
SOLUTION PROCESSING OF INORGANIC MATERIALS

Edited by

David B. Mitzi



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Rapid technological progress is transforming our world into one in which electronic capabilities integrate throughout all aspects of everyday life. Cell phones, laptops, digital assistants, and portable media players now provide unprecedented connectivity among people, information, and entertainment. Future advances promise to bring even more seamless integration, including flexible, wearable, and/or very large-area electronics with advanced functionality. Renewable forms of power generation (e.g., photovoltaics) will also hopefully replace carbon-based power sources in order to address both growing energy needs as well as environmental concerns. All of these changes require fundamental invention in the area of electronic materials processing to attain technological/economical viability—including most notably in the area of low-cost deposition of high-quality functional films, which form the basis of modern electronics. Solution-based approaches for thin-film deposition are particularly desirable because of the low capital cost of the deposition equipment, relative simplicity of the processes, and potential compatibility with high-throughput (e.g., roll-to-roll) processing. Although most of the work toward this goal has focused on molecular and polymeric *organic* films, the search for solution-processible *inorganic* materials is at least as important, offering the potential for much higher performance and better thermal/mechanical stability than comparable organic-based systems. This book offers an exploration of the various means of overcoming technological barriers to the solution-deposition and patterning of inorganic electronic components. Throughout the text, emphasis is also placed on providing concrete examples of applications that employ the described solution-processed inorganic films (e.g., transistors, solar cells, and sensors).

In Chapter 1, the issues confronting the solution-based processing of inorganic films will be introduced, with a primary focus on two questions. The first question is why solution processing of inorganics (versus solution-processed organics and inorganics processed by other means) is important in the context of current trends and needs in the electronics and energy industries. The term “macroelectronics,” or low-cost, potentially large-area and/or flexible, high-performance electronics (e.g., from flexible displays to solar panels and antenna arrays), will be introduced as an important future direction of technology evolution. The second question relates to what needs to be achieved, with respect to film performance, fabrication costs, and device characteristics, in order to have the desired impact on selected applications.

Chapter 2 introduces techniques for solution deposition (e.g., spin coating, spray coating, printing, and stamping) and discusses some of the basic concepts common to the solution deposition of inorganic materials, using chemical solution deposition (e.g., sol-gel, chelate, and metal-organic deposition) as an example. The concepts explored include the issues of substrate surface preparation, solution properties, film formation, crystal nucleation and growth, removal of reaction products during heating, and thermodynamic phase stability. Many of the issues introduced in this chapter reappear in later chapters.

After discussion of basic issues confronting solution-based film deposition, the next chapters address specific developments in the deposition of three important classes of electronic materials—chalcogenides (Chapter 3), oxides (Chapter 4), and silicon (Chapter 5)—with discussion of both the deposition techniques as well as the device results employing these films. The focus in these chapters is on how to get a relatively insoluble inorganic material into solution so that it can be deposited on a substrate, and the common theme is the formation of a soluble precursor that can be thermally and cleanly decomposed to yield the desired phase. Once in solution, spin coating is used as the primary means of delivering the inorganic material to the substrate. Relatively high-performance solar cells and thin-film transistors (TFTs) have been demonstrated using these approaches.

Beyond spin coating, Chapters 6–8 explore other means of delivering the inorganic material to a substrate. For example, spray pyrolysis and spray CVD (Chapter 6) represent a promising direction for high-throughput deposition. Particular emphasis is placed on the development of single-source precursors for use in the spray-based preparation of photovoltaic components. Chemical-bath-based techniques are described in Chapter 7. Rather than effecting a rapid chemical reaction of sprayed precursors on a heated substrate (as for spray deposition), the reaction between soluble metal salt and chalcogen source occurs more slowly in a chemical bath under more mild thermal conditions. Chemical bath deposition, electrodeposition, and electroless deposition are each explored as a means of depositing films for solar cells and superconductors. Successive-ionic-layer-adsorption-and-reaction (SILAR), ion layer gas reaction (ILGAR), and electrochemical atomic layer epitaxy (ECALE) deposition are described in Chapter 8 and rely on the sequential deposition of the cationic and anionic components of the desired inorganic materials. Film thickness is controlled in these techniques by the number of dipping cycles completed.

