R&D Prospects of Organic Electronic Devices

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OVERVIEW: Organic electronics is of enormous technological interest for its ability to integrate circuits, batteries, sensors, and other functionalities on flexible plastic substrates using solution and printing processes at near room temperature, and a wide range of organic devices are now being actively researched and developed. Recently organic EL displays incorporating OLEDs reached the marketplace, and we are already beginning to see the emergence of viable devices based on organic semiconductors. Already positioning itself to become a major player in the new emerging organic electronics business, Hitachi Group is moving rapidly ahead with R&D on organic TFTs, organic actuators, and other organic devices, and has already verified the operation of prototype devices built using solution-processed materials anticipating the growing use of solution and printing-based processing.

INTRODUCTION

IN society where networks penetrate every corner of the country and broadcasting and communications have converged to a substantial degree, a network environment has been put in place enabling people to fully exploit information in every sphere of society. People take for granted enjoyable, seamless and barrier-free interconnection between their individual interface points and all the myriad devices where information is stored around the globe. At the same time, there is ever more diversified demand for greater user-friendliness, easier storage capability, and a host of other requirements. To meet these challenges, we are looking to new electronics for more flexible, wearable, large surface area, multipoint distribution and other novel capabilities that create new value and cannot be easily implemented with legacy technologies.

To create this kind of value, R&D (research and development) initiatives are focusing on a new generation of electronics based on organic semiconductors, oxide semiconductors, and other novel organic technologies in addition to legacy silicon-based semiconductors. Organic electronics in

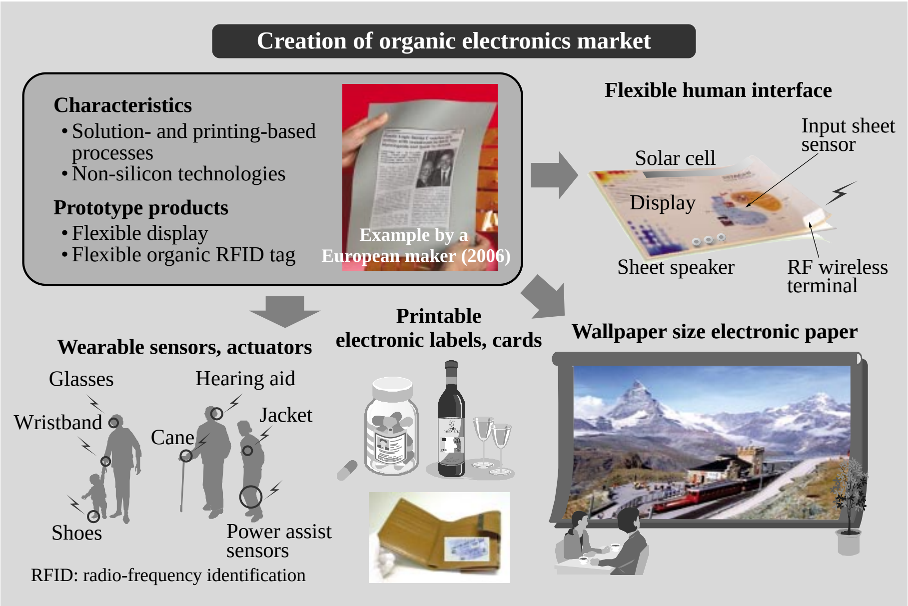


Fig. 1—Organic Electronics Market Outlook.
In 2006 a European-based venture capital company announced its offering of flexible electronic paper. This marked the beginning of the wide open potential of the organic electronics sector, and R&D has now begun to establish flexible electronic devices based on all printing processes.

particular has great potential for realizing these new devices because it offers a way to continually form dense devices on larger area substrates by solution and printing processes without using conventional vacuum and mask-based photolithographic processes. Even compared to traditional silicon technology, organic electronics has significant advantages: fewer steps in the fabrication process, lower equipment costs, and less impact on the environment in the form of lower energy consumption and less use of rare metals. Organic electronics should be thought of not as supplanting legacy technology, but rather as technology that creates new value (see Fig. 1).

This paper provides an overview of Hitachi's recent work on solution-processed small-molecular materials for organic TFTs (thin film transistors) and carbon nanoparticle composites for organic actuators, and evaluates the performance of prototype devices based on these materials. We then outline some of the measurement technology and manufacturing needs and challenges associated with organic materials and devices, highlighting the future technological and business prospects of organic electronics.

