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## Principles of a Three Dimensional Molecular Electronic Memory

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# PRINCIPLES OF A THREE DIMENSIONAL MOLECULAR ELECTRONIC MEMORY

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**Abstract** The principles of using an electronically highly anisotropic insulator as a memory are described. As an example a Langmuir Blodgett (LB) multilayer film of polydiacetylene (PDA), of repeat unit  $[=RC\equiv C-CR=]$ , is considered. Excess injected electrons in a PDALB film reside in the high mobility conduction bands along the PDA backbones which are in the plane of the layer. Diffusion within the layer planes is rapid. The electrons occasionally hop to the next layer plane. N layers can store one N bit word, the presence or absence of electrons in the n th layer denoting a 1 or 0 of the n th bit. Means for writing in the charge, controlling its motion between the layers with fields, and reading out the charge are described. Layers of alternating high and low electron affinity are discussed; they give a much longer storage time in zero field, the electrons then being confined to the high affinity layers.

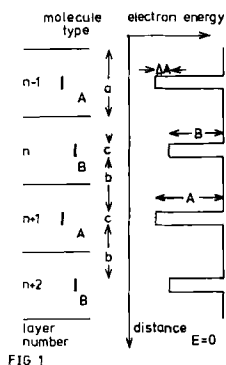


FIG 1

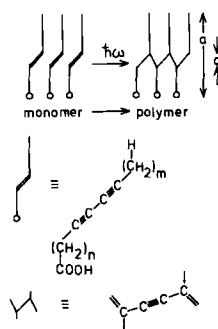


FIG 2

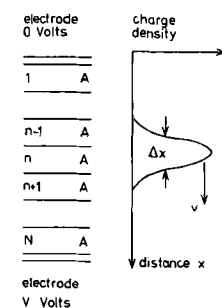


FIG 4

Figure 1 illustrates a Langmuir Blodgett (LB)

alternating multilayer film. Successive monomolecular layers, index  $n$ , of organic molecules A and B, can be built up by the LB technique. The molecules have a conjugated part of width  $c$ , and a non conjugated part. The distance between adjacent conjugated parts is  $b$ , less than the layer period  $a$ . An extra electron injected into the film prefers to live in the conjugated parts of the molecules, and also prefers molecule A to B. Figure 1 denotes electron affinities A and B relative to the affinity of the non conjugated region. The molecules are such that the electron mobility in the film plane within one layer is greater than that between layers. Thus excess electrons are distributed uniformly in the film plane in the conjugated regions, and occasionally hop between layers. The enormous variety of organic molecules allows large variation of the layer parameters  $a$ ,  $b$ ,  $c$ , A and B. Figure 2 shows a polydiacetylene LB film. These have been characterised for a range of parameters  $m$  and  $n^1$ . The monolayer is initially made of monomer. UV light causes polymerisation. The monolayer is retained. Excess electrons on the conjugated polymer backbone are highly mobile<sup>2 3</sup>.

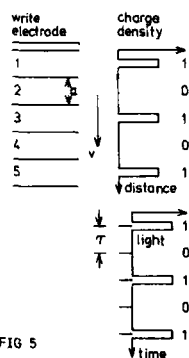


FIG 5

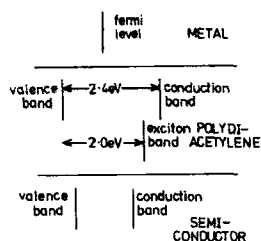


FIG 6

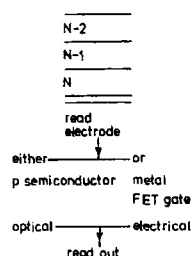


FIG 7

Figure 4 illustrates the motion and spread of a charge sheet in an identical layer film. The voltage  $V$  and field  $E$  cause the charge sheet to drift across the layers with velocity  $v$ . The width  $\Delta x$  of the sheet increases with time  $t$  due to diffusion according to

$$(\Delta x)^2 = D t.$$

The Einstein relation between the drift velocity  $v$  and diffusion coefficient  $D$  is

$$v/E = (k_B T/e) D.$$

From these assumptions alone, a delta function charge sheet can travel a distance of  $N$  layers and spread by less than one layer spacing provided that

$$V > V_1 = N^2 (k_B T/e).$$

Consider an identical layer film. There is a characteristic time  $\tau$ , (or probability  $1/\tau$  per unit time) for electron hopping between layers. Then by arguments due to Mott<sup>5</sup>,

$$1/\tau = V \exp[-2 k b],$$

$$k^2 = 2 m A / \hbar^2.$$

Here  $V$  is a hopping attempt rate, taken as a phonon frequency of  $10^{14}$  Hz.  $k$  measures the spatial decay rate of the electron wavefunction through the non conjugated region of forbidden energy  $A$ ;  $A$  is taken as 3 eV. For  $b = 1$  nm then  $\tau = 0.5 \mu s$ ; for  $b = 0.7$  nm then  $\tau = 2.6$  ns. At low fields  $v$  is linear in  $E$ ; the mobility is