The next three chapters (Chapters 9–11) focus on the deposition of nanostructured or microstructured films and entities. Porous oxide thin films are, for example, of great interest due to potential application of these films as low-K dielectrics and in sensors, selective membranes, and photovoltaic applications. One of the key challenges in this area is the problem of controlling, ordering, and combining pore structure over different length scales. Chapter 9 provides an introduction and discussion of evaporation-induced self-assembly (EISA), a method that combines sol-gel synthesis with self-assembly and phase separation to produce films with a tailored pore structure. Chapter 10 describes how nanomaterials can be used as soluble precursors for the preparation of extended

inorganic films. In this respect, nano-entities (e.g., nanoparticles, nanorods, nanowires, and nanotetrapods) provide an exciting pathway to tailor material properties through size/shape selection, compositional flexibility, and formation of core-shell structures. Chapter 11 focuses on how functional structures can be assembled from nanowire building blocks (i.e., nanowire electronics). In recent studies, fluids have been used to disperse nanowires, and these fluids are used to solution-deposit and orient these entities onto a substrate, yielding an array of nano- or micro-entities. A “holy grail” for this type of research would be to have the capability to chemically and physically functionalize the substrate and nano-entities such that they would self-assemble into relatively complex and predetermined patterns on a substrate.

In addition to depositing and characterizing blanket films, modern electronics relies on the ability to pattern and assemble the resulting insulating, semiconducting and metallic entities into functional devices. Many of the solution-based techniques offer a natural opportunity to achieve this goal during deposition. Chapter 12 gives an overview of patterning techniques that are unique to solution processing, such as ink-jet printing, flexography, gravure, and screen printing. All of these techniques rely on the ability to put the inorganic material or a precursor into solution (i.e., the formation of an ink) and there will therefore also be a discussion of what is needed to make an optimal ink for the different solution-based patterning techniques. Chapter 13 continues with the theme of printing by providing an introduction to rubber-stamping approaches, focusing on techniques that can be used to deposit and pattern single-crystalline micro- and nano-entities on a substrate (no heating of the substrate required). The versatile transfer printing process enables facile integration into heterogeneous 2D and 3D electronic devices and circuits. Although the approaches described in Chapter 13 are primarily “dry” techniques (no solutions required), they are included because they represent an exciting new direction in the low-cost processing of inorganic materials and involve related issues with respect to the stamping process.

Finally, the concluding chapter will discuss the potential implications of the above-described thin-film deposition techniques with respect to technology, highlighting common issues and imminent (or actual) applications of solution-processed inorganics. Although solution-based inorganic film technology is largely in its infancy, commercialization efforts are beginning to ramp up. It is hoped that the current book will give the reader not only a snapshot of the state-of-the-art and a primer on the basics of solution-processing of inorganic materials but also a view of critical areas that need to be addressed (from a materials point of view) before the new technologies can become a commercial reality, thereby giving a direction for future research in the field.

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August 2008*

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Introduction to Solution-Deposited Inorganic Electronics

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1.1 BACKGROUND AND MOTIVATION

1.1.1 Electronics Technologies

Two thrusts currently dominate efforts in electronics research. In both thrusts, the business opportunities stem from society's desire for a more pervasive and integrated electronics environment. However, the technical methods and strategies for achieving this goal are fundamentally different. The first and most widely discussed thrust focuses on what is popularly referred to as Moore's Law and the seemingly endless progression to smaller device feature sizes and the increasing numbers of transistors integrated onto a chip.¹ These chips (i.e., microelectronics) have enabled everything from laptop computers to cell phones, from smart cards to smart toys. The essence of the success of Moore's Law is that by creating technology to make devices smaller, the density and performance increases and the functionality goes up, whereas cost/function goes down. This amazingly successful thrust has created a technological revolution and has been an engine for worldwide economic growth because it results in faster and more compact products for computing and communications.

While over the last 40 years microelectronic integrated circuits based predominantly on silicon technology have made possible our current capabilities in everything from computers and phones to appliances and toys, even greater opportunities would exist if the circuits could be made more lightweight,

flexible, and inexpensive. Everything from flexible displays, to radio frequency identification (RFID) tags that conform to a product's shape, to large and pliable "sensor sheets" that are integrated into airplanes, bridges, or even people to monitor and augment their physical condition, could become possible.² This concept is much newer, and the required technology is not nearly as mature. The distinguishing feature of this newer approach is that small device size is not a critical factor. Rather than fabrication of smaller devices and circuits, described below are two microelectronics-related electronics technologies that have become successful by fabricating modest-sized devices over larger and larger glass substrates (large-area electronics). This work is just now being extended to plastic substrates to provide reduced weight and novel form factors.

