Ultrafast Dynamics of Laser-Excited Electron Distributions in Silicon

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Time-resolved photoelectron spectroscopy is used to directly observe the energy relaxation of optically excited electrons in silicon with 150 fsec resolution. We observe an electron-electron thermalization time of < 120 fsec, an extremely fast *initial* electron cooling rate, followed by an electron-phonon thermalization time of ~ 1 psec, and overall a strong energy dependence to the electron scattering rate. Here, we also report a new effect in two-photon photoemission unique to ultrashort laser pulses, resulting in a sensitive new monitor of electron dynamics.

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A detailed microscopic understanding of hot electron relaxation in materials can be obtained through the use of ultrafast optical probing techniques. Ultrafast lasers have been applied extensively to the study of hot electron relaxation in direct gap semiconductors such as GaAs and InP [1], as well as to metals [2]. In contrast, there have been very few such studies of Si because conventional optical pump-probe methods are difficult to interpret for an indirect gap material. This is unfortunate since understanding hot electron behavior in Si is key to understanding and predicting the properties of state-of-the-art Si devices [3,4]. Presently, dc transport measurements are used to obtain information about carrier scattering for Si device simulations. However, dc transport cannot provide a microscopic description (i.e., state resolved) of the carrier dynamics since it integrates over all energies and can only measure moments of the distribution function and not the distribution function itself [5]. Here we show that by using an ultrafast laser pump-probe approach, the time evolution of an entire electron energy distribution function in *silicon* can be obtained. This time- and energy-resolved approach gives a much more complete picture of the electron dynamics.

In this Letter, we report the first subpicosecond (150 fsec) time- and energy-resolved measurement of the relaxation of optically excited electrons in Si. This is accomplished using a laser pump-probe format by analyzing the *photoelectron* spectrum generated by an ultrashort uv probe pulse. By this method, we obtain *directly* the time evolution of the photoexcited electron distribution function (bulk and interface) in Si with 150 fsec resolution. These measurements would not be possible by either reflectivity/transmission or luminescence schemes [1,6].

Variations of time-resolved laser photoelectron spectroscopy have been applied previously [2,7–11]. In silicon, the first observation of laser-excited bulk conduction band (CB) electrons was reported by Long and coworkers [7]. Here 65 nsec laser pulses were used in a two-beam experiment. Subsequently, Rowe *et al.*, used 1–3 psec pulses to study electron dynamics in Si on a time scale much shorter than had ever been done previously [8]. As will be seen here, however, the most dramatic changes in the distribution function occur for times < 1 psec after the optical excitation.

We also report a new effect in two-photon photoemission with ultrashort laser pulses. Under appropriate conditions, we measure a *depletion* in the probe-induced two-photon photoemission from the valence band (VB), when the pump pulse precedes the probe. A simple model shows this effect to give a sensitive new monitor of electron dynamics, even in regions of low density of states.

The ultrafast pump-photoemission-probe experiments were done using a 2 eV photon energy pump beam followed by a 4 eV photoemitting probe. The measurements were carried out at room temperature on a Si(100) sample (1 Ω cm, B) held in UHV at a pressure 2×10^{-10} torr. A clean Si surface was obtained by removing the oxide cap in UHV at $\sim 1050\,^{\circ}$C [6]. Consistent with the expectation of little or no band bending for this sample [8], we observed no surface photovoltage shift [6]. The kinetic energy spectra of the photoemitted electrons, $N(E)$, were obtained by time-of-flight (TOF) analysis. Such spectra were collected for a variety of pump-probe delay times. The photoelectron kinetic energy E_{KE} is related to the initial CB or surface state energy, E_{CB}, in the Si by $E_{\mathrm{CB}}=E_{\mathrm{KE}}+\chi-h\nu_{\mathrm{probe}}-\Delta\phi_d$, where $\chi=E_{\mathrm{vac}}-E_{\mathrm{CBM}}$, and $\Delta\phi_d$ is the contact potential difference between the sample and the detector.

