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# Adatom and rest-atom contributions in Ge(111)$c(2\times8)$ and Ge(111)-Sn($7\times7$) core-level spectra

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We have identified the adatom contribution in the Ge 3*d* core-level spectra from the clean Ge(111)$c(2\times8)$ surface, shifted 0.17 eV to higher binding energy compared to the bulk. This adatom component vanishes in the Ge(111)-Sn($7\times7$) surface core-level spectra where Sn occupies the adatom site. Moreover we report the observation of an earlier proposed difference between the rest atoms in the $c(2\times8)$ structure, and also a shift to lower binding energy for the rest atoms in both structures studied.

The atomic origin of surface-shifted contributions in core-level spectra from the clean Ge(111)$c(2\times8)$ and Si(111)($7\times7$) surfaces is, although the geometrical structure models are widely accepted, still an open question. Albeit the Si(111)($7\times7$) surface is one of the most well-studied surfaces there still remains some confusion in the literature over the assignment of the so-called $S_2$ component to either adatom[1] or rest-atom[2] emission.

Earlier core-level spectroscopy studies on the clean Ge(111)$c(2\times8)$ surface have shown two surface-shifted components on the low-binding-energy side relative to the bulk binding energy.[3-5] These shifted peaks were interpreted as corresponding to rest atoms and a mixed contribution from adatoms and the second-layer atoms binding to adatoms. The weaker peak with the larger shift ($S_2'$) is normally attributed to rest-atom emission,[3-5] while the stronger peak ($S_1'$) was assigned to both adatoms and second-layer atoms binding to adatoms.

The clean Ge(111) surface displays a $c(2\times8)$ structure after sputtering and annealing, see Fig. 1. The unit cell is believed to be built up of one $c(2\times4)$ cell and one $(2\times2)$ cell each comprising one adatom, called $A_{2\times4}$ and $A_{2\times2}$, and one atom in the layer below the adatoms called rest atoms, $R_{2\times4}$ and $R_{2\times2}$, each having an unpaired dangling bond, see, e.g., Refs. 6 and 7. In this second layer there are also six atoms per unit cell binding to adatoms thus giving three different groups of surface atoms, adatoms, rest atoms, and atoms binding to adatoms. However, by scanning tunneling microscopy[6] (STM) a buckling of the surface was observed, a finding which also has been supported by a recent theoretical treatment.[7] The buckling was more pronounced in the rest-atom layer with a large difference between the two subcells, whereas the adatoms appeared to be almost equivalent. A slight excess of electron charge near $R_{2\times2}$ relative to $R_{2\times4}$ was predicted by Takeuchi and co-workers,[7] which actually was reflected by the filled-state STM images.[6] The voltage dependency of the STM images also verified an earlier proposed charge transfer from the adatoms to the rest atoms.[8] This charge transfer would lead to one photoemission component shifted to higher binding energy and one shifted to lower binding energy.[3] However, the one shifted to higher energy has not been observed; therefore it was assumed that the charge transfer cannot give a complete picture.

The Ge(111)-Sn($7\times7$) structure is believed from a number of techniques[9-13] to be essentially the same as the Si(111)($7\times7$) geometry. This structure, known as the dimer adatom stacking fault model[14] comprises 12 adatoms per surface unit cell, seven rest atoms, three in each unit half and one in the corner hole. Furthermore, there are 36 second-layer atoms binding to the adatoms and finally 18 dimer atoms per ($7\times7$) surface unit. By scanning tunneling microscopy[13] the topmost adatom layer of the Ge(111)-Sn($7\times7$) surface was found to consist mainly of Sn. A photoemission study of this system may therefore clarify the discussion about the origin of the ($7\times7$) $S_2$ peak, since the contribution from adatoms in the Ge 3*d* spectra would be very small.