Given that microelectronics and large-area electronics are both electronics technologies, it might be assumed that the second is derived from and will evolve with the mainstream semiconductor industry. However, microelectronics is driven to produce smaller feature sizes and higher complexity chips. There are, however, many applications where microelectronics is not an appropriate technology, and in fact, it represents too complex or costly of a solution. Thus, the requirements and drivers are so different that few, if any, of the mainstream integrated circuit (IC) technologies are applicable to this second and newer thrust. While sharing many concepts with microelectronics, the second thrust is NOT for the most part derived from the IC industry and does not really benefit from its learning curve, but rather it originates from needs not adequately addressed by conventional microelectronics. It has different drivers, product attributes, and metrics and will be successful in its own product space, or by complementing conventional ICs to create solutions that neither could provide individually. Because of this distinction, varieties of names have been used to describe this non-microelectronic, large-area electronics technology. Because the device dimensions are generally large compared with microelectronics and product applications are physically large compared with microchips, one popular name for this form of electronics is "macroelectronics."³

1.1.2 Commercial Macroelectronic Technology

The most successful application of macroelectronics, the flat panel display (FPD) industry,^{4,5} now rivals the microelectronics industry in revenue; yet, from an electronics perspective, it is based on nothing more than manufacture of modest-sized transistor switches distributed over glass substrates as large as a meter on a side.⁶ Within 10 years, the FPD industry has almost reached the \$100B mark (see Figure 1.1), whereas more traditional semiconductor industry growth has become relatively mature with slowing growth prospects. Another interesting aspect of the FPD story is that it has been accomplished while undergoing rapid changes in the manufacturing technologies. As shown in Figure 1.2, the size of the glass panels used have progressed rapidly through multiple manufacturing generations, which means that the panel size has

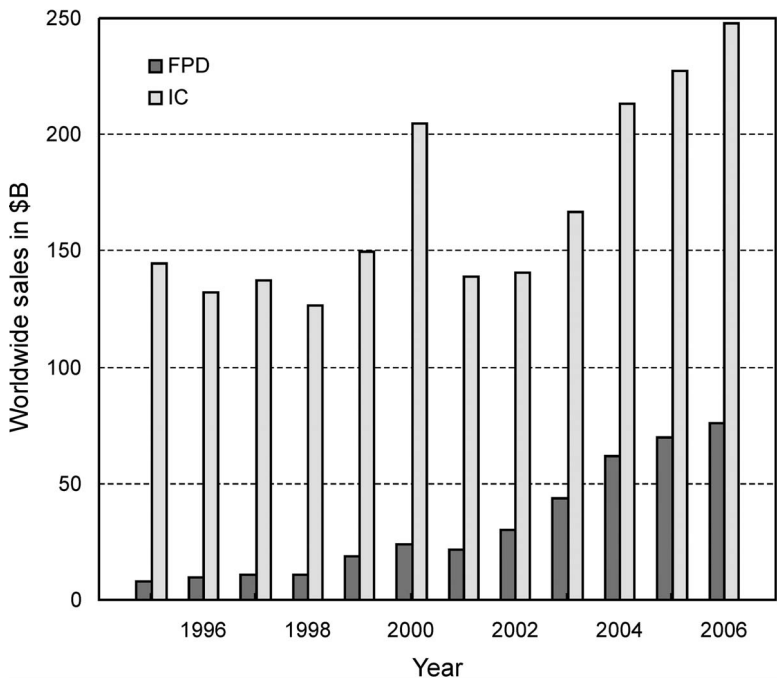


Figure 1.1. Growth of semiconductor and flat panel display industries. [Data Source: Semiconductor industry sales data from Semiconductor Industry Association (SIA) and flat panel display data from Displaysearch Corp, San Jose, CA.]

