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ETHYLENE AND COADSORBED HYDROGEN ON Si(100)-(2x1): STRUCTURE, BONDING, AND DECOMPOSITION

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The effect of post-adsorbed atomic hydrogen on adsorption, desorption and decomposition of ethylene on Si(100)-(2x1) has been studied using high-resolution electron energy loss spectroscopy (HREELS), temperature programmed desorption (TPD), and low-energy electron diffraction (LEED). HREEL spectra show that ethylene, in the absence of hydrogen, rehybridizes from sp^2 to sp^3 and forms a di-σ bonded structure to the surface. After low post-exposures to atomic hydrogen, the observed Si-H mode and the absence of significant change in the chemisorbed ethylene spectrum indicate that the surface dangling bonds still exist after ethylene adsorption, and that the adsorption of ethylene is accompanied by cleavage of the original Si-Si dimer bond. In addition, the hydrogen-saturated dangling bonds are found to stabilize the di-σ bonded ethylene, leading to increased decomposition at higher temperatures. However, higher exposures of atomic hydrogen convert the initial (2x1) reconstruction of the ethylene-saturated surface to a (1x1) structure. Furthermore, the thermal desorption peak of molecular ethylene is shifted up by approximately 100 K. HREELS data show that the C-C bond still exists, and, by using atomic deuterium, a C-D mode is observed. We explain our data by an atomic hydrogen-driven conversion of the di-σ bonded ethylene to a mono-σ bonded surface ethyl. Thermal activation leads to decomposition of about 60% of the initial ethylene in contrast to the mainly molecular desorption in the absence of hydrogen.

I. INTRODUCTION

Unsaturated hydrocarbons such as ethylene and acetylene are important precursors for the growth of SiC thin films by chemical vapor deposition (CVD) and chemical beam epitaxy (CBE). Because of the increasing interest in SiC as a wide band gap material for high temperature device applications, recent work has focused on understanding the elementary chemical reactions of these molecules on a silicon substrate [1,2]. Earlier studies have shown that unsaturated hydrocarbons, like acetylene, ethylene, and propylene, chemisorb on a Si(100) surface with high probability, whereas saturated hydrocarbons do not chemisorb [3,4,5]. At higher temperatures, acetylene is found to decompose on the surface, whereas ethylene mainly desorbs molecularly. Consequently, the former seems to be a better candidate for SiC thin film formation. However, these studies are still idealized insofar as the influences of any coadsorbates are concerned. In particular, hydrogen is known to play an important role in many CVD processes, either as a reaction product (e.g., from silane, disilane, and diethylsilane) or as a carrier gas. The effect of *preadsorbed* hydrogen on the adsorption and decomposition of hydrocarbons has been studied and its influence is mainly one of site-blocking, which prevents subsequent hydrocarbon adsorption [3,6]. In contrast, few results have been reported on the effect of post-adsorbed hydrogen [7]. In this work, we shall present a detailed study of the structure, bonding, and thermal decomposition of ethylene under the influence of post-adsorbed hydrogen. To understand the elementary reactions induced by atomic hydrogen, it is necessary to know the bonding configuration prior to the exposure of hydrogen. Recently, the controversy found in the literature regarding the structure and bonding of acetylene and ethylene on Si(100) has been resolved [8,9,10]. Because of its importance, we start with a brief presentation of our results for ethylene adsorption in the absence of hydrogen. The discussion of post-adsorbed hydrogen is then divided into low- and high-exposure regimes.

II. EXPERIMENTAL DETAILS

The experiments were carried out in an ultrahigh vacuum (UHV) chamber (base pressure 7 x

10^{-11} Torr) equipped with a HREEL spectrometer (LK-2000-14-R), a four-grid rear-view LEED optics, an Auger electron spectrometer with a single-pass cylindrical mirror energy analyzer, an ion sputter gun, a pin-hole gas doser, a tungsten filament to produce atomic hydrogen, and a differentially pumped quadrupole mass spectrometer (UTI-100C) with a cryoshroud. The chamber is pumped by a 1000 l/s turbomolecular pump.

An external load-lock and a UHV sample transfer system described elsewhere [11] allow fast loading of samples into the chamber. Briefly, the silicon specimens are mounted using two molybdenum tabs to a transferable molybdenum sample holder, which slides into the end of the manipulator. Frequent sample exchange makes a direct sample-thermocouple connection difficult. Therefore, a chromelalumel thermocouple is spot welded close to the sample holder. Because of the temperature difference between sample and thermocouple, the measured temperatures are calibrated using an optical pyrometer and known TPD peaks at various temperatures. Using liquid nitrogen cooling and a combination of radiative and electron bombardment heating, sample temperatures between 90 and 1500 K are accessible.

