Polarization-dependent time- and angle-resolved laser photoemission study of transiently excited carriers on the InSb(110) surface

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The electron dynamics of transiently photoexcited carriers at an *in situ* cleaved InSb(110) surface was studied in normal emission using polarization-dependent time- and angle-resolved photoelectron spectroscopy. The photoexcited peak was found to be of even parity, and the measured total decay time was significantly shorter than on all clean III-V semiconductor cleavage surfaces previously studied using this technique. The very high mobility of the conduction-band electrons in InSb is believed to contribute to the fast decay via rapid diffusion of carriers away from the surface region. [S0163-1829(98)01835-9]

I. INTRODUCTION

Studying the carrier dynamics in III-V semiconductors is important because of their potential applications in high-speed electronics and optronics. In particular, very small devices and quantum-well heterostructures involving these materials, where surface and interface phenomena become of greater importance, have gained much interest during the last decade. InSb has the smallest band gap of all the common III-V semiconductors, 0.18 eV at room temperature (RT), which makes InSb a suitable material for detectors in the mid-infrared region. The small band gap is accompanied by extreme values of several other physical properties that are closely related to each other, such as the conduction-band effective electron mass, electron mobility, and diffusion constant. The mobility of the conduction-band electrons ($100\,000\ \mathrm{cm}^2/\mathrm{V\,s}$ at RT) is ~ 5 and ~ 12 times higher than the electron mobilities in InAs and GaAs, respectively.[1] This makes InSb is an ideal material for magnetic-field Hall probes,[2] and should also make it an interesting compound for ultrafast electronics. While previous time-resolved measurements on InSb have been focused on recombination times of transiently excited carriers in the bulk material,[3] here we report time-resolved pump-and-probe photoemission measurements performed on the cleavage surface of this compound. This experimental technique makes it possible to follow the time development of electrons photoexcited to states above the ground-state Fermi level, emphasizing effects in the surface region of the material under study, and has been used to investigate transiently excited states on several other III-V semiconductor cleavage surfaces.[4–6]

When a (110) cleavage surface of a III-V semiconductor is created, the bulk electronic structure is complemented by new electron energy states which are bound to the surface. Most closely related to the band-gap region is the fact that the electron in the broken bond at the cation (In) is transferred to the anion (Sb) broken bond, producing empty and filled dangling-bond surface bands that are conventionally named C_3 and A_5, respectively. In order to minimize the total energy of the perturbation introduced by the surface, the In-Sb zigzag chain in the surface layer is tilted by $\sim 29°$, the In atoms moving into and the Sb atoms moving out from the surface plane. This surface relaxation pushes the A_5 band downward and the C_3 band upward, in many cases into the projected bulk valence and conduction bands, respectively, so that these surface-related bands thus become surface resonances instead of true surface states in most of the surface Brillouin zone (SBZ). For InSb(110) in particular, however, photoemission studies have found the filled A_3 band at the $\bar{\Gamma}$ point (the SBZ center) to be ~ 80 meV above the valence-band maximum (VBM).[7] The energy location of the empty C_3 surface band at $\bar{\Gamma}$ has been predicted by theoretical calculations to be ~ 1.5 eV above the VBM,[8–10] and results from inverse photoemission measurements have located this state at 1.4 eV (Ref. 11) and 1.9 eV (Ref. 12) above the VBM, respectively.

