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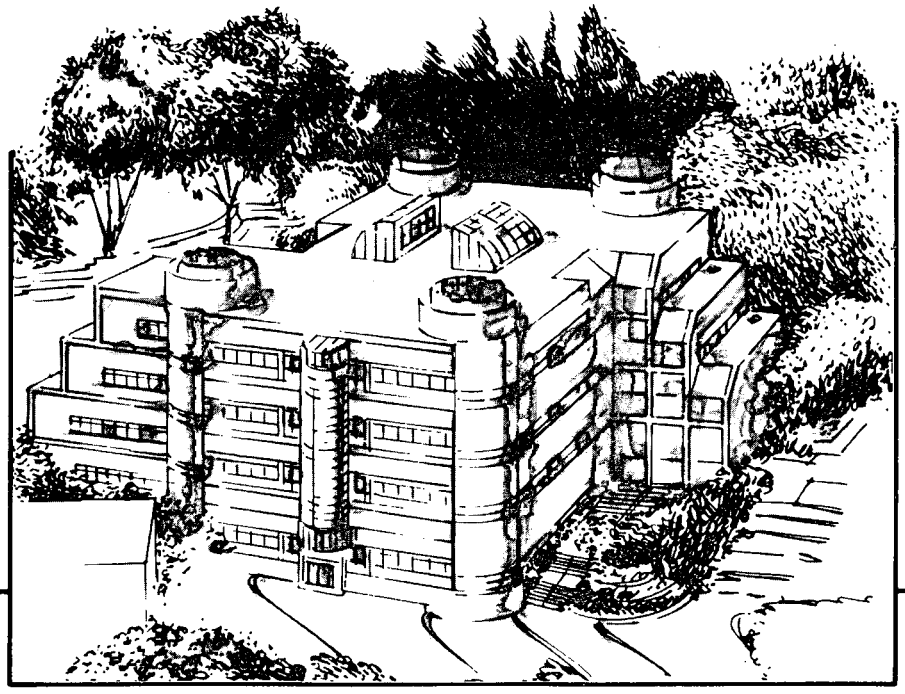

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ABSTRACT

We have studied from first principles the quasiparticle properties of the 2×1 reconstructed (111) surface of Ge. Quasiparticle energies are calculated using the *GW* expansion of the electron self energy operator. The calculations explain a spectrum of experimental results obtained from photoemission, inverse photoemission, optical absorption, scanning tunneling microscopy, *etc.*, for this surface. We also present a quasiparticle theory for the photoelectric threshold and examine the effects of many body corrections for this quantity.

Introduction A recent theory[1] based on Hedin's *GW* approximation for the electron self energy operator has enabled us to calculate and predict the quasiparticle excitation energies at semiconductor surfaces at the accuracy level of 0.1 eV. In this contribution, we report some recent results[2] for the quasiparticle properties at the Ge (111)-2×1 surface using the scheme developed by Hybertsen and Louie. Our theoretical results, which are obtained based on the π-bonded chain reconstruction model[3], are in very good agreement with a host of experimental results. We have also computed the photoelectric threshold energy for this surface within the quasiparticle scheme, and thus gone beyond the standard local density approximation (LDA)[4] for this quantity.

The Structural Model and Calculational Details The quasiparticle energy calculations are based on a π-bonded chain geometry[3,5] of the 2×1 reconstructed Ge (111) surface with significant buckling. The structural parameters were determined from a LDA total energy calculation using the supercell technique with 24 atoms. Using a 32 atom supercell gives rise to changes less than 0.05 eV for the band gap. The wavefunctions are expanded in a plane wave basis with energy cutoff $E_{cut} = 8\ Ry$. The difference in elevations of the two top layer atoms, *viz*, the buckling of the π-bonded chain, is 0.57 a.u..

In the *GW* approach[1], the electron self energy can be expressed as:

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

where G is the dressed single particle Green's function and $W = \epsilon^{-1}V$ is the dynamically screened Coulomb interaction. The static dielectric matrices $\epsilon_{\vec{G},\vec{G'}}(\vec{q},\omega=0)$

are calculated with use of the Hybertsen-Louie model[1] for elements with $|\vec{q}+\vec{G}|^2 \leq 4.8\ Ry$. 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. The dynamical effects in the screened Coulomb interaction W are accounted for by the generalized plasmon-pole model[1]. The projected bulk qausiparticle bands are calculated on equal footing to achieve accurate band alignment.

