Disproportionation Phenomena on Free and Strained Sn/Ge(111) and Sn/Si(111) Surfaces

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Distortions of the √3 × √3 Sn/Ge(111) and Sn/Si(111) surfaces are shown to reflect a disproportionation of an integer pseudocharge, Q, related to the surface band occupancy. A novel understanding of the (3 × 3)-1U (“1 up, 2 down”) and 2U (“2 up, 1 down”) distortions of Sn/Ge(111) is obtained by a theoretical study of the phase diagram under strain. Positive strain keeps the unstrained value Q = 3 but removes distortions. Negative strain attracts pseudocharge from the valence band causing first a (3 × 3)-2U distortion (Q = 4) on both Sn/Ge and Sn/Si, and eventually a (√3 × √3)-3U (“all up”) state with Q = 6. The possibility of a fluctuating phase in unstrained Sn/Si(111) is discussed.

Disproportionation, namely the spontaneous differentiation of initially equivalent sites into states of unlike valence or charge, is well known in solid state chemistry, for example in organic charge-transfer salts and also in transition metal and mixed valence rare earth compounds. Common features are an enlarged unit cell, due to ordering of the disproportionated sites, and the presence of a well defined quantum number (e.g., the valence) that is integer, even when the actual charge imbalance is generally not integer. Here we propose that a disproportionation, driven in this case by a different physics, but equally characterized by integer valences, is at the origin of the well known but only incompletely understood two-dimensional phase transition observed in 1/3 monolayer Sn-covered Ge(111) and Si(111) surfaces. Moreover we present theoretical suggestions that the disproportionated state could be changed, or even removed altogether, by external strain.

The 1/3 monolayer Sn-covered Ge(111) and Si(111) surfaces have received considerable attention since the discovery of a transition from a room-temperature phase with √3 × √3R30° periodicity to a low-temperature 3 × 3 phase, first seen in Pb/Ge(111), then in Sn/Ge(111)2,4, and unsuccessfully searched for in Sn/Si(111).8 The main reason of interest lies in the electronic driving force behind the transition, namely the presence of a half filled surface state, suggested by a two-dimensional surface charge-density wave (SCDW) mechanism. Recent X-ray data show that the transition is accompanied by static freezing and long-range ordering of a 3 × 3 periodic structural distortion, consisting mainly of a “buckling” of Sn adatoms by ~ 0.35 Å along the surface normal. In the distortion, adatoms are generally believed to follow a “1 up, 2 down” (1U) pattern, but there is evidence that under some as yet unclear circumstances a non-negligible portion of the surface distorts with the opposite phase, namely a “2 up, 1 down” (2U) pattern.11,12 The precise mechanism underlying the phase transition has led to debate. While the driving role of the partly filled surface states is unquestioned, the 2D Fermi surface area and nesting properties of Sn/Ge(111) do not fit a 3 × 3 periodicity as expected for SCDWs.11,12 Due to the large electron-electron repulsion, a Mott insulator or a spin-density wave state with negligible distortion could prevail, as in the isoelectronic case of SiC(0001).13 The large observed distortion and the order-disorder nature of the phase transition14,15 however rule out both the weak-coupling SCDW and the Mott insulator. First-principles electronic structure calculations, initially negative,14 later correctly favored the 1U distortion,16,17 with surface electronic bands in agreement with experimental18,19 results.
The calculated energy gain was about 10 meV/adatom, mostly of Jahn-Teller nature. Multi-band and bond-density wave aspects were also pointed out as crucial factors that stabilize the 1U distortion relative to the Mott insulator.12 Surprisingly, these calculations showed no energy gain for a 2U distortion, contrary to the known readiness of 2U to show up experimentally in Sn/Ge(111).19 The order-disorder character of the phase transition, well confirmed by simulations,20 is in agreement with the persistence of a 1U-like Sn 4d core level splitting in nominally undistorted Sn/Ge at high temperature.21 However a puzzling 2U-like persistent core splitting in apparently undistorted Sn/Si17,22 remains unexplained. Finally, substitutional defects play an important role. A Ge (Si) adatom replacing Sn acts as an electron donor in the Sn/Ge (Sn/Si) surface, triggering a local distortion of roughly 2U type.23 However the defect is also likely to exert a negative local strain, effectively squeezing the neighboring Sn adatoms outwards relative to the substrate, so that strain and charge donation apparently conspire. One is eventually led to wonder about the general role of strain, and about whether some of these open questions could be addressed by studying primarily the...
effect of strain on these surfaces. We report here the surprising results of a theoretical study of the Sn/Ge(111) and Sn/Si(111) systems under uniform strain. Besides predicting new strain-driven phase transitions, we find that these surface distortions are in the nature of disproportionation phenomena.

