Observation of oscillatory relaxation of surface photovoltage effect by time-resolved soft X-ray photoemission spectroscopy with synchrotron radiation

Photoinduced phenomena in semiconductors have attracted technological interest in the development of optoelectronic devices, such as solar cells, that have directly led to solutions to problems in global energy issues. In photovoltaic and photocatalytic elements, the most fundamental event is the generation of photovoltage (PV). In the PV effect, an electron-hole pair, created 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 bulk (the surface photovoltage 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. An overall simple picture of the PV effect has been widely accepted, however, the details of the mechanism have remained uncertain. It is of note that, in semiconducting materials, the carriers have been known to respond nonlinearly even under a moderate external field. Such non-equilibrium behaviors have attracted interest in the field of fundamental physics, and their possible applications in optoelectronic technology have also recently been investigated.

The temporal evolution of dynamical phenomena has been empirically probed by time-resolved experiments by various methods, among which the measurement by photoemission spectroscopy has an advantage in being able to trace electronic states (valence bands or molecular orbitals) and chemical shifts (core-level states) directly in *real time*. At the soft X-ray beamline **BL07LSU**, we developed a photoemission spectroscopy system with a time-of-flight spectrometer and with femtosecond-pulse lasers for time-resolved measurements [1]. Pulses of SR and lasers are stably synchronized with jitter time of better than 10 ps and their time delay is limited by time resolution of the SR pulse width (50 ps). With the present system, we performed detailed time-resolved photoemission spectroscopy to elucidate the relaxation mechanism after the PV effect.

Figure 1(a) shows Si 2*p* photoemission spectra of the Si(111)7×7 surface, one of the most famous Si clean crystal surfaces, on an *n*-type Si wafer [2]. Upon laser irradiation, the core-level shift directly corresponds to the variation in the Si bulk band and, thus, to the generation of photovoltage at the surface [3] (Fig. 2). Figure 1(b) shows a plot of the energy variation in the Si 2*p* 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 density (stage I) but deviates from linearity above ~10 μJ/cm^2/pulse. Above ~100 μJ/cm^2/pulse (stages II, III), the power dependence saturates. In the conventional surface PV picture, photovoltage increases with photon density, as shown in stage I, and the behavior in stages II, III is extraordinary.

Figure 3 shows time-resolved Si $2p_{3/2}$ core-level spectra after laser irradiation at delay times from 0 to 70 ns [3]. The relative binding energy was measured

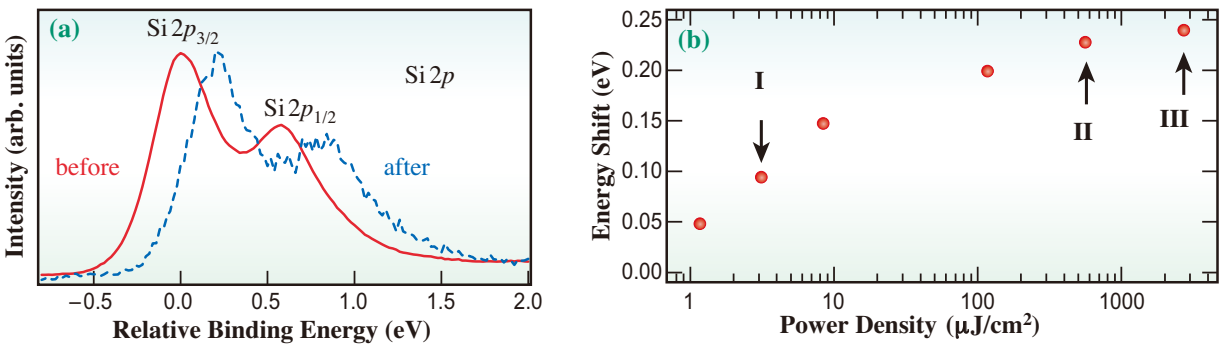

Fig. 1. **(a)** Si 2*p* core-level spectra (hν = 253 eV) before and after the laser irradiation are shown as solid (red) and dashed (blue) lines, respectively. The power density of the pump laser (hν = 1.51 eV) was 2700 μJ/cm^2/pulse. **(b)** Energy shift of Si 2*p* spectra, measured at different power densities or photon densities. The delay time between the pump laser and probe synchrotron pulses was set at 1 ns.

