Carbon bonding site in Si(001)$c(4\times4)$ prepared by hydrocarbon decomposition

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We have reexamined the structural models of Si(001)$c(4\times4)$ induced by carbon, which is important for the initial C incorporation, using high-resolution photoemission. Through a proper thermal treatment after the thermal decomposition of the typical carrier gas molecules of C_2H_2 and C_2H_4, a well-ordered $c(4\times4)$ surface was reproducibly prepared, which exhibits only a single well defined C 1*s* component with a binding energy of 282.8 eV. This indicates that the $c(4\times4)$ surface is made of a unique C bonding configuration in contrast to some structure models. From the angular variation of the C 1*s* photoemission intensity, we confirm that the unique C bonding site corresponds to the incorporation into the subsurface layers rather than a metastable surface adsorption.

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An investigation of the initial reaction of carbon with silicon surfaces provides a fundamental understanding of the heteroepitaxy of the important materials such as diamond[1,2] and silicon carbide[3] and of the formation of $Si_{1-x}C_x$ and $Si_{1-x-y}Ge_xC_y$ alloy films for noble electronic devices.[4]

The Si–C complexes on Si surfaces have been prepared by using various C sources[5] but typically by thermal decomposition of unsaturated hydrocarbon molecules. In that case, the initial surface reaction proceeds roughly through three different steps: (i) the initial adsorption of C sources on Si surfaces (molecular adsorption), (ii) thermal decomposition into atomic C (atomic adsorption), and (iii) the incorporation of C into the Si layers (surface alloying). Although the molecular adsorption stage of the hydrocarbon molecules is well characterized,[6] the atomistic details of the following steps are still unclear.[7,8] Especially, the atomic adsorption structure of C or CH_x reaction intermediates on the surface and that of the subsurface incorporated C atoms are not yet determined.

An issue of particular interest related to the C atomic adsorption and incorporation is the formation of the $c(4\times4)$ phase on the surface. The $c(4\times4)$ phase is universally observed for intentional or even unintentional C doses on Si(001)[5–15] and is the unique ordered phase found during C adsorption or incorporation process. That is, this phase is thought to be an important intermediate stage before the formation of a stoichiometric Si–C network, for example, a precursor to the formation of initial SiC islands/layers in SiC heteroepitaxy on Si(001). However, in spite of such importance and vigorous investigations so far,[5–15] the atomic and chemical structure of the $c(4\times4)$ surface is not clearly determined yet. In more detail, it has been believed that the $c(4\times4)$ surface has both surface and subsurface C species as mainly suggested by C 1*s* photoemission results. The structures and chemical states of such surface or subsurface species have been uncertain.

In this report, based on high-resolution C 1*s* photoemission using synchrotron radiation and careful surface preparation, we clearly show that the $c(4\times4)$ surface contains only a single well-defined C bonding configuration, which corresponds to the subsurface C incorporation. This result restricts the possible structure models significantly and, indeed, denies most of the available structure models containing surface C species as their building block.

We measured core-level photoemission spectra on a soft x-ray beam line (BL-8A1) connected to an undulator of the synchrotron radiation source at the Pohang Accelerator Laboratory (PAL) in Korea.[16] The endstation is equipped with a high performance electron analyzer (SCIENTA-2002, Gamma Data, Sweden).[17] Before exposing to C_2H_2 or C_2H_4, a well-ordered Si(001)2×1 low-energy-electron diffraction (LEED) pattern was observed after a typical cleaning procedure by heating.[18,19] The $c(4\times4)$ phase was prepared by back-filling the chamber with C_2H_2 (C_2H_4) and with a Si(001)2×1 substrate held at 600 °C (700 °C).[18,19] We optimized the gas doses to about 8 (200) L for C_2H_2 (C_2H_4) by maximizing the $c(4\times4)$ LEED spot intensities and minimizing the backgrounds simultaneously. The large difference in the optimal doses between C_2H_2 and C_2H_4 is due to the inherent difference in the reactivity and thus in the sticking coefficient on the surface of these molecules.[18,19] The gas sources were carefully purified by cycles of freezing and pumping. All C 1*s* (Si 2*p*) spectra were obtained at room temperature (RT) using a photon energy of 330 (135) eV. The overall instrumental energy resolution was better than 150 meV and the angular acceptance was ±8°. The C 1*s* photoemission spectra were analyzed by a standard nonlinear-least-squares fitting procedure using Voigt functions with Lorenzian and Gaussian widths of 0.12 and 0.35 eV, respectively.[6]

