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Surface Science 488 (2001) 387–392

SURFACE SCIENCE

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Adsorption of chlorine on the Si(0 0 1)-2 × 1 surface

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Received 21 February 2001; accepted for publication 7 May 2001

Abstract

It is shown that the room-temperature dissociative adsorption of Cl_2 on the Si(0 0 1)-2 × 1 surface results in the bonding of Cl atoms to both the up- and down-dimers which then become symmetrical. At saturation coverage the Si 2p core-level spectra exhibit only a single Cl-induced component with emission twice as strong as that from the up-dimer of the clean surface and with a core-level shift of $+930 \pm 8$ meV. These results were obtained using an analysis in which the intensities of the core-level spectra from the individual Si layers are constrained by an escape depth. It facilitates the identification of components down to the second subsurface layer and yields an inelastic mean free path of 3.4 ± 0.2 Å at a photon energy of 140 eV.

Keywords: Photoelectron spectroscopy; Silicon; Chlorine; Growth; Single crystal epitaxy

Chlorine adsorption on the buckled Si(0 0 1)-2 × 1 surface has been studied extensively in recent years [1–11]. The topics cover both the interface structure and its etching pathway on an atomic scale. It is now commonly understood that Cl_2 adsorbs dissociatively on the surface and forms a strong polar bond with Si without disrupting the 2 × 1 periodicity. Upon annealing, $SiCl_x$ molecules are etched off resulting in the Cl-induced pitting [5,10]. Although a number of reports have attempted to determine the structure of the Cl-covered surface, they have failed to demonstrate conclusively how the chlorine orients on the surface at room temperature (RT). Two different models have been proposed. One states that the two chlorine atoms bond to the up- and down-dimer dangling bonds, making it symmetrical, but with the bond tilted at a 15° angle [5,7,9,11]. However, this traditional view has recently been challenged by the proposal that only the charged up-atom in adjacent dimers receives the chlorine atoms, without disrupting the buckled structure [2,4]. We hereafter denote the first model as the 2SiCl model, and the second the $SiCl_2$ model. Intriguingly, both models claim support from the same set of angle-resolved photoemission data [4,9]. There is insufficient experimental evidences in the literature to resolve this controversy.

Si 2p core-level photoemission has become a touchstone in the study of surface-atom configurations [12–14]. For example, Si 2p core-level

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0039-6028/01/$ - see front matter
PII: S0039-6028(01)01163-3

spectra have been used to determine the dimer symmetry upon the adsorption of alkali metal atoms on Si(0 0 1)-2 × 1 interface [13,15,16]. For Cs, the dimers remain buckled, while for K, they revert to the symmetric orientation. In the latter case, the intensity of the symmetric dimer signal at saturation is twice as strong as that of the up-dimer atom in the clean surface, providing a conclusive demonstration that the buckling has been removed. Ab initio calculation for alkali adsorption has successfully determined the adsorbate geometry, thus giving rise to the double-layer model [7]. The same method of calculation has also been applied to the Cl/Si(0 0 1)-2 × 1 interface and leads to the conclusion that the best configuration is the 2SiCl model. Accordingly, Si 2p cores should exhibit dimer feature similar to those of the case of K adsorption, except for a change of the sign of the surface core-level shift (SCLS) due to the different adsorbate electronegativities; that of K is smaller than that of Si, while that of Cl is larger.

Our recent success of incorporating the inelastic mean free path λ directly in the model function to analyze the Si 2p core-level spectra [13] allows us to relate the relative intensities of the emission from the bulk and any of the individual surface layers to the single parameter λ. In this report we apply this approach to the Cl/Si(0 0 1)-2 × 1 interface. We present novel Si 2p core-level spectra that yield conclusive support to the 2SiCl model.

Photoemission experiments were performed at the Synchrotron Radiation Research Center (SRRC) in Hsinchu, Taiwan, ROC. A Si(1 0 0) surface was preoxidized according to the Ishizaka method and annealed stepwise to 875°C in the photoemission chamber to obtain a clean Si(0 0 1)-2 × 1 surface. The chlorine was obtained by the controlled electrolysis of AgCl in a heated electrochemical cell. The clean Si(0 0 1)-2 × 1 surface was exposed at RT while a current of 10 μA was flowing through the cell. The Cl coverage is characterized by the exposure time. Photoelectrons were collected via an 125 mm hemispherical analyzer (OMICRON Vakuumphysik GmbH) in a UHV chamber with the base pressure better than 2.2×10^{-11} Torr. The pressure during deposition from the well-degassed AgCl cell was no greater than 5×10^{-11} Torr.

