

Rapid Research Note**Dynamics of the phonon-induced electron transfer between semiconductor bulk and surface states****Andreas Zeiser^{*,1}, Norbert Bücking¹, Jörg Götze¹, Jens Förstner¹, Patrick Hahn², Wolf Gero Schmidt², and Andreas Knorr¹**¹ Institute for Theoretical Physics, Nonlinear Optics and Quantum Electronics, Technical University Berlin, Hardenbergstr. 36 PN 7-1, 10623 Berlin, Germany² Friedrich-Schiller-Universität, Institut für Festkörpertheorie und -optik, Max-Wien-Platz 1, 07743 Jena, Germany

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The coupling of surface and bulk states at semiconductor surfaces through electron–phonon interaction is discussed. The governing equations are derived from a microscopic theory in the framework of the density matrix theory. To gain a first insight, model wave functions are used to simulate the dynamics of nonequilibrium electron distributions in three- and two-dimensional states, coupled by Fröhlich interaction. Typical time scales for the coupling are found to be in the order of few hundreds of femtoseconds.

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Femtosecond spectroscopy is able to resolve the temporal dynamics of the relaxation of hot electron distributions in semiconductor bulk material and nanostructures [1, 2]. Recently, similar relaxation phenomena have been observed at semiconductor surfaces [3, 4]. In this note, we theoretically investigate the phonon-induced electron equilibration and transfer using a density matrix theory [1, 5].

We assume that the reconstructed surface (boundary between crystal and vacuum) forms a new periodic structure in the direction parallel to the surface ($\mathbf{r}_{\parallel} = (x, y)^T$). The Bloch theorem can be applied in these directions leading to a two-dimensional wave vector \mathbf{k} inside a surface Brillouin zone (BZ) [7] with the electron wave function: $\psi_{\mathbf{k}}^{\alpha}(\mathbf{r}) = S^{-1/2} \exp(i\mathbf{k} \cdot \mathbf{r}_{\parallel}) v_{\mathbf{k}}^{\alpha}(\mathbf{r})$. $v_{\mathbf{k}}^{\alpha}$ is the Bloch function, defined on the whole z -axis, and S is the surface area. Two-dimensional surface bands can be described by choosing $\alpha = \lambda_s$ as band index. Despite the symmetry breaking by the surface, bulk states can nevertheless be labeled in a first approximation with their band index $\lambda^{(3d)}$ from the infinite crystal, and their three-dimensional wave vector $\mathbf{k}^{(3d)}$, which lies inside a three-dimensional BZ. Since the parallel translational symmetry is in our case smaller than in the infinite case, there is no bijective correspondence between the projected bulk BZ and the surface BZ. However, for the dynamics near the $\bar{\Gamma}$ (surface BZ) resp. Γ (bulk BZ) points, this plays only a minor role and we identify $\mathbf{k} = (\mathbf{k}_x^{(3d)}, \mathbf{k}_y^{(3d)})^T$. Therefore, in our notation, we use for the bulk states the compound index $\alpha = (\lambda^{(3d)}, k_z^{(3d)})$. Similarly the bulk and surface phonon modes are labeled by κ and the two-dimensional wave vector \mathbf{q} , analogous to α and \mathbf{k} for bulk and surface electrons.

Including the kinetic energies of electrons and phonons as well as their interaction in the Hamiltonian [8, 9], we have used Heisenberg equations to derive a coupled set of differential equations including electron–phonon many body correlations. Markovian and second order Born approximation [8, 9] are used to truncate higher order correlations. The phonons are assumed to be a thermal bath for the electrons and are described by

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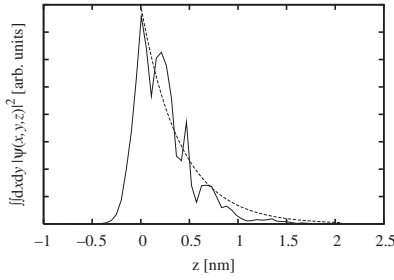


Fig. 1 Electron probability of C₁ surface state of InP(100) 2 × 4 mixed dimer, averaged with respect to parallel directions (solid line) and exponential fit (dashed line).