Figure 1 shows the C 1*s* spectra of the Si(001)$c(4\times4)$ surface prepared by decomposing C_2H_2 (C_2H_4) at 600 (700) °C. These decomposition temperatures are typical in most of the previous works,[12,13,15] which will be explained in more detail below. The C 1*s* spectra from the as-prepared surfaces without any post-annealing [Figs. 1(a) and 1(c)] are composed of two components: the major and dominant one with a binding energy of 282.80 eV (C_1) and the minor of 283.30 eV (C_2). The C 1*s* spectra of the $c(4\times4)$ surface in the previous reports[13,15] commonly involved two components; the major one is consistent with C_1 but a minor one (denoted CP_1 hereafter) has a higher binding energy by 1.0–1.5 eV than C_1, which is not matched with the present

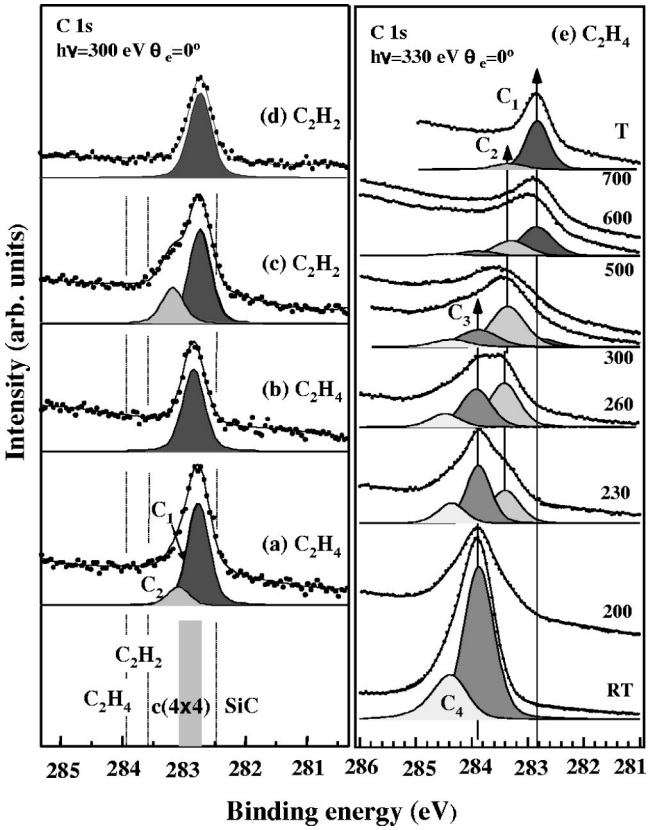

FIG. 1. C 1*s* photoemission spectra of the C-induced $c(4\times4)$ phase on Si(001) taken with a photon energy ($h\nu$) of 330 eV along the emission angle $\theta_e=0°$ (the surface normal). The surfaces of (a) and (c) were prepared by exposing C_2H_4 (200 L) at 700 °C and C_2H_2 (8 L) at 600 °C, respectively. Post-annealing of the surfaces for (a) and (c) at 700 °C for 2 min changes the spectra into (b) and (d), respectively. For comparison, the C 1*s* binding energies of C_2H_2 and C_2H_4 molecules or SiC on Si(100) are indicated by the vertical lines. (e) Similar C 1*s* spectra for a series of post-annealings of C_2H_4 dosed on Si(100) at RT.

spectra. Considering the significantly improved energy resolution of the present study, we guess that the C_2 component was not resolved between the broad components of CP_1 and C_2 in the previous studies; the apparent full-widths-at-half maximum of the previous results were 0.9–1.5 eV in contrast with the present value of ~0.5 eV.[13,15]

So as to understand the discrepancy on CP_1, we first exposed additional C_2H_2 (C_2H_4) molecules on $c(4\times4)$ at RT. The subsequent C 1*s* photoemission measurements clearly showed an extra component, at the same binding energy with CP_1 of the previous reports. The binding energy of CP_1 is further consistent with that of C 1*s* for C_2H_2 (C_2H_4) *molecules chemisorbed* on the clean Si(001)2×1 surface[6] [see also Fig. 1(e)]. This indicates clearly that the remnants of the C_2H_2 (C_2H_4) gas could chemisorb without dissociation rather rapidly after preparing the $c(4\times4)$ surface probably during the cool down of the surface.