In this paper we present results from Ge 3*d* core-level photoemission experiments on the clean Ge(111)$c(2\times8)$ surface and the Sn-induced ($7\times7$) dimer adatom stacking fault structure. In the Ge(111)$c(2\times8)$ surface core-level spectra we have used a four-component deconvolution uncovering the adatom contribution, shifted 0.17 eV to higher binding energy. Furthermore, observation of an earlier proposed difference between rest atoms in the $c(2\times8)$ structure is reported. Finally, we argue for a

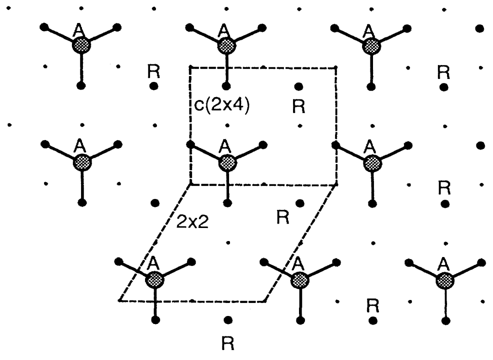

FIG. 1. Top view of the atomic model for the Ge(111)$c(2\times8)$ surface. Large hatched circles represent adatoms, marked *A*. Second-layer atoms are represented by black dots, rest atoms are indicated with a *R*, and bulk atoms by smaller black dots.

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rest-atom origin of the peak shifted to lower binding energy in the Ge(111)-Sn(7×7) spectrum, based on the fact that the adatoms are mainly Sn.

The experiments were performed at the National Synchrotron Radiation Facility MAX-LAB (Lund, Sweden) using a modified SX-700 monochromator. The photoemission spectra were recorded by a 200-mm-radius hemispherical analyzer of Scienta type.[15] In connection with the photoemission chamber is a preparation chamber comprising evaporation sources, sputtering, and a low-energy-electron-diffraction (LEED) optics, sample heating as well as cooling possibilities. Photoemission experiments were performed both at room temperature and at liquid-nitrogen temperature, and the experimental settings were chosen to give a total resolution in the range 80–90 meV, which was measured from the width of the Fermi edge of a tantalum foil in contact with the sample.

The samples were cut from a 0.004–0.01-Ω cm Ga-doped Ge(111) wafer. Excellent $c(2\times8)$ LEED patterns were achieved after repeated cycles of Ar sputtering and annealing at 650 °C for 10 min. During this annealing process the pressure was kept below $5\times10^{-10}$ Torr. Cleanliness of the samples was checked with photoemission spectra from the O 1*s* and C 1*s* core levels and from the valence band, which showed typical features of the clean surface.[16] The (7×7) reconstruction was prepared by deposition of 0.4 monolayer (ML) of Sn from a tungsten filament evaporator, and subsequent annealing at 500 °C for a few minutes.

A set of selected Ge 3*d* core-level spectra from the $c(2\times8)$ structure recorded at liquid-nitrogen temperature is shown in Fig. 2. The experimental spectra are decomposed using four different spin-orbit doublets. Analysis using only three components proved to be insufficient to give a satisfactory fit for all photon energies used. Evaluation of several spectra recorded at different photon energies resulted in the same energy shifts and comparable intensity ratios between the surface components, thus giving a physical argument for the extra contribution.

All values used for the spin-orbit splitting ($\Delta_{SO}$), the branching ratio ($B_r$), the Lorentzian width ($W_L$), and the Gaussian width ($W_G$) are summarized in Table I, together with the energy shifts obtained for the three surface components. The components are labeled *B* (for bulk), $S'_1$, $S'_2$, and $S'_3$. Identification of the bulk component was achieved by using a high photon energy and thereby increasing the mean free path of the photoemitted electrons, which enhances the bulk contribution in favor of the surface peaks. The effect of cooling the sample was a 25-meV decrease in the Gaussian width, from 0.275 eV at room temperature to 0.250 eV at liquid-nitrogen temperature.

