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Addressing of Optoelectronic Memory of Thin Film Zinc Porphyrin with Crossed 5 μm Indium Tin Oxide Arrays

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We report here the preparation and characterization of an optoelectronic memory device based on a single layer of organic thin film (~0.9 μm thick) of zinc octakis(β-decoxyethyl)porphyrin, sandwiched between two crossed indium tin oxide (ITO) arrays. The ITO lines in the array were 5 μm wide and were separated from each other by a 5 μm gap. Data (in the form of an electric charge) could be independently stored at and retrieved from an intersection of the crossed ITO lines with irradiation. Each intersection defined one memory pixel (5 × 5 μm) and there was no cross talk with nearby pixels under the test conditions, clearly demonstrating its potential application as an information storage device using a molecular thin film.
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Zinc octakis(β-decoxyethyl)porphyrin (ZnODEP) is a flat molecule with eight long hydrocarbon chains.[1] In the crystal, molecules are regularly stacked to form individual columns and the nonionic alkyl tails serve as an insulating coating, leading to a bundle of electrically insulated one-dimensional molecular "wires."[1] Even within the same molecular column, the intermolecule separation is ~4 Å,[1] significantly larger than those in inorganic substances. This produces an intrinsic characteristic of a crystal structure consisting of discrete molecules that can be considered an "orientated molecular gas."[2,3] This structure has an inherent advantage over inorganic materials as a medium for high-density charge trapping and, therefore, information storage, because charge carriers are localized on individual molecules and can be trapped for long times on structural defects or impurity sites.[2-4] In principle, the theoretical size of one memory element could be as small as a single molecular column representing the ultimate density in data storage.[5,6] We have demonstrated previously that an individual pixel could be as small as a few tens of nanometers with a configuration of a sharp scanning tunneling microscopy (STM) tip/organic film/indium tin oxide (ITO).[5,7] While this tip-type movable structure is simple and convenient for testing the possibility of ultrahigh density data storage, it is not useful for most memory applications where a fixed rigid device is more desirable. Nor is it useful in examining cross talk among different pixels. This led us to the present study of an alternative configuration as shown in Fig. 1, in which each 5 μm wide ITO line served as an independent electrode and was individually externally addressable.

When a bias voltage was applied to two of the crossed ITO fingers (such as column 3 and row D), the organic film was subjected to the electric field at only that particular intersection (designated as pixel 3D). Thus, Fig. 1 illustrates a total of 25 memory elements. Figure 2a shows the current as a function of bias voltage from pixel 3D with and without irradiation. The dark current is negligible over the potential range of −1 to +1 V. Essentially the same result was seen with the other pixels. Note that in this and other measurements discussed below, the whole film, *i.e.*, all 25 pixels, were irradiated simultaneously with no attempt made to illuminate just one particular ITO intersection. The optoelectronic properties in each pixel appeared to be basically the same as those seen with the large area ITO/ZnODEP/ITO cells reported previously.[5] A steady-state short-circuit photocurrent (I_{sc}) appears in these symmetric sandwich cells as a result of preferential charge injection at the irradiated interface between ITO and ZnODEP film. In this case, electrons from the excited state of ZnODEP molecules are injected into the irradiated ITO contact (termed an anodic current) while positive charges move to the opposite electrode.[1,5,7-13] The relation between I_{sc} as a function of time without bias (the short-circuit photocurrent) from pixel 4D is shown in Fig. 2b.

As with the previously reported large ZnODEP cells, reversible charge trapping and detrapping was also seen with the 5 μm pixels (each pixel contains about 10^{10} molecules).[5] For example, pixel 4D was charged under a bias voltage of 1 V (applied to the ITO lines 4 and D with the irradiated side positive) under illumination. Pixel 4D was kept at short-circuit conditions without light for about 130 s, and then irradiated (Fig. 3b). The dependence of I_{sc} on time was different from that shown in Fig. 2b. The I_{sc} is in the opposite direction (from anodic into cathodic upon irradiation). This is a result of the trapping of holes in the ZnODEP at the irradiated interface during irradiation at 1 V bias and the photodischarge process that occurs at short circuit (detrapping).[5-8] Similarly, when the same pixel was charged under the opposite bias, −1 V, the photodischarge current also reversed its direction (Fig. 3a). Such a reversible charge trapping and detrapping has been proposed for information writing and reading in data storage.[5-8]

The key experiment in this study, however, is the investigation of possible cross talk among neighboring pixels by writing data at one pixel and noticing the effects on neighboring pixels under different conditions. A number of different experiments were carried out to test for cross talk. First, pixel 4D was charged under a bias of 1 V

