Polymers for flexible displays: From material selection to device applications

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Abstract

With digitalization, plenty of information is being exchanged through electronic media, and consumers are demanding high quality, convenient, and portable digital devices. Currently, flat panel displays, such as liquid crystal displays (LCDs) and plasma display panels (PDPs), satisfy them with regard to quality. Convenience and portability will be realized with flexible displays in the future. Polymers are very promising materials for flexible displays with many advantageous characteristics including transparency, light weight, flexibility, and robustness. They are also some of the least expensive materials and are suitable for mass production via roll-to-roll processes. In this review, we will discuss the kinds of polymers that are used, where and how polymer materials are used and the challenges to overcome in developing flexible displays.

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Keywords: Electro-optic material; Encapsulation; Flexible display; Flexible substrate; Transparent electrode

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1. Introduction

The topic of flexible displays has prompted many popular news stories. How do we define a flexible display? Flexible displays can be classified according to degree of flexibility: flat displays are made of plastic or another non-glass backplane, but only for the benefit of lightness or ruggedness; formed displays are bent once, such as a curved automobile dashboard, but do not flex further; flexible displays may be bent or flexed during use, but not over a range that includes folding or rolling; rollable displays are as flexible as fabric [1]. Recently, the literature on flexible displays has been expanding. It now includes a book on flexible flat panel displays written by Crawford [2] and a special edition of the Proceedings of the IEEE on flexible displays [3].

The prospects for flexible displays are promising, although the timing still depends on technical and manufacturing developments [4,5]. Electrophoretic displays such as electronic papers using plastic substrates, which have a relatively simple structure, are just beginning to be produced in quantities approaching high volume. Displays that are intended to flex or roll during use may reach the market in several years, pending further developments in backplane and fabrication processes. The near-term revenue in dynamic signage and mobile phones will lead to the development of larger and more sophisticated displays with flexibility and rollability. Fig. 1, which has been adapted from the data of the iSuppli Flexible Display Report, shows the market prospects for flexible displays from 2007 to 2013 [1].

Polymers are very promising materials for flexible displays with many advantages. They are transparent, light in weight, flexible, and robust. Polymers are a good alternative to the glass substrates that have been actively used for flat panel displays such as liquid crystal displays (LCDs) and plasma discharge panels (PDPs). Glass is so rigid that it is very difficult to use in a flexible display. Polymers have mechanical properties that vary from strong rigidity, such as in engineering plastics, to softness, such as in rubber or polyethylene films. They are some of the least expensive materials and are suitable for mass production via roll-to-roll (RTR)
processes. Therefore, polymers are being considered as the key materials for flexible displays in various application areas including transparent substrates, electrodes, active materials for organic light-emitting devices (OLEDs), LCDs and organic thin-film transistors (OTFTs), dielectric materials, and coating materials. All polymer-based flexible displays are being investigated.

### Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq&lt;sub&gt;3&lt;/sub&gt;</td>
<td>tris(8-hydroxyquinoline) aluminum</td>
</tr>
<tr>
<td>AMLCD</td>
<td>active-matrix liquid crystal display</td>
</tr>
<tr>
<td>a-Si</td>
<td>amorphous silicon</td>
</tr>
<tr>
<td>a-Si:H</td>
<td>hydrogenated amorphous silicon</td>
</tr>
<tr>
<td>AZO</td>
<td>aluminum-doped zinc oxide</td>
</tr>
<tr>
<td>BCB</td>
<td>benzocyclobutene</td>
</tr>
<tr>
<td>CNT</td>
<td>carbon nanotube</td>
</tr>
<tr>
<td>COC</td>
<td>cyclic olefin copolymer</td>
</tr>
<tr>
<td>CRT</td>
<td>cathode ray tube</td>
</tr>
<tr>
<td>CTE</td>
<td>coefficient of thermal expansion</td>
</tr>
<tr>
<td>DP-PPV</td>
<td>poly(2,3-diphenyl-1,4-phenylene)</td>
</tr>
<tr>
<td>ELA</td>
<td>excimer laser annealing</td>
</tr>
<tr>
<td>EPD</td>
<td>electrophoretic display</td>
</tr>
<tr>
<td>ECR-PECVD</td>
<td>electron cyclotron resonance plasma-enhanced chemical vapor deposition</td>
</tr>
<tr>
<td>e-paper</td>
<td>electronic paper</td>
</tr>
<tr>
<td>F-CuPC</td>
<td>hexadecafluorocopper phthalocyanine</td>
</tr>
<tr>
<td>FIrpic</td>
<td>iridium(III) bis[4,6-difluorophenyl]pyridinato-N,C&lt;sup&gt;2&lt;/sup&gt;0] picolinate</td>
</tr>
<tr>
<td>FOLED</td>
<td>flexible organic light-emitting device</td>
</tr>
<tr>
<td>HMDS</td>
<td>1,1,1,3,3,3-hexamethyl-disilazane</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>LC</td>
<td>liquid crystal</td>
</tr>
<tr>
<td>LCD</td>
<td>liquid crystal display</td>
</tr>
<tr>
<td>LEP</td>
<td>light-emitting polymer</td>
</tr>
<tr>
<td>LITI</td>
<td>laser-induced thermal imaging</td>
</tr>
<tr>
<td>LTHC</td>
<td>light-to-heat conversion</td>
</tr>
<tr>
<td>LTPS</td>
<td>low-temperature poly-silicon</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>nc-Si</td>
<td>nanocrystalline silicon</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl pyrolidone</td>
</tr>
<tr>
<td>NONON</td>
<td>silicon nitride–silicon oxide–silicon nitride–silicon oxide–silicon nitride</td>
</tr>
<tr>
<td>NPB</td>
<td>N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine</td>
</tr>
<tr>
<td>OLED</td>
<td>organic light-emitting device</td>
</tr>
<tr>
<td>OTFT</td>
<td>organic thin-film transistor</td>
</tr>
<tr>
<td>OTR</td>
<td>oxygen transmission rate</td>
</tr>
<tr>
<td>PAR</td>
<td>polycarbonate</td>
</tr>
<tr>
<td>PC</td>
<td>polycarbonate</td>
</tr>
<tr>
<td>SCO</td>
<td>polycyclic olefin</td>
</tr>
<tr>
<td>PDMS</td>
<td>poly(dimethylsiloxane)</td>
</tr>
<tr>
<td>PDLC</td>
<td>polymer-dispersed liquid crystal</td>
</tr>
<tr>
<td>PDP</td>
<td>plasma discharge panel</td>
</tr>
<tr>
<td>PECVD</td>
<td>plasma-enhanced chemical vapor deposition</td>
</tr>
<tr>
<td>PEDOT/PSS</td>
<td>poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PEEK</td>
<td>polyetheretherketone</td>
</tr>
<tr>
<td>PEN</td>
<td>polyethylene naphthalate</td>
</tr>
<tr>
<td>PES</td>
<td>polyethersulphone</td>
</tr>
<tr>
<td>PET</td>
<td>polyethylene terephthalate</td>
</tr>
<tr>
<td>PF</td>
<td>polyfluorene</td>
</tr>
<tr>
<td>PI</td>
<td>polyimide</td>
</tr>
<tr>
<td>PLED</td>
<td>polymer light-emitting diode</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PMSSQ</td>
<td>poly(methyl silsesquioxane)</td>
</tr>
<tr>
<td>PNB</td>
<td>polybromobenzene</td>
</tr>
<tr>
<td>PPV</td>
<td>poly(p-phenylenevinylene)</td>
</tr>
<tr>
<td>PVA</td>
<td>poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PVP</td>
<td>poly(4-vinyl phenol)</td>
</tr>
<tr>
<td>QR-LPD</td>
<td>quick response liquid powder display</td>
</tr>
<tr>
<td>RF</td>
<td>radio frequency</td>
</tr>
<tr>
<td>R,G,B</td>
<td>red, green, blue</td>
</tr>
<tr>
<td>SAM</td>
<td>self-assembled monolayer</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SMOLED</td>
<td>small molecule organic light-emitting device</td>
</tr>
<tr>
<td>SLS</td>
<td>sequential lateral solidification</td>
</tr>
<tr>
<td>SUFTLA</td>
<td>surface-free technology by layer annealing</td>
</tr>
<tr>
<td>SWNT</td>
<td>single-walled carbon nanotube</td>
</tr>
<tr>
<td>TBAHA</td>
<td>tris(4-bromophenyl)aluminum hexachloroantimonate</td>
</tr>
<tr>
<td>TCO</td>
<td>transparent conducting oxide</td>
</tr>
<tr>
<td>TDATA</td>
<td>4,4′,4″-tris(N,N′-diphenylamino) triphenylamine</td>
</tr>
<tr>
<td>TFT</td>
<td>thin-film transistor</td>
</tr>
<tr>
<td>TF-TCNQ</td>
<td>tetrafluoro-tetra(cyano) quinodimethane</td>
</tr>
<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>T&lt;sub&gt;m&lt;/sub&gt;</td>
<td>melting temperature</td>
</tr>
<tr>
<td>TMT</td>
<td>TCO–metal–TCO</td>
</tr>
<tr>
<td>TPD</td>
<td>1,4-bis(phenyl-m-tolylamino) biphenyl</td>
</tr>
<tr>
<td>TS-SLS</td>
<td>two-shot sequential lateral solidification</td>
</tr>
<tr>
<td>UHB</td>
<td>ultra-high barrier</td>
</tr>
<tr>
<td>VHF</td>
<td>very high frequency</td>
</tr>
<tr>
<td>WVTR</td>
<td>water vapor transmission rate</td>
</tr>
</tbody>
</table>
In this review, we will discuss what, where, and how polymer materials are used and the challenges to overcome in the flexible display field.

2. Polymer substrates

In flexible displays, the flexibility depends on the substrate. Three kinds of substrates are considered to be flexible: thin glass, metal foil, and plastic. Thin glass films are bendable and have the highly desirable qualities of glass [6]. However, they are brittle. This property limits their application as flexible substrates. Metal foils can also handle high-process temperatures and provide a good barrier to moisture and oxygen, without the problems of breakability [7]. However, metal only works for non-transmissive displays and cannot handle multiple bends. In addition, it is an expensive material to use in large displays. Therefore, metal foils are good candidates for small and early applications of flexible displays. Plastic is the key material of choice, as it allows reasonable tradeoffs in mechanical, optical, and chemical performance. It is an inexpensive and useful material for in-line production via RTR processes. Multilayer-engineered substrates will be required for most practical applications.

2.1. Potential polymer candidates for flexible substrates

There are several polymers that are candidates for flexible substrates as shown in Fig. 2, which lists substrates in terms of glass transition temperature ($T_g$) [2,8]. These polymers are divided into three types, including crystalline, amorphous, and solution-castable amorphous.

Thermoplastic semi-crystalline polymers available for flexible displays include polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and polyetheretherketone (PEEK) [9,10]. PEEK, whose $T_g$ and $T_m$ are ~140 and 340°C, respectively, is known be at the upper limit of semi-crystalline polymers that can be melt-processed because polymers with a $T_g$ of higher than 140°C will be degraded significantly during a melt process. Heat-stabilized semi-crystalline polymers provide good dimensional stability above their $T_g$, which expands their upper operating temperature. The second group, amorphous polymers, includes polycarbonate (PC) and polyethersulphone (PES) [11,12]. These are non-crystalline thermoplastics that can be melt-extruded or solvent casted. The last group is the amorphous polymers that cannot be melt-processed, such as modified PC, polyarylate (PAR), polycyclic olefin (PCO) or polynorbonene (PNB), and polyimide (PI) [13–15]. Fabric materials [16], ultra-thin polymer films [17], and glass-reinforced plastic [18] have also been used as substrates. Fig. 3 summarizes the $T_g$’s of the candidate polymers for flexible substrates.

Table 1 shows a comparison of the characteristics of polymer materials suitable for flexible substrates. Polyesters such as PET and PEN have advantages with regard to clarity, coefficient of thermal expansion (CTE), chemical resistance, moisture absorption, and price while their upper operating temperature and surface roughness are not so good.
PES has good clarity and a high upper operating temperature but has poor solvent resistance and is expensive. On the other hand, PI has high thermal stability and good mechanical and chemical properties but is orange-colored and expensive. Recently, however, many technical advances have been aimed at producing colorless PI by incorporating fluorine, sulfone, or non-aromatic groups [19–25].

2.2. Property requirements that apply to flexible substrates

Currently, OLEDs, which require the most stringent conditions of the flexible display devices, are based on glass substrates because they are perfectly satisfactory for flat panel applications. To replace glass, a plastic substrate needs to mimic the properties of glass, including its clarity, dimensional
stability, thermal stability, barrier properties, solvent resistance, low CTE, and smooth surface, as well as possess good optical properties [2,26]. The minimum property requirements of a polymer substrate to be applied in flexible displays are shown in Table 2, which summarizes various reported literature values up to the early 2007. Substrate materials affect the following processes: barrier coating, electrode deposition, patterning, and thin-film transistor (TFT) fabrication. Therefore, a circumspect approach to selecting the proper substrate materials is required.

