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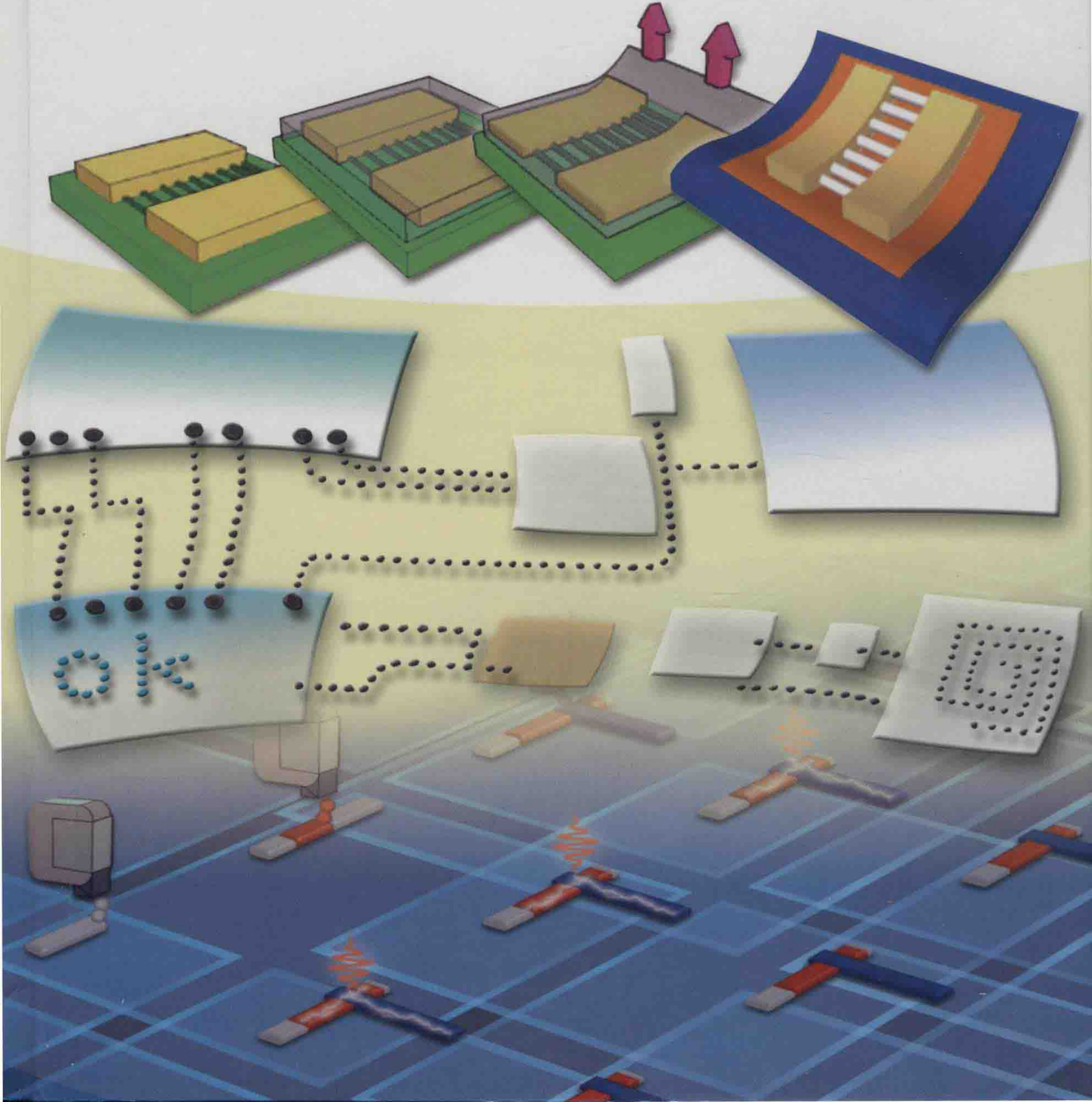
Mario Caironi and Yong-Young Noh

Large Area and Flexible Electronics



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Overview

Mario Caironi and Yong-Young Noh

Flexible and large-area electronics has the potential to mark a further technology revolution in electronics – much like the way the transition from circuits based on discrete components to integrated circuits did – by enabling the pervasive integration of electronic functionalities in all sorts of appliances, their portability, and wearability. Applications are countless: from personal devices (e.g., wearable health monitoring devices) to large-area sensors (e.g., electronic skin, biomedical devices), and smart tagging of products with radio-frequency identification tags. A huge driving force comes from the display industry, with the goal to develop flexible and/or rollable displays deployable on demand to be integrated with portable devices (e.g., smartphones or tablet PC). Conformable large-area sensor arrays (e.g., digital imagers) or chemical and biological sensor arrays also constitute another great opportunity, especially in the case of digital X-ray devices for biomedical and security applications and human healthcare systems. Lightweight, flexible, and easy-to-integrate solar cells are also one of the interesting perspectives opened by this technology, with a view to developing distributed microgeneration sources of different types to serve an information society, necessitating portability, and to provide embedded power supply to low-power, energy-independent, wireless sensor networks.

