Multivalley Electron Population Dynamics on the Ge(111):As Surface

Armin Rettenberger* and Richard Haight
IBM T. J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
(Received 1 September 1995)

Electrons excited to energies well above the conduction band minimum of Ge are observed to populate valleys centered at the $\overline{\Gamma}$ and $\overline{M}$ points of the Brillouin zone on the As-terminated Ge(111) surface. The valley centered at $\overline{M}$ is a surface resonance, located 0.3 eV above the Ge conduction band minimum. The subpicosecond population dynamics are followed directly with harmonic laser photoemission. The time evolution of the excited electron gas temperature was measured and a cooling rate was determined.

PACS numbers: 73.25.+i, 78.47.+p, 79.60.Dp

When electrons in a semiconductor are excited to empty states well above the conduction band minimum (CBM), a multitude of processes conspire to rapidly dissipate this excess energy. One important process involves energy relaxation through the emission of phonons, resulting in the generation of lattice heat. In addition to energy relaxation, momentum transfer can send electrons to other locations within the Brillouin zone. The transition probability for this process depends importantly upon the density of final states to which the electron scatters. In Ge, deformation potential scattering can drive electrons into energetically accessible satellite valleys. The probability for this process is particularly high if the final state is large [1]. Such conditions, as we will describe, exist on the As-terminated Ge(111) surface.

The As-terminated Ge(111) surface, discussed in detail by a number of investigators, is a model unreconstructed semiconductor surface [2–5]. The termination of the Ge surface with As results in the formation of an occupied nonbonding lone pair state which resides 0.4 eV below the Ge valence band maximum (VBM), and a highly dispersive antibonding state, shown in Fig. 1 which resides 0.4 eV above the Ge VBM. Figure 1 displays the bulk band structure projected onto the (111) surface and the calculated quasiparticle surface bands [5], particularly appropriate when comparing to photoemission spectra. The minimum of the empty surface band is found at the $\overline{\Gamma}$ point of the surface Brillouin zone (SBZ). Electron dynamics within the $\overline{\Gamma}$ valley were previously studied in detail for this surface [6], where it was shown that electrons scattered from bulk Ge states into the zone center surface state on a picosecond time scale. Since the bottom of the surface band resides within the Ge bulk band gap, electrons remained trapped in this state at the surface for times approaching a nanosecond.

Inspection of the calculated band structure for this surface (shown in Fig. 1) suggests that further scattering within the Brillouin zone is possible. In particular, a satellite valley energetically degenerate with bulk Ge states exhibits a minimum at the $\overline{M}$ point in the SBZ. In this Letter we describe experimental observations of ultrafast scattering of electrons into and out of this resonance satellite valley with femtosecond (fs) laser photoemission. Excitation with pulses of 610 nm light creates a highly excited electron gas whose time evolution is probed with vacuum ultraviolet pulses which photoemit both valence and excited electron populations. In order to aid in our investigations we have employed a unique parabolic mirror time-of-flight analyzer (PMTFA) whose large collection solid angle [7] permits the observation of electrons throughout the entire SBZ. With this approach we have directly studied the ultrafast population dynamics both at the SBZ center, where electrons are ultimately trapped, and in the $\overline{M}$ resonance, located 0.5 eV above the minimum of the surface state. We show directly that population in the $\overline{M}$ resonance grows within ~400 fs to its maximum and then decays completely within 2 picoseconds (ps). Furthermore, by deconvolving the various scattering contributions to the shape of the photoemission signal collected from the evolving electron gas, we have been able to extract the surface temperatures

