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Switching effect in Cu:TCNQ charge transfer-complex thin films by vacuum codeposition

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We demonstrate the operation of an organic switching device using a uniform poly-crystalline Cu:7, 7, 8, 8-Tetracyanoquinodimethane (TCNQ) charge transfer (CT)-complex thin film that is prepared by vacuum vapor codeposition. Characteristic CT-absorption at $\lambda=600\text{--}1200\text{ nm}$ was observed in the complex film in the UV-visible spectrum and the cyano stretching peak in the IR spectrum shifted to a higher (more than 29 cm^{-1}) wave number than that of a pristine TCNQ film, suggesting the formation of a CT-complex in the evaporated thin film. Reproducible electrical switching characteristics were observed in the indium tin oxide/Al/(Al₂O₃)/Cu:TCNQ/Al structure. The device exhibited a clear threshold from low impedance to high impedance at an applied voltage of $10.0\pm2.0\text{ V}$ and a reverse phenomenon at a negative bias of $-9.5\pm2.0\text{ V}$. In this study, we demonstrate that a thin Al₂O₃ layer between the aluminum (Al) anode and Cu:TCNQ layers creates reproducible switching. © 2003 American Institute of Physics. [DOI: 10.1063/1.1600848]

There has been a growing interest in organic electronic devices such as organic light emitting diodes (OLEDs),¹ organic solar cells,² organic transistors,³ and organic switching devices^{4–13} due to the unique electrical and optical properties of organic materials. Recently OLEDs, in particular, have demonstrated significant improvements that have provided highly efficient full-color-display applications. The introduction of thin film transistors (TFTs) is indispensable and high performance organic TFTs have been anticipated for the active matrix driving of OLED displays. In this letter, we focus on a switching phenomenon using a Cu:7,7,8,8-Tetracyanoquinodimethane (TCNQ) charge transfer (CT) complex, which will be useful for organic TFT applications.

Observation of switching phenomena by a Cu:TCNQ CT complex was first reported by Potember *et al.*^{4–7} Cu:TCNQ CT-complex films with a grain size of a few micrometers were formed with a solution growth method on a precleaned Cu substrate that was dipped into a solution of degassed acetone: acetonitrile (1:1) saturated with TCNQ.⁵ Cu:TCNQ films that were $\sim 10\text{ }\mu\text{m}$ thick were formed with this method having a poly-crystalline morphology on a Cu substrate and their switching characteristics were first reported with a sandwiched structure of Cu/Cu:TCNQ/Al. However, most devices have a serious problem with homogeneity in the Cu:TCNQ films, leading to a lack of reproducibility in device characteristics. To solve these problems, we fabricated a Cu:TCNQ switching device by vacuum codeposition which

allows precise control of Cu and TCNQ contents. In this letter, we report on the reproducible switching characteristics of a Cu:TCNQ codeposited film.

Organic and metal layers were deposited by high-vacuum ($1\times 10^{-3}\text{ Pa}$) thermal evaporation onto a clean glass substrate pre-coated with an indium tin oxide (ITO) layer (300 nm thick) with a sheet resistance of $\sim 20\text{ }\Omega/\square$. The substrate was degreased with solvents and cleaned in a UV-ozone chamber (Nippon Laser & Electronics Lab., NL-UV253). First, a 20-nm-thick Al layer was thermally deposited on an ITO coated glass substrate and successively transferred into an UV-ozone chamber (12 min, O₂ 1 atm) to form a thin Al₂O₃ on an Al layer. We found that this procedure to form the thin Al₂O₃ layer was crucial to obtain reproducible switching characteristics. Next, a 100-nm-thick Cu:TCNQ layer was deposited via thermal codeposition onto the Al₂O₃/Al/ITO layer. Finally, a shadow mask with 1 mm diameter openings was used to define the cathode consisting of a 100-nm-thick Al layer, and then the ITO/Al/(Al₂O₃)/Cu:TCNQ/Al device structure was completed. Here, we stress that when we fabricate the devices without breaking vacuum, it was very hard to obtain reproducible switching effect, suggesting formation of a thin Al₂O₃ layer is responsible for the switching effect. We fabricated an ITO/Al₂O₃/Cu:TCNQ/Al device in a similar manner where a thin Al₂O₃ layer was directly deposited on an ITO substrate by rf sputtering (100 W, $\sim 2.4\times 10^{-1}\text{ Pa}$). In these devices, various deposition ratios of Cu:TCNQ, namely, 0:1 (0 atm/mol %), 1:2 (33 atm/mol %), 1:1 (50 atm/mol %), 3:2 (60