While this scenario has been considered as a mere vision until only a few years ago, the first examples of nonflat displays have made their appearance, alongside first prototypes of flexible photovoltaic modules and plastic imagers. However, most of these very promising applications are still at the research or development level, mainly because of the immaturity of technologies that would enable their ubiquitous spreading. Given the huge interest, different technologies are being developed to fulfill the requirements of the aforementioned applications. These technologies comprise the assembling of small, discrete components on large, flexible substrates, interconnected by flexible, printed, conductive tracks (Figure 1a). While this may be a suitable approach where area is not a constraint and for small production volumes (e.g., real-time monitoring of vibrations in large constructions such as bridges) [1], *integration* obviously offers a technological advantage for mass applications. Integrated flexible electronics is being developed mainly through two different

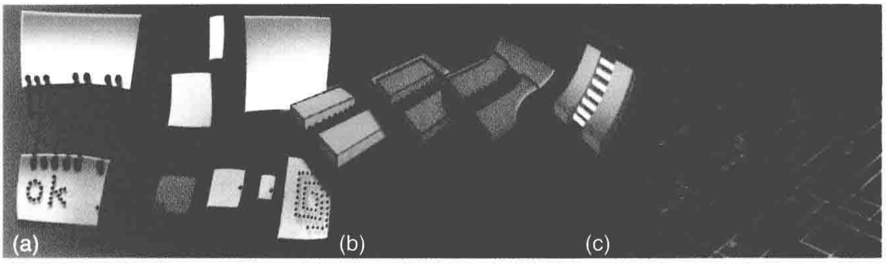

Figure 1 Illustrative representation of the main approaches toward flexible, large-area electronics. (a) Patterning and interconnections of discrete components on foils. (b) Growth of highly ordered structures and their successive transfer onto a flexible substrate. (c) Direct printing of functional inks on flexible substrates.

approaches: (i) the growth followed by sawing or exfoliation of highly ordered crystalline semiconductors and their subsequent controlled transfer onto a flexible substrate (Figure 1b), and (ii) the direct patterning on the substrates of functional materials composing the electronic systems, either via physical vapor deposition methods or by solution-based graphic art printing techniques (Figure 1c).

A widely investigated approach toward large-area flexible electronics is based on organic semiconductors within the framework of π-conjugated molecules [2], a class of materials offering a cost-effective alternative and highly tunable properties through chemical synthesis. Organic semiconductors are very suitable for the above-mentioned applications because they allow easy processing directly on the target substrate with a high degree of freedom of shape, without requiring transfer processes, with different deposition techniques: small molecules can be patterned through vacuum thermal evaporation, a process compatible with roll-to-roll fabrication lines, or, alternatively, small molecules and also polymers can be made soluble by suitable solubilizing side chains. The possibility to treat organic semiconductors in the form of functional inks, enabling a layer-by-layer approach to the realization of complex electronic devices, adds the clear advantage of resorting to low-temperature and high-throughput printing processes. These aspects, together with the superior mechanical properties offered especially by polymers, have made this class of semiconductors among the ones most commonly associated and studied toward the development of flexible electronic applications [3]. This has been a promise of organic electronics for long time. Indeed, the development toward real applications has been progressing much more slowly than predictions. The reasons for this are many, among which we can clearly indicate a technological limitations in the available printing techniques, which were not developed to pattern high-resolution electronic circuits. Another is related to the limited charge mobility of organic semiconductors. Both these problems are now finding very solid answers in the development of printing tools and methodologies enabling finer patterning with high reliability ($<10\,\mu m$)

and in the advanced synthesis of stable and high-performance materials (record mobility values exceeding 10 $cm^2 V^{-1} s^{-1}$).