The n-type (Sb, 10^{18} cm^{-3}) Si(100) samples were prepared by argon ion sputtering and annealing as described previously [8]. After this procedure, the clean Si(100) surface showed a sharp two-domain (2x1) LEED pattern, and any contamination was below the AES noise level (< 0.001 relative to the Si(LVV)-peak). To exclude any problems arising from aging of the samples due to frequent sputter-and-anneal cycles (known as "fogging"), the experiments were performed on four different samples. No differences in the results due to different crystals were found.

The ethylene gases, C_2H_4 (99.99% purity; Matheson) and C_2D_4 (99.8% purity, 96% isotopically pure; Cambridge Isotopes), were used without further purification. A 5-μm pinhole doser maintained a chamber pressure below 2 x 10^{-10} Torr during exposure to ethylene (using a backing pressure of 1 Torr). The exposures are approximately 3 x 10^{12} molecules/($Torr^{-1}$ s^{-1} cm^{-2}) in terms of the backing pressure. Atomic hydrogen and deuterium were generated by dissociation of the respective molecules with a hot (1800 K) spiral tungsten filament positioned approximately 5 cm from the sample. The atomic hydrogen exposures are reported here in terms of molecular hydrogen. An exposure of 1 Langmuir (1 L = 10^{-6} Torrs) of molecular hydrogen corresponds to 1.4 x 10^{14} atoms cm^{-2}.

The HREEL spectrometer utilizes a primary beam energy of 7 eV with an incident angle of 60° with respect to the surface normal. All spectra are recorded in the specular direction if not stated otherwise. A resolution between 8 and 10 meV (FWHM) was routinely achieved with a counting rate of 3 x 10^5 s^{-1} for a clean Si(100) surface.

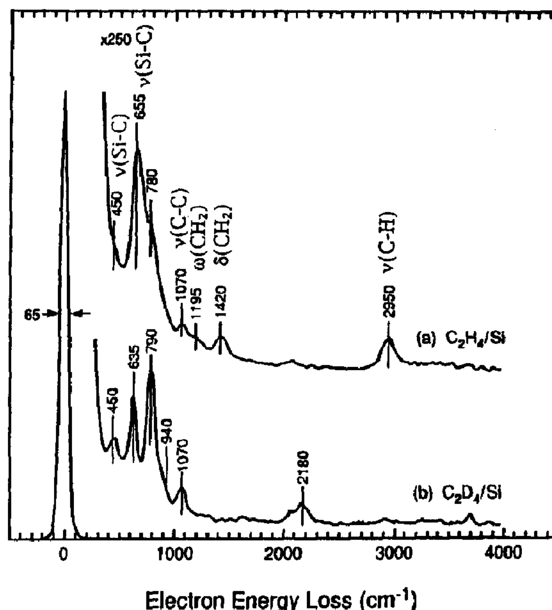

Figure 1: HREEL spectra of adsorbed ethylene on the Si(100)-(2x1) surface at 100 K: (a) C_2H_4/Si(100); (b) C_2D_4/Si(100). The spectra are magnified by a factor of 250 with respect to the elastic peak. The spectra are measured in the specular direction, with an impact energy of 7 eV.

III. RESULTS

Figure 1 shows the HREEL spectra of adsorbed C_2H_4 and C_2D_4 on the Si(100)-(2x1) surface at 100 K and saturation coverage (ethylene exposure of 9 x 10^{14} molecules/cm^2). Seven energy loss peaks at 2950, 2080, 1420, 1070, 780, 655, and 450 cm^{-1}, and a shoulder at 1195 cm^{-1} are observed in the hydrogenated spectrum, (a). In the spectrum for deuterated ethylene, (b), five energy loss peaks appear at 2180, 1070, 790, 635, and 450 cm^{-1}, with a shoulder around 940 cm^{-1} and a weak shoulder at

2080 cm^{-1} [12]. Our results are similar to those from a previous HREELS study [13]. Comparison with infrared spectra of organosilicon compounds allows an assignment of the peaks [14], as summarized in Table 1 and discussed in detail elsewhere [9].

Table 1: Vibrational energies (in cm^{-1}) and their assignments for saturation coverage of ethylene on Si(100)-(2x1) at 100 K.

