Nanometer-Scale Dynamics of Charges Generated by Radiations in Condensed Matter

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Chapter 1. General Introduction

Nanosicence and nanotechnology have been one of the most famous terminologies in this several years for not only academic research fields but also industrial applications such as cosmetic, health care, and so on. Regarding the technology to inspect nanometer-scale topology, microscopes such as an atomic force microscope and a scanning tunneling microscope were developed and have served as the indispensable tool for the direct observation of ultra-small structure with high resolution on nanometer scale or less. Although the state-of-the-art microscope technologies provide the method to approach ultra-small structures with high-spatial resolution, their time-resolutions have not been enough to investigate the chemical and physico-chemical reactions which occur on femto-, pico-, and nano-second time scale. With respect to the spectroscopies of bulk materials without spatial resolution, ultrahigh-time resolution have been achieved with the advent of femto- or atto-second laser, which enables us to explore many kinds of chemical reactions.

The objective of the present work is to elucidate nanometer-scale dynamics of transient charges generated by radiations (photon and electron beam in this case) in condensed matter (organic solvents, polymers, and organic semiconductors). The polymers employed are a resist used as a mask in the lithography, and conjugated polymers/molecules which are expected to serve as a key material for next-generation high-informative society. Picosecond pulse radiolysis and time-resolved microwave conductivity techniques were used for the investigation of such an ultrafast nano-scale dynamics. The author developed and improved these measurement systems, and carried out experiments and computer simulations.

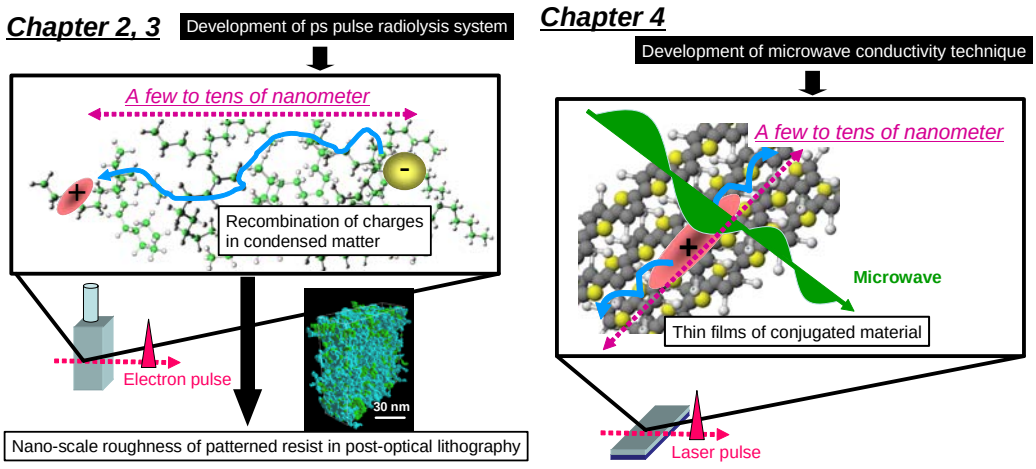

Figure 1. Graphic abstract of this thesis.

Chapter 2. Picosecond- and Nanometer- Scale Dynamics of Charges by Pulse Radiolysis

Pulse radiolysis is one of the most powerful tools to investigate ultra-fast chemical reactions induced by radiations. In order to perform direct observations of short-lived chemical intermediates and elucidate their nanometer-scale dynamics, firstly the author developed sub-ps and ps pulse radiolysis, demonstrating a significant improvement in the extension of

available wavelengths, high signal-to-noise ratio, and high time-resolution (Figure 2).