2.2.1. Clarity
Clarity is the most important property for bottom emissive displays, and a total light transmission of >85% over 400–800 nm coupled with a haze of less than 0.7% are typical of what is required [2]. Table 3 shows the properties of commercial base films [18]. PC and cyclic olefin copolymers (COC) have a high optical transparency. Common PIs are not generally good enough for transparent devices, but transparent flexible PI substrates whose average optical transmission is about 86% in the visible light range at 250 μm thickness have been reported. This fluorine-containing aromatic PI is known to reduce intra- or intermolecular charge transfer complex formation and to possess colorless transparency [19].

2.2.2. Thermal stability
Thermal stability is another important issue for polymer substrates. Polymer substrates are
exposed to high temperatures during manufacturing processes such as barrier coating [27], electrode deposition [28], patterning [29], and silicon-based TFT fabrication [13,30]. In particular, TFTs are very sensitive to dimensional changes due to thermal or mechanical stress [31].

There are two factors that have to be considered when selecting polymer materials with the proper thermal stability: CTE and \( T_g \), where the polymer chains start to move to relax the stress that is stored during the processes. In general, inorganic or metal layers used for barrier or electrode layers have much lower CTEs than polymer substrates, and the dimensions of the polymer change significantly at \( T_g \) [32]. Polymers with high \( T_g \)s such as PI and PES are better choices in this regard. For example, Lim et al. used aliphatic cyclic PI [20] and fluorinated PI [19] as flexible substrates. A low CTE is also advantageous for making dimensionally stable designs for devices [15]. A mismatch of CTE between layers gives rise to strain and cracking under thermal cycling during device fabrication. High-temperature processes, such as the low-temperature poly-silicon (LTPS) process, require plastic substrates that can withstand very high temperatures with CTEs of around 10–20 ppm/K or less to enable film deposition and device annealing at temperatures of up to 350 °C.

<table>
<thead>
<tr>
<th>Properties</th>
<th>PET</th>
<th>PEN</th>
<th>PC</th>
<th>COC</th>
<th>PES</th>
<th>PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (mm)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Total light transmittance (%)</td>
<td>90.4</td>
<td>87.0</td>
<td>92.0</td>
<td>94.5</td>
<td>89.0</td>
<td>30–60</td>
</tr>
<tr>
<td>Retardation (nm)</td>
<td>Large</td>
<td>Large</td>
<td>20</td>
<td>7</td>
<td>&lt;10</td>
<td>Large</td>
</tr>
<tr>
<td>Reflective index</td>
<td>1.66</td>
<td>1.75</td>
<td>1.56</td>
<td>1.51</td>
<td>1.6</td>
<td>–</td>
</tr>
<tr>
<td>Glass transition temperature (°C)</td>
<td>80</td>
<td>150</td>
<td>145</td>
<td>164</td>
<td>223</td>
<td>300&lt;</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (ppm/°C)</td>
<td>33</td>
<td>20</td>
<td>75</td>
<td>70</td>
<td>54</td>
<td>8–20</td>
</tr>
<tr>
<td>Water absorption ratio (%)</td>
<td>0.5</td>
<td>0.4</td>
<td>0.2</td>
<td>&lt;0.2</td>
<td>1.4</td>
<td>80</td>
</tr>
<tr>
<td>( H_2O ) barrier (g/m²/day)</td>
<td>9</td>
<td>2</td>
<td>50</td>
<td>–</td>
<td>80</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 4. Thermal mechanical analysis of PET and heat-stabilized PEN film [33]. Reproduced from MacDonald, Rollins, Eveson, Rustin, and Handa by permission of Society for Information Display, California, USA.

**Table 3**

Properties of base film for polymer substrates (reproduced from Ito, Oka, Goto, and Umeda by permission of Japanese Journal of Applied Physics, Tokyo, Japan)
Polyesters such as PET [33] and PEN [34] have actively been researched as flexible substrates, although their $T_g$s of 78 and 120°C, respectively, are too low to apply to OLED. MacDonald et al. [35] reported heat stabilization processes to impart the thermal and dimensional stability necessary to support OLED manufacture. Fig. 4 gives a thermal mechanical analysis of 125 μm PEN and heat-stabilized PEN films. Heat-stabilized films exhibit minimal shrinkage, of the order of <0.1% and typically <0.05%, when exposed to temperatures of up to 180°C for 5 min. In addition, once heat stabilized, the $T_g$ effects are essentially negated and the PEN film remains a dimensionally reproducible substrate up to 200°C. This is within the performance requirements of a flexible substrate for an OLED display.

Ito et al. developed a new idea to employ flexible fibrous glass-reinforced plastic (FRP) substrates for flexible displays to offer a low CTE of 14 ppm/°C and a high transparency of about 89% at 400 nm [18]. New polymer substrates with a high thermal stability, named OPS® [36] and AryLite® [37], have also been reported.

2.2.3. Surface properties

Surface qualities such as roughness and cleanliness are essential to ensure the integrity of subsequent layers including barrier and conductive layers. Semi-crystalline polymer films do not possess good surface properties compared to amorphous polymer films. Surface defects that remain in the substrates are detrimental to the performance of the active layer of OLEDs, whose thickness is around 100 nm, while picks greater than 50 nm in height are observed on common optical grade PEN films. They will create defects like pinholes on the thin films of barriers and electrodes, forming dark spots in OLEDs [38]. The defects will also lead to cracks when displays are bent. To provide a defect-free surface, scratch resistant or planarizing layers are coated to smooth over all the underlying substrate surface defects [39]. The coated film, called a surface engineered film, ensures good integrity for subsequent barrier layers and conductive coatings.

2.2.4. Chemical resistance

Polymer substrates have to be exposed to a wide range of solvents and chemicals as well as moisture during manufacturing processes, including cleaning, coating, and patterning processes. In general, semi-crystalline polymers such as PET and PEN have strong resistance to solvents, while amorphous polymers have poor solvent resistance. A typical list of the materials that the substrate must be compatible with includes methanol, isopropanol, acetone, tetrahydrofuran, n-methylpyrrolidone, ethyl acetate, sulfuric acid, glacial acetic acid, hydrogen peroxide, and sodium hydroxide. Coated polymer substrates with a variety of organic or inorganic layers or a hard coating layer are used to prevent the invasion of solvents and moisture [2].

2.2.5. Mechanical properties

For the RTR process as well as for display performance, mechanical properties have to be carefully considered [40]. Flexible OLEDs (FOLEDs), which demand stringent requirements among the display technologies, usually contain a polymer substrate, organic–inorganic multi-barrier-layer, brittle transparent inorganic anode, light-emitting layer, TFT layer, metal cathode, and encapsulating layers as shown in Fig. 5 [41]. When the devices are bent, the mechanical discrepancy at the interface between the organic and inorganic materials generates mechanical failure in devices. For those devices inorganic thin films may be the source of the failure due to their brittle properties [42]. In this sense, all-organic-based devices are the best choice for rollable displays. However, certain devices such as FOLEDs require inorganic films, and it is important to understand and improve the mechanical limits of these materials [26].

The failure of devices depends on the arrangement, thickness, and properties of all the layers. Adhesion at the interfaces between the different layers under thermal cycling and environmental testing, wetting characteristics, and the ability to withstand flex testing are critical to determining their robustness in use [35]. Flexible displays have
the advantage of mass production through a RTR process. Therefore, it is essential to understand the mechanical properties required of flexible substrates.

3. Barrier coatings

Inorganic transparent oxide films (e.g. silicon and aluminum oxide) on polymer films have been widely used as gas barrier materials for food and medical packaging. They provide at best only two to three orders of magnitude improvement over the oxygen transmission rates (OTR) of polymer substrates, whether deposited by plasma-enhanced chemical vapor deposition (PECVD), sputtering, or evaporation [42].

However, electronic devices, especially OLEDs, demand more stringent barrier confinement. For an OLED lifetime of $>10,000$ h, the requirements include water vapor transmission rates (WVTR) of $10^{-6}$ g/m²/day and OTR of $10^{-5}$ mL/m²/day [26,43]. Fig. 6 shows the relative barrier properties and requirements for electro-optic devices.

3.1. Mechanisms of device failure

Flexible displays, especially OLEDs, are extremely sensitive to water vapor and oxygen, which bring about their degradation. There have been many mechanisms proposed for the degradation of OLEDs including cathode oxidation, detachment of the organic layer from the anode, diffusion of the emitting layer material into the hole transport layer, detachment of the organic layer from the cathode, electrical shorts, electrochemical reactions at the electrodes, oxygen-activated photochemical damage, and oxidation of polymers by oxygen originating from ITO.

Dark spots resulting from exposure to ambient conditions were found to be due to cathode delamination by Liew et al. [44]. When the dark spots on the cathode were peeled off and the cathode was newly deposited, the OLEDs gave uniform emission, indicating that the origin of the dark spots was cathode delamination. They suggested that the nucleation of the dark spots takes place at the organic/cathode interface during the deposition of the cathode.

Nüesch et al. investigated the influence of oxygen and water [45]. The electrochemical reduction of water at the cathode/organic interface leads to hydrogen evolution, creating bubbles below the cathode surface. Dark spots grown in a pure oxygen atmosphere are different from those grown in a water atmosphere, showing perfectly circular behavior and obeying linear growth kinetics for devices.

Kim et al. [46] looked at the black spots in an electroluminescent polyfluorene system with poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT/PSS) on ITO as the anode and Ca/Al as the cathode. The non-emissive disks surrounding the pinhole defects are characterized by a localized electrochemical reaction with reduction of the normal doped PEDOT/PSS to the dedoped material and oxidation of the active metal.

Wang et al. used micrometer-sized silica particles to create uniformly sized pinholes on the protective cover so that oxygen and moisture would give rise to artificial dark spots [47]. They monitored in situ the linear growth of the dark spots with respect to particle diameter as well as time and suggested that dust contamination may be the major cause of dark spot formation, showing the distribution of the dark spots is Gaussian.

Chua et al. showed that, due to the roughening of the polymer/electrode interface caused by metal migration, the close proximity of metal protrusions leads to an increase in local current that degrades the polymer [48]. Subsequent electrochemical and photochemical reactions result in the formation of
volatile species and a large concentration of carbonyl groups that quench luminescence from the polymer.

The degradation problem can be dealt with by sealing the devices in an inert atmosphere. Therefore, encapsulation of the devices and isolation of the active materials from the atmosphere are very important to prolong the lifetime of flexible devices.

3.2. Theories of gas permeation

Inorganic thin films without defects possess good barrier properties applicable to OLED devices. For example, thin glass foils of around 50 µm thickness perfectly satisfy this condition but they are too brittle to apply to flexible displays. Currently, the most effective way to block gas intrusion while retaining reliable mechanical properties is to use multilayer gas barrier films with an alternating organic and inorganic thin-film structure [39]. However, there exist several challenges to understanding the mechanisms in multilayer, thin-film barrier coatings on polymeric substrates [49]. First, direct imaging and characterization of the sizes and spatial density of defects that are 100 nm in diameter are difficult. Second, it is impractical to measure material properties such as effective diffusivity and solubility for each layer in a multilayer system in situ. Third, a simple analysis of single oxide layers deposited on PET may not accurately represent the individual layers existing within a multilayer stack.

Roberts et al. [50] proposed a model for gas permeation where gas and water vapor transport through gas barrier films is comprised of contributions from three components: un-hindered transport through ‘macro-defects’ (>1 nm) in the oxide layer, hindered transport through ‘nano-defects’ (0.3–1.0 nm), and hindered transport through the amorphous lattice of the oxide (interstice <0.3 nm). The presence of nano-defects indicates that the oxide layer is more similar to a nano-porous solid such as zeolite than silica glass with respect to permeation properties as it demonstrates greater permeability and lower activation energy of permeation than the values expected for polymers coated with glass.

Peukert et al. reported the influence of defects and morphology on barrier properties for the case of vacuum web coating of inorganic layers on polymeric films [51]. Simulations performed via a numerical model revealed a complex interaction mechanism of film thickness, defect area, and defect spacing affecting the permeability. They showed that the critical thickness that limits the permeability decreases by increasing the substrate film thickness. When analyzing defect structures with the same total defect area, the total transmission rate of small defects occurring with high frequency exceeds that for large defects with low frequency, indicating the importance of evaluating small defects.

Graff et al. [49] suggested a mechanism of vapor permeation through multilayer barrier films.

