Research News

Materials and Fabrication Needs for Low-Cost Organic Transistor Circuits

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There has been tremendous progress in the area of organic electronic materials and devices recently. However, many challenges and problems remain to be addressed for practical applications of such materials and devices. This article seeks to summarize some of the important recent materials-related research on organic transistors and point out future needs in this area. Special emphasis is directed towards the stability and processability of the active materials.

1. Introduction

Organic transistor circuits have been proposed for applications such as low-end display driving circuits and low-cost memory devices for smart cards and price tags. The key building blocks for these circuits are organic thin-film field-effect transistors (FETs). A thin-film FET consists of materials ranging from conductors and semiconductors, to insulators.[1–8] A typical device structure is shown in Figure 1. Here, the gate electrode is used to control the current flow between the drain and source electrodes confined
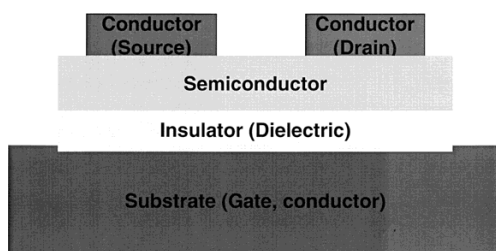

Fig. 1. A typical schematic structure of a thin-film FET. Materials ranging from conductor to semiconductor to insulator are required.

at the interface of the semiconductor and dielectric layer. A transistor is namely p-channel if the major charge carrier is positive, and conversely an n-channel when the major charge carrier is negative. A high-performance transistor should have high current output, fast frequency of operation, and high ratio of currents between the "on" and "off" states (on/off ratio). These parameters require that the semiconducting material has high field-effect mobility (the average charge carrier drift velocity per unit electric field) of at least 10^{-3} cm^2/V s for practical applications.

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A number of organic semiconductors have shown promising transistor performance. Mobilities and on/off ratios in the same range as for amorphous silicon (>0.1 cm^2/V s and >10^6, respectively) have been achieved with organic materials.[9–11] Large-scale integrated circuits based on organic transistors have been demonstrated.[12,13] However, many challenges and problems remain to be solved for practical applications. This article summarizes some of the important recent materials-related advances on organic transistors and future needs.

2. Air-Stable n-Channel Semiconductors

n-Channel semiconductors are important components of p–n junction diodes, bipolar transistors, and complementary circuits. The complementary circuit, which consists of both p- and n-channel transistors, is an ideal circuit configuration for organic semiconductors because it has low static power dissipation and the transistors are "on" only during switching.[14] There are several reasons why only a limited number of high-performance n-channel semiconductors have been discovered so far. First, most organic materials tend to transport holes better than electrons, thus there are less organic n-channel materials available and a great deal of research effort related to light-emitting diodes (LEDs) has been devoted to improving the electron-transporting materials. Second, the performance of n-channel semiconductors is easily degraded after exposure to air since oxygen can act as a trap to oxidize some negative charge carriers. Most of the existing n-channel materials are sensitive to air and moisture, or have relatively low field-effect mobilities. The highest electron field-effect mobility has been reported for fullerenes,[15] but these devices are easily degraded upon exposure to air. In addition, anhydrides and their imide derivatives exhibit n-channel semiconducting properties, but their mobilities remain relatively low.[16,17,31] Recently, we have modified metallophthalocyanines by adding strong electron-withdrawing groups such as −CN,

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−F, and −Cl to their outer rings.[18] In doing so, the lowest unoccupied molecular orbital (LUMO) levels of these molecules are significantly lowered when compared to metallophthalocyanines, and electron injection and transporting are thus made possible. Among them, the hexadeca-fluoro- and hexadecachloro-metallophthalocyanines were found to function as n-channel semiconductors and copper hexadecafluoro-phthalocyanine (structure shown in Fig. 2) showed the best field-effect mobility of ca. 0.03 cm^2/V s. The high mobilities of these compounds are attributed to highly ordered films upon vacuum deposition.[18] A large-scale complementary integrated circuit with 864 transistors has been fabricated using $F_{16}CuPc$ (Pc = phthalocyanine) as the n-channel transistor and α-sexithiophene as the p-channel transistor.[13] In addition, all of the above materials possess remarkable stability in air, and their transistors can be operated in both vacuum and air. These metallophthalocyanine derivatives are the only thin-film n-type materials found to achieve long-term stability in air with mobilities greater than 10^{-2} cm^2/V s (of course, it is desirable to have n-channel materials with higher mobilities in the range of 10^{-1} cm^2/V s).[31] We have also found that the device performance can be affected by atmosphere humidity. Suitable n-channel semiconductors that can resist these environmental effects are desired or, alternatively, a proper packaging method has to be implemented.

