PHYSICAL REVIEW B VOLUME 34, NUMBER 6 15 SEPTEMBER 1986

Surface vibrational spectroscopy studies of aromatic-molecule fragmentation on silicon surfaces

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(Received 31 March 1986)

Cleaved Si(111)2×1 surfaces exhibit a high reactivity when exposed to a thiophene atmosphere. This is similar to the high reactivity of Si(111)2×1 when exposed to other aromatic molecules, and is completely atypical with respect to other semiconductor substrates. In the case of thiophene adsorption, we also observe the annealing-induced fragmentation of the molecule, which is interpreted in terms of a desulfurization process.

I. INTRODUCTION

The adsorption states of aromatic molecules on silicon was the subject of extensive recent investigations with synchrotron radiation photoemission and high-resolution electron-energy-loss spectroscopy (HREELS).[1-4] These studies were stimulated by the discovery of an unexpectedly high reactivity of benzene and pyridine molecules on cleaved silicon, probably due to the cleavage steps. Such reactivity results in stable chemisorption states even at room temperature, a totally different behavior with respect to any other semiconductor surface. The present work extends the investigation to the adsorption of the sulfur-containing aromatic-molecule thiophene, C_4H_4S. Cleaved silicon exhibits again a high reactivity. Upon annealing, however, this high reactivity leads to molecular fragmentation rather than adsorption only.

Thiophene is the simplest molecule in the class of sulfur-containing heterocyclic aromatic systems. On metals, this molecule is a prototype for the study of the hydrodesulfurization process.[5] Photoemission and HREELS investigations of thiophene on Pt(111) revealed that the molecule decomposes at room temperature.[6] This gives rise to an interesting reaction, in which the thiophene sulfur atom is replaced by a platinum atom, suggesting the formation of a metallocycle.

Previous studies[1-4] demonstrated that the adsorption behavior of aromatic molecules on semiconductor substrates cannot be deduced from that on metal substrates. In fact, the typical semiconductor substrate is totally unreactive at room temperature when exposed to aromatic-molecule atmospheres. We have seen, however, that cleaved Si(111)2×1 is atypical. The present study shows that the similarity between these substrates and metal substrates is present for decomposition processes as well as for direct adsorption processes.

Our data show that 1–20 L ($1\ \mathrm{L}=10^{-6}$ Torr s) C_4H_4S exposures of cleaved Si at 85 K results in two different and simultaneous adsorption states. The first state is a chemisorption state, characterized by the removal of a hydrogen atom in α position and the formation of a σ bond between the thiophene α carbon and a silicon substrate atom. The second state is a π-bonded state, with the aromatic ring parallel or almost parallel to the Si surface.

The relative weight of the two states seems related to the quality of the cleave. It is likely, therefore, that the states occur at different adsorption sites. The reactivity of cleavage steps revealed by previous experiments on benzene and pyridine[1,2,4] chemisorption suggest them as sites for the σ-bonded states.

At higher exposures of 30–200 L, a partially ordered multilayer is formed. Upon annealing at ~ 270 K, the thiophene molecules decompose. Our HREELS data do not give any evidence that the C_4H_4 breaks down in this process. No hydrogen adsorption on silicon is detected, while the release of hydrogen atoms from other aromatic molecules produced detectable Si-H vibrational modes.[2,4] This indicates that the C_4H_4 chain is bonded as such to the substrates, i.e., that the process is a desulfurization reaction.

II. EXPERIMENTAL DETAILS

The probe for our study was surface vibrational spectroscopy with HREELS. The experimental system, described in Ref. 2, is located at the Montana State University Center for Research in Surface Science (CRISS). The vacuum chamber has a base pressure in the 10^{-11}-Torr range, and includes a circulating liquid-nitrogen cooling system which can bring the sample temperature down to 85 K.

Reference spectra taken on clean, cold Si(111)2×1, obtained by cleavage at low temperature, reproduced the known features of this surface. The cold substrates were exposed to thiophene vapors, reaching total exposures of 1 to 200 L. The annealing studies were performed by circulating a dc current through a heater close to the substrate. The spectra on annealed samples were taken at the same temperature as the unannealed samples.