Quasiparticle Energies at Ge (111)-2×1 In Table I, we compare the calculated surface-state band gap and band dispersions with available experimental data[6−10]. Optical measurements[7] give a band gap around $0.5 - 0.55\ eV$, somewhat lower than our theoretical value of $0.67\ eV$, whereas a value of $0.65 \pm 0.2\ eV$ is inferred from combined inverse photoemission (IPE) and photoemission (PE) results[6]. A scanning tunneling spectroscopy on the Ge (111)-2×1 surface[8] yields a direct surface gap of 0.65 ± 0.09 eV. The difference between the surface band gap measured by optical processes and that by PE and IPE processes is very similar to the situation at the Si (111)-2 × 1 surface, and is believed to be due to excitonic effects present in the optical processes[11]. Taking the experimental and the theoretical results together, we conclude that the π-bonded chain model represents well the 2×1 reconstruction of this surface. There is, however, one PE experiment[10] which is incompatible with a simple π-bonded 2×1 reconstruction. This is also given in Table I.

The complete surface band structure is depicted in Fig. 1 along with several experiments[6,9,10]. In lining up the experimental data in Fig. 1, the Fermi level is taken to be at $0.1\ eV$ above the valence band maximum (VBM) according to these experiments[6,9,10,12]. Once again, we see the two sets of the PE experiments give quite different occupied bandwidth[9,10].

Theory for the Photoelectric Threshold The photoelectric threshold is defined as the energy of the bulk valence band maximum relative to the vacuum potential level, i.e.,

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

We have used both Ceperley-Alder (CA)[13] and von Barth-Hedin (BH)[14] 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. It is well-known that the exact density functional theory would yield the correct ionization energy for a many electron system[4]. However, 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[2].

We have taken the von Barth-Hedin LDA results and evaluated the many-body corrections to ϕ_{LDA}[1,2] since the *GW* approximation in the electron gas corresponds to the random phase approximation employed in calculating the von Barth-Hedin correlation energies[14]. From Eq. 2, it is clear that the many-body correction to the LDA photoelectric threshold only appears in the E^{qp}_{VBM} term, provided that ϕ_{LDA} is treated at an equal level of approximation. Thus:

$$\phi_{qp} = \phi_{LDA} - \Delta_{VBM} \ , \tag{3}$$

where Δ_{VBM} is the many body correction to the LDA energy of the VBM in the bulk. Following this procedure, we 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[12].

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

	Present Theory		Experiment
	LDA	QP	
$E_g(\overline{J})$	0.24	0.67	0.65 (±0.2)[6]
			0.50 (±0.04)[7a]
			0.52 (±0.03)[7b]
			0.65 (±0.09)[8]
W_{occ}	0.83	0.82	0.80[9]
			0.20[10]
W_{empty}	1.19	1.25	—

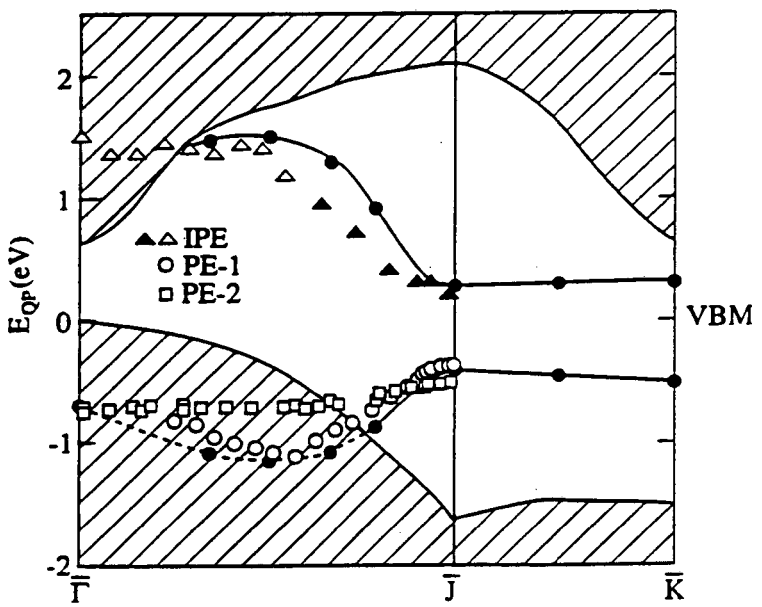

Fig. 1. Quasiparticle surface band structure for Ge (111)-2×1. Shaded regions are the calculated projected bulk states.
(●—●) – Present theory.
(▲) – strong features in Ref.6.
(△) – weak features in Ref.6.
(○) – PE-1 from Ref.9.
(□) – PE-2 from Ref.10.

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