RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 43, NUMBER 14 15 MAY 1991-I

Quasiparticle surface band structure and photoelectric threshold of Ge(111)-2×1

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(Received 15 February 1991)

The surface-state energies of the Ge(111)-2×1 surface are calculated using a quasiparticle self-energy approach. The surface structural parameters are determined through a local-density-functional total-energy minimization resulting in a buckled π-bonded-chain geometry. The quasiparticle energies are computed using a first-order expansion of the electron self-energy operator in the screened Coulomb interaction with a model static dielectric matrix. Our calculated surface-state band gaps and dispersions of both the occupied and unoccupied surface states agree well with experiments. Further, the photoelectric threshold ϕ is found to be 4.73 eV, compared to 4.74–4.80 eV obtained experimentally.

Studies of the electronic properties of the Ge(111)-2×1 reconstructed surface date back to the early 1960s.[1] It has continued to be a subject that attracts much experimental and theoretical investigation.[1–15] Although there has been considerable progress, the structural and electronic properties of this surface remain to be worked out in detail. In this work, we report calculations on the quasiparticle properties of the Ge(111)-2×1 surface based on a π-bonded-chain geometry.[15,16] We have also computed the photoelectric threshold energy for this surface within the quasiparticle scheme,[17,18] and thus gone beyond the standard local-density-functional approximation[19] (LDA) for this quantity for a semiconductor surface.

Previous *ab initio* calculations[15] for a π-bonded-chain model have given a qualitative picture of the electronic structure of the Ge(111)-2×1 surface, but quantitative comparisons with experiments show severe deficiencies of the LDA used. The LDA minimum band gap (at $\bar{J}$) is $\sim$0.2 eV, whereas the measured value is $\sim$0.65 eV from various experiments. Another very important problem encountered in the previous LDA calculation[15] is that the theoretical occupied surface states are too high in energy relative to the bulk valence band by $\sim$1 eV as compared to experiment.

The inherent "band-gap" problem of using LDA eigenvalues for excitation energies in semiconductors has been largely resolved owing to the recent development of a quasiparticle approach in the *GW* approximation.[17,18] In this work, the quasiparticle surface band structure of the Ge(111)-2×1 is calculated using this approach.[17,18] However, the static dielectric matrices, the calculation of which is a very time-consuming step in the self-energy evaluation, are directly obtained from a scheme developed by Hybertsen and Louie[20] based on a model semiconductor dielectric function.[21] The model dielectric matrix has proved very successful in quasiparticle energy calculations for bulk semiconductors.[20] It has also been applied to the clean GaAs(110)-1×1 surface, yielding surface-state results in agreement with those from *ab initio* quasiparticle calculations to within 0.1 eV.[20]

The quasiparticle energy calculations are based on a π-bonded-chain geometry of the Ge(111) surface with significant buckling.[15,16] Figure 1 shows the position of the atoms in our surface structure. The structural parameters were determined from a LDA total-energy calculation. The surface is simulated by a repeated slab geometry to facilitate the calculation in momentum space. Each supercell contains 12 layers (24 atoms). The thickness of the vacuum region between surfaces in the neighboring cells is 12 a.u., which is about 5 layers. In investigating the photoelectric threshold, the thickness of the vacuum is increased up to 25 a.u. to ensure convergence of the results. We have also tested the convergence of the quasiparticle energies with respect to the thickness of the atom-

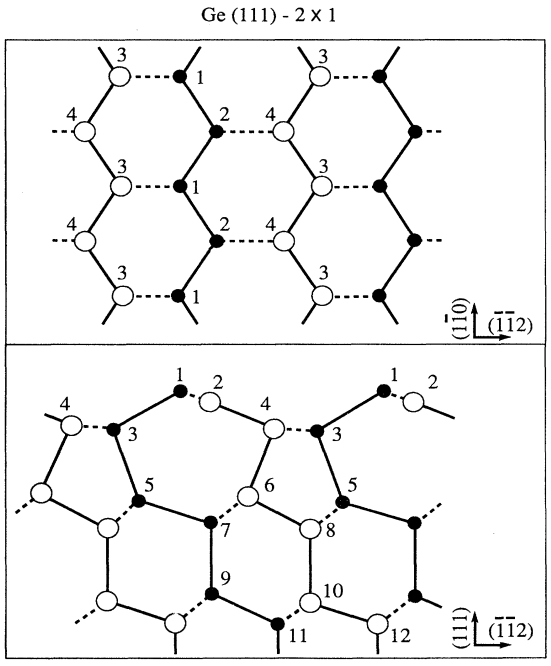

FIG. 1. Schematic view of the atomic structure of the buckled π-bonded-chain reconstruction of Ge(111)-2×1 surface. Upper panel: top view. Lower panel: side view.

ic region in the slab with a 32 atom supercell. Both the surface-state band gap and the lineup of the surface-state energies relative to those of the bulk states do not change by more than 0.1 eV.

