

Invited

Assigning Core-Level Si 2p Photoemission Shifts at the Si/SiO₂ Interface

Sunghee LEE and Mark M. BANASZAK HOLL

Department of Chemistry, Brown University, Providence, RI 02912

Wei Hsiu HUNG and F. R. McFEELY

IBM T. J. Watson Research Center P.O. Box 218, Yorktown Heights, New York 10598

Soft x-ray photoemission of spherosiloxane cluster derived Si/SiO_x interfaces has allowed the direct assignment of observed Si 2p core-level features to specific chemical moieties. The use of these model interfaces to further understanding of the Si/SiO₂ interface will be discussed.

1. Introduction

The structural characterization of solid/solid interfaces remains a challenging problem. Despite years of study, the structure of the technologically important Si/SiO₂ interface remains a subject for controversy.¹ The task of unraveling the structure of this interface has been complicated by a lack of suitable model systems of known structure capable of serving as reference systems for the analysis of spectroscopic results. The problem is particularly acute for a spectroscopic technique such as soft x-ray photoemission where a mixture of initial state, final state, and cross-section effects must be taken into account before proper assignment of spectroscopic features can be made. In an attempt to overcome this difficulty, we have synthesized interface models using clusters of approximately the same dimension as the interface width (10 Å).

2. Results

Three model interfaces have been constructed by the reaction of H₈Si₈O₁₂, H₁₂Si₁₂O₁₈, or H₁₄Si₁₄O₂₁ with a clean Si(100)-2x1 surface.² The clusters have been found to react with the surface dimers, adding a Si-H bond across the dimer atoms. The soft x-ray photoemission spectrum of the interface derived from the cluster is shown in Fig. 1.

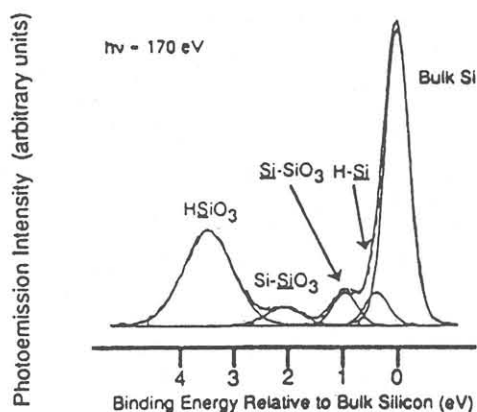


Fig. 1 H₈Si₈O₁₂ Derived Interface

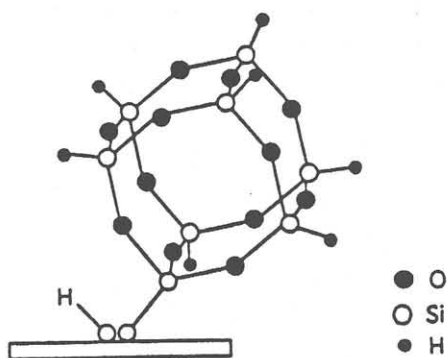


Fig. 2 Schematic of cluster attached to Si(100)

A smooth background has been subtracted from the spectrum and the $2p_{1/2}$ spin-orbit component has been removed, following standard methods, in order to facilitate the apprehension of individual spectral features.³ A schematic picture of the interface is shown in Fig. 2.

Spectra of these model systems provide several key insights regarding the interpretation of photoemission spectra at silicon/silicon oxide interfaces.

First, the assumption that the five peaks observed in the Si 2p core-level spectra of the Si/SiO₂ interface can be assigned to the five formal oxidation states of silicon is demonstrated to be in error. Note that the HSiO₃ fragments ("Si+3") of the cluster are observed at a binding energy of 3.6 eV versus bulk silicon, exactly where "Si+4" is supposed to appear. In addition, the dimer silicon bound to the cluster vertex is shifted to 1.0 eV where "Si+1" atoms are expected, despite being formally "Si+0."

Second, the three different cluster interfaces allow an estimate to be made of the magnitude of final-state core hole stabilization by the bulk silicon. The clusters vary in diameter from 10 Å to 14 Å. Thus, the largest cluster places some HSiO₃ fragments about 4 Å further from the bulk silicon than does the smallest cluster. The total shift observed due to this final state effect is 0.1 eV.

Finally, the model systems provide well-defined chemical species to which photoemission features can be assigned. By making a variety of interface models a library of expected core-level shifts can be developed, facilitating the assignment of interfaces of unknown structure.

¹ *The Physics and Chemistry of SiO₂ and the Si-SiO₂ Interface 2*; Helms, C. R.; Deal, B. E., Ed.; Plenum: New York, 1993.

² S. Lee, S. Maken, M. M. Banaszak Holl, and F. R. McFeely, *J. Am. Chem. Soc.* **116** (1994) 11819.

³ F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, and J. A. Yarmoff, *Phys. Rev. B* **38**, (1988) 6084.