Localized Excitons and Breaking of Chemical Bonds at III-V (110) Surfaces

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Electron-hole excitations in the surface bands of GaAs(110) are analyzed using constrained density-functional theory calculations. The results reveal formation of autolocalized Frenkel-type excitons which merge in microscopic "droplets" due to attraction initiated by exciton-induced unrelaxation of the surface. A substantial weakening of the bonding of the topmost Ga atom is found in such an "exciton droplet." This finding suggests a microscopic mechanism of laser-induced emission of the neutral Ga atoms from GaAs and GaP (110) surfaces.

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Surface electron states, in particular for covalently bound *sp*-electron semiconductors, are very sensitive to the surface geometry. This implies an important role of electron-lattice interaction at surfaces. Coulomb correlations are also enhanced due to weaker screening, reduced dimensionality, and larger effective masses of the charge carriers in the surface bands.

Recent experiments [1,2] show that optical excitation (below the ablation threshold) of the clean GaAs and GaP (110) surfaces can lead to emission of neutral Ga atoms. A superlinear dependence of the Ga yield on laser fluence [1,2] indicates that several electron-hole (*e-h*) excitations are needed to set the Ga atom free. It was argued [1–3] that the effect is due to surface defects which contain weakly bound Ga atoms. The explanation offered in Refs. [1–3] implies that in the presence of *e-h* excitations the adiabatic potential energy surface for these Ga atoms becomes antibonding, which causes their desorption. This mechanism is analogous to the well-known Menzel-Gomer-Redhead mechanism of desorption [4,5]. A specific feature of the scenario [1–3] is that the bond breaking is suggested to occur as a consequence of pairing of holes on the same covalent bond due to a strong electron-phonon interaction. This idea, although supported by semiempirical [6] and model tight binding [7] calculations, has remained a key assumption of the model [1–3].

In the present paper we show that a strong exciton-lattice interaction is an intrinsic property of a defect-free GaAs(110) surface. Even in the absence of defects the *e-h* pairs become autolocalized due to induced surface unrelaxation. We find that the hole density is indeed concentrated on the covalent bonds of the topmost Ga atom.

The (110) surface of III-V compounds maintains the (1 × 1) rectangular symmetry of a bulk (110) crystallographic plane. It relaxes so that the surface cation atoms shift inwards and the anion atoms shift outwards, leaving the cation-anion distance almost unchanged. The relaxation can be described as a quasirigid rotation of As-Fa bonds or as a frozen in "rotational" surface phonon. As concluded from inelastic He scattering [8], this phonon has practically no dispersion; i.e., the As-Ga pairs in different surface cells move almost independently.

Density-functional theory (DFT) calculations reproduce the surface geometry for all III-V compounds quite accurately and reveal two surface bands around the fundamental gap—one occupied and one empty (see Ref. [9], and references therein). The occupied state is predominantly composed of the anion dangling orbitals, and the unoccupied one consists of the cation dangling orbitals. In the following we refer to these band as As-like or Ga-like states as we consider the GaAs(110) surface. Figure 1 shows the surface band structure of GaAs(110) that we calculated using DFT in the local-density approximation (DFT-LDA). We employ a plane wave basis set with a cuttoff of 8 Ry and a slab geometry with a slab thickness of seven layers and vacuum region equivalent to five layers (further details of the calculational method are given in Refs. [9–11]). Since the single-particle

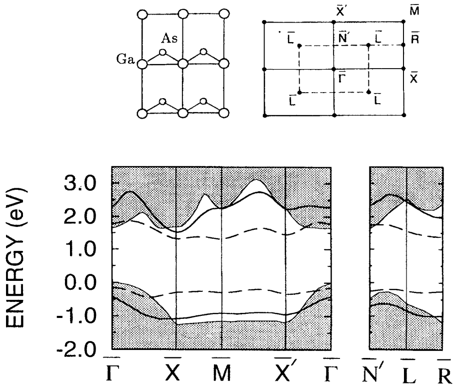

FIG. 1. The calculated energy band structure of the GaAs(110) surface along the perimeter and inside the surface Brillouin zone (SBZ). The shaded regions are projected bulk bands. The dashed lines show surface bands obtained for unrelaxed surface. The energy zero is set at the top of the bulk valence band. The upper panel displays the top view at GaAs(110) surface and the SBZ. The broken lines enclose the smaller SBZ of the (2 × 2) surface cell.

