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High-resolution electron-energy-loss spectroscopy studies of Al adsorption on Si(111)

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We have studied the high-resolution electron-energy-loss spectra at zero momentum transfer ($q=0$) for the $(\sqrt{3}\times\sqrt{3})R\,30°$, $(\sqrt{7}\times\sqrt{7})R\,19.1°$, and 7×7 structures formed when Al is deposited on Si(111)-(7×7) and annealed. For the $\sqrt{3}\times\sqrt{3}$ structure, we found loss peaks at 32.3 and 69.2 meV that agree very well with calculated energies, as well as several other loss peaks of uncertain origin. We have tentatively identified phonon energies for the $\sqrt{7}\times\sqrt{7}$ structure, and demonstrated that for some sample preparations there may be a remnant of the (7×7)-Al structure present for surfaces showing the $\sqrt{7}\times\sqrt{7}$ and even the $\sqrt{3}\times\sqrt{3}$ reconstructions in low-energy electron diffraction.

I. INTRODUCTION

The search for a better understanding of the metal-semiconductor interface is an on-going theme in surface research. Many different techniques have been applied to study a variety of metal-semiconductor systems to further this understanding. It is significant when many techniques have been applied to the same interface, building up a complete picture of its physical properties, and providing a case study for theorists to test their models and calculation methods against.

An example of such a well-studied metal-semiconductor system is the Si(111)-$(\sqrt{3}\times\sqrt{3})R\,30°$:Al reconstruction. We will not attempt a comprehensive review of the literature in this Brief Report. However, the most decisive works include the dynamic low-energy electron-diffraction (LEED) calculations of Huang *et al.*[1] that confirmed that the Al adsorbs at the T_4 site, and the investigations of the electronic structure done by Kinosita *et al.*[2] and Nicholls *et al.*[3]

We report here the results of a high-resolution electron-energy-loss spectroscopy (HREELS) study at zero momentum transfer ($q=0$) for the Si(111)-$(\sqrt{3}\times\sqrt{3})R\,30°$:Al reconstruction. This is the first part of a study that will map out the full phonon dispersion. HREELS data for $q=0$ were previously reported by Kelly *et al.*,[4,5] but at a much lower resolution than the present work. We have found a richer spectrum of loss peaks, and better agreement with the phonon energies calculated by Northrup,[6] including the first sighting of the low-energy phonon he predicted. We also report the HREELS spectra at $q=0$ for the Si(111)-$(\sqrt{7}\times\sqrt{7})R\,19.1°$:Al and Si(111)-$(7\times7)$:Al structures.

II. EXPERIMENT

The equipment and procedures used in this study will be reported in detail in a later publication. Briefly, the Si(111) samples were single crystals cut from a commercial wafer (8–12 Ω cm, P doped). The samples were mounted on Mo sample stubs that were transferred through a load lock, onto a dual-axis manipulator. The samples were cleaned *in vacua* by heating to 900 °C, and then cooling at a rate of about 1 °C/S. Initially, no contaminants could be detected with Auger-electron spectroscopy, but after three or four days a small C peak appeared, at which point we discarded the sample. LEED consistently showed an excellent 7×7 pattern.

Al was evaporated onto the Si from a braided W filament wrapped with 99.999%-pure Al wire. The amount of Al deposited was monitored with a quartz-crystal microbalance, which was placed at roughly $\frac{1}{6}$ the filament-to-sample separation so that it was sensitive to submonolayer coverages at the sample. We relied on the microbalance as a secondary scale for the coverage, using it mainly to quantify the relative amounts of Al used in various experiments, and to determine the best operating conditions for the Al source each time the filament was replaced. We relied on LEED for the primary calibration of the coverage, assigning $\frac{1}{3}$ monolayer (ML) of Al to the coverage that produced the best $\sqrt{3}\times\sqrt{3}$ LEED pattern, $\frac{3}{7}$ ML for the best $\sqrt{7}\times\sqrt{7}$, and 1 ML for the best (7×7)-Al.[7] There was good agreement between the calculated and observed frequency changes of the quartz crystal for the various coverages.

