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

Oyamada, Takahito
Department of Photonics Materials Science, Chitose Institute of Science and Technology (CIST)

Tanaka, Haruo
Rohm Co., Ltd.

Matsushige, Kazumi
International Innovation Center (IIC), Kyoto University

Sasabe, Hiroyuki
Department of Photonics Materials Science, Chitose Institute of Science and Technology (CIST)

他

http://hdl.handle.net/2324/19452

バージョン：published
権利関係：Copyright 2003 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.
Switching effect in Cu:TCNQ charge transfer-complex thin films by vacuum codeposition

Takahito Oyamada
Department of Photonics Materials Science, Chitose Institute of Science and Technology (CIST), 758-65 Bibi, Chitose, Hokkaido, 066-8655, Japan

Haruo Tanaka
Rohm Co., 21 Saiin Mizosaki, Ukyo Kyoto 615-8585, Japan

Kazumi Matsushige
International Innovation Center (IIC), Kyoto Univ., IIC, Yoshida-Hommachi, Sakyo, Kyoto 606-8501, Japan

Hiroyuki Sasabe and Chihaya Adachi
Department of Photonics Materials Science, Chitose Institute of Science and Technology (CIST), 758-65 Bibi, Chitose, Hokkaido, 066-8655, Japan

(Received 21 April 2003; accepted 14 June 2003)

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 $\lambda = 600–1200$ 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/(Al$_2$O$_3$)/Cu:TCNQ/Al structure. The device exhibited 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 $-9.5\pm2.0$ V. In this study, we demonstrate that a thin Al$_2$O$_3$ layer between the aluminum (Al) anode and Cu:TCNQ layers creates reproducible switching.

There has been a growing interest in organic electronic devices such as organic light emitting diodes (OLEDs), organic solar cells, organic transistors, and organic switching devices 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 acetonitrile: acetonitrile (1:1) saturated with TCNQ.$^5$ Cu:TCNQ films that were ~10 $\mu$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 ($1 \times 10^{-3}$ 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 ~20 $\Omega$. 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, O$_2$ 1 atm) to form a thin Al$_2$O$_3$ on an Al layer. We found that this procedure to form the thin Al$_2$O$_3$ layer was crucial to obtain reproducible switching characteristics. Next, a 100-nm-thick Cu:TCNQ layer was deposited via thermal codeposition onto the Al$_2$O$_3$/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/ (Al$_2$O$_3$/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 Al$_2$O$_3$ layer is responsible for the switching effect. We fabricated an ITO/Al$_2$O$_3$/Cu:TCNQ/Al device in a similar manner where a thin Al$_2$O$_3$ layer was directly deposited on an ITO substrate by rf sputtering (100 W, ~2.4$\times$10$^{-1}$ Pa). In these devices, various deposition ratios of Cu:TCNQ, namely, 0:1 (0 at% mol %), 1:2 (33 at% mol %), 1:1 (50 at% mol %), 3:2 (60 at% mol %).
FIG. 2. Absorption spectra and infrared spectra of pristine TCNQ and Cu:TCNQ codeposited films. A characteristic CT band was observed at 600–1200 nm, while there was no significant absorption in the pristine TCNQ layer. The characteristic grain size of ~2 μm was also observed in addition to absorption at 2200 cm⁻¹ for the pristine TCNQ layer. In the IR spectra and this shifted to a higher wave number than that for the pristine TCNQ film. There was also a cyan 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 film (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 observed in addition to absorption at 2200 cm⁻¹.

Figure 3 reveals characteristic electrical switching of an ITO/Au/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/AI 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 ~10³ 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. 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.
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/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 10.0-10nm-thick Al2O3 layers, and a maximum ON/OFF ratio of ~104 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 (~10^4), a high built-in field is formed between the Al/Al2O3 and Cu:TCNQ layer which controls partial charge transfer (ρ) between Cu (donor^1ρ) 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 phenomenon 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 ~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.

This work was supported by Integrated Industry Academia Partnership (IIAP) projects from Kyoto University International Innovation Center and the Grant-in-Aid for Scientific Research of the Ministry of Education, Science and Sports in Japan for financial support of this research.