High-Density Nanosecond Charge Trapping in Thin Films of the Photoconductor ZnODEP

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common sample pretreatment step, dilution, can be effected within the capillary channel manifold. Typical sample preparation steps performed within a conventional flow injection analysis system could also be effected within these devices by electroosmotic pumping of the fluid phase.

Taken together, our results show that the micromachining of capillary channels on planar substrates provides a route to fabricating miniaturized chemical systems on a chip capable of quantitative analysis. Rapid separation of complex sample mixtures combined with sample handling steps such as dilution and injection provide a basis for more complex, miniaturized analysis systems. The application of micromachining techniques to the miniaturization of chemical analysis is very promising and should lead to the development of analytical laboratories on a chip.

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17. The Uniphase/Cyonics laser was operated at an output power of 4 to 5 mW (*15*). Either the beam was directed onto the sample through a 600-μm optical fiber or mirrors and a lens were used to focus the beam to about 40 μm. Emission was collected with a 10:1 or 25:1 microscope objective and then directed into a photomultiplier tube after filtering with an Omega 508- to 533-nm bandpass filter. The signal was electronically filtered and digitally collected with a Macintosh computer equipped with a National Instruments NB-MIO-16 analog-to-digital converter and Labview software or an 8-bit digital LeCroy 9310 oscilloscope (*14, 16*). The potential programs were generated in the computer and applied to the device reservoirs through high-voltage relays and FUG model HCN 12500 power supplies.
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High-Density Nanosecond Charge Trapping in Thin Films of the Photoconductor ZnODEP

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An electrooptical memory effect is observed with solid thin films of the photoconductor zinc-octakis(β-decoxyethyl) porphyrin (ZnODEP) sandwiched between two optically transparent electrodes. Upon irradiation with the simultaneous application of an electric field, electron-hole pairs are generated and separated within the photoconductive layer. These electron-hole pairs become "frozen" within the films when the irradiation is interrupted. These trapped charges can be released by irradiation of the cell, resulting in a transient short-circuit photocurrent. No cross talk between adjacent memory elements separated by ~0.2 micrometer (a density of 3 gigabits per square centimeter) was detected. The charge storage system is robust and nonvolatile. The response time for the write-read beam is in the subnanosecond range, and no refreshing is required for long-term retention of trapped charges.

A nonvolatile, rewritable electrooptical method of data storage has been developed that is based on charge trapping in thin films of a photoconductive material, in this case, ZnODEP, with which high densities and high speeds can be achieved. This information storage method requires a material with a high resistance in the absence of light, good photoconductivity, and the capacity to inject stored charge upon simultaneous application of light and an electric field. Information, as trapped charge, can be written, read, and erased by simultaneous application of an electric field and a light pulse. We also used a scanning tunneling microscope (STM) for charge storage (writing) and charge measurement (reading) within elements as small as 40 nm in diameter.

Photoconductivity has been widely investigated (*1*), and the displacement of charge in photoelectrets upon application of an electric field and light, a phenomenon called persistent internal polarization, has been known for more than 35 years (*2, 3*). Analogous effects are also important in electrophotography (*4*).

Our interest in this approach grew from our investigations of solid-state photocells composed of a solid film of the liquid crystal porphyrin ZnODEP (Fig. 1) held between transparent indium-tin-oxide (ITO) electrodes, first described by Gregg *et al.* (*5*). Such cells produce steady-state short-circuit photocurrents by preferential injection of electrons into the irradiated electrode. While investigating the behavior of such cells under a constant bias with pulsed irradiation or with a pulsed bias under steady illumination, we observed charge trapping.