The primary electron beam energy was 6.5 eV and the incidence angle was 30° throughout the experiments. The energy resolution was primarily determined by the quality of the cleaved surface, and ranged between 12 and 18 meV. The spectra were taken mostly in the specular collection mode, but nonspecular data were collected in some cases.

III. RESULTS AND DISCUSSION

We shall discuss first the results obtained on unannealed substrates. For different exposure levels, we obtained two different kinds of HREELS spectra. Figure 1 shows the typical spectrum produced by 1—20-L exposures. Spectral features appear at 450, 590 (shoulder), 750, 1130, 1590, 2015, 2900, and 3200 cm^{-1}. The broad structure centered at 1130 cm^{-1} is clearly the superposition of different components. The weak feature at 450 cm^{-1} is due to a residual signal from the well-known cleaved Si surface phonon—in fact, its strength decreases as the exposure increases. Its permanence after these levels of exposure indicates that the surface is not yet saturated.

The fact that so many spectral features related to C_4H_4S are observed, and the large width of these features, indicate that either the adsorption site has low symmetry, or there is more than one adsorption state. Previous results on adsorbed C_4H_4S on W(211) suggested two simultaneous bonding configurations, a π-bonded state and a σ-bonded state involving the α carbon.[7] The formation of σ bonds was observed for other aromatic molecules on cleaved Si.[1–4] A chemical reaction leading to a stable σ-bonded state for benzene was obtained for substrate temperatures of 135 K—and it involved the breaking of C—H molecular bonds.[4]

Similar reactions should occur more easily for thiophene due to its higher reactivity,[7] and be possible at a lower temperature of 85 K. Evidence for such reaction, as in the case of benzene and pyridine,[2,4] is the HREELS peak at 2015 cm^{-1}. This is due to bonds between the H atoms released by the reaction and the substrate Si atoms. Quite interestingly, the relatively intensity of the 2015-cm^{-1} peak changes from cleave to cleave for the same exposure level. This corroborates the general hypothesis that the formation of σ bonds for aromatic molecules on cleaved silicon occurs at cleavage steps. It also indicates that the σ-bonded state coexists with another thiophene adsorption state, most likely a π-bonded state as on metal substrates.[1–4]

Other experimental facts confirm the simultaneous existence of two adsorption states. First, the relative intensity of the 2015-cm^{-1} peak decreases as the exposure increases in the range 1—20 L. This indicates that the cleavage steps are saturated after a limited exposure, and only π-bonded states are formed afterwards. Second, the multiple peak centered at $\sim$3000 cm^{-1}, due to molecular C-H stretching modes, contains two components at 2900 and 3200 cm^{-1}, and the 2900 cm^{-1} intensity decreases for increasing exposures. This indicates that the two components of the multiple peak are related to the two adsorption sites, and in particular that the 2900 cm^{-1} is related to the σ-bonded state.

The coexistence of two bonding sites makes the detailed analysis of the HREELS spectral features quite difficult. The symmetry of the π-bonding site is either C_{2v} (if the aromatic ring is parallel to the surface) or lower. The electron-rich sulfur atom is likely to produce deviations from the highly symmetric parallel geometry. As to the σ-bonded state, we expect no symmetry elements at all for the adsorption site. Thus, all molecular stretching modes are expected to appear in the HREELS spectra, together with the Si-H mode due to the released hydrogen and to the Si-C mode for the σ bond.

Table I shows the probable correspondence between HREELS features in Fig. 1 and the thiophene molecular modes.[8] It is clear from the experimental spectra that it is impossible to distinguish from each other, the features related to the two adsorption states, except for the above interpretation of the structure of the $\sim$3000-cm^{-1} peak. As to the Si-C mode, the corresponding HREELS

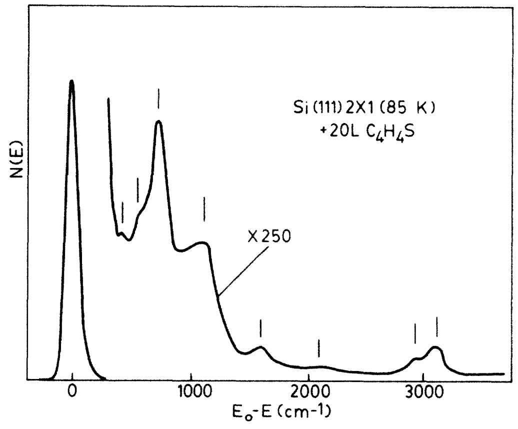

FIG. 1. High-resolution electron energy-loss spectra of cleaved Si(111)2×1 at 85 K, after a 20-L exposure to thiophene.