The pump (2 eV) and probe (4 eV) laser beams were derived from the amplified output of a colliding-pulse mode-locked dye laser operating at ~ 2 eV photon energy [6]. A thin (150 μm) beta barium borate doubling crystal was used to generate the 4 eV probe which was then relay imaged along with the pump to overlap on the sample. The cross correlation between the 2 eV pump and the 4 eV probe was measured to be 150 fsec at the position of the sample. In this report, the 2 eV photon energy pump beam was ~ 0.25 mJ/cm^2 in fluence, giving an excited conduction band electron density of $\sim 10^{19}$/cm^3. We estimate a small rise in surface lattice temperature of $\Delta T\sim 10$ K per pump/probe laser pulse. Note that a 4 eV probe beam is of insufficient photon energy to give one-photon photoemission from the valence band in Si.

The 2 eV pump will excite electrons from both valence

bands (heavy hole and light hole) through the indirect gap into the X valley of the conduction band (see Fig. 1, inset). Surface states can also be excited either directly by the pump or through relaxation from excited CB states. For Si(100), recent calculations [12] show surface dangling bond states to be present in the gap, with one state (π_1^*) extending from nearly the CB minimum (CBM) to about 0.4 eV above the VB maximum (VBM). The distribution of electrons excited by the 2 eV pump into the various states and its time evolution is monitored using the 150 fsec 4 eV probe. Here the excited electrons initially in CB or surface states are promoted by the 4 eV probe to above the vacuum level (Fig. 1) where their kinetic energy is measured ($\chi \sim 3.7$ eV for this surface). These transitions must be indirect for the CB electrons in the present experiment (≤ 0.5 eV above the CBM), since there are no final states accessible by direct 4 eV transitions. For surface states, this transition could be direct because of their different momentum properties. In both cases the final states must be those near the Γ point ~ 4 eV above the initial state. By this method, we observe the photoexcited electrons as they relax within the X valley by electron-electron and electron-phonon scattering, and as they relax into surface states on their way to recombination in the VB. We note the large penetration depth of the 2 eV pump in Si (~ 1 μm); diffusion of excited carriers out of the probed region (~ 100 Å) is expected to be slow ($> 10^{-9}$ sec) [8–10]. These issues have previously been discussed at length by Rowe *et al.* [8].

In our pump–photoemission-probe experiments, two distinct probe-laser intensity regimes were observed and used. Described above is the low probe intensity regime used by previous researchers [2,7–11]. It is characterized by a *linear increase* in probe-photoemission signal with increasing pump fluence. Here, spectra at pump-probe delays $-\tau$ are subtracted from spectra at delays $+\tau$ to reveal the increase in photoemission that results from pump laser population of conduction band states. The resulting spectra (Fig. 1) directly give the hot electron distribution functions in Si at various delay times after the excitation pump beam [13].

Alternatively, we discovered that hot electron relaxation can be probed in a new *high*-probe-intensity regime unique to ultrashort laser pulses (Fig. 2). In this pump-probe experiment, the probe intensity is increased to produce significant two-photon photoemission by *itself*. Now the initial states for the 4 eV probe are in the valence band, the CB or surface states act as intermediates, and (as before) the final states lie above the vacuum level. This is shown schematically in Fig. 2 (top panel). Importantly, transitions from the VB through resonant (or near-resonant) intermediate states will dominate and can occur in many places in the band structure, including to a large energy region (order 1 eV) near X encompassing the CBM [3]. Final states are again reached by indirect 4 eV transitions. At high enough probe intensities (> 100 MW/cm^2), our new finding is that a *depletion* occurs at certain energies in the probe-induced photoemission spectrum when the pump pulse precedes the probe. It can be shown [6] that at high enough probe intensities, two-photon photoemission from the VB will dominate over one-photon photoemission from the excited CB because (a) the VB electron density is $> 10^3$ times higher than that of the laser-pumped CB, *and* (b) the

