Comment on "Dimer Charge Asymmetry Determined by Photoemission from Epitaxial Ge on Si(100)-(2×1)"

The explanation of core-level shifts at silicon surfaces continues to be controversial [1-4]. While it is now generally agreed upon that there exist two surface-related components at the Si(100) surface (S at about 0.5 eV above the bulk line and S' about 0.3 eV below), the assignment of these structures has been questioned by Lin, Miller, and Chiang [3]. The early assignment [1,2], worked out most thoroughly in a Letter by Wertheim *et al.* [2], identifies S with the half layer of outer dimer atoms in an asymmetric dimer model, while S' is identified with the half layer of inner dimer atoms (model 1). Lin, Miller, and Chiang [3] assign S to the full layer of all dimer atoms and S' to the layer of subsurface atoms (model 2). The aim of this Comment is to point out that there exists a third possibility for assigning S and S', which avoids shortcomings in both of these assignments: S is assigned to the outer dimer atoms, S' to the subsurface layer, and the inner dimer atoms coincide with the bulk (model 3).

A drawback of model 1 is the observation that S' persists when saturating the Si(100) surface bonds by a monolayer of Ge, as stressed by Lin, Miller, and Chiang [3] and confirmed by Yang *et al.* [4]. Model 2 is inconsistent with the intensities of surface core levels for several well-defined Si surfaces and interfaces, such as H-, As-, and CaF_2-terminated Si (see Ref. [1] and references therein, particularly Refs. [32-34,60]). Basically, the surface feature S on clean Si(100) is only one-half as intense as the surface core levels of adsorbate-terminated Si surfaces. This discrepancy is much larger than the variations introduced by angular acceptance and fitting procedures. For example, the intensity of S reported in Refs. [1-4] is 17%, ≈ 17%, 14%, and 12% of the total, respectively, compared to surface intensities of (32-43)% for adsorbate-terminated Si surfaces [1]. In the same direction points a result from the recent, thorough reexamination of the Ge overlayer method by Yang *et al.* [4], who find S to be only half as intense as S'. Since S' corresponds to a full layer of subsurface atoms in their assignment, it would be natural to assign S to half a layer of surface atoms. The signal from the other half layer then has to be hidden underneath the bulk peak. One can try to verify this hypothesis more directly by converting asymmetric dimers to symmetric dimers via a monovalent adsorbate, such as Cl. Indeed, it is found that the surface core-level intensity of Si(100) terminated by monochloride [5] is almost twice as large as that of the clean dimer feature S. Although one has to be aware of cross-section modifications by electronegative ligands [1] in these experiments, it has been shown that such effects become significant only with three to four ligands, and are undetectable for a single ligand [1]. Assigning S to a full monolayer instead of half a layer in model 2 also changes the escape depth of the photoelectrons by about a factor of 2, which would be difficult to reconcile with our knowledge of escape depths, as pointed out by Wertheim *et al.* [2]. Model 3 does not suffer from these drawbacks, and avoids introducing additional problems, since it combines the strong features of models 1 and 2, i.e., the half layer of outer dimer atoms for S and the layer of subsurface atoms for S', respectively. A similar analysis [5-7] applies to Ge(100).

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[1] For a review on Si surface core-level spectroscopy, see F. J. Himpsel, B. S. Meyerson, F. R. McFeely, J. F. Morar, A. Taleb-Ibrahimi, and J. A. Yarmoff, in *Photoemission and Absorption Spectroscopy of Solids and Interfaces with Synchrotron Radiation,* International School of Physics "Enrico Fermi," Course CVII, edited by M. Campagna and R. Rosei (North-Holland, Amsterdam, 1990), p. 203.

[2] G. K. Wertheim, D. M. Riffe, J. E. Rowe, and P. H. Citrin, Phys. Rev. Lett. **67**, 120 (1991). The intensity of S is obtained from the peak heights, since areas are not quoted.

[3] D.-S. Lin, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **67**, 2187 (1991).

[4] X. Yang, R. Cao, J. Terry, and P. Pianetta, J. Vac. Sci. Technol. (to be published).

[5] J. A. Yarmoff, D. K. Shuh, T. D. Durbin, C. W. Lo, D. A. Lapiano-Smith, F. R. McFeely, and F. J. Himpsel, J. Vac. Sci. Technol. (to be published). The ratio between Cl-covered and clean surface core-level intensities is 1.9 on Si(100); a similar enhancement of the surface core-level intensity has been found previously when terminating Ge(100) by Cl, see R. D. Schnell, F. J. Himpsel, A. Bogen, D. Rieger, and W. Steinmann, Phys. Rev. B **32**, 8052 (1985).

[6] Recently, an analysis in terms of two shifted surface components has been carried out for Ge(100)2×1 and Ge(100)$c(4\times2)$ by G. Le Lay, J. Kanski, P. O. Nilsson, U. O. Karlsson, and K. Hricovini, Phys. Rev. B **45**, 6692 (1992). The uppermost component is assigned to the outer dimer atoms, as in models 1 and 3. The inner dimer atoms are assumed to be part of the lower surface component, as in model 1. Since the lower surface component is almost 3 times as intense as the upper, it is natural to assume that it also contains the subsurface layer, as in model 3. Note that the dimers must be asymmetric for the $c(4\times2)$ reconstruction.

[7] The Ge 3d spectra for Ge atoms on Si(100) are not addressed here, since it is rather speculative to assume that their structural environment and charge asymmetry are similar to that of a pure Si(100) or Ge(100) surface (see the Comment by Rowe and Wertheim [J. E. Rowe and G. K. Wertheim, preceding Comment, Phys. Rev. Lett. **69**, 550 (1992)]).