Ultrafast carrier dynamics on the Si(100)2×1 surface

Seongtae Jeong
Department of Physics, University of California, Berkeley, Berkeley, California 94720

Helmut Zacharias
Fachbereich Physik, Universität Essen, 45117 Essen, Germany

Jeffrey Bokor
Department of EECS, University of California, Berkeley, Berkeley, California 94720

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We present a study of ultrafast carrier dynamics on the clean Si(100)2×1 surface using time-resolved photoemission spectroscopy. A rapid thermalization inside the surface band is observed, and the carrier relaxation occurs on a time scale of a few hundred femtoseconds to a few picoseconds depending on the initial state energy. The relaxation time increases as the initial state energy decreases with respect to the band minimum. [S0163-1829(96)50248-1]

Understanding ultrafast phenomena in solids is very important for basic science and its contribution to technological innovations in devices and surface chemistry.[1,2] For example, as the size of silicon transistors decreases into the deep submicrometer range, device simulation becomes more complicated because the conventional drift-diffusion model starts to fail. Deeper understanding of electron dynamics is needed to properly estimate device performance and reliability.[3] Hot-electron induced desorption from solid surfaces is another aspect with potential technological impact.[2] Desorption due to the presence of the hot carriers was experimentally demonstrated on metals by several groups[2,4] and theoretical research is still being pursued.[5] Trappe *et al.* showed that hot-electron induced desorption is also possible on semiconductor surfaces[6] and Tien *et al.*[7] presented experimental evidence that hot-electron induced desorption plays an important role in stiction reduction of microelectromechanical systems after ultrashort pulsed laser illumination.

Hot carrier dynamics in silicon is relatively difficult to study using ultrashort pulsed lasers due to the indirect optical band gap. Time-resolved multiphoton photoemission spectroscopy has proven to be particularly effective in overcoming this difficulty. Experiments that measured photoelectric current as a function of laser intensity reported electronic temperatures well above the lattice temperature for nanosecond pulse excitation.[8] The study on Si(111)2×1 surface performed by Halas *et al.*[9] showed the dynamic surface charging plays an important role in carrier dynamics near the surface. A comprehensive study on various silicon surfaces by Rowe *et al.*[10] showed that electron energy relaxation inside the surface band occurs on a time scale shorter than 3 psec. Goldman *et al.* reported that the electron temperature inside the conduction band changes from 1500 to 800 K in less than 60 fsec after excitation.[11]

In this paper, we report on carrier dynamics on the Si(100)2×1 surface[12] after ultrafast laser excitation using time-resolved two-photon photoemission spectroscopy with subpicosecond time resolution. A Ti-sapphire oscillator-regenerative amplifier laser system is used to obtain 0.5 mJ, 800 nm, and 150 fsec pulses at a repetition rate of 1 kHz. An ultraviolet probe beam at 266 nm is produced by frequency tripling using two beta barium borate (BBO) crystals in tandem. The probe pulsewidth is 400 fsec due to the group velocity dispersion between the pump (800 nm) and the second harmonic (400 nm). The polarization of the probe is fixed as p polarization while that of pump can be changed by using half a wave plate. No difference in photoelectron spectra was observed for different pump polarizations.

The vacuum chamber, equipped with low energy electron diffraction (LEED), is kept at a base pressure of 5×10^{-11} Torr. The sample is a p-doped silicon (100) wafer with a doping concentration of 1×10^{15} cm^{-3}. Samples are cleaned before introduction into the chamber by dipping into a buffered HF solution. Further cleaning of the sample, inside the chamber, is performed by heating to 1050 °C for 2 min. After slowly cooling the sample to room temperature, a very sharp 2×1 LEED pattern is observed. The energy of the photoemitted electrons is measured using the time-of-flight technique.