a Bose–Einstein distribution n_q^k (temperature T [10]). A closed system of dynamical equations is obtained, which only contains expectation values of transition amplitudes ($p_{k,k'}^{\alpha,\alpha'}$, $\alpha \neq \alpha'$ or $k \neq k'$) and state occupations (f_k^α). Here we focus on the incoherent electron transfer, which can be described by the equations for the occupations:

$$\dot{f}_k^\alpha = -\Gamma_k^{\alpha,\text{out}} f_k^\alpha + \Gamma_k^{\alpha,\text{in}} (1 - f_k^\alpha), \quad (1)$$

$$\Gamma_k^{\alpha,\text{in/out}} = \frac{2\pi}{\hbar} \sum_{\substack{\alpha',k',q \\ \kappa^\pm}} |D_{k,k',q}^{\alpha,\alpha',\kappa}|^2 \delta(E_k^\alpha - E_{k'}^{\alpha'} \mp \Omega_q^\kappa) \begin{cases} (n_q^\kappa + \frac{1}{2} \pm \frac{1}{2}) & (1 - f_{k'}^{\alpha'}) \quad \text{out} \\ (n_q^\kappa + \frac{1}{2} \mp \frac{1}{2}) & f_{k'}^{\alpha'} \quad \text{in.} \end{cases}$$

Here, E_k^α (Ω_q^κ) is the energy of electrons (phonons). D is the electron–phonon coupling element (for specific examples see below).

To evaluate Eq. (1) a model system for the InP(100) 2 × 4 mixed dimer surface is used. Here an unoccupied surface state exists at about 0.25 eV above the conduction band minimum [6] and time resolved two-photon photoemission experiments suggest, that this surface state couples to the bulk conduction band [3]. For the conduction band dynamics, one three-dimensional band (c) and one two-dimensional band (surface band, s) are taken into account. Both bands have their minimum at the Γ resp. $\bar{\Gamma}$ point, the surface band lying 0.25 eV above the minimum of the conduction band. The energies are taken in effective mass approximation, where $E_k^\alpha = E_0^\alpha + \frac{\hbar^2}{2m_{\text{eff}}^\alpha} k^2$ [10]. In principle, the rates Γ_k^α can be calculated using ab-initio wave functions [6], but the computational effort to evaluate bulk and surface states consistently is very high. Nevertheless, to obtain a first insight in the dynamics, model wave functions are constructed, which consist mainly of Bloch functions of the infinite semiconductor, but different envelope. The bulk wave functions are terminated at the surface. For the Bloch function this leads to $v^{c,k_c}(\mathbf{r}) = L^{-1/2} e^{ik_z z} u^c(\mathbf{r}) \Theta(z)$. Here, $\Theta(z)$ is the step-function, u^c is the Bloch function of the infinite semiconductor, and L is the reference length in z -direction. Guided by DFT calculations [6], cf. Fig. 1, we set the surface state exponentially decaying ($\Lambda = 2.4 \text{ nm}^{-1}$) inside the material: $v^s(\mathbf{r}) = \Lambda^{-1/2} e^{-0.5\Lambda z} u^s(\mathbf{r}) \Theta(z)$, where u^s is a Bloch like function, defined on the elementary cell of the infinite semiconductor.

With these model wave functions, the electron–phonon coupling elements can be calculated. As a first approach, only bulk LO phonons (Fröhlich interaction) are considered. The general matrix element and, as an example, the explicit coupling term between bulk and surface states follow:

$$D_{k,k',q}^{\alpha,\alpha',\text{LO}} = C \int (\psi_k^\alpha)^* \frac{e^{iq^3 d} \mathbf{r}}{|\mathbf{q}^{3d}|} \psi_{k'}^{\alpha'} d^3 \mathbf{r}, \quad D_{k,k',q}^{(c,k_c),s,\text{LO}} = C \frac{1}{|\mathbf{q}^{(3d)}|} \frac{iL^{-1/2} \Lambda^{1/2}}{|q_z - k_z + i\Lambda/2|} D^{c,s}. \quad (2)$$

Here, $C = (e^2 \Omega^{\text{LO}})^{1/2} (2SL \epsilon_0 \epsilon_{\text{phon}})^{-1/2}$, $D^{c,s} = V_{\text{EC}}^{-1} \int_{\text{EC}} u^c(\mathbf{r})^* u^s(\mathbf{r}) d^3 \mathbf{r}$, where V_{EC} is the volume of the elemen-

tary cell of the infinite semiconductor [10]. We demand that u^c and u^s are not perpendicular and estimate the maximum value using the Cauchy–Schwartz-inequality: $|D^{c,s}| \leq 1$.

