Recent Progress in Materials and Devices toward Printable and Flexible Sensors

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Printable electronics present a new era of wearable electronic technologies. Detailed technologies consisting of novel ink semiconductor materials, flexible substrates, and unique processing methods can be integrated to create flexible sensors. To detect various stimuli of the human body, as well as specific environments, unique electronic devices formed by “ink-based semiconductors” onto flexible and/or stretchable substrates have become a major research trend in recent years. Materials such as inorganic, organic, and hybrid semiconductors with various structures (i.e., 1D, 2D and 3D) with printing capabilities have been considered for bio and medical applications. In this review, we report recent progress in materials and devices for future wearable sensor technologies.

1. Introduction

Printing electronics combines several important technologies, such as semiconductor devices manufactured by various printing processes on flexible (sometimes stretchable) substrates. Today, with increasing interest in both printing technology and electronic devices, new innovations combining these two great technologies have been designed to produce novel electronics through low-cost and large-area printing processes. A simple historical roadmap is shown in Figure 1.[1–14]

Printed electronics should include the following key components: i) a flexible (circuit) board to be used as the substrate, ii) the use of inks (semiconductors), and iii) a continuous-printing processing technique (e.g., the slot-die coating process). Historically, the first use of the term “printed electronics” dates back to early 20th century.[15] The technology was initially an attempt to fabricate flexible conductors, which could be applied to various materials while simplifying the interconnections within the complex electronic circuit.[15] By 1950, the printed circuit board (PCB) was developed, which involves copper sheet lamination. Recently, this lamination technology has also been used to fabricate antenna wires for commercial radio-frequency identification (RFID).[16]

The contemporary concept of printed electronics, which includes conductors, semiconductors, and insulators using inks, was initially proposed in the early 1990s. At that time, the goal was to deposit conducting wires using conductive ink. By 1997, Bell Lab had produced a transistor using screen-printing technology for the first time,[17] and, in 1998, UCLA demonstrated an inkjet-printed logo with polymer light-emitting devices (PLEDs).[18]

Printing technology encompasses a variety of processing techniques, such as spray-coating, stamping, and inkjet-printing, all of which enable roll-to-roll processing. Furthermore, recent developments in transfer printing have enabled the transfer of traditional silicon-based devices onto flexible circuit boards or other desirable types of flexible substrates.[19]

Recently, printable technology has found use in various applications, including healthcare, displays, memory, and sensors, showing great promise for future technology.[19,20] This platform enables information to be shared through attaching or implanting the technology in clothes, clocks, and even human skin.

In order to realize feasible wearable technology, significant progress in printing technology is required. At this point, three-dimensional (3D) printing technology is one of the best candidates. If a specific system can be developed that performs a particular task based on information at home by consolidating materials and ideas, it would be a major advancement for future printing technology.[21–23]

In this review, we will discuss the progress of printable sensors, regarding flexible sensor materials and devices. A comprehensive review of printing materials, structures, processing methods and applications will be given. In particular, we will address the technologies employed in user-friendly electronic devices, including wearable technologies. The most fundamental materials and processes used for flexible substrates pertaining to wearable devices will be discussed, followed by recent trends in flexible printable electronic devices including photonic, touch, and biological sensors. Finally, we address the use of 3D printing in designing flexible sensors, which has recently gained popularity.
2. Platform Considerations for Flexible Electronics

2.1. Materials

One of the most important abilities of flexible devices is their mechanical stability under folding or bending without incurring physical damage, a low elastic modulus allowing for such mechanical properties of the devices.[24] Printed material candidates for flexible devices should not only have an appropriate elastic modulus, but also a good electrical performance that can be applied over continuous large-areas at a low-cost. Here, we review materials with conductors, semiconductors, and dielectrics through printed and flexible devices, and also discuss flexible substrates.

2.1.1. Flexible Substrates

The materials and corresponding properties used in flexible circuit boards closely resemble those of printed electronic devices (Table 1), some of which are crucial elements for determining device fabrication methods. The adhesion and radius of curvature are important factors in selecting a flexible-sensor application process. The circuit board’s tensile strength, allowable temperature of desired flexible substrates, and thickness are likewise significant factors for roll-to-roll processing and transferring techniques. Various flexible substrates can be selected for sensor applications. Polyimide (PI), which has a high thermal and chemical resistance, is the most widely used flexible substrate. However, its application in transparent devices is limited by its intrinsic color. Lastly, transparent PI materials have been realized, enabling the production of high-performance sensor devices.[25]

In addition to flexibility, stretchability is a recent feature of interest for electronic-skin (E-skin) and wearable electronic applications. Among device fabrication methods, the most basic and prevalent approach involves the use of poly(dimethylsiloxane) (PDMS),[28] which remains the best choice for stretchable sensor substrates on account of its remarkable flexibility and high thermal and chemical resistance. Most recently, research has been conducted to incorporate stretchability into the sensor structure itself through interconnections and structures such as nanowires and specially designed electrodes for increased flexibility.