II. EXPERIMENT

The experimental setup used in the present measurements is described in detail elsewhere.[13] In summary, the time-resolved photoemission study was performed in normal emission at room temperature, using 150-fs pulses from a tunable, regeneratively amplified titanium:sapphire (Ti:S) laser system set to 780 nm (1.59 eV). The laser system produces ~ 600-μJ pulses at a rate of 1 kHz, and the high peak power (>1 GW) is used to create vacuum-ultraviolet radiation at 130 nm (9.55 eV) by cascaded frequency doubling and tripling in a betabarium borate (BBO) crystal and xenon gas, respectively. A spherical grating is used to select and focus the 130-nm radiation onto the sample. The grating also stretches the probe pulse in time to a pulse width of about 3 ps. Time resolution is accomplished by using the pump-and-probe technique, where the semiconductor samples are pumped by 1.59-eV photons and probed by 9.55-eV photons, which arrive at the sample a well-defined time after the pump pulse by using an optical delay line. The photoelectrons were energy analyzed using a single anode time-of-flight detector with an angular resolution of $\pm 2.5°$ and an energy resolution better than ~ 150 meV for electrons with a kinetic energy of 5 eV. The samples, nominally undoped n-type InSb single-crystal rods [carrier concentration (77 K) $\sim 1\times 10^{14}\ \mathrm{cm}^{-3}$; resistivity (77 K) $\sim 0.148\ \Omega$ cm] with a 5×5-mm^2 cross section, were cleaved *in situ* in ul-

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trahigh vacuum ($<3\times10^{-10}$ Torr). The surface quality and setting of the azimuthal angle were checked by low-energy electron diffraction, which showed a clear (1×1) pattern. The direction of the mirror plane (MP) of the surface, which is defined by the surface normal and the [001] direction (see the inset in Fig. 1), is important to specify together with the polarization of the probe pulse in the present study. We will refer to the two azimuthal directions as the vertical MP and horizontal MP, respectively. The sample normal was directed toward the analyzer, and the light was incident on the surface at an angle of 45°. Light with the electric-field vector perpendicular and parallel to the plane of incidence (equal to the horizontal plane) is denoted s and p polarized, respectively. The pump pulse was p-polarized in all measurements, while the polarization of the probe was changed between pure s and p polarization by using a Berek polarizing compensator placed between the BBO crystal and the xenon gas cell. Since the probe photon energy used in this experiment is 9.55 eV, the estimated escape depth of the photoemitted electrons is ~20–30 Å,[14] and we thus probe several atomic layers into the bulk, as compared to the more surface sensitive measurements using photon energies in the range 30–100 eV.

The polarized radiation from the laser source may be used together with the mirror plane of the surface in order to deduce the parity of the initial state.[15,16] The photoemission transition can be described by the matrix element $\langle f|\mathbf{A}\cdot\mathbf{p}|i\rangle$, where $|i\rangle$ and $\langle f|$ are the initial and final states, respectively, and $\mathbf{A}\cdot\mathbf{p}$ the dipole operator. For an allowed transition, the photoemission transition matrix element must be invariant under reflection in the mirror plane, i.e., have even symmetry, to be nonzero. Since all measurements were done in normal emission, the detector is situated in the mirror plane, and an even final state is required. Therefore, in order to produce an even matrix element, the initial state has to be of the same symmetry as the dipole operator. When the polarization vector is set to be parallel (perpendicular) to the MP, the dipole operator has even (odd) parity.