3. Solution-Processable Semiconductors

The key feature that makes organic semiconductors attractive for low-cost manufacturing is the possibility for them to be deposited from solution, enabling patterning by solution-based processes such as screen printing or ink-jet printing.[7,19–21] However, only a limited number of soluble p-channel organic semiconductors have been reported to show high performance,[10,22,23] and no n-channel semiconductor has had high enough solubility to be directly spun from solution and give high field-effect mobility. Examples of high-performance soluble p-channel semiconductors are oligomeric materials, such as dihexyl-α-tetrathiophene[24] and dihexyl-α-pentathiophene,[25] and regioregular poly(3-alkylthiophene) derivatives (structures shown in Fig. 2).[10,22,23] In order to form transistors with high mobility from solution, the materials have to be soluble and be able to form large-area uniform films, in which the semiconducting molecules are well ordered. The π-stacking between these molecules forms the conducting pathway for charge carriers to hop from one molecule to the other. However, with highly ordered materials it is usually difficult to form smooth uniform films due to their high crystallinity. For example, in the case of oligomeric semiconductors, special solvent, temperature, and surface treatments have to be applied to obtain high field-effect mobility over a large area.[25] In contrast, polymers can easily form uniform films, but it is more challenging to obtain high polymer ordering and their purification tends to be difficult. The polymer that circumvents the two above-mentioned concerns is regioregular poly(3-hexylthiophene).[10,22,23] High field-effect mobility and on/off ratio have been achieved with this polymer. Its only drawback is that it is easily doped by oxygen and the on/off ratio decreases quickly in air. To achieve better device lifetime, the development of high-mobility and highly stable solution-processable materials is important. Structural modifications have been carried out on regioregular poly(3-alkylthiophene)s (PATs), but have not yet resulted in improved performance.[23] Nevertheless, it is interesting to note that the ordering and crystallinity of regioregular PATs are highly sensitive to the nature of the sidechains. Despite regioregularity, the polymers may not be well-ordered, depending on the side groups.[23] The other important consideration, when designing new polymers and choosing fabrication conditions, is that the selected solvent needs to be environmentally friendly. Most of the conjugated polymers are more soluble in chlorinated solvents, such as chloroform and chlorobenzene, which are unacceptable for manufacturing. The best mobility reported for regioregular poly(3-hexylthiophene) was obtained with chloroform as the solvent.[22] However, we have also found that it is possible to obtain high mobility and on/off ratio using more environmentally friendly solvents such as xylenes and p-xylene.[26]
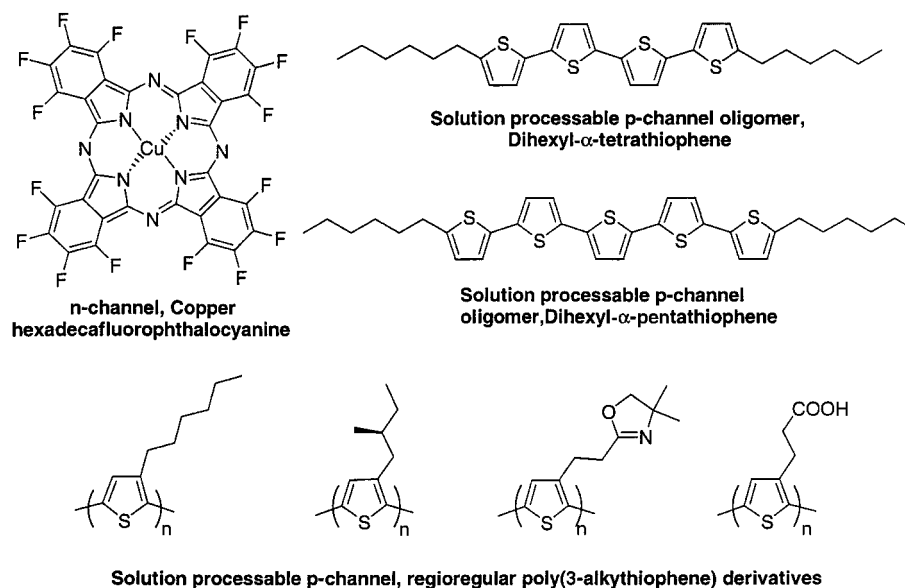

Fig. 2. Schematic structures of typical organic semiconductors.

