DFT-LDA CALCULATIONS OF SURFACE CORE-LEVEL SHIFTS FOR Si(001), Ge(001), AND Ge ON Si(001) (2×1) SURFACES

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Abstract

Converged DFT-LDA calculations for the silicon, germanium, and germanium on silicon (001) (2×1) surfaces favor buckled dimers over symmetric ones. In this paper we comment on the impact of this calculated buckling on the interpretation of experimentally determined surface core-level photoemission spectra. We find that in case of the Si(001) (2×1) surface, dimer buckling leads to a splitting of $\approx$ 1 eV of core energy eigenvalues while the energy levels of the subsurface atoms occur between these two split lines. The core-level splitting between the "up" and "down" surface dimer atoms is essentially the same for Si dimers on Si, Ge dimers on Ge, and Ge dimers on Si (001) surfaces. Although the calculated core-level splitting is substantial, we argue that it should not be interpreted in terms of ionic bonding. Comparison of the calculated initial state effect of the surface core-level shifts with experiments indicate some interesting screening at the surface, which is different for the two different dimer atoms.

Though the (2×1) reconstruction of clean Si and Ge surfaces is well established, details of the atomic relaxation are still unresolved. A powerful means to study the atomic and electronic structure of these surfaces is core-level photoelectron spectroscopy [1-4]. However, there is a recent controversy [5-7] about the correct assignment of the experimentally observed structures to the respective surface, or subsurface, atoms. Consequently, different authors have arrived at different conclusions with respect to buckling and ionicity of the dimer bond. In this paper we focus on a theoretical investigation of this issue.

The (2×1) reconstruction of the Si and Ge (001) surfaces was first proposed by Schlier and Farnsworth [8] in 1959 and has been discussed by many authors during the following years (see, e.g., references in [10]). Recently it was shown that converged DFT-LDA (Density-Functional Theory in the Local-Density Approximation) calculations yield buckled dimers as the lowest energy surface geometry [9, 10]. In the buckled dimer geometry, one of the dimer atoms (the "up" atom) is moved further out from the bulk than it was in the symmetric dimer geometry, while the other

atom (the "down" atom) is drawn towards the bulk. The energy barrier between the two equivalent equilibrium orientations of the tilted dimer was found to be very low and it was therefore predicted that at room temperature rapid flipping should occur (see Fig. 3 in Ref. [10]). This has indeed been confirmed by recent STM experiments [11].

There are two distinct surface lines present in the core-level photoemission spectrum of the clean Si(001) surface, denoted as S and S'. From a line shape analysis, Wertheim et al. [1] concluded that these two surface components, split by 0.62 eV and located below and above the bulk emission, should be attributed to the "up" (S line) and "down" (S' line) atom of the surface dimer. Therefore, the dimer should be buckled and partially ionic.

On the other hand, Lin et al. [2] have studied the evolution of Si-$2p$ and Ge-$3d$ core-level spectra for silicon surfaces with an increasing coverage of germanium. They find that the intensity of the S silicon line decreases with Ge coverage and vanishes for 1 monolayer (ML) coverage, while the intensity of the S' line is not affected until the coverage with Ge reaches 1 ML and then decreases and vanishes. For Ge coverages smaller than 1 ML only the S line of Ge is present, only for higher coverages the S' line of Ge builds up. From this they concluded that there is no detectable (larger than 0.2 eV [1, 7]) core-level splitting between the dimer atoms. Both dimer atoms contribute to one and the same photoemission peak (S), the second surface feature (S') found at high binding energy is attributed to emission from subsurface atoms.