2.1.2. Conductors

Conducting materials are the most important factors of electronic devices as they allow for connection between various components of the device. Printable conductors are highly desirable to avoid the need for photolithography and also to reduce costs.[27] Furthermore, simple solution-based conducting inks can reduce the use of toxic materials. Many kinds of conducting materials and processing techniques have been studied to realize low resistances, low processing temperatures, flexibility, and stretchability. Nanoparticles, nanowires, nanotubes, and thin films can be selected as core materials for specific processing environments.[28–34] In addition, these materials should be processed at low temperatures below 150 °C. Among the potential candidates, metal nanoparticles (i.e., Al, Ag, Au, and Cu) have been considered to be the best for electrical wiring and printing processes due to their ability to form films at low temperatures, while providing good conductivity.[35–38] Moreover, nanoparticle-based inks provide the ability to create precise patterns. On the other hand, one-dimensional (1D) and two-dimensional (2D) materials are difficult to pattern with
good electrical properties.\cite{39,40,41} Recently, these materials have attracted attention in highly flexible and stretchable applications due to their mechanical properties.\cite{42,43} Nanowires have also been considered for transparent conductive materials for solar cells, organic light-emitting diodes (OLEDs), and wearable sensors.\cite{44,45,46} Langley et al. reported representative material properties of printable conductors such as metal oxide, graphene, carbon nanotubes (CNTs), silver nanoparticles (AgNPs), and silver nanowires (AgNWs).\cite{29} With the exception of AgNPs, these materials can be used as transparent conductors. Each material has strengths and weaknesses that can be utilized for specific applications. Nanowire networks are highly compatible with the printing process and a low-temperature processing of nanowire networks is allowed for flexible substrates. Regarding film roughness, nanowire networks have highly rough surfaces compared to metal oxides and Ag films. A rough surface could limit applications in devices such as OLEDs, due to electrical non-uniformity and pin-hole generation. However, some applications (e.g., chemical and biological sensors) do require high surface roughness and surface-to-volume ratio, as well as unique mechanical and electrical properties. In particular, these materials are useful for sensor applications owing to high surface-to-volume ratios and flexibility.

Electrical and mechanical properties of conducting materials have significantly improved for printable electronics and they have been inspiring other printable materials (semiconductors and/or insulators) to develop combined future sensor applications.

### 2.1.3. Metal-Oxide-Based Semiconductors

Metal-oxide-based semiconductors have been widely used in various applications, such as sensors, field-effect transistors (FETs), catalysts, solar cells, and energy harvesting.\cite{48,49,50,51,52,53,54,55}
Chemical, optical, and mechanical sensors have been especially realized through the use of metal-oxide semiconductors. The chemical sensing ability of metal oxides is well known, and originates from the change in conductivity of the materials by absorption or desorption of a gas on the surface. Metal oxides also have the advantage of providing fast film deposition over large areas using simple methods. The simplicity of printable metal-oxide semiconductors has enabled the fabrication of low-cost sensors with high sensitivity and reliability, as compared to traditional Si technologies.

Sensors based on metal-oxide semiconductors are divided into two- and three-terminal structures. Most sensors are constructed using two terminals, consisting of two electrodes and a metal-oxide semiconductor. Three-terminal transistors are used in specific applications such as high-sensitivity sensing, active-matrix operation, and multifunctional devices. The exact sensing mechanism of metal-oxide semiconductors is still questionable. However, partially accepted mechanisms describe trapping of electrons by adsorbed molecules, inducing band banding that is responsible for changes in conductivity, as shown in Figure 2. Many metal-oxide semiconductors have been studied for sensors. These materials are divided into two groups: transition-metal oxides and non-transition-metal oxides. Representative transition-metal oxides such as TiO$_2$, V$_2$O$_5$, and WO$_3$ are used as photoanodes, catalysts, and chemical detectors. Unlike transition-metal oxides, non-transition-metal oxides as ZnO, SnO$_2$, In$_2$O$_3$, and Ga$_2$O$_3$ show good conductivity and high sensitivity. These materials can form the channel layer for the transistors and are useful for multifunction sensors. Composite structures of ZnO–SnO$_2$ have shown higher sensitivity than purely binary oxide structures, where each individual component plays a specific role that leads to synergetic sensing effects. This synergistic effect occurs at heterojunction interfaces between the composite materials, allowing different catalytic actions. Therefore, sensors based on metal-oxide semiconductor are considered desirable for printable sensor applications.