We carried out electronic structure calculations within the gradient corrected local density approximation (GC-LDA) where, in the absence of strain, a stable (3 × 3) 1U distortion was established for the Sn/Ge(111) surface, whereas Sn/Si(111) is still marginally undistorted. We used slab geometries consisting of three Ge (Si) bilayers, a planar 3 × 3 cell with 18 atoms/bilayer, 3 Sn adatoms per cell in the T4 position, and 9 hydrogen atoms saturating the bottom surface of the slab. We employed the PWSCF parallel code with a well checked plane-wave cutoff of 12 Ry and k-summation schemes based on 6 Monkhorst-Pack k-points in the irreducible zone, extended when necessary to 16 and 36 k-points. We strained the slab cell isotropically in the surface plane, by increasing or decreasing its (x, y) sides by up to ±5%, full relaxation allowed along z, the surface normal, so that inside the slab the three dimensional strain tensor was effectively uniaxial. For each strain value, the stable surface geometry was sought for through a series of relaxation runs performed by constraining the value of the adatom buckling \( \Delta z \), (the z-difference between “up” and “down” adatoms) and relaxing all other atomic coordinates, except for the lowest Ge (Si) monolayer, held fixed and bulk-like (or strained), along with the saturating H layer.

Figure 1 summarizes the zero-temperature phase diagram versus strain, the order parameter and energy gain being given for the 3 × 3 distorted state relative to the corresponding fully relaxed \( \sqrt{3} \times \sqrt{3} \) state at the same strain, for both Sn/Ge and Sn/Si. At zero strain, in agreement with experiment and with previous calculations, Sn/Ge is 1U distorted, with \( \Delta z \approx 0.34 \) Å, whereas Sn/Si is 0U (undistorted). Positive strain (in-plane expansion) causes Sn/Ge to lose its distortion, through a 1U-0U transition. By mechanically attracting the Sn adatoms closer to the Ge substrate, strain pushes the half filled dangling bond band upwards in energy towards the middle of the gap. In line with our earlier finding that the 3 × 3 distortion is a multi-band effect in this restored single-band situation the surface reverts to the undistorted \( \sqrt{3} \times \sqrt{3} \) state. The resulting narrow half-filled surface band metallic state should actually be prone to other instabilities. We did check with spin-polarized calculations for a possible antiferromagnetic (Mott-Hubbard) state similar to that of isoelectronic SiC(0001); but up to 5% strain we did not find one, at least in Sn/Ge. Negative strain (in-plane compression) on the contrary pushes the adatoms upwards and that, beyond a critical strain of \( \sim -3\% \), stabilizes a 2U distortion, with a 1U-2U transition in Sn/Ge, and a 0U-2U transition in Sn/Si. Within our approximation, the 2U order parameter \( \Delta z \) at \( \varepsilon = -4\% \) is 0.49 Å with an energy gain with respect to the 0U configuration of 39.5 meV/atom in Sn/Ge, and 0.4 Å with an energy gain of 30 meV/atom in Sn/Si. In both cases the energy gain is suggestive of a 2U-disordered transition at relatively large critical temperature. At still larger negative strains \( \sim -5\% \), all adatoms are finally forced up, with a 2U-3U transition, and an optimal 3U state for both Sn/Ge, and Sn/Si. This state should be seen as uniformly distorted – same symmetry as the “0U” undistorted \( \sqrt{3} \times \sqrt{3} \) state, but with quite different physics as we shall see.