Ab initio ionic pseudopotentials including scalar relativistic effects[22] and the Ceperley-Alder[23] form of the local exchange-correlation potential are employed in the LDA calculations. For the purpose of determining the photoelectric threshold, we have also used the von Barth-Hedin[24] correlation potential. The use of different LDA exchange-correlation potentials does give rise to a sizable change in the LDA photoelectric threshold ϕ_{LDA} as we shall discuss later. The wave functions are expanded in a plane wave basis with energy cutoff $E_{\mathrm{cut}}=8$ Ry. We have taken the surface atomic geometry of Northrup and Cohen[15] and allowed the atoms to relax further under the Hellmann-Feynman forces. Our E_{cut} (8 Ry) is larger than that used in the Northrup and Cohen calculation (5 Ry). We do not find any further appreciable displacements of the atoms. The difference in elevations of the top layer atoms (atoms 1 and 2 in Fig. 1), viz., the buckling of the π-bonded chain, is 0.57 a.u. The band dispersion and the minimum band gap from our LDA calculation are similar to those reported by Northrup and Cohen.[15]

In the GW approximation,[17,18] the electron self-energy can be expressed as

$$\Sigma(\mathbf{r},\mathbf{r}',E)=\frac{i}{2\pi}\int d\omega G(\mathbf{r},\mathbf{r}',E-\omega)W(\mathbf{r},\mathbf{r}',\omega)e^{-i\delta\omega}, \quad (1)$$

where G is the single-particle Green's function and $W=\epsilon^{-1}V$ is the dynamically screened Coulomb interaction. The static dielectric matrices $\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega=0)$ are calculated with use of the Hybertsen-Louie model[20,21] for elements with $|\mathbf{q}+\mathbf{G}|^2\leq 4.8$ Ry. The key feature in the model dielectric matrix is that it is constructed to describe correctly both the long-range and the short-range screening behavior.[20,21] In addition to the charge density, the model static dielectric matrix requires one input parameter, the dielectric constant ϵ_0, at each point in real space.[20] We use $\epsilon_0=16$ in the bulk region and $\epsilon_0=1$ in the vacuum region, and a smooth transition function in the surface region over one-bond length. Details of this transition function are found to be not important. The dynamical effects in the screened Coulomb interaction W are accounted for by the generalized plasmon-pole model.[17] The calculation of Σ requires summations over a large number of bands.[17] We have included 30 bands per atom (thus 720 bands altogether for our 24 atom slab), and 12 special k points in the irreducible wedge of the surface Brillouin zone. The projected bulk bands are calculated on equal footing to achieve accurate band alignment.

In Table I, we compare the calculated surface-state band gap and band dispersions with available experimental data. Among the experimental results, optical measurements[12,13] and direct photoemission[10] from a Ge sample heavily n doped to occupy the surface conduction states appear to give a band gap around 0.5–0.55 eV, which is somewhat lower than our theoretical value of 0.67 eV, whereas a value of 0.65 ± 0.2 eV is inferred from combined inverse photoemission (IPE) and photoemission (PE) results.[11] The difference between the surface band-gap measured by optical processes and that by PE and IPE processes is very similar to the situation in the Si(111)-2×1 surface, and is believed to be due to excitonic effects present in the optical processes.[25] Results from the heavily n-doped samples may be complicated by the heavy doping,[14,25] although a quantitative assessment of doping effects is not available yet. Also, the valence-band widths of the surface states obtained from two photoemission studies[7–9] contradict each other as seen in Table I. Our theory supports the results by Nicholls *et al.*[7,8]

TABLE I. Minimum surface-state band gap at $\bar{J}(E_g)$ and surface-state bandwidths (W^{ss}) calculated in this work as compared to corresponding experimental data. Results are in eV.

	Theory		
	LDA	QP	Experiment
$E_g(\bar{J})$	0.24	0.67	0.65 ($\pm$0.2)[a]
			0.57 ($\pm$0.1)[b]
			0.50 ($\pm$0.04)[c]
			0.52 ($\pm$0.03)[d]
			0.50 ($\pm$0.1)[e]
$W^{\mathrm{ss}}_{\mathrm{occ}}$	0.83	0.82	0.80[f]
			0.20[g]
$W^{\mathrm{ss}}_{\mathrm{empty}}$	1.19	1.25	. . .

