

Thermal decomposition of ethylene on Si(111): formation of the Si(111) $\sqrt{3} \times \sqrt{3}$:carbon structure

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Abstract

Adsorption and thermal decomposition of ethylene on Si(111) have been observed by photoelectron spectroscopy. The evolution of the C 1s and Si 2p core levels upon the adsorption of the ethylene and the formation of C-incorporated surfaces by thermal annealing is analyzed, from which the unique chemical and structural properties of $\sqrt{3} \times \sqrt{3}$ reconstructed phase can be derived. We also discuss the coverage of the C atoms involved and their position on the $\sqrt{3} \times \sqrt{3}$ surface in terms of a structural model.

Keywords: Carbon; Silicon; Synchrotron radiation photoelectron spectroscopy; Surface chemical reaction, Ethylene

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1. Introduction

The incorporation of carbon atoms into silicon surfaces has shown many exotic results such as the ordering of missing rows on Si(100) surface [1] and intermediate surface reconstructions on the way to the formation of silicon carbide (SiC) compounds [2] which are very important materials in semiconductor application. For example, the $c(4\times 4)$ surface made by the C incorporation into a Si(100) consists of 1/8 monolayer (ML) of subsurface C atoms and rearranged Si dimers on top, leading to a $\sqrt{3}\times\sqrt{3}$ -layer like structure. Likewise, the $\sqrt{3}\times\sqrt{3}$ phase has been made by acetylene decomposition at the substrate temperature of 600 °C and studied by scanning tunneling microscopy (STM) and *ab initio* total energy calculations [3-5]. The authors suggested that the $\sqrt{3}\times\sqrt{3}$ phase has a similar structure to the boron-incorporated one where the boron atoms occupy the so-called S_5 site with 1/3 ML below the Si adatoms at T_4 site [6]. Moreover, as a category of group IV adatoms on Si or Ge(111), the Si adatoms on the C-incorporated $\sqrt{3}\times\sqrt{3}$ surface are predicted to drive a phase transition into 3×3 ordering at a low temperature, which is a characteristic of a charge density wave [7]. However since such a property has not been proved from an experimental point of view, some authors have suggested a Mott-Hubbard insulator model [8]. On the other hand, other groups had prepared the same surface by solid C evaporation source and have argued that the surface contains 1 ML of C by x-ray photoelectron spectroscopy (XPS) [9], and that the C atoms form a sheet layer also at the subsurface, from a reflection high-energy electron diffraction (RHEED) simulation [10].

Here, the C-incorporated Si(111) $\sqrt{3}\times\sqrt{3}$ $R30^\circ$ [hereafter referred to as Si(111) $\sqrt{3}\times\sqrt{3}$:C] surface reconstruction is prepared by thermal decomposition of ethylene onto a clean Si(111) substrate. To resolve the above disagreement, and to investigate the chemical bonding nature of the surface, a high-resolution core-level photoelectron

spectroscopy using synchrotron radiation is applied. We discuss the structural properties of the Si(111) $\sqrt{3}$:C reconstructed phase analyzing the depth position and coverage of the C atoms involved in the phase. In particular, the comparison with other surfaces such as ethylene adsorption at top Si surface and SiC_x compound formed from the ethylene decomposition at high temperatures is made by means of analysis of the C 1s and Si 2p core level line shape.

2. Experimental

A p-type Si(111) crystal (Boron-doped, $\square \sim 0.5 \square \text{ cm}$) was cleaned repeatedly by flashing up to 1250 °C after several hours of initial outgassing at 550 °C. High-purity ethylene gas was dosed by back-filling of the chamber through a leak valve. The $\sqrt{3} \times \sqrt{3}$ reconstruction was obtained by dosing 1000 L of ethylene with the sample kept at 627 °C. After the dosing, the sample was kept at the same temperature for 5 minutes longer while the residual gas was pumped down. Once the $\sqrt{3} \times \sqrt{3}$ phase made, the surface keeps stable for a long time as judged from the low energy electron diffraction (LEED) pattern. All the measurements were performed at the beam lines UE56/2 of BESSY in Berlin and 8A1 of PAL in Pohang. In order to obtain comparable data at both experimental stations, the LEED pattern and C 1s core level spectrum for the Si(111) $\sqrt{3}$:C phase were carefully compared. Most of C 1s and Si 2p spectra were taken at photon energies of 330 and 140 eV at room temperature (RT) with linear *p*-polarization geometry. The photoemission data were recorded using a PHOIBOS 100 analyser (Specs GmbH) equipped with a 2D CCD detector, or using a SCIENTA-2002 (Gamadata), both of which give an angular acceptance angle of $\pm 7^\circ$ and similar resolution. The overall