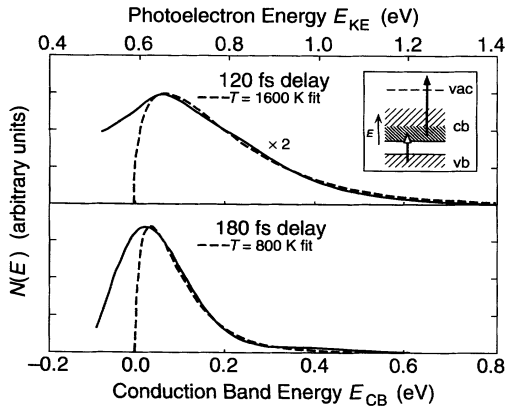

FIG. 1. Pump-probe photoelectron spectra (solid lines): low-probe-intensity regime. The data are fitted to thermal distributions (dashed lines). The CBM is at $E_{CB}=0$. The inset shows examples of pump (open arrow) and probe (solid arrow) transitions responsible for $N(E)$ spectra in the Si band structure.

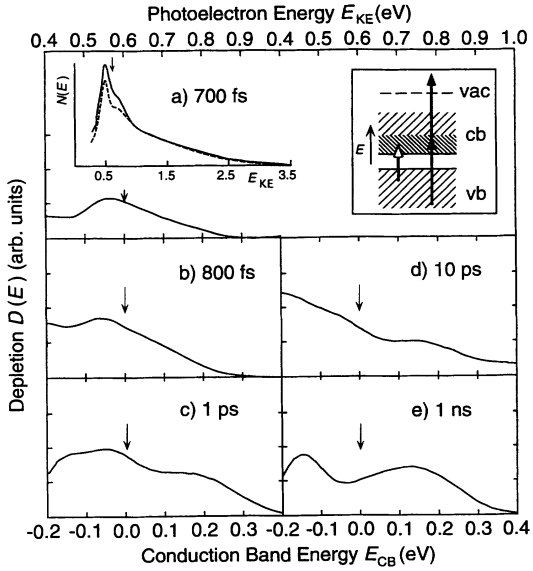

FIG. 2. Pump-probe photoelectron spectra: high probe intensity. Plotted are the depletion spectra, $D(E)$. The top right panel shows examples of transitions (pump, open arrow; probe, solid arrow) responsible for $D(E)$ spectra. The inset to (a) shows the probe-only (solid) and pump-probe photoemission (dashed) spectra for a delay time of 700 fsec. An arrow marks the CBM (at $E_{CB}=0$).

transition probability for two-photon photoemission increases faster (quadratically) with laser intensity than that for one-photon photoemission (linearly). Therefore, the predominant effect of CB population from the pump pulse is to "block" some of the (near-)resonant intermediate states used in the dominant two-photon photoemission from the VB. This gives a depletion, $D(E)$, at photoelectron energies corresponding to those blocked (occupied) states. Our finding that the magnitude of the depletion, $D(E)$ below, has a linear dependence on *pump* intensity follows from this model. We compute the depletion, $D(E)$, from the data: $D(E)=[I_{\text{probe}}(E)-I_{\text{pump+probe}}(E)]/I_{\text{probe}}(E)$, where $I_{\text{probe}}(E)$ is the probe-only photoemission at photoelectron energy E, and $I_{\text{pump+probe}}(E)$ is the pump-probe photoemission at E for some delay time. Under the condition $I_{\text{probe}}^{2\text{ photon}} \gg I_{\text{probe}}^{1\text{ photon}}$, it can be shown that $D(E)$ is proportional to the *fractional* occupation of CB or surface states (at E_{CB}) through which the two-photon transition passed [6]. As a result, an advantage to this scheme is that it has a higher sensitivity especially to near-CBM and surface state electrons [6]. Thus at longer delay times when most of the electrons have relaxed close to the CBM, we use this high-probe-intensity scheme to follow the dynamics.