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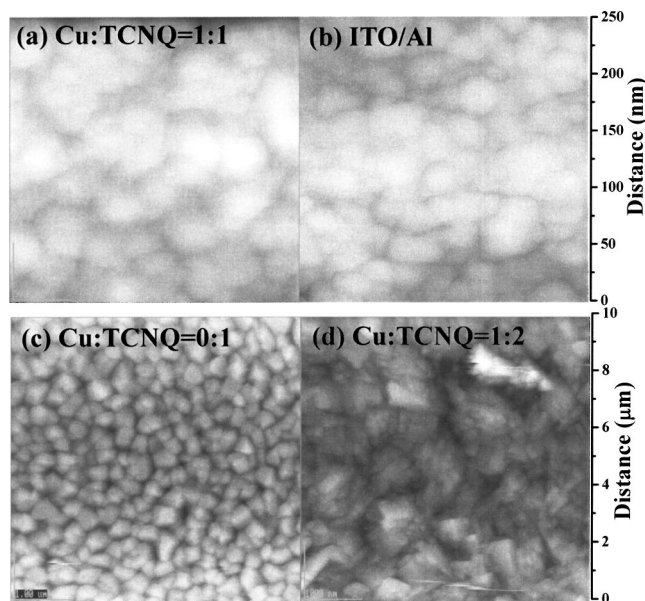


FIG. 1. AFM photomicrographs of Cu:TCNQ layers (100 nm) on aluminum (Al) layer with Cu:TCNQ ratios of (a) 1:1, (c) 0:1, and (d) 1:2. Deposited aluminum layer on indium tin oxide layer (b) is also shown for reference.

atm/mol %), 2:1 (66 atm/mol %) and 4:1 (80 atm/mol %) were employed.

Current density (J)–voltage (V) characteristics were measured using an HP4145 semiconductor parameter analyzer. Before J – V measurement, aging operation was performed. We first applied a cyclic triangular voltage with a minimum voltage of $V_{\min}=0$ V and a maximum voltage of $V_{\max}=1$ V with a frequency of 1 Hz for a few minutes and then increased V_{\max} from 1 to 8 V in turn. The devices settled in high impedance mode during this. Aging is indispensable to induce switching characteristics and all devices undergo this.

We first investigated the film quality of Cu:TCNQ codeposited films on ITO/Al substrates. Atomic force microscopy (AFM) revealed a uniform poly-crystalline texture at a Cu:TCNQ deposition ratio of 1:1 (Fig. 1). The film had a grain size of ~ 50 nm and a depth profile of ~ 20 nm, which coincided well with the surface structure of the underlying Al

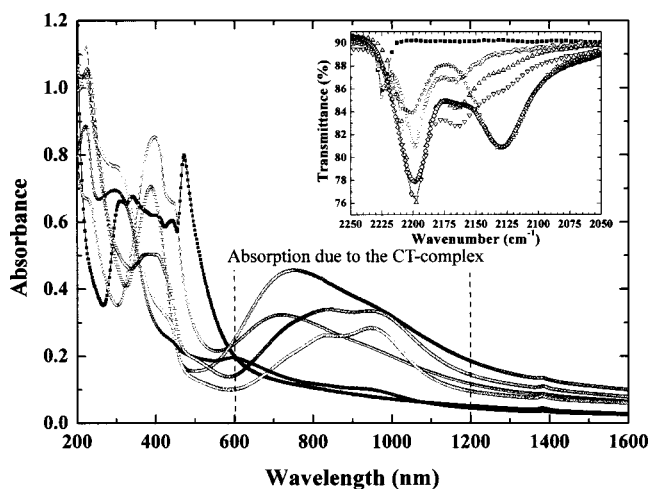


FIG. 2. Absorption spectra and infrared spectra (inset) of Cu:TCNQ CT-complex thin films with various Cu:TCNQ ratios of Cu:TCNQ (atom:mol) = 0:1 (■), 1:2 (○), 1:1 (△), 3:2 (▽), 2:1 (◇), and 4:1 (☆).

