Poster

ELECTRIC FIELD MODULATION OPTICAL SPECTROSCOPY USING FIELD ENHANCEMENT NEAR OPTICAL ANTENNAS

Kenichiro Tanaka and Yoshinobu Aoyagi
Nanoscience Research and Development Support Team, RIKEN, 2-1 Hirosawa, Wako-city, Saitama, Japan
kenichiro@riken.jp (Kenichiro Tanaka)

Electromodulation spectroscopy is one of powerful tools to investigate electronic properties of a material. For instance, the excitonic and electronic structures of a unique quantum-well material $(C_6H_{13}NH_3)_2PbI_4$ were well clarified by electroabsorption spectroscopy. The crystal $(C_6H_{13}NH_3)_2PbI_4$, whose crystal structure is shown in the inset in Fig. (b), is a self-organized crystal, in which the excitons are tightly confined in the inorganic monomolecular layer of $[PbI_6]$ octahedra (~6.37 Å) sandwiched between organic barrier layers consisting alkyl-ammonium chains $[C_6H_{13}NH_3]$ (~ 9.97 Å). In this crystal, the bandgap of the barrier layer is at least 3 eV larger than that of the well layer, and the interfaces between the well and the barrier layer are intrinsically flat; thus the excitons in this crystal behave as an ideal two-dimensional (2D) excitons system. In addition, since the dielectric constant of the barrier layers is much smaller than that of the well layers, the effective Coulomb interaction between electron and hole in the well layer is substantially enhanced, resulting in the enhanced excitons binding energies (image charge effect). Because of this image charge effect and 2D spatial confinement effect, the excitons in this crystal have extremely large binding energy (361 meV), have large oscillator strength (~0.7), and exhibits many fascinating properties. In our previous research, the electroabsorption technique was quite effective to clarify its electronic and excitonic properties, where we observed anomalous blue shifts of the 1s excitons under the applied electric fields perpendicular to the quantum well layers, for which we demonstrated that the image charge effect plays an important role [1].

On the other hand, it was reported recently that the optical field is greatly enhanced at the gap between gold triangles in a bowtie antenna, and the Raman spectra of *p*-mercaptoaniline molecules attached with gold bowtie were observed. In this paper, we report on the electromodulation spectroscopy on the PL of $(C_6H_{13}NH_3)_2PbI_4$ thin film spin-coated on the bowtie antenna, and show that electromodulation spectroscopy can be performed on the enhanced PL at the gap between triangles in bowtie antenna [2].

Gold bowtie antennas were fabricated with electron beam lithography and evaporation technique on a glass substrate. Each bowties are composed of 2 nm Ti adhesion layer and 20 nm gold layers. The obtained sample consisted of multiple bowtie arrays, with 0.5 μm spacing between bowties. The gap lengths between the tips of the triangle in the antennas were varied from 10 nm to 30 nm. A $(C_6H_{13}NH_3)_2PbI_4$ polycrystalline film was then spin-coated onto the substrate. The excitation light source was a cw semiconductor diode laser with photon energy of 2.62 eV. A half-mirror was used to reflect excitation light to the sample through microscope objective (×100). The polarization of the excitation light (E) was parallel to the long axis (x) or short axis (y) with a polarizer. There were about 300 bowties in the spot of the excited light. The same objective collected the PL, which passed through a Raman notch filter to reduce the excitation light, dispersed with a 30-cm monochromator, and detected with a photomultiplier tube. The PL intensities at each wavelength were measured by sweeping the monochromator.

Electromodulation spectroscopy on the PL of $(C_6H_{13}NH_3)_2PbI_4$ were performed, where the electric fields were applied parallel to the quantum well layers and perpendicular to the long axis of the bowtie antennas. Ac electric fields with no dc bias were applied with a frequency of 1 kHz. The PL has dc component P and ac component ΔP; P was measured with a digital multimeter, and the modulated ΔP were decomposed with a lock-in amplifier synchronized at twice the field modulation frequency.