### 2.1.4. 1D-Nanostructure-Based Semiconductors

Since the 1990s, semiconductor nanowire research has become one of the most active research areas owing to its unique properties. In particular, the one-dimensionality of nanowires presents solutions to some key problems, such as the reduction of lattice mismatch, for which conventional thin-film technologies have been criticized. In addition, nanowires are useful for laser applications due to strong laser action without reflectors and long carrier lifetime due to electron confinement effects. Unusually giant piezoresistive effects in Si nanowires were reported. Also, a significant change in thermal conductivity presents the possibility of nanowire use in other applications such as thermoelectric devices. According to Li et al., strong phonon boundary scattering at the nanowire surface can reduce the thermal conductivity in Si nanowires. Also, Hochbaum et al. reported that the reduction in thermal conductivity can be further decreased almost to the amorphous limit by a surface-defect engineering process, which broadens possible applications. The Young’s modulus of nanowires is size-dependent due to surface stress effects. In addition, elastic properties vary depending on the type of materials, the concentration of defects, and the crystallographic orientation.

Wu et al. reported a method to measure the mechanical properties of nanowires through an atomic force microscope tip, and discovered that the yield strength of gold nanowires is 100 times that of bulk materials. They also proposed that nanowire systems had strain hardening effects due to the finite material volume and grain size in nanowires. Furthermore, numerous studies on silver-nanowire-based stretchable and flexible devices have been conducted. Silver nanowires have been regarded as strong candidates to overcome the limitations of indium-tin-oxide (ITO) as transparent electrodes because of their transparent, conductive, and stretchable properties.

Printed devices based on inorganic nanowires have also been developed as grown nanowires are dispersed in organic solvents. Here, we introduce four representative nanowire-coating methods: fluidic alignment, Langmuir–Blodgett (LB), bubble-blown techniques, and electric-field-directed assembly. Huang et al. reported the fluidic alignment technique to assemble and control the nanowire alignment. The key aspects to control the assembly are the fluidic flow rate and time. Depending on the flow rate and time, the angular spread and coverage of nanowires can be controlled. Through this method, conductive networks...
with individually addressable device functions have been successfully demonstrated. In 2003, Yang and Xia introduced the LB approach to assemble close-packed and well-aligned monolayers of silver nanowires. These nanowire monolayers were able to work as substrates for surface-enhanced Raman spectroscopy (SERS). In 2007, Yu et al. described a blown-bubble technique that allowed for uniformity in nanowire alignment, controllable density, and scalability. They utilized a blown-film extrusion, which is highly compatible with polymer films. First, a homogeneous polymer suspension of nanowires was prepared and expanded until bubbles were formed at a controlled pressure. Subsequently, the bubble films were transferred onto the desired substrates. Through this method, they successfully demonstrated large, scalable electronic devices. Based on these methods for printable nanowire films, Fan et al. suggested a roll-to-roll (R-to-R) printing set-up for nanowire-based electronics, as shown in Figure 3.

In addition, Lee et al. recently reported a way to synthesize MoS$_2$ nanowires via a solution process. In the paper, they explained key factors to control the kinetics of growth of MoS$_2$ nanowires, such as the evaporation speed, humidity, and solution concentration. MoS$_2$ nanowires were formed in three different shapes: films, dendrites, and wires, depending on those three factors (Figure 4). Therefore, it is possible to design nanowire-based flexible electronics through those approaches.

### 2.1.5. 2D-Nanostructure Based Semiconductors

After Geim’s first paper about graphene in 2004, many researchers and scientists have taken tremendous efforts to attempt to understand its fundamental properties and technological potential. Unlike other 3D materials, this material can be explained using the Dirac equation, which means that it behaves as massless Dirac fermions. It could also give rise to long-range ballistic transport, in which electrons can move without scattering over large distances, leading to unique electrical and thermal characteristics. In addition, its mechanical hardness is greater than that of diamond, which is considered to be one of the hardest known materials, making graphene a powerful material of high interest for flexible devices. Because of these outstanding properties, it has been regarded as a new future material in various fields and thus, numerous graphene-based applications are discussed in papers. In addition, the advent of transition-metal dichalcogenides (TMDs) has led to much attention in the field of two-dimensional nanomaterials. With the advantage of a monolayer structure, few TMDs, including MoS$_2$ and WS$_2$, have a bandgap. TMDs are layered materials, and when reduced to a single layer, they change from an indirect bandgap to a direct bandgap. Of course, there are other types of TMDs such as metallic NbS$_2$ and VSe$_2$, semi-metallic WTe$_2$ and TiSe$_2$, insulating HfS$_2$, and superconducting NbSe$_2$ and TaS$_2$, that have been actively studied.

