Surface Intervalley Scattering on GaAs(110): Direct Observation with Picosecond Laser Photoemission

R. Haight and J. A. Silberman
IBM T.J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
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Angle-resolved laser photoemission investigations of the laser-excited GaAs(110) surface have revealed a previously unobserved valley of the C_3 unoccupied surface band whose minimum is at $\bar{X}$ in the surface Brillouin zone. Electron population in this valley increases only as a result of scattering from the directly photoexcited valley at $\bar{\Gamma}$. With high momentum resolution, we have isolated the dynamic electron population changes at both $\bar{\Gamma}$ and $\bar{X}$ and deduced the scattering time between the two valleys.

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The two-dimensional surface electronic band structure of semiconductors has attracted great interest due to striking deviations from that observed in the bulk. Termination of the bulk crystal and surface atomic rearrangements can give rise to band-gap states and resonances in both the valence and conduction bands. In the particular case of GaAs(110) a body of work exists in which bands of the surface have been observed and mapped via photoemission and inverse photoemission, yet little is known about surface electronic dynamics, i.e., energy relaxation and scattering rates between surface states.[1-3] Studies of electron dynamics require the population and subsequent probing of normally unoccupied states, i.e., the conduction states of the system, on time scales relevant to energy and momentum relaxation times. In the bulk of semiconductors, such as GaAs, subpicosecond optical probes have been used extensively to investigate electronic relaxation rates and intervalley scattering.[4,5] The extension of such investigations to surfaces enables the study of electronic transport in fundamentally two-dimensional systems. In this Letter we report on the first such studies of electronic energy relaxation and intervalley scattering at a laser-excited semiconductor surface. Using a novel laser photoemission system with <1-ps time resolution to perform a series of excite-probe experiments, we have directly observed a strong electronic emission from a transiently populated band whose minimum is located at $\bar{X}$ in the surface Brillouin zone (SBZ) of GaAs(110). While the existence of this surface-band minimum at $\bar{X}$, labeled C_3, has been suggested from self-consistent pseudopotential calculations,[6] it has not been previously observed. Tight-binding calculations do not predict a band within the surface gap at $\bar{X}$.[7] Since the band gap at the $\bar{X}$ location in the SBZ is significantly larger than the exciting photon energy of our experiment this surface band can only be populated indirectly, from $\bar{\Gamma}$. By combining a picosecond laser photoemission probe with high electron momentum resolution, we have compared, in the same experiment, the time dependence of electron populations in the two valleys. This represents the first time direct surface intervalley scattering has been observed.

Our photoemission studies are carried out as a series of excite-probe experiments. The excitation is an intense ($\sim 300\ \mu J/cm^2$) pulse of red (1.78 eV) light resulting in a carrier density of $\sim(1-3)\times 10^{19}/cm^3$ at the surface. The probe is a weak (10^4-10^5 photons per pulse) pulse of short-wavelength (10.72 eV) radiation which photoemits both valence and transiently excited conduction electrons from the material. A tunable, amplified dye-laser source produces intense pulses of 1.78-eV light of 850-fs duration at 100-Hz repetition rate. Frequency doubling in potassium dihydrogen phosphate and subsequent tripling in Xe gas converts the intense red light into 10.72 eV photons for photoemission. Residual red light for sample excitation is directed through a variable delay line and onto the sample in an ultrahigh vacuum chamber. Spectra are normalized for probe intensity fluctuations by monitoring the 10.72-eV flux on each repetition. GaAs(110) samples, cleaved *in situ,* are positioned at the focus of the 10.72-eV light and photoemitted electrons are detected with a 64-anode, angle-resolving, time-of-flight detector with a resolution of 100 meV for 6-eV electrons.[8] The detector momentum resolution is $\pm 0.06\ Å^{-1}$ at $\bar{\Gamma}$ and $\pm 0.085\ Å^{-1}$ at $\bar{X}$.