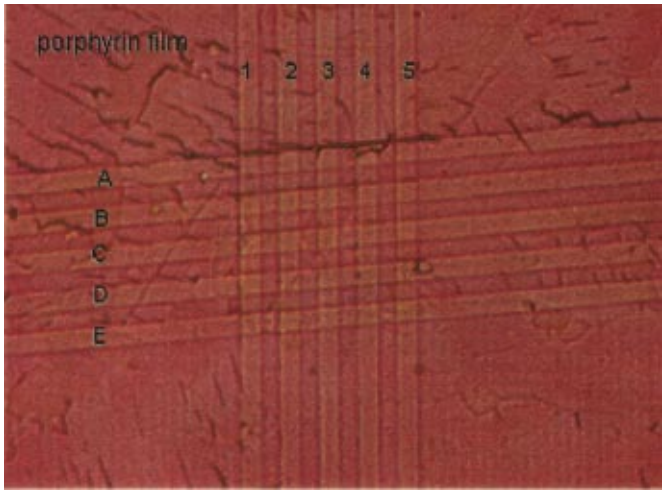

Figure 1. A micrograph of an optoelectronic memory device based on an organic thin film (ZnODEP) sandwiched between two nearly crossed ITO arrays. An individual ITO line (designated as A, B, C, D, E, and 1, 2, 3, 4, 5) is 5 μm wide and is separated by a 5 μm distance from each other. The intersection of the crossed ITO fingers such as column 4 and row D defines one memory element (designated as pixel 4D). A color version of this figure is available in the online edition at http://www3.electrochem.org/letters.html

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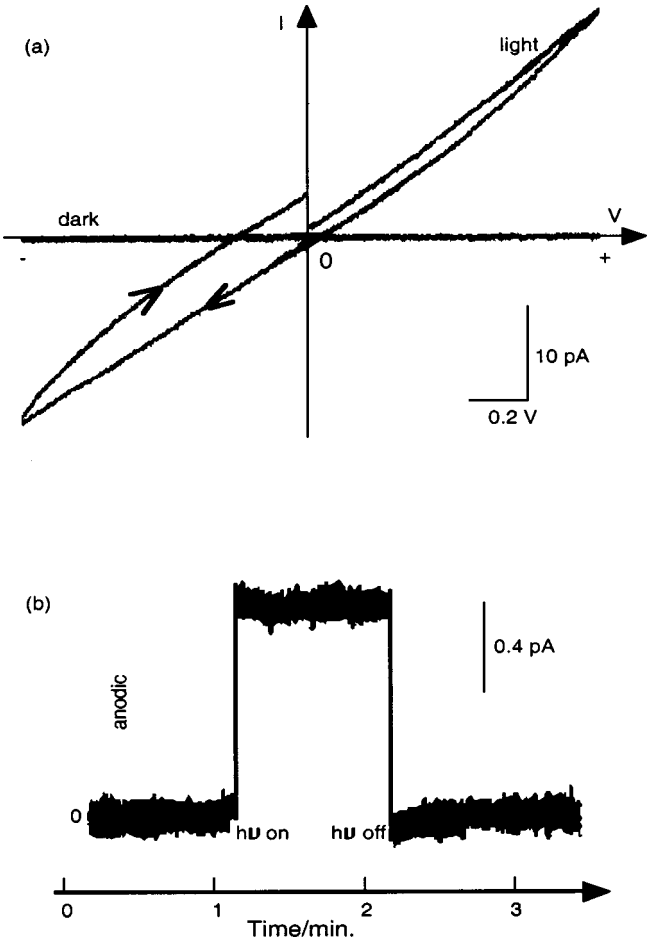

Figure 2. (a) Photo- and dark current as a function of bias voltage obtained from pixel 3D. Scan rate was 50 mV/s. (b) A short-circuit photocurrent as a function of time from pixel 4D without a bias voltage.

