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Ethylene adsorption on Si(100)2×1: A high-resolution photoemission study

M. P. Casaletto,[1] R. Zanoni,[1]* M. Carbone,[2] M. N. Piancastelli,[2] L. Aballe,[3] K. Weiss,[3] and K. Horn[3]
[1]*Dipartimento di Chimica, Università di Roma ''La Sapienza,'' P.le A. Moro 5, I-00185 Rome, Italy*
[2]*Dipartimento di Scienze e Tecnologie Chimiche, Università ''Tor Vergata,'' Via della Ricerca Scientifica 1, I-00133 Rome, Italy*
[3]*Fritz-Haber-Institute der Max-Planck-Gesellschaft, D-14195 Berlin, Germany*

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The adsorption of ethylene on Si(100)2×1 has been investigated at room temperature by high-resolution synchrotron radiation photoemission in the exposure range: 1–1000 L. A consistent picture in favor of molecularly di-σ bonded ethylene is obtained from the analysis of the photoemission spectral features, which shows the progressive decreasing of the surface states in the valence band and the Si $2p$ features related to the surface dimers upon adsorption. By careful fitting of the Si $2p$ complex envelope, the appearance of a component in the Si $2p$ core-level spectrum is evidenced already after 1 L exposure to ethylene. This component, which grows with exposure, is assigned to the formation of two Si-C bonds per dimer as a result of ethylene adsorption. The line-shape analysis by model functions permits us to follow the symmetrization of Si-Si dimers, which are known to be asymmetric on the clean surface, and the growth of a Si-C related spectral component upon adsorption. Relative quantitative analysis of the various peak components suggests that the intensity increase of the new component almost completely parallels the progressive decrease of the surface dimer components. No evidence for carbide formation has been found from the C $1s$ spectrum.

I. INTRODUCTION

The interaction between hydrocarbons and silicon surfaces is a topic of current interest both in basic and applied research fields. Different technological applications can benefit from unravelling the fundamental aspects of the adsorption mechanism. For example, new synthetic routes to the growth of silicon carbide (SiC) thin films can be very useful for microelectronical devices. With the development of diamond thin-film technology, the importance of understanding the Si/C interface has increased particularly as it applies to nucleation and adhesion of the diamond films.[1] Furthermore, a major advance is the discovery that ordered chemisorbed monolayers from multiple functionality hydrocarbons can be formed on a clean Si(100)2×1 surface.[2] The extremely favorable opportunity to attach bifunctional organic molecules to Si(100)2×1 can be achieved by using C═C groups for bonding to the surface, while preserving the second chemical functionality for further surface reaction (polymerization or conversion to other functional groups, such as alcohols and amine). The monolayer functionalization of semiconductor surfaces is of great interest in gas and biochemical sensor development, in molecular electronics, and in the semiconductor industry as passivation layers where an oxide film cannot be used.

In the framework of a systematic investigation carried out in our group on the chemical reactivity of silicon surfaces towards organic molecules [for ethylene see Refs. 3 and 4], we have performed a high-resolution photoemission study of ethylene adsorption on Si(100)2×1 as a function of the exposure.