Closer examination of the distorted geometries reveals a striking feature: the Sn adatoms’ height above the substrate is bimodal, approximately quantized for all strains and states. A given Sn adatom can be either U or D, but not in between. This is reminiscent of static mixed valence, or disproportionated states, where an individual ion site is endowed with a choice between two integer valence states, the overall proportion between them controlled by a chemical potential. The valence state can either fluctuate dynamically with time, or be frozen in a static regular or irregular spatial pattern. In that case, all local properties, including the surrounding ion geometry, display a bimodal distribution. We found, by analysing the electronic structure, that in our case the role of effective valence is played by a surface state occupancy \( q \), which is 2 in all U adatoms, 1 in all adatoms of the undistorted (“0U”) phase, 0.5 in D adatoms of the 1U phase of Sn/Ge, and zero in the D adatoms of 2U phases. This conclusion was established with the help of a separate Sn/Ge calculation, where a single Sn adatom was confined in the 3 × 3 slab cell. The six remaining first-layer Ge atoms were saturated by six hydrogens, effectively decoupling the Sn adatom from its replicas. When a variable electron number was introduced with a net electron excess between −1 and +1 (charge neutrality obtained through a matching uniform positive background), it was found that the population change was restricted to the Sn dangling bond surface state, its occupancy \( q \) correspondingly varying from zero to 2. For each \( q \) value, the total energy was minimized as a function of adatom height \( z \) over the substrate, and the optimal \( z_0(q) \) was determined. The calculations were repeated for various strains and the results reported in Fig. 2 (dashed lines). The comparison of the calculated \( z_0(q) \)’s with the individual adatom heights previously calculated in the 0U, 1U, 2U and 3U stable phases of Sn/Ge is striking and provides a strong evidence of quantization of the individual \( q_i \)’s at four and only four heigh values, corresponding within a few percent error to the occupancies 2, 1, 1/2, and 0 indicated above. These quantized charges \( q_i \) are actually pseudocharges, not to be confused with real, physical electron charges on the adatom. An approximate Mulliken analysis of valence charges showed in fact that the actual charge redistribution among adatoms is always less than 0.1 e. A negligible redistribution of true, total charge is also in good accord with the observed 4d Sn core level splitting, consisting of one deep and one shallow levels in a 1:2 intensity proportion, attributable to U and
D adatoms respectively. Had the true charge imbalance even only resembled that of the pseudocharges, 2 and 0.5 for U and D adatoms, respectively, the sign of the splitting should have been the opposite, and its magnitude much larger. We calculated the magnitude of the core level splitting between U and D adatoms in Sn/Ge-1U in the final-state LDA approximation, and obtained 0.20 eV, in reasonable agreement with 0.32 eV, observed both in (3 × 3)-1U and for the high temperature \(\sqrt{3} \times \sqrt{3}\) phase of Sn/Ge(111). The split core level intensity ratio should be instead 2:1 for a 2U distorted surface, the U and D adatoms being now in that proportion, opposite to the 1:2 of the 1U case. Repeating our core level calculation for the −3% strained Sn/Si(111) (3 × 3)-2U surface we obtained a Sn 4d splitting of −0.20 eV, in qualitative agreement with \(\sim −0.4\) eV observed on the nominally undistorted Sn/Si(111) \(\sqrt{3} \times \sqrt{3}\) surface. We shall return to this point below.

We are now in a position to address directly the physics behind the pseudocharge and its disproportionation, with and without strain, in connection with the electronic structure. In the 0U \(\sqrt{3} \times \sqrt{3}\) phases, the surface state band is isolated inside the gap, each adatom contributing one electron to it, whence \(q_i = 1\) and \(Q = \Sigma q_i = 3\). This is an undistorted metal state, at least within GCLDA. In the (3 × 3)-1U phase, the surface band hybridizes much more with the valence bands, especially with the Ge-Ge bonding state directly underneath the adatom.