Fig. 1 exhibits the Si 2p spectra from a clean Si(0 0 1)-2 × 1 surface and after successively increasing Cl_2 exposure up to saturation monolayer coverage. The data were taken with 140 eV photons and are plotted with the energy referenced to the bulk component B. In the interval from −0.8 to + 0.8 eV, we see a transition with increasing Cl exposure from the characteristic spectrum of the 2 × 1 surface to one approaching the simple spin–orbit spectrum characteristic of bulk Si. Beyond 0.8 eV a new, chlorine-induced Si 2p doublet grows with increasing exposure, as the well-resolved component due to the Si up-dimer atom at −0.5 eV (labeled S(0)u) is attenuated.

The new component (labeled SiCl) has a binding-energy shift of about +0.9 eV for the $2p_{3/2}$ component. The corresponding, well resolved $2p_{1/2}$ component at +1.5 eV makes it easy to follow the intensity of the SiCl contribution. Its growth of intensity follows closely with the rate of reduction of S(0)u, clearly indicating that it is due to the Si surface atoms, which have bonded with Cl atoms. Its intensity increases gradually till saturation

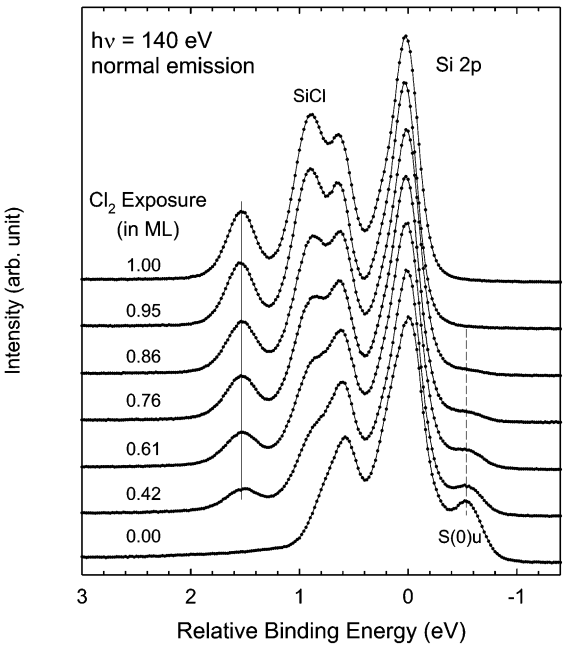

Fig. 1. Si 2p spectra from Si(0 0 1)-2 × 1 from the clean surface and after increasing Cl_2 exposure. The largest exposure is sufficient to produce full monolayer chlorine coverage.

monolayer Cl coverage, ML–Cl, is achieved. Additional exposure does not change the line shape of the 2p cores at all. Moreover, the line shape of the ML–Cl spectrum remains invariant upon annealing up to 420°C. The appearance of only a single chlorine-induced component in Fig. 1 confirms that there is only a single bonding configuration for chlorine at RT deposition.

Using λ as the key adjustable parameter to determine all line intensities in the Si 2p core-level spectrum of the clean Si(0 0 1)-2 × 1 surface, we were able to uniquely identify emission from the first three surface layers and the bulk [13]. This is done by assuming that emission from each atomic layer is layer-wise attenuated according to the formula $S(n) = \xi^n(1-\xi)$, where $\xi = \exp(-d/\lambda\cos\theta)$ and n denotes the nth subsurface layer. θ is the emission angle measured from the surface normal and $d = 1.358$ Å, the Si(1 0 0) layer spacing. Surface-related components are denoted S(0)u for the up-dimer atoms, S(0)d for the down-dimer atoms, S(1) for the first subsurface-layer, S(2)a for the second-subsurface-layer atoms located beneath the dimer rows, and S(2)b for those between the dimer rows. For the clean surface the SCLSs of these components are −510, −14, +189, −200, and +320 meV, respectively. The value of λ is 3.43 ± 0.04 Å at 140-eV photon energy. It will serve as an indicator of the validity of the model function constructed for the analysis of the Si 2p core-level spectra of the Cl-covered surface. This is important because the S(0)d component is hidden under the bulk component, making it impossible to determine directly from its intensity whether Cl bonds to the down-dimer. Misidentification of the fate of S(0)d would lead to an erroneous λ. The method relying on λ-constrained, layerwise intensities consequently provides a criterion to determine whether chlorine bonds to one end or both ends of the dimers.