The adsorption of ethylene on Si(100)2×1 has been intensively investigated by several surface science techniques.[5–10] High-resolution electron energy-loss spectroscopy and low-energy electron diffraction (LEED) studies[5] show that ethylene is molecularly chemisorbed on the surface in the temperature range 77–600 K. A nearly complete rehybridization of both carbon atoms from sp^2 to sp^3 occurs upon adsorption, as suggested by the absence of the C═C bond in the adsorbed species. In the proposed adsorption structure, ethylene is di-σ bonded to two adjacent Si atoms of the dimer, saturating the dangling bonds. Furthermore, when the clean surface is exposed to ethylene, only a small change and no additional spots are observed in the LEED patterns, confirming the (2×1) reconstruction at RT. Although exposure to ethylene does not cause large-scale rearrangement of the original Si surface atoms, changes in the local structure have been observed at 300 K by scanning tunneling microscopy.[6] At low coverage, ethylene molecules prefer to adsorb on top of alternate dimer sites, creating small domains of local (2×2) or $c(2\times4)$ structure. The individual domains are so small (<50 Å) that the change in the reconstruction cannot be detected by any diffraction technique. The most likely adsorption site suggested by angle-resolved photoemission[7] and photoelectron diffraction[8] is a bridging site where the ethylene molecule is adsorbed on top of a Si-Si dimer of the reconstructed surface. The equilibrium molecular bond distance (1.62 ± 0.08 Å) indicated by photoelectron diffraction hints at a single C—C bond in the intact molecule. Therefore, the saturation of the dimer dangling bonds has been hypothesized. At the same time, the Si-Si distance (2.36 ± 0.21 Å) provided by the same technique shows that the Si dimers stay intact and therefore no Si-Si bond rupture occurs upon ethylene adsorption.

The adsorption of ethylene on Si(100)2×1 is found to be stereospecific and almost totally stereoselective, as shown in the report of a stereochemically selective reaction occurring on a solid surface with no intrinsic chirality.[9] In this paper we report, to our knowledge, the first high-resolution synchrotron radiation photoemission study of ethylene adsorption on Si(100)2×1 at room temperature. Only one previous Si $2p$ core-level photoemission study was performed at low

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resolution.[10] High-resolution Si 2p spectra in the exposure range 1–1000 L have been investigated by a careful line-shape analysis to unravel the structural and electronic changes of the Si dimers upon adsorption.

II. EXPERIMENTAL

The high-resolution photoemission experiments have been carried out at the German storage ring BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H.) on the PGM-3 beamline in the photon energy range: 35–600 eV. The overall instrumental resolution (monochromator plus analyzer) was 40 ± 10 meV in the Si 2p region (130 eV photon energy) and below the natural line width in the C 1s range. A UHV analysis chamber (base pressure of $\sim 3 \times 10^{-10}$ mbar) was equipped with a hemispherical electrostatic Scienta SES 200 electron energy analyzer. Photoemission spectra were collected at normal emission, with samples oriented at 30° with respect to the photon beam. The Si(100) crystals were p-type Virginia SC wafers (2.5 Ω cm resistivity). Clean reconstructed Si(100)2×1 surfaces were prepared by direct resistive heating, followed by 30 s flashes at 1373 K. Ethylene (E. Merck, research grade) was further purified by successive freeze-pump-thaw cycles before introduction into the analysis chamber and its purity was checked *in situ* by mass spectroscopy. The adsorption of ethylene on the reconstructed surface has been performed at room temperature in the exposure range: 1–1000 L ($1 \text{ L} = 10^{-6}$ torr s).

III. RESULTS AND DISCUSSION

The photon energy range 35–600 eV permits us to investigate the valence-band region (VB) as well as the Si 2p and C 1s core-level lines. In the following sections, the VB and C 1s results will be briefly commented upon, focusing the attention mainly on the Si 2p line-shape analysis.

A. Valence-band photoemission

The valence-band spectrum of the exposed-Si(100)2×1 surface shows the adsorption-related spectral features already after exposure to 1 L ethylene. Five new features, growing as a function of ethylene exposure, have been assigned to the b_{2u}, b_{2g}, a_g, b_{3u}, and b_{1u} ethylene molecular orbitals. The assignment has been made by comparison with the adsorption of ethylene on differently oriented silicon surfaces. Similarly to the adsorption on Si(111)2×1 (Ref. 3) and Si(111)7×7 (Ref. 4) we find a one-to-one correspondence between gas-phase and adsorbed-related spectral features. The adsorption of ethylene is molecular also on Si(100)2×1, leading to di-σ bonded species on the surface. VB spectra confirm that the adsorption occurs through an electron donor-acceptor mechanism on silicon surfaces. The peak corresponding to the π orbital of the molecule is still present in the adsorbate phase but undergoes an upward shift with respect to the gas phase, thus suffering a destabilization upon adsorption.[3] In contrast to metal substrates, where a shift in the opposite direction has been found, the silicon surface acts as a π donor with respect to the ethylene lowest unoccupied molecular orbital (LUMO), which has a π symmetry as well. Consequently, the C—C bond in the ethylene molecule is stretched and becomes intermediate between single and double. Furthermore, upon adsorption on Si(111)7×7 both adatoms and restatoms are simultaneously involved in bonding ethylene in a bridge site geometry.[4]