instrumental resolution was better than 200 meV for the C 1s and 80 meV for the Si 2p core levels.

3. Results and Discussion

Fig. 1 shows a series of C 1s spectra and a few selected peak fittings of them under the thermal decomposition of ethylene on the clean Si(111) surface. Voigt functions are used for the C 1s fittings with a constant Lorentzian width of 0.15 eV and a variable Gaussian width of 0.65 ± 0.1 eV. In the bottom spectrum, the C 1s line for the ethylene adsorbed by 5000 L on the Si(111) at RT is fitted with two peaks at 283.98 (C1) and 284.46 eV (C1'). The main peak C1 is attributed to Si-C bond formation [11], and another peak C1' which is separated by 0.48 eV from the C1 is assigned to a vibrational loss feature arising from the C-H bond, which is comparable to 0.36 eV for ethylene on Si(100) [12]. At low binding energy side, there is no clear feature which may appear if there is gas impurity or further decomposition of ethylene on the surface [11]. Thus, an ethylene adsorption leads to a non-dissociative reaction with a single chemical state of C on the Si(111) substrate.

After being exposed to ethylene, the substrate is annealed successively for one minute at each elevated temperature as marked on the Fig. 1 and cooled down to RT for the C 1s measurement. As the annealing temperature is increased, new features at the low-binding energy side evolve at 283.39 (C2) and 282.72 eV (C3) at the sacrifice of the ones seen at RT (C1 and C1') on the higher binding energy side. The C2 species is ascribed to an intermediate species formed under thermal decomposition probably due to the of C-H bond breaking [11]. As the temperature increases, the C3 component becomes

dominant and is attributed to a species generated by C-C bond cleavage. Additionally, from the comparison with the C 1s spectrum for the $\sqrt{3} \times \sqrt{3}$ phase in the second spectrum from the top, the C3 is found to be the ingredient connected with the surface reconstruction of Si(111) $\sqrt{3}$:C. Upon higher temperature annealing at 730 °C, another lower-binding peak appears at 282.32 eV, which coincides with the one for the SiC species shown on the top spectrum [13]. This indicates that the C3 species has a different chemical environment from the one for SiC compounds; it is reduced at higher temperatures. Moreover, the C 1s peak for the $\sqrt{3} \times \sqrt{3}$ phase always shows a single feature, with a full width at half maximum of 0.64 eV, as a consequence of the unique chemical bonding state for the C atoms involved in the surface structure. This behaviour is very similar to the C-incorporated c(4×4) surface where C atoms occupy a substitutional site in the 4th layer from the top [2,14]. From an analysis of relative surface sensitivity of the C 1s peaks using different photon energies for the C 1s measurement, the C1 and C2 species turn out to reside only on the top surface while the C3 is located in subsurface region, as discussed below.