![Graph](image_url)  
Fig. 7. Calculated lag-time and steady-state flux for defect spacings of 100 and 1000 µm [49]. Reproduced from Graff, Williford, and Burrows by permission of American Institute of Physics, Maryland, USA.
They used both transient and steady-state vapor permeation measurements combined with classical Fickian diffusion models to determine the mechanism of vapor permeation through multi-barrier structures. They showed that the results obtained are limited not by equilibrium diffusion but by lag-time effects caused by the extremely long effective path length for the diffusing gas, as shown in Fig. 7. It takes a long time to reach a steady state and, once the lag time is exceeded, the water vapor flux will remain at a steady-state value that is substantially higher, $10^{-3}$–$10^{-4}$ g/m$^2$/day, than the WVTR calculated during the transient period. There are several ways to lower the diffusivity and solubility of the polymer inter-layers to improve barrier performance such as inducing hydrophobic moieties or organic/inorganic copolymers, physical modifications through ion bombardment or cross-linking, or chemical modification through reactive etch or plasma surface treatment. However, the range of improvement may be small relative to improvements in the inorganic layer since the effective diffusivity of the inorganic layer is at least four orders of magnitude lower than that of the polymer inter-layers.

Henry et al. proposed a model for the mechanism of water vapor permeation through PET/AlO$_x$N$_y$ gas barrier films [52], identifying that water vapor permeates predominantly through tortuous, nanoscale permeation pathways in the AlO$_x$N$_y$ structure. The nature of this permeation process is the result of the strong chemical interaction of the water molecules with the AlO$_x$N$_y$ pore walls, possibly at N-rich sites. The key requirements to give an ultra barrier condition for optoelectronic devices are to increase the density of the coatings as much as possible to reduce the size and number density of tortuous pathways while maintaining an optimum Al/N ratio.

### 3.3. Barrier coatings on polymer substrates

There have been three research directions in the field of transparent barrier coatings for flexible substrates. The first is focused on the kinds of inorganic materials that will be used. They include silicon oxide [53–56], silicon nitride [57,58], silicone oxynitride [59], aluminum oxide [49], and mixed oxide [60–62]. A perfect layer of bulk oxides, such as SiO$_2$ which makes up glass substrates, of only a few nanometers thickness can reduce the diffusion of water and oxygen to acceptable levels.

The second direction is the structure and the number of barrier layers, which are often called dyads, that are alternatively layered with organic and inorganic materials. A typical single barrier layer provides only two to three orders of magnitude improvement in the barrier properties compared to a bare polymer substrate [39]. To satisfy the requirements of OLEDs, polymer substrates must be coated with multilayer organic–inorganic thin films.

The third is the coating method of thin films. Generally, polymer materials that are used as flexible substrates require low-temperature processes, where the quality of the inorganic films is generally not good compared with high-temperature processes. There has been much research dedicated to finding a way to obtain high-quality films at low temperatures by developing new deposition technologies and improving the deposition processes, including sputter deposition [63], electrobeam deposition [64], and PECVD [65–67]. All these deposition technologies are also available for in-line production through a RTR process, known as web coating [40].

Vitex System developed “Flexible Glass,” which is a commercially available, PEN-based substrate with the company’s Barix barrier that utilizes defect-decoupling layers of vacuum deposited polyacrylate between multiple layers of gas barrier materials such as Al$_2$O$_3$ [39]. This substrate is sufficiently impermeable to moisture and oxygen for application to OLEDs with a low WVTR below $5 \times 10^{-5}$ g/m$^2$/day.

General Electric developed a transparent plastic substrate that provides the high hermeticity that is expected to be required for many organic electronic devices [11]. A PC film with high-temperature capability and a novel single-graded layer ultrahigh barrier (UHB) coating can effectively stop defects from propagating through the coating thickness. The graded UHB coating with a thickness of less than 1 μm can significantly reduce the effective edge diffusion of water through the organic portion of the barrier coating, yielding a low WVTR of $5 \times 10^{-6}$–$5 \times 10^{-5}$ g/m$^2$/day.

For silicon oxide barrier layers, Erlat et al. [68] demonstrated that several PECVD deposition conditions of SiO$_x$, including deposition time, power, pressure, and gas flow rate, can significantly affect the barrier performance. Sufficient time is required for plasma stabilization and the deposition of uniform SiO$_x$ coatings. Coating properties such as
thickness and density, as well as composite properties, are improved with increasing deposition power due to the enhanced excitation and dissociation of the siloxane and O₂ molecules in the plasma. An increase in the substrate temperature improves the mobility of the reactive species and expedites cross-linking of the SiO₂ network, reducing the propensity for porous defects. The system pressure must be sufficiently low and the flow rate of siloxane should be sufficiently high. On the other hand, Wuu et al. [53] increased the deposition temperature from 80 to 170 °C. As the substrate temperature increased, the deposition rate, adhesion, and roughness values were found to increase while the WVTR decreased to a value of nearly 0.3 g/m²/day at 150 °C. Under optimum conditions, the WVTR for PES can be reduced to a level of 0.1 g/m²/day with a double-sided barrier coating of 100 nm on each side at 150 °C.

In the case of silicon nitride layers, Wuu et al. [67] reported SiNx barrier coatings on flexible PES substrates by PECVD for oxygen and water resistant applications. The NH₃/SiH₄ flow ratio has played an important role in SiNx film characteristics, such as bond configuration, transmittance, refractive index, deposition rate, adhesion, WVTR, and OTR. The durability of thin barrier coatings on polymer substrates relies on their coating thickness, and parylene/SiNx/PC resulted in an improved permeation resistance of the coating as well as an improved resistance to crack formation [57]. The WVTR and OTR of the optimized SiNx and parylene multilayers composed of parylene-(600 nm)/SiNₓ(100 nm)/parylene(600 nm)/SiNₓ(100 nm) on the PC substrate can be maintained at levels near 0.01 g/m²/day and 0.1 mL/m²/day, respectively, after 3000-times cyclic bending. The effects of plasma pretreatment for SiNx barrier coatings on Ar, N₂, and O₂ plasma-treated PC substrates were also reported [58]. After Ar plasma treatment for 60 s, the WVTR and OTR of a 50-nm-thick SiNx barrier coating on PC substrate after bending for 6000 times decreased to values near 0.01 g/m²/day and 0.1 mL/m²/day, respectively.

On the other hand, Iwamori et al. [59] developed a new transparent gas barrier material based on silicon oxynitride (SiON) via reactive sputtering in nitrogen plasma. SiOₓNᵧ films have a fine and amorphous structure without pinholes or cracks, increasing the density and showing lower OTR than that of the SiO₂ films. Baik et al. studied the water barrier properties of composite films consisting of silicon oxide and tin oxide, deposited by thermal evaporation on PC substrates [60]. Water vapor permeation through the composite films is significantly affected by the chemical interaction of water vapor with the composite oxide films and the microstructure of the composite oxide films. As the tin oxide is added to the silicon oxide, the polarizability of the composite oxide films increases and the composite films have a more densely packed microstructure with decreasing grain size. Kim et al. [61,62] investigated a variety of inorganic materials and inorganic composites as barrier materials on polymer substrates using the electron beam evaporation system. They showed that a MgO thin film has a lower WVTR value than any other inorganic thin film and that the WVTR of the inorganic film can be dramatically minimized by adopting the inorganic composite.

Weaver et al. [69] reported long-lived FOLEDs fabricated on plastic substrates whose composite barrier consists of alternating layers of polyacrylate films and an inorganic oxide. The permeation rate of water vapor through a flexible substrate was reduced to less than 2 × 10⁻⁶ g/m²/day and resulted in a half-life of 3800 h from an initial luminance of 425 cd/m².

3.4. Permeation rate measurements

Devices such as OLEDs have undergone significant development, but there are no standards for the measurement of barrier properties. Highly sensitive permeation measurements are crucial for the characterization and development of polymeric substrates for flexible display applications, especially OLEDs, which are very sensitive to water and oxygen. The current specifications for the permeation rates of OLED packaging are on the order of 10⁻⁵ mL/m²/day at standard temperature and pressure for oxygen and 10⁻⁶ g/m²/day for water vapor [43]. However, there is no method available commercially for the measurement of ultralow moisture permeation for OLED applications. Therefore, the development of a moisture permeation measurement system will be essential for investigating permeation mechanisms and understanding device lifetime and degradation phenomena. The commercial equipment available from MOCON is limited to a sensitivity of 5 × 10⁻⁴ g/m²/day under varying temperature conditions [70].

Nisato et al. [71] developed a method based on detecting the optical degradation of calcium to
measure the permeation rate of OLEDs. This calcium test method can effectively increase the speed of research and development on thin-film encapsulants suitable for OLED devices by providing quantitative results and sample configurations inaccessible to commercial equipment, which is now limited to \(5 \times 10^{-3}\) mL/m\(^2\)/day for \(\text{O}_2\) and \(5 \times 10^{-3}\) g/m\(^2\)/day for \(\text{H}_2\text{O}\) for 4-in diameter samples of coated plastic. Effective water vapor transmission rates down to \(10^{-6}\) g/m\(^2\)/day were detected. Paetzold et al. [72] proposed the idea of measuring the amount of oxidative degradation in a thin Ca sensor by in situ resistance measurements. The resulting baseline contribution to the WVTR of thin Ca sensor by in situ resistance measurements.

Among the TCOs, ITO has been used most widely as a transparent electrode material. ITO films show high optical transmittance of >90% in the visible light region and a low electrical resistivity \((2 \times 10^{-4}\,\Omega\,\text{cm})\) when deposited on glass substrates under optimized conditions, which include high substrate temperatures of 250–300°C or a post-annealing process. Generally, low-temperature deposition results in high electrical resistance and poor optical transparency.

To overcome these problems, Kim et al. [75] induced pulsed-laser deposition on PET substrates. They obtained an electrical resistivity as low as \(4 \times 10^{-4}\,\Omega\,\text{cm}\) and an average transmittance of 90% in the visible range at the substrate temperature of 100°C. Chung et al. [76] deposited ITO films at room temperature and annealed them through an XeCl excimer laser. They found that excimer laser annealing (ELA) significantly improves the crystal, electrical, optical, and etching characteristics of room temperature deposited ITO. The sheet resistance of irradiated films decreased from \(1.91 \times 10^{-3}\) to \(2.5 \times 10^{-4}\,\Omega\,\text{cm}\), while the optical transmission increased from 70% to 85%. Many other deposition techniques, including radio-frequency (RF) reactive magnetron sputtering [77], sputter-type negative metal ion source [78], and oxygen ion beam assisted deposition [79], have also been reported. Lim et al. [20] prepared FOLEDs using fluorine-containing colorless PI substrate with ITO deposition by RF magnetron sputtering. They found that the sheet resistance of the ITO films on the colorless PI substrate is approximately 20Ω/cm\(^2\) when the sputtering temperature is >150°C and is lower than any resistance values that have been reported previously for ITO films coated onto polymer substrates. Fortunato et al. used a zinc oxide buffer layer between polymeric substrates and ITO films. They reported that the electrical properties of ITO thin films deposited at room temperature on PEN substrates were improved by more than two orders of magnitude by using a zinc oxide (ZnO) buffer layer [80].

On the other hand, there have been many studies replacing ITO with ZnO because ZnO exhibits high

4. Transparent electrodes

Most electro-optic devices such as LCDs, OLEDs, and electronic papers (e-papers) require electrically conductive and transparent electrodes. Indium tin oxide (ITO) thin films deposited on glass substrates have been widely used as transparent conducting electrodes in many electro-optic devices because they possess attractive properties with respect to visible transparency and electrical conductivity [2]. However, ITO thin films have several drawbacks. They are very expensive because indium is one of the rarest material. They require high-temperature processes to get good qualities on glass substrates. Most of all, they are so brittle that they are not easy to apply to flexible displays.

Studies aimed at developing new transparent electrodes include several directions: developing new low-temperature processes using ITO such as pulsed-laser deposition; developing alternative materials to ITO such as zinc oxide; finding new rigid materials available for flexible displays such as transparent polymer electrodes.

4.1. Transparent conducting oxides (TCOs)

There have been remarkable applications of TCOs in the area of flat panel displays such as televisions, computers, electrochromic windows, photovoltaics, and hand-held devices. Coupled with the increased importance of TCO materials, there have been many improvements over several years in the science of these materials [74].
optical transmission and good electrical conduction. In addition, ZnO is more stable in activated hydrogen environments than other TCOs and is not expensive compared to ITO. Ha et al. deposited aluminum-doped zinc oxide (AZO) thin films at the two-substrate deposition temperatures of 100 and 200 °C with a RF magnetron sputtering system on the fluorinated PI substrate [81]. The sheet resistance of the AZO film deposited onto the fluorinated PI substrate at 200 °C and the optical transmission of the AZO/PI film in the visible light range are about $1.94 \times 10^{-6} \Omega \text{cm}$ and 81.47%, respectively. ZnO films with different doping systems were also investigated, such as Zr-doped ZnO thin films [82], Ti-doped zinc oxide thin films [83] and gallium-doped zinc oxide films [84].

