DEVELOPMENT OF SIMULTANEOUS MEASUREMENT OF TIME-RESOLVED MICROWAVE CONDUCTIVITY AND LIGHT ABSORPTION SPECTROSCOPY USING ELECTRON BEAM LINEAR ACCELERATOR

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Abstract

In order to perform conductivity experiments of isolated conductive polymer in non-polar liquid, we developed “time-resolved microwave conductivity” measurement system using X-band microwave. Homodyne system consisting of main and reference arms was adopted, so that good S/N ratio was achieved. Light absorption spectroscopy utilizing nanosecond streak camera is installed into the same geometric set up, which helps us assign the conductivity signals to an intermediate species and evaluate their concentration. After system optimization and development of automatic data acquisition software, typical conductivity kinetics of standard sample was obtained. Charged carrier dynamics and the evaluation of mobilities in σ- and π- conjugated polymers such as polysilane will be investigated by means of dielectric absorption technique. In the future, the ionization source will be replaced by electron beam from L-band linac and pulse radiolysis will be performed simultaneously with the conductivity measurement. The combination of microwave conductivity measurement and light absorption spectroscopy enables us to study the charge transfer dynamics, the conformational effects of polymer on the charge localization, mobility evaluation and so on.

1. INTRODUCTION

Dielectric absorption of microwave[1] occurs owing to the interaction with dipole moment and/or charged carries produced by photo-ionization or direct ionization via radiation such as electron beam. The real and imaginary parts of dielectric constant in dielectric media relate with passed or reflected microwave power and its phase shift, respectively.

Time-Resolved Microwave Conductivity (TRMC) technique[2,3] was developed and has served for the investigation of charged carrier mobility at pulse end. This technique has also been applied for the studies of singlet, triplet, radical species and CT state in condensed, liquid and gaseous phase. The signal detection in these experiments was based on a reflection cell and direct pick-up of reflected microwave from the cell, in order to obtain high time resolution. However in our new system, resonant cavity and homodyne circuit were adopted, so that intense signal and phase change detection of reflected microwave became available.

Target structure in future nanotechnology, whether the technique is bottom-up or top-down, aims at the size of one molecule or one atom. For example, carbon nanotube, which has been extensively investigated worldwide, is expected to serve as a basic element in single electron transistor, wiring and so on. Considering the scale, the intrinsic mobility of charged carrier will play an important role in realizing such a device. Requirement of direct observation of intrinsic mobility in σ- and π-conjugated polymer arises for material screening and evaluation of polymers which is used for organic electro-luminescent device and so on.

Nano-scale gap bridged by carbon nanotube which is fabricated by photo or EB lithography seems to be good solution for the evaluation of conductivity in single molecule, but has problems like contact between the molecule and electrode. The conductivity of the molecule may show several values, depending on the electrode writing process, contact condition such as ohmic or not. Time-of-flight experiments also need samples without pin-hole and impurity.

To address these issues, TRMC is utilized to measure the conductivity in condensed matter. This technique enables us to observe the intrinsic conductivity along an isolated polymer chain without fabricating electrodes via lithographic process.

2. MICROWAVE CIRCUIT FOR TRMC AND SIMULTANEOUS LIGHT ABSORPTION SPECTROSCOPY

Figure 1 shows the microwave circuit for the dielectric absorption measurement. The circuit made by Micro Electro Co. Ltd. was designed for X-band radio frequency of around 9 GHz, and the microwave from Gunn oscillator is divided and guided to the main and signal arms. The microwave in the main arm goes through the circulator and into the resonant cavity. Microwave power in the resonant cavity is adjusted about 3 mW via attenuator in the main arm. Reflected microwave from the resonant cavity is amplified by FET amp. and merges with the microwave from the reference arm in magic tee (mixer).

