# Angle-resolved high-resolution electron-energy-loss study of In-adsorbed Si(111)-(4×1) and -(8×2) surfaces

Kazuyuki Sakamoto,[1,*] Hidenori Ashima,[1] Han Woong Yeom,[2] and Wakio Uchida[1]
[1]*Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*
[2]*Atomic-scale Surface Science Research Center and Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Korea*

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The metallic In/Si(111)-(4×1) surface is known to show a temperature-induced transition into a (8×2) structure. In the present study, we observed a drastic change of the surface free carrier density at 130 K that corresponds to the phase transition. In spite of the decrease in the free carrier density, the (8×2) phase does not show a complete semiconducting character at 90 K. Moreover, we observed two surface phonon modes at 33 and 60 meV that have different dipole activities for the (8×2) phase, and one phonon mode at 61 meV for the (4×1) phase.

The modification of semiconductor surfaces induced by the adsorption of metal atoms has been a topic of experimental investigations for the creation of nanoscale quantum structures with high perfection. Selecting In for an adsorbate, several reconstructions are observed on a Si(111) surface that depend on the coverage.[1–4] Among the In-adsorbed Si(111) reconstructed surfaces, the (4×1) phase is arguably the most interesting one due to the recent observation of the quasi-one-dimensional (1D) charge density wave (CDW) on this phase.[5]

A great number of studies have been done to determine the surface structure,[6–12] electronic character,[5,13–15] and vibrational modes of the In/Si(111)-(4×1) surface.[16] Several models are proposed for the structure of the In/Si(111)-(4×1) surface.[6–12] Among them, the surface structure is suggested to be formed with the reconstruction of surface Si atoms in the recent scanning tunneling microscopy (STM) (Refs. 10 and 11) and surface x-ray diffraction[12] studies. For the electronic structure, the In/Si(111)-(4×1) surface is well known to have a metallic character at a sample temperature of 300 K.[5,13–15] Three surface bands that cross the Fermi level are observed by angle-resolved photoelectron spectroscopy (ARPES),[5,13] and a clear Fermi level crossing and an image-induced surface state by inverse photoelectron spectroscopy (IPES).[14,15] The dispersions of the In-derived three occupied surface bands,[5,13] that of the unoccupied one,[14] and the anisotropic dispersion of the image state[15] suggest the quasi-1D metallic character along the 1D In chains. Recently, the In/Si(111)-(4×1) surface is reported to show a temperature-induced reversible transition into a semiconducting (8×2) phase that is originated by the instability of the metallic phase and by a 1D-CDW using a combined measurement of ARPES and STM.[5] However, the transition temperature is not decided yet.

In the vibrational study of the 300 K In/Si(111)-(4×1) surface, only a long Drude tail originated by the metallic character of this surface is observed, and no vibrational feature is seen due to the presence of this tail in the high-resolution electron-energy-loss spectroscopy (HREELS) study.[16] Since the (8×2) phase is reported to have a semiconducting character,[5] the Drude tail is expected to disappear and the vibrational modes are in anticipation of observation at low temperature. Moreover, HREELS is useful to obtain the information of electronic states close to the Fermi level, because an electronic excited state with rather low energy is detectable from its high resolution.

In this paper, we present the temperature-dependent HREELS study of the In/Si(111)-(4×1) surface. Measuring the temperature dependence of the full width at half maximum (FWHM) of the elastic peak, we determine that a drastic change of the surface free carrier density occurs at 130 K. For the vibrational modes, we observe two surface phonon modes that energies are 33 and 60 meV for the (8×2) phase, and one phonon mode at 61 meV for the (4×1) phase.

