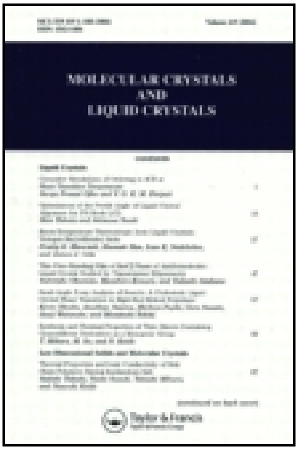

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electrical Properties of Cu-TCNQ Prepared by the Limited Growth

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Version of record first published: 24 Sep 2006

To cite this article: Ning Gu, Hao-Ying Shen, Lan Zhang, Hai-Qian Zhang, Zu-Hong Lu & Yu Wei (1997): Electrical Properties of Cu-TCNQ Prepared by the Limited Growth, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 294:1, 197-200

To link to this article: http://dx.doi.org/10.1080/10587259708032281

Mol. Cryst. Liq. Cryst., 1997, Vol. 294, pp. 197–200
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ELECTRICAL PROPERTIES OF Cu-TCNQ PREPARED BY THE LIMITED GROWTH

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Abstract A new method, limited growth of organometallic films in liquid phase, for preparation of Cu -TCNQ crystallites was adopted herein. Then the electrical properties of the Al/Cu-TCNQ film/Cu sandwichlike structures could be measured. The The transition between the highly resistive and conductive states with different parameters, such as threshold voltage, the shape of I-V curve, can be found depending on different average sizes of Cu-TCNQ grains . The the crystal boundaries may be one of the important factors contributing to the switching mechanism of Cu - TCNQ films has been suggested.

INTRODUCTION

In 1979, Potember et al. reported the observation of rapid, stable and reproducible current-controlled bistable switching phenomena in polycrystalline films of copper-tetracyanoquinodimethane (Cu-TCNQ).[1] It has been proposed that a field-induced solid-state reaction is associated with the switching transition yielding the neutral species of Cu and TCNQ.[2,3] Various diagnostic techniques including infrared, Auger, X-ray, photoelectron, and Raman spectroscopy have been applied to the Cu-TCNQ specimens to investigate the switching mechanism.[4] It possesses a sharp transition point, or threshold voltage (V_{th}), at which the impedance rapidly changes from high level to low level. This V_{th} is proportion to the thickness of the organic films[5]. We are interested to see if the V_{th} is related to the factors except the film thickness. A method has been tried herein to grow Cu-TCNQ films with different features, and a sandwichlike device structure has been fabricated for subsequent for electrical measurements.

EXPERIMENTAL

The copper slice used was oxygen-free. TCNQ was purchased from Tokyo Chem. & Industrial Ltd.(98%). The brief sequence for fabrication of Cu-TCNQ prototype devices studied herein is shown in Fig.1. A square of red copper slice (area: 25 cm²) was cleaned and polished mechanically. Afterwards the cleaned Cu slice was dipped into a solution of 1mM H_2SO_4 to smooth its surface further. Then polyimide(PI) layer was produced on the Cu substrate by spin-casting and chemically treating the PA film. On the surface of PI/Cu sample, a AZ1450 resist was spread by the spin cast

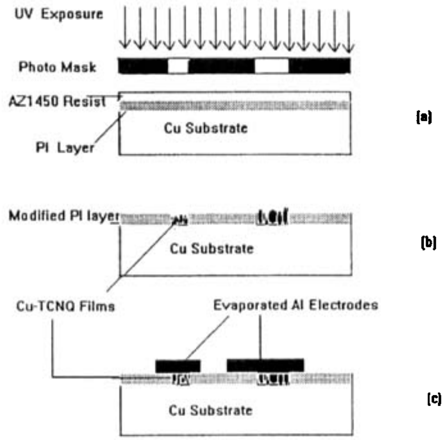

Figure 1: Fabrication sequence of the prototype devices using Cu-TCNQ crystallites prepared by limited growth in liquid phase.

technique. After the sample was exposed by an UV exposure technique and then developed through an alkaline solution, some holes with varied diameters were formed on the surface of AZ resist/PI layer/Cu. The method for forming Cu-TCNQ films in the liquid phase has been called spontaneous electrolysis(SE)[1]. According to SE method, Cu-TCNQ films studied in this paper were prepared by dipping the modified PI layer/Cu substrate sample into a saturated TCNQ/CH_3CN solution at 21℃ for 30 min. Cu-TCNQ crystallites could grow from the Cu substrate in the PI-holes. This technique which provides limited surroundings for growth of Cu-TCNQ crystallites can be called limited SE. Then this sample was dried under a vacuum to remove any trace of solvents. After that, the top layer of Al was produced by evaporation and lithographically patterned to form the top-electrode, as shown in Fig.1(c).

The morphology of Cu-TCNQ films or crystallites was observed by a scanning electron microscope(SEM), S-450. The electrical measurements of this devices were carried out at room-temperature by using the QT-2 Transistor Characteristics Analyzer(DH).

