Oscillatory relaxation of surface photovoltage on a silicon surface

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Time-resolved measurement of photoemission spectroscopy was made to trace a change of surface potential after the surface photovoltage effect on a Si(111) 7×7 surface. Two relaxation processes were found with decay times of nanoseconds and hundreds of nanoseconds, which are explained in terms of the tunneling and the thermionic relaxation schemes, respectively. At the high laser power density, the relaxation has become oscillatory with a temporal period of several tens of nanoseconds.

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I. INTRODUCTION

Photoinduced phenomena in semiconductors have been one of the central focuses in condensed-matter physics. Nowadays, they provide an attractive playground for investigating the nonequilibrium dynamics of electronic states. The related optical technology has seen widespread use; continued studies of surfaces have become significant in revealing photovoltaic and photocatalytic mechanisms that have directly led to tackling the issues of global energy. The temporal evolution of these mechanisms has been empirically probed by time-resolved measurements using various methods such as photoluminescence, reflection, and photoelectron spectroscopies.[1,2] Photoemission measurements have an advantage in being able to trace electronic states (valence bands or molecular orbitals) and chemical shifts (core-level states) directly in real time. There have been a number of time-resolved photoemission experiments[1–10] on the surface photovoltage effect on semiconductor surfaces, the fundamental process in photovoltaics and photocatalysis. In the photovoltage effect, an electron-hole pair, generated by photoexcitation, is split and the two types of carriers are spatially separated. The electron-hole separation is induced by their opposite drift forces near the surface, creating a voltage difference between the surface and the bulk (the surface photovoltage (SPV) effect), and by the difference in their diffusion velocities from the surface (the photo-Dember effect). Relaxation of the effect proceeds through electron-hole recombination at the surface.

In the present research, we performed high-resolution time-resolved photoemission spectroscopy to study the relaxation of the surface photovoltage on the Si(111) 7×7 surface. We discovered that when the power density of the pumping laser is greater than 1000 μJ cm^{-2} pulse^{-1}, the relaxation exhibits damped oscillations with temporal periods of several tens of nanoseconds at delay times faster than 100 ns. Observation of the oscillation likely indicates the existence of the nonlinear effect during the surface recombination process that potentially leads to a new technique of ultrafast optical control of photovoltage at a surface.

II. EXPERIMENT

The photoemission experiment was performed at room temperature at beam line BL07LSU in the synchrotron radiation (SR) facility SPring-8.[11] The time-resolved data were obtained using the one-pump (laser) and multiprobe (SR) methods during several bunch-mode (D-mode) operations of the storage ring. The laser and SR pulse durations were about 35 fs and 50 ps, respectively. The pumping laser was set to provide a photon energy ($h\nu$) of $h\nu = 1.51$ eV with a repetition rate of 1 kHz. A clean Si(111) 7×7 surface was prepared on a heavily doped n-type ($\rho = 0.02\ \Omega$ cm) Si(111) wafer by a cycle of *in situ* resistive heating treatments. Low-energy-electron-diffraction was used to verify crystal surface orientation.

III. RESULTS AND DISCUSSION

At semiconductor surfaces, charges redistribute to compensate for the difference in charge density between the surface and internal bulk. As a consequence, the energy positions of the bulk bands vary with depth from the surface.[12] For a clean Si(111) 7×7 surface on an n-type Si wafer, the Fermi level is positioned in the middle of the bulk band gap,[13] whereas in the crystal bulk it is close to the minimum of the bulk conduction band. Thus, the bulk bands have lower binding energy as these approach the surface (called surface band bending), which assists in forming the so-called depletion-type space charge layer.[12,13] When light irradiates the surface, electrons generated in the bulk conduction band electrically drift away from the surface; holes produced in the bulk valence band drift toward the surface.[14] The accumulation of holes at the surface reduces the original charge distribution, and band bending of the bulk bands vanishes. The nonequilibrium carrier distribution breaks down the charge-neutrality condition, generating a surface photovoltage. As a consequence, the energies associated with the bulk band and core-level states of the Si crystal, the energy difference of which is quantum-mechanically fixed, are shifted accordingly.[8] For a depletion-type space charge layer beneath a Si(111) 7×7 surface on an n-type Si wafer, the SPV shift should be towards higher binding energy, as observed in Fig. 1(a).

