Giant effect of electron and hole donation on Sn/Ge(111) and Sn/Si(111) surfaces

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(Received 4 August 2004; published 23 December 2004)

The charge inhomogeneity at the overlayer and the origin of the two Sn $4d$ core-level components present at the Sn-covered Ge(111) and Si(111) α phases have been investigated. We probe comparatively by high-resolution core-level spectroscopy, the prototypical tin on silicon or germanium (111) systems upon dosing these with a donor (potassium) and an acceptor (iodine). Giant effects are noticed which reveal the bimodal behavior of two types of adatoms with two well-defined, but inequivalently charged, states. We find that the relative weights of these two distinctive Sn atoms, in inverse proportions on Si(111) and Ge(111), can be extrinsically and completely tuned by electron or hole donation. These results shed light on the phase-transition driving force for Sn/Ge(111) and Sn/Si(111) α phases.

During the last few years, the symmetry lowering induced by two-dimensional (2D) phase transitions has been the subject of numerous studies. In particular, the room-temperature (RT) phase observed in one-third of a monolayer of Sn-covered Ge(111) surfaces, ideally containing one threefold backbonded Sn atom (see Fig. 1, top) with α-$(\sqrt{3} \times \sqrt{3})$ periodicity shows a low-temperature phase (LT) with a 3×3 periodicity as the temperature is decreased below 200 K. Such a reversible phase transition has been reported first for Pb/Ge(111),[1] then for Sn/Ge(111)[2] and Pb/Si(111),[3] but astonishingly it has not been found with Sn/Si(111), even when this surface was cooled down to 6 K.[4] Despite extensive stimulating studies, no consensus has been achieved concerning the driving force of this type of low-dimensional phase transition (for a complete review see Petersen *et al.*[5,6]) and its absence on Si(111).[7]

A key point to understanding these phenomena is linked to the elucidation of the origin of the two components that constitute the Sn $4d$ shallow core levels (CLs) on Si and Ge(111), and the reason for their interchanged intensities, because of their implications on the structural and/or charge inhomogeneity at the overlayer. In fact, the existence of two components in the Sn $4d$ CL with different binding energies (BEs) can be related to a single chemical species surrounded by two distinctive electronic environments. However, screening effects may also affect strongly the absolute binding-energy values, within a final-state scenario, which could make difficult a direct photoemission spectra interpretation. Recently, both the influence of defects and local strain have been extensively investigated experimentally[8–10] and theoretically.[9,11] It seems that these two effects, namely, the charge donation and the local distortion, work against each other.

In this context, one may speculate about the general role of the charge distribution at the overlayer and how it will affect the structural environment of these distinct Sn $4d$ CL components. On this basis, the shallow Sn CLs could be analyzed through selective adsorption in order to shed light on the assignment of the Sn $4d$ spectral features. In the past,

these types of doping and/or coadsorption experiments have been frequently used to identify the atomic origin of inequivalent spectral contributions, as it is typically the case of the Si $2p$ CL in the complex Si(111)(7×7) surface reconstruction.[12,13]

In the present work, we report a giant effect of electron and hole donation on the well-defined spectroscopic signatures of the α-$\sqrt{3}$ phases at the Sn/Ge and Sn/Si surfaces, following potassium and iodine adsorption, respectively. Further, we demonstrate that all the Sn-covered Ge and Si phases studied present a bimodal behavior, which differentiates two inequivalently charged Sn sites. We find, that by a giant effect of electron/hole donation the population of these two differently charged sites can be strictly and reversibly tuned.

