Fabrication of organic conductive wires and molecular break junction

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Abstract. Break junction have been proposed as one of methods for making a molecular-scale nano-gaps between the two metallic electrodes. Here we had made organic metallic wire bridges being consist of tetrathiafulvalene-tetracyanouindimethane (TTF-TCNQ) organic charge transfer complex, and then gradually disconnected the bridged molecular wires by a Joule heating to make a molecular-size gap or single-molecular junction. The observed conductance of the initially high conductive wires decreased by a direct current (DC) Joule heating. The conductance exhibited several different behaviors with the stage of the thermal desorption of molecules, and finally disconnected. Significant increase and decrease of the conductance were observed just before the disconnection. After the DC treatment and before the disconnection of the wires, we switched to alternation current (AC) Joule heating to make a single-molecular junction which would work as a single-molecular transistor. During the AC Joule heating, many discrete steps were found in the time evolution of the conductance. The steps were approximately 1 pS or its multiple, and the duration of the step were nearly the same (approx. 300 - 400 s) in the final stage of the AC Joule heating. We conclude that the step height corresponds to the single-molecular conductance and the duration reflects the probability of single TCNQ molecular desorption.

1. Introduction

Many organic and inorganic nanostructures such as nano-dots, nano-wires, and nano-rods etc. have been constructed by bottom-up or self-organization methods. However, it is always difficult to make a wiring in the nanostructures. In addition, an interface double layer and depletion layer are generally formed at an interface of the semiconductor and metallic wires. Although these phenomena cause a contact resistance for the macroscopic devices, they crucially affect for the single-molecular devices because the electronic state of single molecule is fully modulated by the metallic wire contact.

We had proposed novel wire-type organic nano-transistors using a self-aligned formation techniques induced by an external electric field [1-5]. We had developed spontaneous and self-aligned formation techniques of organic nano-transistors using well-known organic conductor TTF-TCNQ [6-16]. Oriented growth and succeeding self-aligned connection were induced by an external electric field.

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during a co-evaporation of the TTF and TCNQ [4-6]. Due to the lack of TTF at the growth tip, nano-TCNQ region was spontaneously formed at the junction. In this way, nano-TCNQ-transistors wired by organic conductive wires were formed[17-19]. These nano-transistor exhibited n-channel field effect transistor (FET) characteristics, which reflected the acceptor nature of TCNQ. The channel length of the spontaneously formed channel was 400 - 700 nm, which was estimated with the AFM potentiometry [20]. These nano-devices were spontaneously formed and free from carrier injection barrier in principle [17].

In this paper, we present the field-induced crystal growth of TTF-TCNQ by making use of static electric field to make connected TTF-TCNQ wires. Then we tried to disconnect these connected wires by DC Joule heating. DC Joule heating was carried out under the constant voltage operation because the constant voltage operation has a self-ceasing effect on the Joule heating. Since the self-ceasing effect was insufficient to make a single molecular junction, we applied AC Joule heating to achieve a single-molecular desorption at around several-molecular junction formed by the DC pretreatment.

2. Experimental details
Field induced selective growth of TTF-TCNQ was carried out using an in-situ observation chamber specially designed for this experiment. The in-situ observation chamber has a large quartz window at the top of the body. The growth of TTF-TCNQ is observed through the window by a long working-distance optical microscope. In this method, one can observe the growth process in real time and without any additional image processing. The shape of designed Cr/Pt electrode is a parallel electrode with several triangular tips. The applied voltage during the field induced growth was in the range of 20 – 60 V. Under a quasi-thermal equilibrium condition, TTF-TCNQ conductive wires are expected to selectively grow from these tips of the electrode and grow along the electric lines of force. With increasing the crystal length, the electric field between the growth tip of two organic conductor increases. Therefore, these organic conductors finally make a connection at each growth tips.

In the DC break junction, constant DC 1 – 3 V was applied to the connected TTF-TCNQ wires according to the sample condition. If the applied voltage is too high, the connected TTF-TCNQ wires immediately burn out. Since there is a high resistive point at the connecting point of two TTF-TCNQ wires, the proper applied voltage is fixed by the electrical resistance of the sample i.e. the connecting point. The constant voltage DC mode is useful to our purpose. Because the electrical current through the connected wires decreases with increasing sample resistance, the Joule heat automatically decreases; this method has an effect to prevent avalanche blow out of the wires in the final stage of the break junction. In addition, AC break junction is conducted to make it possible more critical Joule heating by avoiding the continuous heating. In the AC break junction, applied AC amplitude was selected in the rage of 1 -10 Vp-p, and the frequency was selected to be 7020 Hz. 7020 Hz is near the limit of a time resolution of the lock-in amplifier to measure an electrical conductance.