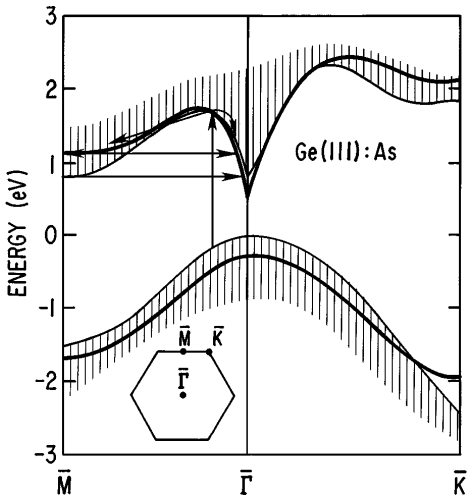

FIG. 1. Quasiparticle band structure diagram of the As-terminated Ge(111) 1×1 surface (after Ref. [5]) showing the bulk projected (hatched regions) and surface bands (solid lines). Arrows show the scattering pathways which result in the transient population of the $\overline{M}$ and $\overline{\Gamma}$ valleys on this surface. Electrons also populate the surface state minimum by intravalley scattering near $\overline{\Gamma}$ (curved arrow).

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and cooling rate of the excited electron population for the first 1.6 ps after excitation.

In this experiment 300 fs pulses of 610 nm light from a synchronously pumped dye laser system are amplified to ~0.6 mJ at a repetition rate of 540 Hz. Approximately 0.12 mJ of this light is split off for photoexcitation of the sample. An adjustable delay line is used to vary the relative arrival time of the excite and probe pulses. The remaining 0.48 mJ of 610 nm light is focused into the Ar gas output of a supersonic pulsed valve located at the input end of a 3 m differentially pumped beam line attached to our ultrahigh vacuum analysis chamber. A comb of odd multiple harmonics [8–13], generated when the intense 610 nm light interacts with the high density Ar gas, is directed to a grazing incidence toroidal grating. Angle tuning of the grating selects the harmonic of interest. For the work described here, 18.3 eV photons were chosen. Photoemission from the excited sample was detected with the PMTFA. Electrons emitted over a wide range of angles from the sample, located at the focus of the paraboloid, are collimated upon reflection from the mirror and directed into a 1 m drift tube. At the end of the tube the drifting electrons strike a multianode array; the subsequent signals are electronically analyzed and sent to a computer. The solid angle subtended by this detector is ~1.1 sr, permitting the simultaneous observation of all areas of the SBZ for the As/Ge surface. Further details of the experimental setup may be found elsewhere [14].

The samples are n-type Ge(111) ($\rho = 0.4\ \Omega$ cm) prepared by sputtering and annealing until a sharp $c(2 \times 8)$ low-energy electron diffraction pattern is observed. The temperature of the sample is raised to and then held at 400 °C during exposure to a flux of As_4 generated from a heated effusion cell. This treatment results in a sharp 1×1 diffraction pattern with exceptionally low background [4]. All measurements to be described were carried out at 300 K.

Figure 2 displays a panel consisting of three spectra showing the time evolution of the transiently excited, normally empty antibonding state of the As/Ge system. Absorption of a pulse of 610 nm light drives electrons into states well above the CBM of the system. The top panel displays the photoemission signal collected near the temporal overlap of the excite and probe pulses ($t = 0$). The zero of energy is chosen as the Ge VBM. The peak at 0.4 eV corresponds to electrons which accumulate near the minimum of the surface state at $\overline{\Gamma}$. A shoulder located at 0.6 eV is also observed and results from electrons which scatter from the bottom of the bulk Ge conduction band into the surface state (see Fig. 1). Both the 0.4 and 0.6 eV features have been identified and discussed in an earlier paper [6].

Quite striking is the appearance of a relatively intense feature located at 0.9 eV, particularly evident in the top two spectra in Fig. 2. If we follow the time evolution of this peak at later delays, as shown in the middle and lower panels, a picture of the evolution of the excited population can be constructed. Note that at 660 fs delay, the 0.4 eV peak has increased in intensity, and we continue to observe the shoulder at 0.6 eV. The 0.9 eV peak, while observable, has diminished significantly in intensity relative to the other peaks. Finally, at 3 ps all evidence of the 0.6 and 0.9 eV features has disappeared and the 0.4 eV peak has intensified further. We also observe a high energy tail of electrons at $t = 0$ which retreats with increasing time. Such a hot electron tail can be fit with a Fermi function for a two-dimensional electron gas to extract a surface electron temperature, which is discussed later in this Letter.

