Shift of surface-plasmon energy across the phase transitions of silicon reconstructed structures for several crystal planes

T. Ichinokawa, N. Yamagami, H. Ampo, and A. Tamura

Department of Applied Physics, Waseda University, 3-4-1 Ohkubo,
Shinjuku-ku, Tokyo 160, Japan

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By electron-energy-loss spectroscopy, energy shifts of the surface plasmon were observed across the phase transitions for several reconstructed structures of silicon surfaces. The surface-plasmon energy shifts by 1.0–1.6 eV, depending on the phase transitions for Si(111) and Si(110) surfaces. A bulk plasmon and other peaks associated with the interband transitions between localized electronic states did not exhibit any notable change. For the Si(100) surface, no shift occurred, corresponding to the nonexistence of a phase transition. The energy shift of the surface plasmon was found to reflect the surface structure change. Two kinds of qualitative interpretation of this shift are presented. One is a change of dielectric function and the other is a change of the electronic density distribution at the surface due to the phase transition.

Silicon has various reconstructed surface structures depending on surface crystal planes.[1-3] It is well known that most of them change their structures with temperature variation,[4-6] impurity stabilization,[7-10] and quenching.[11] A great number of low-energy electron diffraction (LEED) analyses[12-17] were carried out to determine the atomic structures of the reconstructed surfaces. However, complete analyses of them have not yet been performed. As for the electronic structures of these surfaces, a number of investigations of photoelectron spectroscopy[18-21] and electron-loss spectroscopy[22-24] were carried out by many workers. Furthermore, the changes of work function and surface potential for an irreversible structural conversion from the Si(111)2×1 (cleaved surface) to 7×7 (annealed surface) were measured by Auer and Mönch.[25]

In the present experiment, changes of energy-loss (EL) spectra across the phase transitions were observed on the reconstructed structures of silicon surfaces for several planes.

Si(111), Si(110), and Si(100) surfaces were chemically etched and then annealed above 1200 °C at a pressure of 2×10^{-10} Torr to obtain the clean surfaces of the reconstructed structures. LEED patterns of them were observed by a four-grid optics with primary energies $E_p = 30\text{--}120$ eV. The EL spectra of relevant surfaces were measured by a single-pass cylindrical mirror analyzer in a negative second-derivative mode with the primary energy $E_p = 100$ eV. The surface temperature was controlled by electric current passing through the specimen with checking temperature indicated by a thermocouple. The thermocouple temperature had been calibrated by an optical pyrometer.

By the LEED optics, the following structural phase transitions were confirmed. For the Si(111) cleaved surface, two kinds of surface structure changes were observed. One is the conversion from 2×1 to 7×7 structure in a range between 200 °C and 400 °C and the other is the phase transition from 7×7 to 1×1 structure in a range between 840 and 860 °C. For the Si(110) annealed surface, a LEED pattern consisting of a set of rows parallel to the [1$\bar{1}$1] direction, referred to as a Si(17 15 1)2×1 structure by Olshanetsky and Shklyaev,[5] was observed. This structure is called a "16×2" structure in this paper. A phase transition from

the "16×2" to 1×1 structure was observed in a range between 700° and 740 °C. For the Si(100) surface, the 2×1 structure was stable and persisted in a range from room temperature to the melting point. These results agree with those reported in the previous papers except for a phase transition of the Si(110) surface. Olshanetsky and Shklyaev[5] and Jona[15] reported that the Si(110) surface has several reconstructed structures, e.g., 4×5, 2×1, 5×1, "initial," and "X" depending on the heat treatments. In the present experiment, however, these structures were not observed for the clean surface, but they appeared for the surfaces contaminated by nickel and then annealed at different temperatures. These results will be reported elsewhere.

After the confirmation of these structure changes by LEED patterns, the EL spectra were measured across the phase transitions. Figure 1 shows a change of the EL spectra with annealing temperature across the irreversible conversion from 2×1 to 7×7 structure for the Si(111) cleaved surface. The surface peak S_0 reported by Rowe and Ibach[22] is not observable because of an overlapping by an elastic peak. The conversion occurs in a range from 200° to 400 °C. A distinctive change is a gradual decrease of the surface-plasmon energy from 12.2 to 10.6 eV as the annealing temperature increases. The energy shift is irreversible corresponding to the structural conversion. The peak height of the surface plasmon decreases as the annealing temperature increases, but other peaks do not change appreciably across the conversion.

Figure 2 shows a similar result for the phase transition of the Si(111) annealed surface from 7×7 to 1×1 structure. A distinctive change is a gradual increase of the surface plasmon energy from 10.6 to 11.7 eV in a temperature range between 840 and 860 °C. The shift is reversible across the phase transition. The peak heights become lower on the whole with increasing temperature, but peak widths and peak positions except the surface plasmon do not change appreciably.