Emission from states above the Fermi level at the GaAs surface gives rise to strong peaks in the photoemission spectrum when the probe pulse interrogates the system shortly after photoexcitation. Energy distribution spectra recorded under such conditions for emission angles of 0° and 34° are shown in Fig. 1 with the valence-band maximum as the zero of energy. Emission from the occupied valence bands exhibits the strongly angular dependent variations characteristic of crystalline materials. The energetic region just above the valence-band maximum corresponds to the fundamental band gap of GaAs and is devoid of any emission, consistent with the reconstruction of GaAs(110) which sweeps states from the gap. Although the two prominent peaks we observe at 1.4 eV both lie near the conduction-band maximum in energy, their different emission angles indicate that they derive from distinctly different locations within the SBZ. Direct absorption of the pump pulse in GaAs excites electrons to states near the conduction-band maximum

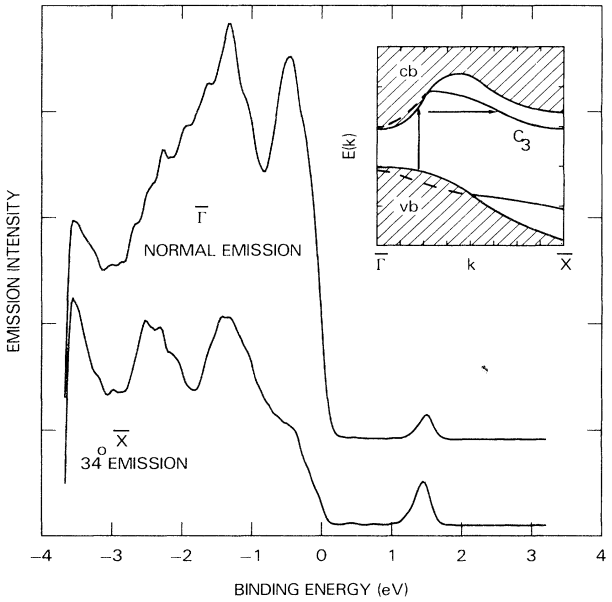

FIG. 1. Excite-probe photoemission spectra from cleaved GaAs(110). The bottom spectrum was collected at an emission angle of 34° relative to the surface normal in the $\bar{\Gamma}$-$\bar{X}$ direction. The top spectrum was collected along the surface normal corresponding to emission from $\bar{\Gamma}$. Inset: The relevant surface and bulk projected (hatched regions) band structure.

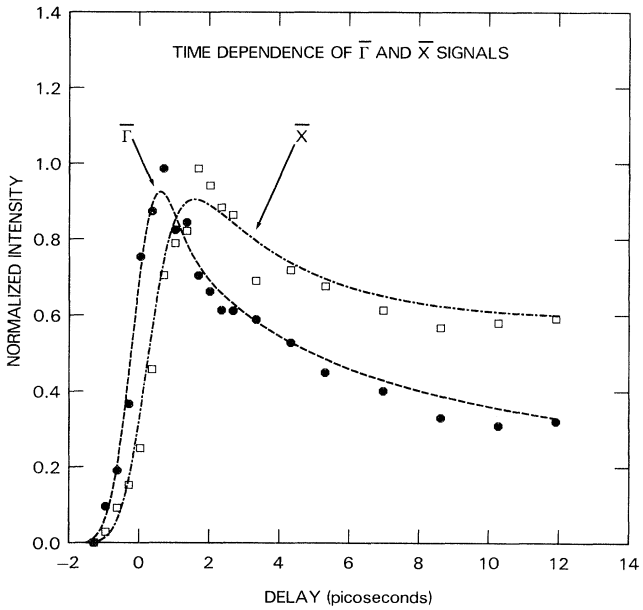

FIG. 2. Excite-probe delay curves for emission from $\bar{\Gamma}$ (filled circles) and from $\bar{X}$ (open squares). Fits from the model calculations described in the text are shown as dashed ($\bar{\Gamma}$) and dot-dashed ($\bar{X}$) curves.

