

## Lifetime measurement of electrons in TiO<sub>2</sub> nano particles Scatter distributed on Si wafer and on SiO<sub>2</sub> using PEEM and fs laser

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**(Introduction)** In the application of TiO<sub>2</sub> nano particles to solar cells, lifetime of electrons in the conduction band is a very important parameter, and there are many studies(refs.1and2). Reported values are largely different among reports. To clarify causes of different values in previous reports enables us to improve efficiency of solar cells, observation of individual TiO<sub>2</sub> nano particles will be important. We have been studying electron transfer dynamics in Au nanoparticle(NP)-TiO<sub>2</sub> NP system by using a photoemission electron microscope (PEEM) having a spatial resolution of 40-nm(refs.3and 4). By using PEEM, we can analyze electrical properties of individual particle. In this paper, we report that lifetime of TiO<sub>2</sub> NP scatter distributed on Si wafer is only 1 ps or shorter and that lifetime component longer than 300-fs was not noticeable for TiO<sub>2</sub> NP distributed on SiO<sub>2</sub>.

**(Experiment)** TiO<sub>2</sub> NPs of nominal size of 100 nm were distributed on a Si wafer and baked for 1 hour in the air at 500degC. The sample was observed by PEEM of 40 nm spatial resolution. The sample was excited both by a fs laser pulse (F) of nominal pulse width of 150 fs and by its second harmonic (SH). By moving a corner cube mirror on a transfer stage, delay time of two pulses was changed by +/- 2 ns.

**(Results)** Figure 1 shows brightness dependence on delay time. The vertical value is the ratio of brightness enhancement when both of F and SH were irradiated to summation of brightness for F and SH only. At delay of 2271.3 ps, more than twice intensity enhancement was observed, and we know F and SH arrived at the same time. A slower decay component should be a signal of long-lived conduction band electrons, because slow decay appeared only at larger delay time and SH comes later at larger delay time, so, we know F excites electrons to conduction band and SH excites conduction band electrons into vacuum.

The time constant of the slow decay was 1ps or shorter. This value is quite shorter than those previously reported values. We interpret that electrons in the conduction band of TiO<sub>2</sub> NP run away to Si wafer.

To confirm our interpretation, we prepared another sample with TiO<sub>2</sub> NP distributed on SiO<sub>2</sub> to prevent run-away of electrons. As shown in Fig.2, slow component was not noticed although very large enhancement was observed at t=0. We interpret this as follows. Due to high barrier of SiO<sub>2</sub>, holes in TiO<sub>2</sub> NP cannot escape. Then, electrons in the conduction band are pulled back by holes and they are difficult to be excited to vacuum.

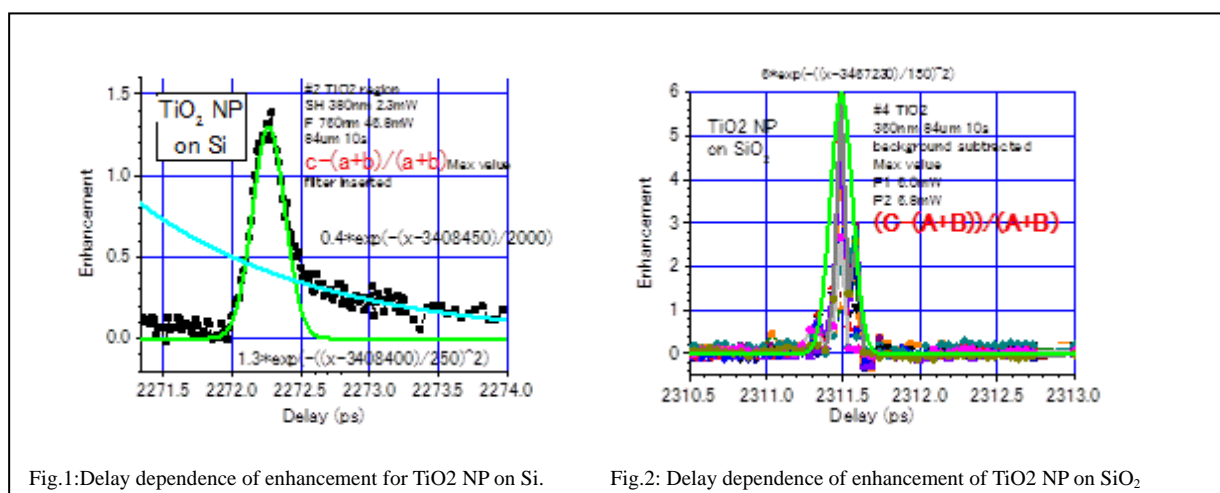


Fig.1: Delay dependence of enhancement for TiO<sub>2</sub> NP on Si.

Fig.2: Delay dependence of enhancement of TiO<sub>2</sub> NP on SiO<sub>2</sub>

(ref.1) L. Du et al.; J. Photochem. Photobio. C: Photochem. Rev. **15** (2013) 21-30

(ref.2) M. Fierz et al, Appl. Phys. **B 68**, 415-418 (1999)

(ref.3) Bochao Li, et al. ; JSAP Spring meeting 2015, 13a-15-9

(ref.4) Bochao Li, et al. ; JSAP Autumn meeting 2015, 13p-2V-4