Picosecond Time-Resolved Photoemission Study of the InP(110) Surface

R. Haight, J. Bokor, J. Stark, and R. H. Storz
AT&T Bell Laboratories, Holmdel, New Jersey 07733

and

R. R. Freeman and P. H. Bucksbaum
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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We report the first use of angle-resolved ultraviolet-photoemission spectroscopy to study electron dynamics in the picosecond time domain on a photoexcited semiconductor surface. Transient population in a normally unoccupied surface state on InP(110) was directly observed. The band minimum for this state was found to lie at $\bar{\Gamma}$ and the surface-band dispersion near $\bar{\Gamma}$ (effective mass) was measured along two surface symmetry directions.

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Angle-resolved ultraviolet-photoemission spectroscopy (ARUPS) is a powerful and well-established tool for the study of bulk and surface electronic states of solids. In a conventional ARUPS experiment, the ultraviolet source is either a rare-gas discharge lamp or synchrotron radiation. Recent advances in nonlinear optics and picosecond-laser technology now provide laser-based ultraviolet radiation sources capable of producing ultrashort pulses at a large selection of photon energies up to 35 eV.[1] In the energy range up to ~25 eV, these sources can provide a *time-averaged* total photon flux comparable to that obtained at typical synchrotron bending-magnet beamlines, with substantially higher peak spectral brightness per pulse. Thus, laser-based sources offer the unique opportunity to apply ARUPS to the study of transient excitations of solids and surfaces in the picosecond time domain. In this Letter, we report the first demonstration of picosecond-time-resolved ARUPS. We have used this technique to study the dynamics of electrons photoexcited by a 50-psec visible laser pulse on a cleaved InP(110) surface.

Surface states are predicted[2-4] and observed[2,5] to lie outside the bulk band gap on the clean (110) surface of InP and GaAs. In particular, an unoccupied surface-state band,[6] labeled C_3 in the notation of Refs. 3 and 4, lies at an energy slightly above the conduction-band minimum (CBM). Excitation of carriers into the bulk conduction band could then lead to population of this surface state as well (see Fig. 1). Using time-resolved ARUPS, we have observed the transient population of the C_3 surface state in InP, located its energy minimum in k space at $\bar{\Gamma}$ (the center of the surface Brillouin zone), and measured the surface-band dispersion along two surface symmetry directions.

Clean InP(110) surfaces, produced by cleavage in an ultrahigh vacuum chamber (base pressure 10^{-10} Torr), were excited by 50-psec pulses of 532-nm laser radiation at a fluence level of 0.5 mJ/cm^2 and repetition rate of 10 Hz. The photoexcited surface was probed by measuring the energy and angular distributions of electrons photoemitted by a synchronized 50-psec pulse of p polarized 118-nm (10.5-eV) laser-harmonic radiation incident at 65° from the surface normal. A time-of-flight electron spectrometer was used with energy resolution of 105 meV at 6.5 eV, and angular resolution of ±2.5°.

Low kinetic energy electrons (below 1 eV) were also produced by multiphoton processes driven by the in-

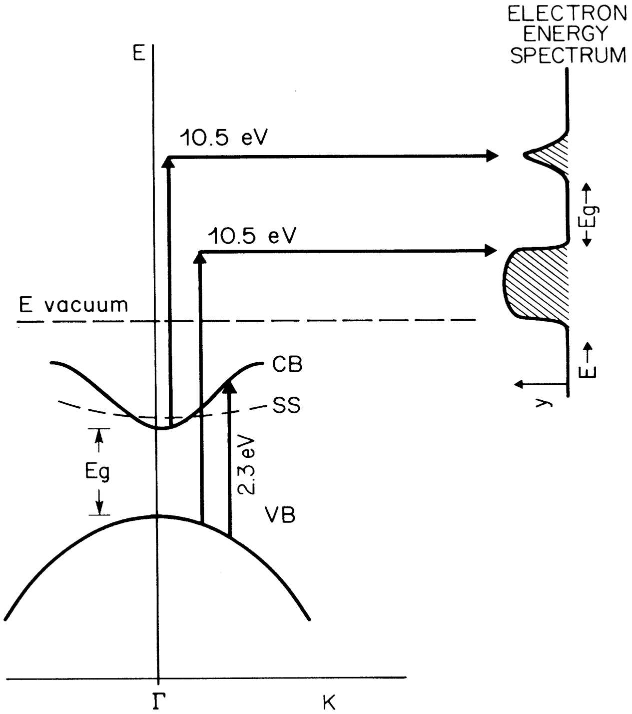

FIG. 1. Schematic band-structure diagram showing the excitation (2.3-eV pump) and subsequent photoemission (10.5-eV probe) from InP. The normally unoccupied surface state is shown as the dashed line.

tense pump pulse. These low-energy electrons are a source of background that hampered previous efforts to develop this technique with use of 4.6-eV probe radiation.[7] A probe photon energy of 10.5 eV effectively separates the electron energy range of interest (2–7 eV) from the low-energy background.