There is one important concern in the application of this method to overlayer systems; namely, scattering of the photoelectrons by the adsorbate layer. The flat background tail in Fig. 1, even at saturation coverage, indicates that the Cl adsorbate does not provide low-energy loss channels. In general, inelastic scattering by an adsorbate layer will attenuate the photoelectrons from all layers by the same amount and will not modify the relative intensities of the line spectrum. Elastic scattering is more insidious, because it changes the direction of the electrons without changing their energy. This has the effect of falsifying λ (when θ is fixed at its geometrical value). This phenomenon can be detected by comparing spectra taken at different emission angles and was found to be significant in the case of alkali metal atom adsorption [13].

Three representative fitted spectra are shown in Fig. 2. In these fits the lifetime width was fixed at 60 meV. Highly consistent values were obtained for the spin–orbit splitting and the branching ratio, which fall with the range of 600 ± 2 meV and 0.53 ± 0.01, respectively. In these spectra, components S(0)u, S(0)d, and S(2)b are simultaneously reduced in intensity by the fractional ML coverage, while the intensity of the S(2)a component is increased by the same factor. The intensity and SCLS of the S(1) component was not significantly modified by the coverage (see below). The average λ obtained from these spectra is 3.42 ± 0.07 Å.

A model function in which intensities are constrained by λ should fit data for all emission angles with identical parameters, requiring only a change in $\cos\theta$. In order to demonstrate the validity of the model function, we simultaneously fit spectral components with identical positions and widths to the ML–Cl spectra taken at 0° and 60° emission angles. In addition, the changes of line intensity with emission angles are helpful in assigning photoemission lines to specific crystalline layers. An example of a simultaneous fit to the spectra with saturation Cl coverage is shown in Fig. 3, and the schematic atomic configuration is shown in Fig. 4. For this surface, the Si 2p core-level spectrum reveals three surface-related components, S(1), S(2), and SiCl, with SCLSs of +178, ∼0, and +930 meV, respectively. The corresponding Gaussian widths are 296, 198, and 278 meV, excluding the instrumental resolution. The bulk width was also 198 meV. The λ's for the 0° and 60° spectra are 3.17 and 3.54 Å, respectively. The 12% increase of λ at 60° relative to the value at normal emission is due to the effect of elastic scattering, which tends to enhance the signals from the deeper subsurface layers [17] at large emission angle.

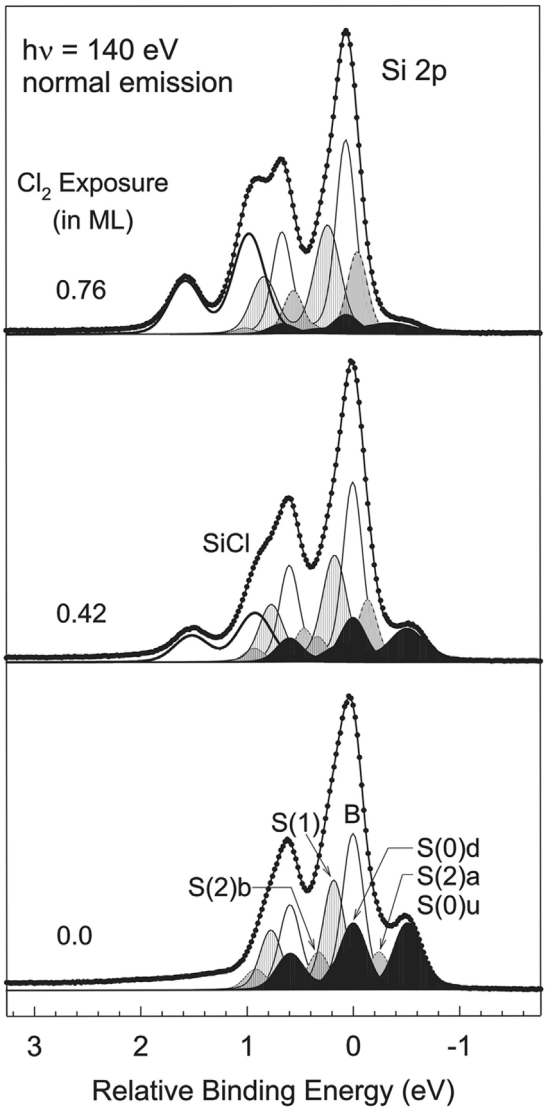

Fig. 2. Results of data analysis (see text) of three representative spectra from Fig. 1. S(0), S(1), and S(2) identify the surface, and first and second subsurface contributions to the spectra.

