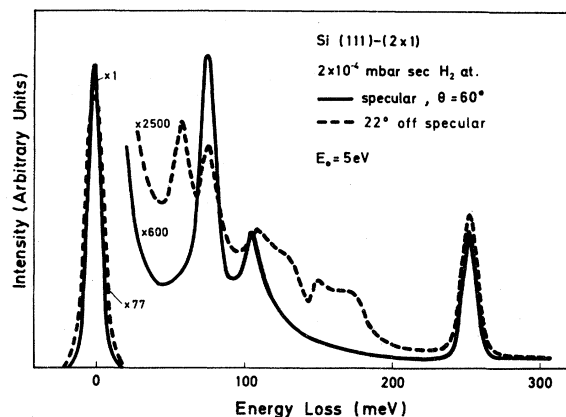
FIG. 7. Comparison of a spectrum taken in specular scattering geometry (solid line) and one taken in off-specular geometry (dashed curve). The most interesting difference between the two spectra is the occurrence of a new sharp loss at 60 meV in the off-specular spectrum. The structure between 100 and 200 meV seems to consist of at least four losses which cannot be assigned at present.

meV which indicates that coadsorption of atomic hydrogen might have the same effect as heating. Concerning the interpretation of the 257 and[24-26] the 77-meV loss one can refer to infrared or Raman data of hydrogenated α-Si. According to these data the structure around 257 meV is attributed to the Si-H stretching modes of SiH, SiH_2, and SiH_3 complexes with frequencies of 250, 261, and 267.5 meV, respectively. As our resolution was insufficient to discriminate between these frequencies it is not possible to make any definite statement on these complexes. We note, however, that especially after high dosage the 257-meV loss becomes very broad, possibly representing a superposition of losses with different frequencies. A similar statement can be placed on the 77-meV loss, as it can be assigned to the wagging modes of SiH, SiH_2, and SiH_3 complexes. Only the structure around 110 meV is attributed to bond-bending modes of the SiH_2 and SiH_3 complexes definitely indicating that at this adsorption stage such complexes already exist. This statement is strongly supported by loss spectra taken after coadsorption of hydrogen and deuterium and off-specular measurements (Figs. 6—8). The spectrum shown in Fig. 6 as a dashed-line curve has been taken after coadsorption of hydrogen and deuterium as indicated. The comparison with the hydrogen spectrum (uppermost spectrum of Fig. 2) shows that only the loss at 97 meV does not scale directly with the mass ratio of deuterium and hydrogen. Assuming, however, a SiH_2 configuration which has a symmetric scissor mode with a frequency of 110 meV, then the corresponding SiHD mode would have a frequency of $\sqrt{3/4}$ times 110 meV,

which agrees almost quantitatively with the measured value. This result is identical to the result obtained by Wagner et al. on Si(111)-(7×7) surfaces.[8]

The comparison of spectra taken in specular and off-specular scattering geometry is reproduced in Fig. 7. It shows essentially the same behavior of the 77- and the 257-meV losses with regard to their response on the change of the scattering angle. This again can be explained, when one assumes that these losses are also attributed to SiH_n complexes with $n > 1$, as only those complexes have stretching and wagging modes with about the same dipole components perpendicular and parallel to the surface. This is especially true for the 77-meV loss which appears much too intense in specular measurements as to be attributed only to a plain bending mode of one single hydrogen on top of a silicon atom.

The most interesting feature in Fig. 7 is the appearance of a new loss at 60 meV in the off-specular spectrum. The fact, that this loss is not observed in the in-specular spectrum clearly indicates that it belongs to a purely parallel mode. Taking recourse to the literature[23] suggests that this loss may be interpreted as a twist mode of a SiH_3 complex which is,
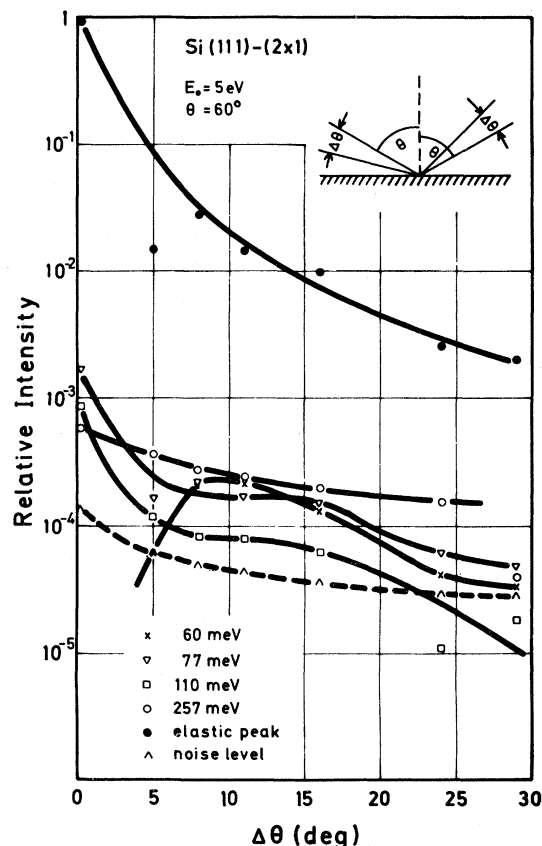

