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Temperature-induced metallization of the Si(100) surface

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We provide evidence for the temperature-induced metallization (TIM) of Si(100) surface. A TIM takes place at about 600 K without any change in surface periodicity. Contrary to previous suggestions, photoemission spectroscopy (PES) reveals that the TIM is not related to the (instantaneous) symmetrization of asymmetric dimers. We suggest that Si adatoms produced at elevated temperatures play a role of donor, giving rise to the TIM.

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Element and compound semiconductor surfaces exhibit a temperature-induced metallization (TIM) upon raising temperature. Much effort has been devoted to revealing the physical origin of the onset of the TIM up to date, especially for the (100) plane. In their combined angle-resolved PES (ARPES) and low-energy electron diffraction (LEED) studies of Ge(100) surface, Kevan and Stoffel[1,2] observed a metallic state above 130 K whose intensity increases as temperature rises. At the same time, a c(4×2) LEED pattern was observed to convert to a 2×1. They suggested that the TIM is related to defects, induced by a flipping motion of dimers, on the disordered-c(4×2) reconstruction.[1,2] A similar increase in metallicity with temperature (up to about 900 K) on Ge(100) was reported in a recent study.[3] The structural phase transition (PT) from a c(4×2) to a 2×1 was also accompanied by the TIM on β-SiC(100) surface.[4] Aristov *et al.* observed a reversible PT from an insulating c(4×2) at room temperature (RT) to a metallic 2×1 at elevated temperature by using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and synchrotron radiation PES (SRPES) measurements. They claimed that two symmetric Si dimers with different heights than each other in a c(4×2) unit cell change to Si dimers with the same height.[4] The structural transformation was attributed to the TIM of β-SiC(100),[4] which was later challenged by Duda *et al.*[5] On the other hand, Si(100) surface, which is the counterpart of Ge(100), exhibits the TIM above 900 K with keeping its 2×1 symmetry.[6,7] In a recent PES study,[8] the intensity at the Fermi level (E_f), which is a measure of the metallic character of the surface, was observed to increase linearly up to about 1100 K. Gavioli *et al.* proposed using high resolution electron energy loss spectroscopy (HREELS) and ultraviolet photoemission spectroscopy (UPS) that an instantaneous symmetric dimer configuration due to fast dimer-flipping is responsible for the TIM of Si(100) surface.[6,7] Up to now, the TIM has been attributed to the local structural transformation or the motion of dimers. However, the reason why semiconductor surfaces start to be metallic at elevated temperatures is not well understood in terms of a structural change of Si dimers. We introduce a concept in this work to account for the TIM.

The Si(100) surface has a relatively simple atomic structure. Its atomic and electronic structure at (or below) RT is now well-established through a number of studies using various surface-sensitive techniques, whereas a few investigations have been performed at an elevated temperature. Of many semiconductor surfaces, Si(100) is used for most of the device fabrication. Some principal processings, such as the formation of high-quality silicon oxide and homoepitaxial growth, are performed at an elevated temperature above RT. Therefore, the study of Si(100) at an elevated temperature is of both scientific and technological importance. It shows peculiar structural and electronic properties depending on substrate temperature. A semiconducting c(4×2) (or 2×2) phase, where asymmetric dimers (Jahn-Teller distortion) are the main building blocks, transforms reversibly to a semiconducting 2×1 at the critical temperature of about 200 K.[9,10] The 2×1 surface has been reported to undergo a TIM above 900 K (Refs. 6 and 7) and then an incomplete melting transition at about 1400 K.[11] Here, we focus on the TIM, whose origin is still an open question among the PTs on Si(100) surface.

In this Rapid Communication, we report experimental evidence for the TIM. The TIM was observed at about 600 K (below than before) without any change in LEED pattern. Core-level spectra show that the number of up-dimer atoms is conserved at temperatures ranged from RT to 1100 K. In electronic band structures at elevated temperatures, the metallic state is visible at Γ and J', which correspond to two minimum points of the empty surface state of an asymmetric dimer model. These results rule out the possibility of the (instantaneous) symmetrization of asymmetric dimers as the cause of the TIM. Si adatoms produced at elevated temperatures are suggested to play a role of donor, filling the empty surface state of asymmetric dimer model.

