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Electric Field Effect of Second-Order Photocurrent in Conducting Polymer Utilizing FET Structure

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Photoconductivity of conducting polymer is an important property that works in many applications of the materials. It is a complex physical phenomenon, depending on many fundamental things, and it is very important to specify the primary physics from the excited electron states to the generations of the free carriers for the application, such as photoelectric converters. Up to now there exist two main approaches for description of photoconductivity [1], one of them is a first-order process that the free carriers are generated after band-band transitions induced by photoexcitation, like in inorganic semiconductors, and the other is a second-order process that the free carriers are generated as a result of reactions with participation of excited species formed upon a light absorption. However it remains uncertain which process take place in conducting polymer.

In conducting polymers, amplitude of photoconduction increases linearly at low excitation light intensity, whereas a nonlinear increase is observed at high excitation light intensity [5,6]. In order to explain these phenomena, we have utilized concepts of polarons and polaron pairs, which enable charge transport between the main chains. Furthermore we proposed a new two-correlated-pulse technique composed of both Pump and Probe light having the wavelength of 400 nm and have succeeded in specifying the origin of the second-order photoconductivity [2]. In addition, by the measurement technique of nonlinear photoconduction, we have also succeeded in directly observing the behavior of polaron pairs and have acquired primary physical knowledge on polaron pairs, such as their lifetime in photoconduction [4-6].

Concerning the measurement of nonlinear photoconduction, the effects of applied electric field in a transverse direction have been investigated [5], however that in a longitudinal direction have not been investigated yet. In this study, we introduced a FET structure in order to investigate what electric field applied in a longitudinal direction from gate electrode affects nonlinear

photoconduction and the formation of polaron pairs. Consequently we measured time-resolved nonlinear photoconduction of conducting polymer utilizing the FET structure in two-correlated-pulse technique to examine a change of the behavior of nonlinear photoconduction by applied gate voltage, and finally investigated for the purpose of obtaining its amplification.

Figure 2 shows the FET structure used in our experiments. As a conducting polymer film, poly(3-dodecylthiophen) (PAT12) (Fig. 1) was prepared by casting method from its chloroform solution on the Si substrate. The channel length and the SiO₂ film thickness were 10 μm and 100 nm respectively.

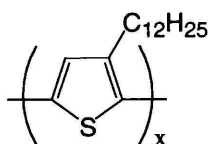


Fig. 1: Molecular structure of PAT12 in this study.

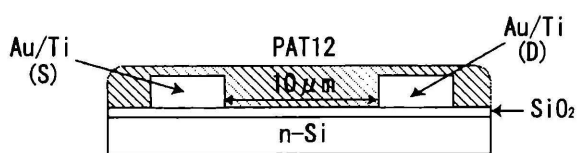


Fig. 2: FET sample structure.

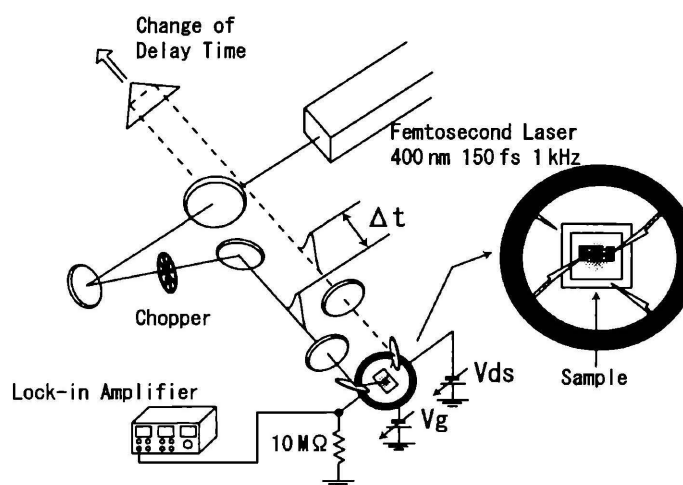


Fig. 3: Scheme of experimental setup of two-correlated-pulse technique.

Figure 3 shows the system of measurement in two-correlated-pulse technique using regenerative amplified high-intensity femtosecond pulse laser as the excitation light source. The wavelength and pulse width of the two-correlated-pulse laser were 400 nm and 150 fs, respectively. First the laser was divided into two parts, one irradiated the sample directly and the other entered the prism to obtain the delay time between two pulses. There were features in the action, which enabled us to think the generative efficiency of the free carriers contributed to nonlinear photoconduction as a function of the delay time under the condition at the constant injection of photons per unit of time.

The laser was focused on and entered the sample. The photocurrent was converted into the voltage by the resistance and detected by the Lock-in Amplifier to perform the time-resolved measurement of nonlinear photoconduction. In addition, in order to enable to be synchronized the excitation light and the Lock-in Amplifier, the chopper was utilized to modulate the laser without the delay time. The measurement was performed under vacuum condition.