The ultrafast time-resolved photoemission results are shown in Figs. 1 and 2. For assignment of the spectral features, we focus on the two-photon photoemission *probe-only* spectrum shown in Fig. 2(a) (inset). The transitions responsible are also shown (top panel, solid arrows). This highly reproducible spectrum is characterized by a peak at low energies followed by a distinct shoulder. When the clean surface is exposed to oxygen, *only* the first peak ($E_{\text{KE}}<0.55$ eV) is affected while the rest of the spectrum is unchanged both in shape and in absolute intensity. We assign this first peak to surface states on Si(100). The shoulder at $E_{\text{KE}}\sim 0.6$ eV is assigned to the CBM. This assignment is confirmed by the energy position of the features with respect to the position of the Fermi level as determined by a gold reference. With $\Delta\phi_d=0.3$ eV (cutoff of the TOF spectra), this assignment gives that the affinity level for this surface, χ, is ~ 3.7 eV, in agreement (to within 7%) with that reported previously [14]. This spectrum is very similar to that presented in Refs. [7–9] using longer laser pulses, and our assignment is identical. Note that this assignment applies to both Figs. 1 and 2 and gives their bottom energy axes, where $E_{\text{CB}}=0$ is the CBM.

In Fig. 1, we show photoemission spectra for pump-probe delay times of 120 and 180 fsec. As described above, these low-probe intensity data represent the hot CB electron distribution function in the X valley at these delay times. The distribution at 120 fsec is distinctly "hotter" than the one at 180 fsec. We find that each data set is well fitted by a thermal distribution. The 120 fsec data are well described by a Boltzmann distribution at 1600 ± 100 K, while the 180 fsec data are well fitted with an 800 ± 100 K Boltzmann distribution. For the fits, we took the density of CB states to go as $E^{1/2}$ and varied the temperature and normalization constant until the best fit was obtained. Here we have not attempted to fit electron energy distributions in the surface states (i.e., below the CBM) [15].

That the hot CB electron distributions are of thermal character at such short delay times is notable, since thermalization will not result from optical pumping without significant electron-electron scattering. If excited electrons in Si scattered only with *phonons* at very short delay times, a thermal distribution would not in general occur for such times. We were unable to distinguish a nonthermal component to the measured distributions even at a delay of only 120 fsec. Thus the electron-electron scattering time in this system for our experimental conditions must be <120 fsec; it must also not be significantly longer than that of electron-phonon.

The extremely fast electron cooling from 1600 to 800 K in <100 fsec is compatible with the electron-phonon scattering rates recently calculated in Si using a pseudopotentials approach [4(a)]. As a simple check, the relevant electron-phonon scattering rate from this calculation is 2–3 collisions with a phonon for each electron in 60 fsec. Combining this with an average phonon energy of ~ 40 meV gives an estimate of the energy loss to be ~ 1200 K in this 60 fsec time scale. This gives agreement with our experiment to within a factor of 2. We are presently in the process of rigorously extracting the energy-dependent scattering rates from our data through use of Monte Carlo modeling. Note that for metals, typical phonon energies are only a few meV making electron cooling rates ~ 10 times slower than for Si [2].

After 200 fsec, the relaxation is found to be much slower. This can be seen in the high-probe-intensity data of Fig. 2. Plotted are probe-only and pump-probe spectra in Fig. 2(a) (inset), and the "depletion" spectra, $D(E)$, in Figs. 2(a)–2(e) for various delays. A schematic of the transitions responsible is also shown (top panel). Again, $D(E)$ is proportional to the *fractional* occupation of CB or surface states at E_{CB}.

