RESEARCH ACTIVITIES II
Department of Molecular Structure

II-A Development of Near-Field Dynamic Spectroscopy and Application to Mesophase Systems

Recent developments in ultrashort pulsed lasers have made ultrafast spectroscopy a mature technique for analyzing dynamic behavior of molecular systems. As for spatial resolution, near-field optical microscopy, which enables spatial resolution beyond the diffraction limit of light, shows remarkable progress in technology in these days. Combination of these advanced optical technologies may offer a direct probe of molecular dynamical processes in mesoscopic systems. It may bring essential and basic knowledge for analyzing origins of characteristic features and functionalities of mesophase systems. We are constructing an apparatus for near-field dynamic spectroscopy with femtosecond temporal resolution and nanometer spatial resolution. Preliminary experimental results are presented here.

II-A-1 Development of an Ultrafast Near-Field Spectroscope and Observation of Dynamic Processes in GaAs Crystal

IMURA, Kohei; OKAMOTO, Hiromi

We have developed an instrument, where a fs pump-probe technique is combined with a scanning near-field optical microscope having a 100-nm spatial resolution, for the purpose of obtaining information on spatially resolved molecular dynamics. We have examined the performance of our instrument and feasibility of applications to the studies of molecular dynamics by using a GaAs crystal.

Experimental set-up consists of an excitation light source, a near-field microscope, and detection systems. The output from a mode-locked Ti:sapphire laser (λ = 780 nm, ~100 fs pulse duration) is split into two beams. The beams are collinearly combined again into one beam after one beam passes through a motorized optical delay line. Positive group velocity dispersion arising from a long optical fiber (for a near-field probe) is pre-compensated by a grating-prism pulse stretcher before the optical beam is coupled to the cleaved end of the fiber. The other end of the fiber has been fabricated as a near-field probe. The near-field probe (commercial) is tapered and Au metal coated, and has an aperture (~100 nm) at the tip. The aperture probe is used to illuminate the sample, and also to collect photoluminescence (PL) from the sample. The PL is detected either by a CCD after dispersed by a monochromator or by a photomultiplier tube after passing through optical filters. To obtain PL images, the sample is raster-scanned beneath the tip, and a sample-tip distance is regulated at ~10 nm by the shear force feedback mechanism. This feedback signal also gives topographic image of the sample.

We have measured the excitation laser power (P) dependence of the PL intensity (I) from the GaAs crystal around 870 nm, and have found a relationship as $I \propto P^{1.5}$. This finding indicates two-photon process involved in the PL. We have performed time-correlated measurements for the two-photon PL from GaAs crystal at ~870 nm. In Figure 1, the PL intensity is plotted against the delay time between the two optical beams. Except for the region around the origin of the delay time, where it shows an interferometric pattern (not shown in Figure 1), a relatively slow decrease of the intensity with delay time is observed. This plot gives information essentially equivalent to that obtained by the time-resolved absorption correlation method (*i.e.*, dynamics in the one-photon excited state). A relaxation time constant 52 ps is obtained by assuming a single exponential decay. The background PL with no delay time dependence is due to the two-photon PL arising from each optical pulse, as well as a single photon inter-band transition.

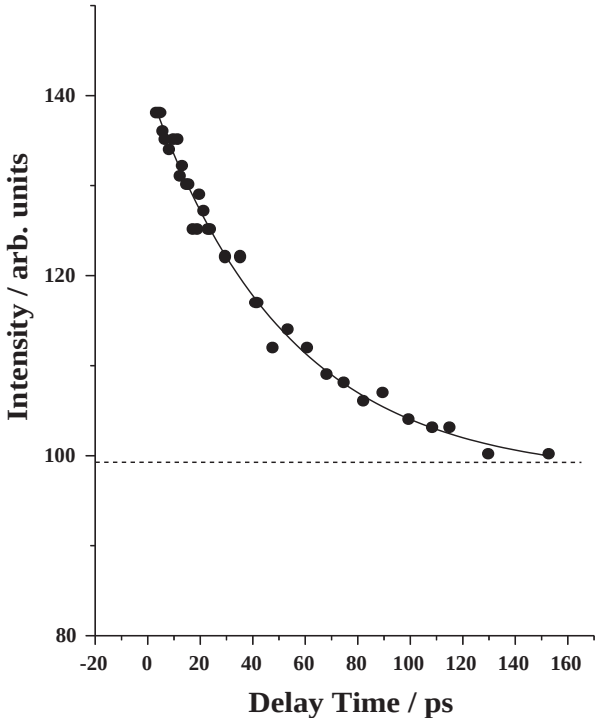

Figure 1. Near-field time-correlated PL signal of GaAs crystal.

II-A-2 Near-Field Autocorrelation Measurements of Femtosecond Light Pulses at a Tip of a 100-nm Apertured Probe by Two-Photon-Induced Photoconductivity

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In ultrafast pump-probe experiments, it is essential to characterize temporal profiles of the pump and probe light pulses. The technique most commonly used for that purpose is based on a Michelson-type autocorrelator combined with phase-matched second harmonic generation (SHG) in nonlinear crystals. For ultrafast experiments under scanning near-field optical microscopes (SNOM), however, such a conventional autocorrelation technique with the SHG crystal is not practical because of unsatisfied phase-matching condition and low radiation energy emerging from the apertured fiber probe. By the use of two-photon-induced photoconductivity in semiconductors, autocorrelation measurements under SNOM are possible. Autocorrelation trace of 470 fs full width at half maximum (FWHM) was reported in SNOM geometry.[1] Utilizing this technique, time resolution of our newly developed femtosecond SNOM apparatus has been measured.

