Ge(111)2 × 1: π-Bonded Chain Model or Not?

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Contrarily to other recent photoemission experiments the authors find that the dangling-bond surface state of Ge(111)2 × 1 has a band dispersion very different from the one predicted by theoretical calculations based on an optimized chain model. The applicability of the π-bonded chain model to Ge(111)2 × 1 is questioned.

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The cleaved Ge(111) surface is found to have the same low-energy electron-diffraction (LEED) pattern (corresponding to a 2×1 reconstruction) as that of Si(111), and it is generally believed that these two semiconductors are likely to have the same reconstruction model. The reconstruction of atoms on the Si(111) surface has been studied extensively for a number of years.[1] Interpretation of the LEED data led to a buckled-surface[2] 2×1 geometry. An important suggestion was recently made by Pandey.[3] He proposed a new type of structural model in which the bonding topology is changed by bond breaking and subsequent rebonding, while approximately maintaining bond lengths. This model has been called the π-bonded chain model. Chadi[4] proposed an alternative structure, the π-bonded molecular model, with slightly different rebonding.

Total-energy calculations have been performed by Pandey[3] and Northrup and Cohen.[5] They show that the buckling distortion associated with the 2×1 reconstruction is unstable with respect to the nonbuckled, relaxed 1×1 surface. Northrup and Cohen[5] have obtained the π-bonded structure from the ideal 1×1 surface using a simple structural path. The energy barrier between the buckled and the chain models is found to be surprisingly small (≃0.03 eV/atom). The comparison between the calculated dispersion of the dangling-bond surface state and the angle-resolved photoemission measurements on single-domain samples by Uhrberg *et al.*,[6] Himpsel, Heimann, and Eastmann,[7] and Houzay *et al.*[8] shows good agreement, although a second structure around $\bar{J}$ has not yet been explained.

In this Letter we report angle-resolved photoemission experiments on 2×1 single-domain cleaved Ge(111). Contrarily to the case of Si there is no agreement with the theoretical surface state dispersion calculated for the π-bonded chain model[9] and the application of this model to Ge should therefore be questioned.

The angular-resolved photoemission spectra have been measured with use of synchrotron radiation from the ACO storage ring (540 MeV) at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Orsay. The spectra were obtained for photon energies between 35 and 50 eV with an overall energy resolution (monochromator plus analyzer) smaller than 300 meV and an angular resolution of ~1°. All energies have been measured with respect to the Fermi level E_F of a Bi sample. However, the energies can also be referenced to the top of valence band E_V by using $E_F - E_V = 0.1$ eV. The samples are p type (2×10^{14} cm^{-3}) and are cleaved in a vacuum of 10^{-10} Torr. Because of the symmetry of the dangling-bond surface state (sp_z) the measurements were performed with the light beam at 30° from grazing incidence.

The crystals were cleaved in the $[\bar{2}11]$ direction which in most cases produced cleaves with large areas of single domains. These domains were sufficiently larger than the light spot (0.5 × 0.5 mm^2) to assure emission from one domain only. The photoemission spectra show very good reproducibility for different cleavages and were measured at $T = 20$, 80, and 300 K. For the spectra obtained at 20 K the LEED indicated that the structure corresponded to a 2×1 and not a 1×1[10] geometry.

In Fig. 1 we show photoemission spectra recorded for various polar angles θ along the $\bar{\Gamma}\bar{J}$ line of the 2×1 surface Brillouin zone for a photon energy of 35 eV. We choose this photon energy because the dangling-bond surface state is maximum and even appears as a sharp peak at $\bar{\Gamma}$. The $\bar{J}$ point is reached around 16°. For angles smaller than 10° the peak has a shoulder on the low-energy side which corresponds to a bulk band (top of the valence band). Polar angles up to 35° have been examined allowing us to cover two Brillouin zones. Data have also been obtained for negative polar angles θ to check the symmetry. The sensitivity of the surface state to contamination was also verified.

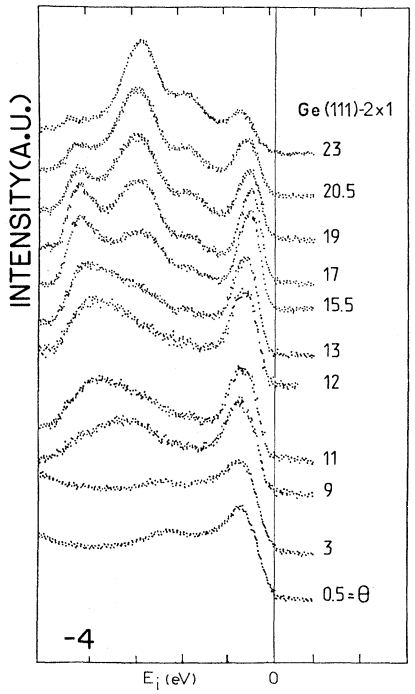

FIG. 1. Angle-resolved photoemission spectra for various angles of emission (θ) along the $\bar{\Gamma}\bar{J}$ line in the 2×1 surface Brillouin zone ($h\omega=35$ eV). The spectra have been taken at 20 K but the sample was cleaved at room temperature.