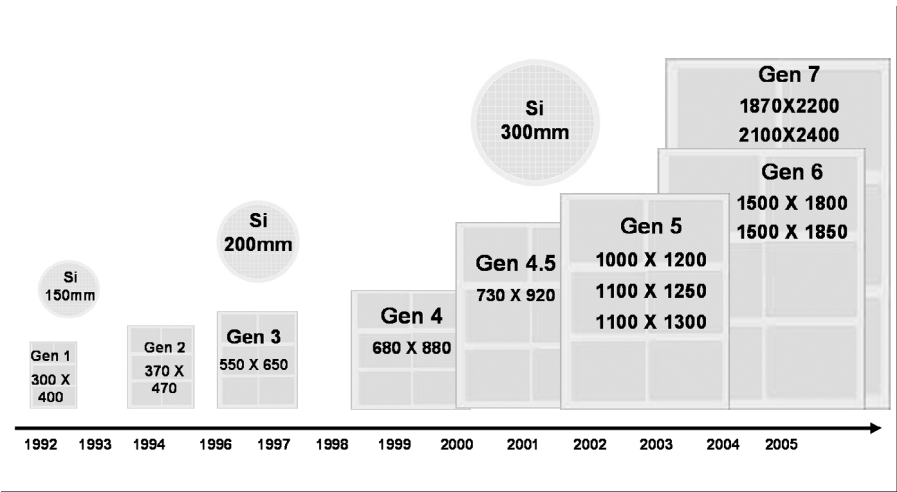


Figure 1.2. Substrate size comparison between Si wafers and glass substrates used in flat panel displays.

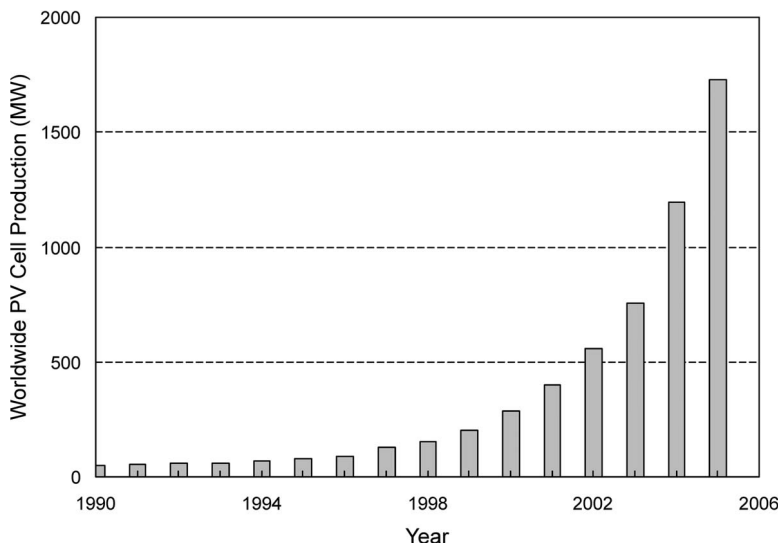


Figure 1.3. Worldwide production volume of photovoltaic modules. [Data source: European Photovoltaic Industry Association, 2006.]

increased by more than 30 times to more than $2\text{ m} \times 2\text{ m}$ for the current eighth-generation production facilities. In contrast, most semiconductor fabrication has been limited to wafer sizes of 300 mm or smaller.

The second large-area electronics technology to reach high volume and revenue, photovoltaics (PV), which is based on “simple” diodes distributed over many hundreds of square centimeters, is also now poised to grow into a major industry as new energy sources become more essential.^{7,8} With the declining stock of fossil fuels and worries about global climate change, solar energy using photovoltaics has become increasingly attractive. The cumulative installed capacity of PV systems has reached over 4 GW and is expected to double every year over the next three years. The annual production volume of PV modules reached the 1-GW milestone in 2004 (see Figure 1.3). With the commencement of a number of a high-volume PV manufacturing facilities over the last two years, production volumes have been growing rapidly ever since, with worldwide manufacturing capacity reaching more than 5 GW in 2007.⁹ Most expansion in photovoltaics is based on crystalline and multicrystalline silicon materials.¹⁰ With the rapid growth of the solar energy market, the availability of reasonably priced silicon feedstock has become a major barrier for future growth. Thin-film technologies offer efficient materials utilization and opportunities for large-area processing. Several companies are building thin-film silicon PV production lines based on large glass substrates (e.g., 4-m^2 glass sheets), which are similar to those employed by the FPD industry. The main barriers for thin-film PV technologies, which need to be overcome in order for thin-film PV to become pervasive, are improved conversion

efficiencies (approaching that of crystalline Si devices) and lower capital cost of some production equipment, especially vacuum deposition tools.¹¹

