

Organic, Bistable Devices with AgTCNQ Charge Transfer Complex by Vacuum Co-Deposition*

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Abstract: The AgTCNQ thin-film was prepared by vacuum vapor co-deposition and characterized by infrared spectral analysis, and then a uniform AgTCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) thin-film layer was sandwiched in a Ti/AgTCNQ/Au crossbar structure array as organic bistable devices (OBD). A reversible and reproducible memory switching property, caused by intermolecular charge transfer (CT) in the AgTCNQ thin-film, was observed in the organic bistable devices. The positive threshold voltage from the high impedance state to the low impedance was about 3.8~5V, with the reverse phenomenon occurring at a negative voltage of -3.5~-4.4V, lower than that with a CuTCNQ active layer. The crossbar array of OBDs with AgTCNQ is promising for nonvolatile organic memory applications.

Key words: organic electronics; bistable switching; crossbar memory

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1 Introduction

The attraction of organic electronics is growing because of their flexibility, simplicity, low cost, and the ability to design and tune electronic and structural properties^[1~4]. There are various organic electronic devices, including organic light emitting diodes^[5~8], organic solar cells^[9], organic field effect transistors^[10~11], and organic switching devices^[12~15]. The bistable switching effect is a key property for information storage and memory. Different kinds of organic thin-films with electrical bistable switching properties are widely researched for potential applications in storage and memory, as organic bistable devices. Generally, there are two methods to use organic bistable thin-film to store data. One way to achieve this is the scanning probe microscope (SPM) technique, including a scanning tunneling microscope (STM)^[16] and an atomic force microscope (AFM)^[17]. With the probe of SPM as an electrode and the substrate as the other common electrode, this method can achieve ultra high density in data recording. For example, the average diameter of the recorded dots on TDME (1, 1, 2-tricyano-2-(4-dimethylaminophenyl) ethynylene) thin-film by STM was only 2.1nm, correspond-

ing to potential storage density of 10 Tbits/cm²^[18]. But this technique cannot be used in practical applications, due to its low efficiency. The other way is a crossbar, also called an X-Y addressable array^[19]. A crossbar array consists of a layer of organic functional thin-film between two sets of electrode wires, including N vertical wires crossing over N horizontal wires, shown in Fig. 1. The simplicity of the crossbar makes fabrication feasible and inexpensive. A crossbar circuit is addressable and integrated with external circuits and systems. Organic nonvolatile memory and even logic computing can be achieved by electrical configuration of crossbar circuits^[20].

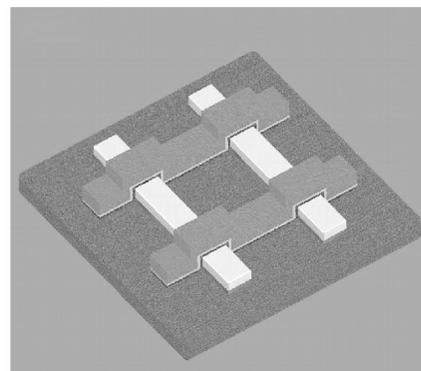


Fig.1 Schematic illustration of Ti/AgTCNQ/Au crossbar array

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Crossbar molecular memory has been researched by HP^[21], Infineon^[22], ST Microelectronics^[23], and others. The Langmuir-Blodgett monolayer thin-film of Rotaxane was used by HP, while self-assembling monolayer thin-films were proposed by Infineon and ST Microelectronics. In addition to the monolayer thin-films mentioned above, various organic thin-films such as CuTCNQ^[24] and AlDCN (2-amino-4,5-imidazoledicarbonitrile) were also proposed for crossbar memory^[25].

In this letter, we focus on a charge transfer complex synthesized by vacuum vapor co-deposition. The infrared spectral analysis on the AgTCNQ thin-film was studied. Organic bistable devices made up of a Ti/AgTCNQ/Au sandwich structure were fabricated with the integrated circuit process, and characterized by current-voltage measurements. The electrical bistable switching phenomenon was observed with a positive threshold voltage of 5V and a reverse bias of -3.5 V. Intermolecular charge transfer induced by electrical field was employed to explain this bistable behavior. The organic bistable devices with AgTCNQ thin-film are promising for organic nonvolatile memory applications.

