

Flexible electronic futures

Robert J. Hamers

Microelectronic devices incorporating organic materials could find a host of applications. That prospect inches nearer with the development of a strategy for growing thin films of the organic semiconductor pentacene.

Virtually all of today's microelectronic devices are made from inorganic materials — silicon and gallium arsenide, for instance. But in the past few years there has been an explosion of interest in devices made from organic molecules for application in devices such as mechanically flexible computers and displays, and even truly 'molecular' computers in which individual molecules replace today's transistors^{1–3}. Organic semiconductors have been known for more than 20 years⁴, and last year's Nobel Prize in Chemistry⁵ was awarded for work in the area. But achieving electronic properties comparable to those of inorganic materials requires high-quality crystals^{6,7}, and these cannot easily be made in the necessary thin-film form by the vapour-deposition methods typically used in microelectronics fabrication. Thin films are needed because they are especially amenable to large-scale circuit fabrication.

On page 517 of this issue⁸ Meyer zu Heringdorf and co-workers report experiments in which they have imaged the

formation of thin films of pentacene, an important molecular semiconductor. Their experiments have produced a notable advance in making thin films of organic semiconductors with the required crystallinity, and led to a new understanding of the factors controlling the growth of these materials as thin films.

Meyer zu Heringdorf et al. used a technique known as photoelectron emission microscopy, or PEEM, to study film formation. In PEEM, the sample is illuminated with ultraviolet light, and photoelectrons that are ejected are imaged using a high-resolution electromagnetic lens system. PEEM provides sub-micrometre spatial resolution and can discriminate between different chemical species (such as silicon and a layer of organic molecules) if they emit photoelectrons at different rates. The imaging capability enables the authors to make movies of pentacene thin films forming on silicon surfaces.

Pentacene consists of five

fused aromatic — benzene-like — rings (Fig. 1). It is one of the most promising candidates for organic electronics, in part because of its chemical and thermal stability, and in part because its planar shape facilitates crystalline packing. By directly observing the surface while pentacene molecules were deposited, the authors were able to glean insight into the microscopic processes controlling crystal formation, and use that insight to achieve a technological advance.

When a simple inorganic material such as silicon or gallium arsenide is deposited onto a surface, the atoms first diffuse across the surface. When enough atoms pack together they form a stable 'nucleus', and further deposition creates 'islands' on the surface. Because organic molecules have more complex shapes and weaker forces binding them into crystals than do their inorganic counterparts, it has not been clear to what extent these classical models of growth can be applied to molecular materials. For example, pentacene (and probably most other molecular semiconductors) can form strong chemical bonds to the silicon surface, and even weak interactions can inhibit diffusion and modify the optimal orientation and packing of the molecules^{9,10} (Fig. 1a).

Using PEEM, Meyer zu Heringdorf et al. found that strongly bonded molecules inhibit nucleation and decrease the crystalline quality of the resulting pentacene film. Why? One likely reason is the close connection between chemical bonding and molecular shape. Whenever molecules break or form bonds, their shape changes. The changes in shape that occur when organic semiconductors (such as pentacene) form bonds to silicon are likely to be especially large. The formation of well-defined crystals requires molecules to nestle together like spoons in a drawer, so even small changes in shape prevent other molecules from packing together with them to form a crystal.

Ideally, film growth will be optimal when the strength of the interaction between the surface and the deposited molecules is strong enough to hold the molecules on the surface, but weak enough to allow them to diffuse and to rotate. To decrease the reactivity between the silicon surface and the pentacene molecules, Meyer zu Heringdorf and colleagues

