# Femtosecond Transfer Dynamics of Photogenerated Electrons at a Surface Resonance of Reconstructed InP(100)

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Time-dependent two-photon photoemission spectra are used to resolve the femtosecond dynamics of hot electrons at the energetically lowest surface resonance of reconstructed InP(100). Two different cases are studied, where electrons either are lifted into the surface resonance via a direct optical transition or are captured from bulk states. These data are the first of this kind recorded with a time resolution below 70 fs. The microscopic analysis shows that electron-phonon scattering is a major mechanism for electron transfer between surface and bulk states.

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The ultrafast optical injection of electrons into nonequilibrium states and the subsequent transfer dynamics to reach an equilibrium situation yield insight into basic transport processes of charge carriers. Especially semiconductors with their well defined initial equilibrium conditions (occupied and unoccupied bands separated by an energy gap) are ideal systems for investigating optically induced quantum transport processes via pump-probe experiments. At semiconductor surfaces the transport processes involve states of different character, such as surface (two-dimensional) and bulk (three-dimensional) states, thus representing a model situation in quantum transport. Hot electron dynamics at the surface of a semiconductor can be considered a model case for corresponding processes that occur at buried interfaces of electronic devices [1,2]. The purpose of this Letter is to analyze surface reconstructed InP as a model system for electron transfer involving a surface resonance and bulk states.

Dynamics of optically generated electrons at the surface of semiconductors has been studied in recent years with various experimental techniques, i.e., transient absorption, time-dependent luminescence, and two-photon photoemission (2PPE) [1–8]. In particular, Rettenberger and Haight have addressed the role of a well-known surface resonance on Ge(111):As [9,10]. The attractive feature of this 2PPE experiment was the high photon energy of the probe pulse that allowed for detecting hot electrons at the $\bar{M}$ point of the surface Brillouin zone. On the other hand, laser pulses of 300 fs or even 700 fs duration made it difficult to determine with sufficient accuracy time constants of 50 and 200 fs that were deduced from the measured time-dependent changes in the 2PPE spectra. Simultaneously, the theoretical analysis relied on the diffusion equation, i.e., a local equilibrium situation, and used rate equations with phenomenological rate constants to fit the data.

In the following we present experimental and theoretical results, which address the ultrafast nonequilibrium transfer dynamics of hot electrons between bulk states and a specific surface resonance, i.e., the energetically lowest surface resonance on In-rich $(2 \times 4)$-reconstructed InP(100), $C_1$ [11]. The cross correlation of about 65 fs (FWHM) allowed a more detailed analysis of the femtosecond electron dynamics in a fully nonequilibrium situation compared to earlier studies of corresponding hot electron dynamics. The so-called mixed-dimer configuration is characteristic for the corresponding surface unit cell of the In-rich $(2 \times 4)$-reconstructed surface of InP(100) [11–13]. The weak dispersion of the $C_1$ resonance on this surface has been calculated predicting the energy minimum at the $\bar{\Gamma}$ point [11] at 0.25 eV above the energy minimum of the bulk conduction band [13]. This has been confirmed already earlier with 2PPE experiments [14].

Two different pathways for populating this surface resonance can be realized with two different photon energies for the pump pulse, i.e., an indirect pathway via bulk states and subsequent transfer to the surface resonance for 2.18 eV photon energy of the pump pulse [15] and alternatively the direct optical generation of electrons in the $C_1$ resonance with 1.75 eV photon energy of the pump pulse. Theoretical calculations have predicted [13] optical transitions that can lift electrons from the $V_1$ and $V_3$ occupied surface states near the top of the valence band to the unoccupied $C_1$ surface resonance [11].

We address here the dynamics of the ultrafast nonequilibrium interplay of both pathways in the quantum transport of electrons. The measured time-dependent 2PPE

 

spectra are discussed within a microscopic kinetic model which includes electron-phonon scattering and can explain the main qualitative features of the experimental signals.