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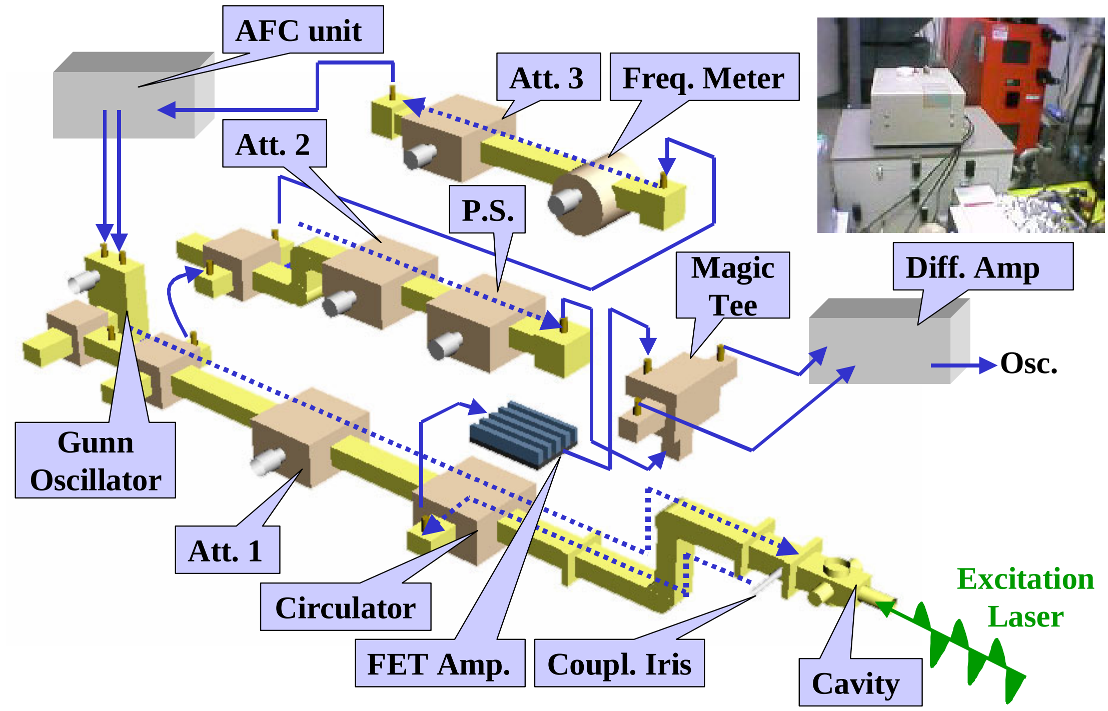

Figure 1 Microwave circuit for the dielectric absorption measurement.

The sample is placed in the position of strongest electric filed in the cavity (Figure 2).

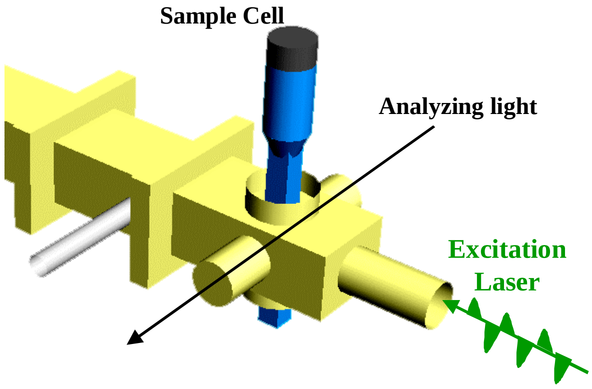

Figure 2 Set up of sample in the resonant cavity.

Resonant cavity has a literal property that it confines microwave of certain frequency (resonant frequency). The microwave frequency is adjusted to the resonant frequency before the transient charged carriers are generated by the excitation laser. Therefore in the cases that the frequency of incident microwave changes from the resonant frequency and/or dielectric absorption (microwave power loss) occurs, the Q value changes, leading to the reflection of the microwave from the resonant cavity. Q value is defined by the following equation.

$$Q_0 = f_0 / \Delta f_0 \qquad (1)$$

The phase difference of microwaves from the main and reference arm is adjusted zero, so that the differential change of Q value is detected. On the other hand, it is adjusted $\pi/2$ in order for the detection of resonant frequency shift.

As described above, our microwave circuit consisting of the main and reference arms is homodyne. For the achievement of long term stabilization of the microwave, a portion of microwave guided into reference arm is also divided and led to automatic frequency controller (AFC) arm. The closed loop from Gunn oscillator, AFC arm, AFC unit and Gunn oscillator has a feedback, but is not used up to date because of an experimental inconvenience. In addition, since TRMC measurement is carried out by one laser pulse and its decay curve falls to base line within usually about 1 ms, AFC feedback loop is not necessary.

Relationship between reflected microwave power and conductivity is described as follows,

$$\Delta\sigma = e\sum_i \mu_i N_i = \frac{1}{A}\frac{\Delta P_r}{P_r} \qquad (2)$$

where $\Delta\sigma$, e, μ_i, N_i, P_r, ΔP_r are conductivity, the electronic charge, mobility of i species, number of i species, reflected microwave power and change of microwave power reflected. A is sensitivity factor and decided from measurable parameters such as resonant frequency, fraction of reflected and incident microwave power, static dielectric constant of resonant cavity including sample for each experimental condition.