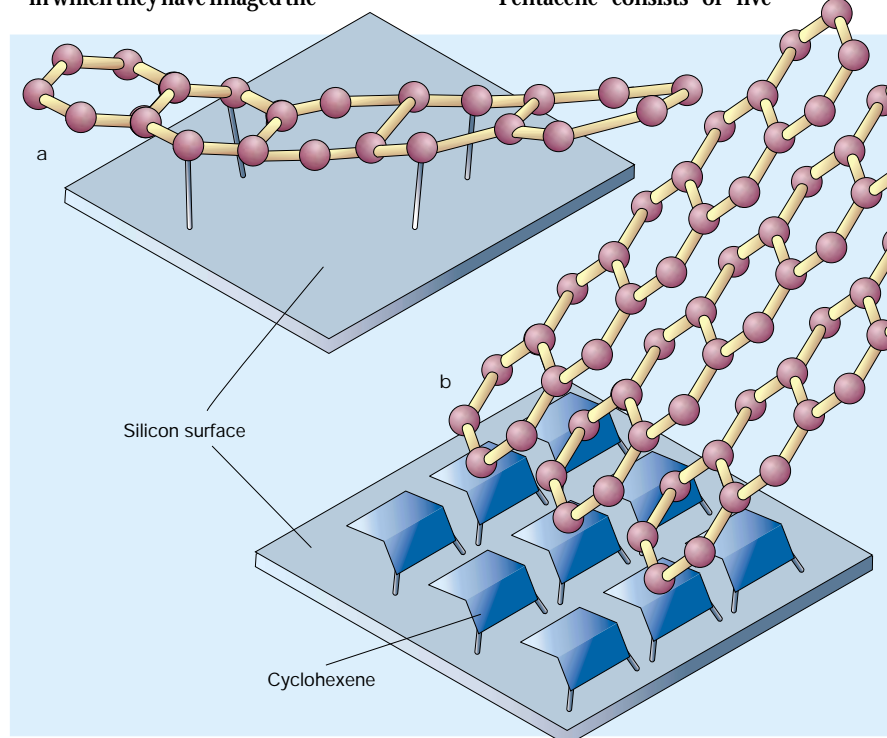


Figure 1 How to make thin-film crystals of pentacene, an organic semiconductor. a, A pentacene molecule that has attached directly to the silicon substrate forms strong bonds to the substrate and so is distorted, inhibiting crystal development. b, The approach used by Meyer zu Heringdorf and colleagues⁸. The silicon has been modified by cyclohexene molecules, which form two bonds with the silicon and coat it with an array of non-reactive C–H bonds. The pentacene molecules can then attach in ordered fashion to the cyclohexene, allowing stable crystal growth.

took advantage of a method for forming ordered organic cyclohexene monolayers on semiconductors¹¹; this method leaves the silicon surface coated with an ordered array of non-reactive C–H groups. The authors hypothesized that any interaction with the deposited pentacene molecules would be weak, and that this would lead to improved growth (Fig. 1b). Their hunch was right. Deposition of pentacene onto these organic-modified surfaces dramatically improves the crystallinity, leading to perfect thin-film crystals approaching 0.1 mm in size — much larger than the size of a single transistor. Similar results were obtained on oxidized silicon surfaces, provided that all of the chemically reactive ‘dangling bonds’ were eliminated. In essence, the new results show that the key to fabricating organic single crystals in thin-film form is to modify the substrate to reduce the bond strength to the organic molecules.

The technological significance of the new results is this: because microelectronic devices are only micrometres (or less) across, it should now be possible to make integrated circuits in which each transistor is made from a single crystal of pentacene, with corresponding improvements in electrical performance. But the results also have broader implications. The trend towards ‘molecular’ electronics is being played out on many length scales, from the micrometre scale of classical microelectronics using organic molecules, down to the use of single molecules³. There is tremendous potential for enhancing chemists’ abilities to design and fabricate ‘designer molecules’ with very specific types of electrical functionality. For instance, specific chemical groups might control the conductivity through a molecule, while other groups might be readily switched between oxidized and reduced states to make a kind of molecular switch^{1–3}.

The practical limitations in this enterprise may not lie in the materials themselves. Rather, they may be in understanding and controlling the properties at the interfaces between organic molecules and the inorganic materials (silicon, metals and so on) that connect them to the macroscopic world¹², and in learning how to coax molecules into assembling themselves into more complex structures. The new work⁸ extends the classical theories of nucleation and growth to more complex organic materials, thereby providing a conceptual link between the two. Given a similar understanding of the electronic properties of the materials and their interfaces, the dreams of cheap, flexible (and perhaps even biodegradable) microelectronics based on organic molecules may soon become a reality. ■

Robert J. Hamers is in the Department of Chemistry, University of Wisconsin–Madison, 1101 University Avenue, Madison, Wisconsin 53706, USA. e-mail: rjhamers@facstaff.wisc.edu

