Core-Level Photoelectron Spectroscopy Probing Local Strain at Silicon Surfaces and Interfaces

Oleg V. Yazyev
Ecole Polytechnique Fédérale de Lausanne (EPFL),
Institute of Chemical Sciences and Engineering, CH-1015 Lausanne, Switzerland

Alfredo Pasquarello
Ecole Polytechnique Fédérale de Lausanne (EPFL),
Institute of Theoretical Physics, CH-1015 Lausanne, Switzerland and
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland

(Dated: March 23, 2022)

Using a first-principles approach, we investigate the origin of the fine structure in Si 2p photoelectron spectra at the Si(100)2×1 surface and at the Si(100)-SiO2 interface. Calculated and measured shifts show very good agreement for both systems. By using maximally localized Wannier functions, we provide an interpretation in which the effects due to the electronegativity of second nearest neighbor atoms and due to the local strain field are distinguished. Hence, in combination with accurate modeling, photoelectron spectroscopy can provide a direct measure of the strain field at the atomic scale.

PACS numbers: 79.60.-i,73.20.-r,68.35.-p

The increasing availability of synchrotron radiation facilities is bearing X-ray photoemission spectra of unprecedented resolution characterizing surfaces and interfaces [1]. The achieved sensitivity is sufficient to distinguish inequivalent subsurface atoms with identically composed first-neighbor shells. Hence, the interpretation of such core-level spectra can no longer be achieved with simple electronegativity arguments, but requires the consideration of the interplay between local strain fields and electronegativity effects of second-nearest neighbors.

These difficulties are strikingly illustrated for the Si(100)2×1 surface and for the technologically relevant Si(100)-SiO2 interface, which have been the objects of numerous highly resolved X-ray photoemission investigations. While the shifts pertaining to the first-layer dimer atoms of the Si(100)2×1 surface have been identified, the other lines appearing in highly resolved Si 2p spectra still lack a consensual assignment [2, 3, 4]. For the Si(100)-SiO2 interface, highly resolved spectra show fine structure in the nonoxidized Si line, with extra components at lower (Siα) and higher binding energy (Siβ) with respect to the Si bulk line [5, 6].

We investigate the origin of the fine structure in Si 2p photoemission spectra at silicon surfaces and interfaces using density functional theory calculations based on pseudopotentials (PPs) and plane waves [7]. To interpret the Si 2p photoelectron spectra at silicon surfaces and interfaces, it is necessary to evaluate core-level shifts with respect to the Si bulk line. Since these shifts mainly result from the relaxation of valence electron states, their accurate determination is possible within a PP scheme, which does not treat core electrons explicitly [8, 9]. We calculated Si 2p shifts including the effect of core-hole relaxation by taking total energy differences between two separate self-consistent calculations. First, the ground-state energy is determined; then the PP of a given Si atom is replaced by another PP which simulates the presence of a screened 2p hole in its core [8].

For the Si(100)-c(4×2) surface we find binding energies of −0.49 eV and 0.02 eV for dimer-up and dimer-down atoms, in good agreement with experimental results [2, 3].

| Theory | Experiment |
|--------|------------|
| Present | Ref. [2] | Ref. [3] | Ref. [4] |
| 1u | -0.49 | -0.49 | -0.49 | -0.50 |
| 1d | 0.02 | 0.06 | 0.06 | 0.06 |
| 2 | -0.01 | | | |
| 3 | -0.14 | -0.21 | -0.20 | -0.21 |
| 4 | -0.26 | | | |
| 3' | 0.24 | 0.22 | 0.20 | 0.23 |
| 4'u | 0.21 | | | |
| 4'd | 0.10 | | | |

FIG. 1: The adopted labeling of Si atoms at the Si(001)-c(4×2) surface. The 4' atoms can be further separated into inequivalent up (4'u) and down (4'd) atoms.
TABLE II: Comparison between calculated and measured Si decomposition in three components.

|            | Theory  | Experiment |
|------------|---------|------------|
| Present    | Ref. [5]| Ref. [6]   |
| α          | -0.21   | -0.25      | -0.22      |
| β          | 0.32    | 0.20       | 0.34       |
| +1         | 0.78    | 1.00       | 0.95       |
| +2         | 1.40    | 1.82       | 1.78       |
| +3         | 2.37    | 2.62       | 2.60       |
| +4         | 3.64    | 3.67       | 3.72       |

The second-layer atoms are found to yield very small shifts (~0.01 eV) while third- and fourth-layer atoms give shifts to both lower (3, 4) and higher binding energies (3′, 4′) with respect to the Si bulk line (Table I). Shifts of deeper layers are negligible.