Vibrational mode	C_2H_4	C_2D_4	Ratio
C-H stretching	2950	2180	1.35
CH_2 scissoring	1420	1070	1.33
CH_2 wagging	1195	940	1.27
C-C stretching	1070	1070	1.0
"SiC" subsurface	780	790	--
Si-C stretching, sym.	655	635	1.03
Si-C stretching, asym.	450	450	1.0

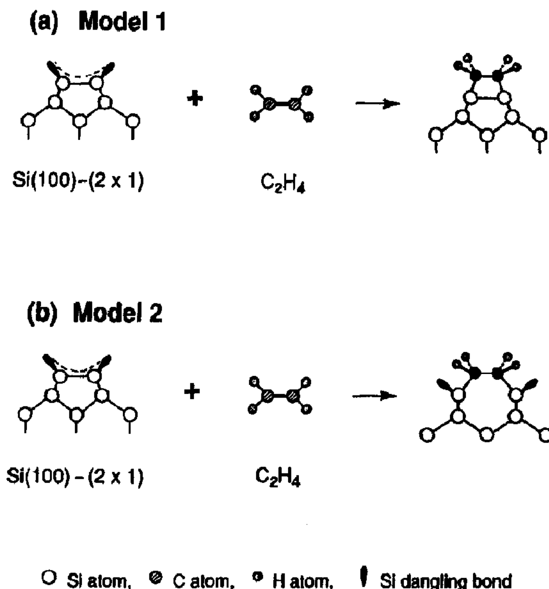

Figure 2: Ball and stick models for di-σ bonded ethylene on Si(100)-(2x1): (a) bonding to the silicon dangling bonds with the Si-Si dimer bond remaining intact [13]; (b) adsorption with cleavage of the Si-Si dimer bond [8, this work].

Our HREELS results confirm a di-σ bonded ethylene which is rehydridized from the gas-phase sp^2 to sp^3. However, these data alone are insufficient to discriminate between the proposed adsorption models shown in Fig. 2. In particular, the question cannot be resolved unambiguously as

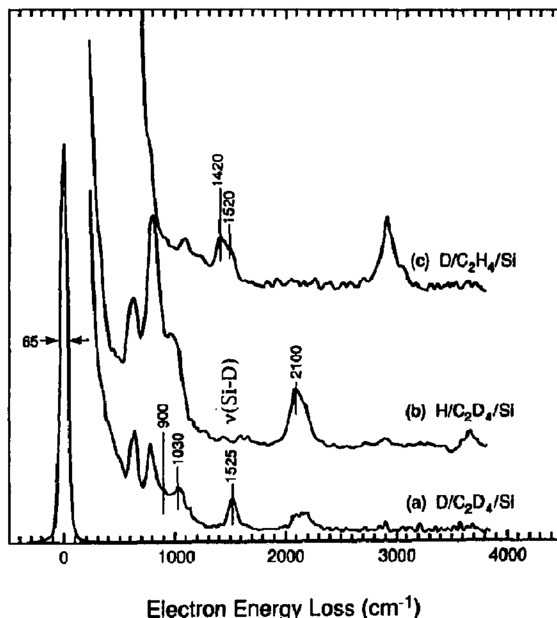

Figure 3: HREEL spectra of the ethylene-saturated Si(100)-(2x1) surface after post-exposure of atomic hydrogen at 150 K: (a) C_2D_4/Si(100) after post-exposure to 4 L of deuterium; (b) C_2D_4/Si(100) after post-exposure to 4 L of hydrogen; (c) C_2H_4/Si(100) after post-exposure to 2 L of deuterium.

to whether ethylene is bonded to the silicon "dangling bonds" or is inserted into the Si-Si dimer bond leaving the silicon dangling bonds intact. To distinguish between these models, we exposed the ethylene-saturated surface to low doses of atomic hydrogen (< 5 L) at temperatures below 150 K. In Fig. 3, the HREELS data are shown for three different isotopic combinations: (a) C_2D_4 after post-exposure to 4 L of deuterium, (b) C_2D_4 after post-exposure to 4 L of hydrogen, and (c) C_2H_4 after post-exposure to 2 L of deuterium.

Comparing the spectra with and without post-dosed deuterium, Figs. 3(a) and 1(b), shows that the spectrum with post-exposured deuterium has, in addition, a strong energy-loss peak at 1525 cm^{-1}: the Si-D stretching mode. The remaining loss features are essentially the same for both spectra. The HREELS data demonstrate clearly that a Si-D bond is formed on the surface upon post-dosing of deuterium and the chemisorbed ethylene is only weakly perturbed. No reactions between the ethylene and hydrogen have taken place, as inferred, for example, by the absence of a C-D stretching