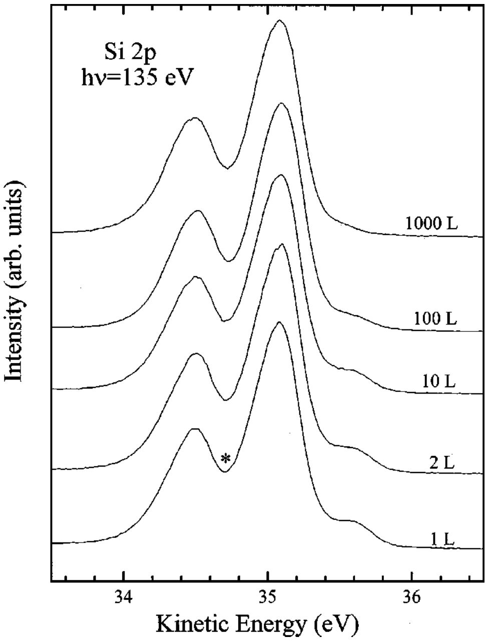

FIG. 1. Si 2p spectra as a function of ethylene exposure at room temperature. The photon energy is 135 eV. The star * indicates the region of the trough depth.

B. High-resolution Si 2p core-level photoemission

Si 2p core-level spectra collected as a function of ethylene exposure in the range 1–1000 L are shown in Fig. 1. Spectra have been recorded at 135 eV photon energy, which corresponds to the highest surface sensitivity.[11] A survey of the high-resolution spectra shows qualitative changes upon adsorption:

(1) There is a remarkable and progressive intensity decrease of the spectral feature on the lower binding energy side for increasing exposures to ethylene. It is still present after an exposure to 100 L ethylene and eventually disappears after 1000 L exposure. This feature has been related to the buckled-up atoms in the Si dimer.[12]

(2) The overall shape of the Si 2p core line does not change significantly upon adsorption. This is particularly evident in the region of the trough depth, marked with a star (*) in Fig. 1, where a Si-C bond would become visible.[13,14] Si 2p photoemission spectra recorded at different photon energies in the same exposure range confirm these qualitative findings.

As already shown by several studies of structural and electronic changes of surface atoms upon adsorption of different molecules,[11,15] further information on ethylene adsorption mechanism on Si(100)2×1 can be achieved by a line-shape analysis of Si 2p core-level spectrum.

1. Curve-fitting of the clean surface

A Si 2p line-shape analysis of the ethylene exposed-Si(100)2×1 needs to consider the clean surface as its start-

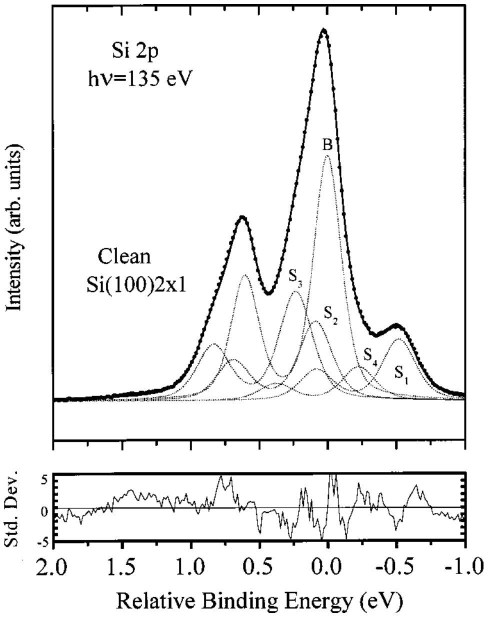

FIG. 2. Line-shape analysis of the Si $2p$ spectrum for the clean Si(100)2×1 surface at room temperature. The photon energy is 135 eV. The scattered curve refers to the raw data, while the solid line to the fitting results. B,S_1,S_2,S_3,S_4 dotted curves denote emission from bulk, up and down atoms in a dimer, second layer and subsurface, respectively. The bottom line refers to the residual of the fitting procedure.