We tried a variety of procedures for producing the $\sqrt{3}\times\sqrt{3}$ structure; the most reliable was to deposit approximately $\frac{1}{3}$ ML of Al, heat the sample to 800 °C, and cool immediately. Similarly, the $\sqrt{7}\times\sqrt{7}$ structure was produced by depositing approximately $\frac{3}{7}$ ML of Al and flash annealing to 800 °C, and the (7×7)-Al structure by depositing approximately 1 ML and flash annealing to 800 °C. Depositing intermediate amounts of Al produced mixed structures, such as $\sqrt{3}\times\sqrt{3}$ and $\sqrt{7}\times\sqrt{7}$, or $\sqrt{7}\times\sqrt{7}$ and (7×7)-Al. Heating to 900 °C for 5 min completely removed the Al from the surface, and restored the familiar 7×7 LEED pattern.

One technical problem involved in working with Al films was their tendency to form alumina any time they were exposed to oxygen. Any alumina near the sample charged up in the spectrometer, severely degrading the resolution. Therefore, prior to depositing Al, all of the native oxide had to be removed from the Mo sample stub. Similarly, when a Si sample was being replaced, all of the Al had to be removed from the sample stub prior to transferring the stub out through the load lock for the mounting of a new sample. These problems could be avoided by sputtering and annealing the sample stub, prior to mounting a Si sample. Subsequently exposing the Mo to atmosphere for 10–15 min while mounting the Si then produced a thin layer of oxide that was easily removed by heating to 900 °C for about 60 min.

The HREELS spectrometer has a dual-pass monochromator and a rotatable analyzer section for angle-resolved measurements. Resolutions of 5 meV were obtained for a Cu sample in the initial trials of this spectrometer. The work reported here was performed with a typical resolution of between 6.2 and 7.0 meV. We worked at zero momentum transfer ($q=0$), with both the incident and scattered angles at 60°. We fit the HREELS spectra with a series of Gaussian curves to locate the positions of the various loss features. The uncertainties for the energies of the loss features was smaller than 1 meV, except where otherwise noted. All of the spectra reported here were taken with an incident electron energy of 3.0 eV, and for sample temperatures between 20 °C and 80 °C.

III. RESULTS AND DISCUSSION

A. Si(111)-($\sqrt{3}\times\sqrt{3}$)R30°:Al

The HREELS spectrum for the $\sqrt{3}\times\sqrt{3}$ reconstruction is shown in Fig. 1. The spectrum is unexpectedly rich with loss peaks. There is one loss peak near 16±2 meV that can only be seen in the spectra with the highest resolution because of its proximity to the elastic peak. There are three well-defined peaks at 32.3, 42.2, and 69.2 meV, and two weaker features at 58±2 and 76.4 meV. Finally, there are several loss peaks in the range from approximately 100 to 125 meV.

The loss peaks between 100 and 125 meV are associated with a small amount of hydrocarbon contamination. Although the pressure in the ultrahigh-vacuum chamber was in the mid-10^{-11}-Torr range, these features appear in the spectrum within a few hours of removing the oxide layer from a new Si sample, and they grew steadily with time. The peak at 16 meV is too close to the elastic peak to see if it shows a similar time dependence. None of the other features showed such a time dependence, so they are probably not caused by the accumulation of a contaminant.

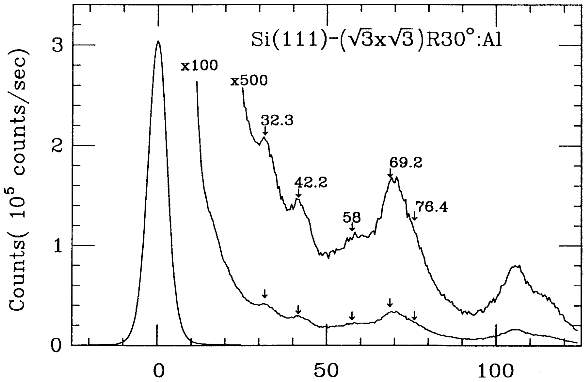

FIG. 1. HREELS spectrum taken for the Si(111)-($\sqrt{3}\times\sqrt{3}$)R30°:Al structure. The energy of the incident electrons was 3.0 eV, and the incident and scattered angles were both 60°. The full width at half maximum (FWHM) for the elastic peak is 6.6 meV.