Figure 1(b) plots the energy variation in the Si $2p$ core-level spectra for a delay time of 1 ns after laser irradiation, taken with various power densities of the pump laser. The energy shift initially increases linearly with logarithmic scale of the power densities but deviates above $\sim$10 μJ cm^{-2} pulse^{-1}. Above $\sim$100 μJ cm^{-2} pulse^{-1}, the power dependence is saturated. Dependence of the surface photovoltage with laser power density is similar to those reported for other semiconductor

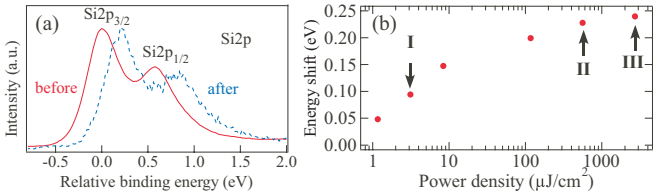

FIG. 1. (Color online) (a) Si $2p$ core-level spectra ($h\nu = 253$ eV) before and after the laser irradiation, shown as solid (red) and dashed (blue) lines, respectively. The power density of the pump laser ($h\nu = 1.51$ eV) was 2700 μJ cm^{-2} pulse^{-1}. (b) Energy shift of the Si $2p$ spectra, measured at different power densities. The delay time between the pump laser and probe synchrotron pulses was set at 1 ns.

surfaces.[3,8,9] The saturation of 0.25 eV is smaller than the surface potential of 0.37 eV (Ref. 15) for Si(111) 7×7 on the present n-type Si wafer. This implies that the bending of the Si bulk band has not yet reached the flat-band condition despite the irradiation by a high-power laser. Since the amount of the bulk band bending is determined in the equilibrium state,[16] the extremely nonequilibrium state, generated by the high-power laser, has likely put the system in a new state which is beyond the perturbation regime of the ground state.

Figure 2 shows time-resolved Si $2p_{3/2}$ core-level spectra after laser irradiation at delay times from 0 to 70 ns. The relative binding energy was measured with reference to the energy position before the pumping. The spectral evolution, taken at laser power densities of 3.1 [Fig. 2(a)] and 560 [Fig. 2(b)] μJ cm^{-2} pulse^{-1}, shows a rise in the binding energy by the surface photovoltage effect, followed by the relaxation of monotonic decay with time. The variation at 2,700 μJ cm^{-2} pulse^{-1} additionally exhibits a temporal oscillation [Fig. 2(c)] containing several frequencies that are higher for shorter delay times. To obtain the time parameters, a part of the data can be parameter fitted [the solid curve in Fig. 2(c)] with the following damped oscillation solution:

$$f(t) = y_0 + (C_1 \cos(\omega t) + C_2 \sin(\omega t))e^{-t/\tau}, \qquad (1)$$

where y_0 is the offset and the C_i are amplitudes of the sinusoidal functions. The frequency (period) of the fitted oscillation is $\omega = 11$ MHz (91 ns); the oscillations at short delay times are likely to have a similar frequency of several tens of MHz (several tens of nanoseconds). One remark is that the frequency (ω) is much lower than either the plasma frequency or those of quasiparticles such as phonons,[17] ruling out their possibility to cause the oscillation.

