A Field Effect Transistor based on the Mott Transition in a Molecular Layer

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Abstract

Here we propose and analyze the behavior of a 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.

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The Field Effect Transistor – the key 3–terminal device in integrated circuit 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.

Materials which might constitute the 2D conducting channel in a FET are classified according to their 2D sheet conductance in Fig. 1. The conductance of the Si–based FET channel forms a benchmark, against which the performance of FET’s fabricated with molecular semiconductor channels compares very unfavorably. However, there exists a class of materials with comparable conductance to Si, namely the poor metals such as the CuO₂ 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 paper we evaluate the concept of a switch based on the novel physical principle of the Mott–Hubbard metal–insulator transition. We shall demonstrate its feasibility on physical grounds, and propose appropriate materials which could constitute the channel in the device.

The Mott–Hubbard insulators (unlike conventional band insulators) have 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 2D Mott insulators are alkali metal layers on GaAs [8], the CuO₂ planes in undoped cuprate superconductors [3], and organic charge transfer complexes [4–6].

The phase diagram for the Mott–Hubbard insulator is well studied in, for example,
cuprate superconductors. It is possible to *metallize* 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 TTF–TCNQ are examples of doped Mott-Hubbard insulators, with 10–40% of carriers.

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 (MTFET), whose essential active elements are illustrated in Fig. 2. The 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 [11] 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 $-\varepsilon_i$, for the $0 \leftrightarrow 1$ transition (ionization level), and as $-\varepsilon_i + U$, for the $1 \leftrightarrow 2$ transition (affinity level). Whichever is the lowest lying excitation will normally 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. 3 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. 3, that provided
the drain potential lies below the upper Hubbard band, \( i.e. \)

\[
e V_{DS} < U - \varepsilon_t,
\]

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 \( \delta \), and gate voltage \( V_G \) is:

\[
e V_G - \varepsilon_t = \delta e^2 / C_{mol},
\]

\( C_{mol} \) in Eq.(3) is the capacitance per molecule and is given by

\[
C_{mol}^{-1} = \frac{1}{\varepsilon} \sum_{i \neq 0} \left\{ \frac{1}{|r_0 - r_i|} - \frac{1}{|r_0 - r_i + 2i(d + R_{mol})|} \right\},
\]

where \( r_i \) are the molecular centers, \( d \approx \varepsilon d_{ins}/\varepsilon_{ins} \), the remaining notations being indicated
in Fig. 2.

From Eq.(3), it is clear that \( V_T = \varepsilon_t/e \) defines the minimum gate voltage required to
have a nonzero concentration 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’s (2) and (3) assuming \( \varepsilon_l = 0.25eV \). For practical application in a 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 0.7eV for 300K operation, fixing the gate voltage at \( \sim 1V \). This implies that \( U \sim 1V \), limiting molecular size to something like \( a_{mol} < 12\AA \), allowing for some screening. Theoretical estimates suggest that (see Table I), in order to have the “ON” gate voltage limited to around \( \sim 1V \), molecules in the channel must be sufficiently large \( (a_{mol} > 6\AA) \). Hence these considerations limit the molecular size to a range \( 6\AA < a_{mol} < 12\AA \). Also the dielectric constant of the insulating spacer between gate and channel must be significantly larger than that of commonly used silica (\( \varepsilon_{ins} = 4 \)). 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 \( D^+A^- \), where at least one of \( D \) or \( A \) is organic; examples are K\(^+\)TCNQ\(^-\), and K\(^+\)C\(_{60}\)\(^-\). It appears that these materials, with their molecule size of \( 6 \sim 12\AA \), and having typically an electronic bandwidth \( \sim 0.5eV \) and a screened Coulomb interaction \( U \sim 1eV \), fulfill the necessary criteria to be used as the conducting channel in the proposed MTFET. Taking as example a system with \( a_{mol} = 10\AA \), if implemented as the channel in a single gate configuration with a high dielectric constant insulating spacer of thickness \( d_{ins} = 50\AA \), the data in Table I gives as the required “ON” gate voltage \( V_G = 0.64V \), and electric field in the spacer \( E = 0.89MV/cm \). 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. Finally, in applications other than in CMOS environments where no low operating voltage is required, the data in
first and third rows of Table I shows that it is even possible to directly use cuprate as the transistor channel, implemented together with a high dielectric insulating spacer.

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

\[ I_{DS} = \mu_h \left( \frac{W}{L} \right) nC_{mol}(V_G - \varepsilon_l/e - \frac{1}{2}V_{DS})V_{DS} ; \quad (4) \]

in the low biased region where \( V_{DS} < V_{sat} \) and \( V_{sat} = V_G - \varepsilon_l/e \). Eq.(4) is derived assuming that the doped hole mobility \( \mu_h \) is constant, as is justified by the doping-dependence of the conductance in cuprates [15]. In eq.(4), \( W \) is channel width, \( L \) channel length from source to drain, and \( n \) is surface concentration of molecules. The \( I_{DS} \) saturates when \( V_{DS} > V_{sat} \) and the saturated current follows:

\[ I_{DS} = \frac{\mu_h}{2} \left( \frac{W}{L} \right) nC_{mol}(V_G - \varepsilon_l/e)^2. \quad (5) \]

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 (4–5) are plotted in Fig. 4 as the I-V characteristics of the MTFET device. They resemble conventional FET characteristics. The trans–conductance per square in the saturation regime can be written as:

\[ G_{sat} = \mu_h n_e \delta, \quad (6) \]

which can be shown to be on the order of several quanta of conductance \( e^2/h \) (or a sheet resistance of a few \( K\Omega \)), consistent with the data from cuprates(see Fig. 1).