The experiment was performed in ultrahigh vacuum chambers equipped with LEED and PES at the beam line 2B1 (Ref. 12) and 3B1 of Pohang Light Source in Korea. A direct current regulated power supply in square wave ranging from 30 to 120 Hz was used to measure the PES spectra at temperatures above RT, as in other works.[6–8] We confirmed that the same spectra were obtained at RT irrespective of the connection to the power supply. When we used SR, the pho-

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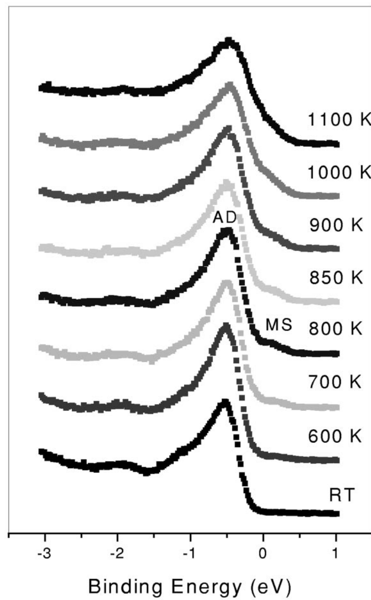

FIG. 1. Angle-integrated valence-band spectra from the Si(100)2×1 surface depending on substrate temperature (RT-1100 K) at normal emission.

ton source was always linearly polarized. The binding energy (BE) is referred to E_f, which is determined by measuring E_f of Ta in electrical contact to the sample. Other experimental details are described elsewhere.[13]

Figure 1 shows angle-integrated valence-band spectra from the Si(100)2×1 surface depending on substrate temperature (RT-1100 K) at normal emission. The incident photon energy and the acceptance solid angle of the spectrometer were 21.2 eV and about 11.4°, respectively. The angle between the incident photon beam and the surface normal (hereafter incident angle) was about 45°. A surface state (AD) originated from dangling bonds of up-dimer atoms is visible at about 0.53 eV at RT. There exists no state crossing E_f. This indicates that the Si(100) surface is semiconducting at RT for low-doped samples. The widths of valence-band features become broad due to phonon broadening upon raising the temperature. A weak shoulder, denoted by MS, appears at about 600 K and then grows up with increasing temperature, while the BE and the intensity of AD do not change regardless of temperature. The metallic feature in PES at elevated temperatures was previously reported,[6] but there are some discrepancies between previous and present experimental results. When compared to previous reports[6–8] the onset temperature of the TIM is quite lower and the state near E_f is distinguishable with AD, which allows us to characterize MS. One feature is that MS is more reactive than AD for the adsorption of oxygen. We could measure the band structure of MS as well as other surface and bulk states.

It has been suggested that the frequency of the dimer flipping motion is so high that the average time spent by the instantaneous symmetric dimers affects the surface electronic structure.[6,7] According to the explanation, the number of the asymmetric dimer should reduce above the critical temperature, at which the TIM takes place. In order to deduce the

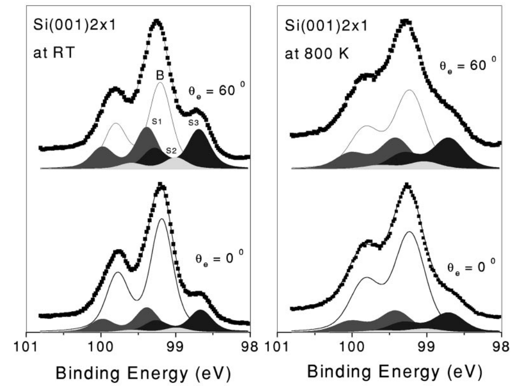

FIG. 2. Fitting results of the surface-sensitive Si 2p core-level spectra from the Si(100)2×1 surface at room temperature (a) and 800 K (b) (emission angle = 0, 60°).