2 Experiment

The deposition of AgTCNQ thin-film was a critical step during device fabrication. A layer of 1nm Ag was evaporated onto the wafer, with a layer of 14.6nm TCNQ evaporated subsequently. The deposition ratio of Ag : TCNQ was 1 : 1 (50atm/mol%). This process was repeated ten times with vacuum at 1×10^{-3} Pa, and the total thickness of Ag is 10nm. After annealing for 120min at 90°C with vacuum at 5×10^{-3} Pa, a layer of AgTCNQ thin-film formed, which was confirmed by ultra violet (UV) and infrared (IR) spectral analysis. The thin-film had a grain size of ~ 100 nm, shown as the inset in Fig. 2.

Like most organic functional materials, the thin-film of the charge transfer complex AgTCNQ was extremely susceptible to damage in the lithography and lift-off processes, leading to uncertain electrical properties. The photo resist, developer, and other organic solvent, such as acetone and alcohol, would penetrate or dissolve with AgTCNQ. Therefore, a protective layer was needed to prevent from contact with organic solvent in the fabrication of AgTCNQ devices. In our previous work, a layer of Cr thin-film was chosen as the protective layer^[26]. Here, we chose Ti instead of Cr as the protective layer for feasible etching. Ti is a good contact metal for organic functional groups because there is little penetration of the organic thin-films^[27].

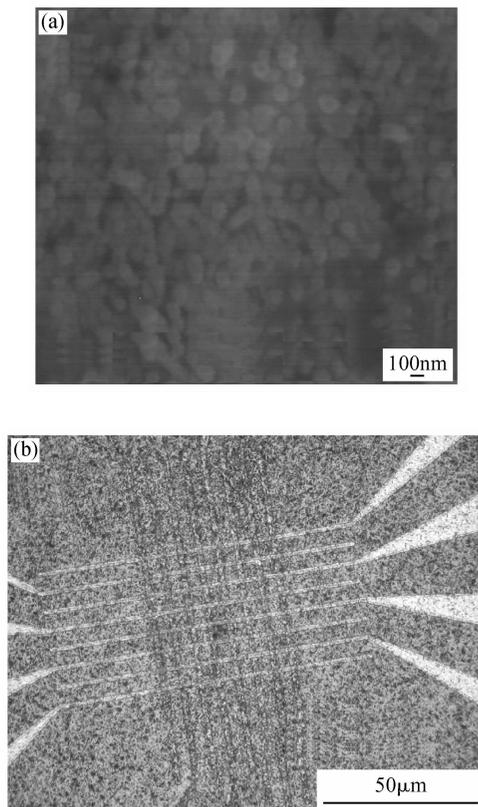


Fig. 2 Images of AgTCNQ thin-film and 8×8 array crossbar devices with AgTCNQ thin-film (a) SEM image of AgTCNQ thin-film deposited by co-deposition; (b) Optical image of 8×8 array crossbar OBDs

The sample was fabricated on 200nm-thick silicon nitride deposited by low pressure chemical vapor deposition (LPCVD) on silicon. The bottom electrodes were fabricated by photo-lithography, e-beam evaporation, and lift-off processes. After the photo-lithography was carried out on an EVG 620 Aligner and descum, a 10nm-thick layer of Cr as an adherence layer and an 80nm-thick layer of Au were deposited on the wafer by a Johnson e-beam evaporation system. Subsequently, an acetone lift-off process was used to remove the unpatterned area. The line-width of the electrodes was $2\mu\text{m}$, and the space of each line was $4\mu\text{m}$, with 8 electrodes in a cell. A layer of AgTCNQ thin-film was deposited onto the wafer by vacuum co-deposition, as presented above. A layer of 20nm-thick Ti was deposited by evaporation to cover the organic thin-film. On the protective layer, the top electrodes with 10-nm-thick Cr and 80-nm-thick Au layers were fabricated through the same process as the bottom ones. Finally, inductive coupled plasma (ICP) etching with CHF_3 and O_2 at powers of 50W and 400W was used to remove the Ti layer down to the substrate. The Ti layer and thin-film under the top electrodes remained. The 8×8 crossbar array with AgTCNQ thin-film is shown in Fig. 2.

