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Two-photon photoemission study of the empty states of InP(100)

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Two-photon photoemission with energy and angle resolution in single-beam and two-beam configurations is used to study the empty states of InP(100). By tuning the photon energies and using the surface barrier as an energy filter, we observe two distributions of electrons photoexcited in the conduction band: the as-excited "ballistic" electrons which fill available empty states and the electrons relaxed down to an energy level located at 0.8 eV above the conduction-band minimum. The bulk or surface origin of this accumulation level is discussed and its association with the X secondary minima is put forward.

Two-photon photoemission (2PP) has appeared recently[1-9] among the few techniques which can probe directly the empty states of semiconductors, such as "negative electron affinity" (NEA), partial-yield, or inverse photoemission spectroscopies. Its principle is to populate or pump these states by photoexcitation and then probe them by photoemission. We report here on single-beam and two-beam nanosecond 2PP measurements with energy and angular resolution, performed on the InP(100) surface characterized *in situ* by various surface techniques. In spite of the quasi-instantaneous nature of photoemission, the nanosecond excitation should bar us from observing as-excited "hot" electrons whose relaxation times lie in the subpicosecond range, since they are greatly outnumbered by those which have relaxed down to band-structure wells. However, we show here that these two kinds of electrons can be selected in 2PP by tuning the "probe" energy and using the surface barrier as a built-in energy filter.

The n-type (10^{18} cm^{-3}) InP(100) samples are prepared under ultrahigh-vacuum in order to obtain an atomically clean and ordered surface.[10] With the energy referred to the conduction-band minimum (CBM), the vacuum level is located at +4.3 eV and the Fermi level at the surface is pinned at −0.35 eV; a filled surface-state band is detected at −1.3 eV by uv one-photon photoemission (1PP) and an empty one at +0.2 eV by electron-energy-loss spectroscopy (EELS),[10] taking into account an exciton binding energy which will be discussed further on. Our 2PP setup involves two dye lasers pumped by an excimer laser whose beams are monitored (pulse duration and energy, impact area) and focused on the sample at normal incidence.[4] Photoelectrons are energy analyzed by a retarding-field analyzer, and/or angle analyzed by rotating apertures, and detected by a charge amplifier. Energy and angular resolutions are about 0.25 eV and 8°, respectively. The primary 2PP data are the relations between the photon flux corrected from the reflectance J_p and the photoelectron flux J_e. J_e is normally proportional to J_p^2 in single-beam experiments and to each J_p in two-beam cooperative experiments, the proportionality factor being the 2PP yield Y_2; however, above a critical flux J_{pc}, the increase of J_e with J_p is no longer quadratic but linear. The single-beam spectra Y_2 and J_{pc} versus photon energy E_p are shown in

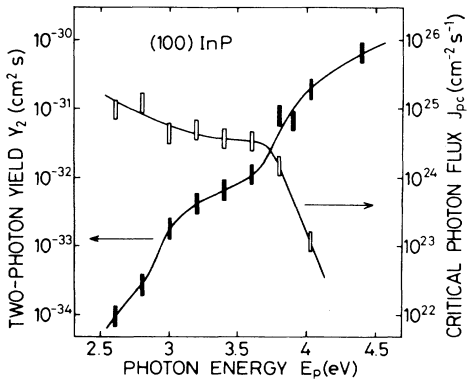

FIG. 1. 2PP yield Y_2 and critical photon flux J_{pc} vs photon energy on InP(100).