ORGANIC DEVICE DEVELOPMENT TRENDS

The key devices at the core of organic electronics include OLEDs (organic light emitting diodes), organic TFTs, organic memories, organic solar cells, and organic sensors and actuators — that together provide a vast array of functions and capabilities. The early basic research on these devices was carried out by universities and research institutes, but the resources needed to move these technologies out of the laboratory and into the marketplace are enormous — especially, resources to develop nanotechnology materials such as solution-processed semiconductors and metallic inks, and to develop processing equipment such as printing and continuous conveyance technologies — so much of the R&D burden has shifted to consortia of leading materials and equipment manufacturers. In terms of applications, other businesses deal with (1) equipment implementing displays, batteries, RFID (radio-frequency identification), and sensors, and (2) systems based on these various kinds of equipment, so we are also collaborating with setup manufacturers and systems-oriented companies as we approach trial applications in the marketplace.

Certainly improving their performance is necessary to turn these devices into viable commercial products, but increasing their stability and reliability by reducing characteristic variation and other refinements is also critically important. Taking the OLED as a case in point, initial work on the low-molecular-weight organic material Alq3 (an aluminum complex) for OLEDs and system development began in 1987, but the material enhancement providing the luminescence and improved decay life sufficient for commercial products didn't come until two decades later. And assuming migration toward solution and printing-based processing, ongoing research is also working to improve the luminous efficiency and reliability of technologies relating to polymer materials and processes.

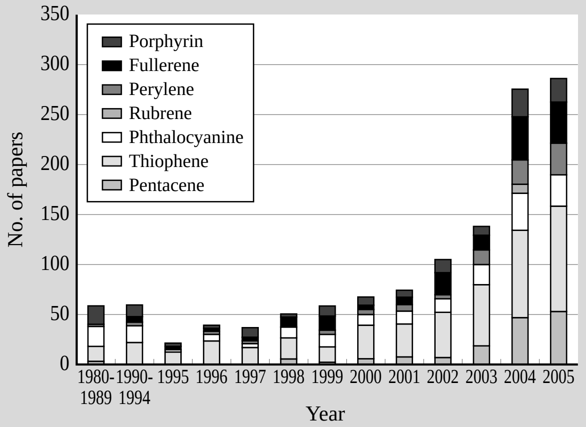
Focusing on organic TFTs, steady work continued since proof of operation of organic FETs (field effect transistors) using polythiophene in 1986 on both polymer and small-molecular-weight materials, and particularly since about the year 2000 there has been an enormous amount of work done on these materials. The performance of TFTs gets better year after year. Many recent studies have been published that deal with the performance of TFTs using the small-molecular-weight organic material pentacene and derivatives, and proven processes and materials approaching a mobility of 10 cm^2/Vs have already been developed. This is significantly better performance than the amorphous silicon TFTs used as pixels in today's LCDs (liquid crystal displays). Now that the potential performance has been demonstrated, R&D is now working to ensure sufficient stability and reliability of organic TFTs. And aside from TFTs, R&D is actively addressing materials, processing, and devices technologies to realize organic solar cells and a host of other organic devices that will see commercial availability as soon as the required performance, stability, and reliability issues are resolved.

Committed to play a leading role in the creation of new value and businesses in the post silicon world of organic electronics, Hitachi, Ltd. has joined forces with research laboratories, Hitachi Group companies, universities, and industry-wide consortia of materials manufacturers, to develop a full range of organic devices — organic TFTs, organic actuators, organic EL (electroluminescence) — as well as the nanotechnology-based materials and basic technologies needed to support organic electronic development.

ORGANIC TFTS

Organic Semiconductor Materials

Beginning around the year 2000 we saw a great increase in the number of papers dealing with organic semiconductor materials, and research in this area has flourished since then (see Fig. 2). Over the last few years the mobility of organic TFTs has started to rival the performance of amorphous silicon devices, and real-world applications will not be far behind. Especially noteworthy is that we are beginning to see the emergence of high-performance semiconductor materials that are created using solution-based processing. Initially, the low-molecular-weight materials for high-performance semiconductors were formed by deposition. Solution-processed materials are high-molecular semiconductors with mobilities some two orders of magnitude below those of low-molecular materials. Leveraging the advantages of processing high-performance materials with wet or solution-based processing will permit the fabrication of high-performance devices by low-cost solution and printing processes.