Figure (a) shows the PL spectra of $(C_6H_{13}NH_3)_2PbI_4$ polycrystalline thin film (~5 nm) near the bowtie antennas at room temperature. The excitation intensity is ~0.5 kW/cm^2. We found clear PL spectra with the peak energies of 2.41 eV for all samples. Though the PL intensity with a gap length of 20 nm is almost same as that with a gap of 30 nm, PL with a gap below 20 nm is substantially enhanced as the gap length is decreased. In addition, the PL intensity of 10 nm gap with the excitation light polarized parallel to the short axis of antennas is much smaller than that with the excitation light polarized to the long axis of antennas, and nearly equal to that of 30 nm gap. These results suggest that the PL intensity is increased due to the optical field enhancement at the gap of optical antennas with the gap length below 20 nm.

The electromodulation PL spectra for the sample with the average gap of 10 nm under several electric fields are shown in Fig. (b). The incident light's polarization (*E*) was parallel to long axis of the bowtie gap (*x*) and perpendicular to the applied electric fields (*y*). The shape of the modulated PL spectrum can be reproduced by linear combination of the first and second derivatives of the PL spectrum with respect to the photon energy, indicating that this electromodulation PL spectrum is originated from both the Stark shift and broadening of the 1s excitons. The obtained result indicates that the phonon-assisted ionization of the 1s excitons occur at room temperature.

In summary, we have performed electro-modulation photoluminescence spectroscopy on an inorganic-organic perovskite-type material $(C_6H_{13}NH_3)_2PbI_4$ thin film at the gap between the gold bowties. This result indicates that electromodulation spectroscopy can be performed on the enhanced PL at the gap between triangles in bowtie antennas.

Acknowledgements:

This work was partially supported by a Grant-In-Aid for Scientific Research from MEXT, Japan, and by the Special Postdoctoral Researchers Program of RIKEN.

References:

[1] Kenichiro Tanaka *et al.*, Phys. Rev. B **71** (2005) 045312, and references therein.

[2] D.P. Fromm *et al.*, J. Chem. Phys. **124** (2006) 061101.

Figures:

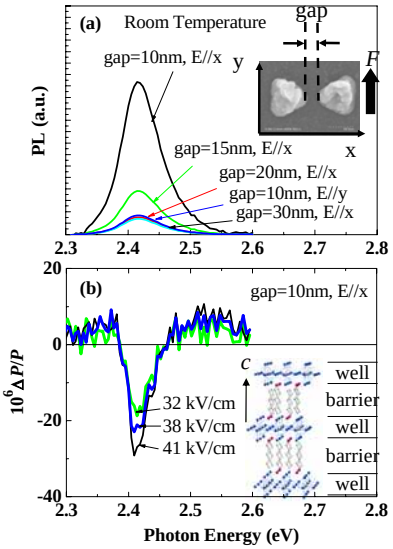

Figure: (a) Photoluminescence spectra of $(C_6H_{13}NH_3)_2PbI_4$ polycrystalline thin film (~5 nm) near the ~300 bowtie antennas with an average gap lengths from 10 nm to 30 nm at room temperature. The excitation intensity is about 0.5 kW/cm^2, and the polarization of the excitation laser (*E*) is parallel to the bowtie antenna's long axis (*x*) or short axis (*y*). The inset shows the scanning electron microscope (SEM) image of a bowtie antenna composed of two-opposing 80 nm-long gold triangles, with a gap length of 10 nm, and the direction of the applied electric field (*F*). (b) Electromodulation photoluminescence spectra of $(C_6H_{13}NH_3)_2PbI_4$ under several electric fields parallel to the quantum well layers near the ~300 bowtie antennas with an average gap length of 10 nm. The inset shows the crystal structure of $(C_6H_{13}NH_3)_2PbI_4$ with the crystal axis *c*.