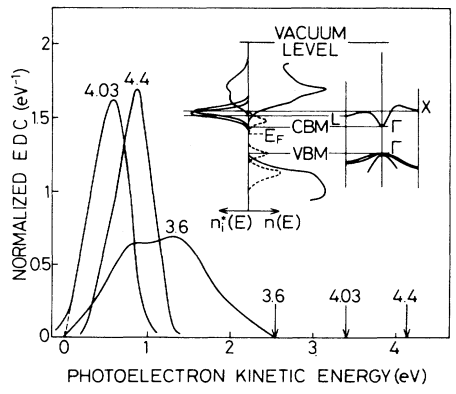

FIG. 2. 2PP energy distribution curves for various photon energies on InP(100), normalized to a unity area. The arrows indicate the maximum kinetic energy allowed by a double photoexcitation process (twice the photon energy minus the work function). The inset shows the relation between the available DOS $n(E)$ (solid curves: bulk states; dotted curve: surface states) and the energy distribution in the intermediate state $n_i^*(E)$ (EDC's brought down by the photon energy); the DOS scale is only indicative.

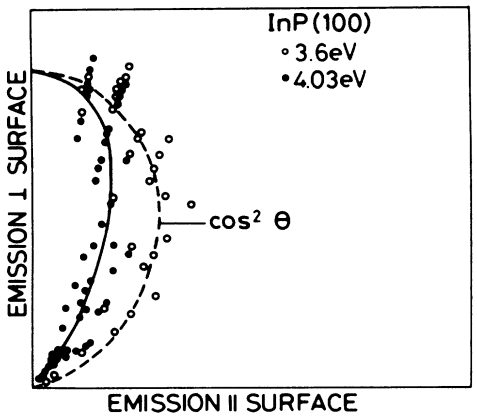

FIG. 3. 2PP angular distribution curves for various photon energies on InP(100), normalized to the same normal emission (the solid curve is a guide to the eye; the dotted curve represents isotropic emission).

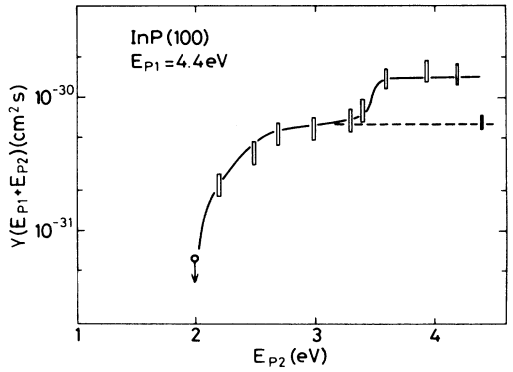

FIG. 4. Cooperative 2PP yield in a two-beam experiment with a fixed beam energy (4.4 eV) as a function of the second beam energy. Open circle: yield lying below experimental sensitivity; full symbol: single-beam yield at 4.4 eV.

Fig. 1. Angle-integrated energy distribution curves (EDC's) and energy-integrated angular distribution curves (ADC's) are reported in Figs. 2 and 3 for various photon energies.

"BALLISTIC" AND "RELAXED" 2PP REGIMES

Two regimes show up in our data. At low E_p, the yield spectrum and the EDC are similar to those of Si,[4] attributed to a double photoexcitation of electrons without energy relaxation at the intermediate level (ballistic electrons). The EDC (whose width increases with $2E_p$ as expected from the increasing range of possible initial states) reflects the joint (initial, intermediate, and final) density of states (DOS),[4] or since the final DOS is featureless (free electrons), the DOS occupied after the "pump" step, just as it does the initial occupied DOS in 1PP. In Fig. 2, we compare this dynamically occupied DOS (EDC at 3.6 eV brought down by the photon energy) with the normally empty available DOS deduced from theoretical calculations.[11] The fair agreement shows that the dynamically occupied DOS is imposed by the available DOS and not by the DOS in the initial state nor by selection rules. In this case, 2PP can be used to determine the empty DOS in a straightforward manner.