To overcome these barriers, the industry is aggressively pursuing both alternative materials and manufacturing methods. Although the major focus of the PV industry is on silicon-based devices, several companies have developed products based on thin-film chalcopyrite and cadmium telluride, as these materials offer opportunities for lower cost production through solution-based processing. Chalcopyrite, or more specifically the Cu(In,Ga)(Se,S)_2 family of compounds, has achieved the highest conversion efficiencies (~20%) of any polycrystalline thin-film material.¹² Several companies have commercialized the technology and are approaching volume production.¹³ Several companies have started producing CdTe in volumes beyond pilot production. Small-area efficiencies of 16% together with simple production technologies make this material very attractive. State-of-the-art commercial CdTe PV modules that have efficiencies in the 9% range are in volume production.¹⁴

1.1.3 Microelectronics Potential

The success of the FPD industry and the rapidly developing PV industry are testaments to the potential for large-area electronics for other system solutions. For example, conformal and flexible form factors are very desirable attributes to provide either portability and/or the ability to install large-area electronics in a variety of locations. These needs are receiving much attention, although fulfilling them is proving to be difficult. Moreover, despite the success of microelectronics, there are applications where it has not been good enough to meet all requirements. Specifically, applications where very low cost is the product driver, rather than performance, can prove challenging for conventional microelectronics. As much as microelectronics has reduced the cost/transistor, the costs are still not low enough to meet the few pennies/item targets for electronic applications that are intended to be disposable, such as RFID tags and product expiration sensors. Similarly, although the number of microelectronic transistors per square centimeters (areal density) has remarkably increased over the last 40 years, the ability to distribute even moderate numbers of transistors over large areas onto a variety of substrates is just beginning to be commercialized for applications such as flexible displays.¹⁵ Transistors at low density can be fabricated over large pieces of glass, but at great sacrifice to performance characteristics compared with mainstream “Moore’s Law” devices.

Although initial applications of large-area electronics have focused on displays and PV, future product opportunities are expected to include sensors, imagers, distributed lighting, electronics that are embedded into clothing or gear already carried (radios, computers), and health monitoring/control of vehicles and even people (Figures 1.4–1.7).^{3,16,17} Figure 1.4 captures a concept long championed by many display manufacturers. It proposes that at some point in the future, the display manufacturing capability will be able to provide

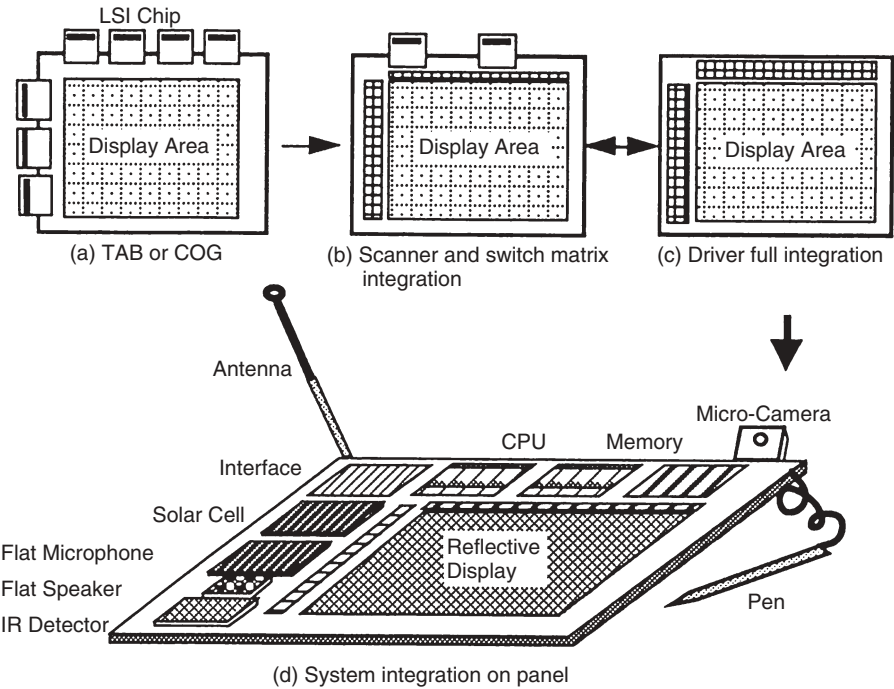


Figure 1.4. Schematic showing the evolution of displays toward a system on a flexible panel. (a) Direct chip on glass attachment technology, moving toward (b) partial display driver integration, (c) fully integrated drivers on glass, followed by (d) a fully integrated “system on a flexible panel,” showing how high-performance thin-film transistors enable display drivers and other system components to be integrated on a flexible metal foil. [Schematic courtesy of Sharp Corp, Osaka, Japan.]

