

Organic electronics: Introduction

by J. M. Shaw
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Guest Editors

For the past forty years *inorganic* silicon and gallium arsenide semiconductors, silicon dioxide insulators, and metals such as aluminum and copper have been the backbone of the semiconductor industry. However, there has been a growing research effort in “organic electronics” to improve the semiconducting, conducting, and light-emitting properties of *organics* (polymers, oligomers) and hybrids (organic–inorganic composites) through novel synthesis and self-assembly techniques. Performance improvements, coupled with the ability to process these “active” materials at low temperatures over large areas on materials such as plastic or paper, may provide unique technologies and generate new applications and form factors to address the growing needs for pervasive computing and enhanced connectivity.

If we review the growth of the electronics industry, it is clear that innovative organic materials have been essential to the unparalleled performance increase in semiconductors, storage, and displays at the consistently lower costs that we see today. However, the majority of these organic materials are either used as sacrificial stencils (photoresists) or *passive* insulators and take no *active* role in the electronic functioning of a device. They do not conduct current to act as switches or wires, and they do not emit light.

For semiconductors, two major classes of passive organic materials have made possible the current cost/performance ratio of logic chips: photoresists and insulators. Photoresists are the key materials that define chip circuitry and enable the constant shrinking of device dimensions [1–3]. In the late 1960s, photoresist materials limited the obtainable resolution of the optical tools to

~5.0 μm (~500 transistors/ cm^2). As optical tools continued to improve, owing to unique lens design and light sources, new resists had to be developed to continue lithographic scaling. Chemists created unique photosensitive polymers to satisfy the resolution, sensitivity, and processing needs of each successive chip generation, and now photoresist materials improve the resolution that could normally be provided on an optical exposure tool. The increased resolution capability of photoresists combined with optical tool enhancements has enabled the fabrication of 1.2 million transistors/ cm^2 with feature sizes of 180 nm, significantly smaller than the 248-nm exposure wavelength of the current optical exposure tool—an achievement that was not considered possible a few years ago.

Polymeric insulators have also been essential to the performance and reliability of semiconductor devices. They were first used in the packaging of semiconductor chips, where low-cost epoxy materials found applications as insulation for wiring in the fabrication of printed wiring boards and as encapsulants to provide support/protection and hence reliability for the chips [4, 5]. Although the first polymeric dielectrics were used in the packaging of chips, IBM recently introduced a polymer that replaces the silicon dioxide dielectric typically used on-chip throughout the industry as an insulator. The seven levels of metal wiring required to connect the millions of transistors on a chip can significantly affect chip performance because of signal propagation delay and crosstalk between wiring. Improvement in interconnect performance requires reduction of the resistance (R) and capacitance (C). IBM was the first to use copper to replace aluminum wiring as a low-resistivity metal, and the first to use a low- k

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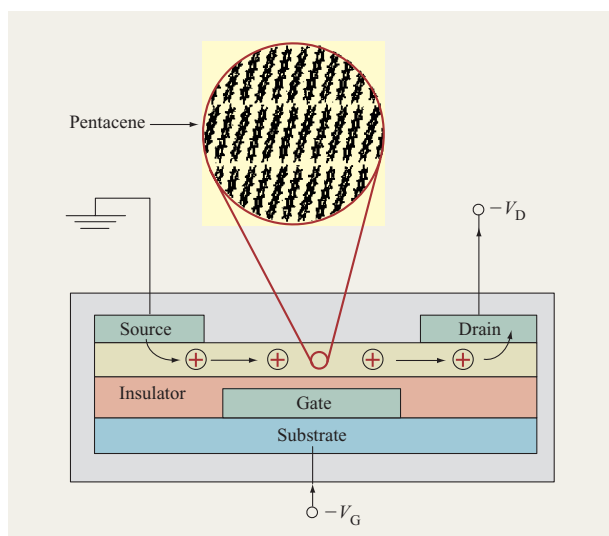


Figure 1

Schematic of organic semiconducting p-type thin-film transistor with top contacts.