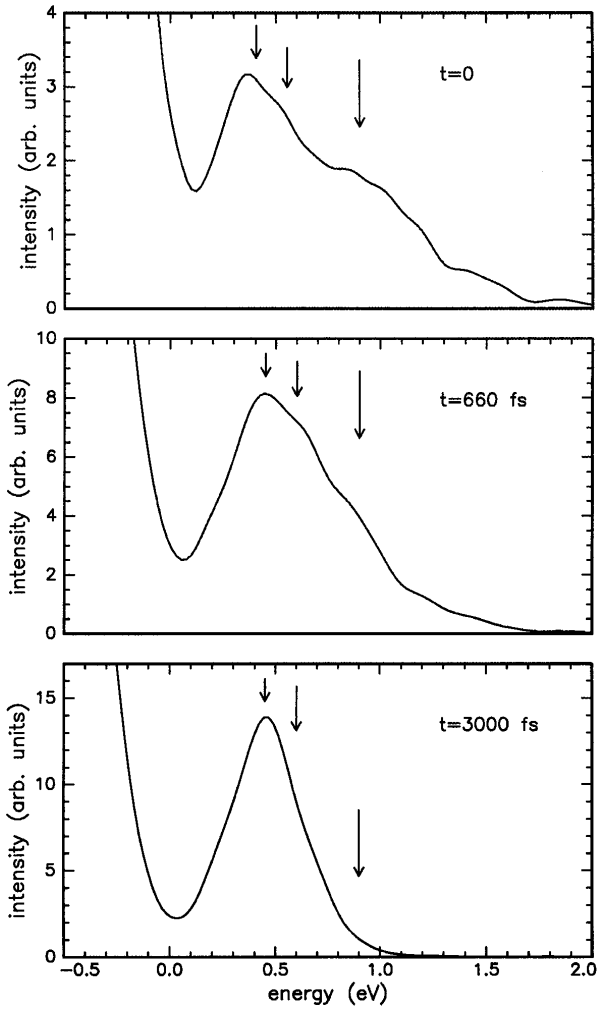

FIG. 2. Top: spectrum of excited surface electron population at $t = 0$. The main peak at 0.4 eV corresponds to electrons populating the minimum of the surface state at $\overline{\Gamma}$. The arrow at 0.6 eV indicates the energy at which electrons scatter into the surface state from the Ge CBM. The arrow at 0.9 eV indicates the center of the peak due to electrons transiently populating the satellite resonance valley at $\overline{M}$. Middle: spectrum collected at 660 fs showing the rapid reduction in $\overline{M}$ population. Bottom: spectrum collected at 3000 fs showing the complete loss of emission from the $\overline{M}$ point, indicating that the population in this satellite valley has been depleted. The 0.6 eV peak has also vanished.

Inspection of the band structure of Fig. 1 helps to explain the features we observe. As discussed earlier, the 0.4 eV peak corresponds to the minimum of the normally empty surface state. The shoulder at 0.6 eV is due to scattering of bulk Ge electrons from the CBM into the surface state near $\overline{\Gamma}$.

The peak at 0.9 eV decays rapidly in time, and its evolution indicates additional dynamics. We note, in Fig. 1, the theoretically predicted existence of a satellite surface valley whose minimum is located at the $\overline{M}$ point (solid line) at an energy of 1.1 eV. Since this surface valley is degenerate with bulk Ge conduction states, it is a resonance and not a bona fide surface state. (A resonance is a surface state which mixes with a degenerate propagating bulk state; the resulting hybridized state exhibits large amplitude at the surface.) Photoexcitation with 610 nm photons (see Fig. 1) produces excited electrons through bulk-bulk, bulk-surface state, and surface state-surface state transitions. Significant absorption occurs only near the zone center. In particular, we emphasize that a direct excitation of the surface resonance at the $\overline{M}$ point is energetically not allowed. Electrons which are directly photoexcited to states near the zone center rapidly thermalize, resulting in a broad distribution of hot electrons. These electrons can then scatter into the resonance at and near $\overline{M}$, a process made particularly favorable due to the high density of states there. Such scattering can occur over a wide range of energies, giving rise to the rather broad peak we observed near 0.9 eV.