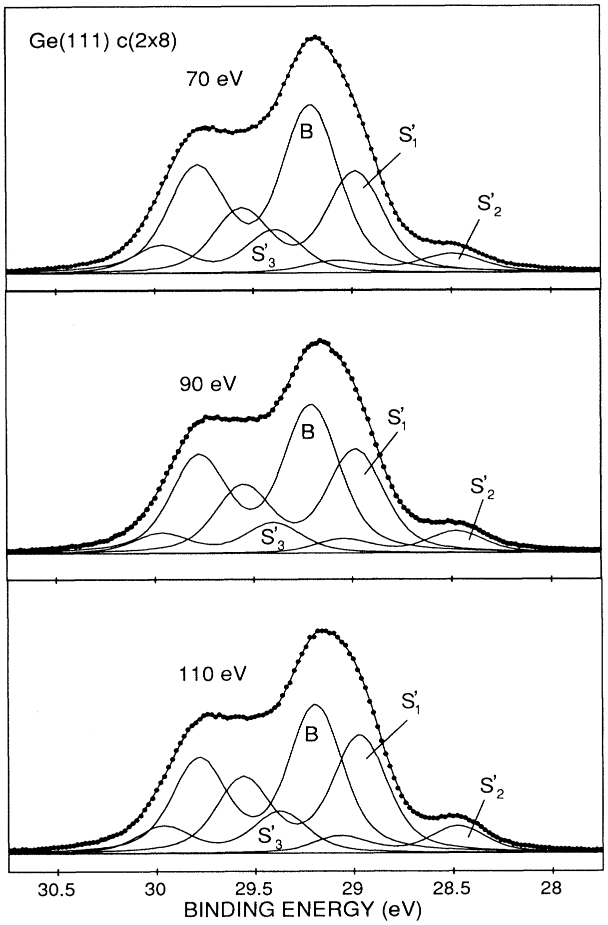

FIG. 2. Core-level spectra from the clean $c(2\times8)$ surface, recorded at different photon energies, marked in the figures, analyzed with four spin-orbit doublets. Labels refer to *B* for bulk and $S'_{1,2,3}$ for the three surface components, respectively; see text.

At least three different sites exist on the Ge(111)$c(2\times8)$ surface and an obvious question is from which kind of atom each core-level peak originates. The structure $S'_1$ in Fig. 2 shows the largest intensity among the shifted components and should accordingly be assigned to the largest number of surface atoms, i.e., the second-layer atoms binding to adatoms corresponding to $\frac{3}{4}$ ML. The intensity of the $S'_3$ peak in the 70-eV spectrum in Fig. 2 is 0.35 of the $S'_1$ intensity, in good correlation with the occupation ratio $\frac{1}{3}$ corresponding to either adatoms or rest atoms. The shift of $S'_3$ to higher binding energy would, according to the argumentation in Ref. 3, suggest an adatom origin of this contribution, thus implying that the only remaining peak, $S'_2$, springs from rest-atom emission. The intensity ratio of $S'_2$ compared to $S'_1$ in Fig. 2 is 0.20 corresponding to emission from 0.15 ML instead of 0.25 ML which is the surface density of rest

TABLE I. Parameters used in the analysis of the spectra. The spin-orbit splitting is denoted $\Delta_{SO}$, the branching ratio $B_r$, the Lorentzian width $W_L$, and the Gaussian width $W_G$. Energy shifts for the different surface components are also tabulated.

| | $c(2\times8)$ | (7×7) | | $c(2\times8)$ | (7×7) |
|---|---|---|---|---|---|
| $\Delta_{SO}$ (eV) | 0.57 | 0.57 | $\Delta E_1$ (eV) | −0.23 | −0.26 |
| $B_r$ | 1.69 | 1.61 | $\Delta E_2$ (eV) | −0.73 | −0.64 |
| $W_L$ (eV) | 0.15 | 0.15 | $\Delta E_3$ (eV) | 0.17 | |
| $W_G$ (eV) | 0.25 | 0.32 | | | |

atoms. However, STM (Ref. 6) and charge-density calculations[7] indicated more electron charge in the propinquity of $R_{2\times 2}$ relative to $R_{2\times 4}$, which when again using the arguments of Aarts, Hoeven, and Larsen[3] would induce a larger core-level shift in the $R_{2\times 2}$ emission. $S_2'$ might, in light of this, stem from merely one kind of rest atom. If so, the estimated surface coverage of 0.15 ML is slightly larger than the ideally expected 0.125 ML. However, a plausible explanation can be achieved from Hirschorn *et al.*,[6] who found small patches of (2×2) intersecting larger $c(2\times 8)$ areas whereas no extended regions of $c(2\times 4)$ could be seen in their STM images. A somewhat stronger $R_{2\times 2}$ emission can accordingly be expected, hence indicating a $R_{2\times 2}$ origin of $S_2'$. This assumption is further supported by the fact that no peak can be seen at lower binding energy than $S_2'$ and $R_{2\times 4}$ emission can be expected, from the above charge transfer argument, to appear at higher binding energy than $R_{2\times 2}$ emission, therefore we believe that $S_2'$ comes from (2×2) rest atoms.