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DFT-LDA eigenvalues, strictly speaking, have no direct physical meaning, to calculate a measurable band structure one has to replace the exchange-correlation potential, V^{xc}, by the nonlocal, energy dependent, complex self-energy, $\Sigma(\varepsilon, \mathbf{r}, \mathbf{r}')$. However, for GaAs and its (110) surface it has been shown [12–14] that in the region of the fundamental energy gap the quasiparticle correction is almost **k** independent; i.e., it shifts the DFT-LDA bands almost rigidly. For conduction bands the shift is about 0.7 eV upwards. For valence bands it is an order of magnitude smaller. Our DFT-LDA band structure has been corrected by the self-energy effect on the conduction band states. The clue to the understanding of the exciton self-trapping is in the link between the surface relaxation and the energy position of the surface states. The relaxation pushes the surface states out of the band gap. It is apparently driven by the energy gain due to lowering of the occupied As band. The *e-h* pair, with an electron in the Ga band and a hole in the As band, should tend to reduce the surface relaxation as this would shift the electron level downwards and the hole level upwards, thus decreasing the energy of the excitation. Both particles thus become self-trapped in a potential well created by the local surface unrelaxation. The localization region is likely to be very compact—about the size of the surface elementary cell, since this "saves" relaxation energy and is not opposed by the weak elastic coupling to neighboring cells. This mechanism of exciton self-trapping is similar to electron localization due to the surface polaron effect [15] which was suggested to be responsible for nonmetallic behavior of the GaAs(110) surface covered with an alkali-metal submonolayer [16,17].

A simple effective mass estimate shows that the exciton binding energy is strongly enhanced at the surface. The effective "surface" Rydberg is

$$\mathrm{Ry}_s^* = 4\frac{m_s^* e^4}{2\hbar^2 \varepsilon_s^2} \approx 16\frac{m_s^*}{m^*}\mathrm{Ry}^*, \tag{1}$$

where the factor of 4 is due to the two-dimensional character of the electron motion, and $\mathrm{Ry}^* = m^* e^4 / 2\hbar^2 \varepsilon_0^2 \approx$ 4 meV is a "bulk" Rydberg with the bulk dielectric constant ε_0. The "surface dielectric constant," $\varepsilon_s = (1 + \varepsilon_0)/2$, enhances the exciton binding energy by another factor, $(\varepsilon_0/\varepsilon_s)^2 \approx 4$. The coefficient, m_s^*/m^*, accounts for the different effective mass at the surface. A rough estimate for GaAs(110) gives $m_s^*/m^* \approx 4$, so that $\mathrm{Ry}_s^* \approx$ 0.26 eV and the corresponding Bohr radius, $a_s^* \approx 8$ Å, is about the size of the surface elementary cell. Therefore the surface excitons are rather of a Frenkel than of a Wannier-Mott type, and the effective mass approximation is actually inadequate. Therefore we use DFT-LDA to study the surface *e-h* excitations and their interaction with the lattice. At first glance this appears not to be justified since DFT is a ground state theory. However, by introducing appropriate constraints (see, e.g., [18]) it is possible to get a meaningful description of the localized *e-h* excitations in the DFT-LDA formalism.

In the Kohn-Sham scheme of DFT the total electron density $n(\mathbf{r})$ is constructed from auxiliary one-particle wave functions $\phi_i(\mathbf{r})$:

$$n(\mathbf{r}) = \sum_i n_i |\phi_i(\mathbf{r})|^2 . \tag{2}$$

The occupation numbers n_i are equal to two for states below the Fermi energy and to zero above (we presume that each state is spin degenerate). Although the Kohn-Sham orbitals $\phi_i(\mathbf{r})$ do not have a direct physical meaning, for GaAs and its (110) surface they are in fact very close to the actual quasiparticle wave functions in the energy range around the band gap [12–14]. Therefore the quasiparticle correction, which leads to almost rigid shift of the conduction bands, does not affect the wave functions of quasiparticles and hence their Coulomb interaction as well as their coupling to the lattice. We therefore presume that setting the occupation number of one level in a valence surface state to $n_i = 1$ and occupying one level in the empty surface state adequately represents the electron density of an *e-h* pair. This means that electron density should be determined via a self-consistent solution of the DFT-LDA equations for $\phi_i(\mathbf{r})$ using Eq. (2) with the just-noted constraint on the occupation numbers.