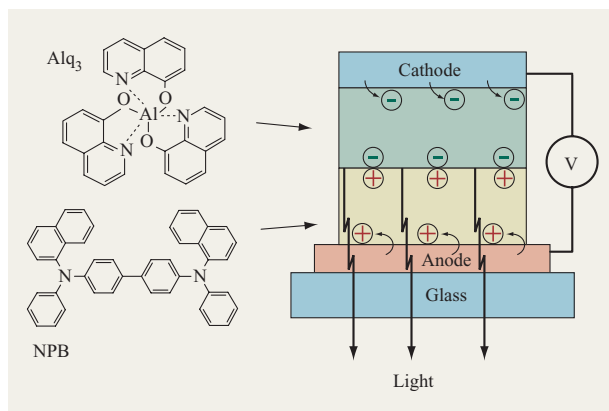


Figure 2

Schematic of typical organic light-emitting diode which uses Alq_3 , tris(8-hydroxyquinolinato)aluminum, as the electron transport and emitting layer, and NPB, N,N'-di(naphthalene-1-yl)-N,N'-diphenylbenzidine, as the hole transport layer.

polymeric material, SiLK** [6] to replace typically used oxide insulators, thereby improving the total interconnect wiring performance by $\sim 37\%$. With continued innovation in materials and design, it is felt that the on-chip wiring will not be a performance limiter for the next decade [7].

Organic materials have also provided performance and reliability for storage products and displays. The density of magnetic storage has increased at a faster rate than even semiconductor devices. Innovations in lubricants, thin-film head materials, and magnetic media have led to these

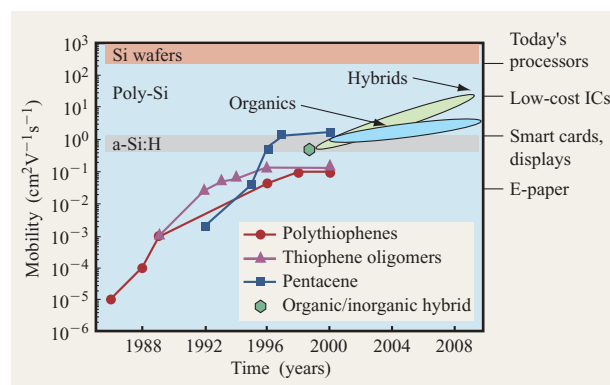


Figure 3

Performance of organic and hybrid semiconductors.

advances. Similarly, the resolution of active-matrix liquid crystal displays (AMLCDs) is approaching photographic quality. The development of liquid crystals, fundamental understanding of alignment layers, and color filters using innovative dyes have contributed to the recent announcement of the IBM "Bertha" display with 200-dpi resolution and wide viewing angle [8].

The ability of chemists to optimize the properties of the organic materials described above has provided key contributions to the growth of the electronics industry. However, it is possible that within the next ten years we may reach the limits of performance improvements in silicon devices, magnetic storage, and displays that can be provided at a reasonable cost. As in the past, basic research on materials may provide a path to new product form factors.

Therefore, it is fitting that this issue of the *IBM Journal of Research and Development* for the first official year of the 21st century should be dedicated to organic electronics. Nontraditional materials such as conjugated organic molecules, short-chain oligomers, longer-chain polymers, and organic-inorganic composites are being developed that emit light, conduct current, and act as semiconductors. The ability of these materials to transport charge (holes and electrons) due to the π -orbital overlap of neighboring molecules provides their semiconducting and conducting properties. The self-assembling or ordering of these organic and hybrid materials enhances this π -orbital overlap and is key to improvements in carrier mobility. The recombination of the charge carriers under an applied field can lead to the formation of an exciton that decays radiatively to produce light emission. (Schematics of semiconducting and light-emitting devices are provided in **Figures 1** and **2**.) In addition to their electronic and optical properties, many of these thin-film materials possess good mechanical properties (flexibility

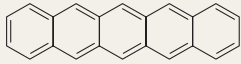
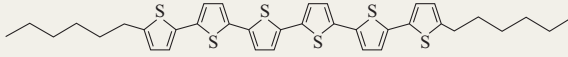
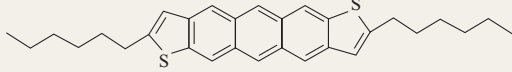
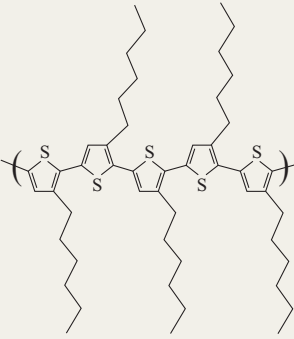
Semiconductor	Representative chemical structure	Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
Silicon	Silicon crystal	300–900
	Polysilicon	50–100
	Amorphous silicon	~ 1
Pentacene		~ 1
α,ω -dihexylsexithiophene		10^{-1}
α,ω -dihexylanthradithiophene		10^{-1}
Regioregular poly(3-hexylthiophene)		10^{-1}
Organic–inorganic hybrid	Phenethylamine–tin iodide	~ 1