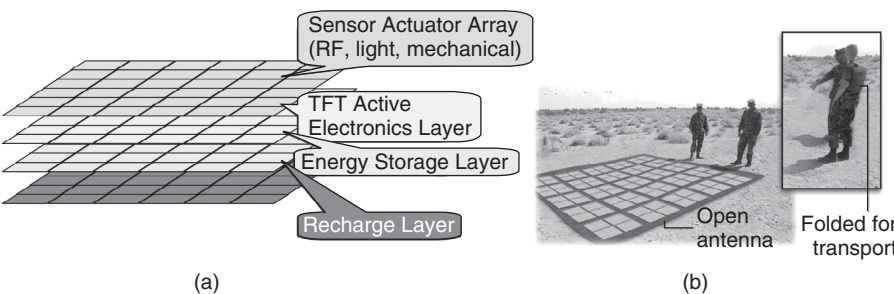


Figure 1.5. Schematic of a fully integrated macroelectronic system and an example of an application concept for macroelectronic systems. (a) Building blocks for a generic macrosystem. (b) Mockup of a large-area antenna array. [Figure courtesy of Sarnoff Corporation. Used with permission.]

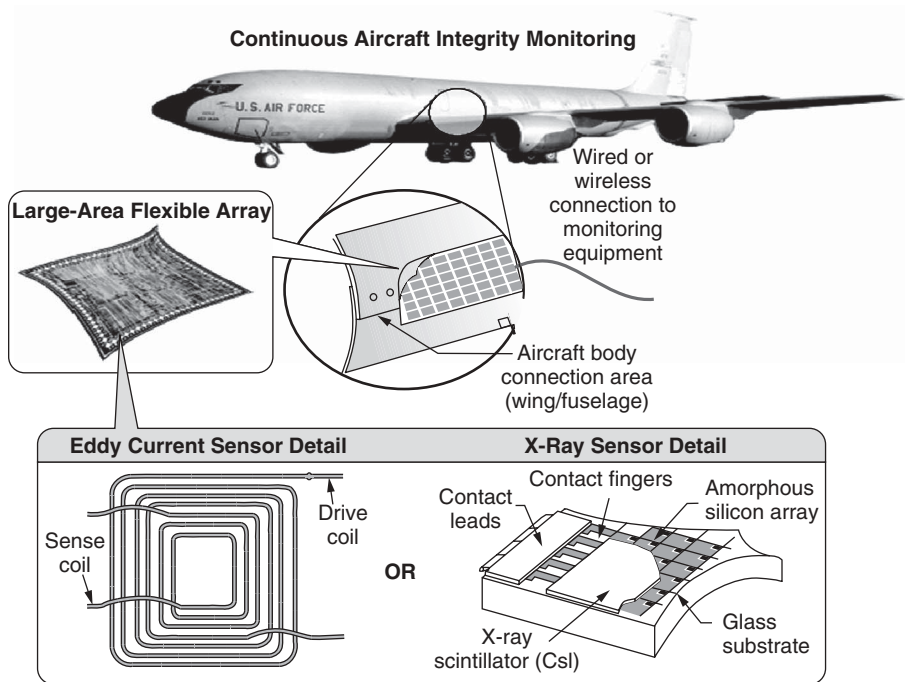


Figure 1.6. Application of large-area embedded flexible control electronics includes structural health monitoring of large objects such as airframes.