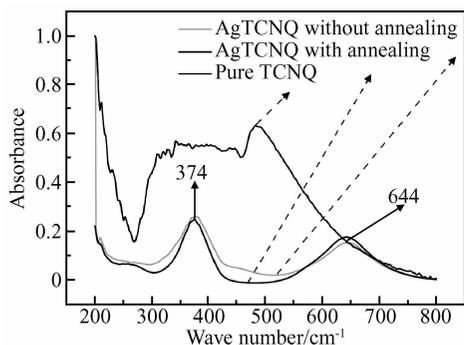


Fig.3 UV spectra of AgTCNQ thin-film with and without annealing and of pure TCNQ thin-film

3 Results and discussion

The electronic transitions correspond to the red- (550~900nm) and blue-band (350~550nm) systems of an isolated TCNQ anion radical. They are both polarized in the molecular plane^[28]. For comparison, the electronic absorption (UV) spectra of AgTCNQ thin-film produced with and without annealing, and pure TCNQ thin-film are studied and shown in Fig. 3. In the red-band region, the typical absorption maximum was at 644nm, while this is 374nm in the blue-band region.

Figure 4 shows the IR spectra of AgTCNQ thin-film produced with and without annealing, and pure TCNQ thin-film. In the AgTCNQ thin-films, the C≡N stretching region was characterized by two bands, a main band at 2195cm⁻¹ and a shoulder band at 2162cm⁻¹. The C=C ring stretching region was characterized by two bands, a weak absorption band at 1579cm⁻¹ and a middle band at 1540cm⁻¹. The C=C wing stretching region was also characterized by two bands at 1361 and 1322cm⁻¹. The peak of C=C-H was at 823cm⁻¹ in AgTCNQ thin-film both with and without annealing. Compared to the spectrum of pure TCNQ thin-film, the C=C ring stretching mode in pure TCNQ at 1543 cm⁻¹ was split into about 1579 and 1540cm⁻¹ in both the AgTCNQ referred to above. Furthermore, the C=C wing stretching in pure TCNQ at 1349cm⁻¹ was split into 1361 and 1322cm⁻¹. In addition, the peak of C=C-H in pure TCNQ bending at 861cm⁻¹ was shifted to 823cm⁻¹ in AgTCNQ thin-film. The appearance of the absorption peak at 1540 and 823cm⁻¹ indicated that TCNQ was changed to TCNQ anion radicals^[28~30]. In contrast to AgTCNQ thin-film without annealing, the absorption peak at 3052, 1543, 1349, 861cm⁻¹ in AgTCNQ thin-film with annealing disappeared, showing that TCNQ was completely changed to TCNQ anion radicals.

We carried out the measurement of electrical properties on a probe station of CASCADE RF1 with

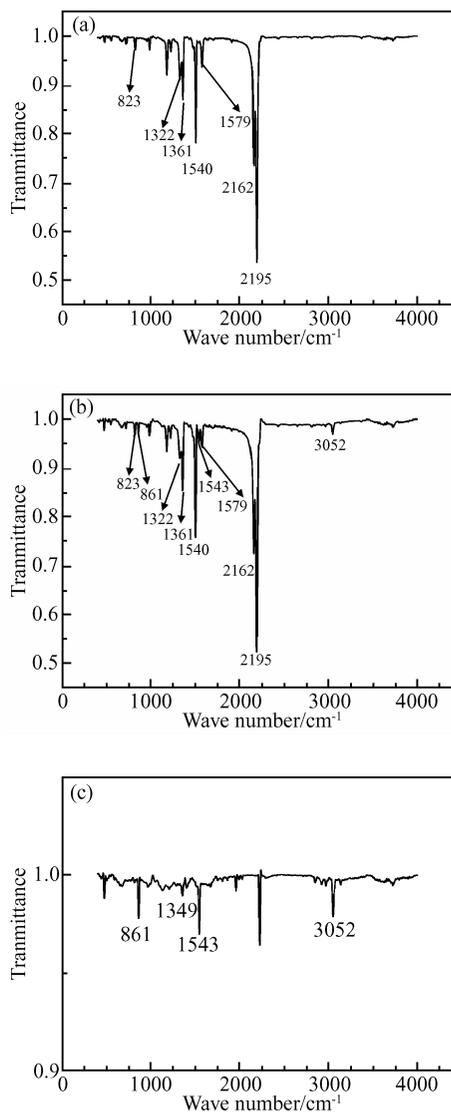


Fig.4 IR spectra of AgTCNQ thin-film with (a) and without (b) annealing, and of pure TCNQ thin-film (c)