Figure 1 shows a photoemitted electron spectrum, using the probe only, from a clean Si(100)2×1 surface. The total number of collected electrons is kept below 0.8 electrons per laser shot throughout this experiment to avoid space charge broadening of the spectra. The photoelectron spectrum taken with the probe only has a sharp peak on the lower energy side; the high energy side has a sharp cutoff at 4.8 eV with an abrupt shoulder around 3.8 eV. These spectral features are similar to what have been reported by other researchers with the same photon energy.[10,13] The electrons with kinetic energy greater than 0.8 eV originate from the valence band via two photon photoemission, while lower energy electrons are believed to come from the occupied surface states via one photon photoemission. These features are shown in the inset of Fig. 1 in which probe-only spectra with different intensities are normalized by the square of the probe intensity. The six spectra overlap above 0.8 eV confirming the two photon photoemission behavior. From the above interpretation, the electrons at the high energy cutoff

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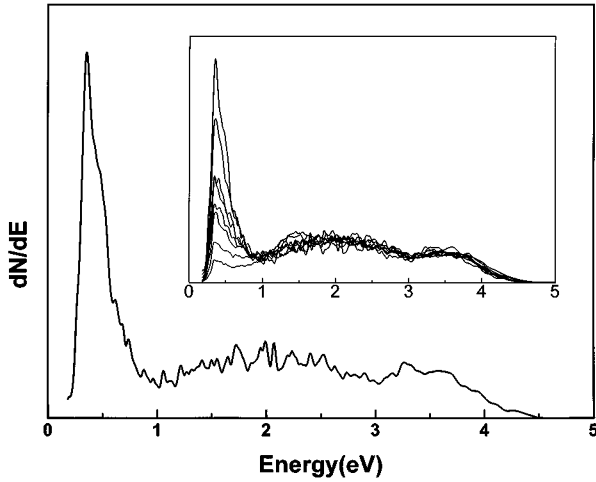

FIG. 1. Photoelectron spectrum from third-harmonic beam (4.66 eV). Inset: photoelectron spectra normalized by the square of the third harmonic intensity.

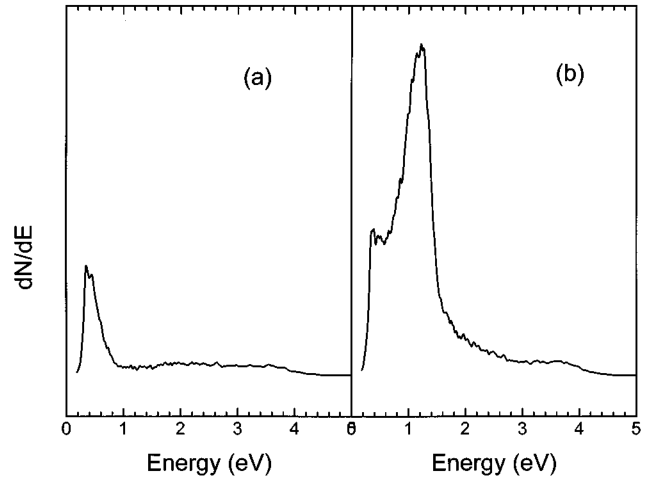

FIG. 2. Pump and probe photoemission spectra at two different time delays: (a) $T=-1.6$ psec, (b) $T=0$ psec.

come from the valence-band maximum (VBM). This can be used to identify the initial states from which photoelectrons originate.

To relate the kinetic energy in vacuum to the energy of the initial states inside the sample, the contact potential and the electron affinity must be known. The kinetic energy of a photoemitted electron is given by the following relation:

$$E_k = n\hbar\omega - (\chi - E) + \phi_d = n\hbar\omega + E - (\chi - \phi_d), \quad (1)$$

where $\hbar\omega$ is the photon energy, n is the number of photons absorbed for photoemission, E is the energy inside the sample measured from the conduction-band minimum (CBM), χ is the electron affinity, and ϕ_d is the contact potential. Measuring the kinetic energy of electrons from the VBM allows the determination of the quantity $\chi - \phi_d$. From relation (1) we find $\chi - \phi_d$ to be 3.4 eV, which is in good agreement with the value calculated in the same way from photoelectron spectra we obtained using the fourth harmonic beam for one photon photoemission from the valence band. Usually, determining initial state energy from a laser-excited photoelectron spectrum is complicated in semiconductors due to the band bending and resultant photovoltaic shift. In this experiment, no photovoltaic shift in photoelectron spectra is observed, in agreement with other studies.[10,11] Therefore, the contribution of photovoltaic shift to the kinetic energy of photoemitted electrons can be ignored in this experiment.

