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ADSORPTION OF H_2S, H_2O AND O_2 ON Si(111) SURFACES

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Electron energy-loss spectroscopy has been applied to the study of Si(111) surfaces covered with H_2S, H_2O and O_2 at room temperature and the surfaces annealed at ~ 600°C. The experimental results strongly suggest that H_2S and H_2O adsorb in the molecular states at room temperature. It is proposed that O_2 is first adsorbed in a molecular state, then adsorbs as atoms, and finally oxidizes forming SiO_2.

ELECTRON energy-loss spectroscopy (ELS) of solid surfaces is a very sensitive tool for the study of the intrinsic and extrinsic surface electronic states.[1–3] This permits us to investigate the chemical bonds of the adsorbates, i.e. whether gas molecules adsorb dissociatively or non-dissociatively on solid surfaces. In this paper, we present ELS results for thermally cleaned Si(111) surfaces covered with H_2S, H_2O and O_2 at room temperature and the surfaces heated to ~ 600°C. The observed differences in the loss spectra strongly suggest that these gases are adsorbed in the molecule-like states on Si(111) surfaces at room temperature.

There has been a controversy about the models for the adsorption of H_2S, H_2O and O_2 on Si(111) surfaces at room temperature. For H_2S and H_2O covered surfaces, the dissociative adsorption model has been proposed by Meyer and Vrakking[4] using Auger electron spectroscopy (AES) and ellipsometry. Fujiwara and Nishijima[3] suggested that H_2O adsorbs as molecules by ELS. For oxygen covered surfaces, the low energy-electron scattering experiments by Ibach *et al.*[5] indicate that O_2 is adsorbed as molecules at the initial stage of the oxidation. Ludeke and Koma[2] proposed that O_2 is adsorbed as atoms using ELS. Recent theoretical calculation by Goddard III *et al.*[6] indicates that O_2 is adsorbed as peroxy radical, or in a molecular state.

The electron spectrometer consists of an electron gun, and two 127° cylindrical analyzers used for the monochrometor and the energy analyzer. The energy-loss spectra were measured in the second derivative mode with a constant resolution of ~ 0.8 eV. The same spectrometer was also used to analyze the surface species by AES. Clean Si(111) surfaces were obtained by heating the samples to ~ 1200°C in the vacuum chamber. Special care was taken to minimize the beam induced effects. The readers are referred to reference 3 for a further detail.

The energy-loss spectrum of a clean surface, curve (a), shows all of the characteristic loss peaks in agreement with those reported by other workers.[1–3] When this surface is exposed to H_2S at room temperature, new peaks appear at 3.7, 4.8 and 8.8 eV, while the peaks attributed to the intrinsic surface-state transitions diminish. The result is shown in curve (b) of Fig. 1. The peak amplitudes are saturated with the exposures of ~ 100 Langmuir (1 L = 10^{-6} torr sec). The peak positions are independent of the exposures and the primary electron energies between 50 to 200 eV within the experimental errors of ± 0.3 eV. These indicate that the three peaks are due to the extrinsic surface states which characterize H_2S adsorption on Si(111) surfaces. The peaks near 10 and 18 eV are due to surface and bulk plasmons, respectively, because they become prominent on increasing the primary electron energy. No evidence has been obtained that multiple adsorption states are involved. The room temperature adsorption of H_2O has been reported elsewhere,[3] and the loss spectrum is shown in curve (c). This result is quite similar to curve (b), which is not surprising due to the similarity of the structural and the electronic properties of the two molecules. However, a difference is found in the electron induced effect, i.e. for H_2O, an electron beam irradiation of ~ 30 min changes the spectra drastically suggesting the decomposition of the molecules, whereas much smaller changes are observed for H_2S in the same period.

The loss spectrum of H_2S adsorption is observed to change substantially on heating the surface to above 500°C. Curve (d) shows the spectrum after three cycles of the successive 50 L H_2S exposure and heating at 600°C. The observed peaks are at 3.4, 5.1, 7.4, 8.9, 10.3, 13.5, 18.1 amd 21 eV. The 2.2 eV peak is either spurious or due to the residual surface-state transition. The above change is attributed to the decomposition of H_2S and the subsequent desorption of hydrogen at ~ 500°C,[7] and the curve (d) is interpreted to correspond to the loss spectrum of a Si(111) surface covered with