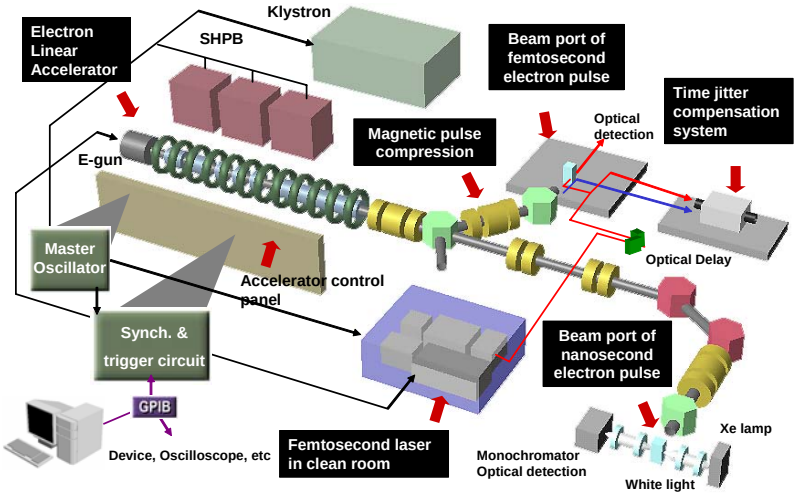

Figure 2. Schematic of subpico-, pico-, and nano-second pulse radiolysis at ISIR, Osaka University.

Using this system, secondly the author measured a geminate ion recombination in liquid alkane (Figure 3 (a)). The kinetic traces was analyzed by diffusion theory and converted to a time-evolution of spatial distribution of positive and negative charges (Figure 3(b)). The results give important information for the post-optical lithographies discussed in the next chapter.

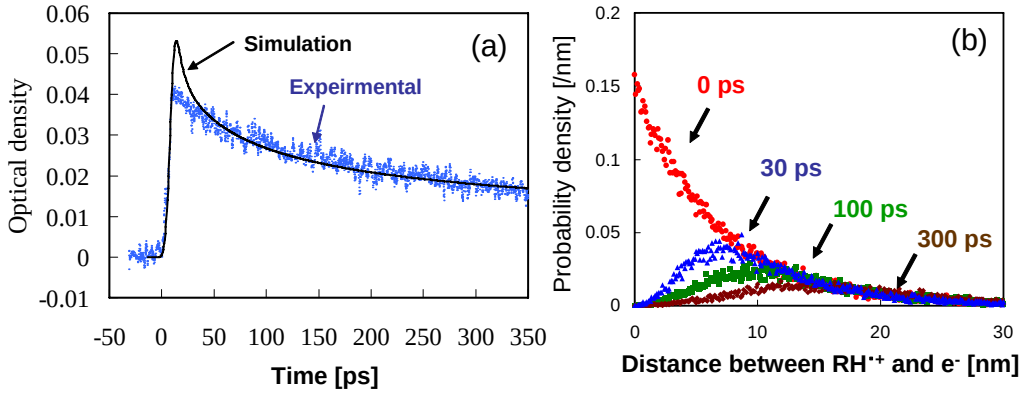

Figure 3. Kinetic trace of cation radicals in liquid n-dodecane monitored at 790 nm by ps pulse radiolysis. (b) Time evolution of distribution function obtained from fitting curve in (a). The horizontal axis indicates the distance between the cation radical ($RH\cdot^{+}$) and the electron (e^{-}).

Thirdly to investigate positive charge transfer from solvent radical cation to solute scavenger, the author examined the decrease of initial yield of solvent radical cations and their accelerated decays in the presence of high concentration scavenger (triethylamine). It was found that the initial yield significantly decreases with the increase of scavenger and this concentration dependence can not be explained by common diffusion theory. The author approached this issue by introducing "adjacent effect" which means immediate charge transfer without diffusion. The author formulated this effect by a statistical model and proved that the model account for the experimental observation. The author also examined this effect by developing original Monte Carlo simulation code to reproduce solvent-solute system (Figure 4). The result gave a good agreement with the experiments and indicated the charge transfer occurs in the first shell of solvent and solute.