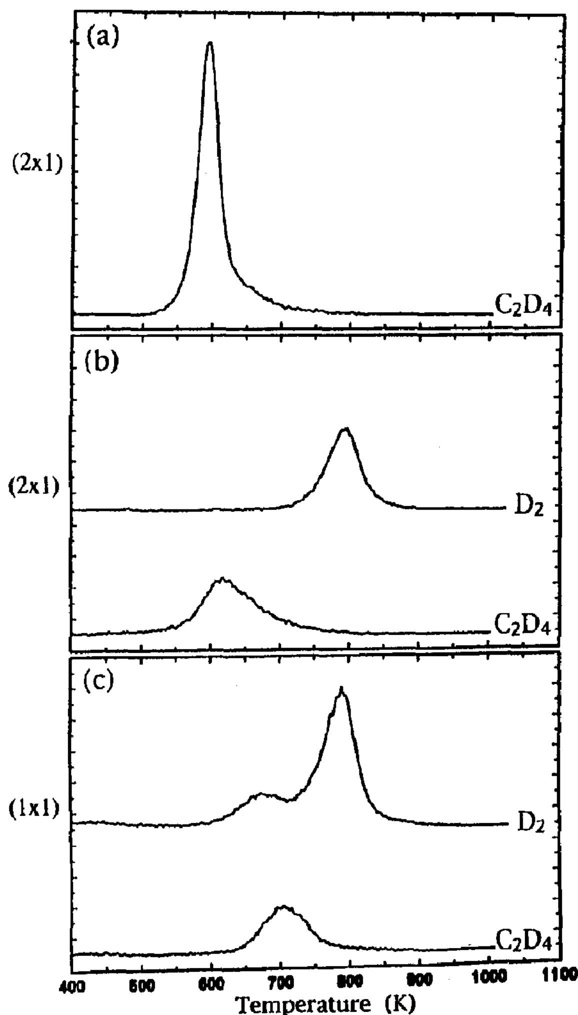

Figure 4: TPD spectra for the C_2D_4-saturated Si(100)-(2x1) surface after post-exposure to atomic deuterium: (a) Without exposure of atomic deuterium; (b) after 5 L deuterium exposure; (c) after 50 L deuterium exposure. The desorption products are molecular C_2D_4 and molecular deuterium. The heating rate was 2 K s^{-1}. The observed LEED patterns for each case are noted on the left side.

vibration at 2180 cm^{-1} in Fig. 3(c), and only a weak intensity for the C-H stretching mode at 2950 cm^{-1} in Fig. 3(b), which is also visible in Fig. 1(b) [12]. The (2x1) diffraction pattern of the ethylene-saturated Si(100) surface does not change after these low exposures to atomic hydrogen, which is expected if the ethylene remains di-σ bonded to the surface.

Figure 4(a) shows the thermal desorption spectrum for a C_2D_4-saturated surface. The slightly asymmetric peak shows the desorption of molecular ethylene takes place at about 590 K. No other hydrocarbon desorption products were observed. This is in agreement with earlier studies which showed that ethylene desorbs predominantly (98%) molecularly [3]. The TPD spectra for a C_2D_4-saturated surface which was post-exposed to atomic deuterium at 150 K are shown in Figs. 4(b) and (c), for a 5 L dosage and a higher dose of 50 L, respectively. The desorption products are molecular D_2 and C_2D_4. The ethylene desorption peak broadens, shifts slightly to higher temperatures, and is reduced in intensity after post-exposure to 5 L of atomic deuterium. After a dose of 50 L, the ethylene desorption peak is shifted up by about 100 K to a desorption temperature of 700 K, and the area of the desorption peak is reduced by about 40%, compared to ethylene desorption in the absence of hydrogen. After an exposure of 5 L, deuterium desorbs around 790 K, which is the desorption temperature for the monodeuteride phase of deuterium adsorbed on Si(100). The deuterium desorption spectrum after a 50 L exposure shows, in addition, a second desorption peak at about 670 K. Again, the deuterium desorption spectrum seen here is similar to the desorption of deuterium from a clean Si(100) surface for higher atomic deuterium dosages at low temperatures. The monodeuteride and the dideuteride desorption peaks, originating from deuterium atoms bonded to a Si-Si dimer and from two deuterium atoms bonded to the same silicon atom, respectively, are clearly seen. In addition, a change in the LEED pattern from a (2x1) to a (1x1) superstructure accompanies the significant upshift in the ethylene desorption peak temperature and the occurrence of a dihydride desorption peak following exposures to atomic deuterium above 10 L.

