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Si 2p Core-Level Shift Assignments: An Analysis of Recent Experimental and Theoretical Studies

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Core-level Si 2p photoemission spectroscopy has been used extensively to explore the structure and reactivity of the Si/SiO_2 interface, a key component of microelectronic devices. However, beginning in 1993, a series of experiments was published in which the binding energy shifts of Si 2p core-levels were measured in a set of model interfaces derived from the clusters $H_8Si_8O_{12}$, $H_{12}Si_{12}O_{18}$, and $H_{14}Si_{14}O_{21}$ (Figure 1).[1] The photoemission features labeled A, B, C, and D refer to the H-Si, $\underline{Si}$-SiO_3, Si-$\underline{Si}$O_3, and HSiO_3 fragments respectively. The results of these experiments could not be reconciled with the almost universally accepted "formal oxidation" state model generally applied to interpret binding energy shifts at the Si/SO_2 interface.[2,3,4] Recently, another model system derived from the reaction of silatrane ($HSi[CH_2CH_2]_3N$) with Si(100) has given similar results.[5] In addition, it was demonstrated that reactions involving H radicals at the interface could easily be interpreted in the light of the recent cluster-based model studies, but could not be explained using the formal oxidation state model.[6]

These studies have raised many questions regarding the correct interpretation of Si 2p core-level photoemission studies.[7] Recently, several group have addressed the issue using *ab initio* theoretical studies. Kageshima and Tabe have published a series of papers in which the binding energy shifts of the silicon atoms are calculated using a non-empirical self-consistent band method.[8] Similarly, Pasquarello, Hybertson, and Car (PHC) initiated a series of *ab initio* density functional calculations aimed at developing a firmer theoretical understanding of the observed Si 2p binding energy shifts.[9] Both group's calculations clearly support the formal oxidation state model, and at the present, cannot explain the results obtained in the cluster-based model experiments.

The current impasse between theory and experiment on Si 2p core-level shifts extends to all aspects of the interpretation. Current disagreements involve the effect of the initial state or coordination sphere of the silicon, the final state or ability of the matrix to stabilize the positively charged core-hole state, and extrinsic effects such as charging.[2,3,4,7,8,9]

Figure 1. Si 2p core-level spectra of model silicon/silicon oxide interfaces
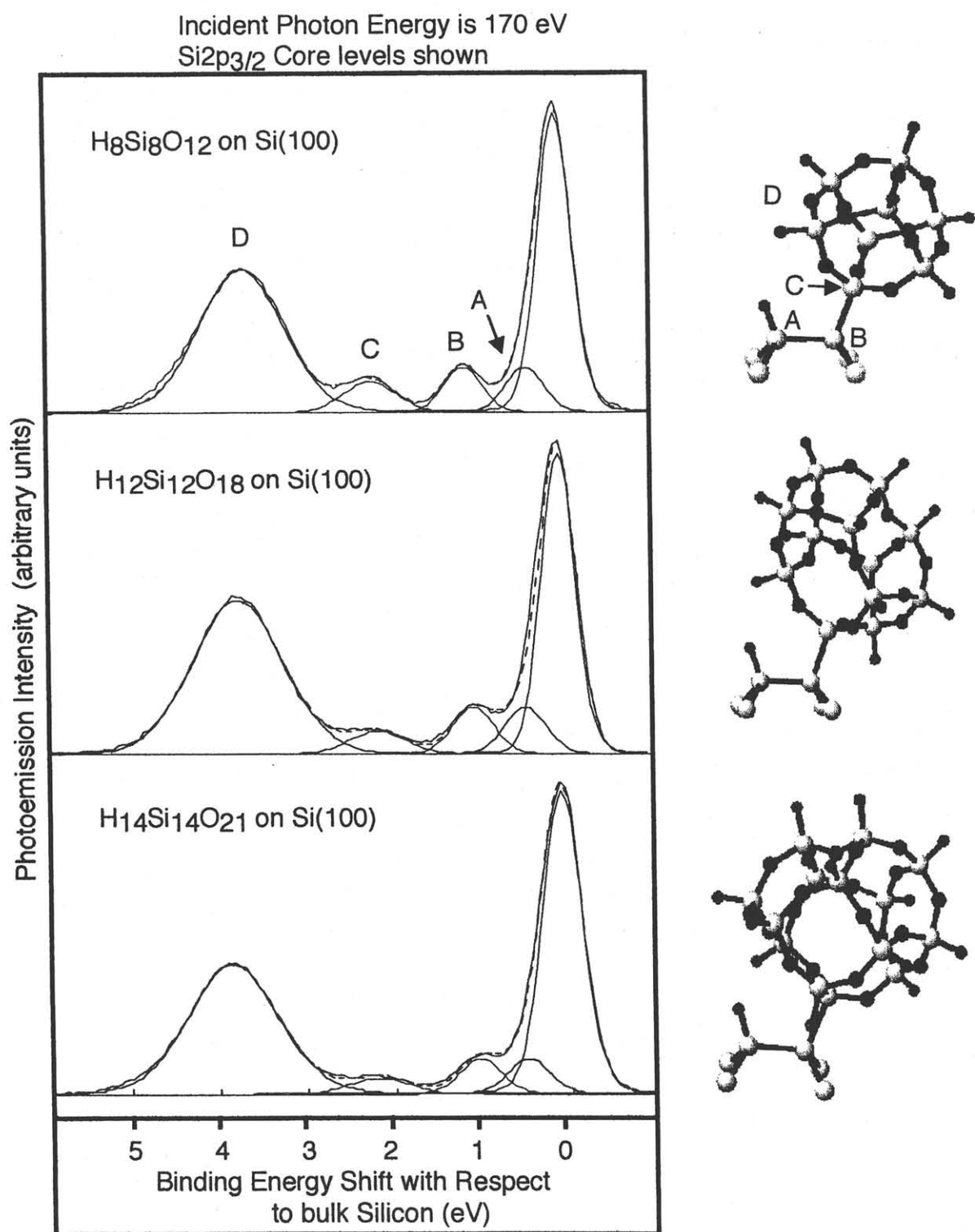
The correct interpretation and understanding of Si 2p core-level spectroscopy is important both in a fundamental sense, and in a practical sense for the interpretation of the structure and reactions taking place at thin dielectric layers. To help facilitate an understanding of the current problems, we will present on overview of experimental and theoretical results published to date. The evidentiary foundations of both the traditional formal oxidation state assignment method and the new approach based on the model interfaces will be discussed. In the context of the discussion, recently obtained results on new silicon oxide cluster systems will be presented. In addition, a recent study in which we have been able to remove initial state effects from consideration, allowing us to directly measure the magnitude of final state and extrinsic effects on the binding energy shift, will be discussed.