Figure 4

Chemical structures and comparison of mobilities of classes of organic and inorganic semiconductors.

and toughness) and can be processed at low temperatures using techniques familiar to the semiconducting and printing industries, such as vacuum evaporation, solution casting, ink-jet printing, and stamping. These properties could lead to new form factors in which roll-to-roll manufacturing could be used to create products such as low-cost information displays on flexible plastic, and logic for smart cards and radio-frequency identification (RFID) tags.

Efforts on these “active” materials initiated in academia and in industrial research laboratories in the 1970s and 1980s have led to a dramatic improvement in performance due to innovative chemistry and processing, as well as the growing ability to understand and control the self-assembly and ordering of oligomers, polymers, and nanocrystals. Research efforts on semiconducting conjugated organic thiophene oligomers [9, 10], thiophene polymers [11–13], and the small pentacene molecule [14–17] have led to improvements in the mobility of these materials by five orders of magnitude over the past 15

years, as shown in **Figure 3**. **Figure 4** shows the chemical structures and reported mobilities of representative classes of organic materials compared to those of inorganic silicon materials. An overview of these materials and associated references are presented in the paper by Dimitrakopoulos and Mascaro in this issue. As each material appears to reach its limit in mobility and saturate in performance, another improved system takes its place. As seen in Figure 4, evaporated films of pentacene have achieved mobilities comparable to that of the amorphous silicon used to fabricate the thin-film transistors (TFTs) which drive the liquid crystal pixels in AMLCD flat-panel displays. Recently a new class of materials, organic–inorganic perovskites [18], has also achieved the mobility of amorphous silicon [19]. While these carrier mobilities are now useful for applications that do not require high switching speeds, all of the previously reported materials operated at high voltages. A method of providing low-voltage operation of these materials was