Figure 2 shows the energy spectra obtained in this experiment for electrons emitted along the surface normal. Zero energy is chosen as our best determination (±50 meV) of the position of the valence-band maximum. Figure 2(a) displays a spectrum for the unexcited surface. When the pump and probe pulses overlap in time as in Fig. 2(b), a new feature appears centered at +1.47 eV. If the probe is delayed relative to the pump by 266 psec the spectrum in Fig. 2(c) is observed. Here the 1.47 eV peak is significantly reduced both in intensity and width. The insets in Figs. 2(b) and 2(c) show a magnified view of this feature. Finally, Fig. 2(d) displays a spectrum obtained with coincident pump and probe pulses after the surface has been exposed to atomic hydrogen.[8] The peaks at −0.6, −1.7, and +1.47 eV have substantially reduced in intensity. We did not observe any recovery of these peaks even after $\sim 5\times10^4$ pump-laser pulses, indicating little or no hydrogen desorption by the pump laser. Sensitivity to adsorbed hydrogen is a generally accepted (although not always conclusive[2]) signature of surface states on semiconductor and metal surfaces. Guided by previous studies[2] of GaAs(110) we assign the peaks at −0.6 and at −1.7 eV to occupied surface states. Band bending[9] at the surface cannot be responsible for the sensitivity of the +1.47-eV peak to surface contamination since we observed identical sensitivity to contamination for both *n*- and *p*-type samples. Furthermore, our study of the angular distribution for this peak (described below) also rules out a bulk identification. We therefore assign this peak to the C_3 unoccupied surface state. Using the band gap of InP at 300 K, 1.35 eV, we determine the energy position of the bottom of the C_3 band to be 120 ±50 meV above the CBM. Our direct measurement of this value agrees with that inferred by van Laar, Huijser, and van Rooy[5] based on measurements of the position of the "surface-exciton" state[10] associated with the indium 4*d* core level.

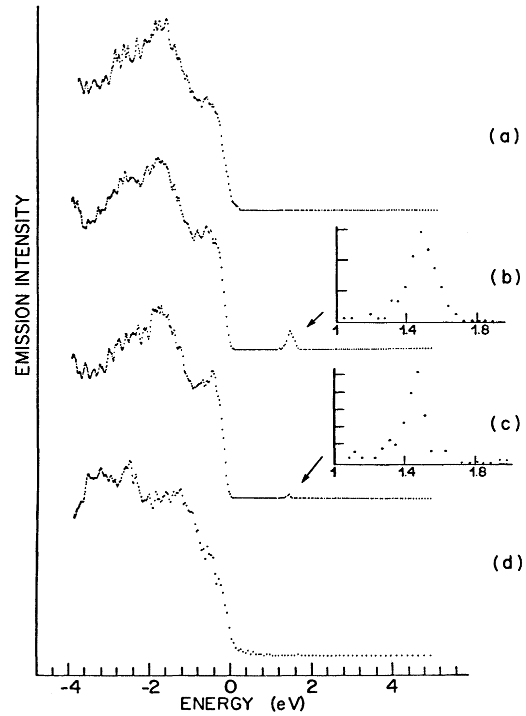

FIG. 2. Pump-probe photoelectron spectra from InP(110) for various relative time delays, *t*. Curve *a*, $t=-133$ psec; curve *b*, $t=0$; curve *c*, $t=266$ psec; and curve *d*, $t=0$ where the surface has been exposed to hydrogen (see Ref. 8). The insets for curves *b* and *c* are magnified views of the 1.5-eV region where the vertical scale has been expanded by a factor of 4.7 and 28, respectively.

The time dependence of the C_3 peak is displayed in Fig. 3, where its integrated intensity is plotted as a function of relative time delay, *t*, between the pump and probe pulses. Since the surface state lies only 120 meV above the CBM, equilibrium is presumably established between the surface and the bulk conduction bands. The data shown in Fig. 3 should thus represent the time dependence of the bulk carrier density *near the surface.* To check this hypothesis, the spatial and temporal evolution of the bulk plasma was calculated with use of a one-dimensional model. The results of this calculation for the bulk carrier density near the surface, with use of a radiative recombination coeffi-

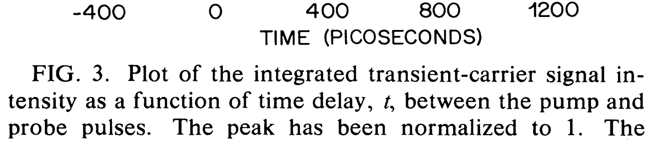

FIG. 3. Plot of the integrated transient-carrier signal intensity as a function of time delay, *t*, between the pump and probe pulses. The peak has been normalized to 1. The dashed curve represents the system time-resolution function. The solid curve is the result of the diffusion calculation as discussed in the text. The effect of finite time resolution is not included in the calculation.

cient[11] of 3×10^{-10} cm^3/sec, an Auger coefficient[12] of 2×10^{-29} cm^6/sec, and a diffusion coefficient, D, of 50 cm^2/sec, is shown as the solid line in Fig. 3. The effects of our finite time and angular resolution were not included in the model. The shape of the curve was found to be largely insensitive to variations in D from 1 to 1000 cm^2/sec; within this range only the overall scale factor varies. The fit of this model to the data indicates that the C_3 surface-state population is equilibrated with the bulk plasma.