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4. Dielectric Materials

There has not been much research on dielectric materials so far even though they are extremely crucial for reliable and high-performance organic electronic devices. The basic requirements for such dielectric materials are that they should have the ability to form thin, pinhole-free films with a high breakdown voltage and good long-term stability. In addition, it is desired that the dielectric material is compatible with organic semiconductors. Specifically, the dielectric films must have low surface trapping density, good surface smoothness, low impurity concentration and must not degrade the performance of ordered organic semiconducting films. Inorganic dielectric materials possess most of the desired features except that they usually have to be deposited under high vacuum or high temperature, which results in substantial cost and incompatibility with plastic substrates. However, they may be advantageous when high dielectric constant materials are desired. In general, organic dielectric materials have relatively low dielectric constants compared to inorganic materials. A high dielectric constant may become important when low device operating voltage is needed.[27] With the same device configuration, semiconducting material, and dielectric thickness, higher current output can be obtained with a higher dielectric constant material at the same applied voltage. Anodized Ta_2O_5 has recently been demonstrated to be a high-performance dielectric material for organic transistors with low operating voltages at around 2 to 5 V.[28] The related anodization process does not require high temperature and vacuum conditions, therefore it is potentially low cost and compatible with plastic substrates. For polymer dielectrics, a number of materials have been reported to give reasonable transistor performance. Examples are poly(methyl methacrylate), poly(vinylphenol), and polyimides. But most evaluations are based on discrete transistors and little is known of the long-term effects of various dielectric materials on device performance. When large-scale integration is needed, it will be critical that the dielectric film has uniform thickness, is pinhole-free over a large area, and is compatible with organic semiconductors. In addition, interfacial diffusion, mixing, and reaction may occur over time and change the characteristics of transistor devices. Such an effect has been observed with several dielectric polymers,[7] which makes proper selection of dielectric materials highly essential for the performance and lifetime of organic electronic devices.

5. Reel-to-Reel Processes for Manufacturing

Many great advantages of processable organic materials can only be realized when combined with compatible fabrication and patterning processes. Conventional photolithography is capable of generating very small feature sizes, but is still relatively expensive for low-end devices. Recently, various printing techniques and non-conventional patterning methods involving stamping or microcontact printing (μCP) and micromolding have shown promising results for organic optical and electronic devices.[7] Polymer LEDs have been ink-jet printed,[20,21] and simple plastic circuits are screen printed on flexible plastic substrates.[19] For organic transistor devices, it is likely that the feature size of the printed electrodes needs to be in the micrometer range in order to have reasonable operating speed and current output. While ink-jet and screen printing have already been widely used for other applications, they are only capable of producing relatively large feature sizes (above 25 μm for ink-jet and 75 μm for screen printing). Non-conventional μCP and micromolding have been actively explored for patterning feature sizes down to 1 μm.[29,30] Metals and conducting polymers have both been patterned to generate high-performance transistors and simple circuits. However, no commercial infrastructure exists for these non-conventional patterning methods even though a possible reel-to-reel fabrication scheme using μCP has been proposed.[30] Other unevaluated issues, such as large-area printing capability and stamp deformation, may limit their applications. A recent method that utilizes photolithography tools was reported.[12] This approach is based on photochemical conversions of polymers from non-conducting to conducting states, achieving a resolution as high as 2 μm. Similar approaches are likely to be important in the future, but they may also retain the problem of high costs associated with photolithography, and may be less flexible than other methods with respect to the materials that can be processed. Ultimately, manufacturable processes (as shown in Fig. 3) that allow reel-to-reel large-area fabrication at low costs are needed. In addition, additive processes will be more desirable since no additional solvents or etchants are needed.
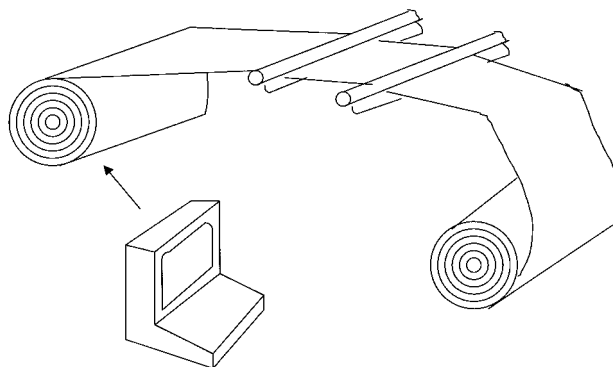

Fig. 3. Reel-to-reel printing processes for the fabrication of organic electronic devices are desired for low-cost applications.

6. Conclusions

In summary, organic materials hold great potential for realizing low-cost flexible electronic devices. The currently available materials have shown a high enough transistor

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performance to be seriously considered for certain applications. Many opportunities exist for new materials design, syntheses, and patterning. Future materials research should put more emphasis on improving the materials' stability and processability. Fundamental issues related to device degradation and interfacial interactions are becoming important for providing guidelines to material improvements. The development of a low-cost patterning process will be extremely critical to fully utilize the merits of all the wonderful new materials.

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