[a]Reference 11.
[b]Reference 6.
[c]Reference 12.
[d]Reference 13.
[e]Reference 10.
[f]References 7 and 8.
[g]Reference 9.

The main features of our theoretical surface band structure can be summarized as follows. The valence surface states bear the bonding π-orbital character along the surface atom chain, whereas the surface conduction band is mainly derived from antibonding π states. The surface states are strongly dispersive along the π-bonded-chain direction, but almost dispersionless in the direction perpendicular to the chain. The dispersion of the occupied surface band is found to be 0.82 eV, with its minimum lying at halfway between $\bar{\Gamma}$ and $\bar{J}$. The maximum of the empty surface band is located at the same $\mathbf{k}$ point. The surface conduction-band width is found to be 1.25 eV. The minimum surface-state band gap, which occurs at $\bar{J}$, is somewhat sensitive to the buckling of the π-bonded-chain atoms, which gives rise to a charge transfer from the more inward atom to the more outward atom (from atom 2 to atom 1 in Fig. 1).

A more detailed account of the surface-state energies is given in Fig. 2, where we show the calculated quasiparticle surface band structure along $\bar{\Gamma}\rightarrow\bar{J}\rightarrow\bar{K}$, in comparison with results from available experiments, including PE,[7–9] and IPE.[11] The theoretical projected bulk bands are represented by the shaded region. Information on the surface band structure deduced from angle-resolved electron-energy-loss spectroscopy[6] (EELS) is also consistent with our theory. However, it is less straightforward to obtain quasiparticle energies from the loss spectrum in EELS measurements[6] than from PE and IPE. In lining up the experimental data in Fig. 2, the Fermi level is taken to be at 0.1 eV above the valence-band maximum (VBM) according to these experiments.[7–9,11]

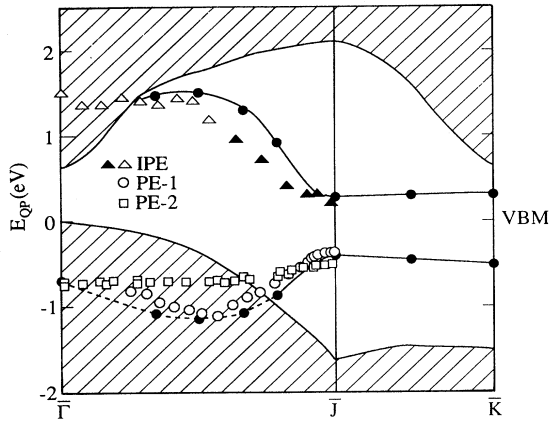

FIG. 2. Theoretical quasiparticle surface band structure for Ge(111)-2×1 compared with results from various experiments. Shaded regions represent the projected bulk bands. (●——●), present theory (dashed line indicates resonances); (▲), strong features in IPE from Ref. 11; (△), weak features in IPE from Ref. 11; (○), PE-1 from Refs. 7 and 8; (□), PE-2 from Ref. 9.

As seen in Fig. 2, the two sets of angle-resolved PE (Refs. 7–9) give quite different band dispersion for the occupied surface states. The one by Nicholls *et al.*[7,8] shows a highly dispersive occupied band with a bandwidth 0.8 eV; the other one by Solal *et al.*[9] only shows a 0.2 eV dispersion. Our theory agrees very well with Nicholls *et al.* and we believe the π-bonded-chain structure in our calculation represents the (2×1) surface reconstruction of the samples upon which PE measurements by Nicholls were carried out. An interpretation of the PE spectra by Solal *et al.* remains elusive up to this point.[11,12]

Experimentally, it was observed[1,2] that for *n*-doped Ge(111)-2×1, the Fermi level almost coincides with the valence-band maximum. One of the suggested possible mechanisms is that the bottom of the conduction surface-state band lies nearly at the same energy as the bulk valence-band maximum, and thus is responsible for the peculiar Fermi-level pinning.[11] Our calculated lowest empty surface state at absolute zero temperature lies at 0.25 eV above the VBM, and is unlikely to be the cause responsible for the observed Fermi-level pinning at the VBM for *n*-doped Ge(111)-2×1 surfaces without a significant band bending. We note that the quality of cleaved surfaces of Ge(111) is, in general, not as good as those of GaAs(110) or Si(111).[2] The presence of a number of steps and other defects on this surface under the experimental conditions[2] indicates that defect states may play an important role in determining the Fermi level.