1. Aviram, A. & Ratner, M. *Chem. Phys. Lett.* **29**, 277–283 (1974).
2. Collier, C. P. et al. *Science* **287**, 391–394 (1999).
3. Joachim, C., Gimzewski, J. K. & Aviram, A. *Nature* **408**, 541–548 (2000).
4. Chiang, C. K. et al. *Phys. Rev. Lett.* **39**, 1098–1101 (1977).
5. <http://www.nobel.se/chemistry/laureates/2000>
6. Crone, B. et al. *Nature* **40**, 521–523 (2000).
7. Schön, J. H., Berg, S., Kloc, Ch. & Batlogg, B. *Science* **287**, 1022–1023 (2000).
8. Meyer zu Heringdorf, F.-J., Reuter, M. C. & Tromp, R. M. *Nature* **412**, 517–520 (2001).
9. Dimitrakopoulos, C., Brown, C. & Pomp, A. J. *Appl. Phys.* **80**, 2501–2508 (1996).
10. Kasaya, M., Tabata, H. & Kawai, T. *Surf. Sci.* **400**, 367–374 (1988).
11. Hamers, R. J. et al. *Acc. Chem. Res.* **33**, 617–624 (2000).
12. Pantelides, S. T., DiVentra, M. & Lang, N. D. *Physica B* **296**, 72–77 (2001).

Demography

Uncertain population forecasts

Nico Keilman

Traditional population forecasts made by statistical agencies do not quantify uncertainty. But demographers and statisticians have developed methods to calculate probabilistic forecasts.

The demographic future of any human population is uncertain, but some of the many possible trajectories are more probable than others. So attempts to forecast demographic aspects of a population, such as its size by a given year, should include two elements: a range of possible outcomes, and a probability attached to that range. Together, these elements constitute ‘prediction interval’ for the population variable concerned. There is a clear trade-off between greater certainty (higher odds) and better precision (narrower intervals). For instance, on page 543 of this issue, Lutz, Sanderson and Scherbov¹ estimate that the odds are 4 to 1 (an 80% chance) that the world’s population, now at 6.1 billion, will be between 5.6 billion and 12.1 billion in the year 2100. Odds of 19 to 1 (a 95% chance) result in a wider interval: 4.3 billion to 14.4 billion.

Demographers have become increasingly concerned about the accuracy of their forecasts, in part because the rapid fall in fertility in Western countries in the 1970s came as a surprise. Forecasts made in those years predicted birth rates that were up to 80% too high and too many young children. The rapid reduction in mortality after the Second World War was also not foreseen; life-expectancy forecasts were too low by 1–2 years; and the predicted number of elderly, particularly the oldest people, was far too low^{2,3}.

Those who use forecasts should be informed about the accuracy of historical predictions. But even more important is the expected accuracy of the current forecast. Statistical agencies traditionally deal with the uncertainty of forecasting population variables by producing two or more predictions of fertility or mortality (or both), and then calculating a range of predictions. For instance, Statistics Norway expects the number of children aged 6–12 in Norway in 2010 to be between 401,000 and 436,000, depending on whether fertility is low or

high — that is, on whether women have an average of 1.5 or 2.1 children, respectively, in 2010. The agency attaches no probability to this interval. Yet those who are planning provisions for education need to know whether the likelihood of this scenario is roughly 30%, 60% or even 90%.

So, during the 1990s, demographers and statisticians developed methods for making probabilistic population forecasts, the aim of which is to calculate prediction intervals for every variable of interest. Examples include population forecasts for the United States, Austria, Germany, Finland and the Netherlands; these forecasts comprised prediction intervals for variables such as age structure, average number of children per woman and immigration flow^{4–8}. Lutz et al.¹ present probabilistic population forecasts for the whole world, and for the 13 large regions that they divide the world into (see Table 1 on page 544). Their most important message is that there is an estimated 85% chance that the world’s population will stop growing before 2100.

Yet probability statements of this kind — which give the expected accuracy of a population forecast — must be interpreted with care, because they vary depending on the statistical method used and its assumptions. For instance, Lutz et al.¹ estimate that there is a 95% chance that the world population will reach 6.6 billion to 11.4 billion in 2050 (see Fig. 2 on page 544). But the US National Research Council (NRC) uses a different method and has calculated that there is a 95% chance that the 2050 world population will be between 7.9 billion and 10.9 billion⁹.

There are three main methods of probabilistic forecasting: time-series extrapolation; expert judgement; and extrapolation of historical forecast errors. Time-series methods rely on statistical models that are fitted to historical data. These methods, however, seldom give an accurate description of the past. If many of the historical facts remain