TABLE I. Curve-fitting parameters for the clean Si(100)2×1 surface. The surface core-level shift (SCLS) of each component is reported in relative binding energy (RBE).

Component	SCLS (eV)	FWHM (eV)	Branching (eV)	Spin-orbit (eV)
B	0	0.2410	0.50	0.602
S_1	-0.523	0.2876	0.50	0.602
S_2	$+0.087$	0.2876	0.50	0.602
S_3	$+0.231$	0.2876	0.50	0.602
S_4	-0.227	0.2876	0.50	0.602

ing point. In Fig. 2 the curve fitting of the clean surface spectrum by a model function is shown. The solid line through the scattered data points is the result of the fitting procedure, while the dotted curves refer to the single components. The residual plot underneath the spectrum is determined by the difference between raw and fitted curves.

In the high-resolution spectrum the Si $2p_{3/2}$ and Si $2p_{1/2}$ components are well resolved and contributions from Si atoms in different chemical environments are evident. The Si $2p$ spectrum has been decomposed by a curve-fitting procedure into one bulklike and four surface-related components, consisting of spin-orbit-splitted Voigt functions, using a nonlinear least-squares analysis. The curve fitting of the clean Si(100)2×1 surface closely reproduces in peak number and energy position the results previously obtained for ethanol adsorption on the same surface.[15] The assignment of all components follows the one reported by Landemark and co-workers.[12,16] In particular, peak B is assigned to the bulklike atoms. Peak S_1, on the low binding-energy side of the bulk component, is assigned to the buckled-up atoms and peak S_2 to the buckled-down atoms in the dimers. Peak S_3 accounts for emission from the second layer and peak S_4 originates from subsurface layers (most likely, emission from half the third layer). The surface core-level shifts (SCLS) obtained for the S_1, S_2, S_3, and S_4 components are, respectively, -0.523, $+0.087$, $+0.231$, -0.227 eV as expressed in relative binding energy (RBE). They are in good agreement with the values -0.500, $+0.062$, $+0.230$, -0.225 eV reported in the literature.[16] The fitting parameters are very similar for all the components, which consist of a $2p_{3/2}-2p_{1/2}$ doublet with 0.602 eV spin-orbit split separation and a branching ratio equal to the statistical value (0.5). The resulting full width at half maximum (FWHM) is 0.2876 eV for all the surface components and 0.2410 eV for the bulk component. A Shirley background subtraction has been performed on the raw data. The curve-fitting parameters of the clean Si(100)2×1 surface are summarized in Table I.

2. Curve-fitting of the exposed surface

Upon ethylene adsorption, the Si $2p$ surface atoms involved in the adsorption process should give rise to new features. While the buckled-up and buckled-down features intensity decreases upon molecular adsorption of ethylene, a new component in the Si $2p$ spectrum should appear, resulting from the interaction of carbon atoms with the surface dimers. The intensity decrease and eventual quenching at high exposures of the Si dimer atoms can be interpreted in terms of dimer symmetrization upon bonding with the bridging ethylene molecules.

The bond formation between the Si dimers and the ethylene molecules does not induce a relevant charge redistribution between the adsorbate and the Si substrate, as indicated by the overall appearance of the spectra, which does not change significantly upon adsorption, except for the low binding-energy region. A new Si $2p$ component is then expected to grow with exposure at an energy position close to that of the buckled-down atoms and compensating for their intensity decrease.

