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

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Abstract

Electron-hole excitations in the surface bands of GaAs (110) are analyzed using constrained density-functional theory calculations. The results show that Frenkel-type autolocalized excitons are formed. The excitons induce a local surface unrelaxation which results in a strong exciton-exciton attraction and makes complexes of two or three electron-hole pairs more favorable than separate excitons. In such microscopic exciton "droplets" the electron density is mainly concentrated in the dangling orbital of a surface Ga atom whereas the holes are distributed over the bonds of this atom to its As neighbors thus weakening the bonding to the substrate. This finding suggests the microscopic mechanism of a laser-induced emission of 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 may actuate a strong electron-lattice coupling at surfaces. Coulomb correlations will typically also be enhanced in surface bands due to weaker screening, reduced dimensionality, and larger effective masses of the charge carriers.

Recent experiments [1,2] show that electron-hole (e-h) excitations at the clean GaAs(110) and GaP(110) surfaces can cause emission of neutral Ga atoms which indicates a strong interaction of the surface e-h pairs with the lattice. In the present paper we investigate an electron density perturbation and related lattice distortion initiated by "pumping" e-h excitations into the surface states.

The (110) surface of III-V compounds maintains the (1×1) rectangular symmetry of a bulk (110) crystallographic plane. However it relaxes as such 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 quasi-rigid rotation of As-Ga bonds or as a frozen in "rotational" surface phonon. As concluded from inelastic He scattering [3], this phonon has practically no dispersion, which means that the As-Ga pairs in different surface cells move almost independently.

Density-functional theory 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. [4] and references therein). The occupied state is predominantly composed of the anion dangling orbitals and the unoccupied one consists of the cation dangling orbitals. Since in the following we consider the GaAs(110) surface, we will refer to these bands as to As-like or Ga-like states. Figure 1 shows the surface band structure of GaAs(110), which we calculated using density functional theory in the local-density approximation (DFT-LDA). We employ a plane wave basis set with a cutoff of 8 Ry and a slab geometry with a slab thickness of 7 layers and vacuum region equivalent to 5 layers (further details of the calculational method are given in Refs. [4,5] and [6]). Since the single-particle 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

non-local, energy dependent, complex self-energy, $\Sigma(E, \mathbf{r}, \mathbf{r}')$. However, for GaAs and its (110) surface it has been shown [7–9] that in the region of the fundamental energy gap the quasiparticle correction to LDA eigenvalues is almost $\mathbf{k}$-independent, i.e., it shifts the bands almost rigidly. For conduction bands the shift is about 0.7 eV upwards. For valence bands it is downwards and an order of magnitude smaller. Our DFT-LDA band structure shown in Fig. 1 has been corrected by the self-energy effect on the lower conduction band states.

The occupied As band agrees well with photoemission data (e.g. [10]) and the empty Ga band is in a qualitative accord with inverse photoemission [11]. Two-step photoemission [12] and optical reflectivity [13] give somewhat different energies of the Ga state. This might reflect the difference of the physical processes involved in the measurement, since inverse photoemission gives the quasiparticle energy of the *empty* state whereas *preoccupation* of the Ga state in two-step photoemission or *creation of e-h pairs* in optical reflectivity measurements implies a presence of polaron and exciton effects. However, importance of these effects becomes more apparent in optical experiments at higher excitation level [1,2], which show that laser irradiation of GaAs and GaP (110), though still below the ablation threshold, causes desorption of Ga atoms. The effect is maximal for the light polarization in $[1\bar{1}1]$ direction, i.e., along the surface Ga-As zigzag chains and practically vanishes for photons polarized in perpendicular direction. As the bulk GaAs lattice has a cubic symmetry, this means that the Ga emission is related to electron-hole excitations at the surface. The yield-fluence relation is superlinear, i.e., several *e-h* excitations are needed to release one atom. To cause the bond breaking these excitations should first become localized, which was attributed [1,2] to surface defects. Our calculations show that even on a defect-free surface a self-trapping of single, double, and triple excitons occurs.

The clue to understanding the exciton self-trapping is in the link between the surface relaxation and the energy position of the surface states. As it can be seen in Fig. 1, 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 shift of this band agrees with the relaxation energy of 0.7 eV, as it results from the total energy calculations. The *e-h*

pair with an electron in the Ga band and a hole in the As band tend to reduce locally the surface relaxation since this would shift the electron level downwards and the the hole level upwards and thus would lower the energy of the excitation. The both particles become then 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 somewhat similar to electron localization due to the surface polaron effect [14] which has been suggested to be responsible for non-metallic behavior of the GaAs (110) surface covered with alkali-metal submonolayer [15,16].

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

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

where the factor 4 is due to the two-dimensional character of the electron motion and $Ry^* = m^* e^4 / 2\hbar^2 \varepsilon_0^2 \approx 4$ meV is a "bulk" Rydberg with the bulk dielectric constant ε_0. The "surface dielectric constant", $\varepsilon_s = (1 + \varepsilon_0)/2$, inhances 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 $Ry_s^* \approx 0.26$ 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-type than of a Wannier-Mott type, and the effective mass approximation is actually inadequate.

