# A new type of organometallic system for high density data storage by scanning tunneling microscopy

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## Abstract

We report a new type of organometallic system, Ag-toluylene 2,4-dicarbamidonitrite (TDCN) composite thin film, for ultrahigh density data storage devices by scanning tunneling microscopy (STM). The Ag-TDCN thin film was prepared on a highly oriented pyrolytic graphite (HOPG) substrate using an ionized-cluster-beam (ICB) deposition method. Marks can be created on the thin film by employing a voltage pulse between the STM tip and the surface of the HOPG substrate. The size of the created marks is about 50 nm and the corresponding data storage density is about $10^{11}$ bits/cm$^2$. The mechanism for the data storage can be attributed to the conductance transition in the complex system. This result shows a great potential for this new kind of organometallic composite system to find application in ultrahigh density data storage. © 1997 Published by Elsevier Science B.V.

Scanning tunneling microscopy (STM), atomic force microscopy (AFM), scanning capacitance microscopy (SCM), and near-field optical microscopy have all been demonstrated to have the ability to make surface modifications on the nanometer scale for high density data storage [1–11]. However, with these probe-based techniques, the manipulation of atoms requires ultrahigh vacuum, low temperature, and a great deal of time. In addition, it is also a problem to distinguish between the recording marks and the existing surface defects, especially with smaller marks. Moreover, the entire storage function of recording, erasing, and reproducing has not been

considered in most studies. Based on the above discussion, it is useful to record and reproduce changes in tunneling current without any change in surface morphology. The phase transition of a sample can, as we know, satisfy this requirement, since the electrical property of the sample may change after the probe action. So far, a few studies on probe-based high density data storage using the phase transition principle [12,13] (e.g., from amorphous to crystalline, or the phase transition in organometallic thin films) have been reported in the last few years. In this Letter we report the high density data storage by STM on a type of organometallic composite, Ag-doped toluylene 2,4-dicarbamidonitrite (TDCN) thin films. The data density on the film is about $10^{11}$ bits/cm$^2$. The possible mechanism can be attributed to the phase transition in the thin films.

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Toluylene 2,4-dicarbamidonitrite (TDCN) is a new organic material of functionality. The TDCN thin film and the Ag-TDCN composite thin film were prepared using an ionized-cluster-beam (ICB) deposition method, and its chemical structure, the synthesis of TDCN, the novel structural property as well as the electrical bistability of the TDCN thin film were described in our previous publication [14]. In the Ag-TDCN charge-transfer complex, the Ag is a donor and the TDCN is an acceptor. Components of Ag and TDCN in the films are critical for obtaining the electrical bistability (electrical switching) and for the high density data storage. The base vacuum of the deposition system is in the order of $4 \times 10^{-7}$ Torr, and during the film deposition the vacuum is about $6 \times 10^{-6}$ Torr. A highly oriented pyrolytic graphite (HOPG) was employed as the substrate of the Ag-TDCN thin film. In the STM experiment, we employ Ag-TDCN films of 100 nm thickness with optimum electrical property. The STM operates in an ambient environment. During imaging the surface of the film, both the constant current mode and the constant height mode were used. For the data storage on the thin film by STM, a voltage pulse was applied on the thin film between the STM tip and the HOPG substrate. In order to know the electrical property of region on the thin film before and after the voltage pulse, the $I$–$V$ relations of the sites on the thin film were measured by (STM).

A typical STM image of the ICB-deposited Ag-TDCN thin film is shown in Fig. 1. The scan area is 160 nm × 160 nm. During the scanning, the STM is
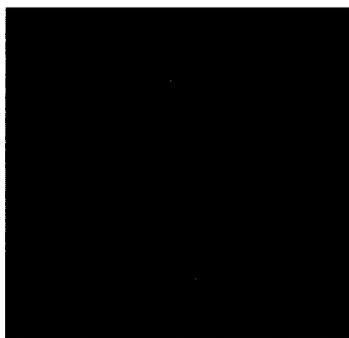