Other materials constituting transparent conducting electrodes, such as antimony-doped tin oxide films [85,86] and multi-oxide combinations including In$_2$O$_3$–ZnO films [87] and Cd–In–Sb–O films [88], were also reported.

4.2. TCO–metal–TCO (TMT) multilayers

TCO films such as ITO have been commonly used as electrode materials in flat panel displays, providing good electrical conductivity and high transparency in the visible region. However, they are too brittle to use as flexible displays. Metal films, on the other hand, have good mechanical properties for flexible display applications but they are not transparent. In this regard, TCO–metal–TCO multilayers such as ITO–metal–ITO have been studied as flexible transparent inorganic electrodes.

Lewis et al. [89] used ITO–Ag–ITO as a transparent electrode for a FOLED instead of ITO. In this case, the ITO layers provided good energy-level alignment for efficient incorporation of holes into the organic layers while the addition of the ductile silver layer gave improved robustness under mechanical strain. ITO–Ag–ITO provided significantly reduced sheet resistance compared to ITO, yielding about $30 \Omega / \text{cm}^2$ and 80% optical transmission at an Ag layer thickness of 8 nm, and improved bending properties both as a function of radius and as a function of cycling. The resistance data for samples bent to a radius of 6 mm as a function of the number of cycles are shown in Fig. 8. After 10,000 cycles the value of $R/R_0$ for the ITO sample was 7.4.

Fahland et al. [90] also examined different layer stacks of the design ITO–Ag–ITO. They found that the layer stack can be optimized to provide sheet resistances below $16 \Omega / \text{cm}^2$ at a total light transmission of over 80% at 550 nm, as shown in Fig. 9. Under these conditions, the ITO was deposited at ambient temperatures because the electrical properties of ITO are of minor importance.

Liu et al. [91] reported ZnS/Ag/ZnS nano-multilayers with a sheet resistance of $3 \Omega / \text{cm}^2$ and a luminous transmittance of about 90%.

4.3. Conducting polymers

Polymers had long been known as electrical insulators when Heeger et al. in 1976 discovered the extremely improved conductive polymer, polyacetylene [2]. With this event, thousands of scientists began to conduct research to develop polymers that are stable in the conducting state and processable at low cost, including polycetylene, polyaniline, polypyrrol, polyphenylene, poly(p-phenylene vinylene), and polythiophene. Recently, polyaniline doped with camphor sulfonic acid (CSA), i.e. PANI-CSA, was found to exhibit metallic conductivity ($> 10^3 \text{ S/cm}$) [92].

Among the conducting polymers as shown in Fig. 10, polyaniline and polypyrrol have already been commercialized in applications for corrosion protection, antistatic materials and fiber sensors. Polyphenylene and poly(p-phenylene vinylene) have been investigated as emitting materials of OLEDs by controlling the effective conjugation length, while thiophene derivatives have been investigated.
as active materials for OTFTs or solar cells by controlling the optical absorption and transport via the organization of the thiophene chains and domains [93].

Conducting polymers have attracted a great deal of attention as potential replacements for ITO in many electronic and optoelectronic devices and especially for flexible displays due to their good mechanical strength and their electrical and optical stability during bending [94,95]. Polythiophene, more specifically poly(3,4-ethylenedioxythiophene) (PEDOT), has been widely studied as the most preferred candidate for transparent conducting-polymer anodes, as it exhibits a very high conductivity of about 300 S/cm and is almost transparent in thin, oxidized films and shows a very high stability in the oxidized state [96,97]. The solubility problem was subsequently improved by using a water-soluble
polyelectrolyte, poly(styrene sulfonic acid) (PSS), as the charge-balancing dopant during polymerization to yield PEDOT/PSS. This combination resulted in a water-soluble polyelectrolyte system with good film-forming properties, high conductivity of about 10 S/cm, high visible light transmission and excellent stability. Films of PEDOT/PSS can be heated in air at 100 °C for over 1000 h with only a minimal change in conductivity. Due to their relatively low conductivity, conducting polymers, especially PEDOT derivatives, have been primarily used as a buffer layer between ITO and a hole-transporting layer, providing a good interface between the ITO anode and the organic hole transport layer [98].

Kim et al. [99] used PEDOT/PSS dispersed in an aqueous solution with added glycerol as the anode for OLEDs. The surface sheet resistance of 130-nm-thick films used in the study was 1850 Ω/cm². Their optical transparency was 90%. Their work functions were in the range of 5.0 ± 0.1 eV, comparable to that of a pre-cleaned and oxygen plasma-treated ITO. Devices using this polymer as an anode showed good external EL quantum efficiency with 0.73% at 100 A/m², which compares well with an OLED using a standard ITO anode. In addition, an induced buffer layer between the conducting polymer and the hole-transporting layer reduced micro-shorts, which lead to a leakage current, with a slight increase in the work function. They also reported a simple method of patterning the conducting-polymer electrode on various substrates including plastics [100].

Joo et al. reported the effects of organic solvents on the charge transport properties of the PEDOT/PSS systems, observing the increase in room temperature DC conductivity of the systems from ~0.8 to ~80 S/cm with a change of solvent [101]. The screening effect due to a polar solvent between dopants and polymer main chains plays an important role in the charge transport properties, such as conductivity and its temperature dependence.

Louwet et al. [102] added high boiling solvents such as N-methyl pyrrolidone (NMP) during the coating of PEDOT/PSS on polyester substrates, which decreases the surface resistance by three orders of magnitude, resulting in transparent conducting electrodes with 350 Ω/cm² and a visual light transparency of 80%.

4.4. Carbon nanotube (CNT) thin films

Nowadays there are a significant number of studies of CNTs, especially single-walled carbon nanotubes (SWNTs), and their applications, including CNT composites, electrical devices, hydrogen storage, field emission devices, nanometer-sized electronic devices, and sensors, due to their unique electrical, mechanical, and optical properties [103]. In the application of flexible electronics, flexible and transparent CNTs are some of the most promising materials because SWNTs have metallic properties as well as semiconductive properties and their electronic behavior, such as their conductivity and their work function, can be adjusted by designing the ways of rolling the graphene sheet.

Martel et al. used transparent SWNT sheets that gave a luminance efficiency of the CNT-based OLED of 1.4 cd/A at the maximum achieved brightness of 2800 cd/m², which is comparable to an optimized ITO anode device made under the same experimental conditions [104]. Zhou et al. [105] applied arc-discharge nanotubes to hole-injection electrodes for OLEDs providing a sheet resistance of ~160 Ω/cm² at 87% transparency. Marks et al. made polymer-based OLEDs using SWNT films on flexible PET substrates [106]. Rowell et al. [107] fabricated flexible transparent conducting electrodes by printing films of SWNT networks on plastic for flexible solar cells. Grüner et al. fabricated transparent and flexible transistors where both the bottom gate and the conducting channel are CNT networks of different densities and parylene N is the gate insulator [108].

On the other hand, Shan and Cho showed that for SWNTs with smaller diameters (<1 nm), the work function is very sensitive to chirality or diameter while for those of larger diameters (>1 nm), there is no significant chirality or diameter dependence as shown in Fig. 11 [109]. For class I tubes, nanotube work functions are very close to the work function of a graphene sheet, ~4.66 eV. For class II tubes, work functions of (n, 0) tubes increase dramatically, while those of (n, n) tubes show a decrease in work function; (6,0), (5,0), and (4,0) tubes are metallic due to σ*-π* hybridization.

There have been various attempts to overcome the low solubility of CNTs, including using various common organic solvents [110,111] or oleum [112], cutting long materials into short, using open-ended pipes with 100–300 nm lengths and forming a stable colloidal suspension in water with the help of surfactants [113], and dissolving full-length CNTs in common organic solvents [114].

For electrode patterning, Wu et al. [115] developed a simple process including vacuum filtering of
a dilute, surfactant-based suspension of purified nanotubes onto a solvent-removable filtrating membrane for the fabrication of ultra-thin, transparent, optically homogeneous, electrically conducting films of pure SWNTs, and the transfer of those films to various substrates. For an equivalent sheet resistance of 70–90% for 50 nm thin films, the electrical resistivity was measured to be $1.5 \times 10^{-4} \Omega \text{cm}$, comparable to commercial ITO. Other methods of deposition or patterning of SWNT, including spin-coat [116], vacuum filtering [117], transfer with poly(dimethysiloxane) (PDMS) stamps [118], line-patterning [119], the Langmuir–Blodgett method [120] and controlling droplets using a gas flow [121], have also been reported.

5. Electro-optic materials

5.1. Liquid crystal displays (LCDs)

Flat panel LCDs have extended their boundaries from small size mobile phones to large-size televisions because they are thin and lightweight and have a low power consumption and excellent resolution. However, there are critical problems of stability when applying conventional LCD technologies to flexible LCDs [122]. Flexing the panel creates forces that will cause the liquid crystal to flow, resulting in cell-gap variations across the panel, visual distortions, and artifacts, which can easily become irreversible [5]. Therefore, it has become a most important challenge to prevent liquid crystal flow under the pressure caused by the deformation that is unavoidable in flexible applications [123].

To ameliorate these cell-gap problems, liquid crystal materials have been separated out in the form of droplets or domains randomly distributed throughout the polymer binders. Technical approaches include polymer-dispersed liquid crystals (PDLCs), pixel-encapsulated liquid crystals, photo-enforced stratification, and encapsulating liquid crystals into polymer capsules.

PDLC films can be made either by phase separation methods [124] or by emulsion methods [16]. Schneider et al. [125] encapsulated liquid crystal by polymerization-induced phase separation in which a homogeneous mixture of photo-reactive monomers and liquid crystals is subsequently exposed to ultraviolet light and the liquid crystals are continuously separated and form dropwise domains to apply to flexible LCDs. They controlled photopolymerization chemically via the fraction of the crosslinker in the polymer/LC composite through the functionality of the pre-polymer to give
large pancake-like droplets, as shown in Fig. 12, of \(~10\mu m\) in diameter and producing very little light scattering. Link et al. reported a technique for producing monodisperse liquid crystal droplets formed into a precisely ordered two-dimensional hexagonal-close-packed monolayer from liquid crystal emulsions, which switch between diffraction and transparency [126]. Chari et al. [127] fabricated single-substrate cholesteric LCDs by colloidal self-assembly. This emulsion-based close-packed PDLC film was fabricated on a moving-web coating machine.

Lee et al. reported a pixel-encapsulated flexible LCD with a multifunctional elastomer substrate fabricated by a replica molding [128]. Fig. 13 shows a process of fabricating a pixel-encapsulated flexible LCD having a multifunctional elastomer substrate, with the scanning electron microscopy (SEM) image of the PDMS elastomer substrate duplicated from the master and the flexible LC cell with a multifunctional elastomer substrate used as the top substrate [128]. Reproduced from Kim, Hong, Yoon, and Lee by permission of American Institute of Physics, Maryland, USA.

**Fig. 12.** Schematic diagram of the flexible encapsulated cholesteric liquid crystal displays [125]. Reproduced from Schneider, Nicholson, Khan, Doane, and Chien by permission of Society for Information Display, California, USA.

**Fig. 13.** A schematic process of fabricating a pixel-encapsulated flexible LCD having a multifunctional elastomer substrate: (a) an elastomer substrate fabricated by a replica molding technique, (b) the SEM image of the PDMS elastomer substrate duplicated from the master, and (c) the flexible LC cell with a multifunctional elastomer substrate used as the top substrate [128]. Reproduced from Kim, Hong, Yoon, and Lee by permission of American Institute of Physics, Maryland, USA.
into a polymer-covered liquid crystal layer [130,131]. As shown in Fig. 14, the paintable LCDs are manufactured by a two-step photopolymerization process. The first UV exposure, using wavelengths beyond the absorption region of the reactive stilbene dye, is through a mask, and the localized polymerization forms an array of polymer walls. During the second UV exposure, using UV light of shorter wavelength in the absorption band of the dye, the polymer sheet is formed. The resulting structures resemble liquid crystal material-filled capsules.

On the other hand, Lee et al. proposed a high-speed flexible display based on a deformed helix ferroelectric liquid crystal in a vertically aligned configuration with a periodic array of columnar spacers on the top sides of in-plane electrodes [132]. The mechanical stability of the flexible display was achieved using a periodic array of columnar spacers formed directly on the top side of the in-plane electrodes by a photolithography technique to give flexibility, uniform alignment, fast response and gray scale capability. Sikharulidze reported an orientational effect in a suspension of nematic liquid crystal with solid nanoparticles, controlled by an optically hidden electrophoretic effect [133]. Polymer wall-stabilized smectic A liquid crystals to be used for bistable flexible displays [134] and liquid crystal microcapsules with a perpendicular alignment shell [135] were also reported.

