Oscillatory relaxation of surface photovoltage effect on a silicon surface observed by time-resolved soft x-ray photoemission spectroscopy

Susumu Yamamoto[1], M. Ogawa[1], R. Yukawa[1], R. Hobara[1], C.-H. Lin[2], R.-Y. Liu[2], S.-J. Tang[2], I. Matsuda[1]

[1] *Synchrotron Radiation Laboratory, The Institute for Solid State Physics, The University of Tokyo*

[2] *National Tsing Hua University, Taiwan*

1. Introduction

Transient electronic structures of photo-excited semiconductors are of fundamental interest and important for practical applications such as photocatalysis and photovoltaics, but little is known about carrier dynamics on photo-excited semiconductor surfaces.

Photoelectron spectroscopy (PES) has been quite successful in providing direct access to electronic structures of materials with surface sensitivity. The extension of PES to time-domain, or time-resolved PES, is now realized by the use of brilliant x-ray short pulses (several tens ps) available at the state-of-the-art synchrotron radiation (SR) facilities. We developed a novel time-resolved PES system at the high-brilliance soft x-ray beamline BL07LSU at SPring-8.

In this article, using the time-resolved PES system, we have studied the relaxation of the surface photovoltage effect on the Si(111)7x7 surface. When the power density of the pump laser is above 1000 μJ/cm^2/pulse, the relaxation has been found to exhibit damped oscillations with temporal periods of several tens ns at delay time faster than 100 ns [1].

2. Experimental

The time-resolved PES experiments were carried out at SPring-8 BL07LSU using a pump (laser) and probe (SR) method [2]. The temporal durations of the laser and SR pulses were about 35 fs and 50 ps, respectively. The pump laser has a photon energy of 1.51 eV with the repetition rate of 1 kHz. A clean Si(111)7×7 surface was prepared by a cycle of in situ resistive heating of a heavily doped n-type (ρ = 0.02 Ω cm) Si(111) wafer.

3. Results and discussion

Figure 1(a) shows Si 2*p* spectra of the Si(111)7x7 surface before and after laser irradiation. As expected for the upward band bending of the n-type semiconductor surface, the Si 2*p* spectrum shifts to the higher binding energy due to surface photovoltage (SPV) effect. Figure 1(b) shows the SPV shift as a function of laser power density. The pump-probe delay time was fixed at 1 ns. The SPV shift initially increases linearly with logarithmic scale of the power

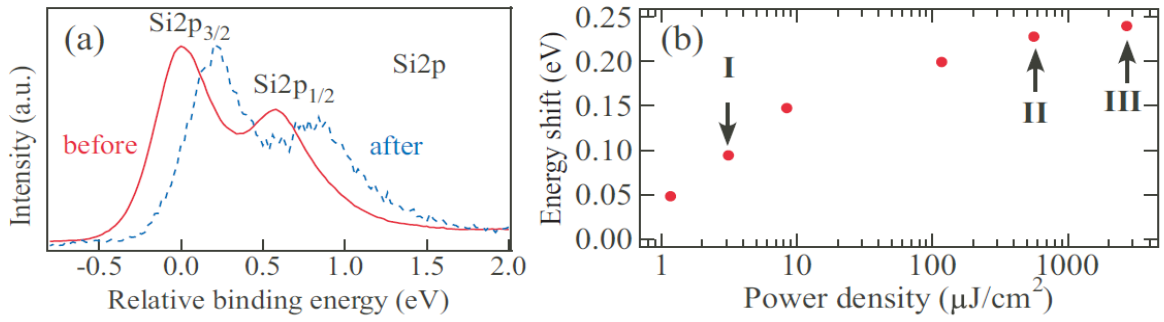

Figure 1: (a) Si 2*p* core-level spectra (hν= 253 eV) before and after laser irradiation. The power density of the pump laser (hν= 1.51 eV) was 2700 μJ/cm^2/pulse. (b) The SPV energy shift as a function of laser power density. The pump-probe delay time was set at 1 ns.

densities (stage I), but deviates above ~10 μJ/cm^2/pulse. Above ~100 μJ/cm^2/pulse (stage II and III), the SPV shift saturates.