at $\bar{\Gamma}$ (see inset). Such electrons, occupying states near the zone center, have near zero crystal momentum and are photoemitted with trajectories along the surface normal. This signal has been observed previously and derives from the C_3 surface resonance whose minimum is at $\bar{\Gamma}$.[9] A similar resonance has been observed on InP(110) as well.[10] The signal at the bottom of Fig. 1 was observed at an angle of 34° to the surface normal along the $(\bar{1}10)$ direction. With 10.72-eV photons, emission at this angle implies a $k_{\parallel}$ of 0.786 Å^{-1}, which corresponds to the magnitude of $\bar{\Gamma}-\bar{X}$ in the surface reciprocal lattice. At the energy and emission angle at which we observe this signal there are no projected bulk bands; i.e., this location corresponds to a band gap at the $\bar{X}$ location of the SBZ. We therefore conclude that the 34° signal we observe derives from a surface band within the band gap of GaAs(110) at $\bar{X}$ in the SBZ. The measured emission intensity from $\bar{X}$ exceeds that from $\bar{\Gamma}$ by a factor of 2.6, as seen in Fig. 1, and suggests a higher density of states at the surface zone edge. The measured angular dependence of the signal near $\bar{X}$ along the $(\bar{1}10)$ (not shown) yielded a FWHM of $\sim 12.5°$ corresponding to electron population between (0.68 and 1.25) $|\bar{\Gamma}-\bar{X}|$. The angular dependence at $\bar{\Gamma}$ is sharper yielding a FWHM of $\sim 7°$ along the $\bar{\Gamma}$-$\bar{X}$ direction. These results indicate that electrons at $\bar{X}$ occupy a greater region in momentum space and we then estimate that the density of states at $\bar{X}$ exceeds that at $\bar{\Gamma}$ by at least a factor of 2. Given the approximate degeneracy of the two bands, the high likelihood of scattering between them accounts for the surprisingly large accumulation of electrons found at $\bar{X}$. Direct photopopulation is ruled out since the projected bulk and surface band gaps at $\bar{X}$ exceed the excitation photon energy by >0.5 eV.[6,11] Instead, electrons at $\bar{\Gamma}$ must emit or absorb a surface-zone-boundary phonon in order to scatter to $\bar{X}$. This scattering process is manifest in the time dependence of the conduction electron signals at $\bar{\Gamma}$ and $\bar{X}$.

The time dependence of signals from both $\bar{\Gamma}$ and $\bar{X}$ is displayed in Fig. 2. Although we have studied the time dependence of the electron concentration at the surface out to >100 ps, we will focus only on the first 12 ps here. Each time scan was taken separately at the two different emission angles on the same sample and during the same experimental run. These data are typical of scans reproduced on other samples with some differences occurring at later times due to variations in the quality of the cleaved surface. We note in Fig. 2 that although both signals begin to rise at -1.30 ps, there is a difference in the rise time and peak positions of the two signals. The $\bar{\Gamma}$ signal exhibits a sharper rising edge and peaks 0.9 ps earlier than the $\bar{X}$ signal. In addition, we note that the decay of the $\bar{\Gamma}$ signal is more rapid than for $\bar{X}$. Direct inspection of the rising edges of the two signals indicates a difference of 0.4 ± 0.1 ps at half height.

The skewing of the $\bar{X}$ time scan to longer times reflects the electron scattering dynamics. Excitation into the $\bar{\Gamma}$ valley results in a hot electron gas with, initially, ~ 350

meV of excess energy $E_{\text{photon}} - E_{\text{bandgap}}$. Rapid thermalization and subsequent longitudinal-optical phonon emission results in relaxation of the electron gas. Since the density of states at $\bar{X}$ is relatively large, intervalley scattering may be more probable than intravalley at $\bar{\Gamma}$, resulting in the rapid population of states near $\bar{X}$. If, at short times, the hot Fermi-Dirac electron distribution can be approximated by a Maxwell-Boltzmann distribution, then scattering between $\bar{\Gamma}$ and $\bar{X}$ can occur at all energies. In addition, electrons at $\bar{\Gamma}$ are resonant with the bulk conduction bands and can directly diffuse into the bulk of the crystal resulting in a loss of signal intensity due, in our experiment, to the short (~20 Å) mean free path of the photoemitted electrons. If equilibrium between the surface and bulk electrons at the zone center is established on time scales significantly shorter than the resolution of the experiment then $N_R = kN_B$ *at the surface,* where N_R and N_B are the surface resonance and bulk electron densities at the zone center and k is the density of states enhancement associated with the surface resonance. To describe the dynamics at the surface and in the bulk we can write

