Study on electron injection dynamics in Au-TiO_2 nanoparticle system (2) –indication of electron transfer by PEEM image of fs-laser excited pair-

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(Introduction) In the development of solar cells utilizing nanoplasmonic, dynamics of electron transfer from light absorbing nano-particles (NP) to electron reservoir NPs is one of the most important subjects to be studied. We chose Au-TiO_2 NP system (ref.1) and we are observing electron emission from NPs with a photoemission electron microscope (PEEM) having a spatial resolution of 30-nm (ref.2). Observation of electron transfer from light absorbing Au-NP to electron reservoirTiO_2-NP by PEEM will be reported.

(Experiment) TiO_2 particles of 100-nm nominal size were mixed in a liquid of Au particles of 10-nm nominal size dispersed by surfactant. A drop was dripped in one-quarter region on a Si wafer of 10 mm size, and the sample was baked at 500degC to form Au-NP attached TiO_2-NP. This region is called mixed region. The sample had also Au and TiO_2 regions. Pulses of 10-fs duration from a femtosecond (fs) Ti: Sapphire laser operated at 80 MHz were sent into a Mach-Zehnder interferometer. The beam from the interferometer irradiated the sample in vacuum. The laser intensity on sample was varied by changing the delay time of two beams in the interferometer.

(Results)

1. PEEM images were observed by Hg lamp illumination as well as fs-laser irradiation. In Au and TiO_2 regions, all bright spots were found at the same positions in both illuminations. On the other hand, in the mixed region, some spots seen in the Hg lamp illuminated PEEM image were not found in the fs-laser illuminated image. This indicates that observed spots are paired Au-NP and TiO_2 –NP and that electrons emitted from Au-TiO_2 –NP pair are generated by transfer of electrons from Au NP to TiO_2 NP.

2. Fig.1 shows changes of brightness of typical NP in each region when delay of two beams were varied. The peak brightness of particles shown here were 2E3 for Au, 1E5 for TiO_2, and 4E5 for Au-TiO_2–mixed regions. L ow intensity of Au-NP image could be attributed to short lifetime of fast electrons. Bright TiO_2 image is attributed to long lifetime of electrons in the conduction band of TiO_2 having a large bandgap. Brighter image of Au-TiO_2 –NP system than TiO_2 –NP can be attributed to electron transfer into TiO_2-NP from Au-NP which is more efficient absorber of 790-nm wavelength fs-laser than TiO_2-NP.

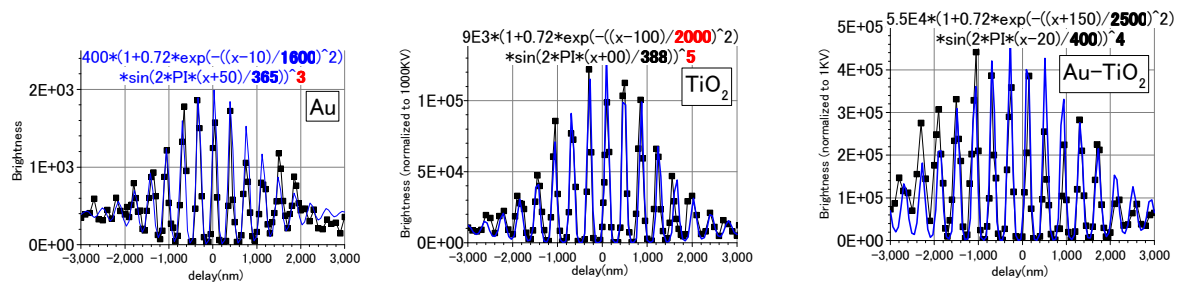

Fig.1: Intensity change of PEEM images of NPs in three regions when delay of two fs-laser beams were varied

(ref.1) L.Du, *et al.* ; J.Photochem. Photobio. C : Photochem. Reviews **15** (2013) 21
(ref.2) Bochao Li, *et al.* ; JSAP Spring meeting 2015, 13a-15-9