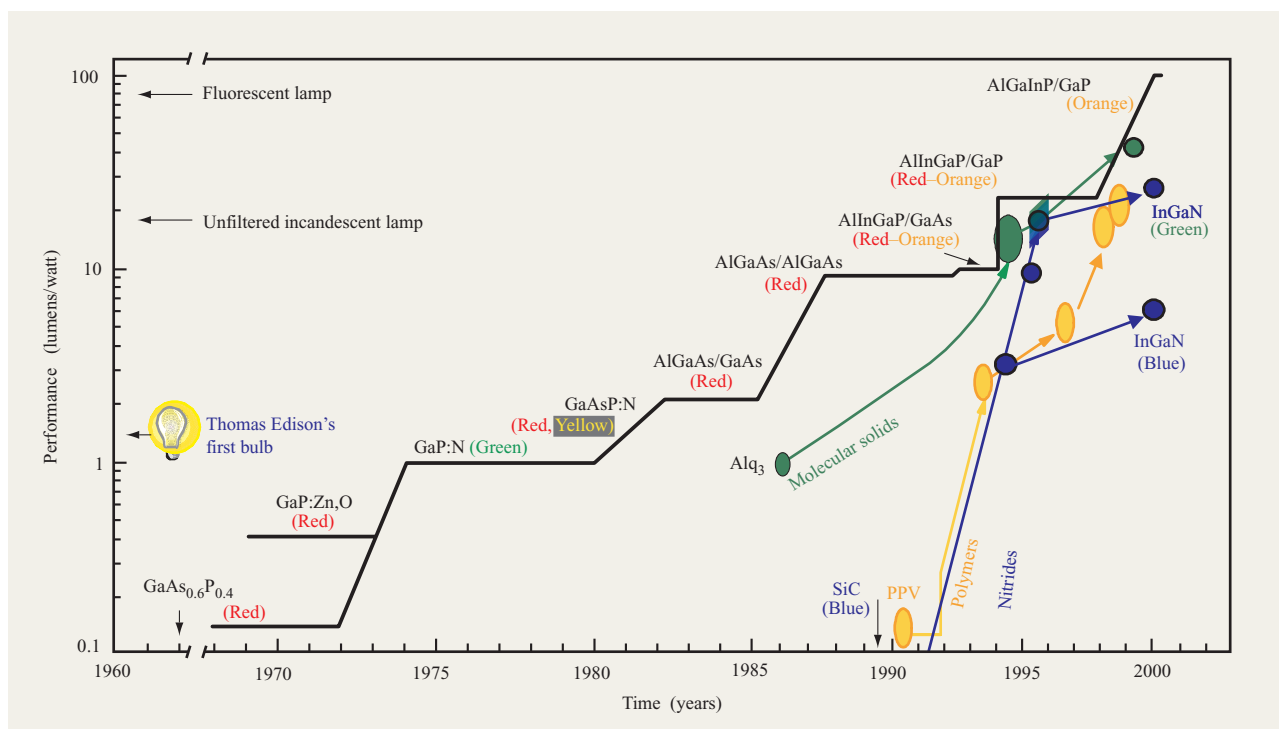


Figure 5

Evolution of LED/OLED performance. (Reprinted with permission from [24]; © 1996 American Association for the Advancement of Science.)

recently reported [16], enabling applications for portable electronics where battery lifetime is a concern.

Since these organic materials and hybrids are polycrystalline, it will be difficult to achieve the mobility of the single-crystal silicon used in high-performance microprocessors. Measurements on single organic crystals of p-type pentacene [17] and an n-type perylene [20] which mark the upper boundary of performance show mobilities of $2.7 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $5.5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ —orders of magnitude lower mobility than single-crystal silicon. However, the organic–inorganic perovskites have demonstrated a Hall mobility of $50 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, providing a possible path to increased performance [21].

The majority of these semiconducting organic materials are p-type, transporting holes (h^+) rather than electrons. While this journal issue focuses on p-type materials, n-type systems are also of interest because they enable the fabrication of p–n junctions, and complementary logic. Some examples have recently been reported in the literature [22, 23].

Further research is needed to improve the mobility and environmental stability of n-type and p-type materials, as well as a fundamental understanding of electron injection, metal contact issues, electron transport, surface modification, and self-assembly. However, organic systems

offer a great deal of flexibility in their synthesis, and as chemists develop new materials and learn how to better order and process them, it is hoped that mobility will continue to improve, perhaps reaching the performance of polysilicon and expanding the applications of such materials for low-cost logic chips.

Similar enhancements in performance have been seen in the development of organic light-emitting diodes (OLEDs). **Figure 5** shows the dramatic increase in luminous efficiency of light-emitting molecular solids and polymers compared to typical inorganic LEDs over a 15-year time scale. Pioneering work was done at Eastman Kodak in 1987 on evaporated small molecules [25] and at Cambridge University in 1990 on solution-processed semiconducting polymers [26]. Currently, the highest observed luminous efficiencies of derivatives of these materials exceed that of incandescent lightbulbs, thus eliminating the need for the backlight that is used in AMLCDs.

The electronic and optical properties of these “active” organic materials are now suitable for some low-performance, low-cost electronic products that can address the needs for lightweight portable devices for the 21st century. This special issue of the *IBM Journal of Research and Development* provides the reader with information

on the status and applications of organic and hybrid conducting, semiconducting, light-emitting, and magnetic materials. The first four papers demonstrate how the synthesis, ordering, and self-assembly of new materials can give rise to improved electronic, optical, and magnetic properties.

The first paper, by Dimitrakopoulos and Mascaro, reviews efforts on organic semiconducting materials, fabrication processes, device designs, and applications, with an emphasis on IBM activities during the last four years. The authors point out that organic semiconductors are limited by the weak van der Waals interactions between molecules, since at room temperature their vibrational energy approaches that of their intermolecular bond energies. Therefore, it may be difficult to further improve the current set of organic semiconductors. However, the next paper, by Mitzi, Chondroudis, and Kagan, reviews the unique electronic and optical properties that have been observed in a new class of materials—organic–inorganic hybrids. These materials offer the potential of improved transport because the inorganic portion of the hybrid material provides stronger covalent or ionic bonds compared to the weaker intermolecular interactions in organic semiconductors, while the organic portion of the system provides the required processability and mechanical properties.

The paper which follows, by Murray et al., describes the synthesis of a different type of organic–inorganic hybrid: a colloidal nanocrystal. It consists of an inorganic core coordinated with an organic monolayer, which provides monodisperse building blocks that self-assemble into ordered superlattices. By tailoring the size and composition of the inorganic core, and the length and chemical functionality of the organic capping layer, the electronic [27], optical, and magnetic [28] properties of these materials can be studied as a function of size, perhaps providing a fundamental understanding of the limits of scaling for storage and semiconductors.