$$\mu = (e/k_B T) (a^2/\tau)$$

At high fields the drift velocity saturates,

$$v = a/\tau, V > N (k_B T/e).$$

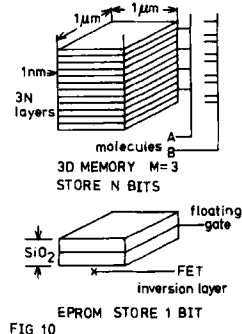
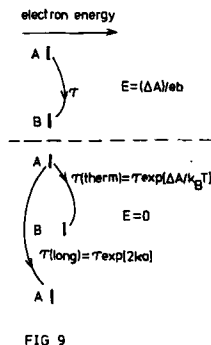
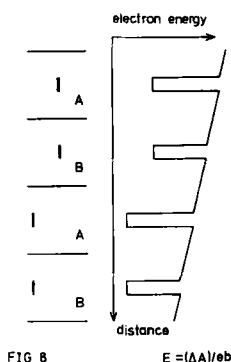
Here back hops against the field become rare as the electrostatic electron energy difference between layers is greater than the thermal energy.

Figure 5 illustrates temporal spatial coherence and writing. If

- 1) a temporal sequence of light pulses of period  $\tau$  is used to photoinject electrons from the electrode,
- 2) the voltage across  $N$  layers is greater than  $V_1$ , then
- 3) a spatial sequence of charge sheets moving at velocity  $v$  is created,
- 4) the spatial period is the layer spacing,  $a$ ,
- 5) the separate sheets do not diffuse together while in transit through  $N$  layers.

If the presence or absence of a light pulse denotes a 1 or 0 bit, then temporal bits are converted into spatial bits. Figure 5 shows writing the sequence 10101. This is a method of writing bits into a multilayer film. Consider, as an example of typical energy levels of the organic layer and of metal and semiconductor electrodes,

the case of polydiacetylene, shown in Figure 6. The energy levels of the polydiacetylene conjugated chain<sup>6 7</sup> are such that the layers are essentially transparent below 2 eV. The Fermi level of a number of metals, and the work function of a number of semiconductors, lie in the gap. So these are suitable photoinjecting electrodes.



Reading, illustrated in Figure 7, is the process of converting a moving spatial sequence of charge sheets arriving at an electrode into a temporal sequence. A p type direct gap semiconductor substrate, of energy levels relative to the film as in figure 6, will fluoresce on arrival of a minority carrier electron charge sheet from the film. The substrate functions as an LED. This optical read out has been considered elsewhere<sup>8</sup>; there it is shown that charge in the film less than the space charge limit can give a usable amount of light on read out. Electrical read out can be obtained using the gate of an FET as substrate electrode. This is sensitive to the total charge in the film. The time derivative of the FET response is due to the arrival of the charge sheets at the electrode. This has been discussed elsewhere<sup>9</sup>.

The alternating layer structure of Figure 1 is drawn in Figure 8 at a critical voltage

$$V = V_A = N (\Delta A/e) (a/b)$$

at which tunnelling from A to B can occur without thermal activation. For  $V > V_A$ , then charge sheets behave as described for the identical layer film. This state is used in the read and write modes. For  $V = 0$  the charges are stored in the A layers. The spatial

coherence of a stored set of charge sheets is destroyed by diffusion in the shortest of the times  $\tau(\text{therm})$  or  $\tau(\text{long})$ . These are illustrated in Figure 9. If  $\Delta A = 0.5$  eV, then the previous numerical example gives, at room temperature:-

b nm	a nm		(therm)	(long)
1	>1	0.5 $\mu$ s	250s	>25s
0.7	>0.7	2.6ns	1.3s	>0.7ms

$\tau(\text{therm})$  can be lengthened by increasing A or lowering the temperature.  $\tau(\text{long})$  can be lengthened by using 2 B layers between each A layer as shown in Figure 10.

The Figure 10 makes an analogy between the molecular memory and an EPROM. Also there are two low affinity B layers between each high affinity A layer. Suppose (M-1) B layers alternate with each A layer. Associate one bit with M layers and use NM layers to hold N bits. The clock time is now  $M\tau$ . In the read and write modes the criteria for the bits to diffuse less than a distance Ma while drifting a distance NMa across the film is again

$$V > V_1 = N^2 (k_B T / e).$$

The critical voltage for tunnelling without thermal activation is now

$$V > V_A = N M (\Delta A / e) (a/b).$$

Together these are the condition for retaining the spatial coherence of the store in the read and write modes.

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