The curve-fitting of the Si $2p$ spectra as a function of ethylene exposure is reported in Fig. 3. In (a), (b), (c), and (d) spectra after 1, 10, 100, and 1000 L ethylene are shown. The solid line through the scattered experimental points refers to the result of the fitting procedure. While the dotted curves represent the peak components, the filled area accounts for the component arising from adsorption. The residual is plotted at the bottom of each spectrum.

In the line-shape analysis of the exposed surface, the main observations are the partial disappearance of the peaks related to the Si dimer atoms and the growth of only one component that accounts for ethylene adsorption. In order to fit the Si $2p$ spectrum after exposure to ethylene, a 1:1 ratio intensity decrease for the dimer buckled-up and buckled-down components has been hypothesized. In all the exposed-surface spectra a spin-orbit split of 0.602 eV and a branching ratio of 0.5 have been imposed. The S_1 component suffers a small energy shift (0.073 eV) upon adsorption, while the S_2, S_3, and S_4 peaks exhibit the same SCLS as in the clean surface. From the curve-fitting procedure, the component arising upon adsorption is localized at $+0.128$ eV RBE and this SCLS remains constant in all the exposure range. The

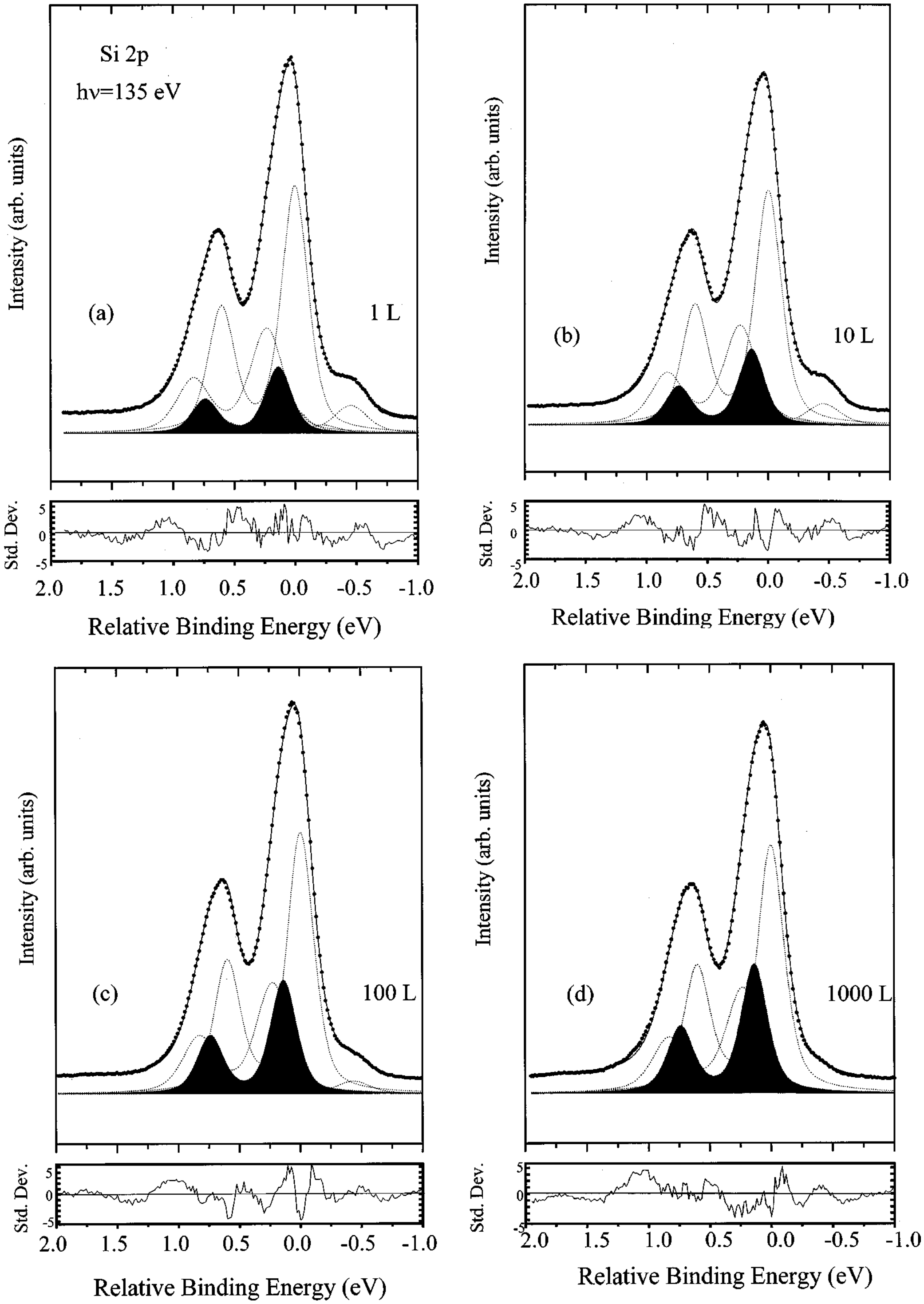

FIG. 3. Line-shape analysis of the Si $2p$ spectra as a function of ethylene exposure at room temperature. The photon energy is 135 eV. Spectra in (a), (b), (c), and (d) refer to 1, 10, 100, and 1000 L ethylene exposures, respectively. The scattered curve refers to the raw data, while the solid line to the fitting results. The single components are plotted as dotted curves and the filled areas show the new Si-C component. The bottom curve represents the residual of the fitting procedure.