FIG. 8. Behavior of the structure and loss intensities of the 60-, 77-, 110-, and 257-meV peaks as a function of the scattering angle.

however, infrared inactive. Therefore, it has to be assumed that the microscopic environment of these complexes is asymmetric. There is supportive experimental evidence for this assumption from our observation of SiH_2 complexes which implies that hydrogen is able to break Si—Si bonds at an early adsorption stage and remove Si atoms from the uppermost layer to create enough asymmetric sites with two or three dangling bonds. This erosive process takes place possibly by a production and desorption of silane. Such a silane production has already been observed directly in thermal desorption spectroscopy (TDS) measurements during high dosages by Günter.[9]

CONCLUSIONS

Our study of the ELS spectra of cleaved Si(111)-(2×1) surfaces after hydrogen adsorption has shown that hydrogen adsorbs even when exposed in molecular form on sites in the vicinity of steps or on step atoms directly in a configuration which does not saturate the dangling bonds. This follows from the strong dependence of the saturation intensity on the step density and from the observation that the 2×1 superstructure was not at all affected by this adsorption process. A discussion as to whether this adsorption is molecular or dissociative is also presented as far as possible but a definite assignment cannot be made at present.

It has further been shown that even at an early adsorption stage there exist SiH, SiH_2, and SiH_3 complexes on the surface and that erosion has to take place in order to provide the suitable adsorption sites. This is also supported by our observation that with increasing dosages the intensity of the elastically reflected electrons gradually decreases while the widths of the loss peaks increase. This can be explained by a roughening of the surface.

ACKNOWLEDGMENTS

[1]J. A. Appelbaum and D. R. Hamann, Rev. Mod. Phys. 48, 479 (1976).

[2]K. C. Pandey, Phys. Rev. B 14, 1557 (1976).

[3]K. M. Ho, M. L. Cohen, and M. Schlüter, Phys. Rev. B 15, 3888 (1977).

[4]K. Hermann and P. S. Bagus, Phys. Rev. B 20, 1603 (1979).

[5]H. Ibach and J. E. Rowe, Surf. Sci. 43, 481 (1974).

[6]T. Sakurai and H. D. Hagstrum, Phys. Rev. B 12, 5349 (1975).

[7]H. Froitzheim, H. Ibach, and S. Lehwald, Phys. Lett. 55A, 247 (1975).

[8]H. Wagner, R. Butz, U. Backes, and D. Bruchmann, Solid State Commun. 38, 1155 (1981).

[9]H.-L. Günter (unpublished), as described in G. Schulze and H. Henzler (unpublished).

[10]G. Herzberg, Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules (Van Nostrand, Princeton, N.J., 1956).

[11]H. Ibach, Phys. Rev. Lett. 27, 253 (1971).

[12]H. Ibach, J. Vac. Sci. Technol. 9, 713 (1972).

[13]G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia, Phys. Rev. B 4, 3398 (1971).

[14]H. Froitzheim, H. Ibach, and D. L. Mills, Phys. Rev. B 11, 4980 (1975).

[15]U. Backes and H. Ibach, Solid State Commun. 40, 575 (1981).

[16]H. Froitzheim (unpublished).

[17]J. Clabes, Jpn. J. Appl. Phys. Suppl. 2, 389 (1974).

[18]U. Scheithauer, private communication.

[19]G. Herzberg, Molecular Spectra and Molecular Structure I, Spectra of Diatomic Molecules (Van Nostrand, Princeton, N.J., 1950).

[20]J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 39, 1487 (1977).

[21]T. Sakurai and H. D. Hagstrum, J. Vac. Sci. Technol. 13, 807 (1976).

[22]K. Hermann, private communication.

[23]H. Froitzheim, Electronspectroscopy for Surface Analysis, Vol. 4 of Topics in Current Physics, edited by H. Ibach (Springer, Berlin, 1977).

[24]G. Lucovsky, R. J. Nemanich, J. C. Knights, Phys. Rev. B 19, 2064 (1979).

[25]M. H. Brodsky, M. Cardona, and J. J. Cuomo, Phys. Rev. B 16, 3566 (1977).

[26]E. L. Freemann and W. Paul, Phys. Rev. B 18, 4288 (1978).