number of surface atoms before and after the transition, Si 2p core-level spectra were measured at several substrate temperatures using a surface-sensitive photon energy (132 eV). The total-energy resolution at the photon energy of 132 eV was about 0.15 eV. The Si 2p core-level spectra at RT in Fig. 2(a) are well fitted with one bulk and three surface components. The BE shifts of S1-S3 components at RT were found to be about 0.20, −0.20, and −0.52 eV, respectively, irrespective of the emission angle. Three surface components (S1-S3) are known to be originated from second layer atoms, impurities or deep layers atoms, and up-dimer atoms, respectively.[14,15] It is difficult to resolve the down-dimer atom component at just about 60 meV higher BE than the bulk component under the measurement at RT. The spectra at 800 K were fitted with the same fit parameters, except for Gaussian width, which were 0.25 eV at RT and 0.38 eV at 800 K, respectively. Fit parameters at RT and 800 K are summarized in Table I, where the relative intensity is normalized to the total intensity and BE shift is relative to that of the bulk component. The BE shifts are independent of substrate temperature, which indicates that the amount of charge transfer from the down-dimers to the up-dimers is the same regardless of temperature. The asymmetric dimers therefore seem to fluctuate between up and down positions with the same tilting angle irrespective of substrate temperature despite the flipping is more frequent at higher temperatures.[16] The intensity of each component (from Fig. 2) and the relative intensity of MS to AD (from Fig. 1), which represents the metallic character of the surface, are depicted as a function of substrate temperature in Fig. 3. The metallicity becomes stronger but the relative intensity of S3 does not change with increasing temperature. This implies that the number of the asymmetric dimers is conserved and the average time spent by instantaneous symmetric dimers does not change at temperatures ranged from RT to 1100 K.

ARPES using SR (BL 3B1) and He I reveals distinctive characters of MS. The state tends to become strong as the photon energy increases from 11 eV to 22 eV. The relative intensity of MS to AD at normal emission decreases at lower incident angle of about 25° when compared to $\theta_i = 45, 65°$. ARPES spectra under the condition of hv = 21.2 eV (He I)

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TABLE I. Relative binding energy and intensity of each component for the Si 2p core level spectra from the Si(100)2×1 surfaces at RT and 800 K. The full width at half maximum for the Lorentzian fit function, branching ratio, and spin-orbit splitting of each component are 0.18 eV, 0.5, and 0.59 eV, respectively. The values in parentheses are for the spectra at 60°.

Component	BE shift	Intensity	BE shift	Intensity
RT			800 K	
B	0	0.689 (0.482)	0	0.692 (0.530)
S1	0.20 (0.18)	0.149 (0.234)	0.19 (0.19)	0.149 (0.210)
S2	−0.20 (−0.21)	0.028 (0.064)	−0.20 (−0.20)	0.025 (0.051)
S3	−0.52 (−0.52)	0.134 (0.220)	−0.52 (−0.52)	0.134 (0.209)

and $\theta_i=45°$ were measured from the Si(100) surface at RT and 900 K along the [010] direction, which is common to two different domains. For the surface at 900 K, MS is clearly visible around normal emission and disappears with increasing emission angle. The state starts to be found weakly around $\theta_e=34°$ and then fades away at higher angles. The resultant band structure at RT and 900 K are mapped in Fig. 4. Band structure at 900 K is almost similar to that at RT, which is consistent with the maintaining 2 ×1 LEED pattern at this temperature, except for the state near E_f. The dispersion does not accord to the symmetric dimer model, in which the state from dangling bond is higher in energy at Γ point.[17] This also excluded the possibility that the TIM is originated from the instantaneous symmetrization of asymmetric Si dimers. Because MS (denoted by dots) at 900 K is visible at only high symmetry points in the 2×1 surface Brillouin zone, we can also rule out the possibility of defects at the surface. Present PES results are similar to those in a previous work in that the state A in Ref. 18 remains at elevated temperature. However, there is a difference that the state B in Ref. 18 is still found up to 1100 K. We compare our experimental results with a band calculation (solid lines) for the asymmetric dimer model[19] along this direction. AD below E_f is in good agreement with the calculation and Γ and J' points, at which MS is found, correspond to two minimum points (denoted by arrows) in energy of the empty state.[19] We observed MS at only Γ point below 700 K, indicating the minimum of the empty state is located at this point. This result strongly supports previous EELS results.[20] The empty surface state is occupied little by little from the bottom as the temperature increases.

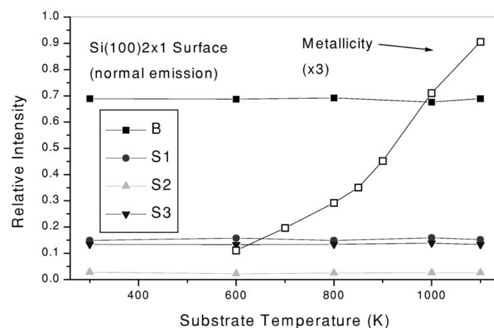

FIG. 3. Intensity of each component in Fig. 2 and the metallicity derived from the relative intensity of MS to AD in Fig. 1 as a function of substrate temperature.

