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A field effect transistor based on the Mott transition in a molecular layer

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Here we propose and analyze the behavior of a field effect transistor (FET)-like switching device, the Mott transition field effect transistor, operating on a novel principle, the Mott metal-insulator transition. The device has FET-like characteristics with a low ''ON'' impedance and high ''OFF'' impedance. Function of the device is feasible down to nanoscale dimensions. Implementation with a class of organic charge transfer complexes is proposed. © *1997 American Institute of Physics.* [S0003-6951(97)00105-8]

The field effect transistor (FET)—the key three-terminal device in computer applications—is beginning to encounter obstacles to further development. Organic-channel field effect transistors, which are contemplated in near-future applications such as smartcards and displays, have been dogged by poor performance, directly traceable to the low carrier mobility in organic semiconductors.[1] The Si FET eventually encounters scaling limitations,[2] as the minimum channel length is estimated to be limited to 300–400 Å. A very significant question often asked is whether there exists an alternative to semiconductor-based FET technology which might offer a solution to such problems?

There exists a class of materials with comparable conductance to Si, namely poor metals such as the CuO_2 plane in cuprate superconductors,[3] or the organic or synthetic metals,[4–6] which belong to the class of doped *Mott–Hubbard insulators*.[7] The unusual intrinsic nature of this class of materials can be exploited in controlling their conductivity. In this letter we evaluate the concept of a switch based on the novel physical principle of the Mott–Hubbard metal-insulator transition.[7] We shall demonstrate its feasibility on physical grounds, and propose appropriate materials which could constitute the channel in the device.

The Mott–Hubbard insulator (unlike the conventional band insulator) has an odd number of electrons per unit cell. It is insulating due to a ''Coulomb blockade'' caused by the repulsive Coulomb interaction U between two electrons on the same site. Assuming one electron per site, propagation is blocked by the potential barrier U required to move an electron on to a nearest neighbor site, provided that the kinetic energy, measured by the intersite transfer integral t, is less than U. Examples of two-dimensional (2D) Mott insulators are alkali metal layers on GaAs,[8] the CuO_2 planes in undoped cuprate superconductors,[3] and organic charge transfer complexes.[4,5]

The phase diagram for the Mott–Hubbard insulator is well studied in, for example, cuprate superconductors. It is possible to *metalize* the insulator by doping with a certain fraction of carriers (say holes), typically 15% carriers per site is appropriate. The holes permit percolation through the lattice without encountering the barrier U. In addition to cuprates, the synthetic metals such as tetrathiofulvalene–tetracyanoquinodimethane (TTF)-(TCNQ) are examples of doped Mott–Hubbard insulators, with 10%–40% of carriers.[4]

Using an appropriate Mott insulator material as a conducting channel, the proposed device operates by gate control of the carrier concentration in the channel. If the carriers are holes, the conduction is termed p-type, if electrons, n-type. Implementation is via an FET–type device, termed a Mott transition field effect Transistor[9] (MTFET), whose essential active elements are illustrated in Fig. 1. The active channel, connecting source to drain when the device is ''ON,'' and acting as insulator when ''OFF,'' consists of a monolayer of the Mott–Hubbard insulating material. The channel is in close proximity to a thin insulating spacer layer, which separates it from the gate (control) electrode.

As in a conventional FET, switching occurs by control of the charge in the channel via the gate voltage.[10] In an enhancement-mode (EM) device, the monolayer is intrinsically insulating; the device default state is ''OFF.'' For a p-type EM device, application of a negative gate voltage induces migration of holes from source and drain into the channel, converting the channel to a p-type metallic conductor, and thus switching ''ON'' the device. Conversely, the n-type EM device can be switched ''ON'' by a positive gate voltage.

An alternative functionality is the depletion-mode (DM) device, in which the channel molecules are intrinsically doped so as to be conducting. The device default state is then ''ON.'' If p-type, the device is switched ''OFF'' by application of a positive gate voltage, and conversely for n-type.