$$\dot{N}_B(z,t) = D\frac{\partial^2 N_B(z,t)}{\partial z^2} + C\alpha f(1-r)e^{-\alpha z - E(t/T)^2} - \frac{N_B(z,t)}{\tau_{B\to R}}, \quad (1)$$

$$\dot{N}_R(t) = \frac{F(t)N_{\bar{X}}(t)}{\tau_{\bar{X}\to R}} - \frac{N_R(t)}{\tau_{R\to\bar{X}}} - \frac{N_R(t)}{\tau_{R\to B}}, \quad (2)$$

$$\dot{N}_{\bar{X}}(t) = \frac{N_R(t)}{\tau_{R\to\bar{X}}} - \frac{F(t)N_{\bar{X}}(t)}{\tau_{\bar{X}\to R}}, \quad (3)$$

where

$$(\tau_{R\to\bar{X}})^{-1} = \frac{2\pi}{\hbar}\rho_{\bar{X}}|\langle\psi_{\bar{X}}|H_{e-p}|\psi_R\rangle|^2.$$

The matrix element is assumed to be a constant, i.e., the scattering rates depend only on the final density of states, $\rho_{\bar{X},R}$. $\tau_{R\to B}$ is the transfer time between surface and bulk, sufficiently short to establish equilibrium. D is the diffusion coefficient, T is the light pulse width, α is the absorption coefficient, f is the excitation photon flux, r is the sample reflectivity, and C and E are normalization constants. Equation (1) describes the time-dependent population density change in the bulk while Eqs. (2) and (3) describe the population changes at the surface due to intervalley scattering. Surface and bulk electron densities are coupled at the zone center. Another important aspect of the intervalley scattering problem involves the inclusion of degenerate band filling. Since complex, detailed energy relaxation calculations[12] are required in order to properly account for such effects, we have instead chosen to mimic the onset of degeneracy with a simple exponential function $F(t)$, which increasingly inhibits scattering from $\bar{X}$ to $\bar{\Gamma}$. At early times, $\bar{\Gamma}$ is directly photopopulated while $\bar{X}$ is completely empty. Scattering to states near $\bar{X}$ is then uninhibited at early times while $\bar{\Gamma}\to\bar{X}$ scattering is possible only if unoccupied states are energetically accessible. Without the inclusion of degenerate filling at $\bar{\Gamma}$ the model substantially underestimates the carrier density at $\bar{X}$ for times greater than ~2 ps. At later times degenerate filling of both valleys limits scattering to the energetic region near the quasi-Fermi level within $kT \pm E_{\text{ph}}$, where E_{ph} is the zone-edge phonon energy (36 meV).[13] We then would expect the decay rates of the two signals to be identical, and indeed this is observed for times greater than ~15 ps. The results of fitting these coupled equations to the data are shown as dashed and dot-dashed curves in Fig. 2. We deduce a scattering time of 0.4 ps and a ratio in the density of states $(\bar{X}/\bar{\Gamma})$ of 2.6. In addition, an enhanced diffusion constant of 500 cm^2/s was required for an acceptable fit. While the room-temperature value of 200 cm^2/s is calculated from the Einstein relation for diffusion, $D = \mu k_B T/e$, the excess excitation energy $(E_{\text{photon}} - E_{\text{bandgap}})$ produces a hot electron gas $[T_e(0) \sim 1300\ \text{K}]$ which would diffuse more rapidly. At later times (5–10 ps) diffusion would decrease as energy relaxation resulted in a cooler electron population.[14,15]