The experiment was carried out in a UHV chamber that is equipped with a HREELS spectrometer, a low energy electron diffraction (LEED) optics, and an Auger-electron spectrometer (AES). The base pressure was below $1\times10^{-10}$ Torr. A VSW IB2000 spectrometer was used for the HREELS measurements. The Si(111) sample, cut from a P-doped (*n*-type) Si wafer with miscut by 2° towards the $[11\bar{2}]$ direction, has an electrical resistivity of 1000 Ω cm and a size of $5\times15\times0.5$ mm$^3$. To obtain the clean reconstructed Si(111)-(7×7) surface, we heated up the chemically prepared sample to 1150 K for 10 min, and then up to 1520 K for 3 sec by direct resistive heating in the UHV chamber. We checked the quality of the surface structure by the observation of a clear (7×7) LEED pattern, and verified the cleanliness by HREELS and AES. The In/Si(111)-(4×1) surface was prepared by *in situ* deposition of In with an effusion cell on the clean Si(111) surface that was heated at approximately 700 K. The formation of a single domain In/Si(111)-(4×1) surface was confirmed by LEED. After cooling down the sample at 90 K, a single domain (8×''2'') LEED pattern was observed. Here, the quotation marks are used to indicate the presence of the streaks and to distinguish the pattern from that of a well-ordered phase.

Figure 1 shows the HREELS spectra of the 300 K In/Si(111)-(4×1) and 90 K In/Si(111)-(8×''2'') surfaces. We also display the elastic peaks of these two surface in the inset, to compare their FWHM's. The energy of the incident

 

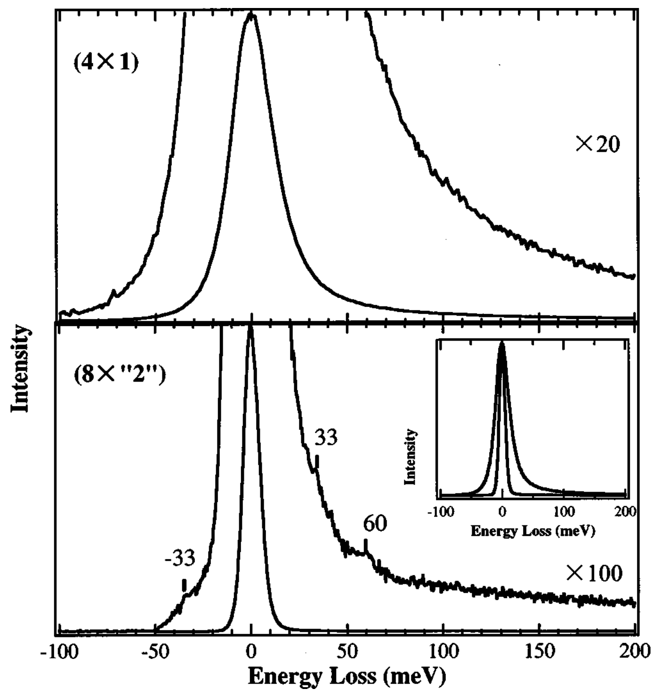


FIG. 1. HREELS spectra of the 300 K In/Si(111)-(4×1) surface and the 90 K In/Si(111)-(8×‘‘2’’) one. The energy of the incident electron is 5.0 eV, and the incident and scattered angles of electrons are both 60° from the surface normal direction for both surfaces. The inset displays the FWHM’s of the elastic peaks of the (4×1) and (8×‘‘2’’) surfaces.

electrons is 5.0 eV, and the incident and scattered angles of electrons are both 60° from the surface normal direction, i.e., the specular condition. The HREELS spectrum of the (4×1) surface shows a long Drude loss tail originated from the 1D metallic character of this surface, and no vibrational feature appears in the spectrum. This result is consistent with the previous HREELS result,[16] and those obtained by ARPES (Refs. 5 and 13) and IPES (Refs. 14 and 15) in which the surface is stated to have a 1D metallic character. After cooling down the sample at 90 K, the Drude tail becomes much smaller than that at 300 K but still observed. Moreover, two loss features are observed at 33 and 60 meV, and one gain feature at $-33$ meV. The presence of the Drude tail indicates that the In/Si(111)-(8×‘‘2’’) surface does not have a complete semiconducting character at 90 K. However, since the Drude tail is originated by the surface free carriers, the large decrease in the density of these carriers is expected by the considerable reduction of the tail’s intensity for the (8×‘‘2’’) surface. To determine the temperature dependence of the surface free carrier density, we have measured the temperature-dependent FWHM of the elastic peak because the elastic peak of the HREELS spectrum is known to broaden due to the presence of the Drude tail for 2D metallic surfaces, and therefore contain information of the surface free carrier density.[17,18] Figure 2 displays the temperature-dependent FWHM of the elastic peak. In Fig. 2, we clearly observe a discontinuity at 130 K. For the Si(111)-(7×7) surface that does not show any transition in the surface structure and has a metallic character at any temperature, the FWHM decreases almost linearly as the temperature goes down.[17,18] Hence, the discontinuity observed in