Source: American Chemical Society (material systems)

Fig. 2—Growth in Number of Papers Dealing with Organic Semiconductor Materials.
Over the last few years the number of papers dealing with organic semiconductor materials has surged, research is flourishing, and applications are even beginning to emerge.

Deposited low-molecular organic semiconductors

The chemical structure of low-molecular compounds can be simply specified, so refining is relatively simple with few impurities. Moreover, the molecules in semiconductor crystal formed by deposition are well ordered, so one expects high mobility. Some of the deposited low-molecular compounds that have been investigated so far include condensed-ring compounds as represented by pentacene, phthalocyanine derivatives(1), oligothiophene derivative(2), and condensed-thiophene derivative. In these compounds, mobilities ranging from 0.1 to 1 cm^2/Vs have been reported. Recently there have even been reported mobilities of around 10 cm^2/Vs that exceed those of amorphous silicon using pentacene and non-deposited single-crystal rubrene(3).

Solution-processed polymer semiconductors

The study of polymer semiconductor materials has a long history, and polythiophenes and other pi-conjugate polymer materials have been extensively investigated. It was apparent early on that such devices could be formed by wet processes without using the massive (and expensive) vacuum equipment used in silicon processes, so devices could be fabricated at very low cost. But in the case of polymer materials, the molecular weight must inevitably be distributed and impurities are far more difficult to remove, so mobilities are 1–2 orders of magnitude less than those of low-molecular-weight materials.

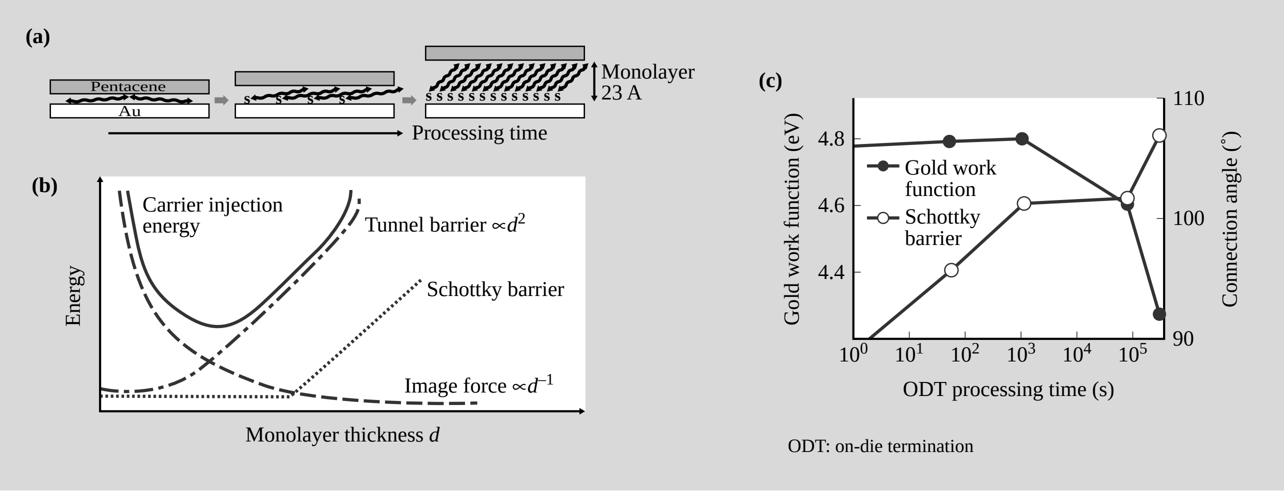
Solution-processed low-molecular organic semiconductors

Low-molecular-weight organic semiconductors provide excellent performance, but their solvents have poor solubility, which makes it hard to achieve the cost savings of solution-based processing that is one of main advantages of organic materials. Recently a number of approaches have been investigated to overcome this problem including the insertion of a substituent group into low-molecular compounds, preparation of soluble precursor molecules, and alternative solution processes.

One introduced substituent group that has proven successful for solubilization is called TIPS (triisopropylsilyl)-pentacene. Mobilities of under 1 cm^2/Vs that rival semiconductor formed by deposition have been reported. A well-known synthetic precursor is pentacene derivative(4). Exploiting this approach, Hitachi Group in collaboration with several material manufacturers investigated a method in which pentacene is dissolved in heated solution, and we achieved a better mobility than deposited pentacene.