The dynamics of scattering from $\bar{\Gamma}$ to $\bar{X}$ at early times are also reflected in the energy distribution of the 1.4-eV peaks (Fig. 3). We note in Fig. 3 that at 0.71 ps ($\bar{\Gamma}$ delay-curve maximum) both the centroid and high-energy edge of the $\bar{\Gamma}$ peak (solid curve in Fig. 3) are higher in energy than the corresponding peak at $\bar{X}$ (dot-dashed curve in Fig. 3). The high-energy edge indicates

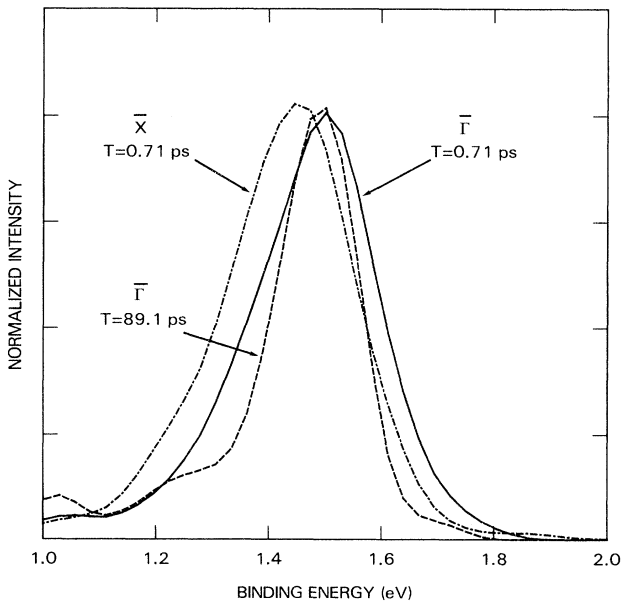

FIG. 3. Expanded views of the excited-electron emission signals for $\bar{\Gamma}$ and $\bar{X}$. The peaks have been normalized for purposes of comparison. Details are described in the text.

the position of the dynamic Fermi level in each valley. At 0.71 ps, the Fermi edge in the $\bar{\Gamma}$ valley exceeds that at $\bar{X}$ by 50 meV. Such a dynamic nonequilibrium at the surface results from the initial photoexcitation which populates only the $\bar{\Gamma}$ valley. The resultant flow of electrons into the $\bar{X}$ valley redistributes the surface electron population and at later times (>3 ps) the Fermi levels equilibrate. Even after equilibration, the Fermi level at $\bar{\Gamma}$ continues to shift to lower energy due to rapid diffusive loss and hence some differences in the edge positions of the two peaks persist. Such a loss of carrier density at the surface results in a reduction of the width of the distribution in the $\bar{\Gamma}$ valley (dashed curve in Fig. 3). The high-energy reduction is a result of cooling of the hot electron distribution within the band and subsequent shifting of the quasi-Fermi level to lower energies as electrons diffuse into the bulk of the crystal. Movement at the low-energy or band-gap side may be due to two effects. Band-gap renormalization is known to occur for electron-hole distributions due to exchange and correlation effects. We note a shift of the low-binding-energy side of 40 meV at $\bar{\Gamma}$ and a shift as well for $\bar{X}$ of 56 meV. These shifts are consistent with values calculated from the formulation of Brinkman and Rice for our excitation densities.[16] In addition, the band gap may narrow as a result of lattice temperature increases due to the emission of phonons from the cooling electron population.[17] We have observed a monotonic increase in the dynamically narrowed band gap with increasing delay times due to these processes. Such effects suggest that for the excitation densities used here, significant distortions of the band structure play an important role in the electron dynamics at short times and may result in a dynamic alteration in the effective mass of excited bands near their minima. We are at present investigating these effects.

In conclusion, picosecond angle-resolved laser photoemission has revealed a new surface-band minimum at $\bar{X}$ in the surface Brillouin zone of laser-excited GaAs(110). We have isolated, with high momentum resolution, the dynamic electron population changes at both $\bar{\Gamma}$ and $\bar{X}$ and deduced the scattering time between the two valleys. These observations suggest that such phenomena, in analogy with the bulk, may play an important role in electronic transport at surfaces and across interfaces.

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