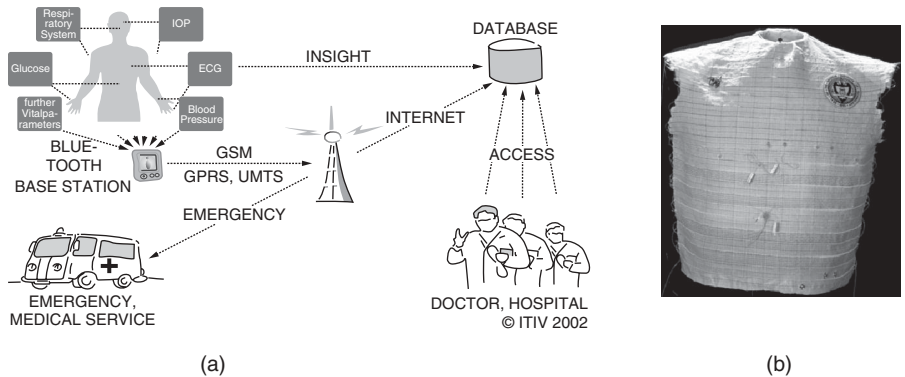


Figure 1.7. Large-area electronic fabrics and health monitoring systems for soldiers and personnel employed in high-risk field operations. (a) Operation of a personnel health monitoring system. (b) Example of a vest with integrated sensors for monitoring body temperature, respiration rate, and other bodily parameters.

not just a display, but also an entire wireless laptop tablet complete with camera, microphone, and solar cell for power. It is unclear when, or even if, such a vision will ever make technical (let alone economic) sense. Nevertheless, the point is that this is one example of a vision that is driving the creation of macroelectronics technology. Figure 1.5 shows yet another large-area concept. Here, the notion is a sensor system that comes integrated with control electronics, energy storage mechanism, and energy harvesting layer, all made via yet-to-be-determined manufacturing technology. Figure 1.6 takes this idea one step further and suggests how a conception suggested in Figure 1.5 might be implemented into an aircraft for structural health monitoring, active flight control and multifunctional applications such as load-bearing structural antennas. Finally, in Figure 1.7, the personal health status application involves a range of sensors, processors, and transmitters integrated within composite materials or mounted on/in human biomaterials (skin/tissues). This assembly is then able to sense and report faults to ensure proper drug usage, or to continuously sense, modify, and transmit physiological and cognitive status. The weight and material integration issues with conventional ICs make these applications impossible or unlikely with a purely microelectronics approach. The major challenge for macroelectronics technology is to enable applications beyond displays that involve large areas and applications that cannot be cost-effectively achieved through traditional packaged-chip fabrication followed by pick-and-place assembly. Nonetheless, these applications will still require sophisticated, high-functionality circuits. The large-scale applications envisioned give rise to the requirement for properties heretofore not associated with IC applications, including the thinness, ductility, and elasticity of electronic components, even during operation. Potentially, cofabrication of electronics and physical structures might be possible. This process would enable the electronics to be built directly onto or within the structure from which it controls, senses, or communicates. Ideally, the electronics would be synergistic with and inseparable from the system. A conceptual model might be the human nervous system. However, the opposite is true for traditional microelectronics, in which passive devices, packaged chips, boards, and boxes are each fabricated separately and only later integrated into the final structure. This difference in manufacturing approach creates major differences for the materials, electronic design, and fabrication methods for macroelectronics versus microelectronics.

1.2 IMPORTANCE OF SOLUTION PROCESSING

Researchers have many obstacles to overcome in the quest to make macroelectronics the “next big thing.” The keys to achieving the desired levels of functionality for a wide range of large-area electronic functions are advances in materials and processes and device structures that can get cost down to pennies (rather than dollars) per square centimeter. Tools and process methods

that provide these devices and their interconnections, at adequate levels of integration and in high yield on a wide range of substrates, must be developed. Some of the required advances in processing and tools will be adopted from the display and photovoltaic industry. However, to achieve the device/circuit performance for more demanding electronic functions, significant improvement in materials and device characteristics must be achieved.

To manufacture flexible integrated circuits, it is not the transistors themselves that are inflexible; it is the relatively thick, bulk wafer on which that the transistors are manufactured. Thinning the wafer to harvest just the upper active circuits is possible but also time consuming, difficult, and expensive. Therefore, in the macroelectronics thrust, the focus is on developing techniques for depositing semiconductors very inexpensively and, in most cases, over a large area on a variety of substrates (to include even plastics and fabrics). The result is a different transistor structure known as a thin-film transistor (TFT; see Section 1.3.1).² The ideal method for fabrication of TFTs for macroelectronics requires that the materials used to create the devices be directly deposited on a thin (and ideally, flexible) substrate. In contrast to microelectronics, with TFTs for macroelectronics, the feature size and level of performance are not the primary drivers. Rather, the processing cost, compatibility with diverse substrates, and attributes of the end item (area, weight, bendability, durability/ruggedness) represent the critical factors. These challenges generally require mild processing conditions not significantly different from the ambient (in contrast to the temperatures and chemicals associated with microelectronics fabrication). Processing under such conditions is much more conducive to a variety of electronic substrates and to the integration of diverse functionality, including computational devices, sensors, photovoltaics, and displays. Therefore, fabrication technologies that promise lowest possible cost while delivering at least adequate electrical performance are of great interest.