Samsung Electronics introduced large area (5.0 in) full color transmissive a-Si TFT-LCDs with a resolution of 400 x 3 x 300 lines (100 ppi) [14]. All the processes of TFT, color filter, and LC were carried out below 150°C on PES films. The overall module, including a backlight unit, is bendable and has a thickness of about 1.2 mm and a weight of 22.0 g, which are one-third of the thickness and weight of normal glass-based displays. Kent Displays developed the first ever reflective cholesteric LCDs on single textile substrates made with simple coating processes by sequential coating of various functional layers on fabric materials [16]. Encapsulation of the cholesteric liquid crystal droplets in a polymer matrix and the mechanical flexibility of the conducting polymers allow them to create durable and highly conformable textile displays.

5.2. Electronic papers (e-papers)

When a TV or computer prevailed in our life, we thought newspapers would disappear. However, we are still getting news from newspapers because of their readability. It is very inconvenient to read long novels on a computer screen. Paper-like readability is the most important target of electronic paper. Omodani studied how to achieve readability in his experiments, presenting the result that it may be possible to improve display readability simply by adopting a free-reading style [136]. Electronic paper can be a thin, high-contrast, reflective display that can be flexed, bent, rolled-up, and folded and, in
particular, it can have a very low power consumption. A portable device that uses this technology will look more like a pad of paper than a standard laptop. Applications of electronic papers include newspapers, magazines, greeting cards, and even cereal boxes, bumper stickers, and wallpaper [137, 138].

Most electronic papers use a bistable property, in which the image is not refreshed until rewritten, and a reflective characteristic, in which the image can be seen through another light source, in comparison with emissive displays such as LCDs or OLEDs. Therefore, they do not require a constant voltage to maintain an image, which greatly decreases power consumption. These electronic paper technologies include cholesteric, ferroelectric, PDLC, electrochromic, electrophoretic, electrodeposition, and OLED techniques. In this section, we will mainly discuss electrophoretic techniques [139].

Electrophoresis means physical motion under an electrical force, while electrophoretic displays switch images by the movement of particles under voltage [140]. Electrophoretic displays are almost invariably reflective and bistable. They have less stringent barrier requirements and can be easily made in large sizes compared to LCDs and OLEDs. The main limitation is a slow switching speed, making electrophoretics a poor choice for video or even rapid scrolling. This largely eliminates the cell phone, game, and parts of the auto market. Electronic paper and electronic books are considered as key applications for electrophoretics because of their bistability [4, 5].

E-ink Corporation uses a microencapsulated electrophoretic material that consists of millions of microcapsules containing charged pigment particles in a clear fluid. A negative voltage applied to the top surface causes the positive white particles to move to the top of the capsule and the surface to appear white, whereas reversing the electric field causes the negative black particles to appear at the top surface and create a dark spot, as shown in Fig. 15. [141, 142]. They fabricated a display on a bendable active-matrix-array sheet, which is less than 0.3 mm thick, has a pixel density of 160 pixels × 240 pixels and a resolution of 96 pixels/in, and can be bent to a radius of curvature of 1.5 cm without any degradation in contrast. They also introduced flexible electrophoretic displays with LTPS TFTs [142] and with OTFTs [9].

Gyricon Media uses a twisting-ball display [143, 144]. Their basic display structure consists of a thin layer of elastomeric material embedded with bichromal. Each sphere sits inside its own cavity, which is filled with silicon oil, allowing the sphere to rotate. The spheres are fabricated such that one hemisphere appears white and one hemisphere appears another color, with each hemisphere having a different permanent charge. In a stable situation, the balls gravitate to one side of the cavity and adhere to the wall. When an electric field is applied across the sheet of elastomer, the ball is released from the side of the cavity so it can rotate to align with the field. After the ball has rotated, it settles again against the cavity wall and becomes stably attached until a reverse electric field is applied. If an image is converted into a planar voltage pattern applied to the surface of the sheet, then the electrical field induces rotation of the balls and the image is transferred to the balls. Light reflected off the balls displays the image.

![Fig. 15. Schematic diagram of the cross section of electronic-ink micro-capsules [142]. Reproduced from Kawai, Miyasaka, Miyazaki, Kodaira, and Inoue by permission of Society for Information Display, California, USA.](image-url)
Sipix Imaging Inc. developed the Microcup\textsuperscript{\textregistered}, in which a particle suspension is deposited into 80–160 µm wide compartments embossed into resin substrates \cite{145,146}. An electrophoretic fluid comprised of charged pigment (TiO\textsubscript{2})-containing microparticles dispersed in a colored dielectric solvent is enclosed and seamlessly top-sealed in the Microcups\textsuperscript{\textregistered}. Color rendition may be achieved either by using a color filter or by sequentially filling and sealing red (R), green (G), and blue (B) electrophoretic fluids in the Microcups\textsuperscript{\textregistered}. Excellent colloidal stability has been observed even after the electrophoretic composition was centrifuged at 1000\textsuperscript{g} for more than 30 min. They also developed new RTR manufacturing processes based on this technique.

Bridgestone Co. presented a new electrophoretic display named Quick Response Liquid Powder Display (QR-LPD\textsuperscript{\textregistered}) \cite{147,148}. This display uses an electronic powder, named liquid powder, which is a high-fluidity material that combines the properties of a powder and a liquid and is highly sensitive to electricity. Fig. 16 shows the cross-sectional structure and the operational principle of QR-LPD\textsuperscript{\textregistered}. Two types of powders, including negatively charged white and positively charged black versions, are put into an area between two ITO-patterned glass plates. The rib forms a cell gap and prevents the powders from mixing. The rest of the space is filled with ordinary air instead of liquid. Using this new material, QR-LPD\textsuperscript{\textregistered} has shown outstanding clarity similar to that of paper along with excellent image stability, quick response, high resolution, clear threshold characteristics, and low power consumption.

Hayes et al. introduced a novel reflective-display principle, in which the optical switch is driven by the so-called electro-wetting effect \cite{149,150}. This principle has the potential for use as a fast, high-brightness color display. Fig. 17 demonstrates the principle of the reflective electro-wetting display. Fig. 17(a) shows the optical stack, comprising a white substrate, a hydrophobic insulator, a colored oil layer, and water. At equilibrium the colored oil naturally forms a continuous film between the water and the hydrophobic insulator. However, when a voltage difference is applied across the hydrophobic insulator, an electrostatic energy is added to the energy balance and the stacked state is no longer energetically favorable. The energy of the system can be lowered by moving the water so that it makes contact with the insulator, thereby displacing the oil (Fig. 17(b)) and exposing the underlying white surface. The balance between the electrostatic and capillary forces determines how far the oil is moved to the side. In this way, the optical properties of the stack when viewed from above can be continuously tuned between a colored off-state and a white on-state, provided the pixel is sufficiently small so that the eye averages the optical response.

Other ideas including electrodeposition \cite{151}, photochromic compounding \cite{152}, fine particles dispersed in a nematic liquid crystal \cite{153}, and hollow fibers \cite{154} have also been reported.

5.3. Polymer light-emitting diodes (PLEDs)

OLEDs have many excellent properties as displays including Lambertian emission, good colors, no cell-gap problem, and the potential for using many promising new solution-processing techniques. In this regard, the OLED is a promising candidate for flexible displays in the future \cite{4}.

However, there exist many challenges yet to be overcome \cite{5}. The biggest challenge is water and oxygen sensitivity, which is a factor on both sides of the display when a polymer substrate is used. We have already discussed this issue in Section 3.

![Fig. 16. The QR-LPD\textsuperscript{\textregistered} architecture and the operation principle \cite{147}. Reproduced from Hattori, Yamada, Masuda and Nihei by permission of Society for Information Display, California, USA.](image-url)
Second is to develop new active materials that have high thermal and mechanical stability, large-area processibility, and high efficiency. Third is to develop new manufacturing processes for FOLEDs, which are not well established at this time[155]. The last challenge concerns active back plain technology, which will be dealt with as the following topic.

OLEDs are classified as small molecule OLEDs (SMOLEDs) and polymer OLEDs (PLEDs). SMOLEDs are being used for the small-sized displays of mobile phones. Small molecules are easily synthesized and purified compared to polymers[156]. Therefore, a large number of high-purity conjugated small molecular materials are commercially available. They are also easy to fabricate in a multilayer structure and more readily allow optimization of the turn-on voltage, luminescence, and efficiency. However, they require a high-vacuum manufacturing system for deposition and they are sensitive to temperature. Therefore, they are difficult to use in a large-area deposition system. On the other hand, conjugated polymers have good film properties and good mechanical and thermal stability but it is difficult to synthesize high-purity conjugated polymers and to fabricate multilayer structures[157]. Most of all, conjugated polymers can be more easily applied to large-area manufacture through cost-effective solvent processes such as spin-coat, ink jet printing, dipping, and spraying. Therefore, polymer materials are an excellent choice for RTR manufacturing as well as flexible displays. In this section, we discuss materials for PLEDs and their fabrication techniques.

5.3.1. Electron injection/transport materials

To optimize electron injection and transporting performance, there are two factors to be considered: how to lower the injection barrier between the cathode and the organic material and how to raise the recombination probability of the carriers. Methods for lowering the injection barrier between the cathode and the organic material include using a cathode of low work function, introducing a buffer layer between the cathode and the organic material.
layer to tune the energy levels, or using organic materials with a higher lowest unoccupied molecular orbital (LUMO) [158].

In the energy-level alignment, lower work function metals such as Mg and Ca are known to be well matched with organic materials, but they are very sensitive to moisture or oxygen compared to higher work function metals such as Ag and Al. Therefore, many attempts to find stable and low work function cathode materials have been reported [156]. The work function of a cathode is also controlled by changing the deposition thickness of the nanolayer of the cathode [159].

As a buffer layer, Elliott et al. prepared a series of tervalent conducting polymers, which have a low work function of <3.6 eV and is tunable, via the thermal polymerization of transition metal diimine complexes [160]. Kim et al. induced polymer-insulating nanolayers between the emitting layer and the aluminum cathode in PLEDs in which a hole is the major charge carrier, showing that a device with a nanolayer of lower dielectric constant provides a higher luminescence quantum efficiency [161]. Shu et al. inserted a layer of non-ionic neutral poly(ethylene glycol)-based surfactant between an electroluminescent layer and a high work function aluminum cathode, which showed comparable or even better device performance than that of control devices using calcium as the cathode [162]. They proposed that when both surfactant and aluminum are used as the cathode, the abundant hole injection through a hole-transporting layer and hole pile-up at the inner side of EL/surfactant interface might cause an effective electric field to induce the realignment of the dipole moment of those polar surfactant molecules, thus lowering the barrier for electron injection.

As organic materials with higher LUMO, metal chelates or metal complexes such as tris(8-hydroxyquinoline) aluminum (Alq3) are the most well-known electron transport materials [163–165]. Organic materials modified with electron withdrawing moieties reduce the barrier of electron injection and block the hole injection. These electron-withdrawing groups include oxadiazole [166–168], azole [169,170], benzothiadiazole [171–173], cyano [174,175], quinoline [176–178], bonyl [179], silole [180–182], and perfluorin [183,184], as shown in Fig. 18. These groups are used as the backbone or pendant group of a small molecule or polymer [185,186] and as the backbone or pendant of an emitting conjugated polymer [187,188].

5.3.2. Hole injection/transport materials

Similar to the case of electron injection/transport, there are several ways to lower the hole-injection barrier between the anode and the conjugated polymers, including using high work function anodes, anode modification, fabricating the multilayer of materials with various ranges of ionization potentials, and modifying conjugated polymers [156]. As discussed in the previous section, TCOs, conducting polymers, and CNTs are considered as flexible transparent anodes.

Surface treatment of the ITO anodes through oxidization by O2 plasma, CF4/O2 plasma, UV ozone treatment as well as acid and base treatment increases the work function nearly to 5 eV [189,190].

An additional hole-injection layer between the anode and a conjugation polymer layer decreases the hole-injection barrier to form cascade-shaped energy levels. These hole-injection materials include a thin layer of platinum [191], metal phthalocyanine [192–194], PEDOT/PSS [96,97], tetra(fluoro)-tetra (cyano) quinodimethane (TF-TCNQ) [195], tris (4-bromophenyl) aluminum hexachloroantimonate (TBAHA) [196], and 4,4′,4″-tris(N,N-diphenylamino) triphenylamine (TDATA) [197].