Cells (Fig. 2) were constructed as previously described (*5*) by capillary filling of molten ZnODEP (*6, 7*) into the 1- to 2-μm gap between two ITO electrodes (area, 0.5 cm^2). Upon solidification, the film was illuminated with a write beam (wavelength, 550 nm) to produce a cathodic current when a negative potential was applied to the irradiated ITO electrode (we choose the sign of the applied potential to be that of the irradiated, or front, electrode with respect to the back electrode). In this writing step, initially vacant traps within the film are filled with electrons (Fig. 3). Because the resistivity of ZnODEP in the dark is very high ($\geq 10^{14}$ ohm·cm), electron movement "freezes" when the light is switched off; the trapped charge remains stored in the

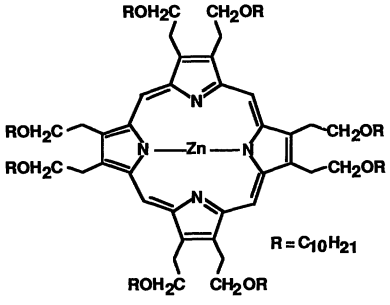

Fig. 1. Structure of the photoconductor ZnODEP.

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dark under open-circuit or short-circuit conditions. The written information can later be read by irradiation of the device with a read beam (wavelength, 550 nm) under short-circuit conditions; the release of electrons from the traps leads to an anodic photocurrent spike (Fig. 3).

In an analogous way, holes can be trapped. When the cell is irradiated under a positive bias, electrons are removed from initially populated traps ("holes" are injected). These trapped holes are again frozen in the dark under both open- and short-circuit conditions. As before, the stored charge is released with a read beam without bias, producing a cathodic photocurrent spike as a result of trap refilling.

The anodic or cathodic photodischarge current spikes can be taken to represent the memory state, "1," compared with an uncharged state, "0." Alternatively, the directional bias during the write phase can be the basis of a three-state (trapped electrons, trapped holes, uncharged) device. The magnitude of the readout current spike depends on the wavelength, intensity, and pulse width of the write beam and the magnitude of the bias. The light pulse and potential pulse need not be precisely synchronized in the write step. In fact, the amount of charge stored is not affected by a longer potential pulse because of the high resistivity of ZnODEP in darkness. Alternatively, the stored charge can be read by measuring the potential at that location at open-circuit conditions (such as with a very high impedance voltmeter) in the dark.

Several factors are of importance in these devices: spatial resolution of the trapped charge, injection (writing) time, stability of trapped charge, and stability of the device to write-read (WR) cycling. The spatial resolution of trapped charge elements depends on a high lateral resistance between storage elements. The geometry of an element of trapped charge is controlled either by the size of the optical beam (optical WR mode) or by the spatial distribution of the applied bias (electrical WR mode).

In the optical WR mode, a bias is applied across the whole surface of the ZnODEP, and a focused light beam is used to illuminate spots on the surface. With a laser beam, this spot has a diameter of ~1 μm. The rise time associated with the optical WR pulse is in the subnanosecond range (Fig. 4). Data can be written optically at different sites (memory elements) on the same sample simultaneously or sequentially. The locations of stored charge can be differentiated quantitatively from the magnitude of current readout. We irradiated the front surface of the device using a bundle of optical fibers with a bias of 1 V. Charge stored by irradiation with individual fibers could be read separately by irradiation of only that memory element under short-circuit conditions without interference from the charge stored in a neighboring element. The very high resistance in darkness thus prevents leakage of charge through the porphyrin film between the two conductive ITO layers or between charged spots within the medium.

In the electrical WR mode, the total surface is illuminated during the write step, and spatial resolution is controlled by a localized electric field, for example, by lithographically deposited electrodes or by the size of a small STM tip. The sharp tip of an STM can be used as a liftable electrode to make a point contact to the film (that is, to confine the electric field to a very small spot). The film was deposited on the ITO substrate by melting the ZnODEP powder. To write, a voltage pulse is applied between the tip and the back contact of the active layer under irradiation, with the photogenerated charge being stored under the tip. As the tip is moved over the surface of the film, charge is deposited at different sites or memory elements. The stored charge can be read by scanning the tip under short-circuit (or reverse bias) conditions over the film surface under illumination and observing the current for the discharge of the elements (Fig. 5). A single element of ~0.2-μm diameter is readily obtainable; this corresponds to a storage density of ~3 gigabits cm^{-2}. In experiments in which the diameter of the stored charge element was mapped with the scanning tip as a function of bias during charging (writing), we found that the size decreased with smaller bias. Hence, even higher storage densities (with less charge stored per element) should be possible. For example, charge has been localized in a spot 40 nm in diameter with a bias of 6 V.