Figure 2(a) shows the C 1s core level spectra measured upon the addition of ethylene for an exposure of 5000 L at RT onto the Si(111) $\sqrt{3}$:C surface which was previously processed by thermal decomposition of ethylene at 627 °C. The position and the shape of the additional peak on the left-hand side coincide with those of the C1 in the figure 1. We interpret this in terms of ethylene adsorbing on the top of the Si(111) $\sqrt{3}$:C, again without decomposition. This occurs since the C atoms for the $\sqrt{3} \times \sqrt{3}$ surface, corresponding to the C3 line, are located in a subsurface region, exposing the surface

with Si atoms which again become reaction sites for the incoming ethylene gas. In order to identify the relative depth population of two different kinds of C atoms, their relative intensity variation is traced by changing photon energy and electron emission angle. In figure 2(a), the relative intensity of the C3 component decreases as the surface sensitivity is increased from the bottom (400 eV and normal emission) to the top (330 eV and 60° emission) spectrum. Since the adsorbed ethylene remains only on the top surface at RT, the relative intensity of the initial C3 component decreases with an increase of surface sensitivity. This is clear from Fig. 2(b) where the relative intensity ratio of C3 component decreases as the photoelectron detection angle increases from the surface normal. The relative intensity of C3 at 60° is reduced by 50 % of that at normal emission. In a simple electron attenuation model, the intensity of photoelectrons is proportional to $\exp(-d/\lambda \cos\theta)$ where θ is the emission angle and λ is the attenuation length, which is several Å at this kinetic energy range (40 ~ 50 eV). Thus the C3 species is located approximately at $d = \lambda \cdot \ln(2.8)$ below the top layer. If we suppose that the C3 species exists only in a single sheet in the Si substrate layers, its position is centred at a depth on the order of the Si bilayer thickness (3.13 Å). However, the maximum intensity occurs at 10° emission in the Fig. 2(b), possibly due to forward scattering from photoelectron diffraction effect. In fact, as shown for the Si(111) $\sqrt{3} \times \sqrt{3}$:B surface [6], there is an intensity modulation of the C3 peak in kinetic energy scans with changing photon energy (not shown here), which means that the C3 component may arise from a specific bonding site in the subsurface region [15].

In order to follow chemical changes of Si surface atoms upon adsorption of ethylene at RT on the Si(111)7×7 surface, a series of Si 2p core level spectra are shown in Fig. 3. The Si 2p doublets are also fitted by Voigt functions with a fixed Lorentzian width of 0.082 eV and a variable Gaussian width of 0.31 ± 0.03 eV after Shirley type background subtraction, while a polynomial background is used for those at 118 eV. The summary of fitting parameters for the spectra in Figs. 3 and 4 is listed in Tab. 1. A photon energy of 140 eV and an electron emission angle of 60° are used to enhance the surface sensitivity whereas the spectra at the normal emission and 118 eV are compared as bulk-sensitive ones. The Si 2p spectrum for the clean Si(111)7×7 is consistent with previous results where surface core-level shifts were resolved from the curve fittings at -0.71, -0.26, 0.28, 0.57, and 0.95 eV of binding energies relative to the bulk component [16]. These are attributed to the rest-atom, dimer or second-layer, pedestal, adatom, and defect atoms. As the ethylene dose increases, the peak at -0.71 eV for rest-atoms is attenuated and the dip between the Si 2p_{3/2} and Si 2p_{1/2} is filled. Since ethylene is supposed to undergo [2+2] cycloaddition on the Si(111)7×7 [17,18], one rest atom-adatom pair is consumed by an ethylene molecule while it produces surface Si atoms bonded to C. Such a result is clearer in Fig. 4(a) which shows curve fittings for a surface dosed with 5000 L of C₂H₄. Two different photon energies with different emission angles are used to discriminate any surface-sensitive components. Due to the longer electron escape depth, all the surface components show reduced intensities at 118 eV in comparison with those at 140 eV. Thus, it is confirmed that the intensities of surface-related peaks at 0.28 and 0.57 eV are increased while those for the bulk and rest-atom (-0.71 eV) decreases. As inferred by Rochet *et al.*, there are other sites involved in the ethylene adsorption in

addition to the rest atom-adatom pair [11]. Moreover, multiply C-coordinated Si atoms may exist on the surface at high doses [18], such that an intensity increase occurs at both the high-binding energy peaks due to the C-Si bond formation.