A remark concerning the calculational method should be made here. To solve self-consistently the Kohn-Sham equations we use an iterative procedure [10] based on the Car-Parrinello scheme [19]. Since this method is aimed at finding the ground state, one might think that iterative evolution of the trial wave functions can interchange the electron and hole levels eventually, bringing all occupied states below the empty ones. However, this does not happen in our case. The reason is that the two levels are separated by the fundamental gap, which is substantially larger than the shift of the one-particle levels due to the *e-h* excitation.

Once the exciton is formed and eventually becomes localized due to the coupling to the lattice, the electron and hole wave functions do not obey translational invariance and the orbitals $\phi_i(\mathbf{r})$ should not be required to the Bloch states. Willing to keep advantage of a plane wave basis, one has to use a supercell which would allow the Bloch states to build the localized wave packets. We performed calculations for a (2×2) surface cell which allows the umklapp processes with wave vectors $\overline{\Gamma}\,\overline{X}$ and $\overline{\Gamma}\,\overline{X'}$ (see upper panel in Fig. 1).

Let us first consider the *e-h* excitation in the $\overline{X}$ point which determines the absorption edge for optical transitions between the surface states [13]. That is, we take the electron and hole states in the $\overline{X}$ point as the trial wave functions and allow them to evolve to the "ground state" which contains a single *e-h* pair in a supercell. Figure 2(a) shows a resulting change of the total electron density. No tendency to the formation of an

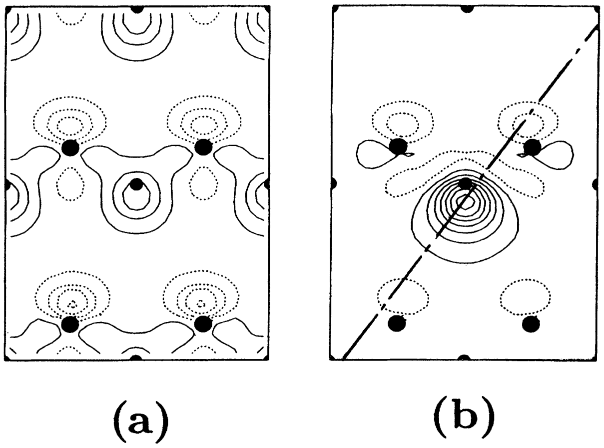

FIG. 2. Top view at the exciton-induced change of electron density: (a) an $\overline{X}$ exciton and (b) an $\overline{L}$ exciton. We display a cut through the (110) plane 0.6 Å above the surface which runs through the middle of the Ga dangling orbitals. Small circles stand for Ga atoms, large for As atoms. The lattice is kept at the ideal ground-state configuration. An increase of the density is shown by the solid lines (electron), a decrease by the dashed lines (hole). Note the difference in scale for (a) the density step is 0.5×10^{-3} bohr^{-3}, for (b) it is 1×10^{-3} bohr^{-3}. The dash-dotted line defines the orientation of the orthogonal plane used for the side view in Fig. 3.

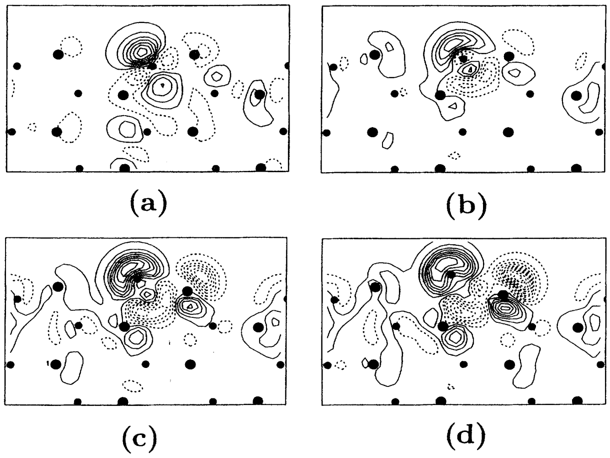

FIG. 3. Side view at the exciton-induced electron density for $\overline{L}$ excitations. Small circles are Ga atoms, large are As atoms. (a) A single excited *e-h* pair. The lattice is kept frozen at the clean surface ground-state geometry. (b) Same as in (a) but for a relaxed lattice. (c) Double *e-h* excitation in a relaxed lattice. (d) Triple *e-h* excitation in a relaxed lattice. Note the difference in scale: for (a) the density step is 1×10^{-3} bohr^{-3}, for (b)–(d) it is 4×10^{-3} bohr^{-3}.

e-h bound state is seen, and the excitation energy E_X is only about 0.08 eV smaller than the band gap. This result is actually apparent since in our supercell, $\overline{X}$ states are allowed to mix only with the states in $\overline{\Gamma}$, $\overline{X}'$, and $\overline{M}$. In all these points the Ga-band and As-band wave functions are equally distributed between the Ga and the As dangling orbitals, respectively, and cannot form a compact wave packet.