Above a photon energy E_p^* (~3.6 eV), the picture changes completely. Y_2 increases rapidly, faster than in Si, and J_{pc} drops down; the EDC switches from a broad to a narrow peak moving as a whole with E_p, and the ADC from isotropic to rather normal distribution (Figs. 1–3); the sensitivity of 2PP to surface treatments increases considerably. In 1PP, the displacement of an EDC peak with photon energy stems from a structure in the initial DOS. Here, since the "probe" step of 2PP is 1PP, it shows that the electrons have relaxed down into an electron accumulation level (EAL) independent of the pump step, located at $E_a = 0.8 \pm 0.1$ eV (see inset of Fig. 2). E_p^* is then the energy necessary to bring the electrons either up to the EAL (~2.1 eV from band-structure data[11]) or from there up to the vacuum level (3.5 eV, in agreement with the experimental value); below 3.5 eV, only the much less numerous ballistic electrons can be probed. This scheme is confirmed by a two-beam experiment, with a fixed energy E_{p1} (4.4 eV) and a variable one E_{p2}. By coupling or decoupling the beams in space or time, the yield involving cooperation of E_{p1} and E_{p2} is plotted versus E_{p2} (Fig. 4). The two thresholds at 2.2 and 3.5 eV can be attributed as follows. Below 2.2 eV, only E_{p1} can pump electrons into the EAL, which E_{p2} is too low to probe, so the yield vanishes. Above this value, E_{p2} also can pump electrons into the EAL, which can then be probed but still only by E_{p1}; the yield levels off at the single-beam yield at E_{p1}, showing that above 2.2 eV the pumping efficiency does not depend on the photon energy. Above 3.5 eV, both E_{p1} and E_{p2} can pump into the EAL and probe it, and the yield doubles. All determinations of E_a from the thresholds and from EDC's are consistent with 0.8 ± 0.15 eV. The ADC further shows that emission from the EAL is rather normal. Since $k_\parallel$ is conserved in the probe step, electrons in the EAL have a low $k_\parallel$ (< 0.07 Å^{-1}). Finally, when all available states in the EAL are saturated by pumping, probing acts on a stationary population, so J_e increases linearly with J_p, which is observed above J_{pc}; the saturation is confirmed by the EDC's which then display a stationary EAL feature plus an increasing high-energy tail. We may describe the yield of the probe step J_e/J_p as the product of the areal saturation density of electrons in the EAL within the escape length (~20 Å), N, and a cross section σ. By comparison to 1PP, where J_e/J_p is 10^{-2} when the whole valence band is involved ($N \sim 10^{16}$ cm^{-2}),[12] we take $\sigma = 10^{-18}$ cm^{-3}. At a photon energy of 4 eV the saturation density $Y_2 J_{pc}/\sigma$ is then 4×10^{10} cm^{-2}; its meaning depends on the nature of the EAL (bulk or surface states).

BULK OR SURFACE ELECTRON ACCUMULATION LEVELS

The observation of an EAL raises two main questions: With what feature of the band structure is it associated? Why and how do electrons accumulate in it? Accumulation in the CBM is expected to be dominant, as shown in InP (Ref. 13) and GaAs (Ref. 14) by NEA photoemission,

but it is not detected here even at photon energies larger than the electron affinity, as in other reported 2PP experiments. In Si(111), no EAL was observed.[4] In ZnTe(110) and InP(110),[7,8] the EAL observed near the CBM may be associated with the CBM itself or with the near-CBM surface state[15,16] and for InP(110) its dispersion indicates a surface origin.[8] Our own data obtained with various probe energies seem to rule out any final-state effect forbidding emission from the CBM. We may then suggest that the many electrons generated in usual 2PP conditions cannot all be accomodated by the CBM and they spill out on higher levels, where they are preferentially observed simply because they outnumber the CBM electrons.