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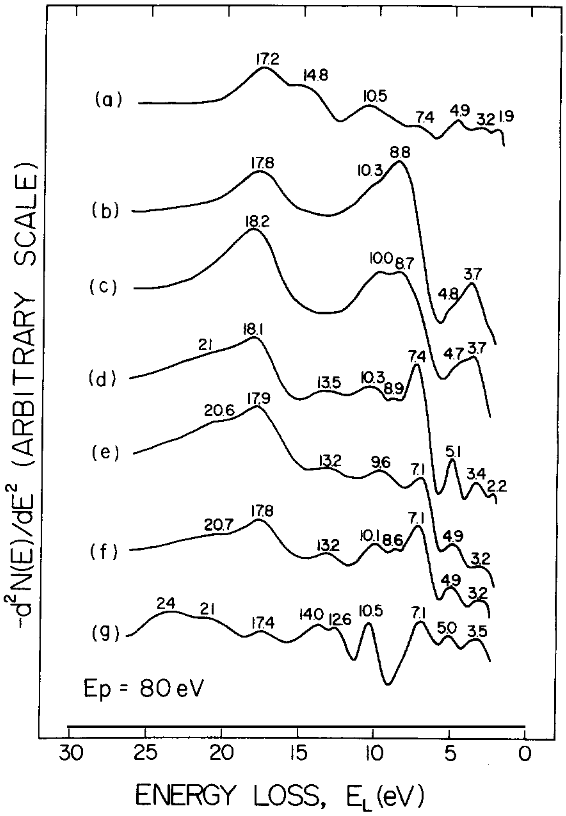

Fig. 1. Negative second derivatives of the electron energy-loss spectra (primary energy = 80 eV) of the Si(111) surfaces: (a) clean surface; (b) after H_2S exposure of 2000 Langmuir; (c) after H_2O exposure of 100 Langmuir; (d) after three cycles of successive 50 Langmuir H_2S exposure and heating at 600°C; (e) after O_2 exposure of 1.2 Langmuir; (f) after O_2 exposure of 100 Langmuir and heating at 700°C; (g) SiO_2 surface.

sulfur atoms. A similar result is observed for H_2O covered surfaces.[3]

Meyer and Vrakking[4] have proposed that H_2S adsorbs dissociatively, and that sulfur and hydrogen atoms form covalent bondings with the dangling bonds of a Si(111) surface. If this is true, the loss spectrum should be a superposition of those corresponding to the Si(111) surfaces covered with sulfur and hydrogen atoms, provided that the lateral interactions of the adsorbates can be neglected. However, no peak is observed at 7.4 eV which is the most prominent of the sulfur covered surface. The lateral interaction is thought to be negligibly small, since no shift is observed of the loss peaks as the surface coverage of H_2S is varied. Therefore, our experimental results show that H_2S adsorbs as molecules at room temperature. A similar discussion has previously been reported for H_2O adsorption.[3]

Curve (e) shows the loss spectrum of a Si(111) surface exposed to oxygen at room temperature. The observed peaks are at 3.2, 4.9, 7.1, 9.6, 13.2, 17.9 and 20.6 eV, which are in general agreement with the previous reports.[1,2] This result is interpreted to indicate that O_2 is adsorbed as molecules in agreement with Ibach and Rowe.[1] When the surface was heated to ~ 700°C for 30 sec, the peak at 9.6 eV disappears. We find a peak at 10.1 eV and a small hump at 8.6 eV as shown in curve (f). It should be emphasized that these peaks do not exist at room temperature, because their center-of-gravity is not at 9.6 eV. The same result is obtained by the electron irradiation for about 10 min (without thermal treatment). We believe that curve (f) is the loss spectrum for O_2 adsorbed as atoms, because the curve is essentially the same as that obtained for a Si(111) surface covered with atomic oxygen produced by three cycles of the successive H_2O exposure and heating at ~ 700°C.[3] Curve (f) is not the spectrum for SiO_2, which is also shown in curve (g), because the peak at 10.1 eV does not have the same origin as the 10.5 eV peak of SiO_2. This is confirmed by the difference in the primary energy dependence of the excitation cross sections, i.e. the latter shows a decrease of the relative cross sections as the primary electron energy is lowered to 30 eV, although the former does not. The survival of the bulk plasmon peak at 18 eV indicates also that the substrate is not oxidized into SiO_2 yet. An additional evidence is the similarity of curves (d) and (f). In connection with this, we want to point out that the surface covered with atomic oxygen is oxidized into SiO_2 by a prolonged electron bombardment, whereas the formation of SiS_2 is comparatively difficult.

Recently, Ludeke and Koma[2] suggested, from the similarity of the observed energy-loss spectra with the excitation spectra of SiO molecules, that oxygen is chemisorbed into a monoxide-like bound state. If this identification is correct, a similar interpretation is applicable to the case of sulfur atoms chemisorbed on a silicon surface. However, the location of the loss peaks for this surface is quite different from the excitation energies of SiS molecules.[8] For example, the main loss peaks at 7.4 eV can not be related to the $E^1\,\Sigma^+\text{–}X^1\,\Sigma^+$ transitions at 4.8–6.2 eV. Therefore, the interpretation by Ludeke and Koma of oxygen adsorption is questionable. Our conclusion is supported by the low energy-electron scattering experiments of Ibach *et al.*[5] and the theoretical calculation of Goddard III *et al.*[6]

As a summary, we have shown that H_2S, H_2O and O_2 are adsorbed as molecules on Si(111) surfaces at room temperature by the comparison of the energy-loss spectra for gas-covered surfaces and the surfaces heated to ~ 600°C. The three stages of the oxidation, i.e. initial adsorption as molecules, then as atoms, and finally as SiO_2, have been distinguished.

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