The experiments were performed in an ultrahigh vacuum chamber equipped with an angle-resolving hemispherical analyzer receiving synchrotron light from the SU8 beam line of the Super-Aco storage ring in Orsay at the Spanish-French station. For more details for the sample preparation and the characteristics of our apparatus we refer the reader to Refs. 14–17. In Fig. 1 we present the Sn $4d$ CL spectra measured at RT for the initial α-$\sqrt{3}$ phases obtained at 1/3 ML of Sn on Si(111) and Ge(111). As previously reported by several groups, the Sn $4d$ CL spectra measured at LT for both substrates are essentially the same as at RT (not shown).[6,15,18–20] The corresponding Sn $4d$ CLs for the Si(111) $\sqrt{3} \times \sqrt{3}$ "mosaic" phase and the Ge(111)2×2 phase, which are formed prior to the $(\sqrt{3} \times \sqrt{3})\alpha$ phases, are also displayed. As already well established, the Sn $4d$ CLs of these two last phases are composed mainly of a single (spin-orbit splitted) component. However, as the mosaic phase is less ordered, its CL peaks are rather broad. For the "mosaic" phase on Si(111), the main spin-orbit doublet is located at lower BE than for the 2×2 phase on Ge(111) by $\sim$0.45 eV (see Fig. 1, bottom).[6,15,18–20] The position of the high binding-energy (HBE) components (designated as *B* in the figure) corresponds to the CL position of the 2×2 phase, while that of the low binding-energy (LBE) ones (labeled as *A*) matches
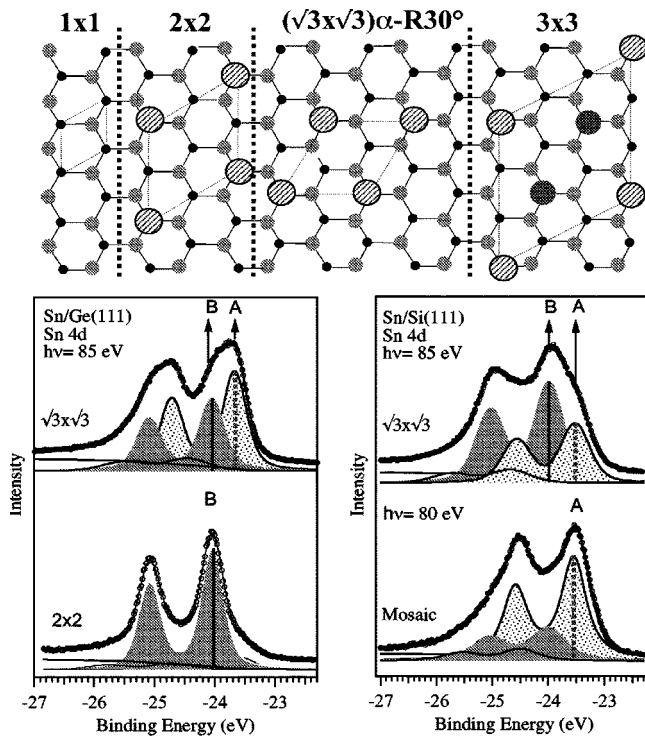
FIG. 1. Top: Ball model of the (1×1), (2×2), $(\sqrt{3} \times \sqrt{3})\alpha$, and (3×3) phases formed by Sn adatoms on Si(111) or Ge(111). Black and gray circles correspond to atoms from the second and first substrates layer, respectively. Dashed circles represent adsorbate Sn atoms. Unit cells are overimposed, representing the symmetry of the Sn overlayers. The (1×1) unit cell is depicted using Si substrate atoms, because it is equal to the (2×2)-Sn structure. Bottom: Sn $4d$ core levels and their decompositions from the adatom surface phases formed by Sn on Si(111) and Ge(111) surfaces. From bottom to top and left to right: Ge(111)(2×2), Ge(111)$(\sqrt{3} \times \sqrt{3})\alpha$, Si(111)$(\sqrt{3} \times \sqrt{3})$ "mosaic," and Si(111)$(\sqrt{3} \times \sqrt{3})\alpha$.