[1] a) Lee, S. L.; Makan, S.; Banaszak Holl, M. M.; McFeely, F. R. *J. Am.Chem. Soc.* **1994**, *116*, 11819-11826. b) Banaszak Holl, M. M.; McFeely, F. R. *Phys. Rev. Lett.* **1993**, *71*, 2441-2444.

[2] Banaszak Holl, M. M.; Lee, S.; McFeely, F. R. *Appl. Phys. Lett.* **1994**, *65*, 1097-1099.

[3] As a lead references for the traditional assignment scheme see: a) *The Physics and Chemistry of SiO$_2$ and the Si-SiO$_2$ Interface 2*, edited by C. R. Helms and B. E. Deal (Plenum, New York, 1993).
b) F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, Phys. Rev. B. **38**, 6084 (1988). c) T. Hattori, Critical Rev. Solid State Mat. Sci. **20**, 339 (1995).

[4] Other authors have explored a variety of reasons why strict adherence to a formal oxidation state model may not be desirable : a) F.J. Grunthaner and P.J. Grunthaner, Mater. Sci. Rep. **1**, 65 (1986). b) S. Iwata and A. Ishizaka J. Appl. Phys. **79**, 6653 (1996).

[5] K. Z. Zhang, J. B. Bender, S. Lee, F. R. McFeely, and M. M. Banaszak Holl, accepted Phys. Rev. B, Rapid Comm.

[6] Lee, S.; Banaszak Holl, M. M.; Hung, W. H.; McFeely, F. R. *Appl. Phys. Lett.* **1996**, *68*, 1081-1083.

[7] F. R. McFeely, K. Z. Zhang, M. M. Banaszak Holl, S. Lee, and J. E. Bender IV, accepted J. Vac. Sci. Tech.

[8] a) H. Kageshima and M. Tabe Surf. Sci. **351**, 53 (1996). b) H. Kageshima and M. Tabe in *Control of Semiconductor Interfaces* edited by I. Ohdomari, M. Oshima, and A Hiraki (Elsevier, New York, 1994) p. 227.

[9] a) A. Pasquarello, M. S. Hybertson, and R. Car Phys. Rev. Lett. **74**, 1024 (1995). b) A. Pasquarello, M. S. Hybertson, and R. Car Phys. Rev. B **53**, 10942 (1996).