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Studies of Acetylene and Oxygen Adsorption on Silicon Surfaces
by Low-Energy Electron Loss Spectroscopy

by

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ABSTRACT

Acetylene and oxygen adsorption on disordered and ordered silicon crystal surfaces of (111) orientation were studied by low-energy electron loss spectroscopy (ELS). There are marked structure-dependent differences in the ELS spectra in the presence of these adsorbates. A model for the acetylene molecule orientation on the silicon (111) ordered surface is proposed to explain the experimental results. ELS data suggest that the electrons in the silicon-oxygen chemisorption bond are more tightly bound on the disordered than on the silicon (111) surface with a (7×7) surface structure.

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Introduction

Electron loss spectroscopy (ELS) with primary electron energy of 50-200 eV has become increasingly popular as a tool for studying surface electronic transitions and collective excitations. The high surface sensitivity of ELS is the result of the short mean free paths of electrons in solids, which are typically $\leq 10 \text{ \AA}$ for 100 eV electrons. Recently, this technique was applied to the study of intrinsic electronic surface states in silicon and of states induced by hydrogen and oxygen adsorption.^(1,2,3) By combining ELS data with experimental results obtained by ultraviolet photoelectron spectroscopy (UPS), information on both the initial occupied and final empty electronic states can be obtained.^(3,4) In addition, by studying excitations from well-defined core levels, final empty states can also be probed by ELS.^(5,6)

In this paper, we present results of ELS studies of: (1) acetylene and (2) oxygen adsorption on silicon crystal faces of (111) orientation which exhibit the (7 $\times$ 7) surface structure or were disordered by ion bombardment using primary electron energies of ~ 100 eV. This constitutes the first energy-loss spectroscopic study of organic molecules adsorbed on silicon surfaces. Based on the experimental data, we put forward a model of acetylene orientation on the silicon (111) ordered surface.

Experimental Techniques

The adsorption experiments were performed inside an ion-pumped stainless steel vacuum system capable of a base pressure of less than 1×10^{-9} Torr. The system is equipped with LEED electron optics, ion bombardment gun, and a quadrupole mass spectrometer. A double-pass cylindrical mirror analyser

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with a coaxial electron gun was used as the primary electron source and energy analyser. The crystal was positioned in front of the analyser with the primary beam at normal incidence. The scattered electrons were analyzed at $\theta = 42^\circ$ over all azimuths. The analyser was operated in the retard-mode and theoretically, the energy resolution ΔE should be $\sim 0.7\%$ of the set pass energy which is 50 eV in all our measurements. However, since no primary beam energy selection was performed, the ultimate resolution was limited by the thermal spread of the incident electrons, which is about 0.6 eV. The spectral features were enhanced by taking the second derivative of the electron energy distribution. This was achieved by modulating the pass energy at a frequency ω and detecting the signal at frequency 2ω . Auger analysis was performed by operating the same analyser in the conventional mode.

The specimen used throughout the experiments was a 2500 ohm-cm p-type silicon crystal, mechanically polished with 0.05 μ diameter Al_2O_3 powders, etched in HF- HNO_3 solution and rinsed in ethanol, and was mounted in a high density alumina holder with a tantalum heater at the back of the crystal. The heater wire was wound non-inductively to minimize the magnetic field generated by the heater current. The major surface contaminants were carbon and oxygen, which were removed by sputtering with an argon ion beam of 2 keV energy and 4 μA current. This gave a disordered surface. Annealing at 800°C for about 30 mins resulted in the formation of the (7×7) structure as detected by LEED.

Acetylene (resp. oxygen) was introduced into the system through a leak valve and the coverage was determined by observing the ratio of the carbon (resp. oxygen) Auger signal to that of silicon as a function of

exposure. We will subsequently call the saturation coverage to be $\theta = 1$, although this may correspond to different numbers of gas molecules per silicon atom on the ordered and disordered surfaces, as discussed below.