An unsaturated $\sqrt{3}\times\sqrt{3}$ structure could be formed by initially depositing too little Al,[7] or by overheating the sample so that too much Al was removed in the anneal. Such a structure gradually degraded over the course of several hours with the intensity of the third-order LEED spots decreasing and the diffuse scattering increasing. HREELS spectra taken at various times as the structure degraded, showed that most of the loss peaks (not including the hydrocarbon peaks) decreased in intensity, while the feature at 76.4 meV grew to eventually dominate the spectrum. Therefore, the feature at 76.4 meV is probably not characteristic of the $\sqrt{3}\times\sqrt{3}$ structure, but is instead associated with a structural element of the degraded surface.

Kelly *et al.*[4,5] reported finding a broad loss peak at 65 meV in HREELS data from the $\sqrt{3}\times\sqrt{3}$ structure. They worked at a significantly lower resolution (12–16 meV) than we have obtained here, so they might have been observing, but not resolving, a combination of the 58.4-, 69.2-, and 76.4-meV loss peaks. Their lower resolution also means that lower-energy peaks would have been obscured by their elastic peak.

Northrup[6] did an evaluation of the force-constant matrix to find the frequencies and eigenvectors for the surface phonons on the $\sqrt{3}\times\sqrt{3}$ surface. He found one phonon at 33 meV and another at 69 meV. These calculated energies are in excellent agreement with the loss peaks we see at 32.3 and 69.2 meV. Northrup identified the lower-energy mode as primarily involving the Al adatom and the Si atoms in the surface layer, while the higher-energy mode involves the stretching of the bond between Si atoms in the second and third layers.[6]

B. Si(111)-($\sqrt{7}\times\sqrt{7}$)R19.1°:Al and Si(111)-(7×7)-Al

In an effort to identify any loss features caused by contamination, we also looked briefly at the HREELS spectrum from the $\sqrt{7}\times\sqrt{7}$ and (7×7)-Al structures. Our resolution was typically lower here (7.0–9.0 meV) than that obtained for the $\sqrt{3}\times\sqrt{3}$ structure, and the uncertainties in the positions of the loss features was 2 meV.

The (7×7)-Al structure was produced by depositing approximately 1 ML of Al, and then flash annealing the sample to 800 °C. LEED displayed the integral-order spots plus weak seventh-order spots adjacent to the integral-order spots. The spots tended to be broader and the diffuse scattering higher than was typically seen for the clean 7×7 surface or the ($\sqrt{3}\times\sqrt{3}$)-Al structure. (A more careful choice of annealing temperature and time might have improved the LEED.) The HREELS spectrum from the (7×7)-Al structure, shown in Fig. 2, has two strong loss peaks at 20 and 56 meV. The latter peak agrees well with the 55-meV peak observed by Kelly *et al.*[5]

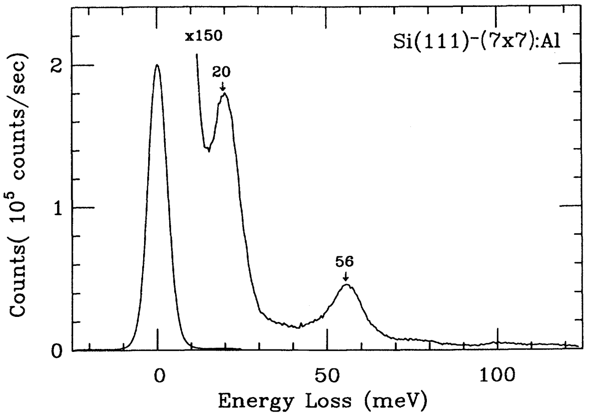

FIG. 2. HREELS spectrum taken for the Si(111)-(7×7):Al structure. The energy of the incident electrons was 3.0 eV, and the incident and scattered angles were both 60°. The FWHM for the elastic peak is 6.6 meV.

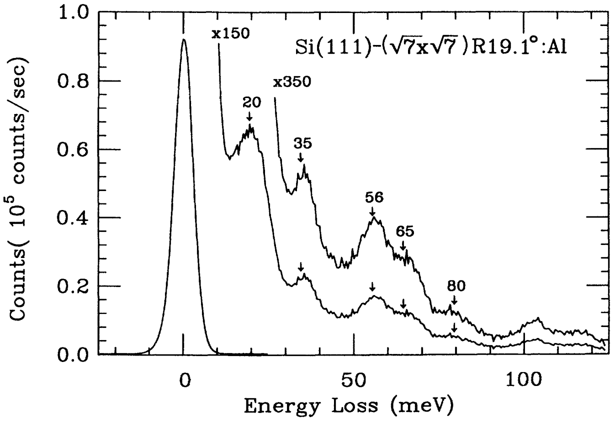

FIG. 3. HREELS spectrum taken for the Si(111)-($\sqrt{7}\times\sqrt{7}$)R 19.1°:Al structure. The energy of the incident electrons was 3.0 eV, and the incident and scattered angles were both 60°. The FWHM for the elastic peak is 6.5 meV.