Figure 2 shows the time evolution of Si 2*p* spectra of the Si(111)7x7 surface after laser irradiation in the delay time of 0 to 70 ns. At lower laser power densities (Fig. 2(a) and (b), which correspond to stage I and II in Fig. 1(b), respectively), the SPV shift shows a monotonic relaxation with time. At the high laser power density (Fig. 2(c), which correspond to stage III in Fig. 1(b)), however, the SPV shift shows an oscillatory relaxation. As seen in Fig. 3(a), the oscillation frequency gets higher at shorter delay times. The frequency (period) of the oscillation is derived to be 11 MHz (91 ns) by fitting the part of the SPV relaxation curve with a damped oscillation equation as expressed below: $f(t) = y_0 + \{C_1 \cos(\omega t) + C_2 \sin(\omega t)\} exp(^{-t}/_{\tau})$, where y_0 is the offset and C_i's are amplitudes of the sinusoidal functions.

The oscillatory relaxation observed at high laser densities was not expected from a simple relaxation process where photo-excited carriers are transported from the bulk to the surface and carrier recombination occurs at the surface. The observed oscillatory relaxation may indicate the existence of non-linear effect for the densely-populated photo-excited carriers at the surface. Development of a theoretical model for carrier kinetics are now underway in order to understand the intriguing physics behind the unexpected oscillatory behaviour observed in this study.

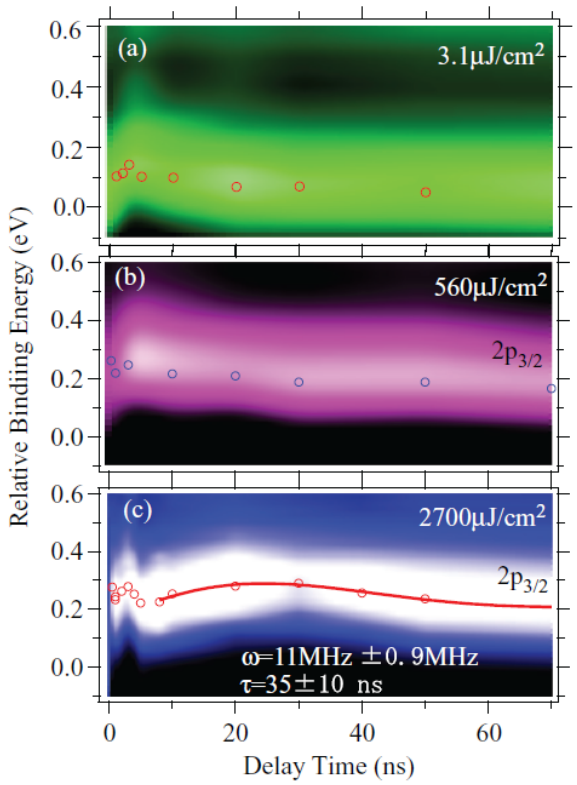

Figure 2: Time evolution of Si 2*p* spectra after laser irradiation with different laser power densities: (a) 3.1, (b) 560, (c) 2700 μJ/cm^2/pulse. The solid line in Fig. 2(c) is the fitted curve with a damped oscillation equation.

References

[1] M. Ogawa, S. Yamamoto, R. Yukawa, R. Hobara, C.-H. Lin, R.-Y. Liu, S.-J. Tang, I. Matsuda, Phys. Rev. B, 87, 235308 (2013).

[2] M. Ogawa, S. Yamamoto, Y. Kousa, F. Nakamura, R. Yukawa, A. Fukushima, A. Harasawa, H. Kondoh, Y. Tanaka, A. Kakizaki, I. Matsuda, Rev. Sci. Instrum., 83, 023109 (2012).