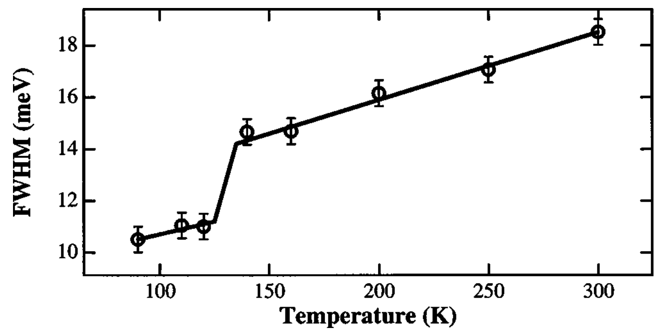


FIG. 2. Temperature-dependent FWHM of the In/Si(111)-(4×1) [In/Si(111)-(8×‘‘2’’)] surface. The energy of the incident electron is 5.0 eV, and the incident and scattered angles are both 60° from the surface normal direction.

Fig. 2 suggests a dramatic reduction of the surface free carrier density at 130 K. Taking into account the appearance of the ×8 spots at a temperature just below 130 K in LEED, we conclude that the (4×1)↔(8×‘‘2’’) transition is accompanied with a drastic change of surface free carrier density.

In order to consider the origins of the two loss features observed in the spectrum of the In/Si(111)-(8×‘‘2’’) surface, we have measured their dispersions. Figure 3 shows the dispersions of the two features measured along the $\overline{\Gamma}$-$\overline{X}$ direction of the (4×1) Brillouin zone. To acquire the dispersion of these two features, we have measured the HREELS spectra changing the incident and scattered angles of electrons, i.e., at offspecular conditions, and used a total energy range of 5.0–15.0 eV for the incident electron to collect the data. During the offspecular measurements, we periodically rotated the analyzer back to the specular direction and repeated the measurement. This procedure helped us to confirm the rotated angle, and to determine whether a certain surface had degraded over time. The inset in Fig. 3 displays the HREELS spectrum measured with an incident electron energy of 5.0 eV, and incident and scattered electron angles of 65° and 55° from the surface normal direction, respec-

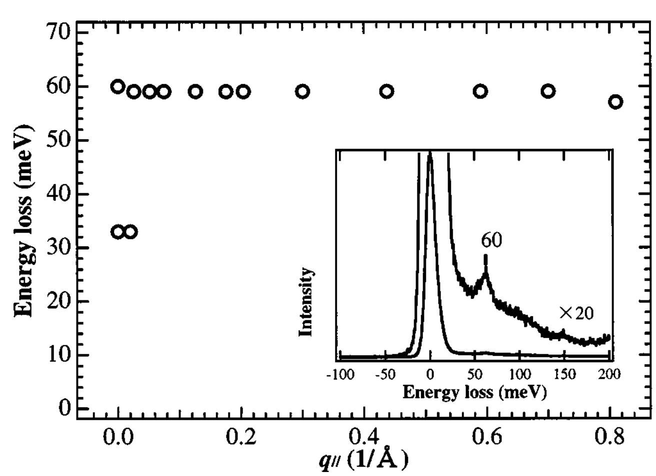


FIG. 3. Dispersion of the surface phonon of the In/Si(111)-(8×‘‘2’’) surface along the $\overline{\Gamma}$-$\overline{X}$ direction. The spectrum shown in the inset is measured with the incident electron energy of 5.0 eV, and incident and scattered electron angles of 65° and 55°, respectively. A total range of 5.0–15.0 eV for the incident electron energy was used to collect the data.