TABLE I. Correspondence between the vibrational modes of the free thiophene molecule and the spectral features of Fig. 1.

C_4H_4S on Si (cm^{-1})	Free C_4H_4S (cm^{-1})
590	$\nu_{23}(453)$, $\nu_{18}(565)$
750	$\nu_1(604)$, $\nu_{19}(686)$, $\nu_{22}(710)$, $\nu_{20}(748)$
1130	$\nu_3(832)$, $\nu_{24},(832)$, $\nu_{10}(872)$, $\nu_{11}(909)$, $\nu_2(1032)$, $\nu_4(1079)$, $\nu_{14}(1252)$, $\nu_{12}(1290)$, $\nu_5(1358)$, $\nu_6(1404)$
1590	$\nu_{15}(1590)$
2900	$\nu_7(2996)$, $\nu_{16}(2996)$
3200	$\nu_8(3093)$, $\nu_{17}(3093)$

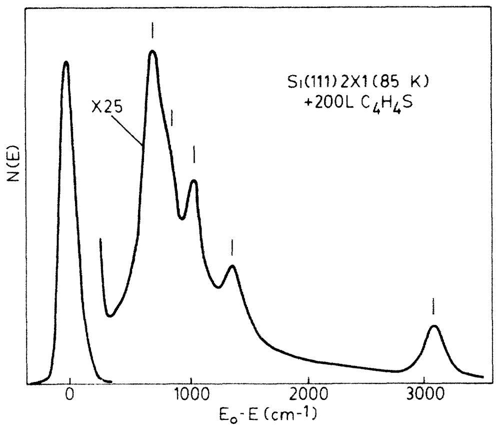

FIG. 2. HREELS data similar to those of Fig. 1, but obtained for a 200-L thiophene exposure.

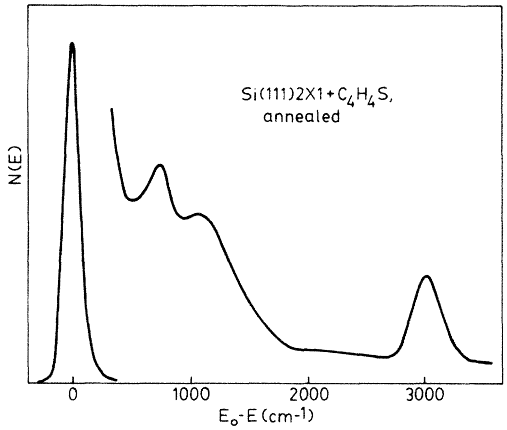

FIG. 3. HREELS data for Si(111)2×1, exposed to 200 L of thiophene while at 85 K, and then annealed to ∼270 K.

features for C_6H_6 and C_5N_5N on Si(111)2×1 are at 540 and 520 cm^{-1}.[2,4] In the present case, this mode contributes to the feature at 590 cm^{-1}. This is confirmed by the fact that the relative intensity of this peak changes with the exposure.

Figure 2 shows the HREELS spectrum produced by 30—200-L exposures of the cold Si(111)2×1 substrate. This spectrum is simpler than that of Fig. 1, and it only contains five features at 720, 850 (shoulder), 1050, 1350, and 3070 cm^{-1}. The absence of the surface phonon peak at 450 cm^{-1} indicates that the surface is completely saturated for these coverage ranges.

