PHYSICAL REVIEW B VOLUME 24, NUMBER 10 15 NOVEMBER 1981

## Rapid Communications

*The Rapid Communications section is intended for the accelerated publication of important new results. Manuscripts submitted to this section are given priority in handling in the editorial office and in production. A Rapid Communication may be no longer than 3½ printed pages and must be accompanied by an abstract. Page proofs are sent to authors, but, because of the rapid publication schedule, publication is not delayed for receipt of corrections unless requested by the author.*

# Evidence for semiconductor-semiconductor interface states: Si(111)(2 × 1)-Ge

P. Perfetti,* N. G. Stoffel, A. D. Katnani, and G. Margaritondo
*Department of Physics, University of Wisconsin, Madison, Wisconsin 53706*

C. Quaresima, F. Patella, and A. Savoia
*Programma Utilizzazione Luce di Sincrotrone, Laboratori Nazionali di Frascati, CP 13, 00044 Frascati, Italy*

C. M. Bertoni, C. Calandra, and F. Manghi
*Istituto di Fisica, Universita' di Modena, Italy*

(Received 16 July 1981)

A direct correlation was found for the first time between theory and experiments on the localized electronic states at a semiconductor-semiconductor interface. The investigation involved synchrotron-radiation photoemission experiments and tight-binding calculations on Ge adatoms on cleaved Si substrates. The theoretically predicted interface states in a region 4–9 eV below the Fermi level were detected in the experimental spectra. These occupied states and their unoccupied counterparts have a fundamental influence on the localized one-electron transitions and on relevant heterojunction parameters in transport processes.

We present direct evidence of the formation of interface states at a semiconductor heterojunction. Photoemission spectra taken on Ge-covered, cleaved Si(111)(2 × 1) reveal two strong contributions to the local density of states in the region 4–9 eV below the Fermi level, $E_F$, as predicted by tight-binding calculations.[1,2] This is the first time that detailed theoretical predictions about heterojunction interface states are confirmed by experimental findings. Therefore our study provides firm evidence that localized states are indeed created during the interface formation between two semiconductors.[1–4] Localized states can have a fundamental role in the optical and transport properties of the heterojunction[5,6] by influencing important interface parameters, e.g., the band bending and therefore the built-in potential. In particular, there is a correlation between the appearance of interface states and the shift of the interface pinning position of the Fermi level.[7]

The existence of heterojunction interface states was traditionally associated with the lattice mismatch between the two semiconductors and the resulting large density of unsaturated chemical bonds in the interface region.[5] In 1977, however, Baraff *et al.*[3] theoretically predicted that heterojunction interface states can be induced by the space-periodicity breakdown even at nearly lattice-matched interfaces such as GaAs(110)-Ge. This prediction was confirmed by pseudopotential calculations by Pickett *et al.*[4] Photoemission experiments by Denley *et al.*[8] revealed states induced by Ge chemisorption on GaAs(110). Their experimental findings, however, matched only part of the theoretical predictions[3,4] leaving substantial uncertainity about the nature of the observed states. In the present work the presence of interface states *not* due to lattice mismatch at the Si-Ge heterojunction is theoretically predicted by tight-binding calculations of the local density of states (LDOS) for different geometries corresponding to one-layer and two-layer Ge films on Si(111). These theoretical predictions are matched by the experimental results. The theoretical results are given for the "on top" chemisorption geometry in Fig. 1 where the LDOS for the deposited Ge layers and for the underlying Si planes is shown. The bulk Si density of states (DOS) for Si and Ge is given for comparison. The interface state peaks $I_1$ and $I_2$ are indicated with shaded areas. The analysis of the band structure shows that the interface states closely correspond to forbidden regions in the projected bulk-Si band structure. These states must be distinguished from the surface states of the Ge film which lie in the band-gap region and give