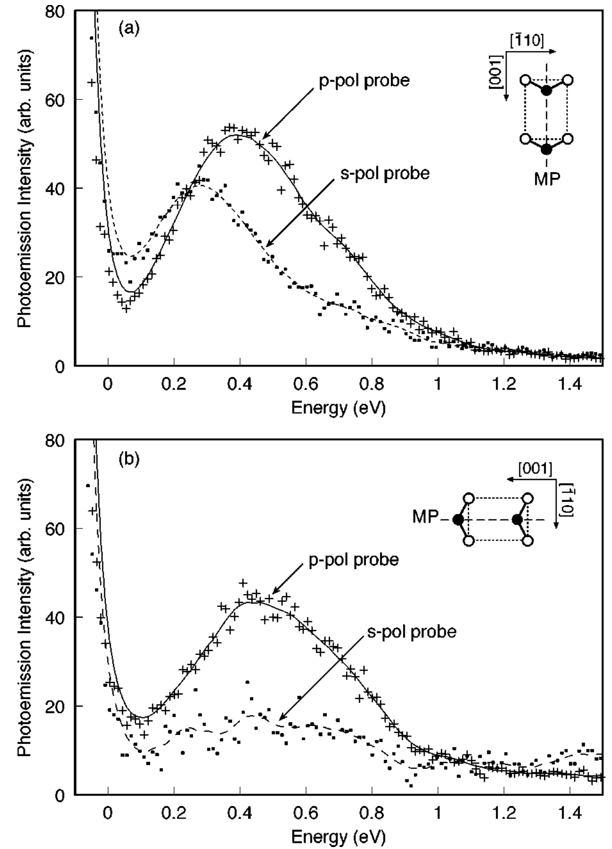

FIG. 1. Pump-and-probe photoemission spectra of the excited peak the at the temporal overlap position for different surface azimuthal directions and polarizations. (a) Vertical mirror plane (MP): polarization vector parallel to the MP using an s-polarized probe. (b) Horizontal MP: polarization vector perpendicular to the MP using an s-polarized probe.

III. RESULTS AND DISCUSSION

Figure 1 shows photoemission spectra at the temporal overlap between the pump and probe pulses for the four possible combinations of MP and probe polarization directions; the insets show the direction of the surface as viewed from the front for each measurement. The pump pulse energy density was ~800 μJ/cm^2 during these measurements, and least-square-fit (LSF) lines are used to guide the eye through the data points. Considering s-polarized probe, the polarization vector will be parallel to the MP in Fig. 1(a), and perpendicular to the MP in Fig. 1(b). The s-polarized probe will, therefore, probe even states in Fig. 1(a) but odd states in Fig. 1(b). The p-polarized probe, on the other hand, has a polarization component along the surface normal and as well as in the surface plane, and will, consequently, probe both even and odd states in Fig. 1(a), but only even states in Fig. 1(b). We can see that, when using an s-polarized probe, the photoexcited peak signal exists only for the vertical MP case [Fig. 1(a)], whereas it disappears when the MP is in the horizontal direction [Fig. 1(b)]. This indicates an even symmetry of the photoexcited peak, which is also consistent with the p-polarized probe spectra. Since a p-polarized probe will have a polarization component along the surface normal, i.e., parallel to the MP, irrespective of the surface azimuthal direction, it will always give a photoemission signal in normal emission for even symmetry initial states. The overall photoemission intensity was slightly higher when recording the p-polarized spectrum, which might explain the larger photoexcited peak in this case. The energy location of the transiently photoexcited peak, ~0.2–1 eV above the VBM, suggests that it originates from the InSb bulk conduction band, since the unoccupied C_3 surface band was found to be located more than ~1.4 eV above the VBM.[12] This conclusion is also supported by the fact that the signal shows even symmetry behavior, as is expected from the bulk conduction-band minimum (CBM) because of its atomic s-like character.[17] Moreover, a rather large bulk signal is expected in the photoemission spectra, because of the above-mentioned relatively long photoelectron mean free path at this low photoemitting photon energy.

The initial-state symmetry behavior is somewhat different from similar pump-and-probe photoemission studies of the InAs(110) cleavage surfaces,[6] but recent studies of GaSb(110) gives the same result.[18] The reason for the different behavior on InAs might be that n-type InAs has been found to spontaneously form an electron accumulation layer within a day after cleavage,[19] even when situated in an UHV

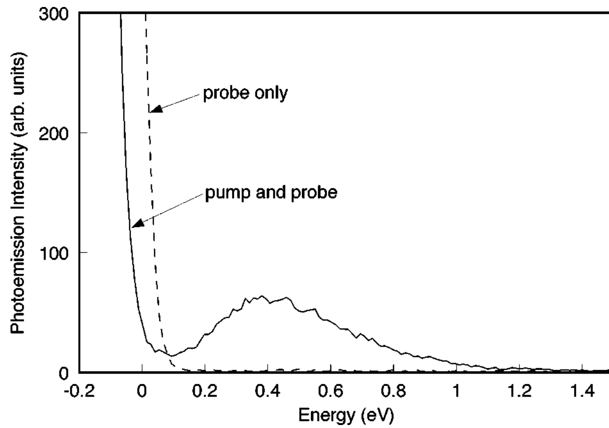

FIG. 2. Photoemission spectra with and without a pump pulse.