To clarify the origin of the deuterium TPD peaks and to address the question of whether there is a chemical reaction between the adsorbed ethylene and the atomic deuterium, an isotopic exchange experiment was performed, the results of which are presented in Fig. 5. The C_2D_4-saturated surface was exposed to 1 L of atomic hydrogen, (a), and to 80 L of atomic hydrogen, (b). The TPD signal was monitored for molecules with masses 2 (H_2), 3 (HD), 4 (D_2), 32 (C_2D_4), 31 (C_2D_3H), and 30 ($C_2D_2H_2$). For display purposes, the baselines of the spectra are shifted. With the 80 L exposure, the spectra again show a shift to higher temperatures for

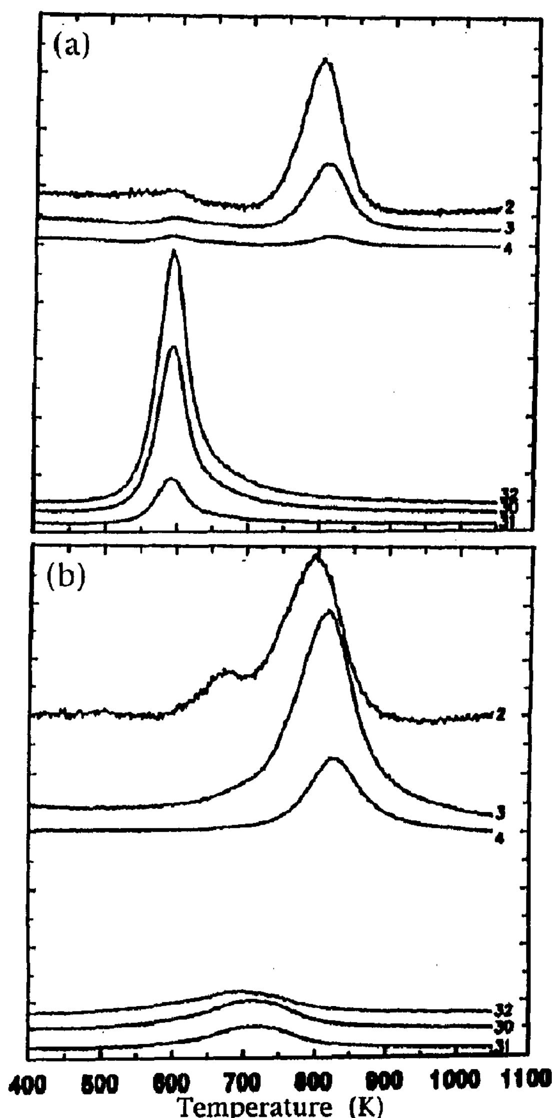

Figure 5: TPD spectra for the C_2D_4-saturated Si(100)-(2x1) surface after exposure to atomic hydrogen: (a) 1.0 L and (b) 80 L. Masses 2 (H_2), 3 (HD), 4 (D_2), 32 (C_2D_4), 31 (C_2D_3H), and 30 ($C_2D_2H_2$) are monitored. Masses 30 and 31 have contributions from the cracking pattern of C_2D_4 (66% $C_2D_3^+$) and due to the isotopic impurity of the C_2D_4 (15% C_2D_3H), respectively. The TPD signals in (a) for masses 30 and 31 originate only from these two effects. The isotopic mixing in (b) is given by C_2D_4:C_2D_3H:$C_2D_2H_2$ = 1:0.45:0.32 after correction for the isotopic impurity and the various cracking patterns.

the ethylene desorption and a reduction in desorption intensity. The monohydride peak for the hydrogen desorption is observed at low exposures followed by a dihydride desorption peak at higher exposures. For the proper interpretation of the isotopic exchange data, i.e., the origin of masses 31 and 30, the cracking pattern of ethylene must be taken into account ($C_2H_3^+/C_2H_4^+$ = 0.6, as determined independently for our system). Additionally, the C_2D_3H isotopic impurity (15%) in the C_2D_4 gas must be corrected for. The TPD spectra for low hydrogen exposure, shown in Fig. 5(a), for masses 30 and 31 originate completely from these two effects. In other words, there is no isotopic exchange within the ethylene molecule up to the thermal desorption temperature. This conclusion has been confirmed by HREELS data (see Fig. 6). The 80 L exposure data in Fig. 5(b), on the other hand, show a strong ethylene peak for mass 31, which indicates isotopic exchange into the ethylene molecule. After correction for the isotopic impurity and the various cracking patterns, the isotopic mixing in (b) is given by C_2D_4:C_2D_3H:$C_2D_2H_2$ = 1:0.45:0.32. The desorption spectra for the hydrogen isotopes show mainly hydrogen from the atomic hydrogen exposure at low doses, see Fig. 5(a). In addition, there is some deuterium seen as HD molecules from the decomposition of the deuterated ethylene which also occurs on a nominally clean Si(100)-(2x1) surface [3]. At higher exposure, see Fig. 5(b), the desorption of the monohydride is observed for all three hydrogen species, H_2, HD, and D_2. It is important to note, however, that the dihydride desorption peak at lower temperatures is only seen for the H_2 molecule, not for HD or D_2. Furthermore, the monohydride peak temperature for H_2 is slightly lower than for HD or D_2. Although our absolute temperature measurement is not accurate, this small shift recorded for different masses within the same TPD run is unambiguous. Both observations underline that hydrogen and deuterium are bonded differently at the onset temperature for thermal desorption and that only the isotopic SiH_2 dihydride species is present on the surface.