The fractional intensity of the SiCl component is proportional to the surface attenuation factor of $(1-\xi)$. Hence, atoms that contribute to this component are those bonded directly to chlorine atoms. Further, its intensity is twice that of the up-dimer atom in the clean surface, which indicates that the buckled dimers have reverted to symmetric orientation, as in the case of K adsorption.

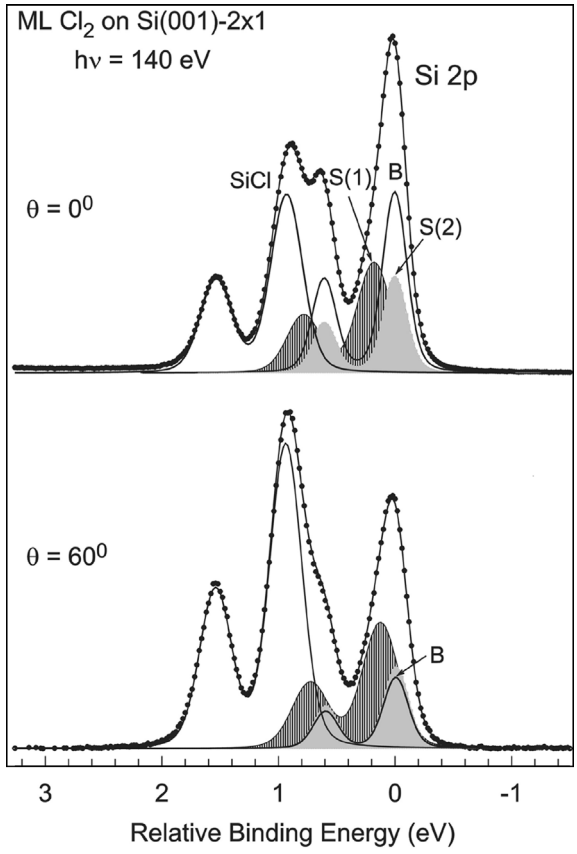

Fig. 3. Result of simultaneous fit to spectra of the Cl-saturated surface taken at 0° and 60° emission angle.

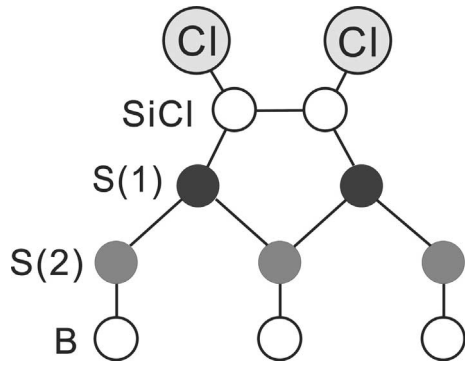

Fig. 4. Schematic side view of the 2SiCl model.

Therefore, the present study definitively supports the 2SiCl model in which dimerization is retained and each surface silicon atom bonds to a single

chlorine atom, saturating all dangling bonds. Note that this conclusion can be qualitatively confirmed by inspection of Fig. 1, where the intensity of the $p_{1/2}$ SiCl component at saturation is seen to be equal to that of the $p_{3/2}$ S(0)u component of the clean surface. This demonstrates that twice as many atoms contribute to SiCl.

The S(1) component is due to atoms in the first subsurface layer, i.e., those directly below the SiCl layer. One of the characteristics of the first subsurface layer is its relative small change in intensity with emission angle [13], which is confirmed in Fig. 3. One of the interesting observations is that the S(1) SCLS is largely unaffected by Cl adsorption and the attendant removal of the buckling, even though the Cl to withdraws charge from the surface Si atoms. This provides confirmation that the dimerization is not destroyed by Cl_2 adsorption. The near identity of the SCLSs of component S(1) in the clean and Cl-saturated surface indicates that chlorine adsorption does not significantly change the charge contour of the S(1) layer from that of the clean surface, a point not mentioned in the calculation [7]. Note that a first subsurface layer, with comparable SCLS, has also been reported for the Sb/Si(0 0 1)-2 × 1 surface with saturation monolayer coverage [12].

