Materials

Univ. of Groningen, Philips Research Lab., Dutch Polymer Inst., Eindhoven Univ. of Technology, Graz Univ. of Technology, Russian Academy of Sciences
Univ. of Illinois, Purdue Univ.:
Semiconducting SAMs versus CNT networks for the next generation of Organic Field Effect Transistors

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A comparison of two potential circuit technologies

The ultimate aim of organic electronics is to produce large circuits with additional functionality, higher speeds than currently available, at significantly lower cost than silicon with the additional benefits of having a flexible (flex) rollable substrate. In terms of current and past technology there has been an impressive improvement in the measured carrier mobility on glass substrates: about an order of magnitude every two years. The progress on flex is less certain, except that the mobility is always somewhat less than on glass and often much less. The improvement on glass is excellent but has involved many process changes for those aiming at circuits as distinct from discrete transistors. It is wise therefore to look at ways of enhancing performance and simplifying processes to minimise the number of later material changes. For many, but not everyone, the aim is to make CMOS. This involves the additional complexity of individually isolating n and p channel devices both during the processing and in the finished circuit. How all this is achieved is the main debate, coupled with the requirements of high yield and reliability. Two recent papers have contributed significantly to this debate.

The first paper [1] from the **University of Groningen**, **Philips Research Laboratories**, the **Dutch Polymer Institute**, **Eindhoven University of Technology**, **Graz University of Technology** and the **Russian Academy of Sciences** present a molecule consisting of on one hand a semiconducting thiophene group and on the other hand an “anchoring group” that are connected by an alkyl chain. The molecule is used to form self-assembled monolayers of the semiconducting thiophene on SiO_2 gate dielectrics of organic transistors.

First the design of the molecule is discussed. The longer the thiophene is, the higher the mobilities can be achieved. An upper limit for the thiophene length however is found because of the worse solubility of longer thiophenes. Different anchoring groups are also explored. It is found that monofunctional anchoring groups give rise to more well ordered monolayers. A Cl-group is selected for its sufficiently high reactivity.

Next, SAMFETs, transistors based on the monolayer semiconducting layer, are discussed. Using XRD the authors show that indeed a monolayer is formed in which the thiophene groups take a herringbone packing. Using SKPM on transistor structures that have only partially been covered with the SAM, the thickness of the monolayer is verified. Simultaneously it is seen that SAM-islands in contact with the electrodes take the same potential as the electrodes while insulated islands of the SAM do not. Transistor performance is characterized. Mobilities are in the range of 0.01 cm^2/Vs and higher. Higher channel lengths show higher mobilities due to contact resistance. This proves that the monolayer is very dense, because in an insufficiently dense monolayer, percolation would be increasingly limited for increasing channel lengths. The high channel lengths that can be reached allow the production of transistors with well-saturated currents at larger VDS.

Finally the low spread of transistor parameters is also demonstrated in practice by integration of over 300 SAMFETs in a 15 bit code generator circuit. A bit-rate of 1 kbit/s is achieved.

Self-assembled organic semiconducting material has been used for the construction of organic transistor with large gate area. For the first time circuits with reasonable size (e.g. 15 bit code generator circuit) have been realised with SAM semiconductors. Not only do the monolayers show a high mobility, their density is shown to allow long channel transistors (up to 40 µm channel length). The bottom-up technique (that is demonstrated) can therefore be combined with top-down techniques (e.g. photo lithography) used for contact definition.

The second paper [2] from **John A. Rogers** et al. at the **University of Illinois** propose the fabrication of an integrated circuit composed of up to 100 transistors on flexible plastic substrate. Those transistors have excellent properties: mobilities of about 80 $cm^2/V.s$, operating voltage of 5 V, I_{on}/I_{off} ratio of 10^5 and subthreshold slope of 140 mV/dec. The active layer is composed from a random network of single walled carbon nanotubes (SWNT).

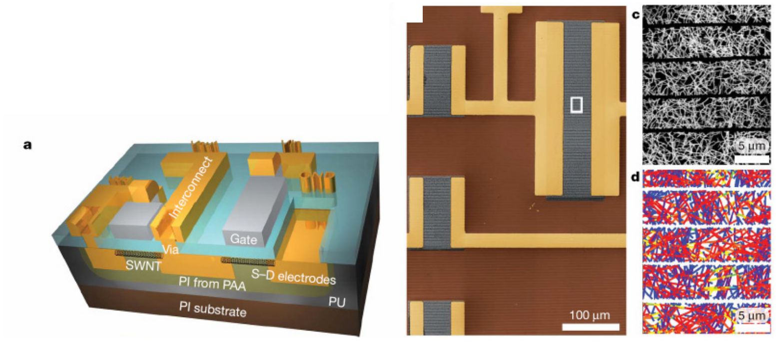

Figure 1: a) SWNT PMOS inverter layout
b) Image of SWNT circuit before before deposition of the gate dielectric
c) A view of the SWNT network strips
d) Theoretical modelling results for the normalized current density distribution in the on state of the device (from higher to lower densities the corresponding colours are yellow, red and blue).
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As the first step towards large-scale integration, the J.A. Rogers group modelled and then built a PMOS inverter (Figure 1a) that operates in the kilohertz range. The active layer is made by a chemical vapour deposition of random networks of SWNT. To prevent short circuits between Source and Drain contacts that can be caused by the metallic SWNT, the authors used soft lithography and reactive ion etching to cut fine lines into the networks. The obtained network strips are oriented along the overall direction of transport with widths designed to reduce the propability of metallic pathways below a practical level without reducing the mobility of the network (Figure 1b, c and d).