Although the amount of charge remaining in the traps is reduced after each reading, many readings can be made before the traps are depleted. The number of possible readouts is increased if the reading beam is weaker than the writing beam. However, because the charge is written under bias and is read under short-circuit conditions, the stored data can be read many times even with a reading beam as intense at the writing beam: In one test with the thin-film cell, the same 10-ns laser pulse was used for both writing and reading, and after ~1500

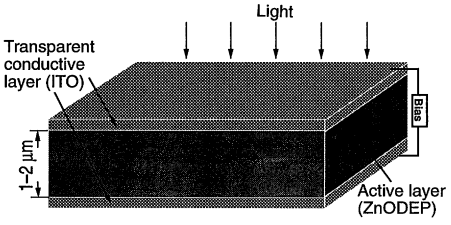

Fig. 2. Schematic diagram of a photocell.

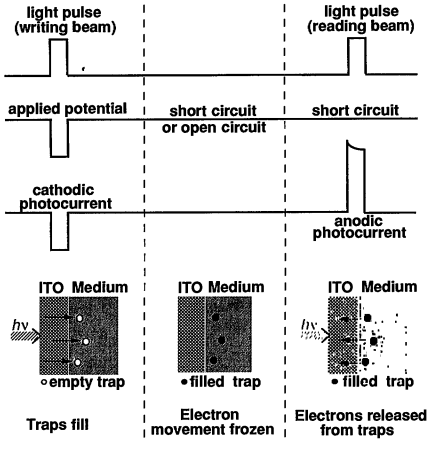

Fig. 3. Operational principles governing an optical memory device based on photoinduced charge trapping and detrapping. Under negative bias, the write beam causes electron storage at trap sites. The stored electrons are released by a read beam under short-circuit conditions.

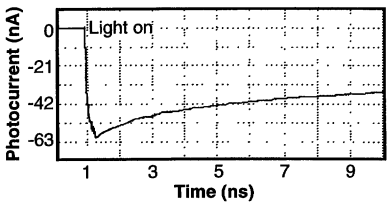

Fig. 4. Photodischarge current as a function of time. The rise time is in the subnanosecond range. A charged spot, written with a 10-ns laser pulse with a bias of +1 V, was irradiated with a read beam, another 10-ns laser pulse under short-circuit conditions.

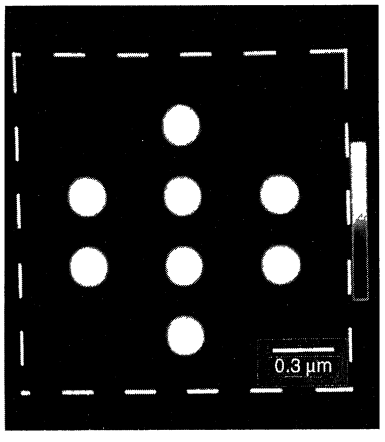

Fig. 5. A discharge current image demonstrating high-density data storage. Data were written under +10-V bias (tip positive) and were read under short-circuit conditions with irradiation by a scan with the STM tip. In this gray-scale image, high read currents appear white and low currents, dark.

readings, the readout signal was still >60% of the first readout current. It is also possible to refresh the stored charge; for example, a potential pulse sequence of the proper width and magnitude could be coupled with a reading beam pulse to rewrite charge. Here, during the first part of the reading beam pulse, a photodischarge results under short-circuit conditions, and during the second part of the reading beam, a potential pulse is applied to recharge the memory element. By this means, the memory element is refreshed after each reading, in a manner analogous to that used for dynamic random access memories (DRAMs).

The cycle life (the number of cycles of charging and discharging) was tested by applying continuous potential pulses of 0 to +0.5 V (pulse width and interval of 1 ms) to the thin-layer cell under constant irradiation, with the memory element charged at +0.5 V immediately after each readout at 0 V. Even after the cell was charged and discharged >1 billion times (a period of ~12 days), the output current of each reading was essentially identical to the first one. This result suggests the absence of irreversible changes in the film during charging and discharging.