that of the $(\sqrt{3} \times \sqrt{3})$ "mosaic" phase. From the α-$\sqrt{3}$ phases for silicon and germanium substrates, the CL spectra are fitted with two components at almost the same binding energies in both cases, but with an interchanged HBE/LBE intensity ratio, that is 2:1 for Si(111) and 1:2 for Ge(111). Ball models representing the 2×2, $(\sqrt{3} \times \sqrt{3})\alpha$ and 3×3 structures are displayed at the top of Fig. 1. We can summarize the fitting parameters as follows: For Ge(111)(2×2) the Gaussian widths correspond to $B:0.31$ and $C:0.50$ eV. A Lorentzian width of 0.24, a spin-orbit split of 1.04 eV, and an asymmetric index of 0.05 in the Ge(111)$(\sqrt{3} \times \sqrt{3})\alpha$ phase, the Gaussian widths are $A:0.30$, $B:0.31$, and $C:0.50$ eV. A Lorentzian width of 0.24, a spin-orbit split of 1.04 eV, a branching ratio of 0.72, and an asymmetric index of 0.05. For the Si(111)$(\sqrt{3} \times \sqrt{3})$ "mosaic" phase the Gaussian width for $A:0.39$ and $C:0.65$ eV. A Lorentzian width of 0.2, a spin-orbit split of 1.04 eV, and an asymmetric index of 0.07, and last, in the Si(111) $(\sqrt{3} \times \sqrt{3})\alpha$ the Gaussian widths are $A:0.39$, $B:0.42$, and $C:0.65$ eV. A Lorentzian width of 0.2, a spin-orbit split of 1.04 eV, a branching ratio of 0.65, and an asymmetric index of 0.07. For simplicity, peak C, with a very small intensity and a BE of 24.5 eV, is not labeled in the figure.
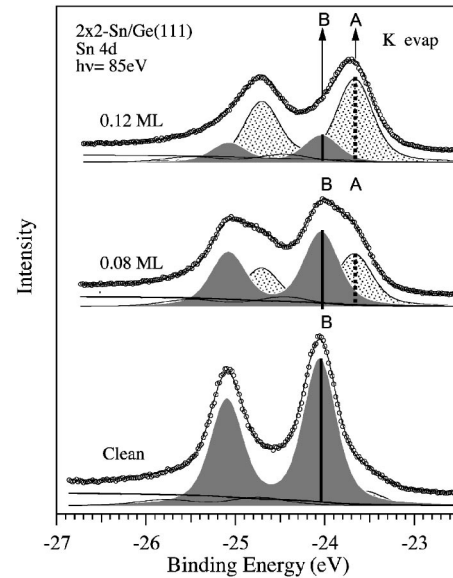

FIG. 2. Sn $4d$ core levels and their decompositions from the 2 $\times 2$ adatom surface phase formed on Ge(111) ($h\nu=85$ eV) at increasing K doses deposited at RT from top to bottom: clean Sn/Ge(111)(2×2), with $\sim$0.08 ML K and $\sim$0.12 ML K coverage.

In order to illustrate first, the electron doping effect in a simple, single-component CL phase, we investigate the impact of adsorbing a strongly electropositive element, potassium, on the 2×2 phase on Ge(111). Surprisingly, while the Ge $3d$ CL is basically unaffected, the effect on the Sn $4d$ CL is spectacular (see Fig. 2). A new component at LBE is evidenced, whose intensity increases with the amount of electron donation provided by the potassium adsorbates at the same BE as the "A" component of the α-$\sqrt{3}$ phases, as well as the "mosaic" Sn/Si phase. Hence, when K is deposited, the intensity of the HBE component is strongly attenuated, while the new LBE component, accordingly increases its intensity. At intermediate K dosing (middle frame in Fig. 2), we are able to stabilize a two-component Sn $4d$ CL line shape, which typically ressembles that observed at the nominal Si α phase (see Fig. 1, middle part). With further dosing we reach, and even pass (top frame), a situation similar to that of the Ge α-$\sqrt{3}$ phase. Next, a corresponding experiment was carried out, upon dosing also with electrons (again K deposition) the "mosaic" phase on Si(111). Remarkably, no significant effect was noticed. We have completed the picture by testing comparatively the influence of electron and hole doping on the Sn/Ge(111) α-$\sqrt{3}$ structure by using, respectively, potassium adsorption on the one hand and iodine (a strongly electronegative species) adsorption on the other hand.