The $\sqrt{7}\times\sqrt{7}$ structure was produced by depositing approximately $\frac{3}{7}$ ML of Al, and flash annealing to 800 °C. In the ($\sqrt{7}\times\sqrt{7}$) LEED pattern, the seventh-order spots were roughly as sharp and intense as those in the clean (7×7) LEED pattern, but the diffuse scattering was always slightly higher. The HREELS spectrum, shown in Fig. 3, contains new loss features at 35 and 65 meV, and a very weak feature in the vicinity of 80 meV. There are also loss peaks at 20 and 56 meV, which had been seen (with considerably more intensity) in the spectrum from the (7×7)-Al structure.

The 35- and 65-meV loss peaks seen for the $\sqrt{7}\times\sqrt{7}$ structure are in the same range of energies as the 32.3- and 69.2-meV phonon losses seen for the $\sqrt{3}\times\sqrt{3}$ structure. Different adsorption sites are involved for the two structures, so we expect different phonon energies, but it seems logical to tentatively attribute the 35- and 65-meV losses to phonons analogous to those found in the $\sqrt{3}\times\sqrt{3}$ structure. Therefore, the lower-energy loss might be caused by Al and Si surface atoms, and the higher-energy loss might be caused by the stretching of the bond between Si atoms in the second and third layers.[6]

In another experiment, we started by growing the (7×7)-Al structure, and then we repeatedly flash annealed to 800 °C until we obtained the $\sqrt{7}\times\sqrt{7}$ structure. The LEED pattern from this surface usually showed higher diffuse scattering than if we had initially deposited just the right amount of Al to obtain the $\sqrt{7}\times\sqrt{7}$ structure, and the HREELS spectrum showed significantly stronger loss peaks at 20 and 56 meV. Annealing again to get the $\sqrt{3}\times\sqrt{3}$ structure, the LEED showed a higher-than-normal diffuse scattering, and now 20- and 56-meV peaks appeared in the HREELS spectrum from this surface. The slight degradation in the LEED patterns, and the increased strength of the 20- and 56-meV HREELS loss features for the $\sqrt{7}\times\sqrt{7}$ structure, and their continuing presence in the spectrum for the $\sqrt{3}\times\sqrt{3}$ structure, suggests that those loss peaks may be caused by a remnant of the (7×7)-Al structure that has not been fully removed in the annealing process.

Finally, we should note that when we first saw that the strength of the loss peaks at 20 and 56 meV seemed to correlate with the amount of Al initially deposited on the Si, we thought that they might be caused by a contaminant originating in the Al source. We subsequently repeated the experiments using a Ta filament instead of W, and also replaced the Al wire with Al purchased from a different supplier, and we found identical results.

IV. CONCLUSIONS

We have measured the high-resolution electron-energy-loss spectra from the various ordered structures formed by Al on Si(111). For the Si(111)($\sqrt{3}\times\sqrt{3}$)R 30°:Al structure, we found loss peaks at 32.3 and 69.2 meV that agree very well with the energies calculated by Northrup,[6] as well as several other loss peaks of uncertain origin. We have also measured the spectra from the Si(111)-($\sqrt{7}\times\sqrt{7}$)R 19.1°:Al and Si(111)-(7×7):Al structures, tentatively identifying phonon energies for the $\sqrt{7}\times\sqrt{7}$ structure, and demonstrating that for some sample preparations there may be a remnant of the (7×7)-Al structure present for surfaces showing the $\sqrt{7}\times\sqrt{7}$ and even the $\sqrt{3}\times\sqrt{3}$ reconstructions in LEED.

We are currently continuing this research by looking at HREELS data from the $\sqrt{3}\times\sqrt{3}$ structure for momentum transfers other than $q=0$ in an effort to map out the phonon dispersions throughout the Brillouin zone. Hopefully, the new data will stimulate further lattice-dynamics calculations, and should lead to a better understanding of the origins of the various loss peaks.

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