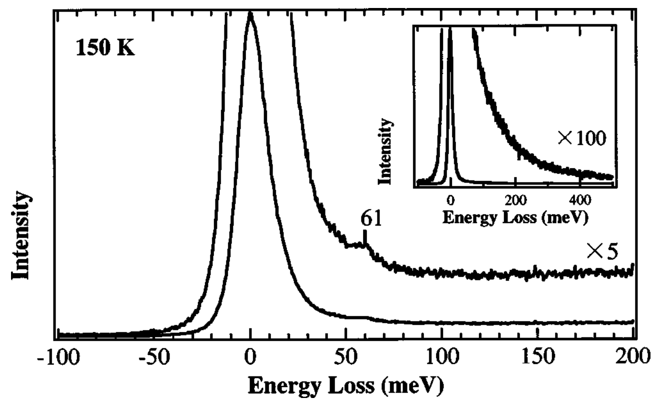


FIG. 4. HREELS spectrum taken for the In/Si(111)-(4×1) surface at 150 K. The energy of the incident electron is 5.0 eV. The incident electron angle of 65°, and scattered one of 55° from the surface normal direction. The inset shows the spectrum measured at the specular condition.

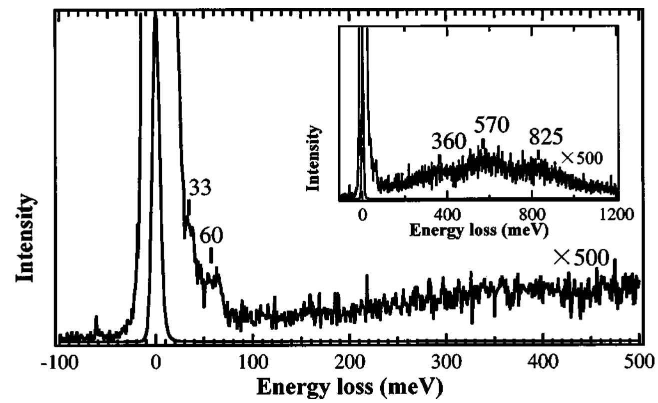


FIG. 5. Electronic excited states of the In/Si(111)-(8×''2'') surface. HREELS spectra are taken with an incident electron energy of 15.0 eV. The incident and scattered angles of electrons are the same as those of Fig 1. The inset shows the same spectrum but with a wide energy loss range.

tively. Among the two loss features, the intensity of the 33-meV feature decreases remarkably as $q_{//}$ varies from 0 like the intensity of the elastic peak. Thus we are not able to observe the 33-meV feature in the inset, and it appears only just around $q_{//}=0$ in Fig. 3. On the contrary, the 60-meV one is observed at any $q_{//}$. These behaviors indicate that the 33-meV feature is a dipole active mode and the 60-meV one is observed by impact scattering. Since the electronic excitations are observed by impact scattering, the dipole activity of the 33-meV feature suggests its origin as a vibrational excitation. For the 60-meV feature, though it is observed by impact scattering, we assign the origin to be also a vibrational excitation because the negligible dispersion of this mode is not able to be explained by the electronic excitation from the large dispersive In-derived occupied states of the In/Si(111)-(8×''2'') surface.[5] Taking into account the mass number of In, the energies of 33 and 60 meV are too large to attribute them as the Si-In vibrational modes, and we consider them to be surface phonon modes. The observation of a phonon mode by impact scattering suggests that it is a mode in which the dipole is parallel to the surface or a Raman-active mode, i.e., a dipole forbidden mode. Therefore, we conclude the 33-meV mode to be a dipole active optical phonon mode and the 60-meV one as a dipole forbidden optical phonon mode.