In Figs. 3(a) and 3(b), we observe that the respective effects are also spectacular and perfectly complementary. As the potassium adsorption progresses, while the Ge $3d$ CL is basically unaffected (not shown), instead the impact on the Sn $4d$ CL is drastic. In order to check if this effect is strictly linked to charge donation, we carried out a symmetric experiment, where instead of donating charge we extract charge upon providing holes to the surface by using iodine adsorption. In Fig. 3(c), the characteristic spectral features of the
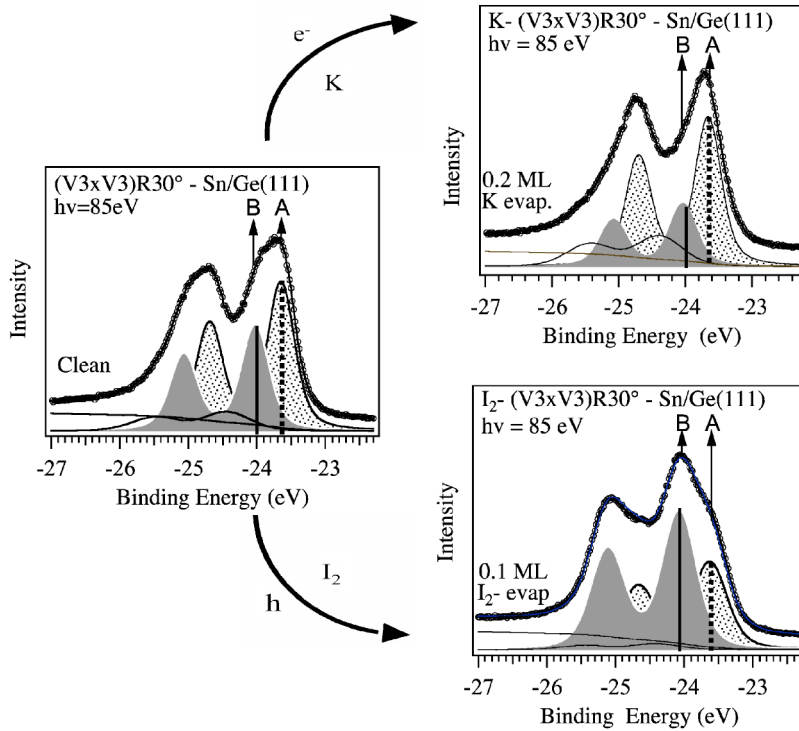
FIG. 3. Sn $4d$ core-level changes on the Ge(111)($\sqrt{3} \times \sqrt{3}$)α, as we dose it with K or I_2, respectively. The results of the fits of the Sn $4d$ CLs are also displayed.

iodine adsorption on the α-$\sqrt{3}$ of Sn/Ge(111) is indicated. In this case, the initially two-component Sn $4d$ CLs with a ~1:2 HBE/LBE component ratio is reversed toward a new balance, approaching with increasing doses to a 2:1 ratio, while the energy position of the two HBE and LBE components did not change, remarkably meeting a situation looking quite similar to that found for the Sn/Si(111) α-$\sqrt{3}$ phase.

Finally, we illustrate in Fig. 4 the electron and hole doping effects on the α-$\sqrt{3}$ phase of Sn/Si(111). The experiment has been carried out in a sequential way; that is, firstly, the electron donation was investigated by K adsorption and in a second step, on the same interface, iodine was deposited in addition. As previously observed on Ge(111), the two-component Sn $4d$ spectrum on Si(111) was transformed after the first step of the experiment (K adsorption) into essentially an almost single component located at the LBE position. This is followed, at the next steps, upon iodine adsorption, by a drastic suppression of the LBE component and a corresponding increase of the HBE one. Hence, besides the fact that the two-component Sn $4d$ CLs in the Sn/Si(111) system follow strictly the same behavior as that in the Sn/Ge(111) one, remarkably we find furthermore that the process is fully reversible.

To summarize, we would like to stress that in all investigated phases the consequence of electron/hole doping results in a bimodal behavior of the shallow Sn $4d$ CL spectral features, meaning that only two energetic positions of the two-component CLs are met: a HBE component and a LBE one. No intermediate position is ever determined upon doping either with holes or electrons. Doping with electrons transfers weight from HBE to LBE (that is from the B to the A component), while conversely, doping with holes transfers weight from LBE to HBE (from A to B).