The photoemission spectrum at 700 fsec delay shows a broad distribution of excited electrons extending from gap surface states to above the CBM ($E_{\text{CB}}=0$). The gap states presumably correspond to the π_1^* dangling bond states of the Si(100) surface [12]. The CB electrons continue to relax in the X valley. In going from 0.7 to 1 psec [Figs. 2(a)–2(c)], there is an increase in electron occupation [$D(E)$] in the CBM region, $E_{\text{CB}}=0$. This indicates that the CB electrons had not yet equilibrated to the (bulk) lattice for these <1 psec delays. By 1 psec, the CB electrons have clearly reached equilibrium with the bulk lattice since beyond this delay relaxation *into* the CBM region is over. Beyond 1 psec, excited electrons are left only to recombine with holes in the VB.

Previous studies of surface recombination in both low and high excitation regimes have shown that the process is dominated by space charge layer (SCL) dynamics at

the surface [9,10,11(b)]. Our data support this finding. Furthermore, they provide the first direct *spectral* observation of CB electron accumulation at the surface due to SCL formation. The principal features of the data to be explained include (a) the development of a shoulder on the high energy side of the CBM by 1 psec, (b) its energy extent, and (c) the long persistence time of excited population [16].

As for Si(111) [9] and Ge(111) [11(b)], our data can be understood by taking into account transient surface charging induced by the intense laser excitation. Specifically, the data can be explained by a positive charging of the surface initially, as in [9] (see also [10]). This subsequently results in a high density of electrons accumulating at the surface with a corresponding depletion of holes (i.e., a SCL). For Si(100), the initial positive charging can result from a high scattering rate of bulk holes into the same surface states that pin the Fermi level just above the VBM [14].

Modeling shows that this electron accumulation can give rise to an electron density *at* the surface (within 10–20 Å) exceeding that in the rest of the excitation volume by a factor > 10 [6,9,10]. Since the penetration depth of the 4 eV probe is ~ 100 Å, this enhancement should give a prominent feature in the spectrum. Band filling for the average CB electron density of $10^{19}/\text{cm}^3$ is only ~ 0.04 eV. For a density 30 times greater, it is 0.3 eV. Therefore, a 30× electron enhancement *at* the surface should appear in the $D(E)$ spectra as a prominent shoulder on the CBM feature out to ~ 0.3 eV. This is what we observe for ≥ 1 psec. The CBM feature itself will have a higher $D(E)$ [Figs. 2(c) and 2(d)] since this state is filled in the rest of the excitation volume (to 0.04 eV), as well as at the surface. The gradual 1 psec formation time of this shoulder [Figs. 2(a)–2(c)] probably reflects the finite drift time of electrons to the surface. At 10 psec, the band filling has increased some more [cf. Fig. 2(d)], evidently due to additional electron drift. This could also account for the increased near-CBM gap surface state occupation. The decrease at 1 nsec in the band filling at the surface, as well as in the electron occupation in both the bulk CBM and gap surface states is consistent with some recombination having occurred by this delay time. Contributing to the long persistence time (> 1 nsec) in these states is the charge separation and high density in the SCL, which inhibit recombination [6,9,10]. Additional measurements are required for a complete quantitative picture. More detailed discussion of our model including deduced surface state scattering rates is presented elsewhere [6].

In conclusion, time-resolved photoelectron spectroscopy has been used to determine for the first time the subpicosecond (150 fsec) evolution of an optically excited hot electron distribution in *silicon*. We have observed an electron-electron thermalization time of < 120 fsec, an extremely fast *initial* electron cooling rate, followed by an electron-phonon thermalization time of ~ 1 psec, and overall a strong energy dependence to the electron scattering rate. At longer delays, the spectra give direct evidence for transient CB electron accumulation at the surface. We are presently combining our experimental results with Monte Carlo simulations to quantitatively extract the energy-dependent scattering rates. Correct scattering rates are essential for understanding the physics and predicting the properties of next-generation Si devices.

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[16] Different results are obtained upon either oxidation of the surface or use of a more highly doped Si sample [6].