 ©1981 The American Physical Society

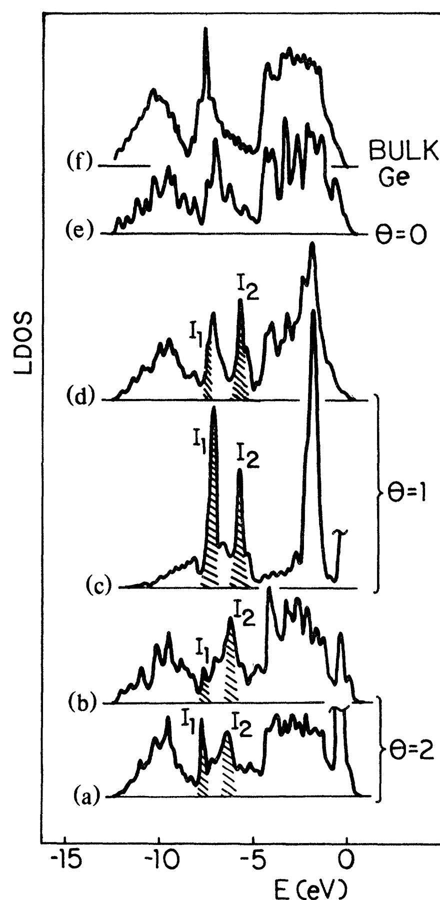


FIG. 1. Theoretical LDOS of two monolayers (a) or one monolayer (c) of Ge on Si and of the first two planes of the Si substrate (b),(d). The bulk-Si DOS (e) and bulk-Ge DOS (f) are given for comparison.

rise to the most pronounced structure in the Ge LDOS. Such Ge surface states persist upon Ge deposition as distinct features of the Ge surface while the shaded structures are localized at the interface and retain this character even for thicker films. Notice that the shape of the LDOS of the Ge film at two-layer coverage already shows the main features of the bulk-Ge DOS. The interface states lie approximately in correspondence with minima of the bulk DOS. Early experiments[9] on Ge on *annealed* Si(111) did not give clear evidence for these interface states. Our present experiments on *cleaved* substrates reveal instead Ge-induced states in agreement with the above theory.

The experimental part of our study consisted of two independent series of experiments carried out at the University of Wisconsin Synchrotron Radiation Center and at the Synchrotron Radiation Project (PULS) of the Laboratori Nazionali di Frascati, Italy, hereafter labeled experiments ($S$) and ($F$). In both series of experiments Si samples ($n$-type, carrier concentrations ranging between $10^{15}$ and $10^{17}$ cm$^{-3}$) were cleaved under ultrahigh vacuum (pressure below $1\times10^{-10}$ torr) and Ge overlayers were evaporated *in situ* (pressure below $3\times10^{-10}$ torr) while being monitored by a quartz crystal oscillator. The clean and Ge-covered surfaces were characterized and studied by Auger-electron spectroscopy, low-energy electron diffraction (LEED), electron-energy-loss spectroscopy, and photoemission spectroscopy. In all these experiments the Ge overlayer was deposited step by step on a room-temperature substrate. In the experiments ($F$) the sample was annealed after each deposition until a ($1\times1$) LEED pattern was observed at $\sim350\,^{\circ}$C. The basic results here reported about electronic states and band discontinuities did not change from annealed to unannealed surfaces. Angle-integrated photoelectron energy distribution curves (EDC's) were measured by cylindrical-mirror analyzers under computer control. The photoelectrons were excited by photons emitted by the storage rings Tantalus (Wisconsin) and Adone (Frascati). The photon monochromators were either a vertical Seya-Namioka or a Brown-Lien "Grasshopper" [experiment ($S$)] or a Jobin-Yvon toroidal-grating instrument [experiment ($F$)]. Photon energies in the range 13–160 eV were used to investigate the valence-band region and the Ge $3d$ and Si $2p$ core levels. From these experiments it was possible to estimate the interface parameters as described in detail in Refs. 7 and 10. In particular, the measured valence-band discontinuity was 0.15–0.21 eV. In this article we are primarily concerned with the novel evidence about Si-Ge interface states. Therefore we shall confine our discussion to the experimental results directly giving that evidence.

Our theoretical and experimental results are compared to each other in Fig. 2. Here the top two curves show the calculated LDOS in the region 3–10 eV below $E_F$ for one monolayer of Ge on Si(111) both for the "on top" chemisorption site already discussed and for a different chemisorption site in which the Ge adatoms sit in a "hollow" position. The LDOS is quite similar for the two geometries and this simplifies the data interpretation but prevents us from identifying chemisorption sites. In particular, both geometries give the two groups of theoretical states identified above as interface states. In detail, the Ge $s$ states give rise to peak $I_2$ which becomes a doublet for the "hollow" site while peak $I_1$ which also becomes a doublet for the "hollow" site has dominant Si $sp$ character. The eight lower curves in Fig. 2 are difference curves between the Ge-covered Si EDC's and the clean-Si EDC's (see Fig. 3). All the difference curves exhibit two peaks at $-5.35\pm0.15$ eV and $-8.1\pm0.15$ eV emphasized in Fig. 2 by shading. These two experimental peaks are identified with the theoretical interface-state features $I_1$ and $I_2$. Notice, in particular, that their intensity de-

