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Nonvolatile memory device based on the switching by the all-organic charge transfer complex

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The authors have investigated the nonvolatile memory device by the amorphous charge transfer complex of 2, 4, 7-trinitro-9-fluorenone and poly(*N*-vinylcarbazole) as a spin-coated active layer. The reversible switching can be controlled by the external electric field and the on/off ratio is more than three orders at 1 V. The device operation might be interpreted as the generation and the extinction of charged carriers in the active layer through the results of the capacitance and the impedance at each state. © 2006 American Institute of Physics. [DOI: 10.1063/1.2360220]

There is much interest in organic electronics such as organic light emitting diodes, organic solar cells, and organic thin film transistors because of low cost, flexibility, and large area applications.¹⁻³ Recently, attentions have been extended to nonvolatile memory (NVM) devices with organic materials as the active layer. The devices showed bistability by the switching behaviors of the cell resistances by the external electric field.⁴⁻¹⁴ There are some reports about their switching mechanism, the field-induced percolation of the nanoparticles in the pentacene layer,⁶ the trapping of the major carriers in poly(*N*-vinylcarbazole) films,⁸ the electric-field-induced charge transfer between the different moieties,⁹⁻¹¹ and the phase transition in the charge transfer (CT) complex of Cu and 7,7,8,8-tetracyanoquinodimethane (TCNQ).¹²⁻¹⁴ But these devices have also some issues, the reproducibility by defects and the dispersion uniformity of the particles and the chemicals in the matrix. The CT complexes composed of the donor and the acceptor molecules in solution would have some advantages within these points of view. The representative CT complex, Cu:TCNQ, also had the reversible switching property but there were also some doubtful points as follows: the homogeneity in the thick film by the wet process¹²⁻¹⁴ and the variation of film texture with the deposition ratio in the thin film by coevaporation.¹⁴ In addition, the reported all-organic CT complexes were incompatible for the practical NVM device.¹⁵⁻¹⁷ The switching behaviors in the mixed-stacked all-organic CT crystals were observed only below 200 K which was too low to apply to a practical device.¹⁶⁻¹⁸ Other devices with all-organic CT complexes also showed switching phenomena at room temperature but these were only write-once read-only memory.¹⁷ Here, we report the programmable NVM device consisting of the all-organic CT complex which was operating at room temperature and easily fabricated by the solution process. The CT complex is made of 2,4,7-trinitro-9-fluorenone (TNF) and poly(*N*-vinylcarbazole) (PVK) which are the well known materials in electrophotography.¹⁹⁻²¹ TNF was synthesized by the nitration of fluorenone, recrystallized from acetic acid,²² and PVK (molecular weight ~90 000) was purchased from Acros Organics. The TNF:PVK CT complex is formed by the direct reaction of two materials in the solution.^{19-21,23} In general, the interaction between CT complex molecules is usually much weaker than the covalent bond, but it is useful

for constructing crystal structures. The TNF:PVK thin film shows the same x-ray diffraction spectra as the PVK thin film and has much rougher surface than the PVK thin film. It is agreed that the thin TNF:PVK film is amorphous, unlike the typical organic CT complexes, and is composed of free TNF and PVK molecules and CT complexes.^{19,20} Figure 1 shows the surface image of the TNF:PVK thin film in the mole ratio of 0.6:1 and the sandwichlike structure of a postulated TNF:PVK CT complex.

The evaluated devices were the cross-point cell structure as shown in Fig. 2. The device preparation involved the subsequent deposition of a 50 nm Al₂O₃ film as an insulator layer and a 50 nm Al film as the bottom electrodes on a silicon wafer by the electron beam evaporation. And then the sample was heat treated at 400 °C for 2 h under atmosphere and was characterized by x-ray photoelectron spectroscopy. The oxidized bottom electrodes were useful to improve the on/off ratio.¹⁴ The TNF:PVK mixture in 1,2-dichloroethane was formed to a 50 nm thin film by spin coating and dried at 50 °C for 30 min under vacuum. Subsequently, 50 nm Al film as the top electrodes was deposited at the rate of 0.3 nm/s. Finally, the prepared device surface except for the electric contact pads was fully deposited with a 50 nm Al₂O₃ film as the passivation layer to protect from outside circumstances during the electric test and the device storage. All deposition processes were carried out under a high vacuum (~8 × 10⁻⁶ Torr) at room temperature. The fabricated devices were typically 1 mm² in active area and characterized by semiconductor analyzer HP 4155A for current-voltage properties, HP 4263B LCR meter for capacitance-voltage properties, and HP 1255A frequency response analyzer for impedance-frequency properties. All electric evaluations were carried out in a black box at room temperature.