Temporal variations of the binding energy in the longer time scale are shown in Fig. 3 at different laser power densities. Complete relaxation of the surface photovoltage effect takes about 1000 ns. The relaxation has been theoretically understood as the radiative or nonradiative surface recombination of carriers that are transferred from the bulk to the surface through or over the surface potential barrier.[9,17] The former is the tunneling transport model and it has been widely adopted in semiconductor devices.[17–19] The latter model corresponds to the thermionic emission process.[9,17]

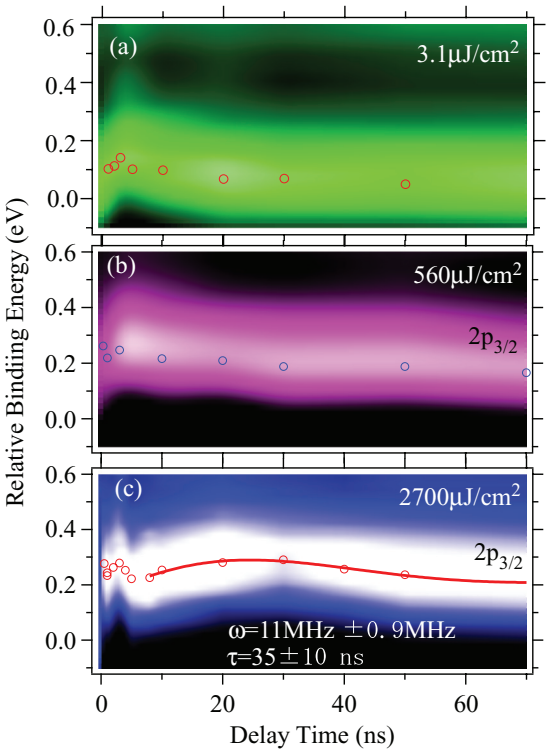

FIG. 2. (Color online) Time evolution of the Si $2p$ spectra, taken at different laser power densities per pulse: (a) 3.1, (b) 560, and (c) 2700 μJ cm^{-2} pulse^{-1}, corresponding to stages I, II, and III, respectively, in Fig. 1(b). The vertical axis represents relative binding energy with respect to the Si $2p_{3/2}$ peak position before the photoexcitation. The open circles correspond to data points. The background is a grayscale photoemission diagram whose points in the region between data points are linearly interpolated. The solid line in (c) is the result of fitting to Eq. (1).

A. Tunneling process

Relaxation of the surface photovoltage effect can be achieved by electron-hole recombination associated with the quantum-mechanical tunneling process of electrons and holes that are spatially separated from each other.[17–19] When free carriers in the bulk tunnel through the surface potential barrier, V_S^*, to meet their counterparts trapped at the surface, the decay (recombination) rate is governed by overlaps of their wave functions and it is given as

$$\frac{dn(z,t)}{dt} = -\frac{n(z,t)}{\tau_{\text{tunnel}}} \exp\left(-\frac{2z}{a_e}\right), \qquad (2)$$

where z is the distance of tunneling. The electron concentration is given as n, while the Bohr radius of a trapped electron is written as a_e. Then, one can obtain

$$n(z,t) = n_0(z) \exp\left\{\frac{-t}{\tau_{\text{tunnel}}} \exp\left(-\frac{2z}{a_e}\right)\right\}, \qquad (3)$$

where n_0 is the initial carrier density. Through the integration of the Poisson equation, $\Delta\phi(z,t) = \Delta V(z,t)/e = -en(z,t)/\epsilon\epsilon_0$, one obtains (where ϕ is the electronic potential) with the help of the sharp-front approximation for the carrier