The insets of Fig. 2 show that the energy width of the C_3 surface-state peak varies with time. Data from a separate set of high-resolution measurements of this effect are shown in Fig. 4. The full width at half maximum drops from its maximum of 154 ± 7 meV at $t=0$ to the instrumental limit of 105 ± 10 meV by $t=260$ psec. Broadening occurs only on the high-energy side of the peak. We attribute this result to band filling. This effect was studied in more detail by measuring the angular dependence of the spectrum at different delay times. The angular distribution of the C_3 signal at $t=0$ was found to peak along the surface normal, with full width at the 10% points of 16° along the $\bar{\Gamma}\bar{X}$, i.e. $\langle\bar{1}10\rangle$, direction, and 13° along the $\bar{\Gamma}\bar{X}'$, i.e. $\langle001\rangle$, direction (notation follows Ref. 3). A measurable amount of upward dispersion (50–100 meV) in the peak position with angle was noted in both directions. At $t=150$ psec, the full width along the $\bar{\Gamma}\bar{X}$ was observed to narrow to 9° from normal.

Since $k_{\parallel}$ is conserved in the photoemission process,[2] after suitable deconvolution of the instrumental response functions, the energy and angular distributions could be used to determine the energy versus $k_{\parallel}$ dispersion relation for the C_3 surface state. The 105-meV-wide C_3 peak taken at $t=260$ psec was used as the instrumental energy-resolution function. The angular distribution taken at $t=150$ psec was used as the angular-resolution function. It was triangular in shape with a full width at half maximum of 5° and a full width at 10% points of 9°. These were then utilized to deconvolve the system response from the data taken at $t=0$. We assume parabolic bands near the $\bar{\Gamma}$ minimum and quote effective masses for the two directions in $k_{\parallel}$ space measured. The band dispersions were obtained by comparison of the amount of band filling, as determined from the total energy width of the numerically *angle-integrated* peak, with the full width of the angular distribution. The band filling of the surface state at $t=0$ was determined as 240 ± 20 meV. We obtain $0.20\leq m^*/m_e\leq0.24$ along $\bar{\Gamma}\bar{X}$, and $0.10\leq m^*/m_e\leq0.15$ along $\bar{\Gamma}\bar{X}'$, where m_e is the free-electron mass. The measured peak shifts with angle were also used to derive the band dispersions, and values consistent with those above were obtained. These values differ significantly from the nearly isotropic bulk-conduction-band effective mass of $0.07m_e$, confirming our identification of this peak as a surface state.

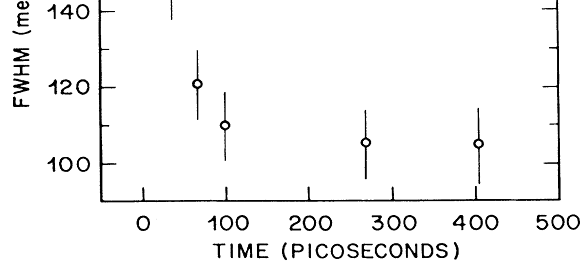

FIG. 4. Time dependence of the full width at half maximum of the 1.47-eV peak.

At present, the cause of observed high sensitivity to the excited surface-state population relative to the bulk-conduction-band population is unclear. With the assumption of equilibrium between surface and bulk bands, a peak band filling in the surface state of 240 meV implies a value of 360 ± 50 meV for the band filling in the bulk conduction band. At 300 K, this corresponds to a degenerate bulk electron density of $(1.8\pm0.4)\times10^{19}$ cm^{-3}. However, appreciable photoemission yield from this population requires the probe photon energy to be tuned to an allowed,[13] direct transition near Γ from the CBM to a high-lying excited-state band. There is no such restriction on photoemission from surface states,[2] since the perpendicular component of momentum is undefined. An extrapolation of recent unpublished ARUPS results of Williams *et al.*[14] to the zone center suggests that an allowed direct transition should indeed occur from the CBM at 10.5 eV in bulk InP. The absence of a bulk signal suggests that either this extrapolation is invalid, or the transition matrix element is particularly small for this transition. Time-resolved ARUPS experiments using a variable-photon-energy probe should help clarify this issue.

In summary, we have used picosecond-time-resolved ARUPS to study the energy and momentum of excited electrons on the InP(110) surface. A normally unoccupied surface state was directly observed to be populated via coupling to bulk photoexcited electrons. The excited surface-band minimum was found to be at $\bar{\Gamma}$, at an energy of 1.47 ± 0.05 eV above the valence-band maximum, and the surface-band dispersion near $\bar{\Gamma}$ (effective mass) was measured along two surface symmetry directions. Picosecond-time-resolved ARUPS offers great potential as a new technique for the general study of transient processes on surfaces. In addition to the study of electron energy and momentum dynamics, it should be possible to observe directly such phenomena as chemical reaction dynamics and ultrafast phase transitions.

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