The HREELS data for a deuterated ethylene-saturated surface after different post-exposures of atomic hydrogen are shown in Fig. 6. The spectra without atomic hydrogen and after post-exposure to 4 L of hydrogen have already been discussed above and are shown again for comparison. With higher atomic hydrogen exposures of 10 and 22 L, the Si-H stretching mode at 2100 cm^{-1} increases in intensity. Two new loss features are also clearly visible: the SiH_2 scissoring mode at 980 cm^{-1} and the C-H

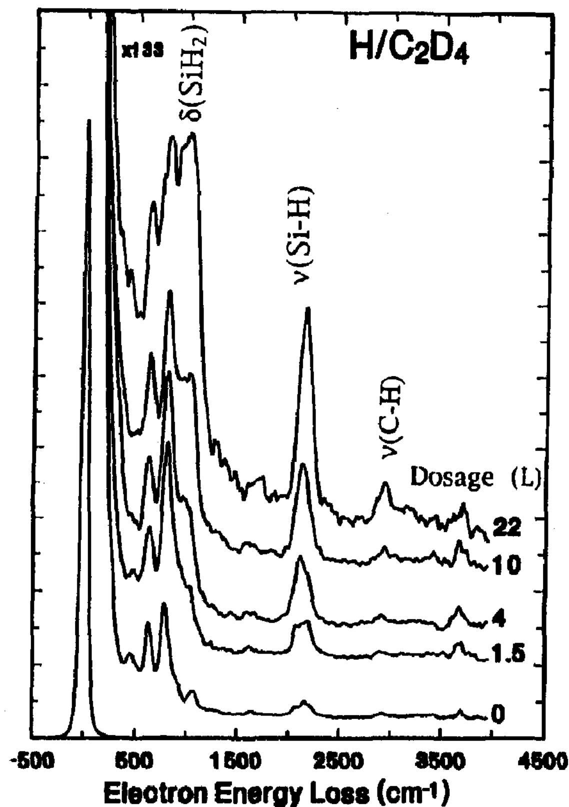

Figure 6: HREEL spectra for the C_2D_4-saturated Si(100)-(2x1) surface after various post-exposures to atomic hydrogen. Only the new vibrational modes are labeled.

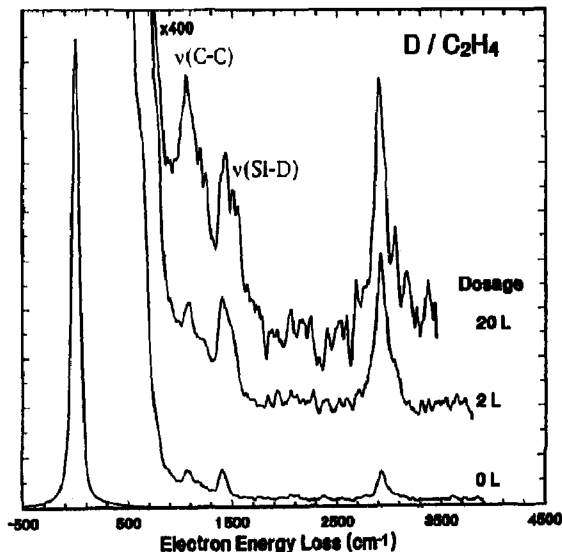

Figure 7: HREEL spectra for the C_2H_4-saturated Si(100)-(2x1) surface after various post-exposures to atomic deuterium.

stretching mode at 2950 cm^{-1}. The latter is increased well above the contribution from the C_2D_3H isotopic impurity mentioned earlier. Figure 7 shows the HREEL spectra for different post-exposures of atomic deuterium to an C_2H_4-saturated surface. The hydrogen isotopes in ethylene and atomic hydrogen have been chosen to examine the loss-energy region around 1100 cm^{-1} which is no longer masked by the strong SiH_2 scissoring mode and CH_2 modes. The low exposure data have been discussed earlier and are shown again for comparison. In Fig. 7, for a deuterium post-exposure of 20 L, a strong peak at 1070 cm^{-1}, the C-C single bond order stretching mode, signifies that even after high exposures to atomic deuterium, the carbon single bond remains intact.