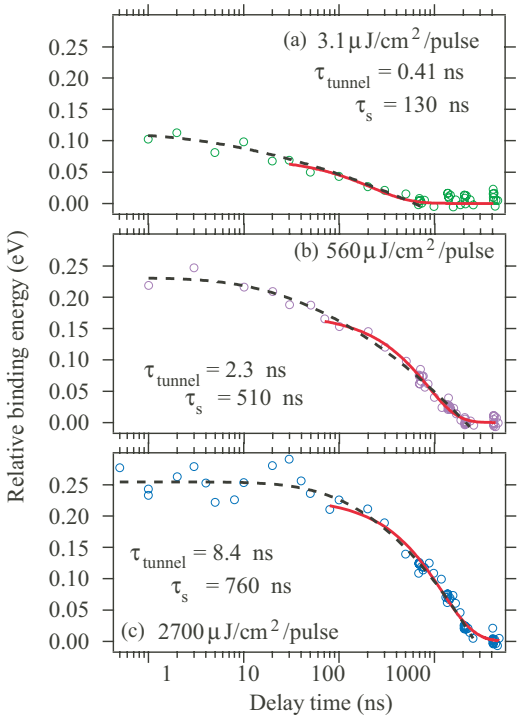

FIG. 3. (Color online) Energy shift of the Si $2p_{3/2}$ core-level peak of a Si(111) 7×7 surface with various delay times after laser irradiation. The power densities of the pumping laser are (a) 3.1, (b) 560, and (c) 2700 μJ cm^{-2} pulse^{-1}, which are indicated in Fig. 1 as I, II, and III, respectively. The experimental data, marked with circles, are parameter fitted with the functions, $V_{\text{tunnel}}(t)$ in Eq. (4) (black dashed lines) and $V_{\text{thermal}}(t)$ in Eq. (14) (red solid lines); τ_{tunnel} and τ_s are the fitted parameters of the time constants of the tunneling and thermionic relaxation models, respectively.

density

$$V_{SPV}(t) = V_{\text{tunnel}}(t) = \frac{e^2}{2\epsilon\epsilon_0} n_0 d^2 \left(1 - \left(\frac{a_e}{2d}\right)^2 \ln^2\left(1 + \frac{t}{\tau_{\text{tunnel}}}\right)\right), \quad (4)$$

where e is the elementary charge and ϵ_0 and ϵ are the dielectric permittivity for a vacuum and the relative permittivity, respectively. Here, the incident carrier density is taken as a constant bulk value, $n_0(z) = n_0$. The depth, d, is the width of the surface potential barrier, V_S^*, or the mean width of the space charge layer.

B. Thermionic process

The thermionic process is one of the relaxation mechanisms established for the surface photovoltage effect.[9] It proceeds by a recombination between a carrier (a hole, for example), trapped at the surface, and the counterpart (an electron), transferred from the bulk over the thermal activation barrier of the surface potential. A decay rate of the trapped holes (the thermionic emission rate) through the thermionic process is proportional to its density, p_{tr}:

$$\frac{dp_{tr}(t)}{dt} = -\sigma_{te} v_{th} n_t \; p_{tr}(t) \quad (5)$$

$$= -\frac{p_{tr}(t)}{\tau_{th}}, \quad (6)$$

where σ_{te} is the thermal cross section of capturing an electron and v_{th} is the thermal velocity of a carrier. In the equation, n_t is the density of the electrons and it is expressed as $n_t = N_c \exp(-V_S^*/kT)$, where N_c is the density of states of the conduction bulk band and V_S^* is the surface potential during the relaxation. By definition,[9,17] the thermal relaxation time τ_{th} is expressed as

$$\frac{1}{\tau_{th}} = \sigma_{te} v_{th} N_c \exp\left(-\frac{V_S^*}{kT}\right), \quad (7)$$

and a solution of Eq. (6) is

$$p_{tr}(t) = p_0 \; \exp\left(-\frac{t}{\tau_{th}}\right). \quad (8)$$

If one defines V_S as the surface potential before the laser irradiation and V_{SPV} as its potential variation by the surface photovoltage effect, V_S^* is equal to $V_S - V_{SPV}$ and Eq. (7) can be written as

$$\frac{1}{\tau_{th}} = \sigma_{te} v_{th} N_c \exp\left(-\frac{V_S - V_{SPV}}{\eta kT}\right) \quad (9)$$