Accumulation in empty surface states fed by the excited bulk will be considered next since the short escape length involved in 2PP, as opposed to the long one involved in NEA photoemission, and the minimization of final-state effects, strongly favors its observation: when at most 10^{19} cm^{-3} electrons populate the CB, and hence only 2×10^{12} cm^{-2} can be emitted, up to 10^{15} cm^{-2} can populate a surface state and be emitted. In InP(110) the EAL at +0.1 eV has been associated[8] with the bottom of an empty surface band found to peak at +0.65 eV by EELS (Ref. 16) and calculations.[17] The EELS transition on InP(100) is 0.2 eV lower than on the (110) surface.[10] Hence, if the EAL's observed at +0.8 eV on the (100) surface and +0.1 eV on the (110) surface are associated with similar surface bands, the binding energy of the core-level exciton involved in the EELS transition depends very strongly on the face: 0.35 eV for (110), 1.25 eV for (110). Though not unrealistic in view of the different electron localizations, such a conclusion cannot be supported now; a direct localization of the surface bands by inverse photoemission will clear up this issue. Under the reverse assumption that binding energies on the (100) and (110) surfaces are similar, the EAL on (100), equivalent to the one observed on (110), is predicted to lie at −0.1 eV, where it cannot be probed even by our highest-energy (4.4-eV) photons. Our +0.8-eV EAL could also be associated with a higher surface state, but it is not clear why this state, probably localized on the anion,[18] is not seen by EELS. Concerning the localization in k space, the electrons in the EAL have a low $k_{\parallel}$ (<0.07 $Å^{-1}$), which, for surface states, means they lie near the center of the surface Brillouin zone whose smallest size is 0.38 $Å^{-1}$. This is not expected since surface bands usually have a low dispersion.[17] The saturation DOS (4×10^{10} cm^{-2}) is also quite low for a surface band. Finally, the EAL should be very sensitive to surface treatments. Preliminary experiments show that oxygen adsorption strongly decreases the surface empty and filled density of states but only slightly reduces the 2PP yield, which merely follows work-function variations. On the other hand, ion bombardment increases the density of gap states, but returns 2PP to its ballistic regime. These data will be discussed at length separately, but, in their present state, they do not support the association of the EAL with a surface band.

If the EAL is associated with bulk states, the obvious candidates are the secondary minima L (+0.6 eV) and X (+0.8 eV),[11,13,19] and especially the X minimum in view of the experimental (E,k) data. The available DOS in these points is consistent with the saturation density (4×10^{10} cm^{-2} within the escape length, i.e., 2×10^{17} cm^{-3}). The steady-state density in the CBM at J_{pc}, evaluated by $J_{pc}[1/(1+Z)]\sqrt{\tau}/D$ where τ [$\sim$1 ns (Ref. 19)] and D ($\sim$100 cm^2/s) are the lifetime and diffusion coefficient of electrons, and Z [$\sim$2.5 (Ref. 19)] the reduced surface recombination velocity, is also 2×10^{17} cm^{-3}: An important part of the photoexcited electrons then accumulate in the EAL. Accumulation in CB valleys has already been observed in InP (Ref. 13) and GaAs (Ref. 14) by NEA photoemission; when the excitation energy is high enough, the transfer of high-energy electrons from the central valley to lateral ones is favored,[20] leading to the Gunn effect. However, data in GaAs and calculations in InP (Refs. 21 and 22) indicate that the transition towards X is less probable than towards L which lies at a lower energy. On the whole, our present data rather point to a bulk origin for the EAL. The effect of ion bombardment may be ascribed to a decrease of lifetime in X at the surface following the creation of new relaxation channels, and described by a surface relaxation velocity analogous to the surface recombination velocity. Finally, it may be noted that whatever the origin of the EAL, its location and its efficiency are the parameters relevant to applications, and 2PP seems to be one of the best methods to determine them directly.

CONCLUSION

2PP is shown to yield direct information about the empty states of InP and about the relaxation processes within the conduction band. This is obtained with nanosecond excitation, i.e., nearly cw with respect to intraband relaxation times, with the help of the surface barrier which forbids probing deep-lying relaxed electrons with low photon energies. We can tune 2PP to observe either the few short-lived hot or ballistic electrons or the many "mild" electrons relaxed down in energy wells. The first regime yields information about the density of empty states in the CB. The second shows that under high-energy injection, an intermediate step in the relaxation is the accumulation of electrons at 0.8 eV above the CBM, probably in the X secondary minimum.

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