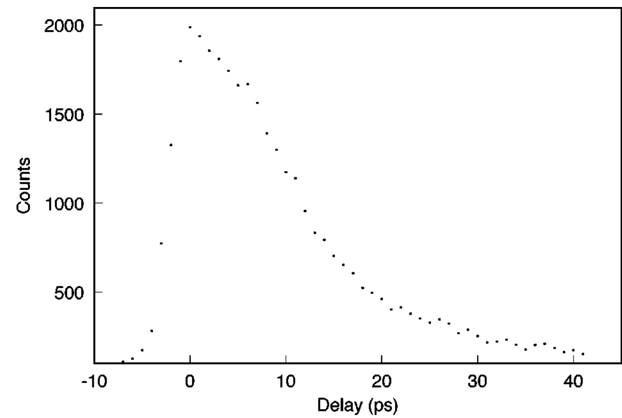

FIG. 3. Decay of the excited peak as a function of relative delay between pump and probe pulses, measured using a p-polarized probe.

environment. In order to investigate such behavior of the cleavage surface of InSb, we exposed a cleaved surface to UHV one day before recording the spectra shown in Fig. 2. With probe only (p polarized), no emission at all was detected from conduction-band states. When applying the pump pulse, apart from a photoexcited peak, the VBM shifted to lower energy by $\sim$75 meV, which indicates a depletion layer at the surface of the n-type InSb at equilibrium, i.e., pinning of the Fermi level closer to the VBM in the InSb band gap. The VBM shift is explained by an upward band bending that is annihilated because of surface photovoltage, which flattens the bands when the surface is optically pumped.[20] Pinning of the Fermi level close to the VBM on InSb surfaces is expected, since the position of the branch point energy is only 0.01 eV above the VBM (see, e.g., Table 3.1 in Ref. 14). Similar results have been reported from previous studies of InSb, both the clean cleavage surface[21] and after deposition of an Au overlayer,[22] even if deposition of Ag at very low temperatures (10 K) has been reported to form an accumulation layer on this compound.[23]

The time-resolved study of the photoexcited peak is performed by measuring the peak at different delays between the infrared pump and the vacuum-ultraviolet probe pulses. By integrating the number of counts in the excited region as a function of delay between the pump and the probe pulses, we obtained a decay spectrum as shown in Fig. 3, recorded using p-polarized probe. We also performed the same experiment using s-polarized probe (with vertical MP) and obtained the same decay time. We can see from the decay spectrum in Fig. 3 that the photoexcited electrons have disappeared almost completely from normally unpopulated region of the photoemission spectrum after $\sim$40 ps. This makes the total decay time of the excited peak on the InSb(110) surface shorter than on all other clean III-V cleavage surfaces studied using this technique.[4–6,18] There are basically three mechanisms that may contribute to the loss of photoexcited signal in this type of measurement: bulk recombination, surface recombination, and diffusion of carriers into the bulk material. The radiative and nonradiative bulk recombination times, obtained from time-resolved photoluminescence and photoconductivity measurements at liquid-helium temperatures, are reported to be longer than 20 ns.[3] Even at RT this decay mechanism should not significantly affect the carrier distribution within the 50 ps studied in the present experiment. The surface recombination rate is enhanced if the density of defect states at the surface increase, since they will act as traps and/or recombination centra. Even when using polished InSb sample surfaces, the surface recombination velocity (SRV) has been reported to be less than 10^4 cm/s.[24] Since a well-cleaved surface is expected to have less defects than any polished surface, and since SRV below 10^3 cm/s is generally less important than bulk recombination,[25] this mechanism should not contribute significantly to the rapid decay of the signal either. Diffusion of carriers into the bulk will take the electrons away from the 20–30-Å thick layer at the surface reachable by the photoemitting probe pulse, because of the finite mean free path of the photoelectrons, and this effect will thus contribute to the loss of signal from the photoexcited and photoemitted peak. The diffusion is driven by the large concentration gradient of photoexcited electrons near the surface, which is created by the short absorption depth ($\sim$100 nm) of the pump pulse radiation. Since InSb has the highest electron mobility of all semiconductors, which in turn as a first approximation is proportional to the diffusion constant, we suggest that the principal reason for the rapid total decay of the photoemitted signal is because of this rapid diffusion of carriers into the InSb bulk. It must, however, be realized that the simple linear Einstein relation between the mobility and diffusion constants[1,2] does not correctly describe the diffusion process in systems that are far from equilibrium (see, e.g., several articles on nonlinear diffusion in Ref. 26).