Because cost/square centimeter is such a major driver for macroelectronic applications, established methods for low-cost manufacture are of great interest. Solution processing for all manner of printed products has a long history and well-developed infrastructure that addresses multiple applications with a wide range of inexpensive materials and patterning methods. Therefore, solution processing has received significant attention, because the essential steps of macroelectronic TFT circuit fabrication can (in principle) all be accomplished using the ordinary, relatively cheap, and widely available technologies used to print ink.^{18–20} One method is a modification of ink-jet printing, and another adapts roll-to-roll processing, which is commonly used to print fabrics and newspapers (for a more detailed discussion, see Chapter 12). Unfortunately, to date, the problem with both of these approaches is the ability to produce transistors that can operate fast enough for potential applications of interest. Although adequate for displays, the TFTs produced easily with these printing methods are much too slow for many applications. Thus, macroelectronics research seeks to exploit this rich printing infrastructure, but with

incorporation of materials required to fabricate higher performance TFT-based electronics.

One means that has been pursued to achieve low-cost, multi-material processing is based on organic semiconductors, because of the well-established potential for compatibility with printing technology.^{21–24} However, to date, inorganic semiconductors have achieved the highest and most stable TFT performance.²⁵ Recent results have provided encouraging results based on solution deposition of inorganic materials rather than requiring the standard vacuum deposition methods. Because of the relatively mature theoretical understanding of inorganic semiconductor devices, and the difficulty of obtaining organic-based TFTs with adequate device characteristics, new ways to solution-deposit and fabricate inorganic semiconductors have received increasing attention, as will be explored in subsequent chapters.

Macroelectronics thus seeks to create a new fabrication methodology based on techniques that are currently alien to microelectronics processing. Ideally, roll-to-roll substrate handling will replace wafer batches, with material deposition via solution processing replacing vacuum evaporation, and material patterning by printing eliminating the need for etching. Given the diversity of materials, devices, and applications that may eventually encompass “large-area electronics technology,” it may well be that no “standard process” and “standard equipment” will ever exist for macroelectronics, as it does for mainstream CMOS IC manufacturing. However, Figure 1.8 provides some idea of

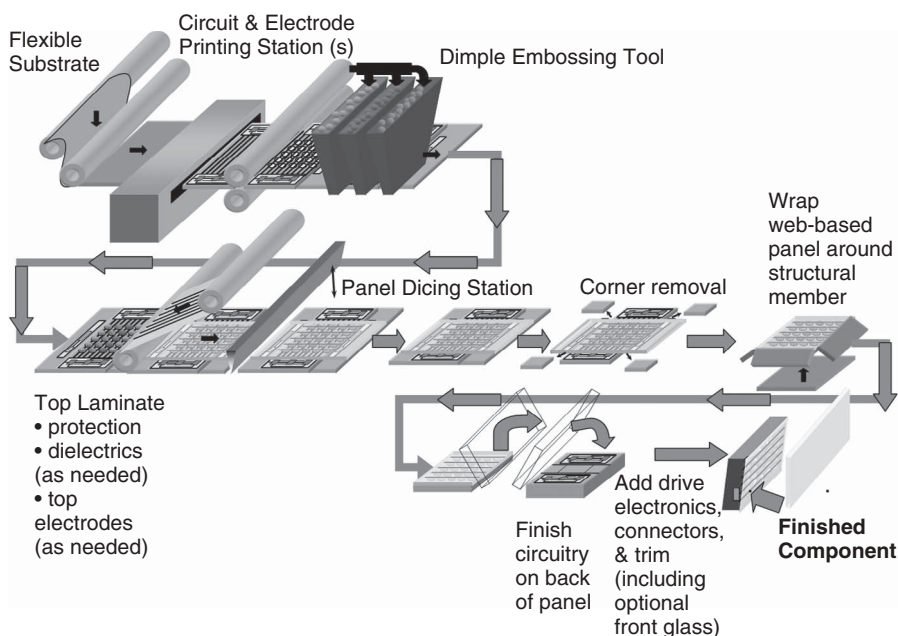


Figure 1.8. Conceptual roll-to-roll manufacturing process.