

Wannier Function Analysis as a Tool for Interpreting Core-Level Photoelectron Spectra

Oleg V. Yazyev*

⁽¹⁾ *Institut de Théorie des Phénomènes Physiques (ITP), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

⁽²⁾ *Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland*

⁽³⁾ *Institute of Chemical Sciences and Engineering (ISIC), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

X-ray photoemission spectroscopy (XPS) involving excitations of core electrons is a versatile experimental technique for the characterization of surfaces and interfaces. However, even in the cases of the Si(100)2×1 surface and technologically relevant Si(100)-SiO₂ interface, which have been the objects of numerous highly resolved XPS investigations, the origin of subsurface XPS signals is not fully understood. 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 2*p* spectra still lack a consensual assignment [1]. For the Si(100)-SiO₂ interface, highly resolved spectra show fine structure in the nonoxidized Si line, with extra components at lower (Si^α) and higher binding energy (Si^β) with respect to the Si bulk line [2]. First principles calculations are able to predict accurately the Si 2*p* core-level binding energies at silicon surfaces and interfaces [3]. Binding energy shifts of the subsurface Si atoms with identically composed first-neighbor shells are caused by electron density displacements due to either the local strain fields or electronegativity effects. In order to distinguish between these two effects, we propose a simple analysis in terms of maximally localized Wannier functions (MLWFs) [4]. Our approach is based on the correlation between the core electron binding energies and the positions of MLWF centers and covalent bond centers [5]. 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. A key result of our work is that XPS spectra in combination with electronic structure calculations and Wannier function analysis provide an atomic-scale probe of the strain in the structure. This confers to photoelectron spectroscopy a new functionality.

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