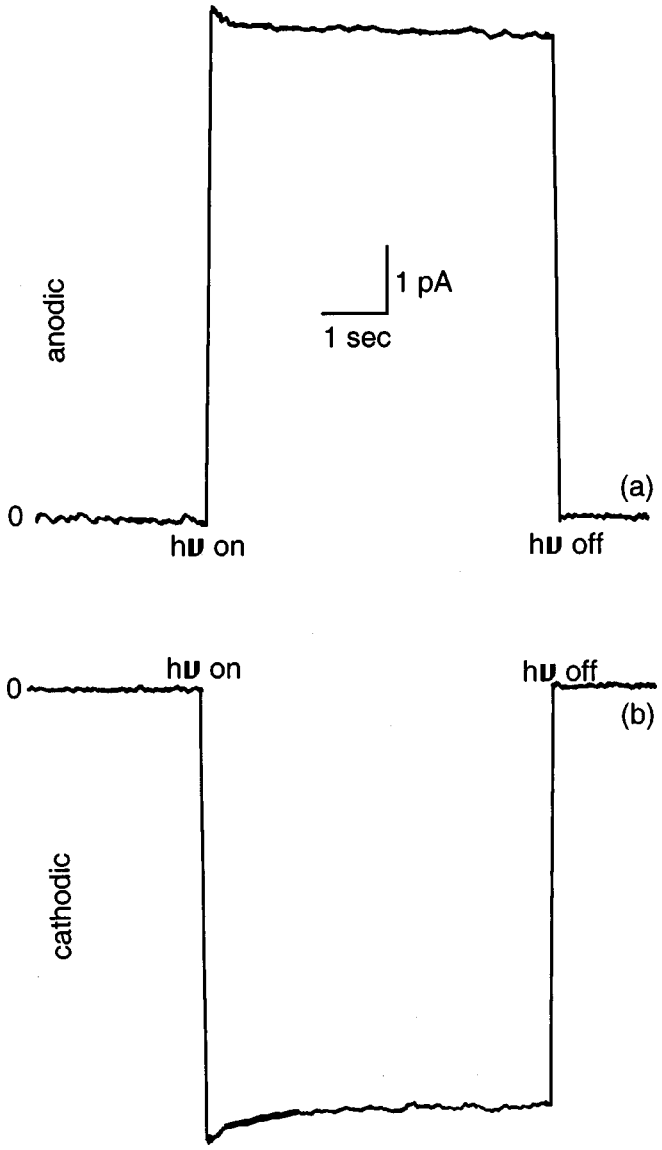

Figure 3. Photodischarge current as a function of time from pixel 4D after the cell had been charged under a bias of (a) −1 and (b) +1 V with irradiation followed by a rest period of 130 s at short-circuit conditions in dark.

with irradiation. Then, ITO lines 4 and D were left at open circuit and a photodischarge attempt was made at the neighboring pixels, such as the previously uncharged pixel 4E (*i.e.*, ITO fingers 4 and E were short-circuited under irradiation). We observed no cathodic I_{sc} there, indicating that data stored at pixel 4D did not affect its closest neighbor, pixel 4E. After this irradiation, the measurement was moved back to pixel 4D, where a photodischarge current in a cathodic direction was seen during irradiation under short-circuit conditions. This means that data written at pixel 4D could be read only at that particular pixel and that short-circuit irradiation of 4E did not affect the data at 4D, showing clearly no cross talk between pixels 4D and 4E. Similarly, cross talk between pixel 4D and 3C was not detected. This was also true for pixels separated by one or more pixels such as pixel 4B and 4D. Systematic investigations of different pixels revealed no cross talk among the neighboring memory elements, crucial for a memory device. Moreover, one pixel was read repeatedly over 1000 times and the readout current was still over 50% of the initial readout signal consistent with our earlier result.[5] Obviously the total number of ITO lines in the array could be extended to several thousands to make a larger memory device in a matrix arrangement.[a,14]

Experimental

In these experiments, a projector light bulb (WKO av/photolamp) was used as a light source (~120 mW/cm^2, absorption coefficients are $\alpha = 0.1\,\mu m^{-1}$ at 510 nm, and $\alpha = 0.45\,\mu m^{-1}$ at 586 nm[9]) that irradiated the sample through an optical fiber. The 5 μm ITO arrays were formed on a glass substrate and each line was progressively increased in width through five steps up to 1.5 mm for electric connection to external instruments. The structured ITO arrays were fabricated by Hewlett-Packard. The ZnODEP compound was synthesized as reported previously.[5-7] A home-made instrument coupled with a universal programmer (EG&G PARC model 175) was used for the measurements. The ZnODEP film was prepared by melting the compound at about 150°C followed by a slow cooling to room temperature similar to a procedure described earlier.[4] Attempts at preparing cells with even smaller ITO array lines, down to 0.5 μm, were not successful to date, mainly because the ITO fingers were often shorted to each other at one or more points. Nevertheless, the 5 μm structure in this study probably represents the highest resolution reported so far with ITO features and shows promise for high-resolution optoelectronic information storage based entirely on a molecular film medium.

[a] An effective charge capacity of the order of 30_C/cm^2 or 10^{18} charges/cm^3 was obtained (see Ref. 14).

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