The S(2) component is split in energy in the clean Si 2p core-level spectrum. This is due to the fact that there are two classes of atoms in the second subsurface layer, those lying directly below a row of buckled dimers and those between the dimer rows. The atomic model indicates that the strains experienced at those two sites are different. In the ML–Cl covered surface the S(2) component appears as a single line. This indicates that the chlorine adsorption has relaxed the strains in that layer, thereby removing the difference between the S(2) atoms in the two sites. The binding energy of S(2) in the Cl-saturated surface is close to that of the bulk component, as one might expect for a deeper layer. As a result it may be mistaken for the S(0)d feature of the clean surface, which has a comparable binding energy, leading to the erroneous conclusion that chlorine bonds solely to the S(0)u atoms without affecting S(0)d. However this $SiCl_2$ model [2,3] is readily excluded in our study, since modeling that component as S(0)d would overshoot the intensity by a factor of $\exp(2d/\lambda)$, or 235%, which rules it out. Alternately, one might merge S(2) with B due to its small SCLS. However, this approach results in a 25% increase of λ, which is unphysical. Moreover, the sudden removal of S(2) in the ML–Cl spectrum cannot be reconciled with its appearance in the submonolayer spectra (see Fig. 2). The existence of the S(2) component has also been confirmed in alkali adsorption on Si(0 0 1)-2 × 1 [13].

In conclusion, exposure to chlorine at room temperature completely saturates the dangling bond of the Si(0 0 1)-2 × 1 surface and removes the buckling of the surface dimer, but does not disrupt the dimerization. The Si 2p core-level spectra reveal emission from the first three surface layers and the bulk. At saturation the core-level shift range from +930 meV for the surface layer bonded to Cl, to +178 meV in the first subsurface layer, and ~0 meV in the second subsurface layer. Although the SCLS of the second subsurface layer is nearly zero, it must be included in the model function for a proper analysis of the 2p spectra because it is resolved in the clean surface. The method used here could be advantageously applied to obtain a more reliable interpretation of the interface structure of other Si(0 0 1) adsorbate systems and could be extended to other surfaces, as well. Future theoretical calculations for silicon interfaces should consider the perturbation of at least the first three surface layers.

Acknowledgements

Dr. G.K. Wertheim's critical comments are gratefully acknowledged. This project is sponsored by the National Science Council under the contract no. NSC-89-2112-M-213-006.

References

[1] Z. Dohnalek, H. Nishino, N. Kamoshida, J.T. Yates Jr., J. Chem. Phys. 110 (1999) 4009.
[2] J.A. Martín-Gago, E. Roman, M.C. Refolio, J.M. Lopez-Sancho, J. Rubio, L. Hellner, G. Comtet, Surf. Sci. 424 (1999) 82.

[3] I. Lyubinetsky, W.J. Choyke, J.T. Yates Jr., Phys. Rev. B 58 (1998) 7950.
[4] R. Lindsay, P.L. Wincott, G. Thornton, N.M. Harrison, Surf. Sci. 398 (1998) 301.
[5] G.A. de Wijs, A.D. Vita, A. Selloni, Phys. Rev. Lett. 78 (1997) 4877.
[6] M. Chander, D.A. Goetsch, C.M. Aldao, J.H. Weaver, Phys. Rev. B 52 (1995) 8288.
[7] P. Krüger, J. Pollmann, Appl. Phys. A 59 (1994) 487.
[8] J.J. Boland, Science 262 (1993) 1703.
[9] L.S.O. Johansson, R.I.G. Uhrberg, R. Lindsay, P.L. Wincott, G. Thornton, Phys. Rev. B 42 (1990) 9534.
[10] M. Chander, D.A. Goetsch, C.M. Aldao, J.H. Weaver, Phys. Rev. Lett. 74 (1995) 2014.
[11] K. Nakayama, C.M. Aldao, J.H. Weaver, Phys. Rev. Lett. 82 (1999) 568.
[12] P. De Padova, R. Larciprete, C. Quaresima, C. Ottaviani, B. Ressel, P. Perfetti, Phys. Rev. Lett. 81 (1998) 2320.
[13] T.-W. Pi, I.-H. Hong, C.-P. Cheng, G.K. Wertheim, J. Electron Spectrosc. Rel. Phenom. 107 (2000) 163.
[14] T.-W. Pi, R.-T. Wu, C.-P. Ouyang, J.-F. Wen, G.K. Wertheim, Surf. Sci. 461 (2000) L565.
[15] Y.-C. Chao, L.S.O. Johansson, C.J. Karlsson, E. Landemark, R.I.G. Uhrberg. Phys. Rev. B 52 (1995) 2579.
[16] Y.-C. Chao, L.S.O. Johansson, R.I.G. Uhrberg, Phys. Rev. B 54 (1996) 5901.
[17] C.J. Powell, A. Jablonski, I.S. Tilini, S. Tanuma, D.R. Penn, J. Electron Spectrosc. Rel. Phenom. 98–99 (1999) 1.