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.(6), 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 of DM operation.

Finally, arrays of quantum dots can be viewed as an extreme limit of the artificially made molecular array. An important distinction should be emphasized however. In quantum dot arrays seen currently in the literature [16], charges propagate via inter–dot tunneling throughout the channel, instead of only at the channel–lead contacts envisaged in our device structure, the entire process of electronic transport is therefore incoherent, which results inevitably in a high “ON” impedance, an unfavorable situation for practical applications. Besides, since the artificial molecules or quantum dots built with current technologies are too large in size (typically $\sim 10\text{nm}$.) to sustain substantial Coulomb interactions, the Coulomb blockade phenomenon or switching can at most be operated at extremely low temperatures.

In conclusion, we have analyzed a MTFET device based on a molecular layer operating on a novel principle, the Mott metal–insulator transition. The channel consists of an array of $\sim 1\text{nm.}$ molecules. The large electronic Coulomb energy of order $\sim 1\text{eV}$ allows operation at room temperature and at a voltage of order $0.5 \sim 1\text{eV}$. “ON” transport is coherent (all molecules are exactly the same) allowing low ‘ON’ resistance. High carrier density permits device function down to $\sim 50$ molecules, i.e. to device densities of order 20 times maximum Si FET density. These characteristics place the proposed device in the category of a possible solution to the fundamental problems which the computer switches is expected to encounter in the next 10–20 years.
|           | ${d_{\text{ins}}} (\text{Å})$ | ${a_{\text{mol}}} (\text{Å})$ | $\epsilon$ | $\epsilon_{\text{ins}}$ | $\delta$ | $E (\text{MV/cm})$ | $V_G (V)$ |
|-----------|-----------------------------|-----------------------------|--------|-----------------|--------|-----------------|--------|
| 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   |

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

[1] F. Garnier, et al, Science 265, 1684 (1994); A. Dodabalapur, et al, Science 269, 1560 (1995); and references therein.

[2] K. K. Likarev, IBM J. Res. Develop. 32, 144 (1988); Y. Taur, et al, IBM J. Res. Develop. 39, 245 (1995).

[3] For example, Bedell et al, High Temperature Superconductivity Proceedings, Addison–Wesley, 1990.

[4] J. B. Torrance, Acc. Chem. Res. 12, 79 (1979).

[5] Z. G. Soos and D. J. Klein, in Molecular Association, edited by R. Forster, Academic Press, London, 1975.

[6] Y. Iwasa, et al, Phys. Rev. B49, 3580 (1994).

[7] N. Mott, Metal–Insulator Transitions, Taylor & Francis, London, 1990.

[8] E. W. Plummer and P. A. Dowben, Prog. in Surf. Sci. 40, 201 (1990); E. W. Plummer, et al, Phys. Low–Dim. Struct. 4/5, 99 (1994)

[9] D. M. Newns, J. Misewich and C. Zhou, USA Patent disclosure #: Y0895–0318.

[10] S. M. Sze, Physics of Semiconductor Devices, John Willey & Sons, 1981.

[11] Device fabrication options follow from functionality; in the EM case, the monolayer can be just the terminating layer of a macroscopic crystalline or amorphous “blob” of $D^+A^-$ material, whereas DM functionality demands that the channel be a true monolayer, with an insulating protective coat.

[12] For this very reason, most inorganic Mott insulators found in nature are not suitable to be implemented in the MTFET for applications in a CMOS logic environment. Their lattice constant $a_{mol}$ are too small, which would inevitably lead to a high operating voltage, if not beyond the breakdown threshold.
[13] S. Yamaguchi, Y. Moritomo and Y. Tokura, Phys. Rev. B48, 6654 (1993); and references therein.

[14] If the kinetic energy, of which a measure is the intersite hopping integral $t$ in the Hubbard model, were large enough relative to $U$, as happens in $K_3C_{60}$, the system can become metallic even for integral occupation, However the 1 : 1 compound $KC_{60}$ is a Class I insulator.

[15] T. Ito, K. Takanaka and S. Uchida, Phys. Rev. Lett. 70, 3995 (1993).

[16] For example, A. A. Middleton and N. Wingreen, Phys. Rev. Lett. 71, 3198 (1993); U. Geigenmüller and G. Schön, Europhys. Lett. 10, 765 (1989); K. Katayama, et al, J. Appl. Phys. 79, 2542 (1995).
FIGURES

FIG. 1. Schematic sheet conductance for various categories of materials.

FIG. 2. Schematic side view of three–terminal molecular transistor. Shown in the inset are energy levels for electrons of individual molecules in the channel.

FIG. 3. 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 $d = 2nm., \epsilon_{ins} = \epsilon = 1$.

FIG. 4. Current $I_{DS}$ versus 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 $G_{sat}^0 = (W/L)\mu_h n e$. The gate voltage is negative in the EM device, with its value increases as one moves from bottom to top curves; while it is positive in depletion mode and decreases from bottom to top curves.