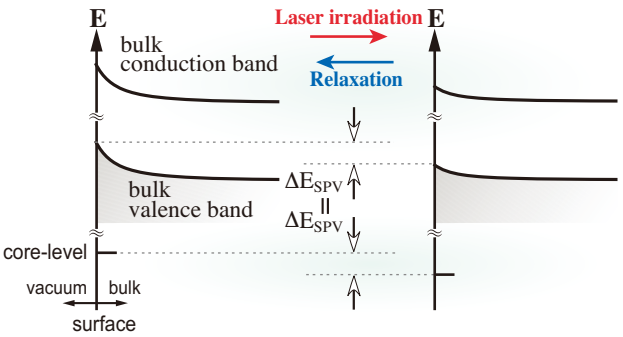

Fig. 2. Schematic of photovoltage effect at semiconductor surface. Bulk bands bend in energy as they approach a surface (surface band bending effect). Energy shift (ΔE_{SPV}) of the bulk band at the surface, induced by laser irradiation, corresponds to that of the core level.

with reference to the energy position before pumping. Whereas the spectral evolution, taken at laser pumping densities of 3.1 (Fig. 3(a)) and 560 (Fig. 3(b)) μJ/cm^2/pulse, shows monotonic decay with time, that at 2,700 μJ/cm^2/pulse exhibits a temporal oscillation (Fig. 3(c)) that includes several frequencies that are higher with shorter delay times. A part of the data can be parameter-fitted (the solid curve in (c)) with the following damped oscillation solution:

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

where y_0 is the offset and C_i's are amplitudes of the sinusoidal functions. The frequency (period) of the fitted oscillation is ω = 11 MHz (91 ns); the oscillations at short delay times are likely to have a similar frequency of several 10 MHz (several 10 ns).

Our experimental data clearly show that, under high laser power density, the excited carriers of the Si(111)7×7 surface layer have long decay times; however, what is unexpected is the observation of periodic behavior in a series of time-resolved spectra (Fig. 3(c)). Typically, surface photovoltage decays continuously with a simple recombination of an electron and a hole, transferred from the bulk. The observation of the oscillation likely indicates the existence of the nonlinear effect during the surface recombination process, which potentially lead to a new technique of ultrafast optical control of photovoltage at the surface. Considerations of theoretical models of carrier kinetics are currently underway in pursuit of a proper understanding of the intriguing phenomena.

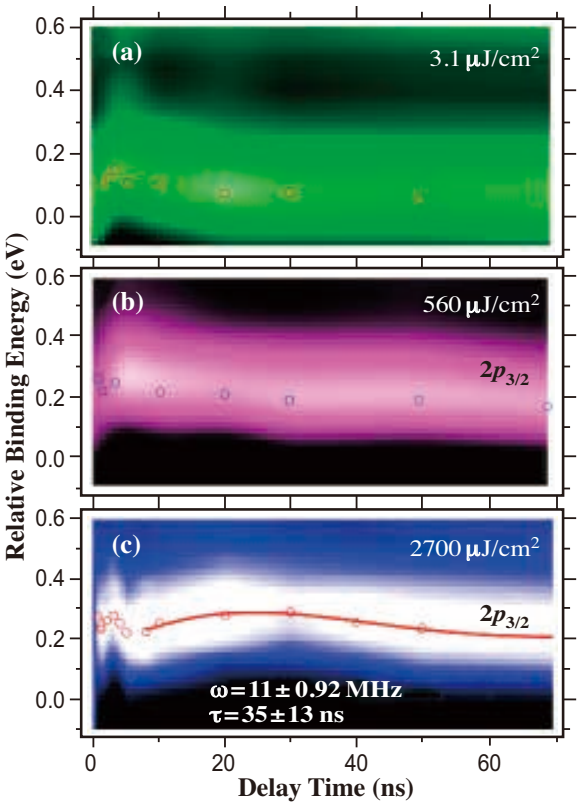

Fig. 3. Time evolution of Si 2*p* spectra taken at different laser power densities per pulse: **(a)** 3.1, **(b)** 560, and **(c)** 2700 μJ/cm^2/pulse, corresponding to stages I, II, and III in Fig. 1(b), respectively. The vertical axis represents relative binding energy with respect to the Si $2p_{3/2}$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

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References

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