Interface Control Technology

In addition to the development of new materials, close control of the interfaces between (1) organic semiconductors and electrodes, and between (2) organic semiconductors and gate dielectrics is also critically important for achieving high-performance organic TFTs. Controlling (1) the semiconductors-electrode interface is important because this directly affects injection efficiency, and controlling (2) the



ODT: on-die termination

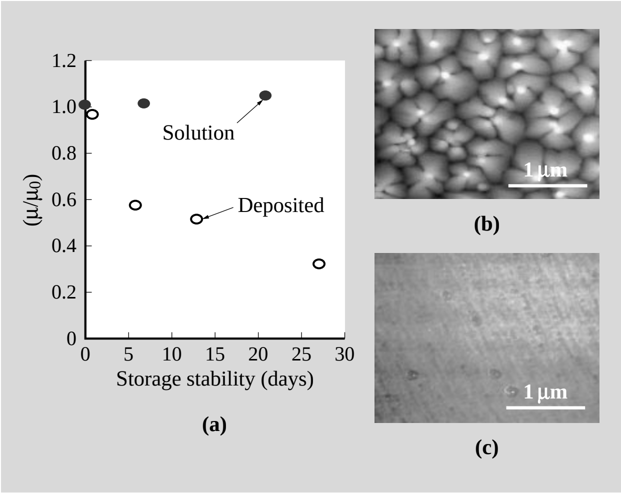
Fig. 3—Control of Carrier Injection from Electrode to Organic Semiconductor by SAMs.
Stages in SAM (self-assembled monolayer) formation over processing time (a), carrier injection model (b), and change in angle on electrode with the change in electrode (gold) work function over SAM (ODT) processing time (c) are shown.

semiconductors-dielectric interface is important because this suppresses electron traps that enhances the transport capability. Addressing (1), we tried modulating the *p*-type/*n*-type by varying the work function of the electrode material.

Hitachi founds a way to control the work function and increase injection efficiency by modifying the source/drain electrode surface using a SAM (self-assembled monolayer)(5). The electrode/semiconductor interface contact resistance R_c is reduced when SAM molecules sparsely bind on the surface in a lying down position as illustrated by the left schematic in Fig. 3(a), but R_c is increased when SAM molecules densely bind on the surface and lift off the substrate and point outwards as illustrated by right schematic in Fig. 3(a). Fig. 3(b) depicts a model of carrier injection energy at the electrode/semiconductor interface. Here again, one can see that when the SAM molecules densely bind on the surface and are in an upright position, the R_c increases. This is because the work function of the gold (source/drain electrode) decreases. Fig. 3(c) reveals that after 20 minutes of processing, the gold work function falls off, and the Schottky barrier increases by a proportional amount. It is assumed that the tunnel barrier also increases. Since there is no trapping level contributing to conduction in SAM molecules, carrier transport from electrode to the trapping level in the semiconductor is only by tunneling through the monolayer. Since the required energy (tunnel barrier) is proportional to two times the monolayer thickness *d*, the energy increases rapidly as the SAM molecules lift off from the substrate. The fact that R_c is reduced more when SAM molecules lie flat and sparsely bind on the surface than when there are no SAM molecules on the surface at all is attributed to image force. When holes from the electrode are trapped in energy levels in the semiconductor, the electrode is temporarily negatively charged. This essentially acts as a force pulling the holes back to the electrode. This image force is one quarter of the distance between the surface of the electrode and the level at which the carriers are initially trapped, which is proportional to one quarter of the thickness of the monolayer. The carrier injection energy at the electrode/semiconductor interface is thought to be the sum of the Schottky barrier, the tunnel barrier, and the image force, and the thickness presented in Fig. 3(b) is the smallest value yet obtained.

Solution and Printing Fabrication Technology

A key advantage of organic TFTs is that they can be fabricated with solution and printing processes alone without deposition equipment, which results in a substantial cost savings. Indeed, a group has already begun to investigate the fabrication of organic TFTs using inkjet and other printing technologies, and solution- and printing-based production of TFTs and other organic devices is projected to emerge as a major new sector in the years ahead. However, at present printing accuracy (alignment) is only 20–30 μm at best, and this is not sufficient for producing the fine patterns demanded by high-performance devices.



(a)

(b)

(c)

Fig. 4—Behavior of Pentacene for Different Processes. Comparison of storage stability for deposited versus solution-processed pentacene TFT (thin film transistor) (a), AFM (atomic force microscope) image of deposition pentacene surface (b), AFM image of solution-processed pentacene surface (c) are shown.

