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Current Oscillation and Pulse Generation Based on Nonlinear Conducting Behaviors in Organic Molecular Systems

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Abstract– Nonlinear conducting behaviors and negative differential resistance in organic solids and their physical mechanism are briefly introduced. The current oscillation and the pulse generation based on the nonlinearity in several materials are shown. The observed phenomena are the relaxation oscillation. The problems and the challenges inherent to the organic materials are discussed.

1. Introduction

The recent development of organic electronic materials is conspicuous. Their luminescence properties, photovoltaic effects and transistor behaviors are intensively studied. Nonlinear responses are widely investigated as well. They range from nonlinear optical effects which are purely electronic responses to nonlinear conducting behaviors, which sometimes involve the dynamics of not only electrons but lattices. In this paper, the author focuses on the nonlinear conducting behaviors and shows the examples and the applications.

The nonlinear conducting behaviors in organic materials have been studied for a long time. Iwasa *et al.* reported the systematic study of the negative resistance in various organic charge-transfer complexes [1]. According to the paper, a wide variety of charge transfer complexes commonly show nonlinear behaviors to the electric field and negative differential resistance (NDR). Up to now, the nonlinear conducting behaviors in various organic complexes have been reported [2]. These studies are partly related to the guideline for development of organic conductors. Such studies aimed at charge transfer between the constituents, so that the open-shell electronic systems are obtained. The open-shell states do not always lead to organic conductors. Various interactions or ordering phenomena, most of which are related to the low dimensional nature, make the systems insulating. Namely, the conducting states and the insulating states are energetically competed. In such situations, the application of electric field or the injection of charge carriers might affect the electronic states and change the resistivity. Actually, several organic charge transfer complexes show nonlinear conductance. Such change of the states is often observed as switching phenomena, which are attractive from the viewpoints of not only materials science but information technology. Though the nonlinear conducting behaviors and the switching effects have long been studied, advanced studies beyond such observations to functionality are quite few. A notable exception is the study by Sawano *et al.* in 2005 [3]. They reported that θ-$(BEDT\text{-}TTF)_2CsCo(SCN)_4$ salts show a current oscillation under the application of static voltage at 4.2 K. In their experiments, the external circuit components were only a series resistor and a voltage source and the frequency was controlled by the external voltage. The author was inspired by the study of Sawano *et al.* and started the study of the application of nonlinear conducting behaviors to the oscillation or other functionality. In this paper, the author reviews a part of nonlinear conducting properties in organic compounds and discusses the relevant functionality. Moreover, the strategy for improvement of the functionality and trials are discussed.

2. Electronic States and Nonlinear Conductivity

In organic charge transfer complexes, several electronic states are energetically competed and the external field might induce the change of the electronic states, leading to nonlinear conducting behaviors. Here, a typical example is shown. In K-TCNQ (TCNQ: tetracyanoquidimethane), TCNQ molecules stack and form one-dimensional columns. K^+ ions also show a one-dimensional arrangement parallel to the TCNQ columns. One electron is transferred from K to TCNQ, so that $TCNQ^-$ molecules form open-shell states. At room temperature, TCNQ molecules are dimerized due to spin interaction between TCNQ molecules and the complex is insulating. Above 395 K, the dimerization disappears and the molecular arrangement is uniform. These two states show different resistivities. It was revealed that, at room temperature, the current injection makes the dimerized state transit to the regular stacking state [4].

Another example of the nonlinearity is observed in TTF-CA (TTF: tetrathiafulvalene, CA: chloranil). In this compound, TTF and CA are alternately stacked and form one-dimensional columns. TTF acts as donor and CA acceptor. The quantity of charge transfer between TTF and CA is dependent on temperature. At low temperature, TTF and CA form dimers, where the degree of charge transfer between TTF and CA, ρ, is beyond 0.5 (here, $\rho = 1$ corresponds to one electron transfer from donor to acceptor) and the compound is regarded as in an ionic state. This state is stabilized by the Madelung energy,

which is the energy gain by an alternating arrangement of positive and negative charges. On the other hand, in the high temperature phase, the degree of charge transfer is small and a neutral state is formed. It was reported that the nonlinear conductance is observed in this compound [5].

The other example is seen in halogen-bridged nickel compounds. In this compound, halogen atoms and nickel atoms are arranged alternately and form one-dimensional chains. The valence of Ni atoms is +3 and the number of d electrons is 7, indicating the formation of open-shell electronic systems. However, due to the strong electron correlation, Mott insulating state is formed. The application of strong electric fields leads to the nonlinear conducting behaviors [6,7]. The origin of this nonlinearity is not clear at present.

Thus, the materials discussed here commonly have open-shell and insulating electronic states and show nonlinear conducting behaviors. The mechanism which makes the open-shell systems insulating might govern the nonlinear conducting behaviors. In some cases, the field-induced breakdown of the insulating mechanism leads to the nonlinear conducting behaviors.

3. Current Oscillation Using Nonlinear Conducting Behaviors

In this section, a method to give rise to current oscillation and pulse generation is shown. By combining the materials showing nonlinear conductance with the external circuit shown in Fig. 1, the spontaneous current oscillation is obtained.