RESULTS AND DISCUSSION

The SEM topography of Cu-TCNQ film prepared by unlimited SE shown in Fig.2. The tightly packed individual crystals are oriented almost along the normaline of the Cu substrate, similar to those reported previously by Potember [1]. The typical crystallite size approximates $1.5 \times 1.5 \times 6$ μm. In contrast, the limited SE method for preparing Cu-TCNQ organometallic salt results in crystallites of different shape: 21 ℃ for 30 min, we obtained Cu-TCNQ crystallites growing in the holes of modified PI/Cu structures. The typical morphology is shown in Fig.3. The diameter of the hole shown in the figure is about 40 μm. It is found that the average size of these Cu-TCNQ crystallites decreases as the holes size decreases, e.g., Cu-TCNQ crystallites with 2.5 μm in average diameter(AD) under the hole diameter 40 μm, 1.7 μm under 20 μm, 1.3 μm under 10 μm, etc.. This phenomenon is related to the "shield effect" . The hole in PI layer causes a local micro-surrounding resulting in insufficient growth of Cu-TCNQ crystallites. For different preparation methods, limited and unlimited SE, the current-voltage (I-V) curves are shown to be different.

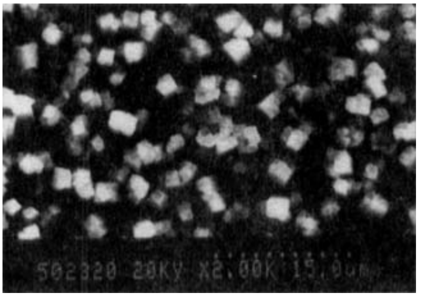

Figure 2: Electron micrograph of Cu-TCNQ film prepared by unlimited growth in liquid phase at 21℃ for 30 min.

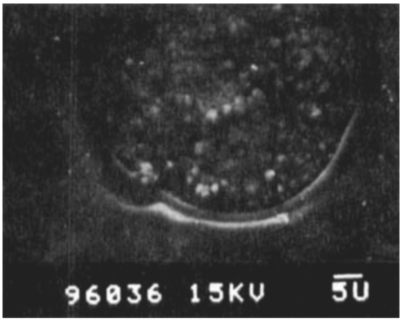

Figure 3: Electron micrograph of Cu-TCNQ organic film prepared by limited growth in liquid phase at 21℃ for 30 min.

With Al metal used as top electrode, we have measured the electrical properties of Al/Cu-TCNQ/Cu prototype device. For different preparing methods, limited and unlimited SE, the current-voltage(I-V) curves are shown to be different. Above V_L (refer to Potember's previous results[1]) but below V_{th} the I-V curve shows super linear or non-ohmic preswitching behavior. At the V_{th}(11 V in this case) an abrupt switching occurs from a high- to low-impedance state. The low-resistance or "on" state is non-Ohmic with a decrease in the impedance, the electrical relationship can then be expressed as $I \sim V^n$ with $n > 1$. When the AV was removed, the device either acted as a threshold switch returning to the "off" state or, under the condition of higher-power dissipation, a memory switch remaining in the "on" state. For comparison, the dc I-V curves of the device Al/Cu-TCNQ/Cu in which Cu-TCNQ films were prepared by limited SE were also measured. A typical curve is shown in Fig.4. This figure also shows switching from a high- to low-impedance state when an applied voltage(AV) exceeds a V_{th}. The difference is that there are intermediate states between the low- and high-resistance state. When the AV exceeds the V_{th} , a rapid jump from this high-resistance state to the a-state shown in the figure occurs; a transition from a-state to b-state can then occur. Afterwards a rapid jump from b-state to c-state and d-state(low-resistance state) occurred. In states c and d, discontinuities(about 0.75 V) also exist. We find that the V_{th} increases as the crystallite AD decreases: for instance, V_{th}=3.5 V for AD= 2.5 μm, V_{th}=8.3 V for AD =1.7 μm and V_{th}= 9.5 V for AD=1.3 μm. This feature is different from

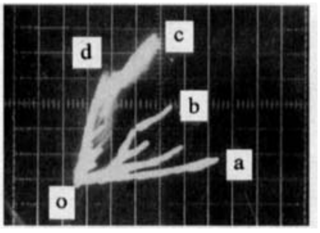

Figure 4: I-V characteristics of the fabricated device based on limited SE Cu-TCNQ crystallites [x-axis: 0.5 V/div; y-axis: 50 mA/div]

Potember's reported results of that V_{th} is proportional to the thickness [5] Comparison of Fig.2 and Fig.3, shows that the formation of Cu-TCNQ crystallites prepared by limited SE is different clearly from those prepared by unlimited method. All contacts between two crystallites involve a great number of boundaries. It is suggested that crystal boundaries play an important role in determining the electrical characteristics of this kind of prototype device. Further investigation is proceeding.

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