In contrast, an *e-h* excitation at the $\overline{L}$ point leads to well localized charge distribution [Fig. 2(b)]. The reason is that eigenfunctions in the four $\overline{L}$ points can combine into wave packets which closely represent dangling bonds of individual Ga or As atoms [15,20]. The localized charge distribution arizes automatically during iterations to self-consistency, although the "starting" charge distribution may look very similar to the one shown in Fig. 2(a). It is clearly seen in Fig. 2(b) that the electron and hole form a compact bound state—a surface exciton.

The exciton density in Fig. 2(b) was obtained by maintaining the reflection symmetry in the plane through the Ga atom. If, instead, a reflection symmetry in the plane through the As atom is requested, the hole becomes entirely localized and the electron is smeared over surrounding Ga orbitals. This state, however, requires higher excitation energy. The total energy calculation shows that the $\overline{L}$ excitation costs 3.1 eV. Comparisons with the energy gap in the $\overline{L}$ point (3.6 eV) gives the exciton binding energy about 0.5 eV.

Figures 3(a)–3(d) show the side view at $\overline{L}$ excitation in the plane indicated by the dash-dotted line in Fig. 2(b). An electron (solid contour lines) resides at the Ga dangling orbital, whereas a hole (dashed contour lines) is distributed over neighboring Ga-As bonds. In Fig. 3(a) the ideal relaxed surface geometry is kept fixed; i.e., it shows the side view at the charge distribution of Fig. 2(b). In Figs. 3(b)–3(d) the lattice has been relaxed according to the perturbed electron density. Therefore we assume that the exciton lifetime is longer than the inverse rotational phonon frequency, ≈0.4 ps. For a single *e-h* pair [Fig. 3(b)] the lattice relaxation lowers the excitation energy to 2.7 eV. In the case of two and three excited *e-h* pairs [Figs. 3(c) and 3(d)] we find that energetically optimal density distribution corresponds to double or triple exciton complexes localized around the same Ga site, but not to separate excitons. Figure 4 shows that this strong exciton-exciton attraction is almost entirely due to the lattice distortion.

Whereas a single $\overline{L}$ excitation is energetically more costly than an $\overline{X}$ excitation, in the case of two or three excited *e-h* pairs the localized double or triple exciton complexes become more favorable. Therefore at sufficiently high excitation level (which is actually determined by exciton kinetics), we expect that the homogeneous state becomes unstable, and autolocalized multiple *e-h* complexes are formed.

From Figs. 3(b)–3(d) a large displacement of the surface Ga atom which holds extra electrons is evident. The electron density redistribution suggests a weakening of the

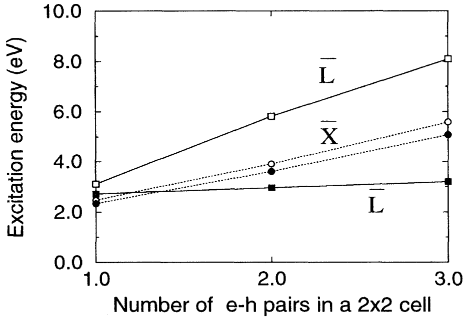

FIG. 4. Excitation energies for different numbers of e-h pairs in a 2×2 surface supercell. $\overline{X}$ excitations (dashed lines) induce a delocalized electron-hole density, $\overline{L}$ excitations are localized: These are a single $\overline{L}$ exciton and double and triple e-h complexes around the same Ga site. The upper curves for both $\overline{X}$ and $\overline{L}$ excitations have been calculated with frozen lattice, the lower curves with relaxed lattice.

bonding of this atom to the substrate as a consequence of a penetration of a hole beneath it. In the examined cases of single, double, and triple excitations a Ga atom remains bound to the surface. This supports the conclusion [1–3] that laser-stimulated emission is due to surface defects, i.e., weakly bound Ga atoms. However, a nonadiabatic desorption of the regular Ga atoms may also be possible if the energy released, due to exciton recombination, could be directly transferred into the local surface vibrations. To explore this alternative a further study of the energy transfer is necessary.

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