A self-assembled monolayer (SAM) has been investigated to manipulate the energy-level offset at the ITO-hole transport layer. Day et al. used SAMs of polar adsorbate molecules with the dipole oriented outward from the surface an artificial dipolar layer where the work function is increased [198,199]. With this method the threshold voltage for light emission can be reduced and the maximum luminance increased. Fujihira et al. enhanced hole injection by fine-tuning of the work function through surface molecular design of ITO [200].

Marks et al. used a SAM with hole transport moieties [201,202]. They modified traditional hole transport molecules such as 1,4-bis(phenyl-m-tolylamino) biphenyl (TPD) and N,N′-bis(l-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) with trichlorosilyl groups and spin-coated them onto the ITO surface, enhancing the ITO-hole transport layer contact via robust covalent bonding, and got dramatic OLED device performance enhancement. Modification with doped π-conjugated polymers [203], a polymer hole-injection layer [204], and hole-injecting conducting-polymer compositions [205] have also been reported.

As hole transport materials, several triarylamine and cabazole derivatives shown in Fig. 19 have been studied. To improve the thermal stability of
conventional hole transport materials containing triarylamines such as TPD and NPB, which have a low glass transition temperature ($T_g$) of below 100 °C leading to crystallization at elevated temperatures, new high $T_g$ hole-injection materials including biphenyl diamine derivatives [206], star-shaped molecules [207], dendrimers with a cabazole dendron [208], and spiro-linked biphenyl diamines [209] were developed. Cross-linking or polymerization also presents good thermal properties. Kim et al. [210,211] synthesized a diamine that has triarylamino moieties and used this product to make a PI film for hole injecting and transport. They also prepared a hole-injecting-transporting layer by in situ mixing hole-injecting and hole-transporting materials by evaporation under vacuum to reduce the number of organic layers in OLEDs. OLEDs with hole-injecting-transporting layers with 25%
hole transport material content displayed the highest efficiency and the longest lifetime, while OLEDs with hole transport materials only exhibited very poor device lifetime despite the higher efficiency [212–214]. Jen et al. thermally cross-linked hole transport layers [215] and Fechét et al. synthesized bipolar transport materials that retain hole and electron transport moieties [216]. Mole-ularly doped polymeric network nanolayers with TPD were also investigated as a hole-injection layer [217].

Other attempts to improve hole transport properties include blending with hole transport polymers, electron transport polymers and light-emitting polymers (LEPs) [218], copolymers containing emitting and hole-transporting moieties [219], and copolymers containing emitting, hole-transporting, and electron-transporting moieties [220].
5.3.3. Electroluminescent polymers
The photoluminescence wavelength of LEPs can be controlled by increasing or decreasing the band gap of the polymer by proper molecular designs [157]. These molecular designs include introducing substituents on the polymer backbone that change the electronic structure of the materials, e.g., by introducing torsion into the polymer backbone via sterically bulky side chains that reduce the effective conjugation length of the polymer or by breaking the chain conjugation with non-conjugated monomers during the copolymerization process [157].

Fig. 20 shows several representative emitting materials for OLEDs.
Poly(\(p\)-phenylenevinylene) (PPV) is the most popular conjugated polymer of the LEPs. It has good thermal stability, good film qualities, and suitable color tunability. However, it has poor solubility, low stability of oxidation and structural defects at the effective conjugating lengths. To improve solubility, a variety of side chains such as alkyl, alkoxy and the bulky cholestanoxy group in PPV have been introduced. Huang et al. introduced silyl groups into a conjugated polymer to afford

![Chemical structures](image-url)
good processability, amorphousness, and good film-forming ability [221,222]. Tsutsui et al. synthesized sterically hindered fluorenyl substituted PPVs, which have excellent solubility and a high quantum efficiency [223,224]. Hsu et al. also introduced fluorenyl substituents to improve solubility and increase steric hindrance in poly(2,3-diphenyl-1,4-phenylene) (DP-PPV) [225]. On the other hand, another problem of PPVs is that electron injection is much more difficult than hole injection, resulting in an imbalance in the rates for electrons and holes and a shift of the recombination zone toward the region near the interface of the polymer/cathode. Jin et al. introduced oxadiazole moieties as electron withdrawing side chains of PPVs, which increases the LUMO energy level and improves device performance [226]. Fluoro groups [227] and cyano groups [228] have been used as electron withdrawing groups. Generally the colors of the PPVs give green to orange-red emissions by controlling the side chains [229]. For blue emissions, Karasz et al. synthesized a series of PPV-related alternating block copolymers containing a conjugated block and non-conjugated block, which can be used directly as blue-green LEPs [230,231]. Shim et al. synthesized PPV-related copolymers containing carbazole or fluorene groups [232]. There were also investigations of polymer blending to give color tuning [233] or high efficiency [234].

PLEDs based on polyfluorenes (PF) are a promising candidate for the next generation of FOLED displays because of their excellent properties, such as good thermal and chemical stability, high quantum yield, good film-forming and hole-transporting properties and, especially, their blue light emission. Polyfluorene homopolymers have a large band gap and emit blue light. Significant efforts have been made to obtain polyfluorene derivatives with a variety of photoluminescence wavelengths. Studies of blue-emitting materials include fluorene/carbazole copolymers for deep blue OLEDs [219,235], polyfluorenes containing bipolar pendant groups [220], quinoxaline-containing polyfluorenes to give high electron affinity [236], copolymers based on fluorene and 2,5-di(2-hexyloxyphenyl) thiazolothiazole [237], and hyperbranched alternating copolymers of tetrabromoarylmethane/silane and 9,9-dihexylfluorene-2,7-diboronic acid [238]. As green-emitting materials, fluorene- and benzothiadiazole-based conjugated copolymers [172], fluorene copolymers containing a phenylene group, biphenylene group, or a thiénylene group [239], and CN-poly(diexylfluorenevinylene) [175] and polydioctylfluorene [240] have been reported. To get red emissions, a narrow band gap comonomer was introduced into the polyfluorene backbone. The low-band gap polymers include fluorene- and benzothiadiazole-based conjugated copolymers [241], copolymers derived from fluorene and benzoselenadiazole [242,243], polymers derived from fluorene and naphthoselenadiazole [244], conjugated polymers containing Eu³⁺ [245], and polyfluorene copolymers containing electron-deficient 2-pyran-4-ylidene-malononitrile moieties [246]. Cao et al. introduced conjugated polyelectrolytes based on polyfluorene, which are soluble in polar solvents such as alcohol due to the ionic side groups that are attached to the conjugated main chain [247,248]. There have also been studies to improve electroluminescent efficiency and stability and reduce intermolecular interaction by introducing cross-linked polyfluorene polymers [249], polyfluorene/PPV copolymers containing the bulky pendant bis(4-alkoxyphenyl) groups in the C-9 position [250], and poly(aryl ether)s containing ter- and pentafluorene pendants [251].

Polythiophenes have high thermal and mechanical stability and stable color tunability but they have poor solubility, short lifetimes, low color purity and are difficult to process [252]. Several investigations of thiophene derivatives were made [253–255].

On the other hand, Kim et al. [256] studied the doping effect of blue light-emitting electron transport molecules in blue organic light-emitting devices. They also fabricated efficient blue OLEDs with charge carrier confining nanostructures formed by wide band gap molecular doping [257]. Alternating terphenylene carbazylenevinylene copolymer [258] and poly(fluorenylenevinylene-terphenylenevinylene) containing phenyl pendant groups [259] also was reported as an emitting material.

Cross-linked polymers have good thermal and mechanical properties as well as good solvent resistance. Hikmet and Thomassen [260] used an electron beam to cross-link electroluminescent polymers while Haarer et al. and O’Neill et al. applied sol–gel processing [261] and radical polymerization [262], respectively. Self-assembled polymers, including polymers using Zn²⁺ to assemble organic building blocks [263], layer-by-layer self-assembled films with water-soluble polymers [264], self-assembling multilayers using the Langmuir–Blodgett technique [265], and polymer-dielectric
nanolayer composites [266] have also been studied. Electroluminescent dendrimers are an exciting new class of materials for OLEDs. Dendrimers have distinct advantages including a modular approach to their synthesis, the ability to utilize a greater range of luminescent chromophores, and, most importantly, the ability to control their electronic and processing properties independently [267,268]. There have also been studies using polyhedral oligomeric silsesquioxanes with organic–inorganic hybrid structures as cores of starlike LEPs [269,270].

Considerable progress has been made with electrophosphorescent OLEDs based on small molecules as the host materials since the utilization of triplet emitters to improve OLED efficiency was proposed [271]. Polymer-based electrophosphorescent OLEDs are important for the solution process. Chen et al. [272] obtained efficient red emission electrophosphorescent PLEDs by simultaneous incorporation of Ir complexes and charge transport moieties into the side chains of polyfluorene while Park et al. synthesized carbazole-based copolymers tethering blue-emitting iridium(III) bis[(4,6-difluorophenyl)-pyridinato-N,C2] picolinate (FIrpic) via covalent bonding [273]. Cao et al. used electrophosphorescent chelating copolymers based on linkage isomers of naphthylpyridine–iridium complexes with fluorine [274]. Samuel et al. used iridium-cored dendrimers for electro luminescent green phosphorescent polymers [275]. Blending host polymers with guest metal complexes was also investigated. In this case, the iridium complexes were modified with fluorines [276] and alkyl groups [277] to provide better solubility with the host polymers.

Hybrid polymer–quantum-dot light-emitting devices are a new area drawing significant attention due to their easy processibility and the ruggedness of the polymers and the exotic optical properties of the quantum dots. A variety of quantum dots such as CdSe/ZnS [278], CdSe/CdS [279], PbS [280] and CdTe [281] have been investigated for application to light-emitting materials. Quantum dots that are dispersed in a hole transport material at different concentrations with different surface modifications [282], a quantum dot monolayer that is sandwiched between the hole-transporting layer and electron-transporting layer [283,284], and a quantum dot using a thermally polymerized hole transport layer [279] were investigated. Ha et al. considered the performance of OLEDs consisting of PEDOT/PSS-Ag nanocomposites with different concentrations of quantum-sized silver nanoparticles as a hole-injection layer, showing that the turn-on voltage significantly decreases when the concentration of the Ag nanoparticles increases [285]. Bulović et al. explored a new method for forming a large-area ordered monolayer of colloidal nanocrystal quantum dots [286].

5.3.4. Patterning technologies

There have been many studies on the fabrication and patterning of active layers for the development of a full-color application. Vapor deposition using shadow masks is the most common way of fabricating small molecule OLEDs (SMOLEDs) demonstrating high performance. However, this technique has difficulties in shadow mask alignment for large area applications.

For a large-area or a RTR application many printing processes are available, including screen, gravure, offset and inkjet. Among them, inkjet printing is a promising technique for RTR processing [287]. The initial impetuses for creating jet-printing technology for displays were the deposition of PLEDs, for which conventional photolithography is difficult because of material sensitivity, and the reduction of the fabrication cost of color filters for LCDs [288]. Presently, jet-printed color filters are the leading application of the technology in production. They are simple and economic processes scalable to large area patterning of OTFTs [289] or PLEDs [290]. The reliability of the inkjet heads is a major challenge in addition to developing solution-processible high-performance materials.
Another currently available patterning technique is laser-induced thermal imaging (LITI) developed by 3M [291,292]. The LITI process utilizes a donor film, a highly accurate laser exposure system, a LEP, and a substrate, as shown in Fig. 21. The donor film consists of a transparent base film with several coated layers. The layer adjacent to the base film is a light-to-heat conversion (LTHC) layer that converts laser energy to heat. The LTHC layer comprises a material that absorbs at the wavelength of irradiation and converts a portion of the incident radiation into sufficient heat to enable transfer in the thermal transfer layer from the donor to the receptor. This technique is also available for large area fabrications through a dry process and can apply to a multi-stacking structure.

Photolithography [293], hot micro-contact printing [294], and radiation-induced sublimation transfer [295] have also been reported.

6. Thin-film transistors (TFTs)

Low-temperature process technologies in TFT fabrication are the most crucial for flexible displays [296]. The TFT processes developed for flat panel display using rigid glass substrates cannot readily be applied for use with flexible plastic substrates due to the limitations of process temperature, lack of dimensional stability, and thermal stresses between the TFT thin films and the substrate.

There are two main approaches for fabricating TFTs on plastic substrates. One is to transfer high-performance poly-silicon or single-crystal silicon TFT devices processed at a high temperature on a glass, quartz, or silicon substrate onto a flexible plastic substrate [297]. This approach provides optimal TFT device performance with respect to mobility, leakage current, stability, and uniformity of the TFTs, whereas it is not a cost-effective process because of the wastage of the glass substrate and the additional cost of the transfer process. Another is to fabricate a TFT array directly on the flexible polymer plastic substrate whereby the TFT, such as amorphous silicon (a-Si), LTPS, or organic semiconductor (OTFT), is fabricated at a temperature less than 150 °C directly on the flexible plastic substrate [298].