Then, in order to investigate the microscopic origins of the observed components, C_1 and C_2, we systematically analyzed the C 1*s* spectra for the decomposition of the molecules at different temperatures. Figure 1(e) shows, for example, the thermal decomposition of C_2H_4 molecules—the molecules were dosed at RT and then annealed at the specified temperatures in series. As reported previously, the C 1*s* spectrum for RT adsorption is composed of the main component C_3 at 283.9 eV and its vibrational satellite C_4 (due to the C–H stretching mode) at 284.4 eV.[20]

The thermal energy provided reduces the intensities of C_3 and C_4 producing a component at 283.3 eV from already 200 °C and subsequently another one at 282.8 eV from 300 °C. The two latter components appearing after annealing can be identified as C_2 and C_1 observed for the $c(4\times4)$ surface from their binding energies. The intensity of C_2 gradually decreases for further annealing and becomes marginal at 700 °C, which is the temperature to form the $c(4\times4)$ phase. The previous calculations and experiments have established that the C_1 component at 282.8 eV corresponds to the atomic C species bonded to four Si nearest neighbors ($C-Si_4$).[8–13,15] Then the intermediate component C_2 can straightforwardly be related to partially decomposed CH_x species or atomic C species with unsaturated bond(s) on the surface.[6,21] Although the detailed atomistic origin of the C_2 component is not clear, this component is obviously related to the transient and metastable bond configurations toward the more stable $C-Si_4$ sites. That is, in relation to the C 1*s* components of the $c(4\times4)$ surface [Figs. 1(a) and 1(b)], it is likely that the C_2 component is not a stable constituent of the surface but a kinetically trapped transient species.

Inspired by the above results, for the purpose of confirming the transient origin of the carbon species related to the C_2 component, we tried further annealing of the $c(4\times4)$ surface at the same temperature as the initial gas decomposition. As shown in Figs. 1(b) and 1(d), a short post annealing (of an order of 1–2 min) is enough to get rid of C_2 completely, leaving well-defined C 1*s* spectra with a single component C_1. This indicates that the C species (site) represented by C_2 converts into the C_1 species, since (i) no desorption of C is reported in this temperature range and (ii) the conversion from C_2 to C_1 occurs even from a temperature as low as 400 °C. The $c(4\times4)$ LEED spots do not show any substantial change during the post annealing while the LEED background intensity tends to diminish slightly. We thus conclude *that the stable carbon atoms involved in the* $c(4\times4)$ *surface have a unique chemical bonding configuration*, which is the fully saturated C atoms with four nearest neighbor Si atoms ($C-Si_4$).

As mentioned above, there is a consensus on the fact that the major C 1*s* component C_1 corresponds to the atomic C species saturated chemically with four Si nearest neighbors.[8–13,15] Through photoelectron diffraction measurement, it was also indicated that the major C species are incorporated into the subsurface substitutional site.[10–12] We also checked the subsurface incorporation of the C atoms related to the present C_1 component through the angle-dependence of the C_1 photoemission intensity as shown in Fig. 2. In this measurement, the polar angle (θ_e) of the emitted photoelectrons was varied toward the [110] axis from the surface normal ([001]) [Fig. 2(b)]. The intensity of the C 1*s* photoelectrons is strongly enhanced around $\theta_e=45-50°$ for both surfaces made from either hydrocarbon molecules.

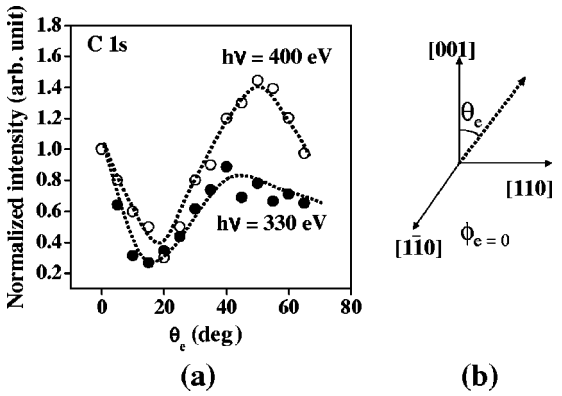

FIG. 2. (a) Polar-angle (θ_e) dependence of C 1*s* photoelectron intensity (the C_1 component in Fig. 1) of Si(001)$c(4\times4)$ prepared by C_2H_2 taken with photon energies ($h\nu$) of 330 and 400 eV. The emission angle is varied towards the [110] axis around $[1\bar{1}0]$ as illustrated in (b).

Since the intensity anisotropy is further enhanced at a higher photoelectron kinetic energy as excited by a higher energy photon beam, this is identified as the forward focusing of the photoelectrons. The forward focusing of photoelectrons indicates the presence of the scatterer atoms along that direction and, thus, shows that the corresponding C atoms are located within a well-defined crystallographic site. Such a site should be within the *subsurface* layer because the forward focusing angle is as high as 45°. This is fully consistent with previous photoelectron diffraction experiments.[10–12] However, it should be mentioned that the present results still cannot exclude the coexistence of some surface C atoms if it has a similar chemical configuration of $C-Si_4$ with a similar C 1*s* binding energy. This is because the surface C species would have no significant forward focusing except for a very grazing emission angle, which is not accessible in the present measurement geometry. Indeed, the previous x-ray photoelectron diffraction analysis with unresolved C 1*s* spectra included a large fraction of surface C species.[11,12] However, the highly coordinated $C-Si_4$ configuration cannot easily be achieved in the surface (topmost) layer as discussed further below for the structure models.