Fig. 1. STM image of the Ag-TDCN thin film deposited on HOPG before the voltage pulse from the STM tip, showing the uniform and planar surface of the film, $V_b = 0.16$ V, $I_t = 0.44$ mA, scan area: 160 nm × 160 nm, scan mode: constant height.
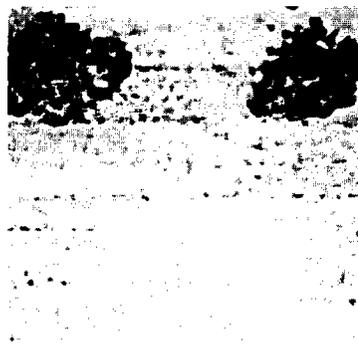


Fig. 2. STM image of the same area as Fig. 1 after two successive voltage pulses ($V = 4.0$ V, $\Delta T = 2$ ms) from the STM tip on the thin film, showing the two dark marks on the STM image of the thin film, $V_b = 0.16$ V, $I_t = 0.44$ mA, scan area: 160 nm × 160 nm, scan mode: constant height.

in the constant height mode, $V_b = 0.16$ V, $I_t = -0.44$ nA. One can see a very uniform and rather planar surface of the ICB-deposited Ag-TDCN thin film in Fig. 1. At one site of the area in Fig. 1, a voltage pulse of 4.0 V and 2 ms from the STM tip was applied on the film. After the voltage pulse, a dark mark (or a hole) on the thin film in the area of Fig. 1 can be created. After two successive voltage pulses, we made two dark marks in the STM image as shown in Fig. 2. For another successive voltage pulse on the film of Fig. 2, we made three dark marks in the STM image as shown in Fig. 3. If we name the dark mark as state '1' of the thin film, the
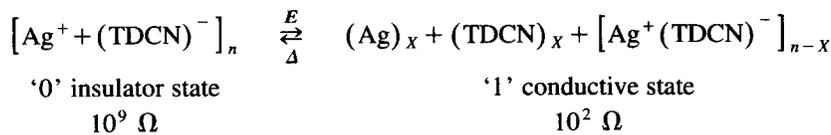


Fig. 3. STM image of the same area as Fig. 1 after three voltage pulses ($V = 4.0$ V, $\Delta T = 2$ ms) from the STM tip, showing the three dark marks on the STM image of the thin film, $V_b = 0.16$ V, $I_t = 0.44$ mA, scan area: 160 nm × 160 nm, scan mode: constant height.

other bright part is then the other state named state '0.' One dark mark is one bit of the '1' data. Therefore a voltage pulse on the functional organometallic thin film can store one bit of data. Based on Figs. 2 and 3, one deduces that the data storage density can reach $10^{11}$ bits/cm$^2$.

In our experiment it is also of importance to ask for identifying the formation mechanism of the dark marks, Is it the surface modification or the phase transition of the thin film from high impedance to low impedance? Sato et al. [12] reported the high density data storage by STM on a composite material, a crystalline and its glassy form, and attributed the recording marks to the phase transition of the material from amorphous to crystalline. Mutsumoto et al. [13] used Cu-TCNQ to carry out high density data storage, and believed also that the possible mechanism was the phase transition. However, they did not give further explanations. To understand the formation mechanism of the formed dark marks, $I$–$V$ curves of the sites were measured by STM before and after the voltage pulses. Before the voltage pulse of the thin film, two typical $I$–$V$ relations were obtained as shown in curves (a) and (b) of Fig. 4. In

curve (a), the applied voltage is from 0 to 1 V, and the tunneling current is 0 nA, which means that the Ag-TDCN thin film is initially an insulator below the applied voltage of 1 V. When the applied voltage increased from 0 to 1.5 V, we can see that the $I$–$V$ relation in curve (b) is different from that in curve (a). The film is initially an insulator, and after the voltage threshold of 1.45 V, it changes from insulator to a conductor. After the voltage pulse, the $I$–$V$ relation of the pulsed sites is shown in curve (c) of Fig. 4, which indicates that the pulsed sites of the thin film were conductor.