The paper by Angelopoulos provides an overview of applications for conducting polymers in the microelectronics industry, with a focus on polyaniline. Until the 1970s, the majority of polymers were classified and used as insulating materials. However, in 1978 it was discovered that electrons could be added or subtracted (chemical doping) from unsaturated polymers such as polyacetylene, polythiophenes, and polyanilines, allowing the flow of current [29]. This opened an entire new field, and for their discovery and development of conducting polymers, Alan Heeger, Alan MacDiarmid, and Hideko Shirakawa were awarded the Nobel Prize in Chemistry last year. These conducting polymers have unique properties in that they combine the electronic properties of metal with the processability and mechanical properties of polymers. While they are still orders of magnitude less conducting

than copper, they are useful for many applications, such as coatings for electrostatic discharge protection, corrosion protection, and electrodes for metallization. Advances in synthesis and ordering or self-assembly of these materials are expected to yield significant improvements in conductivity.

The development and optimization of new organic systems requires innovative methods, techniques, and computer simulation to provide fundamental understanding of charge injection and transport, and to guide the optimization and development of novel materials.

The next three papers provide the fundamental understanding needed to optimize the performance of small-molecule organic light-emitting devices. The paper by Riess et al. investigates the influence of trapped and interfacial charges, showing that the delay time for the onset of electroluminescence at low voltages is controlled by the buildup of internal space charges, which facilitates electron injection, rather than by charge-carrier transport through the organic layers. In general, the control of internal barriers in multilayered structures is key to tailoring device performance. The paper by Alvarado et al. is an overview of spectroscopy and electroluminescence excitation experiments with a scanning tunneling microscope (STM) to study the physical and electronic structures of the organic materials used in OLEDs. Here the role of the top electrode in an OLED is played by the STM tip. Charge carriers are injected from the tip into the organic stack to provide information on emission homogeneity, degradation of emission, energy barriers, carrier mobility, and recombination efficiency. The STM, which was invented in 1982 [30], allowing investigators to “see” at a molecular level, continues to be a key enabler providing fundamental information on the performance limitations of OFETs and OLEDs.

The paper by Curioni and Andreoni describes the use of computer simulations to study *tris*(8-hydroxyquinolato)aluminum (Alq_3), the prototypical electron-transporting and -emitting material used in OLEDs, and its interaction with the metals typically used as cathodes. The work is aimed at gaining insight into the electronic properties of the solid phase of Alq_3 , as seen in Figure 2. The authors propose new derivatives that may have higher intrinsic luminescence.

The last paper, contributed by Howard and Prache from eMagin Corporation, discusses the use of OLEDs for microdisplay applications. Microdisplays, which exploit the dense electronic circuitry in a silicon chip, are providing a new wave of ultraportable information products, including headsets for viewing movies and cellular phones with full-screen Internet access. The requirements for these displays are reviewed, and a case is made to show that OLEDs are the best candidate for transducer technology.

The electronics industry must satisfy the demands of an increasingly complex society for pervasive computing: access to instant information, data handling, and communication. Although organic electronics is a new area, the performance improvements in OLEDs and in organic conducting and semiconducting materials have generated much commercial interest. An OLED material has already led to a commercial product, an automobile display available from Pioneer. In addition, companies such as Eastman Kodak in collaboration with Sanyo Electric, Cambridge Display Technologies together with Seiko Epson, E-Ink in conjunction with Lucent, TDK, Philips Electronics, eMagin, Dupont/Uniax, Covion Organic Semiconductors, Idemitsu Kosan, and Plastic Logic, to name only a few, are developing products and obtaining intellectual property in the field.

There will be continued growth in the field of organic electronics, fueled by the promise of the new products and applications that can be derived from electronically and optically active organic and hybrid materials. These include low-cost and perhaps even flexible displays for e-newspapers and advertising, and low-cost memory and logic devices. Long-term research efforts and innovation are needed to provide new organic semiconductors, organic light-emitters, and conducting polymers with improved performance, processability, and environmental stability to oxygen and moisture. The successful development of these new materials will require increased multidisciplinary partnerships among physicists, chemists, biochemists, and engineers. As improvements in material properties are realized over the next ten years, organic electronics may displace traditional entrenched technologies and manufacturers.

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