Organic TFTs using solution-processed materials

Hitachi has fabricated a prototype TFT array using solution-processed materials. By fabricating the device using solution processing, we obtained a dramatic improvement in storage stability compared to earlier organic semiconductors [see Fig. 4(a)](6). This remarkable improvement is attributed to the fact that, in deposition processing, many nuclei are formed in the initial stage of deposition that are seeds of crystal growths, as shown in Fig. 4(b). A trench is formed at the boundary between crystals that is vulnerable to oxidation, and the oxidation has an adverse effect on the conductivity of carriers in the film. By contrast in solution processing, a very large crystal grain forms that exhibits far fewer of the kind of boundaries one sees with deposition processing, as shown in Fig. 4(c). This not only improves the conductivity characteristic, it also suppresses oxidation which is a prime factor in diminished performance and improves storage stability. We have confirmed the performance of a TFT with a field-effect mobility of less than 1 cm^2/Vs, performance that is more than adequate for a wide range of IC (integrated circuit) applications including display pixel-drive TFTs and RFID elements.

Self-aligned solution-process electrode fabrication method

Because printing resolution is limited to about 20–30 μm, alignment accuracy between the lower electrode (gate) and upper electrode (source/drain) is critically important in terms of improving circuit performance. With the goal of achieving better printing alignment accuracy, Hitachi has proposed a novel photo-irradiation method through the backside for aligning photosensitive self-assembled monolayers(7). The new method enables us to create self-aligned rectangular patterns with 20-μm spacing in a conductive polymer film on plastic substrate. By integrating this approach with printing technology, this will give us the ability to fabricate high-performance devices with all solution-based and printing processes.

ORGANIC ACTUATOR

Organic Actuator

Work began on organic materials such as gels that change shape in response to stimuli and strong dialectic polymers for application to actuators as early as the 1970s. Recently actuators based on such materials as conductive polymers, platinum ionic conductive polymers, and carbon nanotube sheets have attracted scientific and technological interest for their light weight and ability to operate on very low drive voltage(8). Generally, these kinds of actuators only operate when immersed in electrolyte solution, but there are also reports of actuators designed to work in air by incorporating non-volatile ionic liquid into the film. Here we will refer to actuators based on organic materials whose operation can be controlled by electric signals as "organic actuators." Here we will briefly describe some of the organic actuators that have been developed using CNP (carbon nanoparticle) composites.

CNP Composite Actuators

Hitachi has developed two types of organic actuators, one that works in electrolyte solution and the other that works in air(8), (9). The ways that the two devices work are somewhat different, but the materials out of which they are configured are essentially the same. Fig. 5 shows a schematic representation and SEM (scanning electron microscope) micrographs of the materials used in the organic actuators developed in this work. This type of material in which CNPs are dispersed in polymer binder is called CNP composite, and has a number of significant advantages.

(1) Because the materials contain conductive CNPs, their conductivity is high and the conductivity of the material can be set at will by varying the CNP content and type of CNP. By optimizing conditions and varying the percentage of CNP content, the conductivity can be varied by as much as six orders of magnitude.

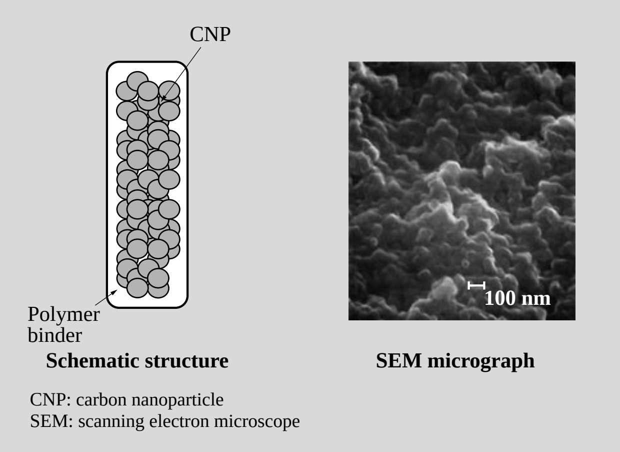


Fig. 5—Schematic and SEM Micrograph of Actuator Material Structure.
Schematic structure and SEM micrograph of the material used in the actuator developed in this work are shown.