The second step of this work is the realization of a SWNT-based four bit row decoder that demonstrates its ability to decode a binary encoded input of four data bits into sixteen individual data output lines at frequencies in the kilohertz range (Figure 2).

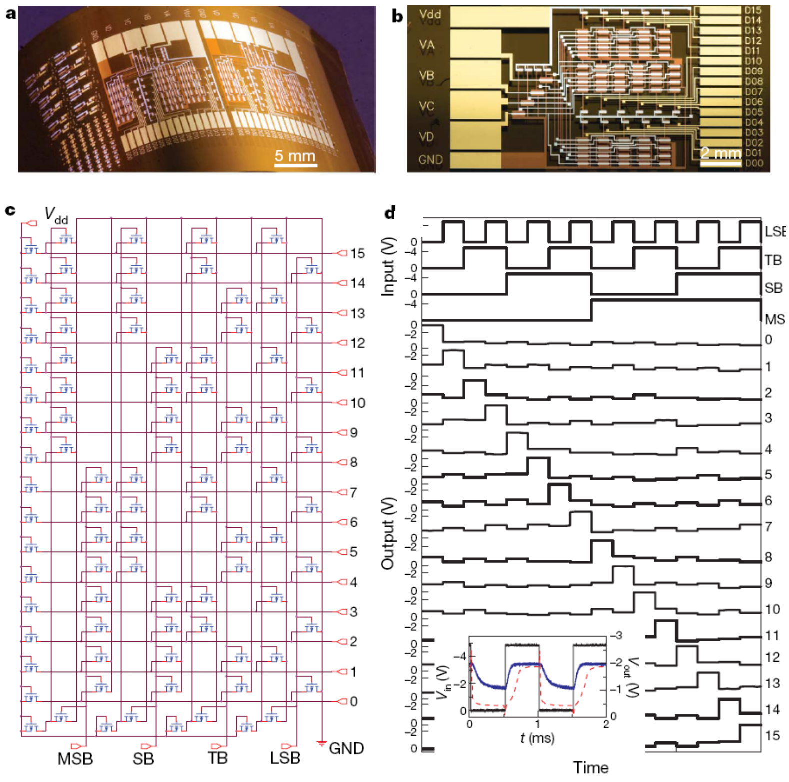

Figure 2: a) & b) Optical images of the SWNT flexible circuit.
c) SWNT circuit diagram.
d) Output circuit characteristics.
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Although the operation frequency of the circuit remains low (1 kHz) due to the higher value of the transistors channel length (100 μm), the development of optimized materials and solution-printing techniques for fabricating SWNT-based integrated circuits used in this work represent some new directions for flexible organic electronics development.

The table attempts to make careful comparisons of the potential benefits of such approaches and the table attempts to do this.

	Self assembly	CNT (non aligned)
Substrate	SiO_2 on Silicon	flex
No. of TFTs	'hundreds'	100
Mobility	0.04 $cm^2V^{-1}s^{-1}$ L_D?	80 to 0.04 $cm^2V^{-1}s^{-1}$
Operating voltage	5 V swing?	-5 V swing?
Speed	5.0 Khz	1 kHz
On-off ratio	10^3 but variable	10^5 but variable
Contact resistance	High	High
Liquid & evaporation	Deposition/solution	Deposition/solution
Circuit configuration	n channel/sat load	p channel
Cross-overs	no	no
Uniformity	Very good	Very poor
Depletion/enhancement	depletion	either (good for circuits)

In many ways the second paper is nearer to becoming a reality because it is on flexible substrates. There does appear to be a problem with the uniformity of the devices and the presence of short circuits. It is virtually impossible to design circuits that have big parameter variations: a 'rule of thumb' is that a circuit is no better than the worst transistor in the array. If the uniformity problems could be solved the nanotube approach would seem to be the best alternative. Neither process is near to a final form. For example it is necessary to have low capacitance cross-overs. This is where one conducting line has to run across a second without a short-circuit between the two. Gate dielectric material provides a possible separation between the two but this is required to have a high dielectric constant for the transistor but a low value of dielectric constant for the crossover. Ring counters or oscillators do not require such cross-overs: almost everything else does. The growth in the market for organic electronics will be coupled with increases in circuit speed. This is in part dependent on the overlap of the gate by the drain and source which can reduce speed by a factor of 4 because of the Miller Effect. Auto-alignment is a must, but the bottom gate geometry has the greatest potential in this respect.

Taking into account of all these factors the self assembly method [1] seems to be more appropriate. This is because of the difficulty in controlling parameter spreads with nanotubes. The final solution may be quite different because the aim in the longer term will involve mixed signal and even RF circuits for auto ID. Then the problem of integrating vertical diodes and non-volatile memory as well as perhaps OLED and PV is an issue.

[1] "Bottom-up organic integrated circuits" ; E.C.P. Smits, S.G.J. Mathijssen, P.A. van Hal, S. Setayesh, T.C.T. Geuns, K.A.H.A. Mutsaers, E. Cantatore, H.J. Wondergem, O. Werzer, R. Resel, M. Kemerink, S. Kirchmeyer, A.M. Muzafarov, S.A. Ponomarenko, B. de Boer, P.W.M. Blom, D.M. de Leeuw : ***Nature*** **455**, 956 (2008).
[2] "Medium scale carbon nanotube thin film integrated circuits on flexible plastic substrates" ; Q. Cao, H.S Kim, N. Pimparkar, J.P. Kulkarni, C. Wang, M. Shim, K. Roy, M.A. Alam, J.A. Rogers : ***Nature*** **454**, 495 (2008).