

Ultrahigh-density data storage on a novel organic thin film achieved using a scanning tunnelling microscope

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Abstract

An organic thin film of *N, N*-dimethyl-*N'*-(3-nitrobenzylidene)-*p*-phenylenediamine with electrical bistability properties was prepared by the vacuum deposition method. The film was observed with a scanning tunnelling microscope (STM). Ultrahigh-density data storage is demonstrated on the organic film, produced by applying a voltage pulse between the STM tip and the substrate of the thin film under ambient conditions. The average size of the recording marks is about 0.7 nm, corresponding to a data storage density of about 10^{13} bits cm^{-2} . The local current–voltage curves of the film suggest that the recorded area is conductive, while the unrecorded region possesses high resistance. The recording mechanism is also discussed.

1. Introduction

Recently, ultrahigh-density data storage has attracted increasing interest [1–6]. To meet the demands of ultrahigh-density data storage, the size of the recorded marks must reach the nanometre scale. Organic materials have received much attention because of their great potential for use in optical or electrical devices. In the past, we have reported nanometre scale recording up to a data density of about 10^{13} bits cm^{-2} on a series of organic thin films [7–12]. Recently, we have succeeded in writing marks 0.6 nm in diameter at their smallest on a new organic film [13]. For application in potential data-recording devices, the recording films must be very stable under ambient conditions. We have reported a recording on an organic thin film of *N'*-(3-nitrobenzylidene)-*p*-phenylenediamine (NBPDA) by means of a STM under ambient conditions [14]. In the NBPDA molecule, there are both electron donors ($-\text{NH}_2$) and electron acceptors ($-\text{NO}_2$). We have discussed the recording mechanism and proposed that the recorded marks were mainly caused by the charge transfer. But in that system the $-\text{NH}_2$ is not stable enough for an

ideal storage medium. So we designed and synthesized a new organic molecule, *N, N*-dimethyl-*N'*-(3-nitrobenzylidene)-*p*-phenylenediamine (DMNBPDA). In the molecular structure, the $-\text{NH}_2$ is replaced by $-\text{N}(\text{CH}_3)_2$. The melting point of NBPDA is 146 °C, while DMNBPDA melts at 172 °C. Thus it can be seen that DMNBPDA is more stable than NBPDA. Because $-\text{N}(\text{CH}_3)_2$ is a better electron donor than $-\text{NH}_2$, charge transfer occurs more easily in the system of DMNBPDA than in that of NBPDA. So the former could be a satisfactory recording medium for data storage. In this paper, we report on the study of ultrahigh-density data storage on DMNBPDA thin films.

2. Experimental details

DMNBPDA was synthesized by our research group. The molecular structure is shown in figure 1. The DMNBPDA thin film was deposited on a freshly cleaved highly ordered pyrolytic graphite (HOPG) substrate by the vacuum deposition method. The evaporation system was at about 1.3×10^{-3} Pa. The organic material was heated to 70 °C in a crucible in the vacuum chamber.

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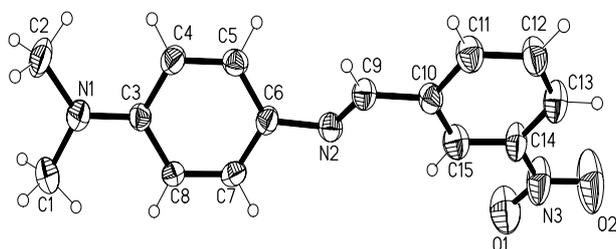


Figure 1. The molecular structure of DMNBPDA.



Figure 2. A typical STM image of a recorded pattern formed by a voltage pulse of 3.5 V applied for 5 ms; scanning conditions: $V_b = 0.39$ V; $I_t = 0.21$ nA.

STM experiments were performed using tips made of Pt/Ir (80/20) wires in constant-height mode by Solver P47 (NT-MDT Co.). The data recording was carried out by applying a series of voltage pulses between the STM tip and the HOPG substrate. To compare the electrical properties of the organic thin film before and after the voltage pulse, the current–voltage (I – V) curves of the unrecorded and recorded regions were separately obtained using the STM. In order to confirm the reliability of the experiments, various samples and tips were used.

3. Results and discussion

Figure 2 is a typical pattern for data recording on the DMNBPDA film, formed by applying a voltage pulse of 3.5 V for 5 ms between the STM tip and the HOPG substrate. The average size of the recorded marks is about 0.7 nm in diameter, corresponding to a data storage density of about 10^{13} bit cm^{-2} . In the image, the shadow effect on each mark is due to the fact that the feedback circuits are not completely nulled during scanning. The recorded marks are very stable during continual scanning for 2 h.

Local I – V characteristics of the films measured before and after the voltage pulse confirmed the conductance transition, as shown in figure 3. The recorded region shows an electrical conductor behaviour, which suggests that delocalized electrons exist in the recorded region of the film. The electrical resistance of the recorded region is much lower than that of the unrecorded region, causing bright dots observed by the STM. Considering the fact that not only strong electron donor groups ($-\text{N}(\text{CH}_3)_2$) but also strong acceptor groups ($-\text{NO}_2$) exist in the of DMNBPDA molecule, we believe that the recording mechanism is probably caused by intermolecular or intramolecular charge transfer. Generally, intramolecular charge transfer is unstable; however, the recorded marks that we observed are very stable. Therefore

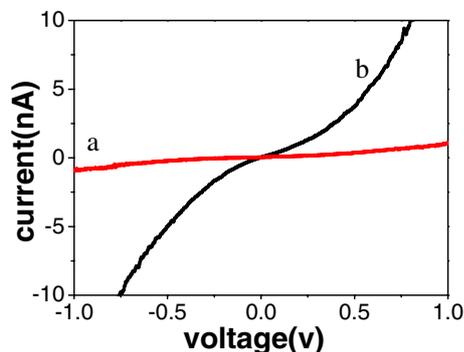


Figure 3. Typical STM I – V relations. (a) The I – V curve before application of the voltage pulse, with high resistance; (b) the I – V curve after application of the voltage pulse, with low resistance.