a Keithley 4200 SCS. The typical current-voltage curve of these crossbar devices with a sequence from curve 1 to 4 is shown in Fig. 5. The initial state had high impedance with a resistance of 106W, corresponding to an OFF state. When the voltage applied was higher than 5V, corresponding to field strength of about 5×10^5 V/cm for a 100nm-thick AgTCNQ thin-film, the resistance of the cross-point was turned down to $10^5 \Omega$ (ON state), shown in curve 1 in Fig. 5. This low impedance state remained when the voltage swept from 5 to 0V, showing the memory effect of this organic bistable device. A reverse switching turned the cross-point to OFF state with a negative voltage higher than -3.5V, corresponding to erasable memory. Moreover, the positive and negative threshold voltages for switching in the repeated test circle were 3.8 and -4.4V, respectively. Figure 5 shows that this OFF state was also stable in curve 4. The operation voltage of these bistable switches with

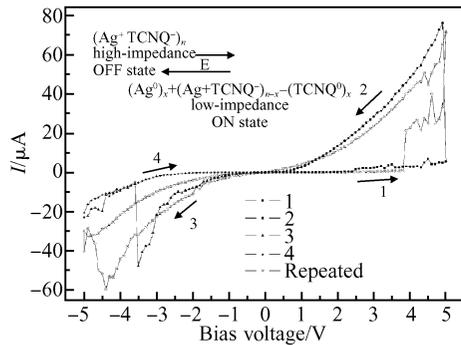


Fig.5 Electrical bistable switching I - V characteristic of Ti/AgTCNQ/Au OBDs. The voltage bias swept from curve 1 to 4, sequentially. The repeated test showed that the bistable switching behaviors were reproducible. The inset shows the mechanism of electrical bistability of AgTCNQ.

AgTCNQ is much lower than with the CuTCNQ sandwich structure^[19], promising a lower power consumption. We believe that this switching effect was induced by charge transfer from donor to acceptor, shown in the inset of Fig. 5. The initial state of AgTCNQ thin-film has a large resistance. When a voltage higher than the threshold is applied, the thin-film is changed into Ag^0 and TCNQ^0 with electrons transfer from TCNQ^- to Ag^+ . This switching is reversible by a reverse bias.

4 Summary

In conclusion, organic bistable devices with AgTCNQ thin-film were fabricated and characterized. The AgTCNQ charge transfer complex was deposited by vacuum vapor co-deposition. UV spectral and infrared spectral analyses of this organic thin-film were studied. A reversible, electrical, and bistable switching effect was observed in the crossbar devices with an operated voltage no higher than 5V, which is much lower than the CuTCNQ complex reported by previous works^[24]. These crossbar organic bistable devices have the potential to be used in organic memory applications.

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基于共沉积技术的 AgTCNQ 的有机双稳态器件*

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摘要: 采用共沉积技术制备了 AgTCNQ 薄膜, 并进行了红外、紫外光谱表征. 利用微电子工艺制备了基于 AgTCNQ 薄膜的有机双稳态器件. 研究发现, Ti/AgTCNQ/Au 双稳态器件具有可逆、可重复的开关存储特性. 将器件从初始的高阻态转变为低阻态的正向开关阈值电压为 3.8~5V, 将低阻态转变为高阻态的负向阈值电压仅为 -3.5~-4.4V, 与通常的 CuTCNQ 器件相比较小. 这种基于 AgTCNQ 交叉结构的有机双稳态器件可应用于非易失性有机存储器.

关键词: 有机电子学; 双稳态开关; 交叉存储器

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