$$= \frac{1}{\tau_s} \exp\left(\frac{V_{SPV}}{\eta kT}\right), \quad (10)$$

where the η should be understood as an ideality factor, as known from diode theory,[9] and τ_s is defined as

$$\tau_s = \frac{1}{\sigma_{te} v_{th} N_c} e^{V_S/\eta kT}. \quad (11)$$

A change of surface potential by the surface photovoltage effect, V_{SPV}, can be given in terms of the fractional charge density,[9,17] $\Delta_n = \Delta n/n_0$, where n_0 is the initial electron density:

$$V_{SPV} = \eta kT \ln(1 + \Delta_n). \quad (12)$$

The decay equation for V_{SPV} can, thus, be obtained from Eq. (12) as

$$\frac{dV_{SPV}}{dt} = -\frac{\eta kT}{\tau_s}\left(e^{\frac{V_{SPV}}{\eta kT}} - 1\right). \quad (13)$$

Solving the equation, one can derive $V_{SPV}(t)$ as

$$V_{SPV}(t) = V_{\text{thermal}}(t) = \eta kT \ln\left(1 - (1 - e^{V_{SPV}(0)/\eta kT}) e^{-t/\tau_s}\right). \quad (14)$$

By fitting the time dependence of the experimental energy shift with Eq. (14), one is able to obtain the relaxation time τ_s. As defined in Eq. (11), τ_s corresponds to the (dark) carrier lifetime before the laser irradiation ($V_{SPV} = 0$) if σ_{te}, v_{th}, and V_S remain constant after the surface photovoltage effect and the following relaxation.

C. Fundamental picture of relaxation after the surface photovoltage effect

Making curve fits of the experimental energy shifts with these functions, Eqs. (4) and (14), it was found that data could not be fitted with one of the functions but were well fitted with their combination: $V_{\text{tunnel}}(t)$ at the delay time faster than $\sim$100 ns and with $V_{\text{thermal}}(t)$ at the slower delay time. The time constants, τ_{tunnel} and τ_s, are given in Fig. 3, showing longer times for the larger power density. The variation of τ_s

indicates that the thermal cross section of the electron capture (σ_{te}), the thermal carrier velocity (v_{th}), or the offset of the surface photovoltage shift ($V_{SPV}(0)$) has changed because of the high-power laser irradiation. The modification of $V_{SPV}(0)$, which is sensitive to the surface charge carrier density, is consistent with the saturation of the surface photovoltage effect at stage III in Fig. 1(b).

Our experimental data clearly show that, under high laser power density, the excited carriers of the Si(111) 7×7 surface layer have longer decay times; however, what is unexpected is the observation of periodic behavior in a series of the time-resolved spectra [Fig. 2(c)]. Typically, surface photovoltage decays continuously with a simple recombination of an electron and a hole, transferred from the bulk.[1–10] The observed oscillatory relaxation most likely indicates the existence of the nonlinear effect associated with nonequilibrium carriers, densely populated at the surface, excited by the high-intensity laser. The surface photovoltage effect in the Si(111) 7×7 surface was previously investigated using a scanning tunneling microscope.[3] There, electron-hole recombination was found to proceed promptly at atomic defects on the surface. Since the oscillatory relaxation in the delay-time region is observed to be faster than 100 ns, the origin is possibly related to the recombination of carriers, transferred by the tunneling process, at such defects on the Si(111) 7×7 surface.

IV. CONCLUSION

In summary, we have carried out time-resolved photoemission measurement on a Si(111) 7×7 surface to trace the relaxation of the surface photovoltage effect at delay times from picoseconds to microseconds. Following the rise of the surface photovoltage effect, two relaxation processes were found with decay times of nanoseconds and hundreds of nanoseconds, which are explained in terms of the tunneling and the thermionic relaxation schemes, respectively. At high laser power density, the relaxation becomes oscillatory with a temporal period of several tens of nanoseconds. An appropriate theoretical model of the carrier kinetics is necessary for the proper understanding of these intriguing phenomena.

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