Two kinds of samples were used in previous PE and IPE experiments: heavily *n*-doped[10] and undoped (or lightly doped)[11] crystals. In the former case, the normally empty conduction surface-state band is partially occupied, allowing for a PE study for these states. In the latter case, both PE and IPE are required for a determination of the surface-state band gap and the dispersion of the conduction and valence surface bands. The difference between these two sets of experiments for the surface-state band gap is only about half of that given by a theory for band-gap shrinkage upon heavy *n* doping.[14] This discrepancy could be ascribed to the use of the effective-mass approximation and the static screening approximation employed in Ref. 14. Both approximations are not well founded when the theory predicts that the band shrinkage is comparable to the band gap itself.[14] The band-gap decrease due to the presence of the doped electrons and the screening seen by these electrons need to be treated on equal footing. Similarly, a self-consistent treatment of the dynamical screening effects in the formation of the excitons is also important for an accurate evaluation of the excitonic effects in the optical spectrum. A simple theory[25] has illustrated how the presence of electron-hole interaction can modify quite dramatically the shape of the surface-state optical absorption spectrum in the case of Si(111)-2×1.

In the calculation of the photoelectric threshold ϕ, a thick vacuum region between slabs is required to give a reliable vacuum level. In investigating the surface band structure, this is less crucial since only relative energies are needed. The photoelectric threshold is defined as the energy of the valence-band maximum deep in the bulk relative to the vacuum potential level, i.e.,

$$\phi = \phi_{\text{vac}} - E^{\text{QP}}_{\text{VBM}} . \tag{2}$$

We have used both Ceperley-Alder[23] (CA) and von Barth- Hedin[24] (BH) correlation potentials in our photoelectric threshold calculations within the LDA. The BH correlation potential is lower by about $\sim$0.5 eV for electron-density parameter r_s from 2 to 6 compared to the CA potential. We find that the results for ϕ_{LDA} depend on the form of the exchange-correlation potential used, although the exact density-functional theory would yield the correct ionization energy for a many-electron system.[26] Within the LDA, the BH correlation potential gives a photoelectric threshold which is 0.26 eV larger than that from the Ceperley-Alder potential. This difference is less than the 0.5 eV difference in the bulk correlation potential itself, because of screening of the surface dipole from self-consistent charge rearrangements. Comparing the charge-density distribution from these two exchange-correlation potentials, we observe a slightly greater penetration of the electron density into the vacuum region in the Ceperley-Alder case, resulting from the higher potential in the bulk region. This gives rise to a dipole potential that screens partially the original increase in potential.[26] However, screening is not as effective as the zero-dipole model would have suggested in this specific case.[27] From the zero-dipole model, one expects that the change in ϕ_{LDA} would be about the change in V_{LDA} divided by $(1+16)/2$—the effective dielectric screening constant. We see that this is not the case here.

We have taken the von Barth-Hedin LDA results and evaluated the many-body corrections to ϕ_{LDA} since the *GW* approximation in the electron gas corresponds to the random-phase approximation employed in calculating the von Barth-Hedin correlation energies. From Eq. (2), it is clear that the many-body correction to the LDA photoelectric threshold only appears in the $E^{\text{QP}}_{\text{VBM}}$ term which is a bulk property and may be obtained from a bulk quasi-

particle calculation. Thus

$$\phi_{QP} = \phi_{LDA} - \Delta_{VBM} , \quad (3)$$

where Δ_{VBM} is the many-body correction to the LDA energy of the VBM in the bulk. Following this procedure,[28] we only find a 0.1 eV increase in the photoelectric threshold within our *GW* approximation. Our final result for the photoelectric threshold is 4.73 eV, in good agreement with the experimental values of 4.74–4.80 eV.[1,2]

In conclusion, the present quasiparticle calculation provides a quantitative analysis and understanding of the experimental electronic spectra of the Ge(111)-2×1 surface, including those from photoemission, inverse photoemission, and angle-resolved electron-energy-loss spectroscopy. This lends a very strong support to the π-bonded-chain model for the reconstruction of the Ge(111)-2×1 surface. It is a good indication of the applicability of the model dielectric matrix approach to quasiparticle self-energy calculations of heterostructure systems. Our theoretical result for the photoelectric threshold is also in excellent agreement with experiment. The many-body correction beyond the LDA to this quantity appears not to play a major role for this surface.

We thank John Northrup for many helpful communications. This work was supported by NSF Grant No. DMR88-18404 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. X.Z. acknowledges support from the Center for Advanced Materials and S.G.L. acknowledges support from the Guggenheim Foundation. Cray computer time was provided by the NSF at the San Diego Supercomputing Center and by the Department of Energy.

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