There are several ways to synthesize graphene and TMDs such as by mechanical exfoliation and chemical vapor deposition. Here, we only focus on methods available for printing processes. In the case of graphene, it can be prepared in a liquid-phase solution. The process involves chemical oxidation of graphite to graphite oxide. Graphite oxide has been mainly produced by the Brodie method, the Staudenmaier method, and the Hummers method. These three methods involve oxidation of graphite in the presence of strong acids and oxidants, and the level of oxidation can vary on the basis of the method, the reaction conditions, and the precursor. After obtaining graphite oxide, it can be readily exfoliated to individual graphene oxide (GO) sheets by ultrasonication. Graphene oxide can be converted back to graphene by chemical reduction, for example, by using hydrazine. This mechanism consists of a combination of hydroxyl groups and hydrogen atoms through a dehydroxylation reaction. After the reduction, the oxygen–carbon bonding is removed and graphene sheets are obtained. The product, however, is typically not entirely reduced, as some functional groups remain.

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**Figure 3.** Illustration for roll-to-roll printing machine for nanowire electronics fabrication. The process includes a patterning process, a transfer, and assembly for nanowire-based transistors having semiconductor channels, source/drain electrodes, and gate electrode. Reproduced with permission.

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groups remain. Therefore, the quality of the graphene produced by this process is not perfect. Despite the non-pristine nature of solution-processed graphene, there are some applications for this kind of graphene, including biological or chemical sensors, as the OH group in the graphene can be replaced with other functional groups to detect target molecules.\textsuperscript{[92]} Also, Coleman et al. introduced a liquid-exfoliation method for TMD materials including MoS\(_2\), WS\(_2\), MoSe\(_2\), TaSe\(_2\), NbSe\(_2\), NiTe\(_2\), and Bi\(_2\)Te\(_3\).\textsuperscript{[96]} They studied many solvents to exfoliate each material and investigated suitable solvents for each material. After exfoliation, the sheets were spray-coated onto the target substrate and the film quality was confirmed by several characterization methods. In 2011, Smith et al. described a liquid-exfoliation method based on aqueous surfactant solutions.\textsuperscript{[97]}

2.1.6. Dielectrics

The electrical performance of FETs depends on the dielectric properties and low interface defect densities between a dielectric and a semiconductor film. Printable dielectric materials used for the gate insulator of FETs include SiO\(_2\), Al\(_2\)O\(_3\), HfO\(_2\), polymers, and organic/inorganic hybrid dielectrics.\textsuperscript{[98–101]} Most inorganic dielectrics require the use of a high-temperature annealing process due to the necessity of high-density films and low leakage currents, and because decomposition of organic compounds from solution occurs readily. On the other hand, organic dielectric materials such as poly(vinyl phenol) (PVP) and poly(dimethylsiloxane) (PDMS) are highly desirable due to the low temperatures required, their high dielectric strengths, and their flexibility. Several dielectric materials and corresponding dielectric constants are shown in Table 2. Compared with high-\(k\) metal-oxide dielectrics, polymer dielectrics have relatively low dielectric constants. Therefore, enhancing the dielectric constant

![Figure 4. Scheme of a solution process for MoS\(_2\) films, dendrites, and nanowires. The MoS\(_2\) structures change depending on the evaporation speed and concentration of the solution, and the humidity. Reproduced with permission.\textsuperscript{[74]} Copyright 2015, John Wiley & Sons, Inc.](image-url)

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric constant ((k))</th>
<th>Material</th>
<th>Dielectric constant ((k))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO(_2)</td>
<td>25</td>
<td>Polymide</td>
<td>3.0</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>10.1</td>
<td>Poly(vinyl phenol)</td>
<td>3.5</td>
</tr>
<tr>
<td>HfO(_2)</td>
<td>25</td>
<td>Poly(dimethylsiloxane)</td>
<td>2.6</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>3.9</td>
<td>Polyethylene</td>
<td>2.4</td>
</tr>
<tr>
<td>PVDF</td>
<td>6.0</td>
<td>Polystyrene</td>
<td>2.5</td>
</tr>
</tbody>
</table>
is necessary to improve device performances of polymer-based dielectrics. Hybrid structures, such as high-k BaTiO₃ nanoparticle-embedded polymer dielectrics, have shown enhanced dielectric constants and leakage currents. Highly stable dielectric properties that can endure strained environments are ultimately required to employ flexible and stretchable sensor applications.

2.2. Processing of Flexible Substrates

Due to the nature of the flexible substrate, the processing conditions are subject to several limitations, as follows: i) low processing temperatures, ii) low coefficients of thermal expansion (CTE) and high surface roughness of the films, and iii) permeability to diffusion of oxygen and water.

First, the processing temperatures must be considered since the glass-transition temperature of flexible substrates is much lower than that of rigid substrates. For example, polyimide (PI) has a glass-transition temperature \( T_g \) between 360 °C and 410 °C. Other polymer substrates have \( T_g \) even lower than that. As such, many conventional semiconductor processes are not feasible, and if used, can compromise device performance.