Let us consider the case where the active component in the layer consists of a single type of molecule. The molecular energy levels relative to the source-drain Fermi level are defined as lying at $-\varepsilon_l$, for the $0 \leftrightarrow 1$ transition (ionization level), and as $-\varepsilon_l + U$, for the $1 \leftrightarrow 2$ transition (affinity level). Whichever is the lowest lying excitation will normally
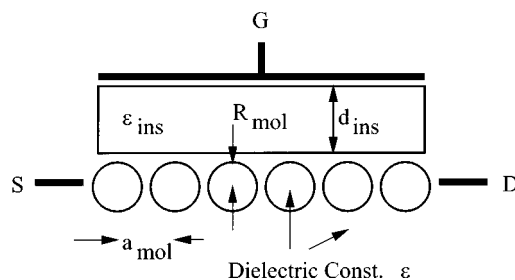

FIG. 1. Schematic side view of three-terminal molecular transistor.
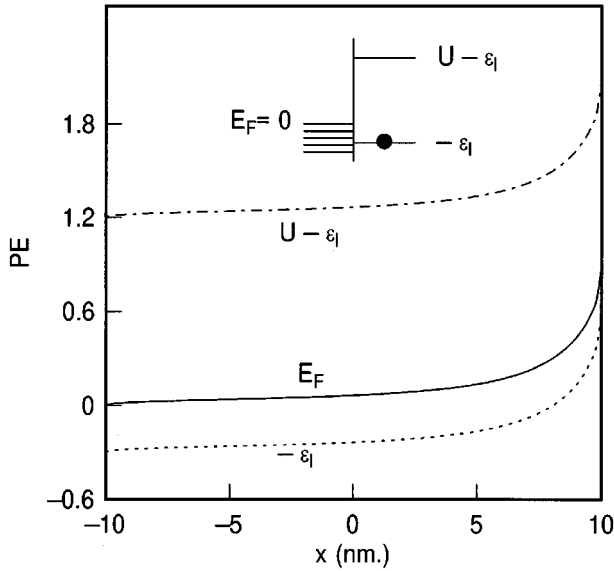
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FIG. 2. Energy variation along channel in the presence of a drain-source bias V_{DS} for the p-type device, calculated treating electrodes and channel as thin plates, with gate electrode infinite. Energy levels in eV are $U = 1.5$, $\varepsilon_l = 0.3$, $V_{DS} = -0.9$, plate separation $d = 2$ nm., $\epsilon_{ins} = \epsilon = 1$. Shown in the inset are energy levels for electrons of individual molecules in the channel.

TABLE I. The gate voltage required for the "ON" state for various parameter sets in MTFET for both single gate and dual gate configurations.

	d_{ins}(Å)	a_{mol}(Å)	ϵ	ϵ_{ins}	δ	E(MV/cm)	V_G(V)
Single gate	50	4	4	40	0.15	4.73	2.71
Single gate	50	10	4	40	0.15	0.89	0.64
Single gate	1000	4	4	400	0.15	0.45	4.77
Single gate	1000	10	4	400	0.15	0.08	1.07
Single gate	100	12	4	4	0.15	4.36	4.87
Dual gate	20	10	4	4	0.15	1.30	0.90

define whether the device is p- or n-type. In the following, we select the p-type enhancement mode case (as shown in the inset, Fig. 2) for analysis in further detail.

In the insulating "OFF" state, the device must be able to sustain a significant source–drain voltage V_{DS} without excessive tunneling current or dielectric breakdown. Fig. 2 shows the potential energy of an electron as a function of distance along the channel, when the p-type EM device is in the "OFF" state, with a potential $-V_{DS}$ applied between the drain and the source gate (assumed at same potential). For most of the channel length, apart from a "healing length" (typically of the magnitude of one or two molecule diameters) near the drain end, the potential is that of the source -gate. It is clear from Fig. 2 that, provided the drain potential lies below the upper Hubbard band, i.e., $eV_{DS} < U - \varepsilon_l$, then the channel should remain insulating.