While the conductivity can be measured by TRMC, it appears as the sum of mobility and number of charged carrier. If one wants to obtain the value of mobility itself, the number of charged carrier must be assigned independently. Simultaneous light absorption spectroscopy helps us assign the conductivity kinetics to a

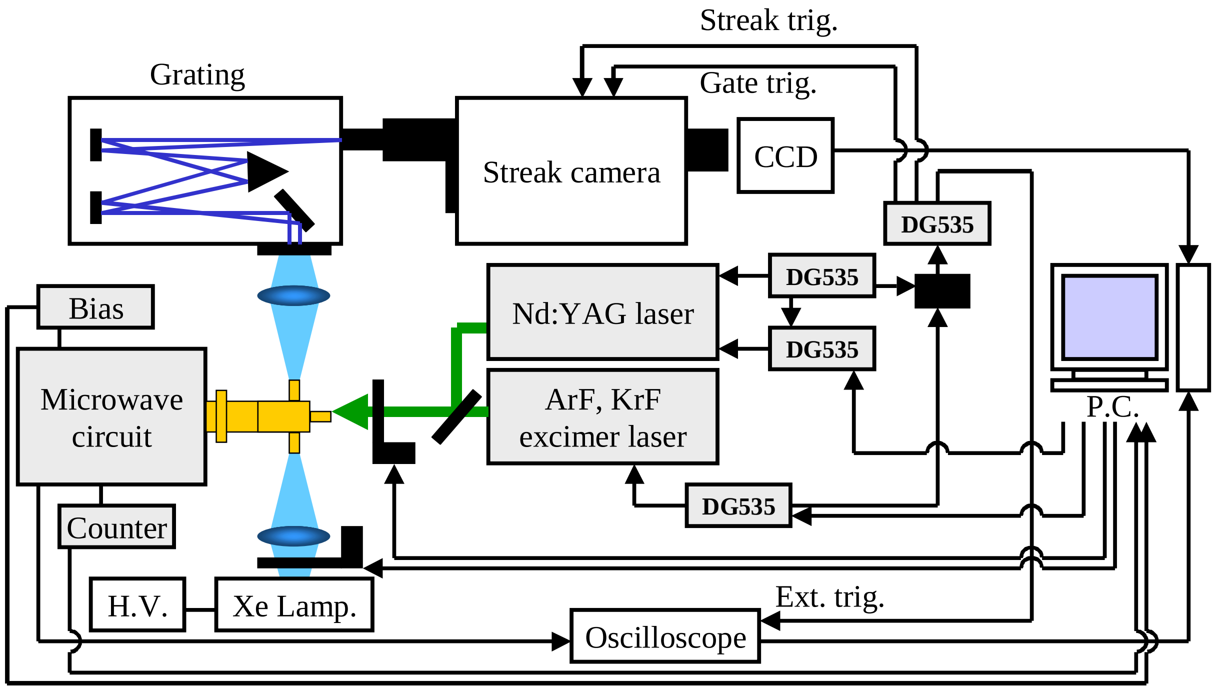

Figure 3 Schematic drawing of simultaneous TRMC and light absorption spectroscopy experiment.

certain species and estimate its concentration. The schematic drawing of simultaneous TRMC and light absorption spectroscopy experiment is illustrated in Figure 3. The nanosecond excitation laser pulses from ArF excimer (193 nm), KrF excimer (248 nm), THG (355 nm) and SHG (532 nm) of Nd:YAG are available up to date.

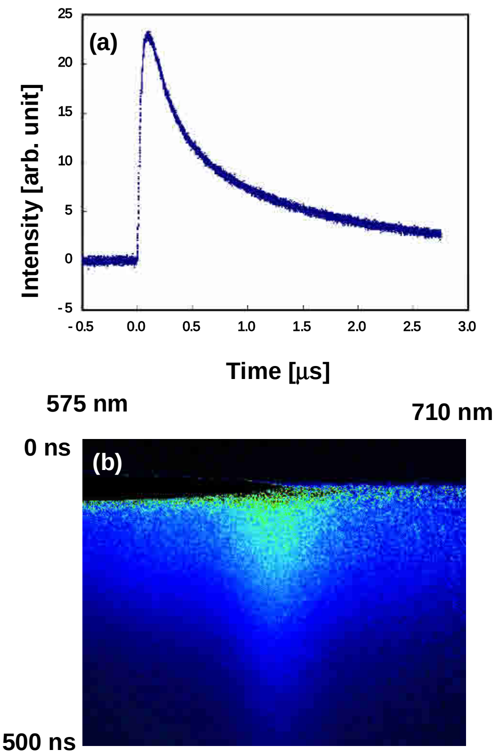

Figure 4 (a)Dielectric absorption kinetics and (b) light absorption spectrum of poly-dioctylfluorene film

Typical dielectric absorption kinetics and absorption spectrum of poly-dioctylfluorene film were observed by using TRMC as shown in Figure 4. The analysis and systematic investigation of this π-conjugated polymer will be performed in the near future.

3. USE OF ELECTRON BEAM FROM LINAC AS AN IRRADIATION SOURCE

The use of electron beam from liniac as an irradiation source has advantages compared to photo-ionization. High-energy electron beam (EB) homogeneously ionize the sample. Namely, high-energy EB shows good transparency for many kinds of organic compounds. Besides, the G value (number of produced species /100 eV absorbed dose) of primary species can be estimated easily.

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