Second, incompatible CTEs should be considered. Flexible substrates usually have a CTE of a higher magnitude higher than that of inorganic materials. Poor dimensional stability with varying processing temperatures limits patterning resolution, causing overlay registration or alignment problems that restrict the scalability of flexible electronics. Also, significant CTE differences leave residual stresses between the substrate and film, resulting in lamination, failure, and a shortened lifespan. Surface roughness is also one of the important factors to be considered. Standard polymer substrates have a high density of bumps and pinholes on the surface. Processing on polymer substrates at moderate temperatures also results in increased surface roughness due to the migration of oligomers to the surface. This roughness degrades device performance and reduces the yield. Figure 5 demonstrates polyimide surface defects as well as a thin, smooth coating, serving as a clean, impermeable interface. Lastly, permeability to diffusion of oxygen and water is an issue to be addressed. Unlike glass or silicon, polymer substrates do not provide sufficient protection to permeants. Encapsulation is required, as exposure to environmental moisture will degrade the device performance.

For surface roughness and the permeability to diffusion of oxygen and water, many inorganic/organic multilayered thin films have been proposed and demonstrate good planarization coating, as well as permeation barriers. In this section, we will mainly focus on novel processing technologies that reduce the processing temperatures of flexible substrates.

2.2.1. Amorphous Metal-Oxide Semiconductors

Metal oxides, especially transparent conducting oxides (TCOs), have been known for decades for wide applications...
in optoelectronic devices.\textsuperscript{113–115} Since the discovery of amorphous indium-gallium-zinc oxide (IGZO),\textsuperscript{116} metal-oxide semiconductors have attracted attention of both academia and industry as a replacement of silicon in active-matrix displays and emerging flexible, wearable electronics.\textsuperscript{117}

With proper selection of post-transition-metal cations, metal-oxide semiconductors have a high electron mobility due to the large s-orbital overlap.\textsuperscript{118} Due to the spherical symmetry of the s-orbital, the amorphous states can provide comparable electron mobility to the crystal states, which can be considered as a large advantage of amorphous metal-oxide semiconductors (AMOS).\textsuperscript{119} The high tolerance of structural defects makes low-temperature solution processing a convenient and feasible approach to deposit films.\textsuperscript{27,120,121}

Traditionally, precursor solutions are made of metal salts dissolved in organic solvents with various additives acting as ligands to improve solubility and prevent hydrolysis.\textsuperscript{122} Furthermore, these coordinated complexes slow down the sol–gel processing to form uniform films on the substrate. To achieve low-temperature processing, alkoxide systems\textsuperscript{123} and combustible methods\textsuperscript{124–126} have been proposed to reduce the activation energy required to complete the chemical conversion. Other forms of energy such as ultraviolet,\textsuperscript{127} microwave,\textsuperscript{128} infrared radiation,\textsuperscript{129} and high pressure\textsuperscript{130} have also been incorporated with an annealing process to reduce the thermal budget. Furthermore, organic salts/solvents inevitably bring in carbon impurities, which hinders the material quality. Several aqueous precursor systems\textsuperscript{131–133} have also been explored, showing comparable results at much lower processing temperatures (as low as 200 °C). Also, aqueous precursors provide reduced viscosity, which can result in ultrathin metal-oxide films. The small thickness yields lower stiffness and interfacial stress, allowing integration of flexible electronics with smaller bending radii. However, low viscosity also limits the processing options.

2.2.2. Organic Semiconductors

Organic electronics are based on small molecules or polymers, while charge transport is dependent on $\pi$-bonding overlapping and hopping mechanisms.\textsuperscript{134} Organic semiconductors can be deposited by vacuum evaporation (small molecules) or solution processes (polymers or small molecules), while solution-based techniques are more suitable for low-cost, large-area deposition. Unlike inorganic semiconductors, where a high processing temperature is required, organic semiconductors only need solvent evaporation after solution deposition. Low-processing-temperature compatibility with various plastic substrates, combined with intrinsic mechanical flexibility, makes organic semiconductors suitable for flexible electronics.

Conventionally, the crystalline domain of small-molecule-based thin films and the transistor feature size usually have similar length scales, causing severe grain-boundary scattering and variation from device to device.\textsuperscript{135} Although polymer-based thin films have much smaller crystalline domains and better uniformity, the complicated interactions between polymer chains make sheet-like lamellae structures more difficult to achieve, resulting in lower field-effect mobility.