We use DFT-LDA to study the e-h excitations and their interaction with the lattice. At first glance such approach appears to be not justified, since DFT is a ground state theory. However, by introducing appropriate constraints (see e.g. [17]) 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 the auxiliary one-particle wave functions $\phi_i(\mathbf{r})$:

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

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 [7–9]. 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 Ga state we adequately represent the electron density of a *e-h* excitation. This means that the 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.

Once the exciton is formed, the electron and hole wave functions do not separately obey translational invariance but only the whole exciton wave function does. Therefore if the Kohn-Sham orbitals in Eq. 2 are required to be Bloch states, the exciton correlations will be missing. We perform calculations using a (2×2) surface cell to allow for the umklapp processes with wave vectors $\overline{\Gamma}\,\overline{X}$ and $\overline{\Gamma}\,\overline{X'}$ (see upper panel in Fig. 1). These processes via the *e-h* Coulomb interaction should help building out of the eigenfunctions of the (1×1) periodical surface the bound *e-h* state. Let us first consider the *e-h* pair in point $\overline{X}$, which determines the absorption edge for optical transitions between the surface states [8]. Figure 2 (a) shows the change of a total electron density due to this excitation. No tendency to formation of the *e-h* bound state is seen and the excitation energy $E_{\overline{X}}$ is only slightly (by about 0.08 eV) smaller than the band gap. This result is actually apparent, since in our (2×2) supercell the $\overline{X}$-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, respectively, the Ga and As dangling orbitals and cannot form a tightly bound state. In contrast, the *e-h* pair in $\overline{L}$-point leads to a localized charge perturbation, as shown in Fig. 2 (b). The reason is that the eigenfunctions in the four $\overline{L}$-points, connected by the "new" reciprocal lattice vectors, can be combined in a wave function with nodes at all Ga (or, respectively, As) sites in a (2×2) cell except one [14,18]. It is clearly seen in Fig. 2 (b) that electron and hole form a compact surface exciton. The localized charge distribution

arizes automatically during iterations to self-consistency, although the "starting" charge distribution can look very similar to the one shown in Fig. 2 (a). The exciton density in Fig. 2 (b) was obtained maintaining the reflection symmetry in the plane through the Ga atom. If, instead, a reflection symmetry for a plane through the As atom is requested, the hole becomes entirely localized and electron is smeared over surrounding Ga orbitals. This case, however, corresponds to higher excitation energy, since the exciton-induced lattice unrelaxation is much smaller (see below). The total energy calculation shows that the $\overline{\text{L}}$-excitation costs 3.1 eV. Comparison with the energy gap in $\overline{\text{L}}$-point (3.6 eV) gives the exciton binding energy about 0.5 eV.

Figures 3 (a-d) show the side view at the localized $\overline{\text{L}}$-excitation in the plane indicated by the dashed-dotted line in Fig. 2 (b). A localization of both an electron (solid contour lines) and a hole (dashed contour lines) is apparent. In Fig. 3 (a) the ideal relaxed surface geometry is kept fixed, i.e. it shows the side view at the charge distribution of the Fig. 2 (b). In the Figs. 3 (b-d) the lattice has been relaxed according to the excited electron density distribution. Therewith we assume that the exciton lifetime is longer than the inverse surface phonon frequency, ≈ 0.4 ps. For a single e-h pair [Fig. 3 (b)] the lattice relaxation lowers the excitation energy down to 2.7 eV. In case of two and three excited e-h pairs [Fig. 3 (c,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 independent excitons.

Figure 4 illustrates that this strong exciton-exciton attraction is almost entirely due to the lattice distortion. If excitons were not interacting, the energy of two or three e-h pairs would be, respectively, two or three times larger than that of a single exciton. As the upper curves in Fig. 4 (for both $\overline{\text{X}}$ and $\overline{\text{L}}$-excitations) show, this simple proportionality is slightly violated due to the Coulomb interaction. The lower curves demonstrate a dramatic effect of the lattice relaxation on $\overline{\text{L}}$-exciton and a very weak one for $\overline{\text{X}}$-excitation. Whereas a single $\overline{\text{L}}$-exciton is energetically more costly than a delocalized $\overline{\text{X}}$-excitation, in the case of two or three excited e-h pairs the localized double or triple exciton complexes become lower in energy. Therefore at sufficiently high excitation level (which is actually determined by the exciton

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kinetics) we expect that the homogeneous state becomes unstable, and autolocalized double and triple e-h complexes are formed. From Fig. 3(b-d) a large displacement of the surface Ga atom which holds extra electrons is evident. The electron density redistribution suggests a weakening of the bond of this atom to the substrate as a consequence of penetration of the hole beneath it. It may be then possible that this surface atom will be set free and emitted as neutral Ga atom when excitons recombine and excitation energy transforms into the local surface vibrations.

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FIGURES

FIG. 1. Calculated energy band structure of GaAs (110) surface along the perimeter and inside the surface Brillouin zone (SBZ). The shaded regions are the projected bulk bands. 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 the GaAs (110) surface and the SBZ. The broken lines enclose the smaller SBZ of the (2×2) surface cell.

FIG. 2. Top view at the exciton-induced change of the 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 solid lines (electron), a decrease by 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 dashed-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 - 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 relaxed lattice; (d) Triple e-h excitation in 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}.

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.