The nominally undoped (unintentional $n$ doping at about $5 \times 10^{14}$ cm$^{-3}$) InP(100) layers were grown in an Aixtron 200 MOCVD (metalorganic chemical vapor deposition) reactor. Growth and surface reconstruction were monitored via *in situ* reflection difference spectroscopy (RDS). Details of the preparation procedure have been described elsewhere [16,17]. Employing a patented device [18] the sample was transferred contamination-free and with preserved atomic order from the MOCVD reactor into a mobile ultra-high-vacuum (UHV) chamber. From there it was transferred further via load-lock ports into any desired UHV chamber, where LEED, ultraviolet photoemission spectroscopy, x-ray photoemission spectroscopy, and RDS measurements were carried out. Thereby, it was confirmed that the subsequent fs-2PPE investigations were addressing the In-rich $(2 \times 4)$-reconstructed surface.

The fs-2PPE measurements were carried out at room temperature with the sample mounted in an UHV chamber with base pressure in the range of $5 \times 10^{-11}$ mbar. The pump pulse of about 40 fs width (FWHM) delivered either 1.75 or 2.18 eV photons, respectively. The probe pulse of 4.66 eV photons with about 50 fs width (FWHM) was more than 1 order of magnitude weaker than the pump pulse. The 4.5 nm absorption length for the latter provided the required high surface sensitivity of the measured 2PPE signals. Pump and probe pulses were incident at 50° against the surface normal and 2PPE spectra were recorded at different delay times between pump and probe pulses. Photoemitted electrons were collected by a homemade time-of-flight spectrometer that was aligned parallel to the surface normal. Photoemission perpendicular to the (100)-crystal face involved electrons emitted from bulk states with appropriate energy in the $\Gamma$-$X$ direction. Photoemission from the $C_1$ surface resonance was detected in a narrow $k_{\|}$ range controlled by the angular acceptance of our spectrometer which is in the range of $\pm 0.025$ Å$^{-1}$ for electrons with 1.0 eV of kinetic energy. The typical energy resolution was on the order of 90 meV. The density of the generated hot electrons was estimated in the range of several $10^{17}$ cm$^{-3}$.

Figure 1 shows experimental and theoretical 2PPE spectra of the In-rich $(2 \times 4)$-reconstructed surface of InP(100) at various delay times between pump and probe pulses. The spectra correspond to the direct optical population of the surface resonance (1.75 eV) from occupied states near the top of the valence band. The peak at about 1 eV kinetic energy dominates the early spectra. With increasing delay time the peak at 1 eV kinetic energy is seen to decrease and a peak near the bottom of the conduction band is formed.

Figure 2 shows analogous curves as in Fig. 1, but for excitation with 2.18 eV photon energy. The spectra correspond to the indirect pathway where initially hot electrons

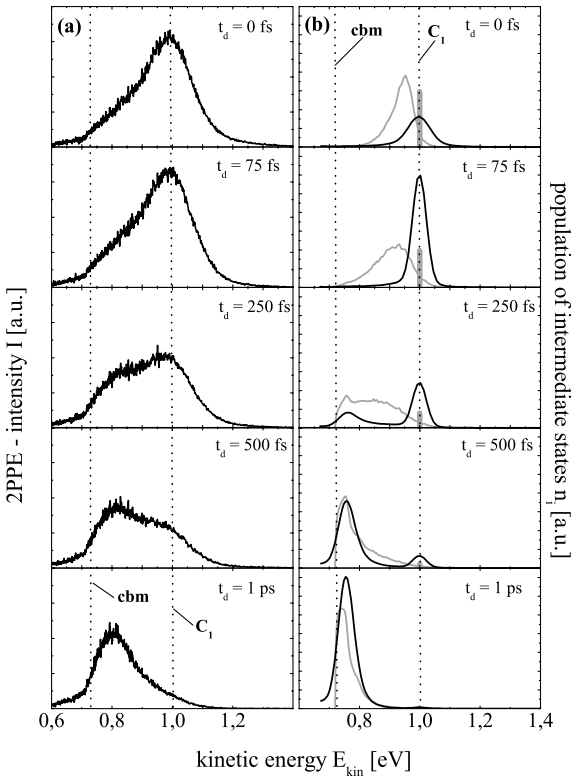


FIG. 1. (a) fs-2PPE spectra measured in normal emission at different time delay $t_d$ (values given as insets on the right) after excitation with laser pulses of 1.75 eV photon energy. The position of the $C_1$ surface resonance and the position of the conduction band minimum are indicated with vertical dotted lines. (b) Calculated fs-2PPE spectra (black curves) and population of intermediate states (gray curves) for different time delay $t_d$ (values given as insets on the right) between pump and probe laser pulses. The population in the surface resonance is shown as a gray shaded vertical bar.