The abovementioned materials show not only the nonlinear conducting behaviors but the NDR behaviors. The schematic current(I)-voltage(V) behavior is shown in Fig. 2(a). At low current, the materials show a linear conductance which is described by Ohm's law. With increase of current, the transition to a low-resistance state is achieved and NDR is observed. After the completion of

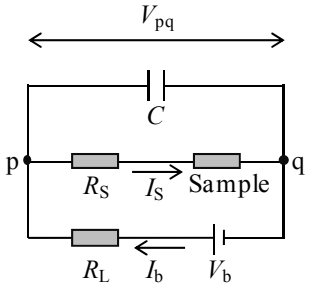

Fig. 1 Circuit for current oscillation using the sample showing negative differential resistance.

the transition to the low-resistance state, I-V curve should show positive differential resistance. However, in a real material, such positive differential resistance is hardly observed experimentally because such recovery of positive differential resistance requires a large current which leads to the breakdown of the sample. In order to get a positive slope in the higher current region, one series resistor R_s is added as shown in Fig. 1. As a result, an S-shaped I-V curve is obtained. Then, a voltage source (voltage: V_b) and a series resistor R_L are connected as shown in Fig. 1. Here, the voltage between the two points p and q (V_{pq}) is discussed. V_{pq} of the path via the sample should be S-shaped, while that of the path via the voltage source should be described by a line (load line) determined by R_L and V_b. The intersection shown in Fig. 2(a) is the solution and the stable point of this circuit. Moreover, a parallel capacitor C is added for the introduction of temporal instability. Resultantly, the intersection of the S-shaped curve with the load line is not reached. After the voltage source is switched on, the charging to the capacitor starts and the operating point reaches the point A through the branch α (Fig. 2(b)). As V_{pq} is also the voltage of the capacitor, the temporal discontinuity of V_{pq} is prohibited. Then, after reaching the point A, it jumps to the branch γ, in which the discharging occurs, and reaches the point B. Due to the continuity of the voltage, it jumps down to the branch α. Then, the

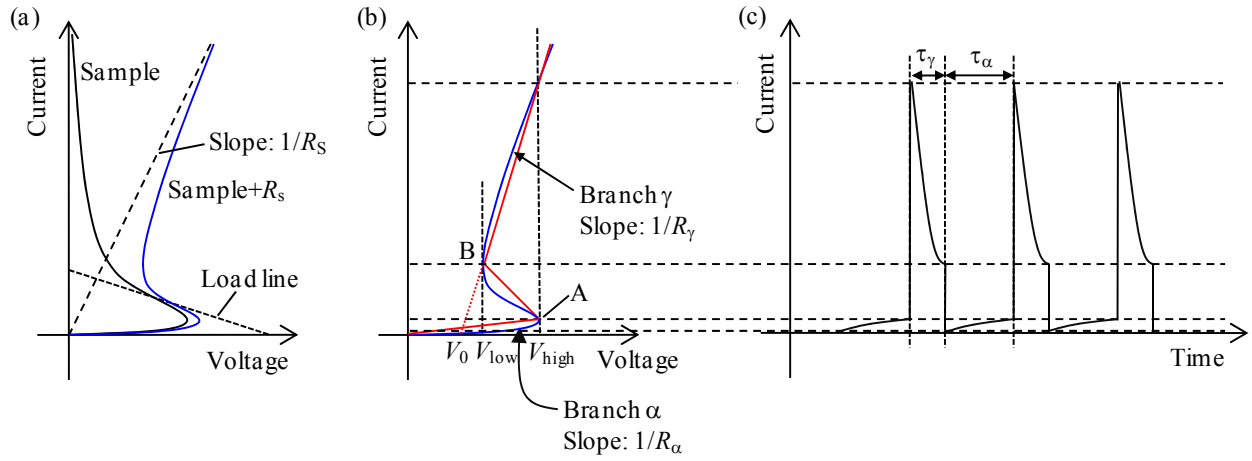

Fig. 2 (a) Typical behaviors of NDR samples and sample+series resistors. Load line is also indicated. (b) Linear approximation of NDR+R_s. (c) Schematic of oscillatory current.

cyclic motion is continued. The schematic of these temporal motions is shown in Fig. 2(c). In the materials, the branch α is the high-resistance state, namely, the insulating state and the branch γ is the low-resistance state, namely, the state in which the insulating mechanism does not work or is weakened.