There is still on average one electron/adatom; however the total pseudocharge \(Q = 3\) per cell disproportionates, \(q = 2\) electrons now filling the U adatom’s dangling bond (Figure 3a), the remaining one shared between the other two D adatoms, each with \(q = 0.5\). The onset of the (3 × 3)-1U ground state in Sn/Ge is thus favored by the small Ge bandgap, and by the consequent energy proximity of the surface band to bulk valence bands. That is consistent with the absence of distortion in Sn/Si(111), and in SiC(0001), where the surface band is more isolated in the wider bandgap. In the strain-induced 2U phase, both U adatoms have \(q = 2\), while D has \(q = 0\). The total pseudocharge \(Q = 4\) now: one extra electron has been drawn from bulk valence bands into the surface band. For strain values in the 2U range, the surface bands (Figure 3b) drop in fact enough in energy to overlap the bulk valence bands, now slightly above \(E_F\). Furthermore, because the difference \(q_U−q_D\) is greater than in the 1U phase (2 compared to 1.5), the optimal distortion is larger (0.49 Å compared to 0.34 Å in Sn/Ge). The 2U distortion amplitudes and energy gains are correspondingly smaller in the stiffer, wide-gapped Sn/Si. Finally, in the \(\sqrt{3} \times \sqrt{3}\)-3U phase, all adatoms are equivalent with \(q = 2\). The surface band lies entirely below \(E_F\), and 3 electrons are transferred from bulk to surface, so that \(Q = 6\). In this sense, the 3U state is fundamentally different from the 0U state, despite its sharing the same symmetry. In all these distorted states, the surface state band breaks up into narrow adatom-localized levels. Their filling and emptying leads to a Jahn-Teller-like energy gain, and that explains the quantization of the pseudocharge \(q\). Negative strain acts as a chemical potential, and disproportionation arises out of the necessity to distribute an increasing electron number through integer surface state occupancies. In chemical terms, U adatoms could perhaps be compared with “tetravalent” Sn, D to “divalent” Sn.

These results and predictions should be amenable to experimental test, particularly if the strains required to provoke the transitions could realistically be introduced, e.g., by heteroepitaxy. Even if our calculated critical strain values are probably affected by systematic errors of order 1–2%, connected with lattice parameter errors and with imperfect handling of incipient strong correlations by the density functional calculation, the strain-induced sequence of transitions seems inescapable. Among the phenomena that are already observed, the 2U patches reported on Sn/Ge seem now very likely to be induced by some local strain. The puzzling 2U core level signature of nominally unstrained Sn/Si is likely to be due to a dynamical, fluctuating 2U state. Assuming in fact a 0U-2U zero-temperature, classical transition to occur in reality at some small positive strain (instead of a small negative strain as in the GC-LDA calculation), the long range order could simply be destroyed by thermal fluctuations, still leaving a local 2U distorted structure.

Of additional interest is the possibility of quantum mechanical fluctuating states, analogous to dynamical mixed valence. Close to the critical strain values separating two classical distortion states, such as 0U-1U, 0U-2U, 1U-2U, 2U-3U, tunneling across low barriers could lead to quantum melting of the classical long-range order. This kind of polaronic state could entail the exotic but real possibility of surface state superconductivity when, as the case for 0U-2U, the pseudocharge fluctuation takes place in units of two, thus realizing a bipolaron state. The large distortions involved suggest however that this novel strong-coupling surface polaronic metals and bipolaronic superconductors might be attainable only at very low temperatures.

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FIG. 1. Energy gained by the (3×3)-1U and 2U distortions against the relaxed undistorted √3 × √3 phase, as a function of strain. (a) Sn/Ge(111); (b) Sn/Si(111).

FIG. 2. Adatom height z as a function of strain in Sn/Ge(111). Open squares: “down” adatoms; filled squares: “up” adatoms; dashed lines: optimal height of an isolated charged adatom (see text).

FIG. 3. Electron bands of Sn/Ge(111) 3 × 3. (a) 1U, zero strain; (b) 2U, strain −4%.