Organic semiconductors are not the only possible candidates that can be directly processed onto flexible substrates. Many other very promising functional materials are being developed, among which metal oxides represent an important class (10–50 $cm^2 V^{-1} s^{-1}$), being especially applied in the field of high-resolution displays. Indeed, vacuum deposition, through sputtering, is enabling the fabrication of backplanes based on indium gallium zinc oxide (IGZO), which has overtaken hydrogenated amorphous silicon in terms of mobility and stability. Other metal oxides are being developed as well, with intense effort also dedicated to enabling solution processability, where the challenge is reducing decomposition temperatures of soluble precursors to be compatible with processing on plastic substrates [4–6].

Colloidal nanocrystals [7, 8] are also very intriguing because, in principle, they offer both solution processability and highly controlled structures, down to atomic levels. Because of their small size, with the associated large surface-to-volume ratio, their properties are highly dependent on surface states, thereby enabling the tuning of their electronic properties. Investigations on quantum dots have stimulated one of the most important fields in nanoscience and nanotechnology. After decades of continuous efforts by researchers in this field, tremendous progress has been made in the synthesis of quantum dots and their potential applications to optoelectronic devices. The implementation of quantum dots in devices relies not only on their intrinsic properties but also on the collective behavior of the dots in the assemblies, with approaches that make the preparation of quantum dots reproducible, facile, and up-scalable, and on the strategies to tune their surface states and chemical composition with the aim to impart novel properties by applying various post-synthetic treatment procedures.

It is important to note that hybrid solution-processable materials have recently received a lot of interest, with the aim to combine the best features of different materials, such as mechanical strength and processability of polymers, with high performances of 1D or 2D structures. Notably, a new emerging class of solution-processable crystals, namely hybrid metal–organic perovskites [9, 10], which are not treated in this book, has opened up vast opportunities for low-temperature fabrication of efficient solar cells and solution-processable optoelectronic devices.

Another important approach to large-area and flexible electronics is the one based on "nanomembranes," [11, 12] where circuits are developed at the wafer level and subsequently sawed or etched with specific processes in the form of thin films to be laminated on plastic carrier foils. A similar approach, which is usually considered under the same category, is the one based on the growth of high-performance 1D or 2D nanostructures (e.g., 1D crystalline nanowires, nanoribbons, or carbon nanotubes; 2D graphene, transition-metal dichalcogenides, and many others) lately patterned on plastics through different techniques such as transfer printing. These approaches allow achieving very high performances, especially in terms of carrier mobility (>100 $cm^2 V^{-1} s^{-1}$)

in transistors, and are therefore suitable for applications where high switching speeds are required (e.g., wireless electronics).

Besides semiconductors, also relevant materials such as conductors (printable, flexible, and/or stretchable) and insulators (dielectrics, substrates) are required. Among conductors, polymeric materials, such as poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and highly conductive metallic inks that can be sintered below 150 °C, are largely available, with the necessity to reduce costs with the challenging development of copper-based inks. Carbon-based conductors, such as those based on graphene, are an emerging opportunity. Regarding dielectrics, the challenge is to develop high-capacitance dielectrics with low leakage, compatible with large-area, flexible applications. Polymeric insulators are good candidates, but they cannot fulfill all these requirements. An interesting alternative is the use of electrolytes, enabling very high specific capacitance through the formation of electric double layers. Above all, high-performance flexible barriers are required to enable stability of applications, especially in the case of organics which are very sensitive to ambient atmosphere.

Book Structure and Aim

The book is divided in two parts. Part A covers materials, which are the key aspect of the field, their physical–chemical properties to provide the fundamentals necessary for a suitable insight, and a critical view point for applications, along with first exemplary applications in electronic devices and circuits. The first six chapters cover semiconductors, Chapters 7 and 8 deal with dielectrics, and Chapters 9 and 10 describe barriers and substrates, respectively. Different approaches for conductors are described case by case in different chapters throughout the book. Part B covers processes and applications, across flexible circuits (Chapters 11–13) and displays (Chapter 15), memories (Chapter 14), solar cells (Chapters 16 and 17), and biosensors (Chapter 18).

A peculiarity of this book is that it puts together areas that are traditionally separated, especially in terms of scientific communities, but all of which tend to the same large-area "macroelectronics" applications from different ends. As we inevitably had to make choices in selecting the topics within this very broad field, our main intention was to select the most exciting examples of approaches and technologies that can really mark the way for new products which will be able to affect in the near future our daily life, hopefully improving it.

The readers will benefit from having collected in a single source valuable information on a very expanding field, as it is the one of large area electronics. They will, first, benefit from receiving an introduction to very different approaches and have the possibility of an in-depth comparison of fundamental properties of different materials, achievable performances, and viable manufacturing methodologies. They will find both fundamental information about materials and an extensive update and description of recently developed devices, with details on the