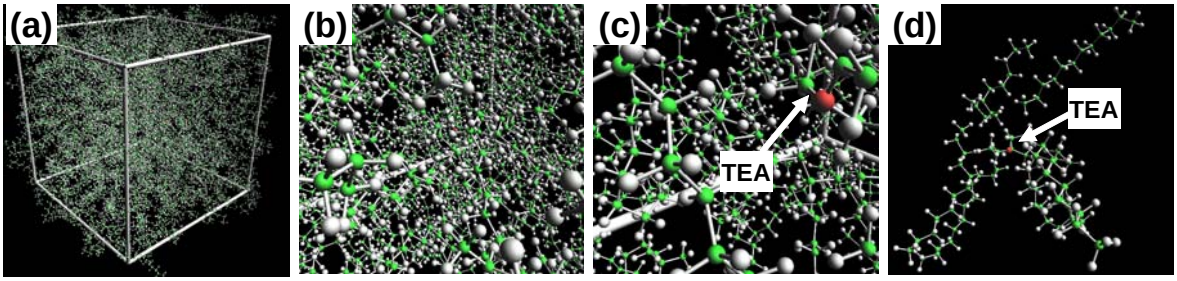

Figure 4. Reproduction of solvent-solute mixed solution by Monte Carlo simulation. (a) Outer-view (b) (c) Inside the box. (d) One solute (TEA) and solvents which are adjacent to each other.

Chapter 3. Nanometer-scale Dynamics of Proton and Acid in Resist Polymer

The progress of electronic devices has been supported by advances in "top-down" nanolithography. The energy of the exposure source would exceed the ionization potential of resist materials at the 32-nm technology node with the deployment of extreme ultraviolet light or an electron beam (EB). Among the issues of nanoscale fabrication with chemically amplified (CA) resists which enables highly-sensitive patterning by acid catalytic reaction during post exposure bake (PEB), line edge roughness (LER) is the most serious concern. The author investigated the dynamics of proton and acid in chemically amplified resist for post-optical lithographies by original Monte Carlo simulation (Figure 5). The dynamics were reproduced on the basis of experimental results of the picosecond pulse radiolysis shown in Chapter 2, where the nanometer-scale time evolution of spatial distribution between positive and negative charges was clarified.

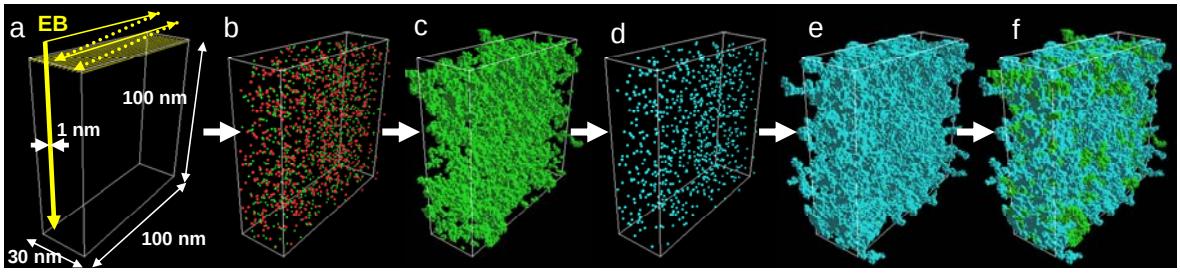

Figure 5. Nanomter-scale dynamics of proton, anion, and acid in EB-CA resist reproduced by Monte Carlo simulation. (a) Irradiated area (b) initial distribution of proton (green) and anion (red) (c) latent image catalyzed by proton (d) initial distribution of acid before PEB (e) latent image catalyzed by acid. (f) Superimpose of (c) and (e).

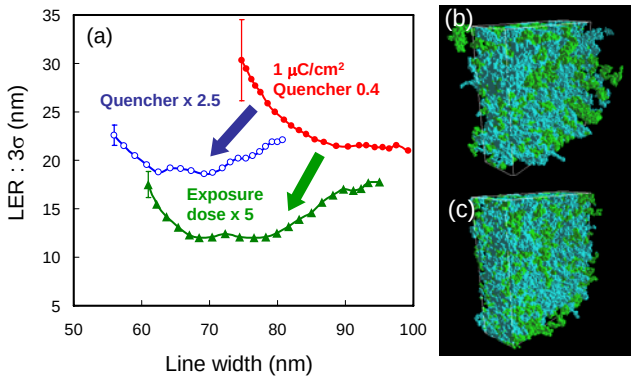

Figure 6. (a) LER dependence as a function of line width (acid diffusion). (b) Latent image which gives the mimimum LER on the red line (b) and the green line (c) in (a).