6.1. Amorphous silicon TFTs

Hydrogenated amorphous silicon (a-Si:H) TFTs are widely used as switching devices in active-matrix LCDs (AMLCDs) at the moment. These devices are generally made from hydrogenated amorphous silicon and silicon nitride layers formed on glass substrates by PECVD with processing temperatures exceeding 300 °C.

Long et al. [15] fabricated amorphous silicon TFTs at a high temperature of 250 °C on PI substrates. However, polymer substrates are normally incompatible with typical high-temperature processes because the maximum working temperature of most polymer substrates is between 100 and 150 °C. On the other hand, the low deposition temperature leads to an excess of hydrogen incorporated onto the growing amorphous silicon surface, which gives a high defect density and poor electronic properties such as low mobility and high gate current-leakage [299,300]. The hydrogen content of the amorphous silicon film deposited by PECVD was reported to be ~20 at% at 100 °C and ~10 at% at 250 °C [301].

To get high-quality amorphous silicon with low hydrogen content on plastic substrates at a low temperature below 150 °C, the concentration of silane gas was controlled [302–304] or new deposition techniques such as very-high frequency (VHF) PECVD [305], hot-wire chemical vapor deposition [306] and electron cyclotron resonance plasma-enhanced chemical vapor deposition (ECR-PECVD) [307] were introduced.

Sazonov et al. [308] fabricated TFTs with amorphous hydrogenated silicon (a-Si:H), nanocrystalline silicon (nc-Si), and amorphous silicon nitride (a-SiNx) films using plasma deposition equipment at process temperatures as low as 75 and 120 °C. The a-Si:H TFTs showed good performance characteristics including field-effect mobilities of 0.8 and 0.6 cm²/V s and threshold voltages of 4.5 and 4 V at 75 and 120 °C, respectively. Won et al. [309] used organic materials that have similar mechanical properties to the plastic substrates as gate insulators, instead of inorganic materials such as SiNx, on PES substrates. They got a field-effect mobility of 0.4 cm²/V s and a threshold voltage of 0.7 V, which were better than the case of a silicon nitride gate insulator where the field-effect mobility and threshold voltage were 0.3 cm²/V s and 5 V, respectively, when they introduced benzocyclobutene (BCB) gate insulators. They also got a field-effect mobility of 0.5 cm²/V s and a threshold voltage of 4.7 V using a poly(4-vinyl phenol) (PVP) gate insulator [310]. Hong et al. [311] developed a 5.0-in transmissive type plastic amorphous...
TFT-LCD with a resolution of 400 × 3 × 300 lines. All the processes of TFT, color filter, and LC were carried out below 150 °C on PES films.

6.2. Low-temperature poly-silicon TFTs

Low-temperature polycrystalline silicon (LTPS) TFTs have good mobility, which is higher than that of amorphous silicon TFTs by two orders of magnitude, and can reduce the channel size of the switching TFTs to increase the emitting zones as well as provide a more stable threshold voltage over the life of the device [312,313]. Many deposition processes have been developed to make low defect and high-quality polycrystalline silicon thin films, including direct deposition [314], solid phase crystallization [315], ELA [317], and sequential lateral solidification (SLS) [318].

But the current LTPS processes for AMLCDs employ a typical process temperature in the range of 450–600 °C to recrystallize the amorphous silicon films via excimer lasers [319]. Therefore, it is difficult to use conventional LTPS TFT processes for polymer substrates that require a low process temperature under 150 °C. To circumvent this limitation, there have been two kinds of investigations, including direct fabrication on plastic substrates and transfer from glass to plastic substrates.

With regard to direct fabrication on plastic substrates, direct deposition, ELA and SLS have been actively studied. Cheng and Wagner [314] monolithically integrated p-channel and n-channel TFTs of nanocrystalline silicon on plastic substrates by direct deposition at a substrate temperature of 150 °C to obtain a high electron field-effect mobility of ~30 cm²/V·s and a usable hole mobility of ~0.35 cm²/V·s. Gosain and Usui [317] created poly-silicon TFTs on plastic substrate at a substrate temperature of 110 °C, except for the temperature rise during excimer laser irradiation for crystallization providing a field-effect mobility of 250 cm²/V·s and sub-threshold swing of 0.16 V/decade. Young et al. [320] also used this technique on a variety of polymer substrates including PI, PAR, polynorbonene (PNB), and PES. Kim et al. [318] employed a two-shot sequential lateral solidification (TS-SLS) technique to obtain high throughput for mass production. In this case, the field-effect mobility and threshold voltage were 181 cm²/V·s and 1.6 V, respectively. A thin-beam crystallization method [321] and ion beam deposition followed by eximer laser crystallization at room temperature [322] have also been reported.

Among the transfer technologies investigated, Akihiko et al. fabricated a bottom gate TFT device layer using an ELA process on a glass substrate and transferred this TFT layer onto a plastic substrate [323]. Fig. 22 shows a schematic flow of the transfer process. First, the stopper layer is deposited against HF etching on a conventional glass substrate. The device layer is formed through the LTPS process and glued to the second substrate with a removable, non-water-soluble glue (Fig. 22(a)). The glass substrate is etched off in hydrofluoric acid (HF) at room temperature (Fig. 22(b)). The etching stopper is also removed in another kind of etching solution. The transparent polymer substrate is stuck onto the back surface of the device layer with a permanent adhesive (Fig. 22(c)) and then the second substrate is detached (Fig. 22(d)). The TFT layer on the
plastic substrate did not do any significant damage to the device layer and the changes in LTPS TFT characteristics with substrate bending revealed a mobility change of 16% under 0.75% compression. Inoue et al. [324] developed a new technology that enables the transfer of thin-film devices from an original substrate to another substrate using laser irradiation, which is called surface-free technology by layer annealing (SUTFLA). A polycrystalline silicon TFT backplane for LCDs with integrated drivers was fabricated using a low-temperature process below 425 °C and successfully transferred from a glass substrate to a plastic film using this technology. They fabricated an all-plastic substrate TFT-LCD having a display area of 0.7 in measured diagonally and a pixel count of 428 × 238. Takechi et al. [325] reported on a very high rate and uniform glass etching with HF/HCl spray for transferring TFT arrays from a glass substrate to a flexible substrate. Using HF/HCl spray etching, they achieved both high etch rates of over 20 mm/min and satisfactory etch-rate uniformity over a 150 mm area with an approximately 5% variation.

6.3. Organic thin-film transistors

There has been a lot of interest in the development of OTFTs in which organic semiconductors are used as active layers because the organic semiconductors are deposited at a low temperature or processed through low-cost solution processes such as spin coating or ink jet printing. In addition, they are compatible with polymer flexible substrates, compared to amorphous silicon processes or low-temperature polycrystalline silicon processes [326,327].

6.3.1. Organic semiconductors

As active materials of OTFTs, pentacene, and thiophene oligomers deposited by vacuum evaporation have been used to elucidate the transport mechanism in the active layer of organic semiconductors. In this case, field-effect mobility was known to depend on the deposition condition of the active layer and its morphology [328]. Traps in the bulk, interface, and grain boundary of the active layer affect the current–voltage characteristics of single crystalline and polycrystalline OTFTs [329,330]. The mobility in polycrystalline oligothiophene increases linearly with grain size, and the temperature dependence of the mobility changes drastically from small grains, where the mobility is thermally activated, to large grains, where the mobility is practically temperature independent [331]. Fig. 23 shows potential OTFT materials that have been studied.

Among small molecular semiconductors, pentacene demonstrates good performance. Under optimized conditions, pentacene TFTs had mobilities ranging from 0.5 to ~3 cm²/V s, which is close to single-crystal mobility [12]. When a cross-linked polyvinylphenol-based copolymer was spin-coated as a dielectric layer, good carrier mobility as large as 3 cm²/V s was reported [332]. OTFTs with a surface-modified alumina dielectric layer showed high mobility of 2 cm²/V s [333]. For alkyl substituted oligothiophenes, the length of the a,a’-substituted alkyl side chains had a notable influence on the TFT performance while the best performance was obtained for molecules with relatively short alkyl chains (2–6 carbons), which had good carrier mobilities as large as 1.1 cm²/V s [334]. Functionalized indolo[3,2-b]carbazole was reported to have mobilities up to 0.12 cm²/V s and a current on–off ratio of 10⁷ [335], and a mobility of ~8 cm²/V s was reported for rubrene [336].

Devices resulting from solution processes generally tend to exhibit poorer performance than those made with thermally evaporated organic small molecular semiconductors, due to their lower crystallinity. As a semiconductor based on small molecules, the conversion of pentacene precursors through heat treatment at 200 °C afforded a highly ordered active layer with a good mobility of 0.89 cm²/V s [337]. Anthradithiophenes that are functionalized with triethylsilyl groups adopt a two-dimensional π-stacking arrangement and exhibit mobilities as high as 1 cm²/V s [338]. Dithiophenetetrathiafulvalene, which forms single crystals driven by π–π stacking with S···S interactions, also showed high mobility of 1.4 cm²/V s [339]. Two symmetrical a,ω-substituted sexithiophene derivatives containing thermally removable solubilizing groups showed overall mobilities as high as 0.07 cm²/V s with on/off ratios of 10⁸ [340]. For polymer semiconductors, especially regioregular polythiophene, a higher molecular weight as well as more strongly π–π interacting building blocks [341] yielded higher mobilities compared with polymers of lower molecular weight. This is in spite of the higher degree of crystallinity of the latter and is due to the fact that charge carriers can travel farther along longer chains before they have to hop to another chain [342]. A polythiophene
A semiconductor incorporating thieno[2,3-b]thiophene, which is stable under ambient conditions, was introduced as a solution processable polymer having a mobility of 0.15 cm²/V s [343]. The carrier mobility is higher in oriented films along the rubbing direction than in isotropic films and can

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**Fig. 23. Examples of organic semiconducting materials for TFTs:**

(a) solution processible pentacene precursor [337], (b) indolo carbazoles [335], (c) dithiophene-tetrathiafulvalene [339], (d) poly(3-hexylthiophene) [341], (e) solution-processed oligothiophenes [340], (f) thienothiophene containing polythiophenes [343], (g) perfluorocarbon-modified polythiophenes [349], (h) metallophthalocyanines [348], (i) carbonyl-functionalized quaterthiophenes [353], (j) trifluoromethylphenyl endcapped materials [351], (k) N-alkyl perylene diimides [350], (l) tricyanovinyl-capped oligothiophenes [354], and (m) ladder polymers [355].
be as high as 0.02 cm²/Vs at room temperature [344]. Poly(3-hexylthiophene) transistors fabricated by spin coating from high boiling point solvents to facilitate the growth of a highly crystalline film exhibited a mobility of 0.12 cm²/Vs [345].

N-type organic semiconductors have recently drawn increased attention because they can be used as n-channel materials of complementary circuits, which are profitable with low power consumption [346]. To get a higher performance from n-type OTFTs, n-channel semiconductors need to have high electron affinities with electron withdrawing groups and also high mobilities, similar to those of p-type semiconductors, as well as stability against atmospheric oxidants such as O₂ and H₂O [347]. Metallophthalocyanines with strong electron withdrawing groups were used in an n-channel active layer that exhibited a mobility of 0.03 cm²/Vs [348]. Electron-deficient perfluoroarene substitution for electron-rich thiophene rings lowered LUMO energies while preserving rod-like molecular architectures, achieving n- and p-type activities and a high n-type activity with a mobility of 0.08 cm²/Vs [349]. Dianhydride or diimide moieties containing naphthalene and perylene derivatives have been actively studied because of their relatively large electron affinities and π-stack structure and π-orbital interactions. OTFTs based on N-alkyl perylene diimides achieved very high saturation electron mobilities as high as 1.7 cm²/Vs by carefully adjusting film growth conditions and linear mobilities of 0.3–0.6 cm²/Vs [350]. Yamashita et al. developed a new π-electron system with trifluoromethylphenyl groups showing n-type performance with electron mobilities of 0.12–0.30 cm²/Vs [351] and thiazole oligomers with trifluoromethylphenyl groups showing very high mobilities of 1.83 cm²/Vs [352]. Quaterthiophenes functionalized with carbonyl groups as electron withdrawing groups [353] and origothiophenes capped with tricyanovinyl groups [354] have also been reported as high mobility n-channel semiconductors and ambipolar transport semiconductors. Babel and Jenekhe introduced conjugated ladder polymers as n-channel active layers through a solution spin-coating process [355]. The field-effect mobility of the electrons yielded mobilities as high as 0.1 cm²/Vs, which is comparable with p-type polymer semiconductors.