A similar band structure at elevated temperature was also observed for the Ge(100)2×1 surface. When compared to the Si(100), MS is relatively weak at J' point, which can explain the reason why MS is visible at only Γ point in previous reports.[1,2] It should be noted that the TIM occurs without any change in LEED pattern above RT. The simultaneous structural transformation in previous reports would

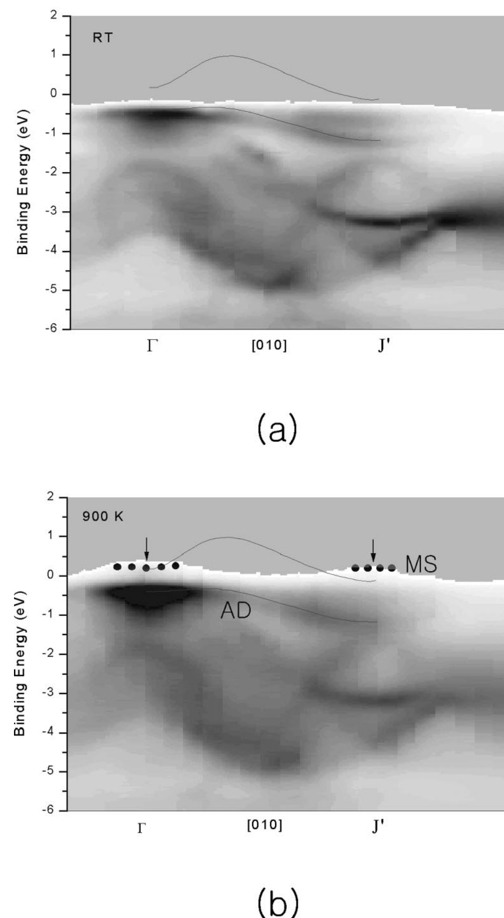

FIG. 4. Experimental band structure for the 2×1 surface at room temperature (a) and 900 K (b) along the [010] direction taken with He I (hν=21.2 eV). The notations at bottom indicate the symmetry points of the 2×1 surface Brillouin zones. The dots and solid lines stand for experimental and theoretical band dispersions, respectively, and the dark background represents high photoemission intensity.

be accidental and the TIM is likely to depend on sample conditions.

Where do the electrons occupying the empty state come from at elevated temperatures? Thermal excitation can be a possible source but the substrate temperatures in this work are too low to excite electrons in valence bands thermally. Furthermore, AD still remains after the complete disappearance of MS upon oxidation, which strongly rules out the possibility. Therefore, we consider that a donor giving its electron to the empty state is produced at an elevated temperature and its population increases upon raising temperature. As observed for highly n-doped Si(100) surface,[21,22] the empty state can be occupied by the electrons of dopants. However, we observed the TIM for lightly p-doped surface as well as the lightly n-doped one and could not find any trace of the correlation between dopants and the TIM. By comparing our PES results with previous STM or reflection electron microscopy (REM) data at elevated temperatures, we find a clue to the electron source. Microscopy images show that Si adatoms are produced near the onset temperature of the TIM.[23] Si adatoms behave as if they possess positive charges.[24] These results suggest that Si adatoms play a role of donor, filling the empty state. The increase in metallicity upon raising the temperature can be understood as the growth of its population. Si adatoms should have an effect on the electronic structure of Si(111) surface due to its positive effective charge.[25] Hence, we measured angle-resolved valence-band spectra from a Si(111)7$\times$7 surface with increasing temperature. As temperature rises (up to about 1000 K), the metallicity of the Si(111) surface grows up without any change in LEED pattern. Although the TIM does not take place on the Si(111) because it is already metallic at RT, the increase in metallicity is believed to be comparable with the TIM of the Si(100) surface. Kandel and Kaxiras have shown by using first-principle calculations that the adatoms hopping between different sites in a representative configuration can have positive effective charges on Si(111) surface.[26] Despite there is no calculation on Si(100) surface, the resemblance between both surfaces supports our interpretation that Si adatoms are responsible for the TIM of the Si(100) surface.

In summary, the TIM of Si(100) surface has been investigated. Core-level spectra and electronic band structure at elevated temperatures reveal that the TIM is not related to any structural change of asymmetric dimers. We suggest that Si adatoms produced at elevated temperatures give rise to the TIM.

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