full width at half maximum (FWHM) values are: 0.3231 eV for the surface components; 0.2562 and 0.2537 eV for the bulk and the Si-C components, respectively. The optimized parameters for the ethylene exposed-Si(100)2×1 surfaces are listed in Table II.

A major result of the line-shape analysis is the energy location of the component at +0.128 eV SCLS, which can be assigned to the formation of Si-C bonds. This is the first high-resolution photoemission evidence of Si-C bonds arising from ethylene adsorption on Si(100)2×1. The presence of such a component in the Si $2p$ spectrum already after 1 L exposure to ethylene [Fig. 3(a)] is also confirmed in the valence-band region, showing the typical spectral features related to the adsorbate. In a previous photoemission study of ethylene adsorption on Si(100)2×1 performed at lower resolution,[10] any visible structure related to the formation of

TABLE II. Curve-fitting parameters for the ethylene-exposed Si(100)2×1 surface. The surface core-level shift (SCLS) of each component is reported in relative binding energy (RBE).

Component	SCLS (eV)	FWHM (eV)	Branching ratio	Spin-orbit (eV)
B	0	0.2562	0.50	0.602
S_1	−0.450	0.3231	0.50	0.602
S_2	+0.083	0.3231	0.50	0.602
S_3	+0.231	0.3231	0.50	0.602
S_4	−0.227	0.3231	0.50	0.602
Si-C	+0.128	0.2537	0.50	0.602

TABLE III. Intensity ratio of all the surface components relative to the bulk as a function of ethylene exposure. $\Delta S_1+\Delta S_2$ denotes the total intensity decrease of the Si dimer atoms upon adsorption.

	S_1	S_2	S_3	S_4	Si-C	$\Delta S_1+\Delta S_2$
Clean	0.30	0.42	0.53	0.17		
1 L	0.14	0.17	0.53	0.05	0.26	−0.41
10 L	0.12	0.15	0.53	0.04	0.31	−0.45
100 L	0.06	0.07	0.53	0.02	0.43	−0.59
1000 L			0.53		0.52	−0.72

a Si—C bond was excluded at least up to 82.5 L ethylene. For higher exposures (2330 L ethylene) a component with a +0.5 eV SCLS was introduced in the Si $2p$ spectrum.