Figure 3 shows a variation of EL spectra across the phase transition from "16×2" to 1×1 structure for the Si(110) surface. The surface plasmon energy increases gradually from 10.1 to 11.2 eV in a range between 700 and 740 °C. The shift is reversible across the phase transition. Surface
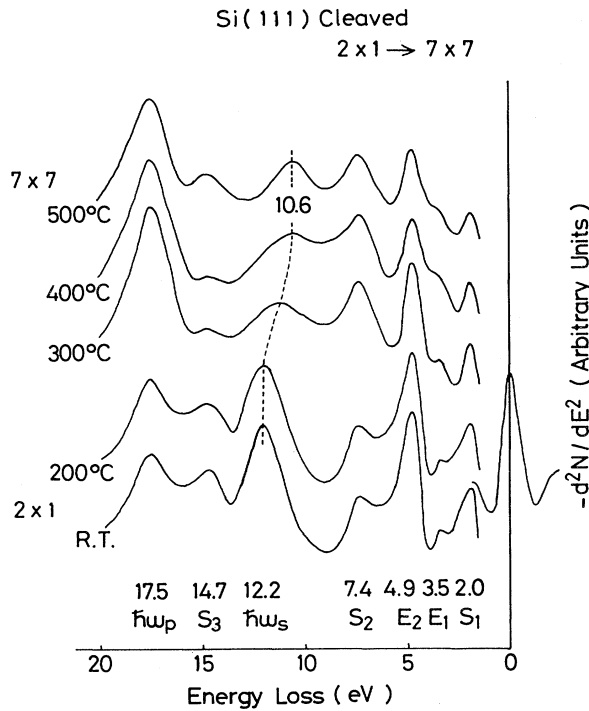
FIG. 1. Variation of EL spectra in a negative–second-derivative mode with the annealing temperature across the structural conversion from 2×1 to 7×7 for the Si(111) cleaved surface. $E_p = 100$ eV.

FIG. 3. Variation of EL spectra in a negative–second-derivative mode across the phase transition from "16×2" to 1×1 for the Si(110) surface. $E_p = 100$ eV.

peak heights of S_2 and S_3 are much weaker than those of other surfaces.

Figure 4 shows the EL spectra for the Si(100)2×1 surface. In this case, any peak shift is not observed from room temperature up to the melting point corresponding to the nonexistence of phase transition. The surface-plasmon peak is observed at 11.3 eV and an appreciable change is the lowering of the S_1 peak with increasing temperature.
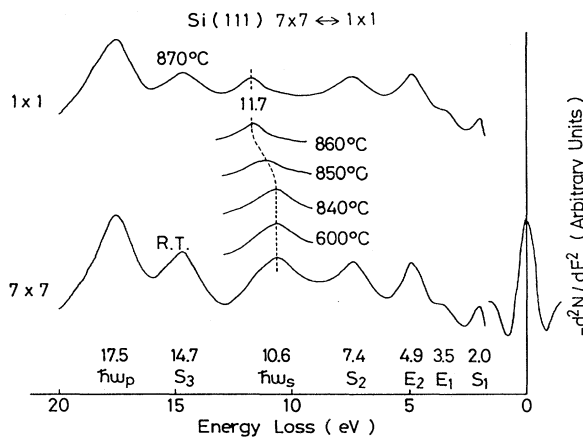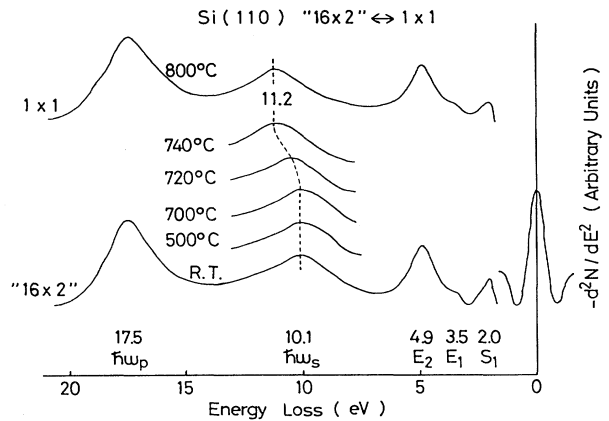
The data of the present experiment are summarized as follows: (1) The surface-plasmon energy is closely correlated with the surface crystal structure, whereas other peaks associated with the interband transitions and bulk plasmon excitation have no correlation with the phase transition. (2) The cleaved surface of the Si(111)2×1 has the maximum surface plasmon energy (12.2 eV) among the measured surfaces and it is close to a calculated value of $\hbar\omega_p/\sqrt{2}$ (12.4 eV). Other reconstructed surfaces have lower values than this. (3) As for the Si(111) surface, the surface plasmon energy for the 2×1 structure of the cleaved surface is the largest and that for the 7×7 structure is the smallest. The value for the 1×1 structure of a high-temperature phase is intermediate between them.