are generated in higher lying bulk states and then captured by the surface resonance. Excitation with 2.18 eV photon energy produces an initial distribution of hot electrons with a peak at about 1.35 eV kinetic energy. The peak at 1 eV kinetic energy rises with a delay, passes through its maximum height, and finally disappears via feeding into the peak close to the conduction band minimum. In both, Figs. 1 and 2, the peak at 1 eV kinetic energy is attributed to photoemission from the electron population in the $C_1$ surface resonance with a contribution from isoenergetic bulk states.

To analyze the experimental results on a microscopic footing, we apply a many body density matrix theory, including relevant bulk and surface states [19–21]. The corresponding Hamiltonian includes the coupling of the electronic states via the electric field (pump and probe pulses) as well as the electron-phonon interaction [22]. To obtain dynamical equations for the 2PPE signal determined by the vacuum electron occupancies, we use Heisenberg equations to set up a system of equations which

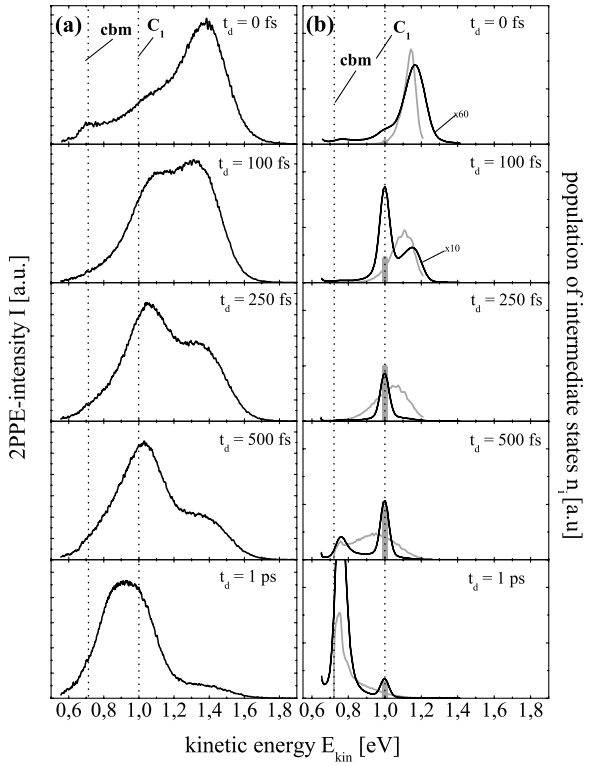


FIG. 2. (a) Experimental curves as in Fig. 1 but for excitation with laser pulses of 2.18 eV photon energy. (b) Calculated curves as in Fig. 1 but for excitation with laser pulses of 2.18 eV photon energy.

is truncated by correlation expansion in second order Born and Markovian approximation [21,23]. The phonons are assumed to be a thermal bath for the electronic degrees of freedom and are described by a thermal Bose distribution. The remaining terms include polarizations and densities of the electonic state [24]. For instance, the 2PPE signal is proportional to the density of the free electron band. In particular, a coupling between surface and bulk states appears. The coupling parameter determines the time scales and the dynamics.