In order to verify that the 0.9 eV peak is actually emission from the $\overline{M}$ point we performed the following experiment. Electrons at the $\overline{M}$ point in the SBZ have a parallel wave vector, $k_{\parallel} = 0.908$ Å^{-1}. As a result, when photoemitted with 18.3 eV photons, these electrons are emitted at an angle of 28° from the surface normal, given by $k_{\parallel} = 0.51\sqrt{E_{\mathrm{kin}}}\,\sin(\theta)$ Å^{-1} where E_{kin} is the photoemitted electron kinetic energy. Although our PMTFA collects electrons over a wide range of angles permitting a view of the entire SBZ, an appropriate tilting of the sample by 25° relative to the parabolic mirror [shown in the inset of Fig. 3 (top)] significantly reduces the detection of the $\overline{\Gamma}$ electrons (normal emission) while electrons from the $\overline{M}$ point are collected. Comparison of spectra from normal and tilted emissions are shown in Fig. 3 together with an inset which indicates the geometries employed. The spectra were collected near $t = 0$. Note that for the tilted geometry, the band gap is wider and the peak of the signal is located at 0.9 eV. This position, as can be seen in Fig. 3, lines up well with the 0.9 eV shoulder present in the normal emission spectrum and provides additional proof that the 0.9 eV peak originates from the satellite resonance valley at $\overline{M}$. Our identification of the $\overline{M}$ minimum at 0.9 eV is 0.2 eV lower than the theoretical value [5] for this resonance. This small difference may be due to the combined uncertainties of the calculation and experiment in addition to dynamical effects associated with the rapidly evolving electron gas.

We can also interrogate the dynamics in the resonance valley. Figure 3 (bottom) displays the intensity of the $\overline{M}$ emission as a function of delay time. The edge of the $\overline{M}$ signal rises within approximately 400 fs but displays a somewhat slower decay. The population of the $\overline{M}$ valley is completely depleted beyond 2.3 ps in the delay curve. This rapid decay of population is driven by several processes including coupling of electrons into bulk Ge states where they can relax to the Ge CBM or diffuse away from the surface. It is also possible for electrons to return to empty states near the zone center. All of these processes rapidly deplete the population in the $\overline{M}$ resonance resulting in the observed short residence time. It is important to note here that we are measuring the population dynamics of the coupled $\overline{\Gamma}$-$\overline{M}$ system and not the inherent "lifetime" of the resonance such as that which

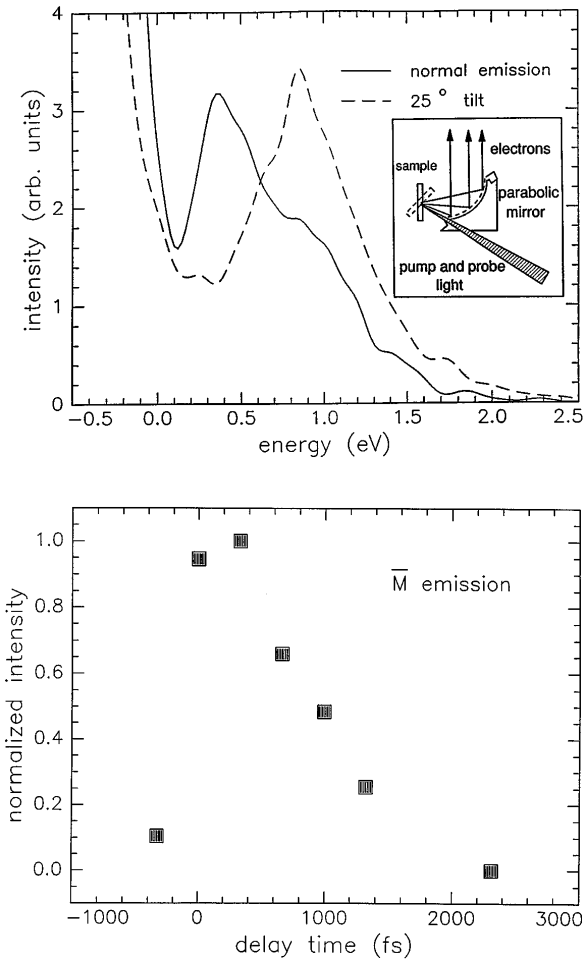

FIG. 3. Top: excited electron spectra collected at normal emission (solid line) and with the sample tilted off at 25° (dashed line) near $t = 0$. The 25° signal has been scaled by a factor of 2 for direct comparison. Bottom: normalized $\overline{M}$ emission as a function of time.