The pump pulse also generates photoemitted electrons. With increasing pump fluence, the number of photoelectrons increases rapidly. The space charge effect thus sets an upper limit to the pump fluence we can use. The maximum pump fluence level in this experiment set by this consideration is found to be 1 mJ/cm^2. The carrier density produced for 1 mJ/cm^2 fluence at 800 nm is estimated to be 2.7×10^{18} cm^{-3}. When the pump beam is incident on the sample with an average power of 200 mW, a rise in sample temperature was observed through the thermocouple attached onto the sample holder plate. The increase was about 10 °C. The peak temperature rise in the excitation region was estimated to be less than 100 °C.[7]

Figure 2 shows pump and probe spectra taken at two different time delays. Figures 2(a) and 2(b) show the spectra taken at $T=-1.6$ and 0 psec, respectively. Negative time delay means the probe precedes the pump. The spectrum at $T=-1.6$ psec is the same as the sum of the pump-only spectrum and the probe-only spectrum, as expected, and can be considered as background. The spectrum taken at $T=0$ psec [see Fig. 2(b)] shows a double peak. The peak around 0.3 eV is present at all time delays with small change in strength and the peak around 1.2 eV shows significant change in strength as a function of time delay between the pump and probe.

Figure 3 shows photoelectron spectra taken at different time delays between the pump and probe with the spectrum at $T=-1.6$ psec [shown in Fig. 2(a)] subtracted from each spectrum. The electrons from the CBM appear with a kinetic energy of 1.2 eV from relation

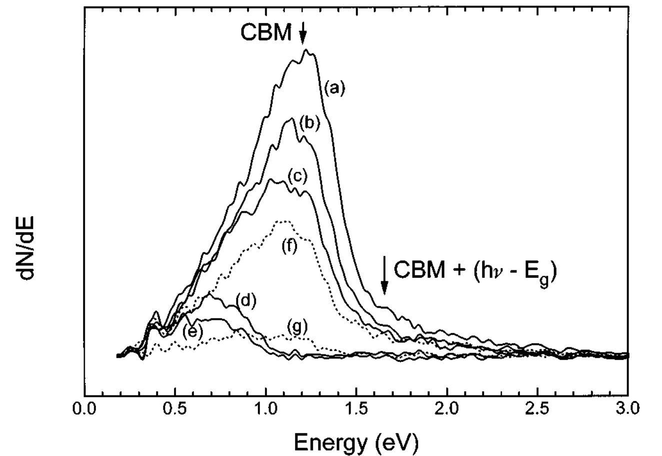

FIG. 3. Time-resolved spectra at different time delays: (a) $T=0$ psec, (b) $T=0.13$ psec, (c) $T=0.33$ psec, (d) $T=1.07$ psec, (e) $T=2.4$ psec, (f) $T=-0.27$ psec (dashed line), (g) $T=-0.47$ psec (dashed line).

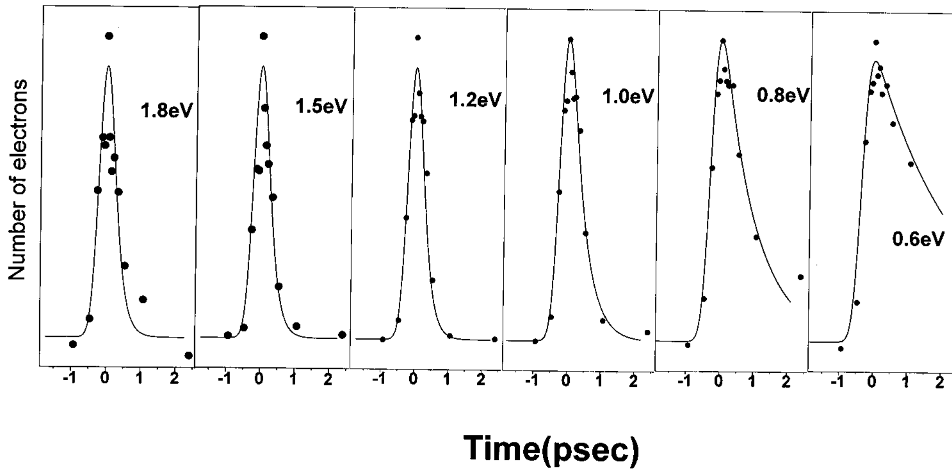

FIG. 4. Transient peak strength as a function of time delay between pump and probe. Different spectra correspond to different energy positions.