Results and Discussion

A. The Clean Surfaces

The energy loss spectrum for the clean, ordered Si(111)-(7×7) surface is shown in the topmost curve of Fig. 1. This is identical to that of Rowe and Ibach,⁽¹⁾ except that the E_1 transition shows up much more clearly here, probably as a result of better resolution. The peaks labelled E_1 and E_2 are attributed to bulk interband transitions, whereas $\hbar\omega_p$ and $\hbar\omega_s$ are due to bulk and surface plasmons, respectively. S_1 is due to transitions from the surface dangling bond state and S_2 , S_3 arise from the back-bonding states,⁽¹⁾ which appear only as shallow shoulders on the disordered surface, as shown in the topmost curve of Fig. 2. The spectrum from the disordered surface shows a weak shoulder slightly above the surface plasmon peak. This peak disappears on annealing and/or prolonged exposure to ultra-high vacuum (~ 30 min in 5×10^{-9} Torr). This behaviour suggests that it is a surface-related transition, and from its transition energy of 11.6 eV, this energy loss peak probably arises from back-bonding state transitions.⁽⁷⁾

B. Effect of Acetylene Exposure on the Ordered and Disordered Silicon Surfaces

On the Si(111)-(7×7) surface, exposure at room temperature to acetylene causes attenuation of peaks due to bulk and surface transitions, except for the S_2 transition which becomes stronger with increasing acetylene coverage. (Fig. 1). The rate of attenuation of other surface-related peaks, viz.

S_1 and S_3 , as a function of exposure is small. In fact, after 2000 L ($1\text{L} \equiv 10^{-6}$ Torr-sec) of acetylene exposure, a weak S_1 peak still remains. Above $\theta = 0.5$, the E_1 transition at 3.2 eV is dominated by a growing neighboring acetylene-related peak at 3.6 eV. Another peak at 8.4 eV shows up as a shoulder of the 7.3 eV transition. At saturation of the surface with adsorbed acetylene, the LEED pattern showed very weak one-seventh order spots and no new structures. Thus, these results indicate that acetylene does not form an ordered overlayer on the Si(111)-(7 $\times$ 7) surface. Flashing the crystal to 800°C produces an acetylene peak in the quadrupole mass spectrometer, indicating that most of the C_2H_2 is not decomposed on the surface.

The energy loss spectrum of the silicon (111) surface with the (7 $\times$ 7) structure saturated with acetylene differs significantly from that of the acetylene-saturated disordered silicon surface (Fig. 2). The relative strengths and positions of loss peaks are different, e.g. on the disordered surface, there are two well-developed peaks at 7.0 and 8.4 eV, while on the ordered surface we observe a strong peak at 7.3 eV and a weak shoulder at 8.4 eV. This suggests that the bonding sites of acetylene are different on the two surfaces. In addition, the dangling bond transition S_1 is completely removed on the disordered surface by the adsorption of 0.25 monolayer of acetylene, while it is still present on the Si(111)-(7 $\times$ 7) surface even at saturation. The latter observation indicates that acetylene molecules sit on certain preferred sites which appear to be much less accessible for bonding on the ordered (111) crystal face than on the disordered silicon surface.

A recent study of the surface crystallography of acetylene on the platinum surface of (111) orientation⁽⁹⁾ indicates that acetylene sites in a two-fold bridge position between two platinum surface atoms. Let us assume a similar model for the adsorbed acetylene on the silicon (111) ordered surface, with its π orbitals overlapping with the silicon dangling bond orbitals. The silicon crystal field will cause the splitting of the acetylene π orbitals. Assuming that the π electrons have the same final state in energy loss experiments, one would see two or more neighboring energy loss peaks. This is indeed observed on the (7 $\times$ 7) surface, viz a strong 7.3 eV peak and a weak 8.4 eV shoulder. By placing acetylene molecules randomly (as evidenced by LEED) on the ordered silicon surface in bridge positions, there will still be silicon surface atoms not bonded to any acetylene molecules, which explains the incomplete removal of the S_1 transition. The incomplete coverage of all bridge sites is also indicated by the observed smaller carbon to silicon Auger peak ratio (~ 0.02) on the ordered silicon surface as compared to the corresponding ratio (~ 0.03) on the disordered silicon surface after saturation.

This interpretation of bonding can be further tested by ultra-violet photoelectron spectroscopy since the presence of split peaks due to the π orbitals of acetylene and the variation of their relative intensities in the UPS spectrum as a function as the polar angle should be detectable.