To compare these experimental results with a theoretical prediction of core-level shifts, we have extracted the effective potential from our total-energy calculations, and averaged it within spheres centered at atomic positions. Differences of this averaged potential between different atoms reflect differences in core-level single-particle binding energies, $\varepsilon^{\text{initial}}$, of the respective atoms. The measured XPS electrons then have the energy

$$E^{\text{XPS}} = \varepsilon^{\text{initial}} + \hbar\omega + E^{\text{relax}},$$

where $\hbar\omega$ is the photon energy and E^{relax} is the energy provided by the many-electron system in order to screen the XPS-created core hole. In a simple picture of the photoemission process, differences in the electronic screening of the core hole between surface and bulk atoms are neglected. Within this assumption, all calculated binding energy differences would be comparable to the splitting between the respective (i.e. bulk and surface) photoemission peaks observed in the core-level spectra. While this procedure might be questionable for the comparison between bulk and surface derived structures [4], it appears reasonable for comparing the core-level energies of the two different dimer atoms. A screening process that discriminates between the "up" and "down" atom of the dimer in such a way that the calculated core-level splitting is exactly cancelled is not known, although it is possible in principle.

For the buckled Si(001)(2×1) surface we find that the core levels of the "up" atom are shifted towards smaller binding energy by about 0.55 eV with respect to the bulk. On the other hand, the core levels of the "down" atom have a binding energy that

is larger by about 0.45 eV than in the bulk. Therefore, the total surface core-level splitting between both dimer atoms amounts to 1 eV. This splitting is reduced to about 0.7 eV in the p(2×2) ordering of buckled dimers, though the buckling angle and the dimer bond length are now slightly larger than in the (2×1) structure. The different atoms in the first and second subsurface layer are also not equivalent, their core-level energies vary within about 0.3 eV range, scattering around the bulk core energies and lying always between the dimer lines. This result is in full agreement with the analysis of Wertheim *et al.* [1].

While our value of the surface core-level splitting is substantial, we do not find any charge transfer, neither to nor from any of the two dimer atoms. (Charge transfer is defined here as the difference in the spherically integrated electron density around atoms.) We thus question the usefulness of the common assumption, to immediately identify core-level splitting with charge transfer. The core-level splitting is caused by the spatially varying "background potential", due to charge redistribution in the interatomic region and the overall decay of the crystal potential towards the vacuum region.

Our results cannot be reconciled with the analysis of Lin *et al.* [2], because we think that a difference in effective screening of more than 0.5 eV between the "up" and "down" dimer atoms is implausible. Our calculations show that Ge dimers on Si give rise to the same splitting of core levels as Ge dimers on Ge. Therefore we cannot understand Lin's Ge $3d$ photoemission spectra if we assume simple layer-by-layer growth of Ge on Si. Rowe *et al.* [5] suggested that Ge atoms initially substitute the "up" Si atoms in surface dimers. This line of reasoning would explain in a natural way the results of Lin's experiment and at the same time would be in agreement with our calculations.

Our results for Si and Ge look quite similar, especially in the respect that in both cases the initial-state energies of the core electrons for the two surface dimer atoms are shifted above and below the bulk level, whereas the experimental energies (which include the final-state screening) show a different result: Experimentally, the surface S and S' lines are found both above the bulk lines in Ge [3, 4] and above and below the bulk level in Si [1, 2]. This corroborates the view that the measurement of binding energy differences between surface and bulk atoms by core-level spectroscopy might be considerably affected by final state screening effects [4]. In fact, the calculated initial-state splitting of the dimer core electrons for Ge is about 0.8 eV, whereas the measured core-level splitting of the S and S' line is 0.4 eV [3].

One possibility to solve this puzzle would be to assume that

$$E_{\text{bulk}}^{\text{relax}} \approx E_4^{\text{relax}} \approx E_3^{\text{relax}} \approx E_1^{\text{relax}} < E_2^{\text{relax}}.$$

Here $E_{\text{bulk}}^{\text{relax}}$ is the final-state screening energy of a core hole in the bulk, and E_i^{relax} are the sreening energies of core-holes at the "up" atom ($i = 1$), the "down" atom ($i = 2$) and the two different second-layer atoms ($i = 3$, $i = 4$). Due to a larger relaxation energy for the "down" atom, the respective photoemission peak could

be shifted in such a way that it coincides with the bulk line (within experimental resolution). If this is true, the S' peak has to be attributed to subsurface atoms (while the S peak is still assigned to the "up" atoms). Recently, based on an analysis of XPS photoemission intensities, Himpsel [6] has suggested such an assignment of experimental photoemission peaks. Additional calculations are under way to test this possibility.

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