One can now physically dope the channel by applying a negative voltage $-V_G$ to the gate electrode relative to the source and drain electrodes. The molecular array will then tend to switch to the metallic state once its lower Hubbard band moves up to the Fermi level of the leads. The actual density of available charge carriers in the array is determined by the electrostatic equilibrium established at a given gate voltage. Neglecting electronic kinetic energy, which is a relatively small effect, the relationship between doping, or the average hole density per molecule δ, and gate voltage V_G is $eV_G - \varepsilon_l = \delta e^2 / C_{mol}$, where C_{mol} is the capacitance per molecule and is given by

$$C_{mol}^{-1} = \frac{1}{\epsilon} \sum_{i \neq 0} \left\{ \frac{1}{|\mathbf{r}_0 - \mathbf{r}_i|} - \frac{1}{|\mathbf{r}_0 - \mathbf{r}_i + 2\mathbf{i}(\widetilde{d} + R_{mol})|} \right\}, \quad (1)$$

where $\mathbf{r}_i$ are the molecular centers, $\widetilde{d} \approx \epsilon d_{ins} / \epsilon_{ins}$, the remaining notations being indicated in Fig. 1.

From the foregoing, it is clear that $V_T = \varepsilon_l / e$ defines the minimum gate voltage required to have a nonzero concentra-

tion of charge carriers in the molecular layer. If $\delta = 0.15$ is taken as the typical fraction of carriers required to adequately be in the "ON" (metallic) state (based on cuprate data[3]), the required "ON" gate voltage can be specified for a given set of parameters. In Table I we collect some values calculated from Eq. (1) assuming $\varepsilon_l = 0.25$ eV. For practical application in a complementary metal-oxide semiconductor (CMOS) logic environment, the gate voltage must lie below the breakdown threshold that both the insulating spacer and the molecular channel can sustain, but lie above about 0.7 eV for 300 K operation, fixing the gate voltage at ~ 1 V. This implies that $U \sim 1$ V, limiting molecular size to something like $a_{mol} < 12$ Å, allowing for some screening. Theoretical estimates suggest that (see Table I), in order to have the "ON" gate voltage limited to around ~ 1 V, molecules in the channel must be sufficiently large ($a_{mol} > 6$ Å). Hence these considerations limit the molecular size to a range 6 Å $< a_{mol} < 12$ Å. Also, the dielectric constant of the insulating spacer between gate and channel must be significantly larger than that of commonly used silica ($\epsilon_{ins} = 4$). With these considerations in mind, the best candidates for the conducting channel of the MTFET device can only be found in *synthetic materials* or *artificially made structures*.

The molecules need to be reasonably closely packed so that electronic wave functions between neighboring sites are well overlapped. Suitable proposed materials are the charge transfer salts[4,5] $D^+ A^-$, where at least one of D or A is organic; examples[11,12] are $K^+ TCNQ^-$, and $K^+ C_{60}^-$. It appears that these materials, with their molecule size of 6~12 Å, and having typically an electronic bandwidth ~ 0.5 eV and a screened Coulomb interaction $U \sim 1$ eV, fulfill the necessary criteria to be used as the conducting channel in the proposed MTFET. Taking as an example a system with $a_{mol} = 10$ Å, if implemented as the channel in a single gate configuration with a high dielectric constant insulating spacer of thickness $d_{ins} = 50$ Å, the data in Table I give as the required "ON" gate voltage $V_G = 0.64$ V, and electric field in the spacer $E = 0.89$ MV/cm. The latter is well below the typical breakdown threshold. On the other hand, if implemented in a dual gate configuration,[9] a regular organic insulator such as polyimide or even silica will perform satisfactorily (Table I), thus the requirement for high dielectric constant materials is not essential.