(2) Material with particular properties can be used for the polymer binder as required. Ionic conductive material can be used for the actuator that operates in electrolyte solution, and material having a large thermal-expansion coefficient can be used for the actuator that operates in air. Moreover, by using a soluble polymer material that can be implemented as a kind of ink, the actuators can be formed by printing, which is very advantageous.

(3) The material consists of conductive particles and polymers, which means that the actuators can be implemented as extremely lightweight and flexible actuator film.

Organic actuators implemented using these CNP composites are known as CNP composite actuators. Let us next take a closer look at the air-stable actuator that works in atmosphere.

Air-stable CNP Composite Actuator

Fig. 6 shows a schematic revealing the operating principle of the air-stable CNP composite actuator(10). If a difference in electrical potential is applied at opposite ends of the actuator film, current flows through the film and Joule heating is produced because the CNP composite actuator is conductive. The Joule heating causes the temperature of the actuator film to rise, and the film expands as a result of thermal expansion. Then when voltage to the film is cut off, the film returns to its normal temperature and shape as it cools down. This ability to change the shape of the film by controlling the thermal expansion with electric signals can be harnessed to use the device as an actuator. This makes the device air-stable in contrast to the earlier CNP composite actuator that only works in electrolyte solution, and since an opposing electrode apart from the film itself isn't needed, the drive system can be implemented very simply which is another major advantage.

In order to obtain a certain amount of displacement with this actuator, Joule heating that produces a certain amount of temperature change must be applied to the actuator film. Also note that, to obtain the same amount of Joule heat, the required voltage will vary if the electrical resistance of the film differs. Or to put it differently, the required drive voltage can be adjusted and controlled by varying the resistivity of the actuator film. Since it is easy to change the electrical

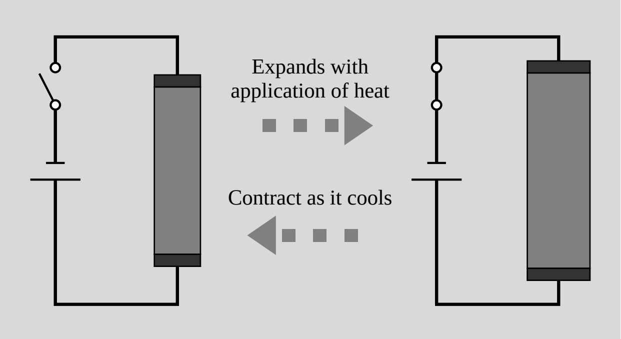


Fig. 6—Operating Principle of CNP Composite Actuator that Works in Air.
Exploiting change in shape by thermal expansion that is controlled by electric signals, the device can be used as an actuator.

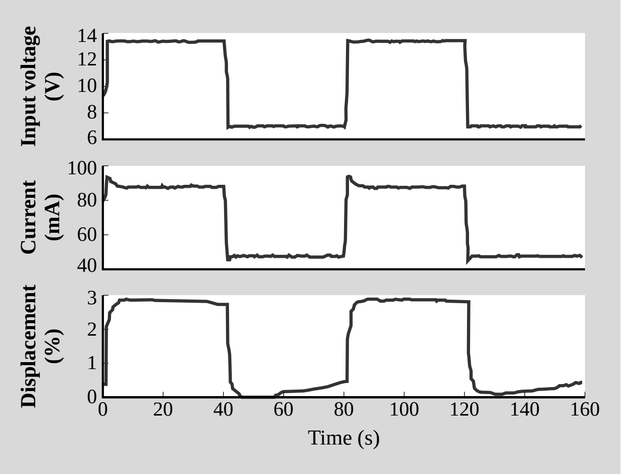


Fig. 7—Film Current and Displacement of the CNP Composite Actuator that Works in Air.
Current that flows in the actuator layer and the change in displacement of the actuator layer are shown.

TABLE 1. Characteristics of the CNP Composite Actuator
Characteristics of the CNP composite actuators that operate in electrolyte solution and in air are shown.

Characteristics	Works in electrolyte solution	Works in air
Operating principle	By charge stored in electric double layer	Thermal expansion accompanying self-generated heat
Rate of expansion/ contraction	Maximum 4% Practical 2%	Maximum 4% Practical 2%
Drive voltage	Several volts	Several volts to several tens of volts
Operating speed	Follows input signals exceeding 30 Hz	Follows input signals exceeding 30 Hz
Generated response	Max. about 5 MPa	Max. about 5 MPa
Life	100,000 expansion/ contraction cycles	10,000 expansion/ contraction cycles
Features	Practically no energy required to maintain shape	Easy device fabrication because configuration and processing are simple

conductivity of CNP composites, the drive voltage can be easily set at any value at will. Moreover, because binder is also used as necessary, polymer with a large thermal expansion rate can be used for the binder to produce a large displacement.