The SCLS value of the spectral feature related to the formation of adsorbate-substrate bonds (+0.128 eV) is unusually small for Si—C bonds. In the literature SCLS values in the range: +0.21 to +0.5 eV have been reported for Si—C single bonds following the reaction of hydrocarbons on Si(111)7×7.[13,14] Si $2p$ core-level spectra of saturated hydrocarbon-dosed Si(111)7×7 surfaces show chemically shifted components with 0.48±0.05, 1.00±0.05, and 1.50 ±0.05 eV SCLS for methane, neopentane, and adamantane adsorption, respectively.[13] This has been attributed to the formation of $\mathrm{Si(CH}_y)_x$ $(x=1-3;y=0-3)$ type surface species. Since chemical shifts have been shown to be additive with the number of bonds on a particular Si atom (e.g., for oxygen and fluorine),[17,18] SCLS between +0.4 and +0.5 eV are expected for Si-C bonds and +1.0 and +1.5 eV for a di- or tricarbide species, respectively.

In a high-resolution core-level photoemission study of alkyl-terminated Si(111)7×7 surfaces, a Si $2p$ component shifted to higher binding energy has been attributed to the presence of a Si—C bond at the interface.[14] Chemical shifts in the range +0.21 to +0.27 have been observed for alkyl chains with a different number of carbons atoms.

From our line-shape analysis performed on an ethylene-exposed Si(100)2×1 surface, the presence of any component in the energy range +0.21 to +0.5 eV can be readily excluded for all the investigated exposures. The fact that the value of the energy shift resulting from the Si $2p$ curve fitting is unexpectedly small for a Si—C bond suggests a complex adsorption process, with a charge redistribution possibly involving not only dangling bond saturation, but also a π interaction between the ethylene empty π orbital and substrate levels of suitable symmetry.[3] An electron donor-acceptor mechanism, with back donation from the silicon surface to the ethylene LUMO and a consequent net charge transfer from Si to C, can account for such a small SCLS.

3. Relative quantitative analysis

On a qualitative basis, the Si $2p$ line-shape analysis clearly shows that the intensity of the new component increases with the exposure, while that of the surface dimers correspondingly decreases and finally disappears at high exposures. In a simple approach, it is reasonable to expect that this intensity decrease can be recovered by the increase of the Si-C component. The analysis of the relative quantitative ratios of all the components can address this point. In Table III, the ratios of the intensity of each peak relative to the bulk are reported as a function of ethylene exposure. The progressive intensity decrease of S_1 and S_2 peaks, expressed as $\Delta S_1+\Delta S_2$, is closely compensated for the increase in the Si-C component, at least within the experimental error (±10%).

C. C 1*s* core-level photoemission

The C 1*s* photoemission spectrum of the ethylene exposed-Si(100)2×1 show an asymmetric peak, which can be fitted with two components, with FWHM=0.657 eV and a relative energy shift of 0.516 eV. The asymmetry towards higher binding energy excludes the formation of silicon carbide (SiC), which is known to produce a chemical shift in the opposite direction. The different electronegativity between C and Si atoms should give rise to a SiC component at lower binding energy with respect to the aliphatic carbon, shifted by 1.2–1.4 eV.[14] No evidence for carbide formation has been found from the analysis of the C 1*s* core line. The asymmetrical shape towards higher binding energy can be accounted for the unresolved ethylene vibrational progression.[19]

IV. CONCLUSIONS

The adsorption mechanism of ethylene on Si(100)2×1 has been investigated by high-resolution synchrotron radiation photoemission as a function of the exposure at RT. Analysis of the photoemission spectral features confirms that ethylene is molecularly di-σ bonded to the surface and shows the progressive decreasing of the surface states intensity and the appearance of a component in the Si $2p$ core spectrum. Line-shape analysis by model functions allows following the symmetrization of the Si-Si dimers and the progressive growth of a new component as a function of ethylene adsorption. This component exhibits a very small SCLS and can be assigned to the formation of two Si—C bonds per dimer. The intensity increase of the Si-C related component closely parallels the progressive decrease of the surface dimer components, as shown by the relative quantitative analysis of the various peak components. Finally, the C 1*s* spectrum shows no evidence for carbide formation.

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*Corresponding author. Fax: +39-06-490324, Email address: r.zanoni@caspur.it

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