The details of the chemical changes of the Si atoms upon Si(111) $\sqrt{3}$:C phase formation are shown in the peak fitting results in Fig. 4(b). On the Si(111) $\sqrt{3}$:C surface, the relative intensities of most surface-related components are enhanced compared with the spectrum for C₂H₄-adsorbed surface on the Fig. 4(a). There are four major surface components at -0.27, 0.30, 0.60, and 0.99 eV of relative binding energies [19]. Of the fitted components, two peaks at 0.60 and 0.99 eV show an increased emission intensity at $\hbar\omega = 118$ eV, a different behaviour from that shown on the C₂H₄-adsorbed surface in the Fig. 4(a) where most surface components show decreasing intensities under bulk-sensitive conditions. This different trend suggests that the two peaks do not arise from top surface components, but from interface Si atoms bonding to the C in a subsurface region.

components for clean surface	binding energy (eV) / relative intensity		
	Clean Si(111)	C ₂ H ₄ /Si(111)	Si(111)- $\sqrt{3}$:C
bulk	0.00 / 0.453	0.00 / 0.411	0.00 / 0.341
dimer & second	-0.26 / 0.043	-0.27 / 0.053	-0.26 / 0.098
rest-atom	-0.71 / 0.043	-0.67 / 0.016	-0.78 / 0.027
pedestal	0.28 / 0.348	0.27 / 0.311	0.33 / 0.271
adatom	0.57 / 0.105	0.51 / 0.172	0.60 / 0.155
defect	0.95 / 0.007	0.82 / 0.036	0.91 / 0.065
new			1.27 / 0.029

Table 1 Fitting parameters of Si 2p spectra at $\hbar\omega = 140$ eV for three different surfaces shown in Figs. 3 and 4. The spin-orbit splitting and branching ratio are 0.605 eV and 0.5, respectively, for all the spectra.

We assumed that the strong Si 2p emission at the high binding side arises from the charge transfer from Si to the more electronegative C atoms, which is probably accompanied by a large structural change. The question is that how many of the C atoms are involved in this structure. First, from the decrease in the intensity for the rest atom upon 5000 L exposure ($0.043 \rightarrow 0.017$) in Tab. 1, one can roughly estimate the C coverage for the C1 species on the top surface as about 0.4 ML referring the previous result [11]. Second, by taking account of the comparable C 1s intensities of the C1 and C3 components in the Fig. 1, and the photoelectron intensity attenuation from the deeply located C3 species, the amount of C atoms involved in the $\text{Si}(111)\sqrt{3}:\text{C}$ phase may reach up to 1 ML. The minimum coverage should be at least much more than $1/3$ ML, which was proposed by means of the earlier studies with STM and related total energy calculations [3,4]. In fact, an earlier experimental study suggested the C coverage of 1 ML [9], even though a higher C coverage is predicted to cause an unstable $\text{Si}(111)\sqrt{3}:\text{C}$ phase from *ab initio* calculation [5], Therefore, more sophisticated structural models should be considered for a correct atomic geometry on this surface. A simple starting model might be the Si-terminated $\text{SiC}(0001)\sqrt{3} \times \sqrt{3}$ surface which consists of a Si adatom at T_4 site and Si-C bilayer underneath [20].

4. Conclusion

The $\text{Si}(111)\sqrt{3}:\text{C}$ reconstructed surface is prepared through thermal decomposition of ethylene on the $\text{Si}(111)$ surface. The details of the chemical changes of the C and Si atoms for related surfaces are compared in terms of C 1s and Si 2p core level line shapes using photoelectron spectroscopy. The singlet feature of C 1s and its intensity variation

upon the change of electron emission angles for the $\text{Si}(111)\sqrt{3}:\text{C}$ phase indicate that the C atoms occupy a unique subsurface site. This C species is unstable under heat treatment and shows a different binding energy from that of the SiC compound which is formed at a higher temperature. The enhanced emission on the high binding energy side in the Si 2p spectra implies a large structural change made by C incorporation into the substrate. Based on the present and previous studies, the C coverage for the $\text{Si}(111)\sqrt{3}:\text{C}$ seems to be close to 1 ML, which again requires a new structural model.

