Chronology of Carriers at Semiconductor Surfaces Studied by Time-Resolved Photoemission Spectroscopy

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Photoemission spectroscopy using synchrotron radiation has been the significant experimental method to *probe* electronic structure of semiconductor surfaces *directly*. Recently, we have developed time-resolved photoemission spectroscopy system at synchrotron radiation beamline to *trace* temporal variation of electronic state at semiconductor surface *in real time*[1,2].

Surfaces have been known to play crucial role in relaxation of the surface photovoltage effect (SPV) effect, the basic process in photovoltaics and photocatalysis. On the other hand, surfaces have been also known to change their electronic properties significantly even with submonolayer adsorption of foreign atoms. Thus, it is inferred that relaxation of the SPV effect is highly sensitive to surface characters that can be regulated by surface treatments. In the present research, we have systematically performed time-resolved photoemission experiments to trace the relaxation process in *real time* on various semiconductor surfaces with distinct surface electronic structure, surface disorder, and surface potential. The temporal variation was monitored by the one-pump and multi-probes method using pulses of laser and synchrotron radiation at SPring-8 BL07LSU.

On the metal-covered Si(111) surface system, the time evolution does depend on the surfaces and the relaxation essentially proceeds in two steps, a fast process at the initial stage and the following slow process. The former and the latter can be described in terms of the tunneling and the thermionic relaxation schemes, respectively. The transition between the two mechanisms was found at the certain amount of the surface potential, which likely corresponds to the critical width for the tunneling transport. The crossover can be understood by breakdown of the quantum tunneling regime by the increase in width of the space charge layer during the relaxation.

On the Si(111)7x7 clean surface[3], 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.

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