The example of the current oscillation in K-TCNQ is shown in Fig. 3 [8]. A clear oscillation is achieved at room temperature. The oscillation is stably continued. The observed phenomenon is similar to the blinking of a neon tube which is known as the Pearson-Anson effect [9]. This phenomenon is classified as a relaxation oscillator. Judging from Fig. 3 (upper right), the oscillatory waveform is not sinusoidal but pulse trains. This comes from the fact that the sojourn times on the branches α and γ (τ_α and τ_γ, respectively) are different. Using the linear approximation of the two branches shown in Fig. 2(b), the oscillation period T and the ratio are described as follows [6]:

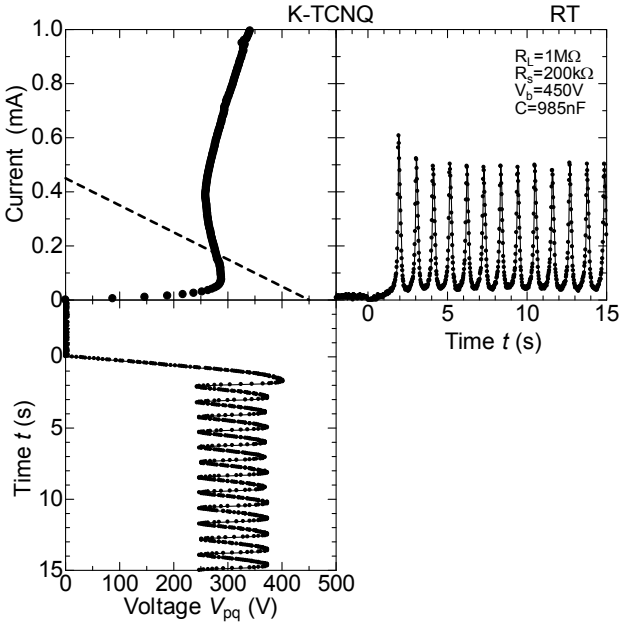

Fig. 3 (Upper left) *I-V* characteristic of K-TCNQ and a series resistor (dots) and the load line (dotted line). (Upper right) Temporal profile of current oscillation. (Lower) Temporal profile of voltage. Reprinted from the paper: H. Kishida *et al.*, *Appl. Phys. Express*, vol. 4, 031601, 2011. © 2011 The Japan Society of Applied Physics.

$$T \approx \tau_\alpha + \tau_\gamma = \frac{R_L R_\alpha}{R_L + R_\alpha} C \ln\left(\frac{V_{low} - E_1}{V_{high} - E_1}\right) + \frac{R_L R_\gamma}{R_L + R_\gamma} C \ln\left(\frac{V_{high} - E_2}{V_{low} - E_2}\right) \quad (1)$$

and

$$\frac{\tau_\gamma}{\tau_\alpha} = \frac{R_L + R_\alpha}{R_L + R_\gamma} \cdot \frac{R_\gamma}{R_\alpha} \times \ln\left(\frac{V_{high} - E_2}{V_{low} - E_2}\right) / \ln\left(\frac{V_{low} - E_1}{V_{high} - E_1}\right). \quad (2)$$

Here, $E_1 = R_\alpha V_b / (R_L + R_\alpha)$ and $E_2 = (R_L V_0 + R_\gamma V_b)/(R_L + R_\gamma)$. Parameters are defined in Fig. 2(b). These equations indicate that the oscillation period and the pulse width can be controlled by the external circuit parameters. The examples of the control by the capacitance, the voltage and R_L in halogen-bridged nickel compounds are shown in ref. [6,7].

Specific circumstances of the organic crystals should be considered. In the low-resistance state, a relatively large current flows and the temperature change due to the joule heating might affect the *I-V* curve. As a result, the current and the voltage do not trace the static *I-V* curve. This heating effect might be reduced by the decrease of the sample size.

4. Strategy for More Stable Oscillation and Trials

The abovementioned mechanism induces phase transitions or changes of electronic states with each oscillation period. They are often accompanied by the change of lattice, namely, the change of position or form of molecules. Because it sometimes leads to a macroscopic damage to the crystal such as cracks, it is not preferable. In order to avoid this, the phase transition in which the lattice change is smaller should be used. One example is the field-induced breakdown of Mott insulating state. The other is the case that the long-range Coulombic interaction induces the ordering of the charge configuration, which leads to an insulating state without the help of lattice deformation. If the field-induced resistivity change is observed using the charge-ordered state of the organic compounds, it is preferable because the lattice change is expected to be small. The nonlinear conducting behaviors in such materials are reported in ref. [10,11], in which the target material is α-(BEDT-TTF)$_2$I$_3$ (BEDT-TTF: bis(ethylenedithio)-tetrathiafulvalene). This compound shows the charge-ordering below 135 K. The nonlinear conducting states are optically revealed by the electronic Raman scattering method [11]. By using this compound, Ito *et al.* achieved the current oscillation whose period is 63 msec [12].

Another target system is the materials which have a higher symmetry. To this end, the constituent molecule should be also a symmetric material. For example, the coronene complexes are a possible candidate. Actually, one coronene complex, $(coronene)_3Mo_6Cl_{14}$, has a cubic lattice and shows charge disproportionation in the crystal [13]. This might lead to a more controllable field-induced change of the state.

5. Conclusions

Spontaneous current oscillation and pulse generation based on the NDR behaviors in several open-shell electronic systems such as organic charge transfer complexes and halogen-bridged nickel compounds were achieved. The oscillation is explained by alternating occurrence of high-resistance state and electric-field-induced low-resistance state. The oscillation includes the alternating phase change or phase transitions. Therefore, to improve the oscillatory behaviors, we should consider the system in which the motion of the lattice is smaller.

Acknowledgments

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