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Captions

Fig. 1 A series of C 1s spectra upon dosing of 5000 L of C₂H₄ on Si(111) followed by annealing for 1 min. at the marked temperatures. The $\sqrt{3} \times \sqrt{3}$ and SiC_x surfaces are made by dosing the C₂H₄ on samples kept at 627 °C and 700 °C, respectively.

Fig. 2 (a) C 1s spectra measured upon adsorption of C₂H₄ onto Si(111)- $\sqrt{3}$:C surface. From the bottom, three spectra are stacked with increasing bulk to surface sensitive conditions (b) Relative intensity plot of the C3 component with respect to electron emission angle from the surface normal at $\hbar\omega = 330$ eV.

Fig. 3 Evolution of Si 2p spectra upon adsorption of C₂H₄ from 2 to 5000 L on Si(111) surface at room temperature.

Fig. 4 Si 2p core level spectra and their curve fitting results for two different surfaces: (a) 5000 L of ethylene dosed on the Si(111)-7x7 and (b) Si(111)- $\sqrt{3}$:C.

Tab. 1 Fitting parameters of Si 2p spectra at $\hbar\omega = 140$ eV for three different surfaces shown in Figs. 3 and 4. The spin-orbit splitting and branching ratio are 0.605 eV and 0.5, respectively, for all the spectra.