IV. DISCUSSION

The HREELS, TPD and LEED data show clearly that two distinct regions occur for post-adsorbed atomic hydrogen on an ethylene-saturated Si(100)-(2x1) surface. For low exposures to atomic hydrogen, hydrogen is found to saturate the dangling bonds as was clearly observed in the HREELS data (Fig. 3) discussed here and in more detail elsewhere [9]. After coadsorption, the (2x1) reconstruction of adsorbed ethylene is maintained. For higher exposures, the atomic hydrogen converts the ethylene to an adsorbed ethyl group, which leads to the observed (1x1) LEED pattern. The incorporation of atomic hydrogen into the ethyl group and the presence of a C-C single bond were clearly shown by HREELS data (Figs. 6, 7). Based on these results, a mechanism for the chemical reaction of ethylene with post-adsorbed hydrogen is proposed in Fig. 8. To keep track of the origin of the hydrogen, the model is shown for deuterated ethylene. For low exposures, here indicated by up to two hydrogen atoms per two silicon surface atoms (or per one Si-Si dimer on the clean (2x1) surface), the saturation of dangling bonds leads, upon thermal activation, to desorption of molecular ethylene (C_2D_4) and subsequent monohydride desorption as in the absence of ethylene. Electronic stabilization of the ethylene by post-adsorbed hydrogen is indicated by the broadening and small upshifting of the ethylene desorption peak. With this stabilization, some ethylene decomposes to surface carbon, liberating molecular hydrogen that desorbs molecularly (not shown in Fig. 8).

The change in branching ratio, clearly seen in the TPD data, with stabilization of a hydrocarbon molecule was used previously to explain why acetylene adsorbed on Si(100)-(2x1) mainly decomposes and the similarly bonded ethylene on the same surface mainly desorbs upon thermal activation [1].

Further post-exposure to atomic hydrogen is found to break one of the Si-C bonds, leading to an ethyl group bonded to the surface. This explains the emergence of a (1x1) LEED pattern. The vibrational spectroscopy clearly shows the incorporation of hydrogen into the newly formed ethyl group and the presence of a C-C single bond. The ethyl group can either decompose via α-hydride elimination, or undergo β-hydride elimination, liberating ethylene [15]. In our case, the ethyl group is stabilized by the formation of silicon dihydride, as shown in Fig. 8. Upon heating, the dihydride must desorb first (nearly the ideal dihydride desorption temperature) to reopen the reaction path for β-hydride elimination and desorption of ethylene. The expected significant shift in ethylene desorption temperature above the dihydride desorption has been unambiguously observed. Furthermore, the mechanism predicts the

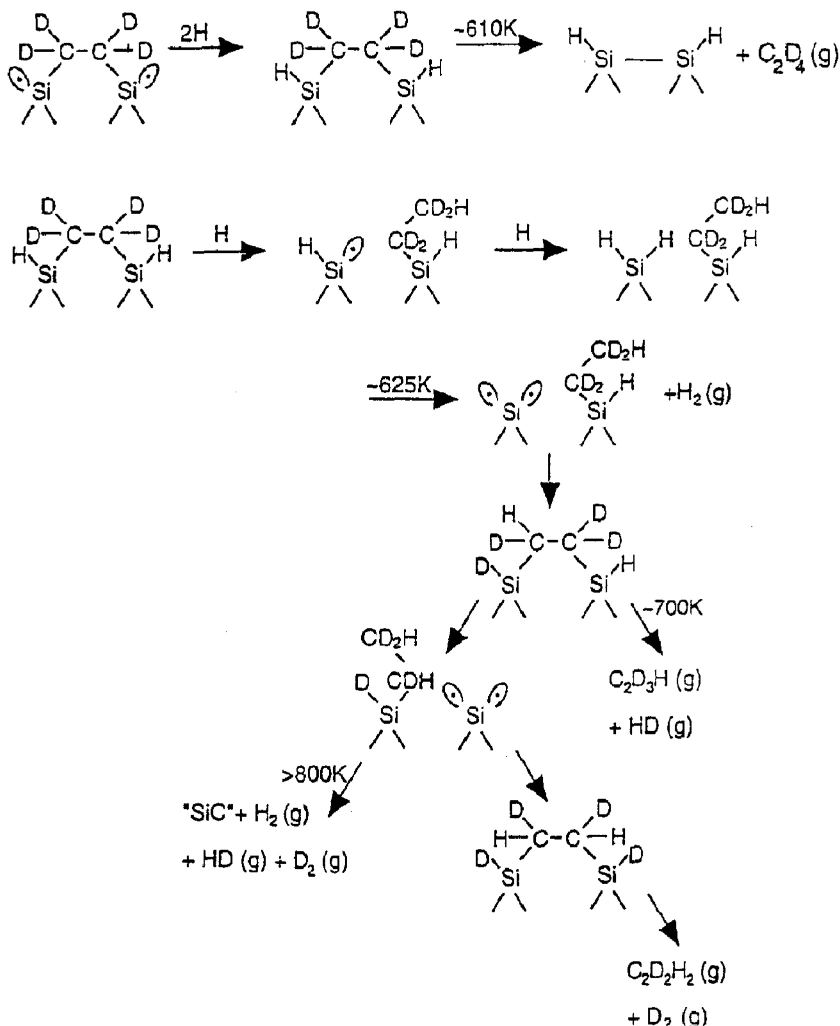

Figure 8: Schematic reaction and decomposition mechanism for ethylene upon post-exposure to atomic hydrogen on the Si(100)-(2x1) surface.