The biggest issue in organic electronics is the poor device performance resulting from the nature of the disordered film and hopping conduction, which can be improved with stacking of the conjugated backbone. To facilitate charge transport, the active layer would have $\pi$-conjugated polymers with $\pi-\pi$ stacking in the direction of current flow. Aside from molecular design, the detailed deposition technique also affects the formation of self-organized ordered structures. To improve the degree of self-organization, a slow annealing is proposed to control the film growth rate.\textsuperscript{136} For example, high-boiling-point additives, such as diiodooctane (DIO), are added to slow down the evaporation of solvents.\textsuperscript{137} Besides self-organization, other approaches have been used to try to align the polymer chain by substrate patterning or shearing. For example, surface modification prior to the deposition of channel materials, based on self-assembled monolayers (SAMs), can affect the nucleation and growth of organic semiconductors, dramatically impacting semiconductor crystalline domain size and carrier mobility.\textsuperscript{138,139}

Other approaches to modify molecular packing and alignment include zone-casting,\textsuperscript{140} dip-coating,\textsuperscript{141} droplet-pinned crystallization,\textsuperscript{142} and solution-shearing methods.\textsuperscript{143–145} A unique method to create a single-crystal pattern is using microcontact printing,\textsuperscript{146} which will be discussed later. However, since translating these small laboratory results into reliable and large-area manufacturing remains challenging, there is still a long way to go for organic electronics.

2.2.3. Transfer and Stamping

Another method for the processing of flexible electronics is called the transfer and stamping process. Instead of processing directly onto a flexible substrate, devices are fabricated onto a rigid substrate and later transferred onto the flexible substrate. The key procedures, as shown in Figure 6, involve the fabrication of a high-quality semiconductor on the source substrate, removal from the carrier substrate, transfer of elements with the use of an elastomeric stamp, and removal of the stamp. This technology can be applied to various nanomaterials, such as metal oxides,\textsuperscript{147} CNTs,\textsuperscript{148–150} graphene,\textsuperscript{151} silicon,\textsuperscript{18} organic materials,\textsuperscript{152} and compound semiconductors.\textsuperscript{153–156} These procedures can be repeated to allow 3D stacking of heterogeneous integration,\textsuperscript{157,158} demonstrating multifunctional sensing systems.\textsuperscript{159} With the capability of delivering nanomaterials to selective areas, transfer printing can disperse nanomaterials over large areas in material-efficient layouts. Furthermore, devices can be transferred on broad classes of substrates, even paper,\textsuperscript{159} and stretchable elastomers.\textsuperscript{160}

One of the most attractive points is that the transfer and stamping process allows for a high-temperature process since the pre-transfer process is completed on a rigid substrate. Thus, devices based on the transfer process promise high performance and reliability. On the other hand, it is accompanied by some disadvantages, such as complexity and high cost. Therefore, we can further develop the field of flexible electronics, considering both the advantages and disadvantages.
2.3. Mechanics for Flexible Devices

There are two different scenarios under a bending test. The first mechanical model is based on the assumption that the thin film covers the entire substrate; we call it the simple mechanical model. Another model explains the mechanical failure accounting for the effects of film edges and finite device sizes, removing the assumption of the first model. The second model suggests three different failure modes: cracking, slipping, and delamination. Based on these different modes, we can understand failure mechanics for flexible devices. In addition, conformal devices have recently attracted attention for flexible electronics. In Section 2.3.3, we cover the mechanics of conformal devices, such as the stiffness calculation and the adhesion-energy calculation.

2.3.1. Simple Mechanic Models

Here, we discuss the simple mechanical model for films subject to bending on a substrate.\[161\] Figure 7 illustrates a schematic model for a film on foil under bending. To put it simply, if the foil-substrate and the film have identical Young’s moduli \(Y_s = Y_f\), labels the strain at the surface of films can be given by:

\[
\varepsilon = \frac{h_f}{2R} (1)
\]

However, in the case of different Young’s moduli \(Y_s \neq Y_f\), the strain at the top surface of the films can be described by:

\[
\varepsilon = \left(\frac{h_f + h_s}{2R}\right) \left(1 + 2\eta + \chi\eta^2\right) / \left(1 + \eta + 1 + \chi\eta\right) (2)
\]

where \(\eta = h_s / h_f\), \(\chi = Y_s / Y_f\), and \(h\) is each thickness. In addition, if devices are placed in a neutral mechanical plane (NMP), we can develop strain-free devices under bending conditions. The simplest way to set the device into an NMP is to use an encapsulation layer. If the stiffness of the device is negligible, the devices can be situated where \(Y_e\) and \(h_e\) are young’s moduli and thickness of the encapsulation layer:

\[
Y_e h_e^2 = Y_f h_f^2 (3)
\]

Through the above mechanics, we can understand how much strain the devices suffer under bending. However, the calculation assumes that the film covers the whole substrate, although this situation is not always followed. In the next section, we will discuss more-general situations.