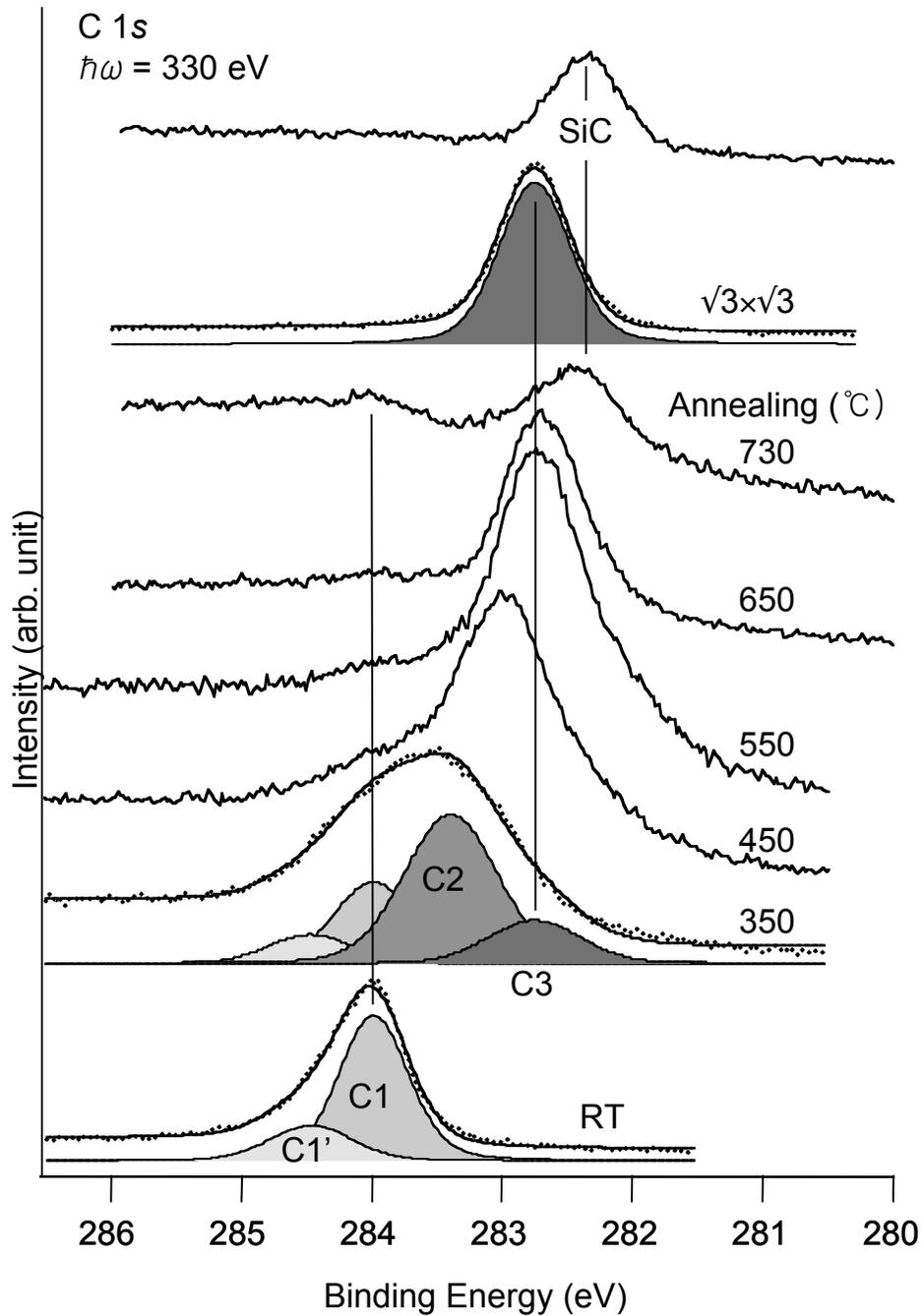


Fig. 1 A series of C 1s spectra upon dosing of 5000 L of C_2H_4 on Si(111) followed by annealing for 1 min. at the marked temperatures. The $\sqrt{3}\times\sqrt{3}$ and SiC_x surfaces are made by dosing the C_2H_4 on samples kept at 627°C and 700°C , respectively.

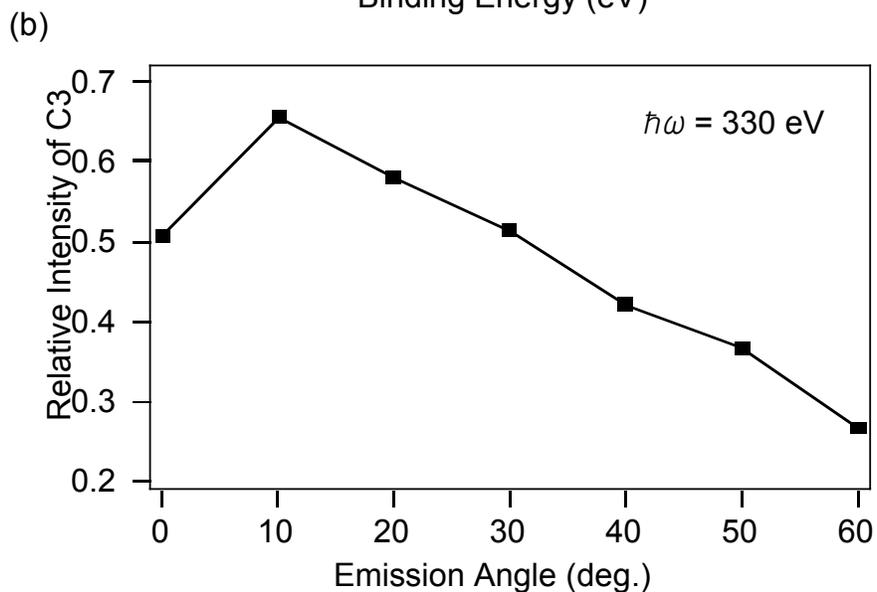
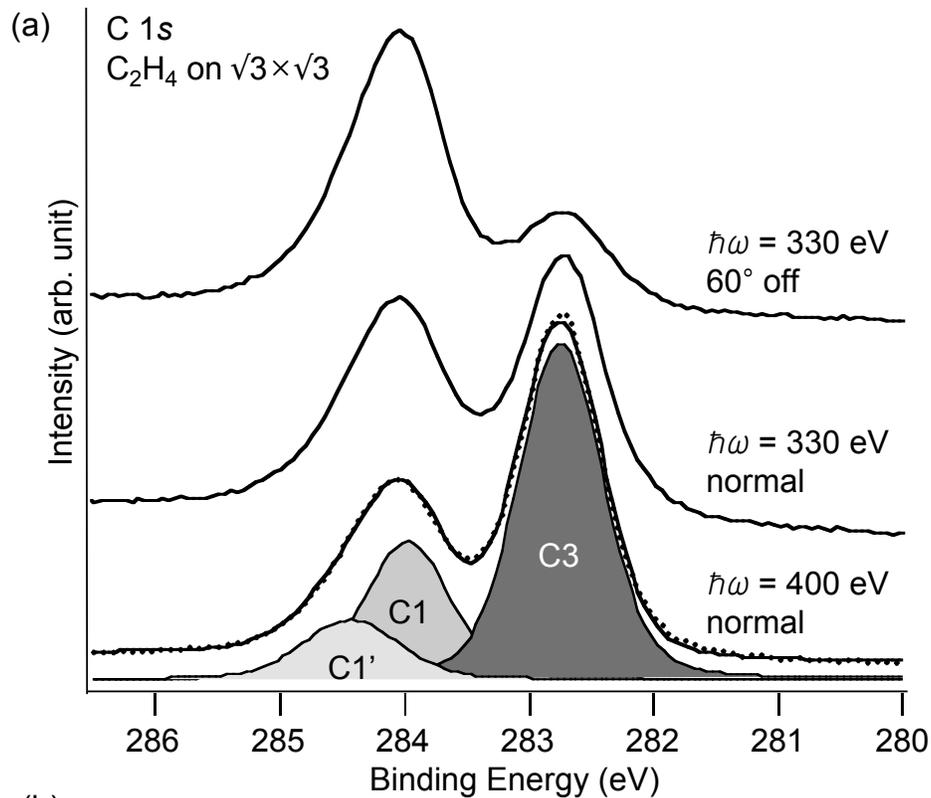