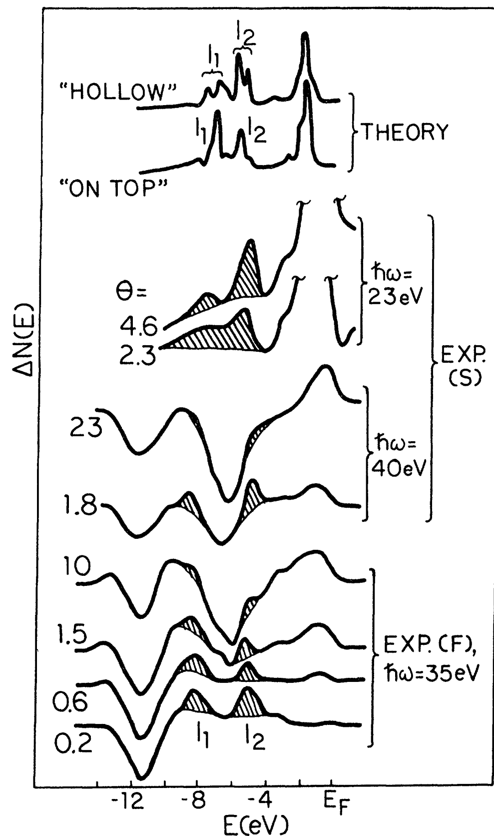


FIG. 2. Top two curves show the calculated LDOS for one monolayer of Ge on Si(111) with the adatoms either in a "on top" site or in a "hollow" site with respect to the substrate atoms. The eight lower curves are EDC difference curves obtained by subtracting the EDC's for Ge-covered surfaces from the EDC's of the clean-Si surface (see Fig. 3). The four lower curves correspond to experiments ($F$) and to a photon energy of 35 eV while the two remaining curves correspond to experiments ($S$) and to photon energies of 23 and 40 eV. The shaded areas emphasize the interface states. The nominal overlayer thickness, Θ, is shown in equivalent monolayers at the left-hand side of each curve.

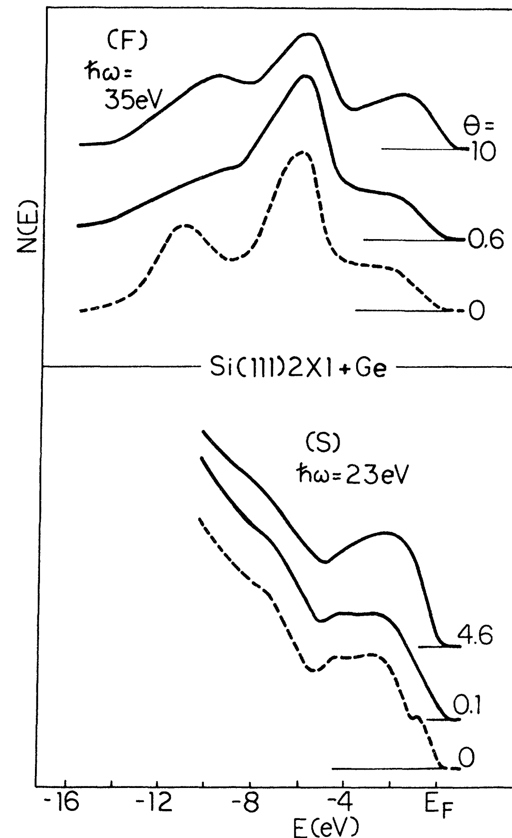


FIG. 3. EDC's for the clean Si(111) (2 × 1) surface (dashed line) and for the Ge-covered surfaces (solid line). The upper and lower curves correspond to experiments ($F$) and ($S$).

creases as the overlayer thickness increases for the $\hbar\omega = 35$ and 40 eV spectra. This is consistent with the interface localization of the states if one considers the high surface sensitivity of the EDC's at these photon energies.