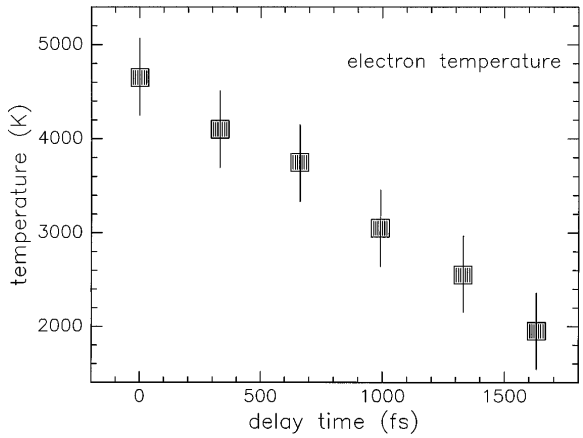

FIG. 4. Time dependence of the excited surface electron temperature.

would be inferred from linewidths typically observed with inverse photoemission [15,16].

We have also analyzed our data in order to determine the temperature of the excited electron population on the surface. The large collection angle of the PMTFA permits the observation of hot electrons higher up in the empty surface bands which might otherwise escape detection in an angle resolved approach. We have extracted the electron temperature by first removing the 0.6 and 0.9 eV peak contributions from the excited state photoemission spectra. For a two-dimensional band, the density of states is a constant (in the approximation of parabolic bands). As a result, the product of the density of states with the Fermi function simply returns the Fermi function, scaled by a constant, which was then convolved with the detector resolution function and fit to the spectra. The change in the surface electron temperature with time is shown in Fig. 4. The initial temperature, determined at the temporal overlap of the excite and probe pulses is found to be 4650 $\pm$ 400 K. This temperature is reasonable considering that excitation with our 610 nm (2.036 eV) photons results in electrons with energies as high as 1.6 eV above the antibonding surface state minimum. Indeed, at very early times (as in the top spectrum in Fig. 2) we see electrons at energies approaching 2 eV above the VBM of Ge. In the top two spectra of Fig. 2 we observe an energetic electron tail which retreats rapidly with increasing delay time. Figure 4 exhibits the temperature extracted from fitting the Fermi function to the spectra collected for different delay times. We see that the temperature of the excited electrons drops from 4650 to $\sim$1950 K within the first 1.6 ps. This translates into a cooling rate at early times of $dE/dt = (1.5 \pm 0.3) \times 10^{11}$ eV/sec. To our knowledge no previous measurements of electron cooling rates at a semiconductor surface have been carried out. Electron energy loss studies have been carried out in two-dimensional quantum well systems (GaAs/GaAlAs) [17,18] where screening and hot phonon effects are known to slow cooling rates [19,20]. For 150 Å quantum wells and an electron density of $2.5 \times 10^{11}/\text{cm}^2$ cooling rates up to 0.3 eV/ps were measured [18]. However, these measurements are difficult to compare with directly since polar optic (Frölich) scattering is dominant in GaAs but does not occur in monoelemental Ge. In addition, excitation conditions in those experiments leading to different electron densities and excess electron energies make direct comparison difficult. Nevertheless, in the present experiment where we estimate the peak surface electron density to be $\sim 5 \times 10^{12}/\text{cm}^2$, cooling rates are also expected to be slowed by screening and hot phonon effects.

We wish to thank Brian Tonner and the Synchrotron Radiation Center at the University of Wisconsin for the use of the toroidal grazing incidence grating. We also thank Paul Leiderer and Johannes Boneberg for stimulating discussions and comments.

*Present address: Universität Konstanz, Postfach 5560, D-78434, Konstanz, Germany

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