2.3.2. Three Different Failure Modes

Many transistors have patterned channel layers, which means that the channel layers do not cover the entire substrate. In such a case, the patterned layer size and edge can critically affect the mechanical properties of devices. We refer to a study...
by Park et al. to explain the three different failure models.\[162\]

We adapted a beam theory, which includes all key influences to explain this mechanical modeling. The substrate is defined as a beam of length $L$ that subject to a compressive force. If the $dL/L$ is over a critical strain $\pi^2 h_s^2/12L^2$, where $h_s$ is the thickness the beam starts to bend. While $dL/L$ increases, the axial compressive force can be expressed by:

$$F = \pi^2 E h_s^4/12L^2$$

where:

$$E_s = E_s/1 - \nu_s^2$$

$E_s$ and $\nu_s$ represent the Young’s modulus and the Poisson ratio of the substrate respectively. The device structure consists of an active film, an adhesive layer, and the substrate. Here, the active film and substrate are modeled as beams, whereas the adhesive layer is modeled as a shear lag model because of its low stiffness compared with the active film and the substrate. Since the adhesive layer plays a role in releasing the stress applied from the substrate to the active film, the surface strain of the active film can be much smaller than the nominal strain $\epsilon_{nom}$, defined by $h_s/2R_{nom}$, where $h_s$ is the substrate thickness.

To understand what happens during bending, we need to determine the maximum stress in each case. In the case of slip and delamination at the interface, an understanding of the shear and peeling stresses between the active film and adhesive layer is required. The maximum shear stress is expressed by:

$$\tau_{max} = \frac{\pi G_a h_s}{3h_s L} \left( \frac{dL}{L} - \frac{\pi^2 h_s^2}{12L^2} \right)$$

where $G_a$ is the shear modulus of the adhesive layer, and:

$$\lambda = \frac{G_a}{h_s \left( \frac{1}{E_s h_s} + \frac{1}{E_t h_s} \right)}$$

Thus, the slip between the active film and the adhesive layer happens when the maximum shear stress reaches the critical shear strength, which depends on the given information.

In addition, the maximum peeling stress between the active film and adhesive interface is expressed by:

$$\sigma_{max} = \left[ \beta G_a h_s \left( \frac{2\chi \lambda}{\lambda^2 + \frac{\lambda}{2}} + \frac{\lambda}{\lambda^2} \right) + E_s \right]$$

$$\times \frac{\pi}{\chi' h_s L} \left( \frac{dL}{L} - \frac{\pi^2 h_s^2}{12L^2} \right)$$

$$\chi = \left[ \frac{E_s}{h_s} \left( \frac{1}{E_s h_s} + \frac{1}{E_t h_s} \right) \right]^2$$

$$\beta = \frac{3(1 - \nu_s) \left( \frac{1}{E_s h_s^4} - \frac{1}{E_t h_s^4} \right) h_s}{4(E_{nom}^3 + 1) \left( \frac{1}{E_s h_s^4} + \frac{1}{E_t h_s^4} \right) + 6(E_{nom}^3 + 1) \frac{h_s}{E_s}}$$

where $\nu_s$ is Poisson’s ratio of the adhesive layer. Delamination occurs when the maximum peeling stress reaches the critical tensile stress, which can be calculated for a given situation.

In the case of fracture mode, the maximum tensile stress should be addressed, and can be expressed by:

$$\sigma_{crack} = \left[ G_a h_s \left( \frac{2\chi \lambda}{\lambda^2 + \frac{\lambda}{2}} - \frac{2h_s \chi'}{3\lambda^2} \right) + E_s \right]$$

$$\times \frac{3\pi}{\chi' h_s L} \left( \frac{dL}{L} - \frac{\pi^2 h_s^2}{12L^2} \right)$$

The crack happens once the maximum tensile stress reaches a critical tensile stress, which is calculated on the basis of the given situations.\[163,164\]

From the above mathematical representations of bending, we can anticipate the failure mechanism under bending stress. For example, the failure mechanisms of Si membranes were investigated as a function of the Si thickness as shown in Figure 8.\[162\]

### 2.3.3. Conformal Device Mechanics

Device conformity on uneven substrates is an important component that must receive considerable attention. Small stiffness properties are desired to achieve conformal coverage over the uneven surface.\[165\] Since the conformal contact strongly depends on the stiffness and adhesion energy of a device, it is necessary to study the underlying mechanics of conformal contact for the successful demonstration of conformal devices. Thus, here we cover numerical models such as stiffness and adhesion energy through overlapping cylinder models.