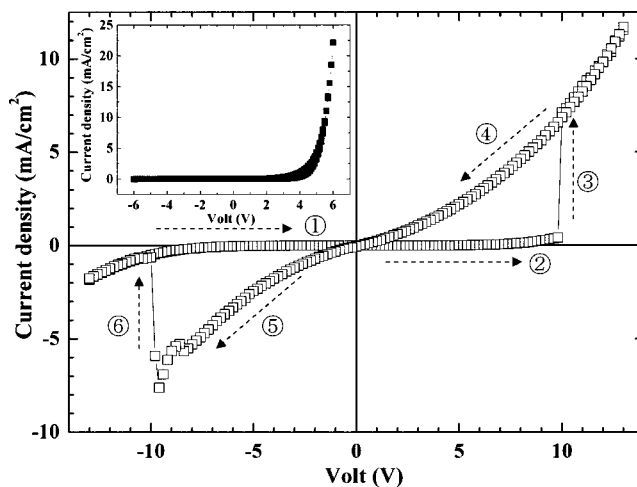


FIG. 3. J – V characteristics of an ITO (300 nm)/Al (20 nm)/(Al₂O₃)/Cu:TCNQ (1:1, 100 nm)/Al (100 nm) device. (Inset) J – V characteristics of an ITO (300 nm)/Cu:TCNQ (1:1, 100 nm)/Al (100 nm) device.

layer, resulted in a uniform dense poly-crystalline Cu:TCNQ layer. At Cu:TCNQ deposition ratios of 0:1 and 1:2, however, large uneven poly-crystalline textures with a characteristic grain size of ~ 2 μ m were observed, resulting in failure to deposit a uniform metallic cathode electrode. Consequently, we employed a Cu:TCNQ ratio of 1:1 to fabricate the devices.

The absorption spectrum of Cu:TCNQ codeposited films confirms the formation of a CT complex. Figure 2 summarizes the absorption spectra for pristine TCNQ and Cu:TCNQ (1:2, 1:1, 3:2, 2:1, and 4:1) deposited films. A characteristic CT band was observed at 600–1200 nm, while there was no significant absorption in the pristine TCNQ film. There was also a cyano stretching peak (2200–2160 cm⁻¹) for the complex films (Cu:TCNQ=1:2, 1:1, and 3:2) in the IR spectra and this shifted to a higher (more than 29 cm⁻¹) wave number than that for the pristine TCNQ (2226 cm⁻¹) (inset of Fig. 2). In the Cu:TCNQ with deposition ratios of 2:1 and 4:1, additional vibration at 2129 cm⁻¹ was also observed in addition to absorption at 2200 cm⁻¹.

Figure 3 reveals characteristic electrical switching of an ITO/Al/Cu:TCNQ/Al device. The device has a clear threshold from low impedance to high impedance at an applied voltage of 10.0 ± 2.0 V and a reverse phenomenon at a negative bias of -9.5 ± 2.0 V, when we progressively apply a voltage as indicated by the circled numbers. This characteristic switching phenomenon was observed more than 1000 times. However, we observed no switching effect in the ITO/Cu:TCNQ/Al device, suggesting that the Al layer plays an important role in switching (inset of Fig. 3).

Figure 4 has the switching characteristics of Cu:TCNQ devices with various Cu:TCNQ ratios. We observed the switching effect only with Cu:TCNQ concentrations of 1:2, 1:1, and 3:2 and no switching effect with concentrations of 0:1, 2:1, and 4:1. In particular, the Cu:TCNQ (1:1) thin film resulted in the largest ON/OFF ratio of $\sim 10^3$ at 5.0 V. In the case of high Cu concentrations, on the other hand, Cu atoms presumably formed a conductive channel in the complex films, leading to the lack of a switching effect. Also, the lack of switching characteristics in the TCNQ neat layer suggests

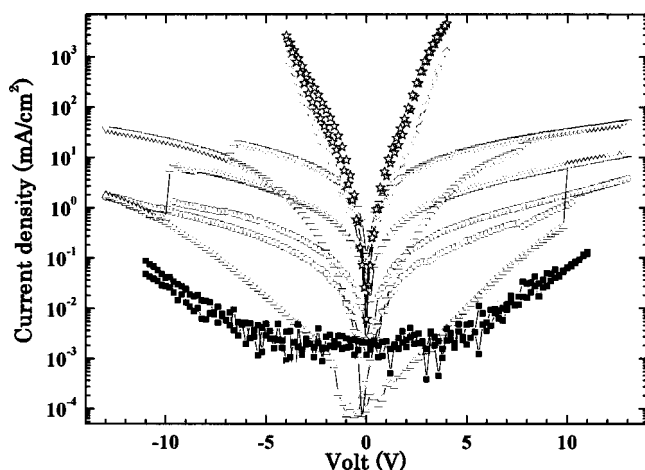


FIG. 4. J - V characteristics of ITO (300 nm)/Al (20 nm)/(Al₂O₃)/Cu:TCNQ (1:1, 100 nm)/Al (100 nm) devices with various Cu:TCNQ ratios; Cu:TCNQ=0:1 (■), 1:2 (○), 1:1 (△), 3:2 (▽), 2:1 (◇), and 4:1 (☆).

that charge transfer between Cu and TCNQ is also responsible for switching.