(This figure is in colour only in the electronic version)

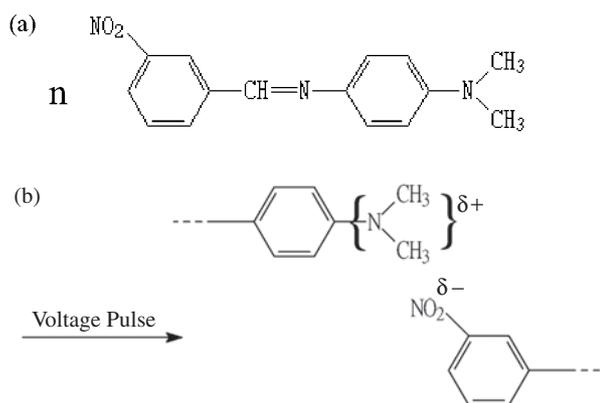


Figure 4. The intermolecular charge transfer mechanism of data recording for the DMNBPDA thin film. (a) The high-resistance state related to the unrecorded region of the DMNBPDA thin film; (b) the low-resistance state related to the recorded region of the film.

the recording mechanism is probably caused by intermolecular charge transfer.

We have calculated the three-neighbour molecular system of the NBPDA by the method of density functional theory (DFT) [15]. The result indicates that electron transfer is confined to just the two-nearest-neighbour molecular system and induced by a strong electric field. Considering that the $-\text{N}(\text{CH}_3)_2$ in the DMNBPDA molecule is a better electron donor than the $-\text{NH}_2$ in the NBPDA molecule, intermolecular charge transfer would happen under a certain electronic field. A schematic explanation of the recording mechanism is shown in figure 4. Figure 4(a) relates to the unrecorded area of the thin film, without the delocalized electrons. The region is composed of separated DMNBPDA molecules and is in a high-resistance state. When a crucial voltage pulse is applied to the film, charge is transferred from $-\text{N}(\text{CH}_3)_2$ of one molecule to $-\text{NO}_2$ of another molecule, i.e. the π -electron is delocalized in the system and the resistance of the system becomes lower, as shown in figure 4(b).

4. Conclusions

We have succeeded in developing an organic thin film of DMNBPDA with electrical bistability. Ultrahigh-density data

storage is realized by applying a voltage pulse between the STM tip and the HOPG substrate. The recording marks are very stable; their average size can reach 0.7 nm in diameter. Intermolecular charge transfer has been proposed as the recording mechanism.

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References

- [1] Sato A and Tsukamoto Y 1993 *Nature* **363** 431–3
- [2] Kado H and Tohda T 1995 *Appl. Phys. Lett.* **68** 188–91
- [3] Chou S Y, Krauss P R and Renstrom P J 1996 *Science* **272** 85–7
- [4] Kolb D M, Ullmann R and Will T 1997 *Science* **275** 1097–9
- [5] Dujardin G, Mayne A, Robert O, Rose F, Joachim C and Tang H 1998 *Phys. Rev. Lett.* **80** 3085–7
- [6] Piner R D, Zhu J, Xu F, Hong S and Mirkin C A 1999 *Science* **283** 661–3
- [7] Ma L P, Song Y L, Gao H J, Zhao W B, Chen H Y, Xue Z Q and Pang S J 1996 *Appl. Phys. Lett.* **69** 3752–3
- [8] Gao H J, Sohlberg K, Xue Z Q, Chen H Y, Hou S M, Ma L P, Fang X W, Pang S J and Pennycook S J 2000 *Phys. Rev. Lett.* **84** 1780–3
- [9] Song Y L, Ma L P, Xie S S, Pang S J, Jiang L and Zhu D B 2000 *Mater. Sci. Eng. B* **76** 79–82
- [10] Li J C, Xue X L, Li X L, Liu W M and Hou S M 2000 *Appl. Phys. Lett.* **76** 2532–4
- [11] Shi D X, Song Y L, Zhang H X, Jiang P, He S T, Xue S S, Pang S J and Gao H J 2000 *Appl. Phys. Lett.* **77** 3203–5
- [12] Ma L P, Yang W J, Xie S S and Pang S J 1998 *Appl. Phys. Lett.* **30** 3303–5
- [13] Shi D X, Song Y L, Zhu D B, Gao H J, Zhang H X, He S T and Pang S J 2001 *Adv. Mater.* **13** 1103–5
- [14] Ma L P, Yang W J, Xue Z Q and Pang S J 1998 *Appl. Phys. Lett.* **73** 850–2
- [15] Hou S M, Zhao X Y, Yang C, Xue Z Q, Yang W J and Chen H Y 1999 *J. Vac. Sci. Technol. B* **17** 2467–10