On the other hand, in the four-probe current–voltage $(I$–$V)$ measurement of the sample, we previously found the electrical bistability of thin films [14,15]. The films of electrical bistability possess an electric field threshold. Also, the film is initially in a high impedance state. If the applied electric field is below the voltage threshold, it would maintain the high impedance, and when the applied electric field exceeds the threshold, the film would become to have the conductive state. The film transition can be described as follows:

$$\left[ Ag^+ + (TDCN)^- \right]_n \quad \underset{\Delta}{\overset{E}{\rightleftarrows}} \quad (Ag)_x + (TDCN)_x + \left[ Ag^+ (TDCN)^- \right]_{n-x}$$

'0' insulator state $\qquad\qquad$ '1' conductive state

$10^9 \ \Omega$ $\qquad\qquad\qquad\qquad$ $10^2 \ \Omega$

where $\Delta$ represents heating, which can recover the recorded regimes from state '1' to state '0'. Comparing the $I$–$V$ curves in the STM measurement with the results by the four-probe $I$–$V$ measurement, one can find a common point, i.e., both the electric field between the STM tip and the substrate and between the two electrodes in the four-probe $I$–$V$ measurement can cause the conductance transition of the Ag-TDCN thin film. In both cases the voltage thresholds are almost of the same order of magnitude, which suggests that the electrical property of the pulsed sites of the thin film changed greatly from insulator to conductor. To further evidence the formation mechanism of the dark sites, we employed different samples with different thicknesses and different components of Ag and TDCN in the thin film, and we found that though the voltage pulse from the

STM tip was the same as that described above, no dark mark could be made on the thin films of no electrical bistability. Only on the thin films with the electrical bistability and at a suitable voltage pulse from the STM tip the dark mark can form, which further demonstrates that the possible mechanism of the mark formation is caused by the phase transition from the high impedance to the low impedance of the functional organometallic composite thin films.

In our STM investigation of ultrahigh density data storage, it should be noted that the voltage bias should be set below a certain value at the initial scanning of the sample. Otherwise, the film would shift from a state of high impedance to one of low impedance, and it would become impossible for the film to conduct the data storage. So in the STM studies, we initially applied a low voltage to prevent
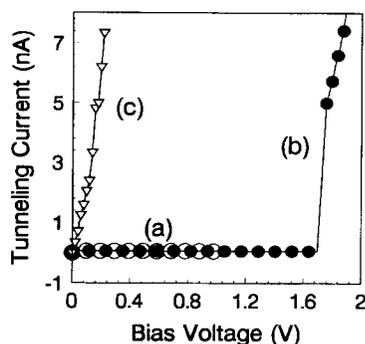
Fig. 4. STS results of the Ag-TDCN thin film: (a) before voltage pulse, the applied voltage is below 1 V; (b) before voltage pulse, the applied voltage is from 0 to 1.8 V; and (c) after the voltage pulse. Curve (a) indicates that the thin film was initially an insulator when the applied voltage is below the voltage threshold. Curve (b) indicates that the film becomes a conductor when the applied voltage exceeds the voltage threshold of 1.7 V, which is the conductance transition of the thin film from the high impedance to the low impedance. Curve (c) is the $I-V$ relation of the pulsed site of the thin film, which indicates that the pulsed-regime is conductive.

the film to transform to a state of low impedance (conductor), in other words, to retain the high impedance of the film in state '0'. From the above description, it is reasonable to infer that it is the transition of the electrical property of the Ag-TDCN thin films that makes possible ultrahigh density data storage on the charge-transfer organometallic composite thin film by STM.

In summary, we have found a new kind of physical system of electrical bistability, Ag-toluylene 2,4-dicarbamidonitrite (TDCN) organometallic composite thin films, to carry out ultrahigh density data storage. The storage density is about $10^{11}$ bits/cm$^2$. The possible mechanism of the mark formation in the STM image is due to the phase transition of the

thin film conductance before and after the voltage pulse on the organometallic functional thin films. This conductance transition possesses better properties of the film, such as writing/erasing, shorter transition time ($\sim$ ns), and stability, which gives this type of films great potential with respect to ultrahigh density data storage.

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