Test of the significance of diffusion can be performed by deliberately locking photoexcited electrons close to the surface. This was done by Haight and co-workers[27,28] by evaporating a few layers of Ge onto different surfaces of a GaAs substrate. Since Ge has a smaller band gap than GaAs, the CBM offset between the two materials will hinder electrons photoexcited into the Ge conduction band from diffusing into the bulk GaAs. The ‘‘delayed diffusion’’ effect was demonstrated when depositing Ge on the GaAs(110) surface.[27] Interestingly, however, performing the same procedure on a GaAs(111) substrate[28] was shown to give a shorter total decay time ($\sim$30 ps), i.e., an even shorter time than obtained in the present study. The very fast decay was in this case attributed to the formation of defects at the heterostructure interface, which will provide rapid nonradiative decay channels. As stated above, however, a high surface

density of such defects is not expected on a clean cleavage surface.

Since the type of decay spectrum shown in Fig. 3 only indicates the decay time of total amount of carriers that are reachable by the probe pulse in the excited region, and does not show any change of shape of the excited peak during the decay, we also recorded a complete photoemission spectrum at all delay times. A compound spectrum based on the LSF lines from such p-polarized spectra with vertical MP is shown in Fig. 4. The figures on the right hand side of the spectrum indicates the relative delay between the pump and probe pulses. Electrons are first excited into levels as high as ~ 1.6 eV above the VBM, but due the initial rapid relaxation from these states and the finite pulse width of the probe pulse (~ 3 ps), they are not possible to monitor in the present experiment. It can, however, be seen that electrons relax in the conduction band within 3 ps after excitation, filling states at the CBM, and finally decay away from the photoemission spectra. No double-peak structure, as was found on InAs and attributed to a weak accumulation layer,[6] could be detected.

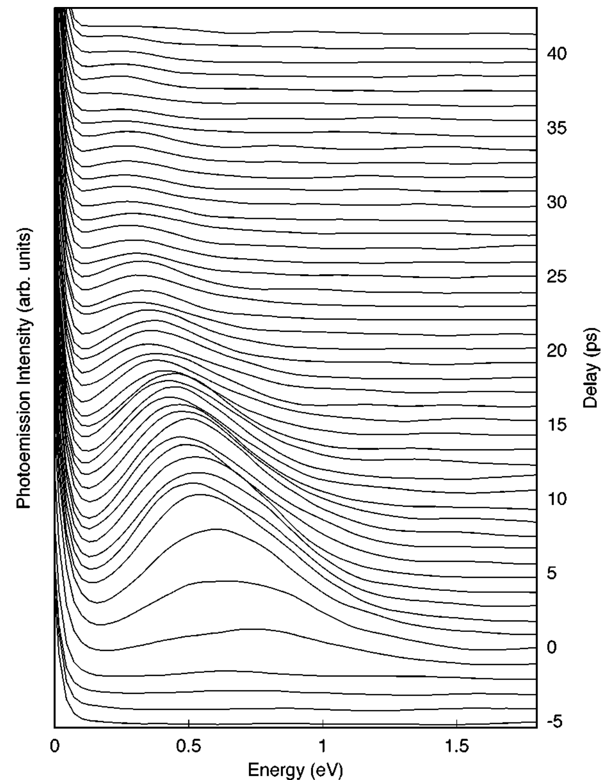

FIG. 4. A compound spectrum constructed from an excited peak photoemission spectrum at all delay times used in Fig. 3; the figures on the right indicate the delay time.