predominance of H_2 for the dihydride desorption, as is also observed experimentally. At these high temperatures, the conversion between an adsorbed ethyl group and ethylene might be reversible before the molecule finally decomposes to surface carbon and hydrogen or desorbs. This would explain the

observed isotopic exchange of more than one hydrogen atom within the ethylene molecule. For the highest exposures of atomic hydrogen, a small probability for a direct reaction between gas phase atomic hydrogen and the hydrocarbon, as in a gas-phase reaction, must also be kept in mind [16].

V. CONCLUSIONS

We have shown that ethylene adsorbed at low temperatures is di-σ bonded to silicon by insertion into the Si-Si dimer bond on the clean Si(100)-(2x1) surface. Low exposures of atomic hydrogen saturate the dangling bonds on the silicon, which leads to the stabilization of the adsorbed ethylene. Therefore, the branching ratio between thermal decomposition and molecular desorption is increased. High exposures of atomic hydrogen, on the other hand, lead to a σ-bonded ethyl forming a (1x1) surface reconstruction. The ethyl is significantly stabilized by the formation of a silicon dihydride blocking the possibility of hydrocarbon desorption via β-hydride elimination. Therefore, about 60% of the initial ethylene decomposes, leaving carbon on the surface and liberating hydrogen. This is in contrast to the mainly molecular desorption of ethylene in the absence of post-adsorbed hydrogen. The dramatic effect of hydrogen reported in this study, highlights the importance of understanding the role of such coadsorbates for a better fundamental understanding of CVD or CBE processes.

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REFERENCES AND NOTES

1. C.C. Cheng, P.A. Taylor, R.M. Wallace, H. Gutleben, L. Clemen, M.L. Colaianni, P.J. Chen, W.H. Weinberg, W.J. Choyke and J.T. Yates, Jr., Thin Solid Films 225 (1993) 196.
2. P.A. Taylor, M.J. Bozack, W.J. Choyke, J.T. Yates, Jr., J.Appl.Phys. 65 (1989) 1099.
3. L. Clemen, R.M. Wallace, P.A. Taylor, M.J. Dresser, W.J. Choyke, W.H. Weinberg, J.T. Yates, Jr., Surf. Sci. 268 (1992) 205.
4. P.A. Taylor, R.M. Wallace, C.-C. Cheng, M.J. Dresser, W.J. Joyke, W.H. Weinberg, J.T. Yates, Jr., J. Am. Chem. Soc. 114-17 (1992) 6754.
5. B.D. Thoms, P.W. Lorraine, W. Ho, J. Chem. Phys. 97 (1992) 2759.
6. M.J. Bozack, W.J. Choyke, L. Muehlhoff, J.T. Yates,Jr., J. Appl. Phys. 60 (1986) 3750.
7. M.J. Bozack, P.A. Taylor, W.J. Choyke, J.T. Yates, Jr., Surf. Sci. 179 (1987) 132.
8. C. Huang, W. Widdra, X.-S. Wang, W.H. Weinberg, J. Vac. Sci. Technol. (in press).
9. C. Huang, W. Widdra, W.H. Weinberg, Surf. Sci. Lett. (submitted).
10. A.J. Mayne, A.R. Avery, J. Knall, T.S. Jones, G.A.D. Briggs, W.H. Weinberg, Surf. Sci. 284 (1993) 247.
11. X.-S.Wang et al., J. Vac. Sci. Technol. A (in press).
12. The weak energy loss peaks at 3700 and 2900 cm^{-1} in Fig.1(b) are caused by physically adsorbed water and a C_2D_3H impurity in the C_2D_4 gas, respectively.
13. J. Yoshinobu, H. Tsuda, M. Onchi, M. Nishijima, J. Chem. Phys. 87 (1987) 7332.
14. D.R. Anderson in *Analysis of Silicones*, A.L. Smith, Ed. (John Wiley, New York, 1978, p.247).
15. M.A. Rueter, J.M. Vohs, Surf. Sci. 262 (1992) 42.
16. C.C. Cheng, S.R. Lucas, H. Gutleben, W.J. Choyke, J.T. Yates, Jr., Surf. Sci. Lett. 273 (1992) 441.