(1), with $\chi-\phi_d=3.4$ eV. The transient peak in Fig. 3 appears above and below the conduction-band minimum (CBM). Electrons with kinetic energy less than 1.2 eV cannot come from the conduction band but instead must come from the surface states of the Si(100)2×1 surface. The dynamics of the transient peak and the positions of the double peak in Fig. 2 are what would be expected from the surface band structure of the Si(100)2×1 surface.[13–17] We believe that the transient peak is attributable to surface states. There are two reasons why we believe this is the case. First, the strength of the peak was sensitive to the contamination from the residual gas inside the chamber, becoming weaker after about one day. Furthermore, if the sample is reheated up to 1050 °C for 2 min, the peak becomes strong again. The second reason is that there is no direct transition from the bulk X valley to states above the vacuum level in this range. Photoemission from the X valley would require indirect transitions. On the other hand, emission from surface states does not have to satisfy momentum conservation along the sample normal and this transition has a higher probability than the indirect transition from the X valley, as was argued in Ref. 10.

Figure 3 shows several noticeable features. First, in the spectrum at $T=0$, the kinetic energy of electrons extends up to 3 eV. When electron-hole pairs are generated from 800 nm illumination, the maximum electron excess kinetic energy above the conduction-band minimum would be only 450 meV, as indicated in Fig. 3. The reason why electrons are observed with excess kinetic energy of up to 1.8 eV above the conduction-band edge can be explained by rapid thermalization among the carriers. Due to carrier-carrier scattering, kinetic energy is redistributed among the carriers. Figure 3 shows that the carrier-carrier scattering takes place faster than the temporal resolution of this experiment. The spectral shape of the transient peak cannot be fitted with a simple Maxwell-Boltzmann distribution because what is observed is the product of the carrier distribution function and the surface density of states. Second, with an increase in the time delay between the pump and probe, the carrier distribution moves toward lower energy, indicating carrier cooling. The cooling time is comparable to the pulsewidth for electrons above the conduction-band minimum. At time delays longer than 1 psec, the number of electrons above the conduction-band minimum drops below the noise level.

Relaxation features are more visible when the number of electrons in the transient peak is plotted as a function of the delay between the pump and the probe. Figure 4 shows data for electrons with kinetic energies of 1.8, 1.5, 1.2, 1.0, 0.8, and 0.6 eV, respectively. The solid line fit to the experimental data was obtained by solving a simple generation-relaxation equation, assuming a Gaussian temporal pulse shape and a constant relaxation time. The rising edge is primarily determined by the pulsewidths of the laser beams and the risetime is around 0.22 psec. The relaxation time for each curve is taken as 0.2, 0.2, 0.2, 0.4, 1.0, and 2.5 psec, respectively. It is clear that the relaxation time becomes shorter as the initial state energy changes from inside the bulk band gap to above the bulk conduction-band minimum. It is interesting to note that this kind of fast electron relaxation dynamics has been observed for a variety of metal systems.[18–20] One word of caution is that relaxation times given above should not be taken literally as single particle lifetimes at given energies because the population dynamics at a certain energy level might involve population feeding from the higher-lying states[19] and density-dependent carrier-carrier scattering as well as population decay and photoexcitation. These effects can only be dealt with by solving the Boltzmann transport equation beyond the simple relaxation time approximation. The simple energy-dependent relaxation time approximation serves the need for our qualitative discussion.

Particularly noteworthy is the absence of the coupling between the bulk and surface states. If there is strong population feeding between the surface states and bulk states, the surface states whose energy is below the conduction-band minimum would show very slow decay dynamics because the carrier recombination time in silicon is known to be considerably longer than the time scale of our study. But here we see fast relaxation decay below the conduction band, as has been observed in Ref. 10 for silicon. This can be interpreted as the absence or negligible contribution of carrier feeding from the bulk states. Therefore, the transient signal is dominated by photoexcitation into the surface states followed by relaxation inside the surface states.

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