Figure 4 shows the time-resolved characteristics of nonlinear photoconduction of PAT12 at different gate voltage (V_g). The excitation light intensity and the source-drain voltage (V_{ds}) were 1.5

$\mu\text{J/pulse}$ and -10 V , respectively. In the delay time $\Delta t=0$, the peak caused by nonlinear photoconduction was observed.

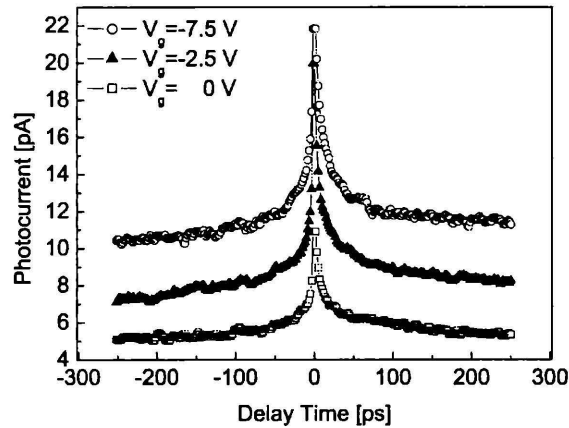


Fig. 4: Modulated photocurrent as a function of delay time of PAT12 at different V_g ($V_{ds}=-10\text{ V}$).

Figure 5 shows the dependence of photocurrent of PAT12 on V_g . In V_g from 0 V to -2.5 V , linear photocurrent ($I_1=I_{|\Delta t|\gg 0}$) was not only increased but nonlinear photocurrent ($I_2=I_{\Delta t=0}-I_{|\Delta t|\gg 0}$) was prominently increased. However as applied high negative V_g , I_2 was gradually decreased whereas I_1 was hardly changed.

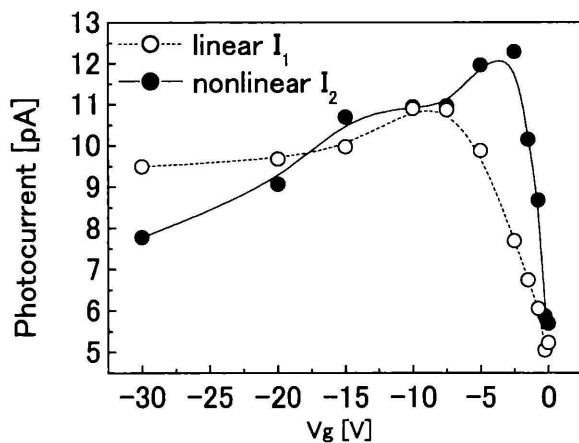


Fig. 5: Dependence of photocurrent of PAT12 on V_g ($V_{ds}=-10\text{ V}$).

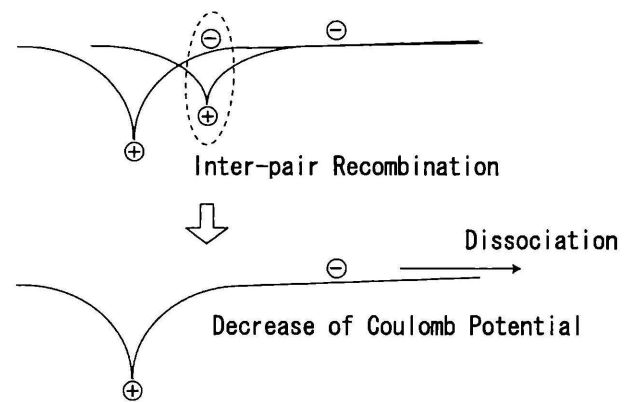


Fig. 6: Process of inter-pair recombination.

Essentially, the generations of the free carriers contributed to nonlinear photoconduction in conducting polymer are taken place as a result of inter-pair recombination (Fig. 6) [3]: after the state at high densities of polaron pairs are formed by the enhancement of excitation light intensity,

newly generated polaron pair by the collisions of two polaron pairs are dissociated. Because of two remaining charges having longer inter-charge distance they are increased their chance to be free charge. Thus, for conducting polymer having relatively low mobility, nonlinear photoconduction can be taken place prominently.

According to previous reports [5,6], nonlinear photoconduction in electric field applied parallel to the substrate has been observed, in addition, V_g applied to the perpendicular direction enables to promote the hopping of polaron pairs between main chains and form the state at high densities of polaron pairs in the channel. In consequence, because inter-pair recombination is performed effectively, it is considered that nonlinear photoconduction is amplified. However as applied high negative V_g , because the dissociations of polaron pairs are performed prominently and their chances of inter-pair recombination are decreased, it is considered that only nonlinear photoconduction can be gradually decayed.

In conclusion, we performed the time-resolved measurement of nonlinear photoconduction in PAT12 utilizing FET structure, and photoconduction contributed in its second-order process was observed. It was also found that V_g applied in FET structure enables to increase the densities of polaron pairs in the channel and modulate nonlinear photoconduction of PAT12.

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