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

Recently, Lin, Miller, and Chiang [1] presented new data that purport to resolve a long-standing controversy about the interpretation of the dimer-bond reconstruction of Si(100)-(2×1) and Ge(100)-(2×1) surfaces. About ten years ago core-level photoemission [2] was interpreted in terms of two distinct surface sites, although only one shifted peak, labeled S, was observed. The other component was assumed to have a negative shift, resulting in a partially ionic dimer bond in agreement with theoretical predictions. This component at larger binding energy, labeled S', has appeared in a number of experiments [3,4], but Ref. [1] asserts that the new data show that this signal is due only to subsurface atoms. Thus the dimer core-level splitting is so small that the dimers are best described as covalent.

Here we provide an alternative interpretation of the data in Ref. [1], which is more consistent with known details of strain and electronegativity differences that are important in surface reconstruction on Si(100) and Ge(100). We also resolve the factor of 2 difference in electron escape implied by the previous interpretations [2-5] without large, chemically induced changes in core-electron cross sections [1].

Our interpretation emphasizes that at the growth temperature of $\sim 350\,^\circ$C significant coverage dependent alloying takes place. At low coverage the Ge-containing dimers will be predominantly of mixed composition, containing one Si and one Ge atom. The reduced dimer symmetry implies buckling will be in a direction determined jointly by the electronegativity difference and size of Si and Ge. Ge, being slightly more electronegative and larger, will then preferentially become the up atom, which is known to gain electron charge with a core-level shift to smaller binding energy. As a result the Si surface signal S is initially attenuated with Ge deposition, without loss of the S' signal, while the Ge S signal grows, as the data show. Only when all the up atoms have become Ge will it be favorable to replace Si down atoms with Ge.

The identification of S with both dimer atoms and S' (which had not been resolved in earlier work [6] by some of these authors) with the subsurface layer encounters a number of difficulties.

(1) It leads to escape depths which are larger by a factor of 2 than those obtained for Si in well documented cases; see, e.g., the extensive footnote 49 of Ref. [3].

(2) Considerable evidence exists that alloying will occur at relatively low growth temperatures [7-9], smearing the Si-Ge interface. The change in the Si $2p$ spectra in Ref. [1], as the Ge coverage is increased from 2.1 to 4.5 ML (monolayers), argues against pure layerwise growth.

(3) Strain strongly influences the surface structure of mixed Ge-Si composition [10,11]. A study of surface segregation in the equiatomic GeSi alloy [10] shows that compressive strain makes the subsurface layer unfavorable for Ge. This effect should be even more pronounced for the smaller Si lattice, so that the identification of S' with Ge in the second layer is questionable.

(4) The intensities of the S and S' components in their analysis are at variance with those obtained from data with better statistical significance [4]. In particular, the intensity of the S' component, which is equal to or greater than that of S, indicates that it is not exclusively from the subsurface layer.

At first sight, our model appears to require that the coverage calibration differ by a factor of 2 from that reported in Ref. [1], since $\frac{1}{2}$ ML of Ge atoms suffices to cover the surface with mixed Ge-Si dimers. However, entropy considerations and the experimental evidence in Refs. [7-9] and [11] suggest that the mixing of Ge and Si includes deeper layers during the early stages of growth. At about 1 ML of deposited Ge strain effects [9] probably favor the formation of a near-equilibrium distribution of Ge and Si in the first few layers, with comparable amounts of Ge in the surface and deeper layers. The S' signal begins to disappear beyond this coverage, at which only the up atoms of the dimer have been replaced by Ge. By 2 ML of deposited Ge atoms the equilibrium distribution is complete and the dimers consist entirely of Ge in agreement with Figs. 1-3 of Ref. [1].

In summary, we have presented an alternate interpretation of the data reported in Ref. [1] that appears to be more consistent with a wide variety of results than that originally offered.

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