Having established switching between the metallic and insulating states of the correlated molecular array, the analysis is straightforward for the source-drain current in the "ON" state. Within the gradual-channel approximation,[10] it is given by
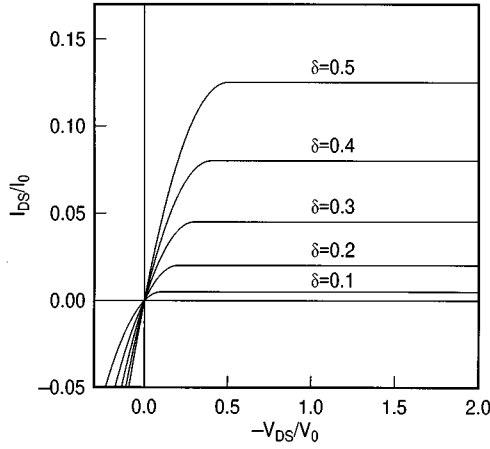
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FIG. 3. Current I_{DS} vs drain-source voltage $V_{DS}(=-V)$ in the channel under various gate voltages, corresponding to source-end doping $\delta = 0.1 - 0.5$ (from bottom to top curves). The current I_{DS} and the voltage V_{DS} in the curve are expressed in terms of $I_0 = G_{sat}^0 V_0$ and $V_0 = e/C_{mol}$, respectively, where $G_{sat}^0 = (W/L)\mu_h ne$. The gate voltage is negative in the EM device, with its value increasing as one moves from bottom to top curves, while it is positive in depletion mode and decreases from bottom to top curves.

$$I_{DS} = \mu_h \left(\frac{W}{L} \right) n C_{mol} \left(V_G - \varepsilon_l/e - \frac{1}{2} V_{DS} \right) V_{DS}, \qquad (2)$$

in the low biased region where $V_{DS} < V_{sat}$ and $V_{sat} = V_G - \varepsilon_l/e$. Equation (2) is derived assuming that the hole mobility μ_h is constant, as is justified by the doping dependence of the conductance in cuprates.[13] In Eq. (2), W is channel width, L channel length from source to drain, and n is the surface concentration of molecules. The I_{DS} saturates when $V_{DS} > V_{sat}$ and the saturated current follows:

$$I_{DS} = \frac{\mu_h}{2} \left(\frac{W}{L} \right) n C_{mol} (V_G - \varepsilon_l/e)^2. \qquad (3)$$

The hole concentration in the saturation regime has dropped to zero at the drain end of the channel ("pinch effect"), which occurs first at $V_{DS} = V_{sat} = V_G - \varepsilon_l/e$.

The results [Eqs. (2) and (3)] are plotted in Fig. 3 as the $I-V$ characteristics of the MTFET device. They resemble conventional FET characteristics. The trans-conductance in the saturation regime can be written as:

$$G_{sat} = \mu_h (W/L) n e \delta, \qquad (4)$$

which can be shown to be on the order of several quanta of conductance e^2/h (or a sheet resistance of a few kΩ) in a poor metal, consistent with the data from the example of the cuprates.

Although charge propagates coherently within the channel in the "ON" state, we expect that tunneling occurs at the channel-lead contacts. Detailed analysis shows, however, that the (insulating) edge region at the contact is confined only within one or two molecular diameters in the "ON" state. Tunneling conductance has been estimated to be of the same order of magnitude as Eq. (4), indicating that the edge effect does not significantly affect the characteristic low "ON" impedance.

There are two possible fabrication approaches to the device. Simple deposition of a thick layer of channel material on top of the prepared gate-insulator/source-drain structure (a) is confined to EM, where the material is insulating and will not short out the device, and (b) requires that the molecules arrange themselves satisfactorily at the oxide interface. A more designer approach is to exploit the rapidly developing self-assembly technology, enabling formation of a molecular monolayer, which permits either EM or DM operation. Arrays of quantum dots can be viewed as a form of the artificially made molecular array, though coherent inter-dot tunneling such as occurs with molecules is difficult to achieve.[14]

In conclusion, we have analyzed a MTFET device based on a molecular layer operating on a novel principle, the Mott metal-insulator transition. It is believed that high carrier density permits device function down to ~50 molecules, i.e., to device densities of order 20 times maximum Si FET density.

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