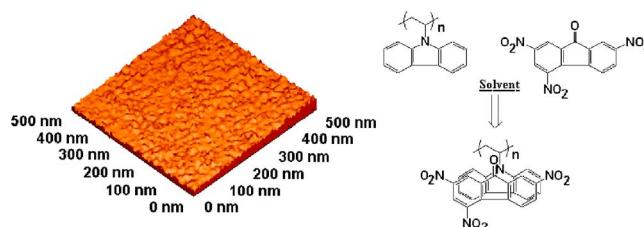


FIG. 1. (Color online) Surface image of the TNF:PVK thin film in the mole ratio of 0.6:1 by atomic force microscopy and the chemical structure of a postulated TNF:PVK CT complex.

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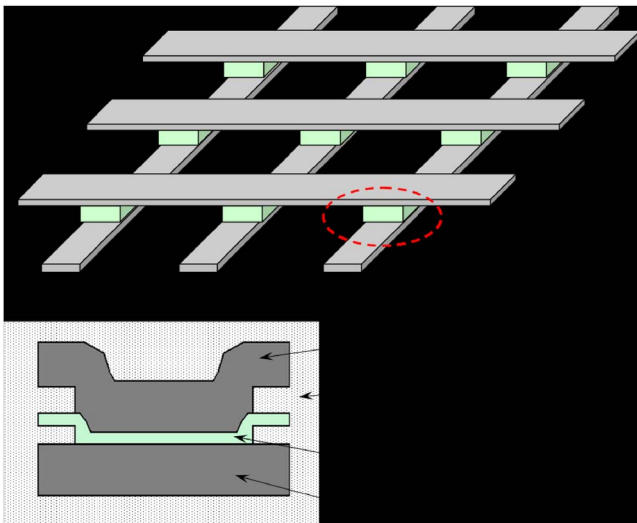


FIG. 2. (Color online) Schematic diagrams of the cross-point cell structure and the cross section of the organic device. The Al_2O_3 layers protect the organic active layer from the breakdown at the electrode edges and the outside circumstances during the electric test and the device storage.

First, we investigated the electric properties depending on the composition of the CT mixture. The maximum on/off ratio with the stable switching property was observed in the TNF:PVK mixture of 0.6:1 with the highest dielectric constant¹⁹ and the saturation density of CT complex molecules in the mixture.²⁰ The current-voltage curves in Fig. 3 showed general properties of the stabilized device with the TNF:PVK mixture of 0.6:1. The current abruptly changed from $\sim 10^{-8}$ to $\sim 10^{-4}$ A at 2.5 V during the forward bias scan. The on state with the low resistivity was continuously kept during the second forward bias scan from 0 to 3.5 V. During scanning of the reverse bias from 0 to -5 V, the current was suddenly decreased at -4.2 V and the device was changed from the on state to the off state with the high resistivity. Each state was maintained after disconnecting the external electric field and the on/off ratio of current at 1 V was more than 10^3 . Also, the devices often showed a 10^5 of on/off ratio during the first bias scan and the variations of the erase and the write voltages were about 1.5 V. These might be related to the variations of the fabrication processes and the material preparations for the CT complex devices. The

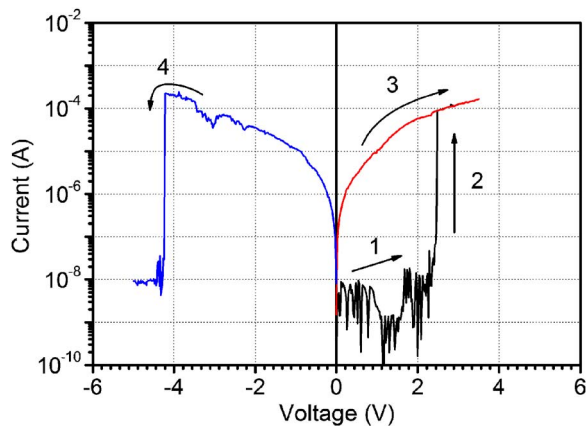


FIG. 3. (Color online) Typical current-voltage curves at the TNF:PVK thin film in the mole ratio of 0.6:1: Curve 1, forward bias (off state); curve 2, turn on (write); curve 3, forward bias (on state); and curve 4, turn off (erase).