The photocurrent output of a GaAsP diffusion type photodiode was detected by a lock-in amplifier. The signal has been confirmed to be of quadratic response (Figure 1A). Femtosecond light pulses were obtained from a mode-locked Ti:sapphire laser (pulse duration <100 fs). Normal group velocity dispersion arising from the optical fiber for the apertured probe was pre-compensated by a grating pair. Figure 1B shows the autocorrelation trace of the Ti:sapphire laser pulses at a tip of a 100-nm apertured fiber probe. The FWHM obtained is ~100 fs, which indicates that dispersion by the fiber is successfully pre-compensated in our apparatus. The spatial uniformity of the detector sensitivity was also examined (Figure 1C), by scanning the probe with the distance between the detector surface and the probe tip kept constant. There was no detectable correlation between the topographic structure and the photocurrent image. The dark spots found in Figure 1C may be ascribed to defect sites of the semiconductor.

Reference

1) W. Schade, J. Preusser, D. L. Osborn, Y. Y. Lee, J. deGouw and S. R. Leone, *Opt. Commun.* **162**, 200 (1999).

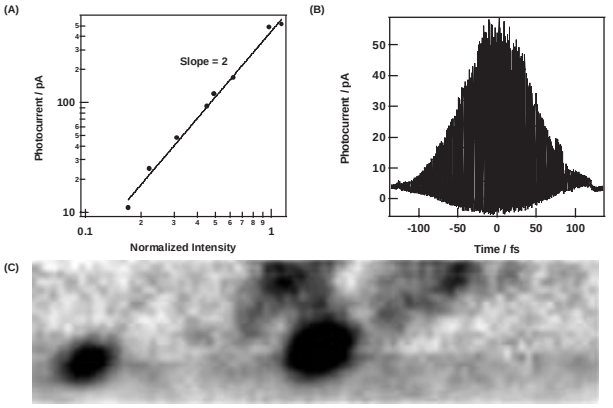

Figure 1. (A) Peak diode current as a function of normalized incident pulse energy. Solid line shows a quadratic fit to the data. (B) Autocorrelation signal obtained at the tip of the 100-nm apertured probe. (C) Spatial image (area size: 5 μm × 1.25 μm) of photocurrent.

II-A-3 Structure and Photophysics of PIC J-Aggregates Studied by Scanning Near-Field Optical Microscopy

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Molecular assemblies such as J-aggregates have received much attention over the past decades because of their characteristic optical properties. The J-aggregates are characterized by a strong and sharp optical absorption band, called J-band, which is red-shifted with respect to the monomer absorption. It has been interpreted that the strong absorption arises from the interactions between the monomeric molecular transition dipoles. Intermolecular interaction between dipoles causes the coherent delocalization of excitons over an aggregate. Pseudoisocyanine (PIC) dye is known as a typical molecule which forms a J-aggregate. Barbara and co-workers[1),2)] have studied PIC J-aggregates by scanning near-field optical microscopy. We have also observed structures and photophysics of PIC J-aggregates to examine performance of the scanning near-field microscope we have constructed recently.

PIC J-aggregate was prepared in PIC-PVS (polyvinylsulfate) hot solution and spin coated onto a substrate (cover glass). Spin-coated J-aggregate was excited by the second harmonic (527 nm) output of Nd:YLF laser through a sub-wavelength-sized (100 nm) aperture probe. J-band fluorescence from the aggregate (~575 nm) was collected by a high NA objective lens and detected by a photomultiplier tube. In order to investigate structures of the J-aggregate, the sample is scanned beneath the probe by keeping the sample-probe distance constant. Fluorescence and simultaneously obtained topographic images proved that produced J-aggregates have fibrous structures. The aggregates are longer than 10 μm in length, 10–150 nm in width, and 1–50 nm thick, depending on the sample preparation condition. We have also investigated the polarization characteristics of the near-field fluorescence for the fibrous J-aggregates. It has been found that the fluorescence from the J-aggregate depends little on the polarization of the excitation light. On the other hand, polarization of the fluorescence is strongly correlated to the fiber direction as seen in Figures 1(c) and (d). The latter observation indicates that the direction of transition dipole for the J-band fluorescence lies along the long axis of the J-aggregate as reported before.[2)] Time-resolved spectroscopic studies of the aggregates are under progress.

References

1) D. A. Higgins and P. F. Barbara, *J. Phys. Chem.* **99**, 3 (1995).
2) D. A. Higgins, P. J. Reid and P. F. Barbara, *J. Phys. Chem.* **100**, 1174 (1996).

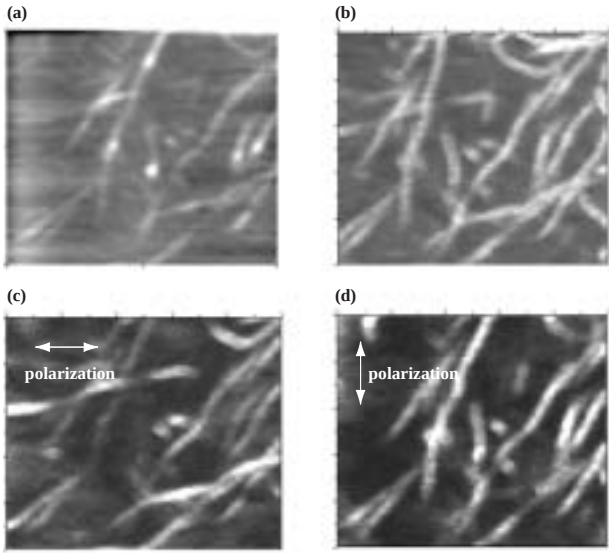

Figure 1. Observed images of J-aggregates (scan range 5 μm × 5 μm). (a) Shear-force topography. (b) Unpolarized fluorescence image. (c) Horizontally and (d) vertically polarized fluorescence images.