Fig. 2 (a) C 1s spectra measured upon adsorption of C_2H_4 onto $Si(111)-\sqrt{3}\times\sqrt{3}$:C surface. From the bottom, three spectra are stacked with increasing bulk to surface sensitive conditions (b) Relative intensity plot of the C3 component with respect to electron emission angle from the surface normal at $\hbar\omega = 330$ eV.

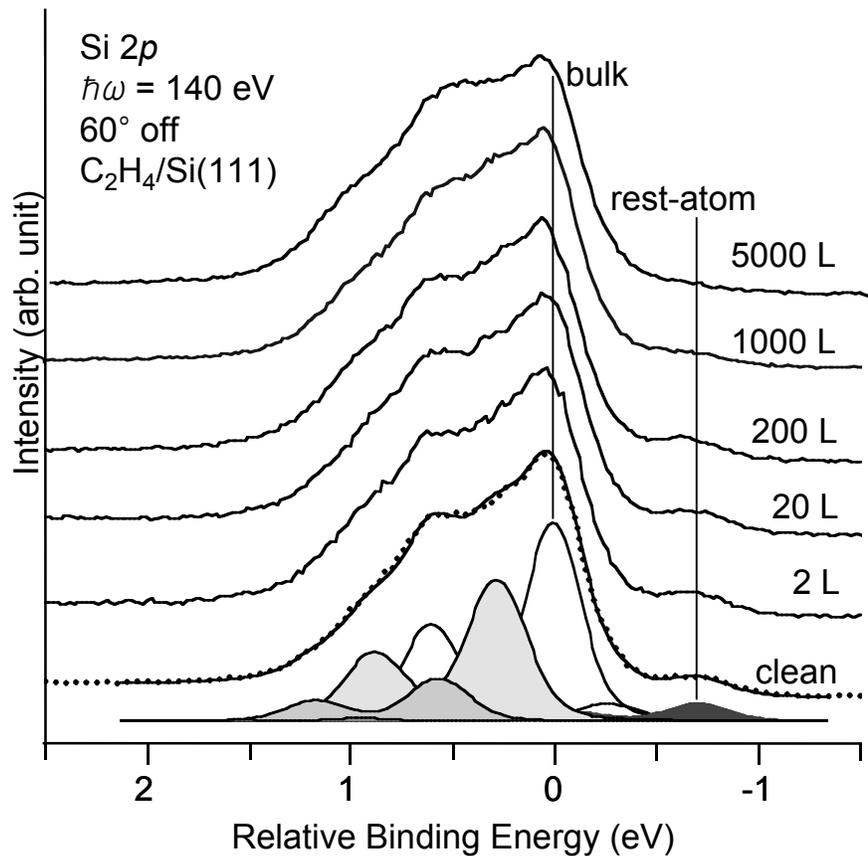


Fig. 3 Evolution of Si 2p spectra upon adsorption of C₂H₄ from 2 to 5000 L on Si(111) surface at room temperature.

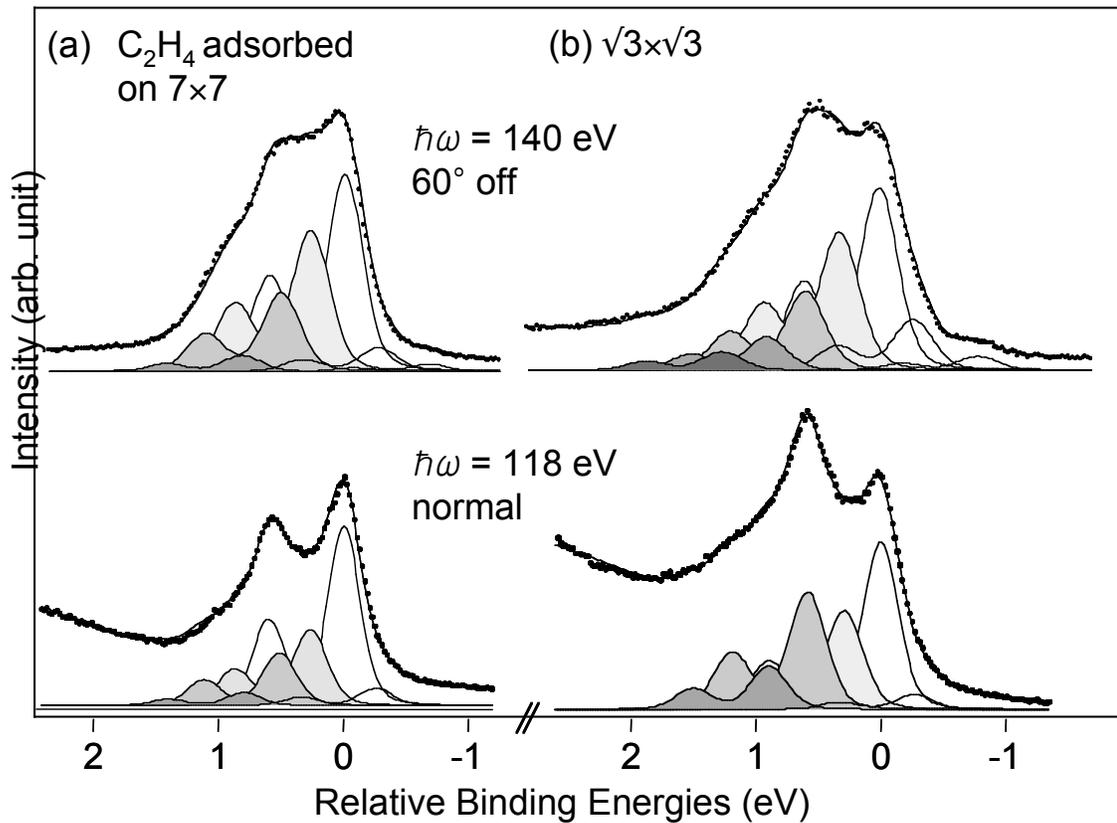


Fig. 4 Si 2p core level spectra and their curve fitting results for two different surfaces: (a) 5000 L of ethylene dosed on the Si(111)-7x7 and (b) Si(111)- $\sqrt{3}\times\sqrt{3}$:C.