The scattering equations (Eq. (1)) are numerically calculated for two different situations: (i) initially all electrons occupy the surface state (Fermi–Dirac distribution) and relax to the conduction band; (ii) initially all electrons occupy the conduction band (Gaussian distribution), energetically above the surface state. In both cases, the coupling strength is taken to have its maximal possible value ($D^{c,s} = 1$).

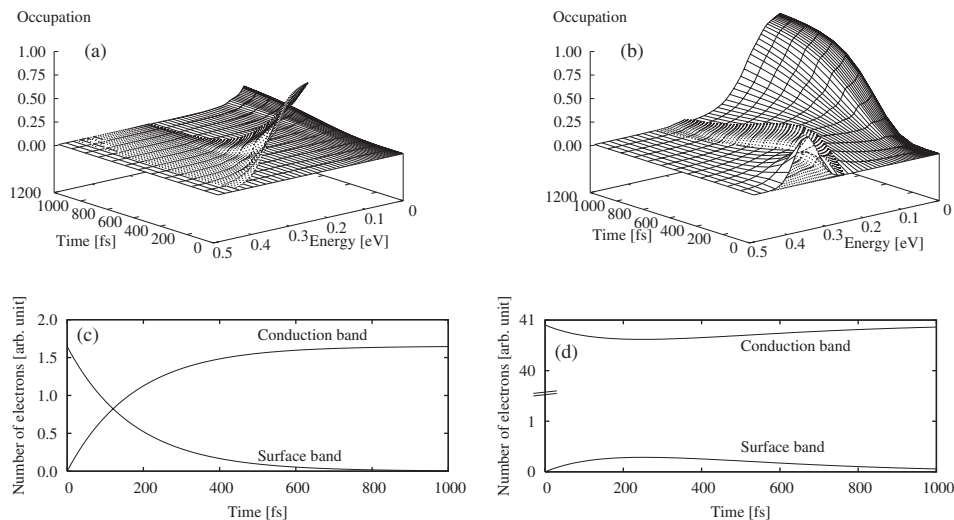


Fig. 2 Electron occupation dynamics (a, b) of bulk band (0 eV) and surface band (0.25 eV) for (i) and (ii). Time dependence (c, d) of total number of electrons in surface and bulk band for (i) and (ii).

(i) Figure 2a, shows the temporal and energetic interplay of the surface occupation (initially peaked at 0.25 eV, at the minimum of the surface state) and the bulk occupation (bottom at 0 eV). Within several hundred femtoseconds, the surface electrons relax through phonon emission to the bottom of the conduction band, forming a Fermi distribution. Using the total number of electrons in each band (Fig. 2c) the time constant for the electron transfer is estimated to be 175 fs [11] by assuming an exponential decay.

(ii) Figure 2b shows the equilibration and electron transfer of hot bulk electrons to isoenergetic surface states. As the surface band has less states than the conduction band the total number of electrons in the surface band is small compared to the conduction band (cf. Fig. 2d). At about 200 fs [11], the electrons scatter back to the bulk band and totally vacate the surface band.

In conclusion, electron transfer at semiconductor surfaces can be initiated by electron–phonon interaction and will contribute to explain recent experiments [3]. Future work should focus additionally on the ab-initio calculations of the matrix elements and the contribution of electron–electron interaction.

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- [10] I. Waldmüller et al., in: *Nonequilibrium Physics at Short Time Scales*, ed. by K. Morawetz (Springer, Berlin, 2004).
- [11] The effective masses are $m_{\text{eff}}^s = 0.2$ and $m_{\text{eff}}^c = 0.068$ and the offsets $E_0^s = 0.25$ eV and $E_0^{(c,k_z)} = \frac{\hbar^2}{2m_{\text{eff}}^c} k_z^2$, respectively. The energy of the LO phonons was set to $\Omega^{\text{LO}} = 43$ meV, the temperature to $T = 300$ K and $\varepsilon_{\text{phon}} = 41.54$.
- [11] Note that, as the coupling strength $D^{c,s}$ is varied, also the obtained relaxation times vary, according to an inverse quadratic dependence $\tau \sim (D^{c,s})^{-2}$. The calculated times can be viewed only as a lower boundary (Eq. (2)).