Fig. 7 shows the current flow through the film and the typical change in the amount of displacement in the film when a rectangular wave is input at both ends of a CNP composite actuator film. The film expands when voltage is applied, and returns to the original shape when the voltage is withdrawn. As long as the temperature continues within a certain range, this reversibility between shapes continues. But in contrast to the CNP composite actuator that works in electrolyte solution, once the shape has been changed, the current cannot be interrupted in order to maintain that shape. In other words, power is consumed just to maintain the shape.

Table 1 shows a summary overview of the properties of the two CNP composite actuators, one that works in electrolyte solution and the other that works in air. To facilitate comparison between the two devices, we used the same CNP composite in both devices: we used Ketjenblack from Lion Corp. for the CNP and Nafion from E. I. du Pont de Nemours & Co. (Inc.) for the binder.

Note that the CNP composite actuator films are produced using solution processes. This means that, by devising CNP composite materials, actuators can be readily fabricated by a range of printing methods. Harnessing this technology will open the door to all kinds of new developments: tactile transmission devices responsive to touch, a dynamic Braille device that represents characters with the touch of slightly protruding keys, objets that can be used for sales promotion, and many more.

ORGANIC MATERIAL DEVICES: MEASUREMENT AND FABRICATION CHALLENGES

R&D on the application of organic materials to devices has been going on for decades, and we are now beginning to see the emergence of actual applications. The advantages and additional value of all the features of organic devices — pliancy, flexibility, and printable solution-based processing — that are so difficult to achieve with ordinary silicon technology are starting to become apparent. But when fabricating flexible devices, obviously the substrate must be flexible as well, so this requires different methods of conveyance and different alignment mechanisms that used with conventional silicon wafers and glass substrates. Particularly when plastic is used as a flexible substrate, warpage and deflection induced by thermal processing must be taken into account, which means that three-dimensional alignment — that is, alignment on the Z-axis in addition to the normal two-dimensional alignment — is required.

In manufacturing, quality control is essential for improving productivity. However, the ability to fabricate devices by solution and printing processes opens the way to roll-to-roll processing, which demands rather different technologies for inspection and quality control purposes. Moreover, because these materials are organic, conventional optical and electron beam-based inspection techniques may have a detrimental effect on the device performance, thus requiring controls on the wavelength of inspection light and the accelerating voltage of electron beams. The migration to organic technologies will thus entail a number of challenges, as well as the development of new inspection techniques based on new measurement technologies and quality control technologies.

CONCLUSIONS

In this paper we surveyed recent development trends in organic devices, detailed recent work on organic TFTs and organic actuators based on CNP composites, and evaluated the performance of prototype devices built using new organic materials. We also noted the challenges of developing measurement and fabrication technologies tailored for organic materials and devices, and commented on the future prospects of the emerging organic electronic sector. According to data compiled by several independent market survey firms, the market for organic EL displays and other organic device products will begin to see very rapid and sustained growth beginning around 2015. For any company that wants to be a part of this emerging new growth market, it is essential to get involved in the business and the manufacturing of products while the market is still small. By getting involved at this early stage, we intend to seize the initiative by developing our products to a high-quality finished form, and by amassing a wide range of intellectual property and know-how relevant to organic electronics.

As detailed in this paper, Hitachi has fully demonstrated the practical viability of organic electronics — displays, RFID, actuators, and other devices — based on solution-processed materials by investigating new nanotechnology materials, processes, and devices, and by verifying the performance of organic devices. Indeed, the first step has already been taken by demonstrating that the implementation of device and circuit arrays and integration of functional capabilities are possible, and significant business opportunities will also arise in materials and equipment manufacturing. Then at the next stage, proving of operation of these integrated organic devices and forging ties with a full range of other businesses that provide materials, make fabrication and measurement equipment, and provide setup and system services will be critically important. With the goal of forging a new organic electronic business in the years ahead, Hitachi is committed to ongoing research and development to enhance device performance by reducing characteristic variation and improving reliability, and moving ahead to develop functionally integrated technologies based on solution and printing processing.

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