For the Si(100)-SiO₂ interface, we adopt a model structure which incorporates a realistic transition region [10]. Calculated binding energies are given in Fig. 2 along the direction orthogonal to the interface plane. The binding energies of oxidized Si atoms increase almost linearly with oxidation state [9], and show quantitative agreement with experimental values (Table I). The focus of the present investigation is on nonoxidized Si atoms, which give shifts with a significant spread near the interface. The simulated spectrum associated to these Si atoms could be decomposed into three components (Fig. 2 inset), yielding shifts for the Si^0 and Si^3 lines of ~0.21 eV and 0.32 eV, which also agree with experimental data (Table II).

Binding energy shifts of Si atoms with identically composed first-neighbor shells are caused by electron density displacements due to either the local strain fields or electronegativity effects. We carried out an analysis in terms of maximally localized Wannier functions (MLWFs) [11] in order to distinguish between these two effects [12]. For the Si(100)-c(4×2) surface, we find that, apart from the shifts associated with the dimer atoms, the other shifts mainly result from the local strain induced by the surface reconstruction. For the interface, the Si atoms with second-neighbor O atoms contribute to the Si^α line, while the Si^β line originates from bond elongations of Si atoms without second-neighbor O atoms. From the experimental shift of about 0.3 eV, we infer the occurrence of Si atoms with an average bond length elongation of ~0.05 Å.

In conclusion, we revealed the physical mechanisms underlying the fine structure in Si 2p photoelectron spectra at silicon surfaces and interfaces. Maximally localized Wannier functions offer a powerful tool to identify core-level shifts originating from the electronegativity of farther neighbors. A key result of our work is then that the remaining lines provide an atomic-scale probe of the strain in the structure. This confers to photoelectron spectroscopy a new functionality in addition to the detection of chemical composition.

* Electronic address: oleg.yazyev@epfl.ch

[1] F. J. Himpsel et al., in Proceedings of the International School of Physics Enrico Fermi, edited by M. Campagna and R. Rosei (Elsevier, Amsterdam, 1990), p. 203–236.
[2] E. Landemark et al., Phys. Rev. Lett. 69, 1588 (1992).
[3] P. De Padova et al., Phys. Rev. Lett. 81, 2320 (1998).
[4] H. Koh et al., Phys. Rev. B 67, 073306 (2003).
[5] J. H. Oh et al., Phys. Rev. B 63, 205310 (2001).
[6] S. Dreiner, M. Schürrmann, and C. Westphal, J. Electron Spectrosc. Relat. Phenom. 144-147, 405 (2005).
[7] R. Car and M. Parrinello, Phys. Rev. Lett. 55, 2471 (1985); CPMD version 3.9.1, Copyright IBM Corp 1990-2004, Copyright MPI für Festkörperforschung Stuttgart 1997-2001, http://www.cpmd.org.
[8] E. Pehlke and M. Scheffler, Phys. Rev. Lett. 71, 2338 (1993).
[9] A. Pasquarello, M. S. Hybertsen, and R. Car, Phys. Rev. Lett. 64, 1024 (1995); Phys. Rev. B 53, 10942 (1996).
[10] A. Bongiorno, A. Pasquarello, M. S. Hybertsen, and L. C. Feldman, Phys. Rev. Lett. 90, 186101 (2003).
[11] N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).
[12] O. V. Yazyev and A. Pasquarello, Phys. Rev. Lett. 96, 157601 (2006).

FIG. 2: Calculated Si 2p shifts at the Si(100)-SiO₂ interface along an orthogonal direction to the interface. The Si^α correspond to oxidized Si atoms with n O neighbors (n=1 - ▲, 2 - △, 3 - ▷, 4 - ◤), and are color-coded in the atomistic model. Nonoxidized Si atoms (Si^0) with (α) and without (•) second-neighbor O atoms are distinguished. Inset: simulated spectrum for Si^0 (Gaussian broadened: σ=0.08 eV) and its decomposition in three components.