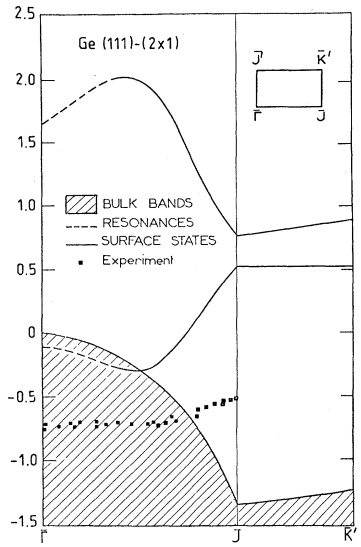

FIG. 2. Surface state dispersion from $\bar{\Gamma}$ to $\bar{J}$ for the chain model obtained by Northrup and Cohen (Ref. 9) and our experimental points (squares).

In Fig. 2, the initial energy of the surface state versus the momentum vector K along the $\bar{\Gamma}\bar{J}$ direction is given. The band-structure calculation of Northrup and Cohen,[9] based on the π-bonded chain model, is also shown.

The measured dispersion in our experiment along $\bar{\Gamma}\bar{J}$ is of the order of 250 meV. This is in contradiction with the π-bonded chain model calculated by Northrup and Cohen[9] which gives 850 meV. Another prominent surface state, labeled σ, is predicted in a gap in the projected band structure roughly 8 eV below the top of the valence band and halfway between $\bar{\Gamma}$ and $\bar{J}$. This state disperses upwards and is associated with σ bonds between the surface atoms in the chain. We have not observed this state, but we note that at 8 eV below the Fermi level, this state should be broadened by Auger transitions. In addition, the polarization that we have used is not the most favorable for observing this state.

The absolute position of the theoretical result is 0.8 eV higher than the experimental value. One source of uncertainty in the theoretical position of the surface state energy is the interpretation of the local density eigenvalues as removal energies. As pointed out by Northrup and Cohen[9] the assumption that the difference between the eigenvalues of occupied states is equal to the difference in the removal energies may be invalid when comparing surface states, which are confined to two dimensions, with itinerant-electron bulk states.

The comparison between theory and our experimental data is very poor. There is fair agreement between the theory and the results of Nicholls *et al.*[11] who have found a totally different energy dispersion and a bandwidth for the surface state of 800 meV. We explore the origins of the differences between the experimental results below.

The experiment by Nicholls *et al.* is done with use of 10.2-eV photons which means that the kinetic energy for the emitted electrons is around 6 eV. For this energy the electron mean free path is very large and the contribution of bulk states is very important. This can be seen by examining Fig. 1 of Ref. 11. The surface state appears as a sharp peak only for $\theta\geq37°$. Below this value three structures are observed and it is possible that there is a large contribution of bulk structure to these peaks.

Hence, if we consider our results as valid then we conclude that the measurements are inconsistent with the chain model. What are other possible models?

(a) One alternative structure to the chain model

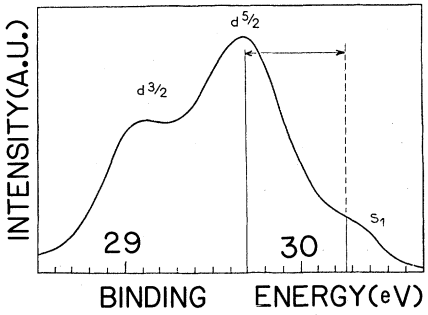

FIG. 3. Angle-resolved photoemission spectra from Ge $3d$ levels for Ge(111)2×1. Emission (S_1) from surface $3d$ levels is seen on the low-binding-energy side of the bulk level for the surface-sensitive spectrum ($h\omega=50$ eV).

is the π-bonded molecular (or dimer) model.[12] The chain and molecular models differ only by the rebonding of atoms in the third layer. However, the dispersion calculated by Nielsen *et al.*[12] for Si(111)2×1 is of order 500 meV and the band disperses downward between $\bar{\Gamma}$ and $\bar{J}$, in contradiction with the experiments.

(b) Another possibility is the buckling model.[2] Self-consistent pseudopotential calculations for Si give an upward dispersion of 0.3 eV[13] for this model. The similarities of the calculations for Si and Ge would lead one to expect the same kind of dispersion for Ge(111)2×1, in very good agreement with the experiment. However, the calculations by Northrup and Cohen[9] show that the buckling model gives a metallic surface in contradiction with experiment. In addition, the buckling model has a higher total energy than the ideal or chain model.

To obtain an estimate of the possible charge transfer for an ionic buckled surface, we have performed a photoemission experiment on the $3d$ levels of Ge. This is shown in Fig. 3. The photon energy is chosen so that the photoelectrons have a kinetic energy (~15 eV) not too far from the minimum of the electron mean free path. We consider only the $d^{5/2}$ component of the spin-orbit-split d levels. There is a strong surface state S_1, at −0.580 eV from the bulk state; it disappears with contamination. Self-consistent calculations of surface core-level shifts of semiconductors have not been reported to our knowledge. However, the charge transfer dq between surface atoms has been calculated. For the buckling model Northrup and Cohen[14] have found that the up atoms gain 0.1 electron. In the case of the chain model the surface should be covalent but in fact a small charge transfer exists as a result of the nonequivalence of atoms in the top-layer chain and the charge transfer is of the order of 0.02 electron.[14] In the case of Si(111)2×1 the measured $2p$ core-level shift (~ −0.37 eV)[15,16] has been converted into a charge transfer by using an empirical conversion factor of 2.2 eV/electron which has been derived from the Si $2p$-level shifts induced by adsorbed oxygen.[17] It is clear that the much larger value obtained for Ge (−0.58 eV) is again in contraction with a small charge transfer expected for the chain model.

In conclusion, we have shown that the properties of the surface states (valence band and core) are not consistent with the present chain model and so the reconstruction of Ge(111)2×1 is still an open question.

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