Readout can also be implemented by measuring the voltage produced by the photoinduced charge in the dark. Because no charge flows during a voltage measurement, depletion of the stored signal does not occur in this read mode. Charge generated and stored by a low intensity writing beam (~10 $\mu W\ cm^{-2}$) under a small bias (+0.5 V) was read continuously in the dark with a high input impedance voltmeter (Orion Research Model 701A pH meter) with no perceptible change for >2000 hours. The readout voltage was constant at 20 mV with no evidence of decay. The nature of the trap sites for charge storage in a polycrystalline ZnODEP film is not clear; studies of other systems (8) suggest that they might be crystal defects, grain boundaries, or chemical impurities.

The approach described here for trapping charge in a photoconductive thin film appears promising as a means of information storage. Current state-of-the-art Si-based DRAMs contain 64 megabits (each with a cell size of ~1 to 2 μm^2) and have addressing speeds of 30 to 50 ns (9). We have demonstrated high-density, high-speed writing and long-term stability and cycle life. The structures involved are simple and inexpensive. Although we have used an STM [which has also been recently used in a capacitive mode for charge storage in a nitride-oxide-silicon (NOS) system (10)] to write and read data, high-resolution lithographics might also be useful in the fabrication of memory devices based on this system. The experimental results reported here were obtained with ZnODEP, but other photoconductive materials have shown similar properties in preliminary experiments.

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Electron Diffraction and Imaging of Uncompressed Monolayers of Amphiphilic Molecules on Vitreous and Hexagonal Ice

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A new approach is described for probing domains of ordered self-assemblies of amphiphilic monolayers at the aqueous solution interface. The method has potential importance for the study of membrane structure, Langmuir-Blodgett films, and nucleation processes of two- and three-dimensional crystals. Electron diffraction (ED) patterns indicative of two-dimensional crystalline self-assembly were obtained from samples, which were examined by cryo-electron microscopy, of monolayers of water-insoluble amphiphiles on vitrified aqueous substrates. The apparent hexagonal symmetry of an ED pattern from a $C_{16}H_{33}OH$ monolayer was interpreted in terms of multiple twinning. Monolayers of the $C_{31}H_{63}OH$ and cadmium salt of $C_{19}H_{39}CO_2H$ that were studied by dark-field techniques displayed faceted two-dimensional crystallites with a maximal size of 1 to 2 micrometers. Epitaxial nucleation of hexagonal ice by the $C_{31}H_{63}OH$ monolayer has also been demonstrated by ED.

Interfacial self-assembly of molecules into ordered two-dimensional (2D) aggregates is important to many fields (*1*–*3*), including crystal nucleation, the formation of mono- and multilayers, and molecular electronics. A method for the direct demonstration of such microscopic properties of amphiphilic monolayers in situ is grazing incidence x-ray diffraction (GIXD) by synchrotron radiation (*4*). This method has revealed that water-insoluble amphiphilic monolayers in the uncompressed, relaxed state are highly crystalline. This finding contrasts with the generally accepted view that monolayers need to be well compressed to exhibit 2D crystallinity. The GIXD method has allowed measurement of the structure and the growth and dissolution properties of self-aggregated monolayers as a function of parameters such as molecular length, temperature, solvent, and additives (*3*). Surface x-ray techniques do not yield direct images of the 2D crystal domains. Such domain morphologies have been examined by epifluorescence and Brewster angle microscopy. However, these methods are applicable only to domains larger than 1 μm in diameter and have not unambiguously revealed self-assembled monolayers on solutions displaying faceted 2D crystals (*5*). Atomic force microscopy has shown that domain structures in Langmuir monolayers of stearic acid, $C_{18}H_{39}CO_2H$, transferred from water onto polyethyleneimine-covered mica have fairly well faceted grains as small as 2 to 3 μm (*6*). Transmission electron microscopy (TEM) studies of mono- and multilayers of amphiphilic molecules that had been transferred (in a partially compressed state) from a water surface onto a solid support did not reveal submicrometer features in the domains (*7*).

The self-aggregating ability of amphiphilic monolayers on water suggests that one could fast-freeze the water subphase

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