In Fig. 3 the analysis of a Ge 3*d* spectra from the Ge(111)-Sn(7×7) surface using three components is shown. Adding a fourth peak in the analysis gave no significant improvement of the fit. As can be seen in Table I the Gaussian width has now increased to 0.32 eV, which is 70 meV larger than for the clean surface. Possible reasons are the random mixture of Sn and Ge in the adatom layer, seen with STM,[13] and even in subsurface layers giving rise to slightly different chemical shifts and also the presence of two different halves of the unit cell. Moreover, band bending within the sampling depth shows up as a broadening of the core-level spectra.[17] The band bending manifests itself by a shift of the bulk binding-energy position, which at a photon energy of 70 eV is about 35 meV lower in the (7×7) case than for the clean $c(2\times 8)$ surface. The result is in good agreement with what DiCenzo *et al.* found.[5]

The strongest surface peak ($S_1$) should, as for the clean surface, be attributed to the largest surface atom population which is the second-layer atoms binding to adatoms, corresponding to $\frac{36}{49}$ ML. The energy shift of this contribution is 0.26 eV to lower binding energy which is somewhat larger than for the clean surface. This change may be ascribed to the chemical difference of the adatom. Ge has a somewhat larger electronegativity than Sn,[19] hence one might expect a shift to even lower binding energy for the second-layer atoms binding to adatoms in the (7×7) structure than on the clean surface when substituting Ge adatoms with Sn.

The remaining $S_2$ peak, shifted 0.64 eV to lower binding energy and with an intensity of 0.19 of the $S_1$ intensity, thus has its origin in either dimers, rest atoms, or adatoms. A dimer core level would have an intensity relative to $S_1$ of 0.5 since there are $\frac{18}{49}$ ML of dimers; thus $S_2$ is too weak to have a dimer origin, and, since Sn is believed from surface x-ray diffraction[11] and STM (Ref. 13) to replace Ge adatoms, the only possible atoms left are the rest atoms for which the intensity ratio is expected to be 7/36. There are seven rest atoms and 36 atoms binding to adatoms per surface unit cell, which is close to 0.19. In addition, a charge transfer from adatoms to rest atoms was predicted by a theoretical study on the Si(111)(7×7) surface,[18] which is similar to the Ge(111)-Sn(7×7) surface. Thus a shift of the rest-atom core level to lower binding energy in the same fashion as the $c(2\times 8)$ rest-atom shift can be expected. However, the magnitudes of the shifts cannot be expected to be exactly the same since the (7×7) surface is metallic in contrast to the semiconducting $c(2\times 8)$ reconstruction, and differences in the charge transfer may also be expected simply because the adatom to rest-atom ratios are not similar in the two structures.

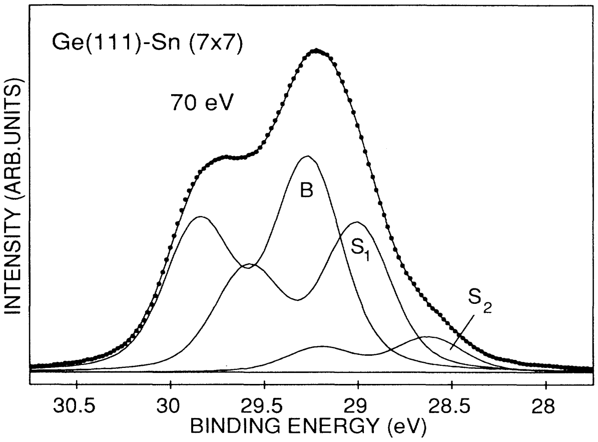

FIG. 3. Ge 3*d* spectrum of the Ge(111)-Sn(7×7) structure at 70-eV photon energy.

In summary, from the analysis of several core-level spectra acquired from the clean Ge(111)$c(2\times 8)$ surface we argue that analysis using four separate spin-orbit components is adequate and that the finding of a peak shifted to 0.17 eV higher binding energy compared to the bulk is correlated to adatoms. This assignment is supported by the direction of the shift to higher binding energy, predicted by the charge transfer from adatoms to rest atoms, the intensity ratio, and the fact that this component is absent in the spectra from the Ge(111)-Sn(7×7) surface where Sn has replaced the Ge adatoms. The component shifted to lower binding energy previously assigned to all rest atoms in the $c(2\times 8)$ structure, is suggested here to spring only from rest atoms in the (2×2) part of the $c(2\times 8)$ unit cell reflecting an earlier proposed difference between the rest atoms in the two subcells. In the (7×7) structure the $S_2$ component, shifted to lower binding energy, is attributed to rest atoms, justified by the intensity ratio and most of all the presence of this contribution when the number of Ge adatoms is expected to be very small.

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