For the spectral range of the experiment, the typical optical properties of InP can be well described by a model system with three bulklike bands (valence and conduction band, free electrons in the vacuum) and one surface band energetically close to the conduction band; cf. Fig. 3(a). Close to the $\Gamma$ point we apply the effective mass approximation to describe the corresponding energy dispersions. In addition, we assume that surface bands are unoccupied and all electrons are initially excited from the valence band. The wave functions exhibit translational symmetry parallel to the surface: $\psi^{\alpha}_{\vec{k}_\parallel}(\vec{r}) = Ce^{i\vec{k}_\parallel\cdot\vec{r}_\parallel}v_\alpha(\vec{r})$. Here $\alpha$ has the meaning of a band index for the two-dimensional surface band, whereas for three-dimensional bands it contains the bulk band index and the wave vector component perpendicular to the surface [e.g., $\alpha = (v, k_\perp)$, $v$ valence band] [24]. In order to develop an intuitive picture we

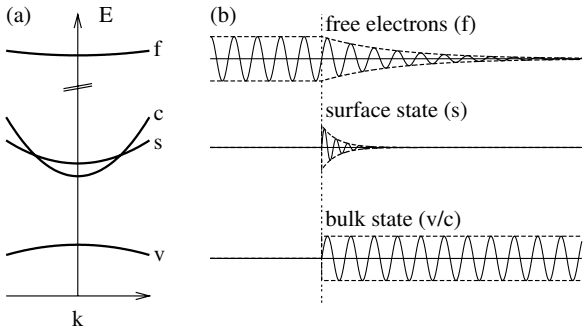


FIG. 3. Sketch of the energies of the four band system (cut through $k_\perp = 0$) (a) and of the model wave functions (b).

model the 2PPE process by assuming simple model wave functions; cf. Fig. 3(b). The ansatz is inspired by calculations concerning surface states [11], free electron waves [25], and usual bulk wave functions. Bloch functions of the infinite crystal are used as carrier waves, varying the envelope for the different states. Bulk wave functions are taken of the infinite crystal and decay abruptly at the surface. This also applies to the surface state, but inside the crystal exponential damping is assumed. The decay constant ($\lambda = 2.4\ \mathrm{nm}^{-1}$) is taken from a fit of density-functional theory calculations [11]. The free electrons (vacuum states) are taken as incoming waves at a finite step potential [26]. Inside the crystal the wave functions are also damped exponentially to account for a finite penetration length [25]. All material parameters are taken from Ref. [27], whereas the electron-phonon coupling strength (only LO phonons with constant dispersion) between the conduction and the surface bands, as well as the dipole moments containing the surface state have been approximated by bulk values. The dipole moment for the bulk-surface transition matrix element has been determined to reproduce the experimental ratio of bulk and surface occupancies generated by the first excitation pulse. For the electron-phonon coupling matrix elements (Fröhlich coupling) the largest possible coupling strength within our model wave functions (Cauchy-Schwartz inequality for the wave function overlap) has been chosen.

All the major qualitative features of the experimental signals such as peak positions and time evolution are reproduced by the numerical integration of the equations of motion. There remain, however, some quantitative differences. In the calculated curves (Fig. 1) the peak at 1 eV, i.e., that of the surface resonance, continues to rise over the complete length of the pump pulse, whereas in the experimental curves this peak reaches the maximum value already at an earlier time thereby indicating a much faster decay process. For the calculated curves LO-phonon scattering is assumed as the only mechanism for depopulating the surface resonance whereas further scattering processes could actually speed up the depletion process. Indeed, electron-electron scattering and also scattering with sev-

eral phonon modes is conceivable. Calculations of phonon induced intervalley scattering using deformation potentials have produced time constants of about 30 fs [28]. The influence of electron-electron scattering is suggested by the much broader linewidth of the experimental compared to the calculated peaks. The calculated curves show a decrease in the magnitude of the 2PPE signal with increasing energy of the bulk states which is not seen in the experimental curves. Applying a simpler model [29] we have shown before that such a behavior can result from the assumption of an unrealistic final state. Details about the very early time behavior should emerge in the future from better time-resolved experimental data, and future calculations should take into account electron-electron scattering and also scattering involving several phonon modes and should explore the influence of the final states.

In conclusion, our results demonstrate femtosecond electron transfer between a two-dimensional surface resonance and three-dimensional bulk states in InP(100). Electron-phonon coupling is determined as an important mechanism for electron transport between surface and bulk states.

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