The simplicity of the spectrum in Fig. 2 suggests a state which is ordered at least in part, and most likely corresponds to condensed C_4H_4S multilayers. Table II shows that a one-to-one correspondence can be established between spectral features in Fig. 2 and the molecular modes which are totally symmetric, i.e., energy-loss active, in C_s symmetry. This symmetry means that the molecular plane is not parallel to the surface, but tilted—as suggested by the presence of the S atoms in the molecule. Independent evidence for this conclusion is provided by 14° off-specular spectra. These are not different from the specular spectra, confirming that the multilayer is not in a very symmetrical state.

HREELS experiments were performed on substrates first exposed to more than 30 L of thiophene, and then annealed. The HREELS results changed for an annealing temperature of ∼270 K, as shown in Fig. 3, and remained unchanged for further annealing at higher temperatures, up to ∼330 K. We did not observe a conversion of the multilayer adsorption state to the low-exposure adsorption state. This argues against the hypothesis of strong thiophene thermal desorption.

TABLE II. Correspondence between the vibrational modes of the free thiophene molecule which are dipole active for the C_s symmetry and the spectral features of Fig. 2.

C_4H_4S on Si (cm^{-1})	Free C_4H_4S (cm^{-1})
720	ν_{23}(453), ν_1(604), ν_{22}(710)
850	ν_3(832), ν_{24}(832)
1050	ν_2(1032), ν_4(1079)
1350	ν_5(1032), ν_6(1404)
3070	ν_7(2996), ν_8(3093)

The spectrum of Fig. 3 exhibits broad features with no clear correspondence to the thiophene molecular modes. In particular, we can identify only one resolved peak at 3020 cm^{-1}, in the spectral region of the C-H stretching modes. These facts indicate that the thiophene molecules are decomposed. The question then arises—does the decomposition involve the fragmentation of the C_4H_4 chain. Good evidence against this hypothesis is given, as discussed above, by the absence of the Si-H stretching mode at 2015 cm^{-1}. All other aromatic molecule adsorp-

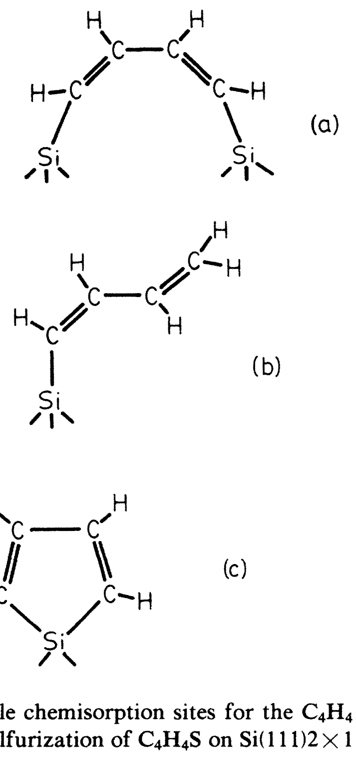

FIG. 4. Possible chemisorption sites for the C_4H_4 chain produced by the desulfurization of C_4H_4S on Si(111)2×1.

tion processes leading to the release of H atoms—including the initial adsorption of thiophene—give instead such modes.

We conclude, therefore, that the observed decomposition process is a desulfurization reaction. This process should also produce atomic sulfur adsorbed on the surface. Some evidence for the presence of atomic sulfur is provided by the appearance of a very weak and broad feature near 480 cm^{-1} after annealing. This is close in energy to the Si-S-Si vibrational peak observed after the annealed-induced decomposition of H_2S adsorbed on $Si(111)7\times 7$.[9]

We can speculate that the two most likely chemisorption geometry for the C_4H_4 chain are those shown in Figs. 4(a) and 4(b). The case of Fig. 4(c), which could be suggested by the analogy with C_4H_4S on Pt(111),[6] does not seem likely in this case. In fact, it would require a complete rearrangement of the bonding situation of the corresponding Si atoms, which is unlikely to be energetically favorable.

ACKNOWLEDGMENTS

This research was supported in part by the National Science Foundation (NSF), Grants No. DMR-84-21212 and No. DMR-82-05581. We are grateful to the staff members of the Montana State University Center for Research in Surface Science (supported by the NSF, Grant No. DMR-83-09460) for their excellent technical support.

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