These results agree nicely with the latest theoretical results predicting a disproportionation phenomena on Sn-covered Ge(111) and Si(111) surfaces.[11] By using the gradient corrected local-density approximation (GC-LDA), Tosatti's group has found for both systems that the ground state depending on the surface strain can be characterized by a disproportioned state with two distinctive sites of unlike valence or charge.[21] In the present work, the spontaneous charge disproportionation is extrinsically tuned by electron or hole donation of appropriate coadsorbed atoms.
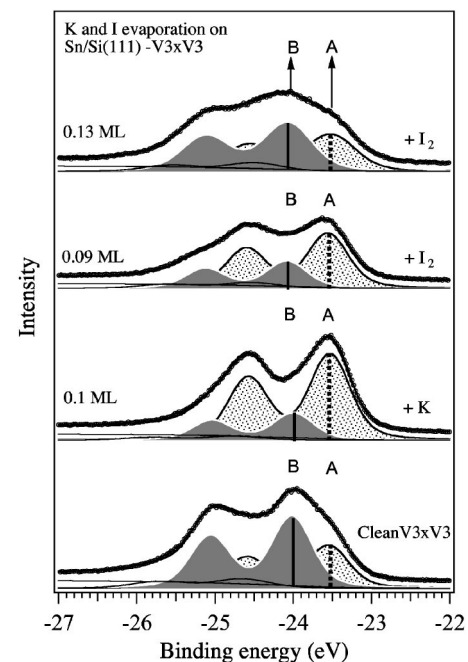

FIG. 4. Sn $4d$ core-levels evolution on Si(111)($\sqrt{3} \times \sqrt{3}$)α by deposition of ~0.1 ML K and after adding ~0.09 ML I_2, and I_2 coverage. The results of the fits of the Sn $4d$ CLs are also displayed.

To illustrate this mechanism let us consider only a local fraction of the surface including an Sn atom and four Ge atoms underneath, affected by a close electron or hole coadsorbed donor. The neutral group ideally represents a small cluster of the unreconstructed α-$\sqrt{3}$ phases, characterized by a half filled dangling bond band. Reference 11 shows that at the minimum of the surface band (around the M point in k space), the wave function presents a well-defined antibonding character between the adatom and the substrate (for Sn/Ge or Sn/Si). Consequently, when the dangling bond is filled by electron donation from, i.e., potassium, all Sn-Ge bonds weaken, increasing the adatom-surface distance, favoring the existence of "up" Sn adatoms. This effect is clearly observed by a remarkable intensity increase of the "A" component. On the contrary, if the dangling bond is emptied by hole donation induced by iodine coadsorption, accordingly with the wave-function antibonding character, the Sn-Ge bonds strengthen stabilizing a down Sn adatom. In this case a notable intensity increase of the "B" component has been recorded in all investigated phases.

Consequently, our results can be interpreted as if the relative intensities and energetic positions of the two components of the Sn $4d$ CLs are dictated by the respective "up" and "down" population of the Sn adatoms. Hence, this may suggest that the unique difference between the 1:2 and 2:1 intensity ratio Sn $4d$ CLs for the Ge(111) and Si(111) α-$\sqrt{3}$ phases, corresponds to "2 up, 1 down" and "1 up, 2 down" overlayer structures, respectively. If this interpretation is confirmed, its compatibility with the available STM results published by Melechko *et al.* in Ref. 8 may be reviewed. Also, the 0.35 A "buckling" of the Sn overlayer in the Sn/Ge(111),[22,23] may be partially responsible of the measured $4d$ core-level splitting. Summing up, the measured binding-energy splitting may be the consequence of a surface pseudocharge redistribution together with a distinctive structural environment associated to "up" and "down" adatoms. That is also consistent with the absence of the (3 $\times$3)Sn/Si(111) phase at low temperature, which can be rationalized assuming that the characteristic temperature of the order-disorder transition in this system, if it exists, should be even lower than the temperature range investigated so far. Although, evidently to ensure this scenario a detailed structural study of the α-$\sqrt{3}$ Sn/Si(111) phase should confirm that a distorted overlayer characterizes this surface at room and low temperatures.

In summary, we have found the link between the charge doping and the respective Sn $4d$ CLs. We emphasize the key role of the surface charge redistribution on the stabilization of the buckled ground state, even though the core-level shift cannot be only associated to a charge imbalance. Evidently, $4d$ core-level electrons are energetically quite far away from the Fermi energy, so it is not obvious if this charge redistribution has a delocalized or a rather localized character. On the other hand, it has been probed that these shadow core levels are very sensitive to any structural change or pseudocharge redistribution. Hence, the drastic CL modifications induced by doping could be certainly compatible with a surface charge disproportionation, which may have only a partial degree of charge localization.

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