IV. SUMMARY

In summary, we have performed a polarization-dependent time- and angle-resolved photoemission study of normally unoccupied states at and near an *in situ* cleaved InSb(110) surface. The transiently photoexcited peak was found to be of even symmetry, consistent with the bulk CBM, and we also found that the total decay time of the photoexcited signal is significantly shorter than as measured from the other clean III-V cleavage surfaces using the same technique. We conclude that this result stems from the extremely high electron mobility in InSb, which leads to a rapid diffusion of carriers away from the surface region that is reachable by the photoemitting probe pulse.

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[1] C. M. Wolfe, N. Holonyak, Jr., and G. E. Stillman, *Physical Properties of Semiconductors, Prentice Hall Series in Solid State Physical Electronics* (Prentice-Hall, Englewood Cliffs, NJ, 1989).
[2] A. Bar-Lev, *Semiconductors and Electronic Devices*, 2nd ed. (Prentice Hall, Englewood Cliffs, NJ, 1984).
[3] R. D. Grober, H. D. Drew, G. L. Burdge, and B. S. Bennet, J. Appl. Phys. **71**, 5140 (1992).
[4] R. Haight, J. Bokor, J. Stark, R. H. Storz, R. R. Freeman, and P. H. Bucksbaum, Phys. Rev. Lett. **54**, 1302 (1985).
[5] R. Haight and J. A. Silberman, Phys. Rev. Lett. **62**, 815 (1989).
[6] H. S. Karlsson, G. Chiaia, and U. O. Karlsson, Surf. Sci. Lett. **407**, L687 (1998).
[7] R. Manzke and M. Skibowski, Phys. Scr. **T31**, 87 (1990).
[8] R. P. Beres, R. E. Allen, and J. D. Dow, Phys. Rev. B **26**, 5702 (1982).
[9] M. Schmeits, A. Mazur, and J. Pollman, Solid State Commun. **40**, 1081 (1981).
[10] C. Mailhiot, C. B. Duke, and D. J. Chadi, Phys. Rev. B **31**, 2213 (1985).
[11] H. Carstensen, R. Claessen, R. Manzke, and M. Skibowski, Phys. Rev. B **41**, 9880 (1990).
[12] W. Drube, D. Straub, and F. J. Himpsel, Phys. Rev. B **35**, 5563 (1987).
[13] H. S. Karlsson, G. Chiaia, and U. O. Karlsson, Rev. Sci. Instrum. **67**, 3610 (1996).
[14] W. Mönch, *Semiconductor Surfaces and Interfaces*, 2nd ed. Springer Series in Surface Sciences Vol. 26 (Springer-Verlag, Berlin, 1995).
[15] J. Hermanson, Solid State Commun. **22**, 9 (1977).
[16] W. Eberhardt and F. J. Himpsel, Phys. Rev. B **21**, 5572 (1980).
[17] G. P. Williams, F. Cerrina, G. J. Lapeyre, J. R. Anderson, R. J. Smith, and J. Hermanson, Phys. Rev. B **34**, 5548 (1986).
[18] H. S. Karlsson and U. O. Karlsson (unpublished).
[19] H. S. Karlsson, R. Viselga, and U. O. Karlsson, Surf. Sci. **402–404**, 590 (1998).
[20] M. Alonso, R. Cimino, and K. Horn, Phys. Rev. Lett. **64**, 1947 (1990).
[21] G. W. Gobeli and F. G. Allen, Phys. Rev. **137**, A245 (1965).
[22] C. A. Mead and W. G. Spitzer, Phys. Rev. Lett. **10**, 471 (1963).
[23] V. Y. Aristov, M. Bertolo, P. Althainz, and K. Jacobi, Surf. Sci. **281**, 74 (1993).
[24] G. V. Beketov and A. I. Liptuga, Mater. Sci. Forum **173-174**, 215 (1995).

[25] D. E. Aspnes, Surf. Sci. **132**, 406 (1983).
[26] *Semiconductors Probed by Ultrafast Laser Spectroscopy*, edited by R. R. Alfano (Academic, Orlando, FL, 1984), Vols. 1 and 2.
[27] R. Haight and J. A. Silberman, Appl. Phys. Lett. **57**, 1548 (1990).
[28] R. Haight, M. Baeumler, J. A. Silberman, and P. Kirchner, Surf. Interface Anal. **19**, 301 (1992).