There have been various structure models for the $c(4\times4)$ phase up to now without any conclusive experimental evidence to support a specific model. The earlier structure models even did not consider the presence of the C atoms.[22–24] At first, the present C 1*s* observation rules out one of the most sophisticated $c(4\times4)$ structure model proposed through STM image analysis and *ab initio* calculations. Within this model shown in Fig. 3(a), carbon atoms substitute the first and second layer Si atoms forming a cluster of six carbon atoms (one C–C dimer and four back-bonded C atoms). The C–C dimer atoms in the topmost layer and the back-bonded C atoms in the second layer have distinctively different chemical bonding configurations of three C nearest neighbors with one dangling bond and three Si plus one C nearest neighbors, respectively. These two different chemical bonding configurations would definitely result in different C 1*s* binding energies; considering the large C 1*s* binding energy difference between diamond and cubic SiC of ~4 eV,[25] the replacement of one C–Si bond with a C–C bond could yield a C 1*s* energy shift of 0.5–1.5 eV.

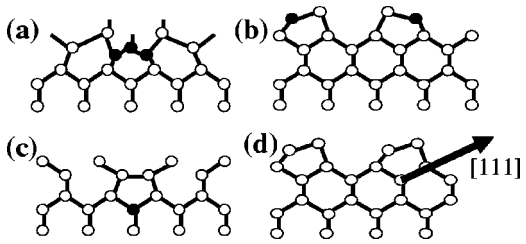

FIG. 3. Atomic structure models (side view) proposed previouly by (a) Leifeld *et al.*, (b) Simon *et al.*, and (c) Norenberg *et al.* The open and solid circles denote Si and C atoms, respectively. (d) The structure model of the clean Si(001)2×1 surface for comparison. The arrows indicate the forward scattering (focusing) direction from a subsurface substitutional site.

The alternative structure models have single C sites in the first layer or in the fourth layer as drawn schematically in Figs. 3(b) and 3(c).[9,13] Simon *et al.* introduced a mixed Si–C dimer on the first layer as the basic building block with some extra C distributed randomly under the second layer [Fig. 3(b)]. This is in contradiction to the present results indicating that the major, and plausibly the only C spieces is incorporated into the subsurface layers.[26] Furthermore, the previous *ab initio* calculations[7,8] support that carbon atoms favor to be incorporated into the third layer, although these calculations did not include the $c(4\times4)$ surface structure. Such a "deep" carbon incorporation was also confirmed for a lower coverage structure on Si(001) in a very recent STM and theoretical study.[27] The remaining structure model shown in Fig. 3(c) is consistent with the unique subsurface incorporation of C atoms. However, this model did not elaborate the surface reconstruction, which is believed to be significant from the STM studies.[14] This is further supported by the Si 2*p* spectra shown in Figs. 4, where the surface component (at ~0.5 eV in the figure) due to the asymmetric dimers on the clean Si(001) surface almost disappears on the $c(4\times4)$ surface. That is, we suggest that the structure model for the $c(4\times4)$ surface has to feature (i) a unique C site in the subsurface layers with $C-Si_4$ bonding and (ii) the reconstruction of the surface Si atoms being compatible with the characteristic STM image.

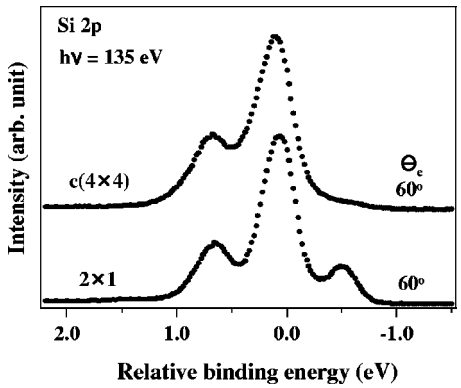

FIG. 4. Si 2*p* photoemission spectra of the C-induced $c(4\times4)$ phase on Si(001) taken with a photon energy ($h\nu$) of 135 eV along the emission angle $\theta_e=60°$ for extreme surface sensitivity.

In summary, we showed through high-resolution C 1*s* and Si 2*p* photoemission study using synchrotron radiation that the C atoms of the C-induced Si(001)$c(4\times4)$ surface are stabilized at a unique chemical configuration. The angular variation of C 1*s* photoelectron intensity indicates further that the unique C site corresponds to the subsurface incorporation. We note that a careful treatment is required to prepare a uniform $c(4\times4)$ phase because of the transient C bonding configurations and the narrow range of the annealing temperature needed. This result rules out most of the previous structure models for the $c(4\times4)$ phase. More extensive modeling and experimental studies are thus required for the $c(4\times4)$ surface structure.

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