C. Effect of Oxygen Exposure on the Disordered Silicon Crystal Surface

Changes in the surface transitions on the disordered silicon crystal surface with increasing oxygen coverage are similar to that observed for

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the Si(111)-(7×7) surface,⁽²⁾ as shown in Fig. 3. Surface transitions S_1 and S_3 are removed. Peaks associated with oxygen appear at 3.4, 4.9, 7, 8.3, 9.5, and 12.8 eV, in complete agreement with results of Ludeke and Koma.⁽⁸⁾ Previously, on the silicon (111) surface with the (7×7) structure, splitting of the surface plasmon peak was observed, which was explained as due to the appearance of an oxygen-related transition close to the surface plasmon energy, viz ~11 eV.⁽²⁾ However, no such splitting was observed on the disordered surface. Instead, the corresponding oxygen transition occurs at a slightly larger transition energy of 12.8 eV.

It was previously shown that the chemical composition of the surface is most likely that of silicon monoxide, SiO, since the energy loss peaks agree closely with those in the U-V absorption spectrum of gaseous SiO.⁽⁸⁾ In this circumstance, and assuming that the final state of the transition (an exciton level) is unchanged,⁽⁴⁾ the larger transition energy of this oxygen level indicates that the electrons in the SiO bond are more strongly bound on the disordered surface. This is probably a result of the more "open" structure on the disordered surface, thereby affording more neighbors for the adsorbed oxygen atom. This explanation is consistent with the observation that on the Si(100)-(2×1) surface, which also has a fairly open structure, the corresponding oxygen transition is at ~13 eV.⁽⁴⁾

This interpretation is further substantiated by our preliminary data on oxygen desorption from silicon surfaces (Fig. 4). The surface was first saturated by a monolayer of oxygen and then heated to 750°C. The oxygen concentration on the surface was then monitored by Auger electron spectroscopy as a function of time. As can be seen from Fig. 4, oxygen is removed faster from the ordered surface than from the disordered surface,

which is indicative of the stronger binding force on the latter surface. No attempt was made to estimate the difference between the desorption energies on the two surfaces, because at 750°C, oxygen desorption is accompanied by partial reconstruction on the disordered surface, which would undoubtedly alter the silicon-oxygen binding.

Conclusions

We have used electron loss spectroscopy, (ELS), to study and compare chemisorption processes occurring on both ordered and disordered silicon surfaces of (111) orientation. These studies indicate that the adsorption of acetylene on the Si(111)-(7×7) surface takes place on preferred sites, arising mainly as a result of the overlap between the silicon surface dangling bond orbitals and the π orbitals of the C_2H_2 molecules. To explain the ELS and Auger data, we propose that on the ordered silicon surface with the (7×7) structure, the acetylene molecule predominantly sits between two silicon atoms in a bridge position.

By comparing the difference in the oxygen-related transition at 12.8 eV on the disordered and ordered silicon (111) surfaces, we conclude that the electrons in the chemisorbed silicon-oxygen bond are more strongly bound on the disordered surface. This conclusion is substantiated by ELS results on the Si(100) surface.⁽⁴⁾ This is mainly the result of different atomic environments surrounding the chemisorbed oxygen atom.

The purpose of these studies was to examine the effects of an electron donor (C_2H_2) and an electron acceptor adsorbate (O_2) on the electronic surface states of clean ordered and disordered silicon. There are differences, especially in the changes induced by the two different species on the S_1

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dangling bond transition: oxygen appears to remove this surface state on both surfaces while acetylene does not on the ordered Si(111)-(7x7) surface. It would be of importance to verify the relationship between chemical bonding and electronic surface states. UPS studies of the bonding of these same adsorbates on the same silicon surfaces would also be necessary to provide additional information to establish this correlation.

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Figure Captions

- Fig. 1. Electron loss spectra of the silicon (111)-(7×7) surface with various coverages of acetylene.
- Fig. 2. Electron loss spectra of the silicon (111) disordered surface with various acetylene coverages.
- Fig. 3. Loss spectra of the silicon (111) disordered surface with various oxygen coverages.
- Fig. 4. The oxygen concentration on silicon surfaces as a function of time after the surfaces have been saturated by a monolayer of oxygen. The substrate temperature is $(750 \pm 5)^\circ\text{C}$. The two curves are scaled to give the same oxygen signal at $t = 0$.

XBL 7512-10069

Figure 1

XBL 7512-10071

Figure 2

XBL 7512-10068

Figure 3

XBL 7512-10070

Figure 4

0 0 1 3 4 4 5 7 5 1 0

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