The right-hand side of the difference curves in Fig. 2 exhibits a positive signal introduced in the bottom half of the Si gap and in the upper part of its valence band by bulk-Ge $p$ states. In fact the measured valence-band discontinuity[7] places the Ge valence-band edge above the Si valence-band edge—as one can see from the linear extrapolation of the EDC leading edges in Fig. 3 (notice, however, that while the extrapolation is straightforward for the $\hbar\omega = 35$ eV EDC's where the clean-surface-states signal at the top of the valence band is weak, the $\hbar\omega = 23$ EDC's require instead a correction for the surface-state shoulder immediately below $E_F$). Notice that the intensity of this bulk-Ge feature increases with the overlayer thickness while the intensities of the interface features decreases beyond a few monolayers. The remaining features in the region 8–11 eV below $E_F$ of the difference curves ($F$) are due to bulklike Ge $s$ states displaced in energy with respect to the bulk-Si $s$ states by the valence-band discontinuity.[7]

The observed interface state at −8.1 eV provides a natural explanation for two of the Si(111)(2 × 1)-Ge electron-energy-loss spectral features,[2] i.e., the peaks at transition energies of 8.0 and 29.6 eV. The final-state identification for these peaks is made difficult by the possibility of large excitonic shifts.[11,12] However, this problem is solved by noticing that the *difference* between the above transition energies, 21.6 eV, coincides with the measured distance between $I_1$ and the Ge 3$d$ core level. Therefore those two transi-

tions have $I_1$ and Ge $3d$ for initial states and the same final state — probably one of the empty Si-Ge interface states predicted by the theory[1,2] and modified by excitonic interaction.[12]

We emphasize that the interface evolution described in Ref. 7 for Si(111)(2 × 1)-Ge essentially coincides with the appearance of the interface states here discussed — and presumably of the corresponding unoccupied localized states.[1,2] The unoccupied localized states influence the pinning position of $E_F$ and therefore the built-in potential of the Si-Ge heterojunction. On the other hand it is not clear if and how the interface states influence the band discontinuities. The measured valence-band discontinuity, 0.15–0.21 eV, is not very far from the tight-binding value calculated by Harrison,[13] 0.38 eV. The discrepancy could actually be eliminated by taking into account the effects of lattice mismatch[14] and therefore the interface states would not seem to play a major role in determining that particular parameter. Besides the above indirect effects the interface states could obviously have a direct role in transport properties as intermediate steps in recombination processes.[5]

This work was supported in part by the NSF, Grant No. DMR 78-22205. One of us (P.P.) acknowledges partial support of the University of Wisconsin Graduate School Research Committee. The experiments ($S$) were made possible by the expert assistance of the University of Wisconsin Synchrotron Radiation Center (supported by the NSF, Grant No. DMR 74-15089). The experiments ($F$) were made possible by the collaboration of the staff of the PULS, Frascati, and in particular of M. Capozi.

---

*On leave from PULS-INFN, Laboratori Nazionali di Frascati, CP 13, 00044 Frascati, Italy.

[1]S. Nannarone, F. Patella, P. Perfetti, C. Quaresima, A. Savoia, C. M. Bertoni, C. Calandra, and F. Manghi, Solid State Commun. 34, 489 (1980).

[2]P. Perfetti, S. Nannarone, F. Patella, C. Quaresima, F. Cerrina, M. Capozi, and A. Savoia, J. Vac. Sci. Technol. (in press).

[3]G. A. Baraff, J. A. Appelbaum, and D. R. Hamann, Phys. Rev. Lett. 38, 239 (1977).

[4]W. E. Pickett, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. 39, 109 (1977).

[5]A. G. Milnes and D. L. Feucht, *Heterojunctions and Metal-Superconductor Junctions* (Academic, New York, 1972).

[6]F. Bernabucci, G. Margaritondo, P. Migliorato, and P. Perfetti, Phys. Status Solidi A 15, 621 (1973).

[7]G. Margaritondo, N. G. Stoffel, A. D. Katnani, H. S. Edelman, and C. M. Bertoni, J. Vac. Sci. Technol. (in press).

[8]D. Denley, K. A. Mills, P. Perfetti, and D. A. Shirley, J. Vac. Sci. Technol. 16, 1501 (1979); P. Perfetti, D. Denley, K. A. Mills, and D. A. Shirley, Appl. Phys. Lett. 33, 667 (1978).

[9]G. Margaritondo, N. G. Stoffel, A. D. Katnani, and F. Patella, Solid State Commun. 36, 215 (1980).

[10]A. D. Katnani, N. G. Stoffel, H. S. Edelman, and G. Margaritondo, J. Vac. Sci. Technol. (in press).

[11]G. Margaritondo and J. E. Rowe, Phys. Lett. A 59, 464 (1977).

[12]G. Margaritondo, A. Franciosi, N. G. Stoffel, and H. S. Edelman, Solid State Commun. 36, 297 (1980), and references therein.

[13]W. H. Harrison, J. Vac. Sci. Technol. 14, 1016 (1977).

[14]A. D. Katnani, R. R. Daniels, and G. Margaritondo (unpublished).