Deplete excitation ? of defects states in TiO_2 nano particles observed using PEEM and fs laser

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(Introduction) TiO_2 nano particles (NP) is a very usefull and widely used material and understanding its electronic strucuture is imporatnt. In order to evaluate electron affinity of individual paricles, we obsrved TiO_2 NP distributed on a Si wafer by using PEEM (photoemeission electron microscope) and fs laser. We reported that brightness jump was observed at 740 -750 nm and at 780-790nm(ref.1). However, it is difficut to attribute this gap to band gap, electron affinity, nor ionization energy.

Latelely, we came to know that defcts states lie at 0.8eV below conduction band minimum in TiO_2 NP (ref.2). The existence of defects state explains most of our observed results. In the latest pump-probe experiment, largest brighnes enhancement was observed at relatively low laser power when power of a laser for excing electrons to conduction band is varied. We interpret this being caused by depletion of defects states.

(Experiment) Vacuum level and valnce band maximum were observe by using EUPS developed at AIST (ref.3). TiO_2 NPs of nominal size of 100 nm were distributed on a Si wafer and baked for1 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). At the delaytime of maximum PEEM image brghtness enhabcement (t=0), power of F beam was varied.

(Results)

EUS observation gave valence band maximum 2 eV below Fermi level and vacccum level of 4.6 eV, indicating ionization energy of 6.6 eV. When band gap is 3.2 eV, conduction band minimum locates at 1.2 eV above Fermi leve.

Right figure shows dependence of enhancement on F laser power. Enhancement is a ratio of difference of brightness between that when F and SH are irradiated atthe same ime and summation of F only and SH only. Enhancement showed the maximum at F power of 100 mW and decreased at larger power.

Smaller enhancement at larger F laser power can be interpreted by depletion of defects states by a strong excitation.

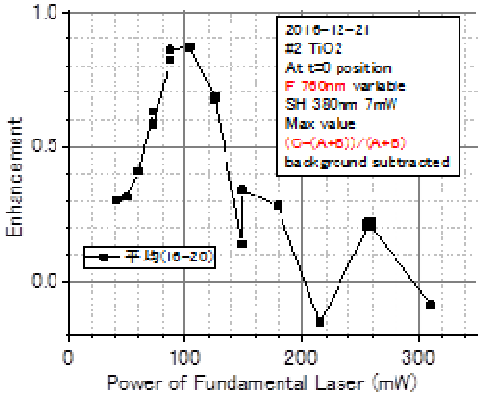

Fig.1. Dependence of enhancement on F laser power.

references

(ref.1) Bochao Li, et al. ; JSAP Spring meeting 2016
(ref.2) Adam Argondizzo et al, Physical Review B 91, 155429 (2015)
(ref.3) T.Tomie and T.Ishitsuka; *Synthesiology* **9** (2016) 216