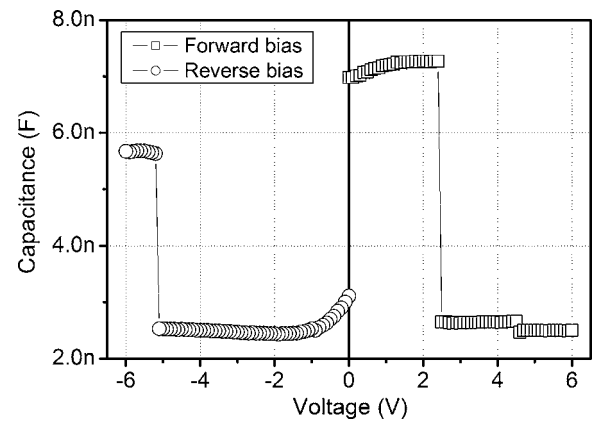


FIG. 4. Typical capacitance-voltage curves at the TNF:PVK thin film in the mole ratio of 0.6:1. (forward bias: $0 \rightarrow 6$ V, Reverse bias: $0 \rightarrow -6$ V).

switching behavior was not reported in the previous study using the TNF:PVK thick film, but it could be explained in view of the CT complexes with the ionic and the neutral crystals.^{21,24} In the thin TNF:PVK films, there may be no ionic-stacked domains with high electrostatic interaction between the CT complexes because of the amorphous film with the abundant defects and the off state in the as-received device. But the interaction between TNF and PVK molecules might be the ionic state and/or the neutral state. In the case of the ionic state, some TNF:PVK CT complexes may undergo a reverse polarity in the antiferroelectrically ordered stacks during the high electric field. And the current may be abruptly increased by succeeding multiplication of charge carriers in the higher electric field (on state). The amorphous CT complex may have many antiferroelectrically ordered stacks because of the random orientation of CT complexes. If the interaction is a neutral state, some of the complexes might be thermally activated to the ionic state which has been proposed as the carriers of the electron current. These ionic CT complexes will promote intermolecular electron transfer in the favorable direction under the electric field. The successive multiplication of ionic state will induce the device to the on state. In the switching behavior, the amorphous CT complex may be much efficient to create and keep the charge carriers which are preserved by abundant defects for a long time.

The capacitance-voltage characteristics in 100 KHz were also conducted to investigate the dielectric conditions of the CT complex during the bias scan in the range from 0 V to 6 and -6 V. As shown in Fig. 4, the device capacitance was suddenly decreased at 2.5 V and abruptly increased at -4.2 V. These changes occurred at the same switching voltages in the I - V characteristics, which may be related to the generated charges in the system or the injected charges from electrodes. In this system, the abrupt changes of capacitances may be attributed to the generated charges in the CT complexes because the injected charges may gradually change the device capacitance with electric field and the recombination of carriers cannot increase the capacitance at the high electric field.²⁴ The generated charges may also disappear suddenly by the external electric field and the device capacitance may return to the former state. The generated charge may be related to the charged defects from the ionic state of the CT complex at the high electric field.

The impedance-frequency characteristics were carried out to understand the properties of conduction carriers at

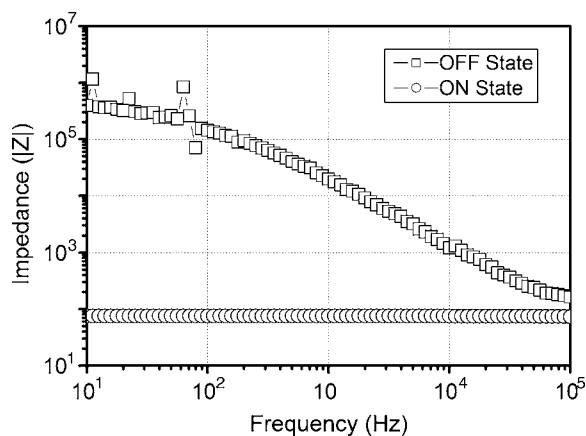


FIG. 5. Impedance-frequency curves followed by each state of the device at the TNF:PVK thin film in the mole ratio of 0.6:1.

each device state. Each state shows different impedance curves with frequency in Fig. 5. The impedance did not change up to 10^6 Hz at the on state but it seems to be proportional to $1/\omega C$ at the off state, where ω is the angular frequency and C is the capacitance. The consistent impedance at the on state may be due to the existence of the charge carriers from the CT complex.¹³ In the off state, the generated charges may disappear in the stabilized CT complex.

In summary, we demonstrated a reversible and programmable NVM device by the amorphous all-organic CT complex at room temperature which showed more than 10^3 of the on/off ratio and less than 6 V in the operation voltage. The switching phenomena of the TNF:PVK CT complex at room temperature may be due to the amorphous structure with low electrostatic interaction and abundant defects, unlike the usual crystalline organic CT complexes. The switching behavior in the device may originate from the generation and the extinction of charged carriers in the active layer.

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