The author revealed the dependence of LER of latent images on line width (acid diffusion length), exposure dose, and quencher concentration, i.e. increase of exposure dose and/or quencher gives smaller LER and minimum LER point exists during the acid diffusion process (Figure 6).

Chapter 4. Dynamics of Charge Carriers by Time-Resolved Microwave Conductivity

In order to get insight into the intrinsic nature of charge carrier mobility and dynamics in organic semiconductors, the author developed an in-situ time-resolved conductivity (TRMC) and transient optical spectroscopy (TOS) system and applied to electrode-less measurement of photoconductivity in thin films of σ and π conjugated polymers and molecules. In conventional direct-current method such as time-of-flight and field effect transistor, there are many problems e.g. interface interaction between semiconductor and metal electrodes, grain boundary, and charge injection. Oh the other hand, the TRMC technique which is an alternating-current method can eliminate these factors and reflect a nanometer-scale charge transport property.

The author investigated regioregular polythiophene (RR-PT) films upon addition to tetracyanoethylene (TCNE) as an electron acceptor, and discussed the dynamics from the viewpoints of additive concentration, film morphology, and dependence of excitation wavelength. Figure 7 (a) shows the photoconductivity signal converted to the product of quantum efficiency of charge carrier generation (ϕ) and sum of mobilitiyes ($\Sigma\mu$) upon exposure to 355 and 532 nm laser pulse. The $\phi\Sigma\mu$ increases with the TCNE concentration, meaning the increase of ϕ and/or Σμ. The fluorescence from RR-PT shown in Figure 7 (b) resulted in exponential-type quenching with TCME concentration, suggesting electron transfer from RR-PT to TCNE. The kinetic traces of TRMC and transient photoabsorption at ca. 465 nm coincided to each other over four order of time scale. This indicates both signals originate from the same species: positive polaron in RR-PT. The intensity of transient photoabsorption increase to some extent with TCNE concentration; however, this is not enough to account for the significant increase of $\phi\Sigma\mu$. From these experiments, the author deduced that the increase of $\phi\Sigma\mu$. is due to the increase of mobility which probably arises form the matching of molecular orbital of RR-PT and TCNE rather than the enhancement in micro-ordering of the molecules.

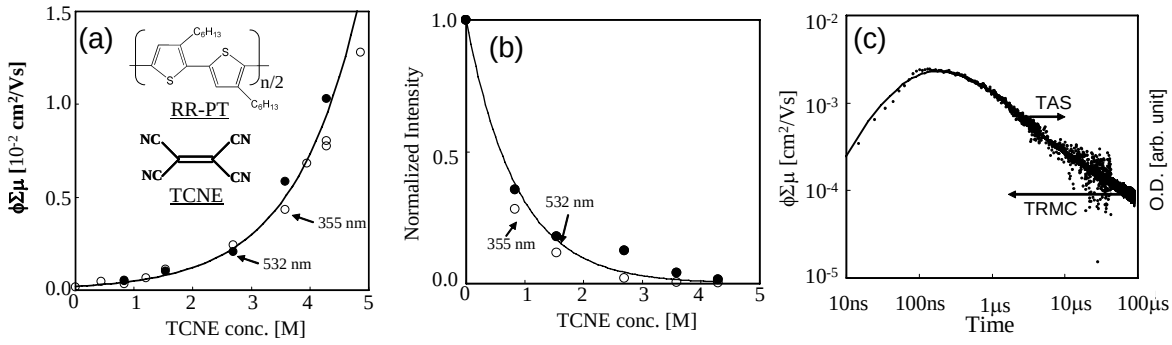

Figure 7. (a) Photocunductivity signal obtained by TRMC in the mixture films of RR-PT and TCNE upon exposure to 355 and 532 nm laser pulse. (b) Fluorescence intensity as a function of TCNE concentration. (c) Kinetic traces of TRMC and transient photoabsorption spectroscopy (TAS).

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