Semiconductors including n- and p-type materials have seen big improvements in performance in the past few years. The adoption of complementary structures that incorporate both p- and n-type transistors for OTFTs presents many advantages, including reduced power dissipation and improved noise margins compared to p- or n-type transistors. Organic complementary transistors also have greater robustness in addition to better processability and compatibility with flexible substrates compared to inorganic complementary transistors. Organic complementary circuits using hexadecafluorocopper phthalocyanine (F-CuPc) as the n-type semiconductor and a-sexithiophene (a-6T) as the p-type semiconductor have been introduced [346]. Solution-processed ambipolar organic field-effect transistors, which transport both holes and electrons, were fabricated using polymers based on interpenetrating networks as well as narrow band gap organic semiconductors [356].

6.3.2. Gate dielectric materials

Recently, there has been much interest in the use of new dielectric materials as gate insulators to boost OTFT performance because improvements in the charge carrier mobility of organic semiconductor materials have begun to plateau around the mobility of amorphous silicon TFT [357]. High dielectric constant gate insulators generally are known to accumulate more carriers on the interface of insulators and semiconductors are known to exhibit a low operation voltage [358]. However, Veres et al. [359] reported when a low dielectric constant gate insulator is used for a device, performance is significantly improved with increased mobility, reduced threshold, and lower hysteresis because of reduced energetic disorder and carrier localization at the interface. The surface roughness of an inorganic gate insulator is an important parameter affecting OTFT performance; a rougher gate surface hinders the movement of charges because of the roughness of the valleys and results in smaller pentacene grain size and lower hole mobilities [360]. The evolution of pentacene thin films as revealed by photoelectron emission microscopy showed the growth mechanisms and dynamics of pentacene thin films on the inorganic gate layer [361]. Fig. 24 shows several examples of gate dielectric materials for OTFTs.

Inorganic gate insulators that have high dielectric constant values compared to organic insulators were deposited by anodization to create anodized ultra-thin metal oxides with extraordinarily low leakage, high breakdown field strength, and low-operating voltage [362]. The procedure to produce a polymeric smoothing layer resulted in an order of
magnitude improvement in charge mobility relative to the rough dielectric [363]. The chemical treatment that creates the silicon oxide surface through SAMs of organic trichlorosilanes led to a higher mobility, a 20-fold improvement over the mobility on bare silicon oxide, in a polyfluorene copolymer [364]. The electric dipoles of SAMs with fluorines and amino groups affected the accumulation of holes and electrons in the transistor channel [365]. Phosphonate-linked SAMs have greatly improved electrical properties showing a near-zero threshold voltage [366]. Dielectric interface chemistry was reported to affect n-type performance via interface electron trapping [367].

In addition to their superior compatibility with flexible substrates, polymeric insulators can produce smoother surfaces and allow more freedom to fabricate both top and bottom gate devices and inexpensive large-area applications by solution processes compared to inorganic insulators. Several polymer gate insulators including PI [370], BCB [371,372], poly(vinyl phenol) (PVP) [373], poly(vinyl alcohol) (PVA) [374], silsesquioxane polymers [375], and parylene polymers [376] have been investigated.

**Fig. 24.** Examples of gate dielectric materials: (a) 1,1,1,3,3,3-hexamethyl-disilazane (HMDS) [368], (b) poly(methyl silsesquioxane) (PMSSQ) [369], (c) polyimide (PI) [370], (d) benzocyclobutene (BCB) [372], (e) poly(4-vinyl phenol) (PVP) [373], (f) poly(vinyl alcohol) (PVA) [374], (g) parylene polymer [376], and (h) self-assemblable silane-based materials [377].
previously. The operating voltage and power dissipation of organic devices were dramatically reduced by exploiting the self-assembly of silane-based molecular dielectrics with a thickness of 2.5 nm, providing operating voltages of 2 V or less [377]. Surface-initiated ring-opening methathesis polymerization was used to form thin-film polymer-dielectric layers with thicknesses of < 100 nm to > 2 μm [378]. Marks et al. reported that blending of commercially available polymers and organosilane cross-linking agents affords robust, smooth, adherent, pinhole-free, high-capacitance, low-leakage ultra-thin gate dielectric materials [379]. Gate dielectric multilayers containing a UV-cured PVP-poly(methyl methacrylate) (PMMA) layer and a PMSSQ layer showed improvements in OTFT performance with mobility improved by as much as 50 times to 0.15 cm²/V s and an on/off ratio of 10⁶ [380]. Maliakal et al. [381] used a novel core-shell-nanoparticle based gate dielectric with titanium oxide as the core material and polystyrene as the flexible shell to achieve 3.6-fold enhancement in the dielectric constant and mobilities approaching 0.2 cm²/V s.

The solution processabilities of electrodes, semiconductors, and dielectrics for OTFTs have propelled the current surge of research with their probabilities of low-cost and large-area manufacturing coupled with their outstanding features of being physically compact, lightweight, and flexible. Sirringhaus et al. [382] developed the direct inkjet printing of all polymer transistor circuits, including via-hole interconnections based on solution-processed polymer conductors, insulators, and self-organizing semiconductors. They also fabricated a polymer-based transistor device with a channel length of 500 nm by surface-energy-assisted inkjet printing [383]. Halik et al. [384] developed a process for the fabrication of fully patterned all-organic pentacene TFTs on flexible polymer substrates using PEDOT/PSS for the gate electrode and for the source and drain contacts and cross-linked PVP as the gate dielectric layer. All jet-printed polymer TFT [385] and a self-aligned self-assembly process [386] have also been reported.

6.4. Others

Transparent oxide semiconductors have recently been proposed as active materials for TFTs while transparent electronic devices formed on flexible substrates are expected to meet emerging technologi-
7. Encapsulation

In the previous section, a multilayer barrier structure on plastic substrates was demonstrated, which protects devices, especially OLEDs, from moisture or oxygen [39]. A single layer of an inorganic compound such as SiO₂, Al₂O₃, SiNₓ, or MgO can be adequate as a barrier layer for LCDs. A very dense and amorphous single layer also can be used as an encapsulant for an OLED on glass. But in a flexible display, it may be difficult to maintain the integrity of a single-layer barrier, especially if it is composed of oxides or nitrides because they tend to crack readily under tensile stress. Multilayer barriers present the most robust and forgiving properties in this regard. A defect in one layer does not affect or does not add to a defect in another layer [11].

To completely prevent gas ingress into the devices, two kinds of gas sealing structure are needed on the top and bottom sides. This gas sealing technology is called encapsulation or passivation. To date, most OLED devices have been encapsulated by sealing the device in an inert atmosphere such as nitrogen or argon using a metal that can be secured by a bead of UV-cured epoxy resin. And a getter such as calcium oxide or barium oxide is incorporated into the package to remove residual water incorporated in the package or diffusing through the epoxy seal over time [27]. However, this kind of encapsulation is impossible to apply to the flexible display system.

There are a couple of ideas considered as next generation encapsulation technologies for flexible displays as substitutes for the metal can [27]. One is to use barrier-coated polymer films, which have a transparent or opaque organic/inorganic multilayer structure, in place of the metal can. This approach has the advantages of allowing more flexible process conditions as well as robust mechanical properties. Another is a multilayer thin-film encapsulation where multilayer thin films are directly deposited on the OLED structures, providing a thinner device structure compared to the polymer film encapsulation. We have already discussed barrier-coated polymer films in the previous section. In this section, thin-film encapsulation will be described. The required conditions for thin-film encapsulation of OLED displays include high transparency for top emitting OLEDs, low-stress materials, low processing temperature, densely packed and highly conformal coating, pinhole-free coating and compatibility with the active components of OLEDs.

The multilayer barrier structure consists of transparent organic layers that planarize the substrate surface and decouple defects in the oxide as well as allow for greater flexibility in an otherwise rigid coating plus transparent inorganic metal oxide layers that act as a practical diffusion barrier. Chwang et al. [393] encapsulated passive matrix, FOLEDs on flexible plastic substrates using an organic/inorganic multilayer barrier encapsulation technology. The displays, based on electrophosphorescent OLED technology, were deposited on barrier-coated plastic substrate and hermetically sealed with an optically transmissive multilayer barrier coating encapsulation with alternating Al₂O₃ and polyacrylate layers. Preliminary lifetime to half initial luminance of the order of 200 h was achieved on the passive matrix driven encapsulated 80 dpi displays, and a 2500 h lifetime was achieved on a dc tested encapsulated 5 mm² FOLED test pixel. Visser et al. fabricated similar alternating stacks of polymer and low-temperature inorganic oxide layers with a plasma-protective buffer deposited between the OLED device and the barrier structure via the Vitex system, which demonstrated water permeation in the range of 1 × 10⁻⁶ g/m²/day [394]. Van Assche et al. [395] investigated the a-SiNₓ:H deposition process with only 3 plasma deposited silicon nitride layers separated by a thin organic layer showing a water permeation rate of below 10⁻⁵ g/m² per day and OLED lifetimes of over 500 h at 60 °C and 90% RH.

Lifka et al. [396,397] proposed a novel multilayer stack of silicon nitride–silicon oxide–silicon nitride–silicon oxide–silicon nitride (NONON) as thin-film encapsulation. They used a combination of PECVD silicon nitride and PECVD silicon oxide. In this case, the silicon oxide changes the chemical interface of a defective area and therefore enables the growth of silicon nitride, reducing the number of pinholes through stacking of these layers. The water permeability of a single NON stack deposited at 85 °C was measured to be less than 1 × 10⁻⁶ g/m²/day. Yoshida et al. [398] encapsulated a full-color OLED display using SiON as a moisture barrier film on the substrate and SiN as a passivation film on the device. The display was approximately 0.2 mm thick, weighted approximately 3 g, and it was bendable. The estimated half-luminance decay time was more than 5000 h with an initial luminance of 1000 cd/m², which is equivalent to that of a device.
on a glass substrate. Akedo et al. [399] developed plasma-CVD SiNₓ/plasma-polymerized CNₓ:H multilayer films to improve the longevity of passivated OLEDs for automobile applications. The films had highly effective barrier against moisture even at high temperatures because the thermal stress of the films was released by the soft CNₓ:H layers and no cracks were produced.

Kim et al. [61,62] investigated a variety of inorganic materials and inorganic composites as passivation materials on polymer substrates using the electron beam evaporation system. They showed that the MgO thin film had a lower WVTR value than any other inorganic thin film, and that the WVTR of inorganic films can be dramatically minimized by adopting an inorganic composite as a passivation material.

8. Roll-to-roll (RTR) processes

The current method of producing display panels, circuit boards, and other electronic devices is a batch process using conventional vacuum deposition and lithography pattern technologies on silicon wafers or glass substrates. On the other hand, the RTR process is currently a well-known technology to the film manufacturer in diverse areas such as newspapers, labels, etc. [40].

RTR processing offers a significant advantage compared with the conventional batch process, as it increases throughput by allowing for greater levels of automation and by eliminating the overhead time involved in loading and unloading panels into lithographic imaging tools and chemical processing stations. This leads to lower contamination levels and, thus, higher yields due to the minimal human handling that is needed to process the substrates [5]. However, there are many challenges including display backbone manufacturing, where electronics are fabricated on a plastic substrate with precision and high yield, and fabrication of TFTs for active-matrix backplanes.

Current research includes two kinds of approaches: the transfer of current processes from glass substrates to new RTR processes or the development of new technologies available for RTR processes [400]. However, there are many challenges to achieving real RTR processes [401,402].

Fig. 25. Technical challenges for flexible displays.
9. Conclusions

Flexible displays will be the ultimate choice in the future in the display industry because of their many advantages including convenience, portability, and large-size applications as well as low-cost production through RTR processes.

However, there are many challenges to surmount, as summarized in Fig. 25. The thermal stability, solvent resistance, thermal expansion coefficients, and gas absorption of polymer substrates need to be improved so that they are as good as glass substrates. OLEDs require almost perfect encapsulation against water vapor. Electrodes such as anodes or cathodes should endure repeated stress and be available for web coating. Active materials of the displays should demonstrate high performance and stability as well as solvent processibility applicable for inkjet processes. With regard to TFTs, low-temperature processes need to be developed and their performance and stability should be improved to apply for TFTs as well as OLEDs.

With good properties and processibility, polymers have attracted the attention of many scientists as potential flexible display materials, including transparent substrates, transparent electrodes, and active materials for OLEDs, LCDs and OTFTs, dielectric materials, and coating materials. All polymer-based flexible displays are even being investigated.

In this article, we have reviewed the recent progress in polymer materials that are potential candidates for use in flexible displays. We believe this review will give insights to readers on what, where, and how polymer materials are used and the challenges yet to be overcome in flexible display.

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