To obtain knowledge of the phonon modes of the In/Si(111)-(4×1) surface, we have measured the HREELS spectrum at 150 K, i.e., a temperature just above the transition temperature. We select a temperature of 150 K to except the influence of the (8×''2'') phase that results from the unevenness of the sample temperature at a lower temperature, and because the increase of surface free carrier density should enlarge the intensity of the Drude tail and therefore hide the vibrational features at a higher temperature. Figure 4 shows the HREELS spectrum of the 150 K In/Si(111)-(4×1) surface measured using an incident electron energy of 5.0 eV, and incident and scattered electron angles of 65° and 55° from the surface normal direction. The inset shows the spectrum measured at the specular condition. Comparing the spectrum shown in the inset of Fig. 4 with that in Fig. 1, we recognize the reduction of the tail's intensity that results from the decrease of the surface free carrier density. Although the intensity of the Drude tail becomes small, no feature appears in the spectrum measured at the specular condition. At the off-specular condition, we observe a small feature at 61 meV. Here, the combination of two effects has made the observation of a loss feature of the In/Si(111)-(4×1) surface possible. That is, because the Drude tail originated by the surface free carrier results from dipole scattering, both the reduction of the cross section of dipole scattering at an offspecular condition and that of the surface free carrier density at a low temperature, decrease the intensity of the Drude tail. The small feature at 61 meV has a negligible dispersion and observed at a large range of $q_{//}$ like the 60-meV mode observed for the In/Si(111)-(8×''2'') surface. Since the electronic excitation should not show such a small dispersion on a Si(111)-(4×1) surface, we consider this feature as a dipole forbidden optical surface phonon mode.

Finally, we mention the inconsistency between the electronic property of the (8×''2'') phase obtained in the present result and the recent ARPES study,[5] in which the (8×''2'') phase is reported to have a semiconducting character from the absence of the electronic state at the Fermi level. Three reasons are able to explain the inconsistency. First, the phase transition is not accompanied with a CDW as suggested in the previous report,[5] and the electronic state of the (8×''2'') phase just below the Fermi level is not detected in ARPES from its simply small cross section. Second, due to the instability of the 1D-CDW, the electronic states close to the Fermi level fluctuate and only a pseudo-CDW gap is in existence. The pseudo-CDW gap should have only a small density of states due to the partly metallic character that is caused by the fluctuation of the electronic states, and might not be detected in ARPES due to its small cross section. Third, since there are three metallic surface bands at 300 K, only one of them opens a CDW gap. In order to examine the third reason, we have measured the electronic excited states of the In/Si(111)-(8×''2'') surface. The HREELS spectra shown in Fig. 5 are obtained with an incident electron energy of 15.0 eV, and incident and scattered angles of 60° from the surface normal direction. The inset shows the same spectrum with a wider energy loss range. Since the cross section of dipole scattering decreases using an incident electron with a higher energy, the Drude tail becomes invisible in comparison with the spectrum shown in Fig. 1. Due to the disappearance of the Drude tail, we are able to discuss the electronic states around the Fermi level of the 90 K In/Si(111)-(8×''2'') surface. Moreover, the invisible Drude tail allows us to clearly observe the two loss features at 33 and 60 meV at the specular condition. For the electronic states, a very small but finite intensity is observed in the full range of the spectrum. The finite intensity indicates that the occupied electronic states and the unoccupied ones continue at the Fermi level, and therefore no purely gap exists at the Fermi level. The loss features observed in Fig. 5 hide the electronic information below 60 meV. However, because the CDW gap is estimated to be in the order of 80–160 meV in the ARPES measurement[19] and no feature indicating the presence of a gap is observed in this energy range, we consider that none of the three metallic surface bands open a gap. Therefore, the third reason described above is not appropriate to explain the inconsistency between our present result and the previous ARPES study.[5] Although we are not able to determine the proper origin, we propose two possibilities for the explanation of the inconsistency. First, there is no CDW at all. Second, if there is CDW, the (8×2) phase is partly metallic due to the instability of the 1D-CDW with a significant reduction of the surface free carrier density. The inset of Fig. 5 might be the interband transitions or surface plasmons, though we are not able to fix their origins within the present result.

In conclusion, we have investigated the electronic and vibrational properties of the In/Si(111)-(4×1) and -(8×''2'') surfaces using HREELS. The (4×1)↔(8×''2'') phase transition is accompanied by a drastic change of the surface free carrier density at 130 K. For the vibrational property, two surface phonon modes are observed at 33 and 60 meV in the low temperature (8×''2'') phase, and one mode at 61 meV in the high temperature (4×1) phase. The 33-meV mode is a dipole active mode, and the 60- and 61-meV ones are dipole forbidden optical phonon modes that are not dispersive.

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*Electronic address: sakamoto@surface.phys.tohoku.ac.jp

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