A number of physically different models have been proposed for the reconstruction at the silicon surfaces, e.g., surface defect models,[12,26] rehybridization of the bulk sp^3 bonds at the surface,[27,28] softening of surface phonons,[29–31] and charge-density waves.[32] Auer and Mönch[25] measured

FIG. 2. Variation of EL spectra in a negative–second-derivative mode across the phase transition from 7×7 to 1×1 for the Si(111) surface. $E_p = 100$ eV.
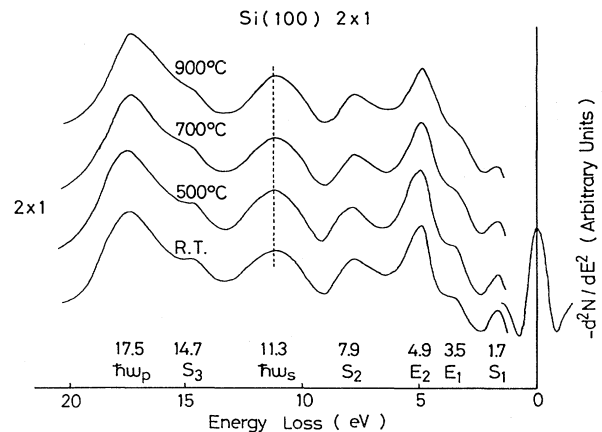
FIG. 4. EL spectra in a negative–second-derivative mode at several temperatures for the Si(100)2×1 surface. Appreciable energy shift of the surface plasmon is not observable corresponding to the nonexistence of the phase transition. $E_p = 100$ eV.

the work function for the structural conversion from the 2×1 to 7×7 surface and showed that the work function decreases by 0.25 eV across the conversion. This result indicates that surface dipoles induced at the 2×1 surface are larger than those at the 7×7 surface. Therefore, it can be seen that surface dipoles induced at the reconstructed surface play an important role in the reconstruction and in the energy shift of the surface plasmon.

To find a clue to elucidate the surface-plasmon shift across the phase transition, we propose following considerations. Present results show that energies of interband transitions do not change appreciably across the phase transitions. This fact means that the joint density of states remains almost the same after the phase transition. Since the EL spectrum is described by an imaginary part of minus inverse dielectric function, and furthermore since the dielectric function is expressed by a joint density of states and an oscillator strength, the shift of the surface-plasmon energy should be ascribed to the change of the oscillator strength with the phase transition. The oscillator strength is more sensitive to the variation of the wave functions than the joint density of states, because the oscillator strength is expressed by a matrix element of a momentum p, while the band structure depends implicitly on the electron wave functions. Thus, the shift of the surface-plasmon energy is attributable mainly to the change of the wave functions. Among the wave functions, those contributing to S_2 and S_3 transitions play an important role, because their excitation energies are close to the surface-plasmon energy. The change of the surface dipoles across the phase transition mentioned above is thought to be explained by the variations of these wave functions. Details of the claculations will be published elsewhere.

Another explanation of the surface-plasmon shift is probable by considering a change of the electron density with the surface structure change. Since the observed change of the peak is restricted to the surface plasmon, the cause of the shift should be considered as the collective nature of the phase transition. There are several theoretical considerations, as for the effect of the surface electron density distribution on the surface-plasmon energy. Eguiluz and Quinn[33] calculated an influence of the electron density profile normal to the surface on the surface-plasmon dispersion. They showed that for surfaces with an electronic density step of thickness a and electronic density n_1, the surface-plasmon dispersion curve is pushed below to a lower frequency than the value (ω_s) of the regular surface plasmon for an abrupt surface $(a=0)$. On the other hand, Forstmann and Stenschke[34] calculated a surface-plasmon dispersion for the aluminum surface covered with a thin selvedge having a different electron density and a different thickness. The result showed that the dispersion curve becomes lower with decreasing electron density and increasing thickness of the selvedge. These aspects suggest that the local variation of the charge distribution at the surface affects the surface-plasmon energy. Further calculations adaptable to the reconstructed surfaces of semiconductors are necessary for quantitative explanation.

Successive experiments are in progress to elucidate the changes of work function for various phase transitions measured in this paper. Measurements of the energy shift of the surface plasmon for various kinds of semiconductors of III-V compounds are also proceeding.

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