To understand the switching mechanisms, we investigated the switching characteristics depending on thickness of the Cu:TCNQ layer and the anode electrodes. Here, we fixed Cu:TCNQ ratio at 1:1 because it had the best switching characteristics. Interestingly, the switching characteristics were almost independent of the Cu:TCNQ thickness (Fig. 5), suggesting that switching is basically an interfacial phenomenon between the electrode and the Cu:TCNQ layer. The anode materials are also crucial in switching. Here, instead of an Al anode, we employed a device structure of ITO/Al₂O₃/Cu:TCNQ(1:1)/Al where the Al₂O₃ layer was formed by rf sputtering to confirm its effect. This was because we found that it was necessary to form a thin Al₂O₃ layer through UV-ozone treatment to obtain reproducible switching characteristics. At Al₂O₃ thicknesses of 0, 1.0, 5.0, 7.5, 8.8, and 10.0 nm, we observed switching effects with 1.0, 5.0, 7.5, 8.8, and 10.0-nm-thick Al₂O₃ layers, and a maximum ON/OFF ratio of $\sim 10^4$ with the 7.5-nm-thick Al₂O₃ layer. We did not observe any switching effects without an Al₂O₃ layer. Thus, these results indicate that a thin Al₂O₃ layer on an Al layer is responsible for the switching effect. Due to the large dielectric constant of the Al₂O₃ layer ($\epsilon \sim 10$), a high built-in field is formed between the Al/Al₂O₃ and Cu:TCNQ layer which controls partial charge transfer (ρ) between Cu (donor⁺ ρ) and TCNQ (acceptor⁻ ρ). It is often observed that neutral TCNQ molecules provide a mixed valence state with existing TCNQ radical anions in TCNQ columns and mixed valence. TCNQ complexes are more conductive than charge transfer complexes with complete charge transfer.⁶⁻⁹ Thus, the external field would convert a significant amount of charge transfer Cu:TCNQ to neutral TCNQ with the application of a forward bias of 10.0 ± 2.0 V and then charge carriers would be subjected to tunneling injection through the thin Al₂O₃ layer into the Cu:TCNQ layer. However, the reverse switching phenom-

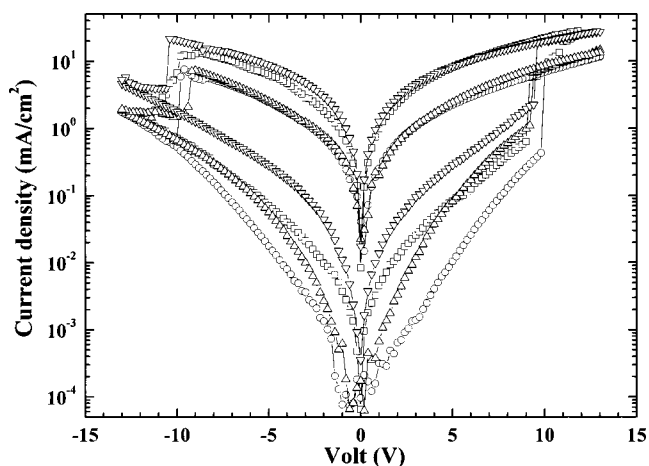


FIG. 5. J - V characteristics of ITO (300 nm)/Al (20 nm)/(Al₂O₃)/Cu:TCNQ (1:1, X nm)/Al (100 nm) devices depending on the Cu:TCNQ thickness; i.e., 50 (□), 100 (○), 200 (△), and 300 nm (▽).

enon from neutral TCNQ into charge transfer Cu:TCNQ would occur with the application of a reverse bias of -9.5 ± 2.0 V. Further researches into understanding the switching mechanism are currently in progress.

In summary, we demonstrated that it was possible to form uniform Cu:TCNQ CT-complex thin films by vacuum codeposition. A device with an ITO/Al/Cu:TCNQ/Al configuration with Cu:TCNQ (1:1) thin film demonstrated reproducible switching characteristics with a large ON/OFF ratio of $\sim 10^4$. We demonstrated that the interface of the Al anode and Cu:TCNQ layers is mainly responsible for high electric field due to the presence of a thin Al₂O₃ layer, leading to electrical switching. Both the formations of uniform Cu:TCNQ and the thin Al₂O₃ layers contribute to occurrence of the switching effect.

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