3. Results and Discussion
Figure 1 is an optical micrograph of grown TTF-TCNQ crystals and wire bridges around the electrode tip. The voltage applied during the growth was 40 V at the left side electrode. Tiny TTF-TCNQ crystals grew from the electrode and some wires made a connection. By an analysis of the time variation of the captured image, the preferential growth from anode and high electric field area is clearly revealed. Incubation time was the shortest and crystal growth rate was the highest in the anode and high electric field area. On the other hand in the cathode side and high electric field area, the incubation time was the longest and crystal growth rate was the lowest (to be published elsewhere). Therefore, a speculated picture of this selective growth was explained by a molecular drift motion of ionized TCNQ along the electric field. Distribution of negatively ionized TCNQ molecules is biased toward the anode by the electric field.

Next, we tried DC molecular break junction to develop a molecular-level nano-gap electrode or nano-transistor. If an electric current through the connected TTF-TCNQ wire is applied, generated Joule heat is concentrated at the high resistant connecting point. The connecting points are originally
high resistant because of the lack of TTF concentration and the low cross section compared to the trunk of the wire. Since TTF has higher vapor pressure compared to TCNQ, TTF molecules at around the junction firstly vaporize, and as a result, the resistance at the junction increases. The increase of resistance causes more concentration of the Joule heat at the junction.

Figure 2 shows the time evolution of the total electrical conductance of the sample under the application of DC 2 V. Characteristic decrease of the electrical conductance was observed. In the initial stage of Joule heating, the conductance slowly decreases. This period is assigned as an initial TTF desorption process, which have an effect to fix the high resistance point. Then after 70 s, steep decrease of the conductance began. This steep decrease of conductance corresponds to the main and successive TTF desorption. After 70 s, characteristic slower decay of the conductance and the significant increase and decrease which was larger than the base noise level were observed until 270 s. This stage corresponds to the TCNQ molecule desorption at the junction because the concentration of the generated Joule heat was accelerated by the vaporization of the TTF. Then, after 270 s, the conductance exhibited the very slow decay and significant increase and decrease exceeding the base noise level. After a large increase of conductance at 440 s, the TTF-TCNQ wires finally disconnected at 460 s. The nearly constant conductance with significant rises indicates that the competition of desorption and adsorption of TCNQ occurred at the heated junctions. We have found no discrete step on the conductance change even after statistical analysis due to the lack of the time resolution and the controllability of the generated Joule heat.

As an advanced trial, AC current application was conducted after the 3rd stage of the DC treatment. The advantage of the continuous and constant AC pulse train application is to prevent an avalanche burning of the junction. Figure 3 shows an example of the time evolution of the total conductance during AC Joule heating. Amplitude of the applied sine wave voltage on this sample was set to 10 V_{p.p}. Since continuous AC voltage generates well-controlled heat pulse train of $V^2/R$ Joule/pulse, AC Joule heating is better than DC method to achieve a single molecular disconnection. If the generated Joule heat is comparable to or slightly lower than the thermal energy required for the single event of TCNQ adsorption, no single event occurs within the single heat pulse. Under this condition, the number of the heat pulse reflects the probability of the single molecular desorption under the supplied thermal energy. In figure 3, discrete steps of total conductance are observed. The difference of the conductance at each step is approximately 1 pS or it’s multiple as indicated in figure 3. Moreover in the final stage, the duration of one step (approximately 300 - 400 s) is almost the same in each step.
The observed discrete increase and decrease of the conductance correspond to the single molecule desorption at molecular junctions. Due to our experimental results, single molecular desorption occurs in every $300 - 400$ s i.e. $2.1 - 2.8 \times 10^6$ pulses. In the final stage of the Joule heating, an electrical current is concentrated at the single molecular bridge as illustrated in figure 4. The heat pulse generated by the single current pulse defines the effective local temperature ($T_{local}$) at the molecular bridge. The single event of molecular desorption stochastically occurs every $2.1 - 2.8 \times 10^6$ pulses. The assumed $T_{local}$ is now under estimation by the molecular dynamics calculation. In addition, it is supposed that there exist many parallel molecular bridges because the conductance oscillation observed in this experiment will cease if the last molecular bridge burn out. In our rough estimation, 20 - 50 molecular junctions will parallel exist.

4. Summary
We had made organic metallic wire bridges of TTF-TCNQ organic charge transfer complex, and then gradually disconnected them by DC and AC Joule heating to make single-molecular junctions. The observed conductance under DC Joule heating exhibited several different behavior with the stage of the thermal desorption of molecules, and finally disconnected. After the DC treatment and before the disconnection of the wires, we switched to AC Joule heating to make a single-molecular junction. During the AC Joule heating, many discrete steps were found in the time evolution of the conductance. These steps were approximately 1 pS or it’s multiple, and the duration of the step were approximately $300 - 400$ s in the final stage of the AC Joule heating. We have concluded that the step height corresponds to the single-molecular conductance and the duration reflects the probability of single molecular desorption.

Acknowledgments
This work was supported by Grant-in aid for Scientific Research and Chiba University Global COE Program from Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. Part of this study was conducted by the support from the “Toyo University nanotechnology Network”, which comprises the “Nanotechnology Network Japan” by MEXT.

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