One of the most important aspects in achieving conformal contact is to estimate the time at which conformal contact begins, which means that the study of critical adhesion energy is essential for the conformal device. First, we start with the stiffness calculation. The stiffness value is a function of Young’s modulus, the width of the device, the thickness of the device, and the distance between the neutral plane and bottom. The equation for stiffness can be shown by:

$$EI = Ebh \left( \frac{1}{3} h^2 - hy + h^2 \right)$$

where $E$, $b$, $h$, and $y$ represent the Young’s modulus, the width of the device, the thickness of the device, and the distance between the neutral plane and the bottom, respectively. In addition, since the adhesion energy relies on the surface-roughness
information, we need this information for numerical modeling. For quantitative analysis, we need to construct a specific model to mimic an uneven substrate. The overlapped cylinder model is a representative method for which, based on the surface roughness information, we can construct a model (Figure 9).

\[ R, 2d, \text{and } r_0 \text{ represent the radius of the cylinder, the distance between two centers, and the arc of radius at } \theta_0 = \sin^{-1}\left[\frac{d}{(R + r_0)}\right], \text{respectively. In addition, the contact angle, } \theta, \text{can be shown to be:} \]

\[ \frac{R \sin \theta}{d - \sin \theta} + \frac{dR \cos \theta}{(d - R \sin \theta)^2} - \left(\frac{\gamma}{\gamma_c} - 1\right) \left(1 - \frac{d}{R \sin \theta} + \frac{d \cos \theta}{R \sin^2 \theta}\right) = 0 \]  

(12)

Here, with the calculation and surface roughness information, we can calculate the critical adhesion energy. The adhesion energy per unit is calculated as:

\[ \gamma = \frac{EI}{2R^2b} \left[1 + \frac{(1 + \lambda)R^2}{(1 - \lambda)^2r^2}\right] \]  

(13)

where \( \gamma, EI, R, b, \lambda, \text{and } r \) are the adhesion energy, the stiffness, the radius of the cylinder, the width of the device, the wavelength, and the arc between overlapped cylinders, respectively. Once the calculated adhesion energy is lower than 10 mJ m\(^{-2}\), it is energetically favorable for the device to fully wrap around the uneven substrate, since the energy value for wet interfaces is 10 mJ m\(^{-2}\). From this analysis, we can estimate when the conformal contact begins under given situations. With numerical modeling, we can design a suitable device structure to make a conformal contact.

3. Sensor Applications

3.1. Electromechanical Sensors

As the tactile sensor for skin-inspired electronic devices has been attractive, various studies on electromechanical sensors have been conducted. Mainly, there are three different types of electromechanical sensors: piezoresistive, piezoelectric, and capacitive-type sensors. Each method is based on different materials and their different properties, which means that each method follows a different mechanism to respond to external strain. Here, we cover the basic physics and representative materials for each case.

3.1.1. Piezoresistive-Type Sensors

Piezoresistive materials can change their resistance under applied mechanical stresses. Studies on piezoresistance started in 1856 with William Thomson. He demonstrated that resistance changed with elongation in some metals, such as iron and copper. However, he did not use the exact term to describe the phenomenon, and the term piezoresistance was coined by Cookson in 1935. Later, Edward Simmons suggested the first metallic strain gauge in 1936 through change in resistance. A breakthrough was made by Bardeen and Shockley.
in 1950. They predicted that a large change in resistivity was possible in semiconductors. Based on the prediction, Smith demonstrated the first measurements of large piezoresistive coefficients in silicon and germanium. With these advances, several sensors based on piezoresistive effects have been investigated. The resistance can be expressed by the following equation:

$$R = \rho \frac{I}{A}$$  \hspace{1cm} (14)

where $\rho$, $l$, and $A$ are resistivity, length and area, respectively. That is, the change in resistance originates from a change in dimension and resistivity. We can express the relative change in resistance in terms of geometric effects and resistivity effects.

$$\frac{\Delta R}{R} = (1 + 2\nu) \varepsilon + \frac{\Delta \rho}{\rho}$$  \hspace{1cm} (15)

In Equation (15), the first term, $(1 + 2\nu)$, represents the geometric effect, and the second term represents the resistivity effect. Since the second term in semiconductors is much larger (around 50–100 times) than that in metals, semiconductors show a bigger change in resistance under stress, which means that sensors based on semiconductors show much more sensitivity than sensors based on metals. The sensitivity of strain sensors based on the piezoresistive effect can be expressed by the following equation called the gauge factor (GF):

$$GF = \frac{\Delta R/R}{\varepsilon}$$  \hspace{1cm} (16)

where $\varepsilon$ is strain and $\Delta R/R$ is relative resistance change. The gauge factor values of several materials are listed in Table 3.

Because of its simple principle, a lot of piezoresistive-type strain sensors based on several materials have been demonstrated over several decades. The most traditional piezoresistive sensors are based on metallic materials, starting as early as 1936. However, their gauge factor value is relatively low, since strain sensors based on metallic materials only depend on a change in dimensions without a change in resistivity, whereas semiconductors based on strain sensors show much better sensitivity since their resistivity and dimension both change once they are subjected to external stress. The resistivity change is attributed to the band structure change of the semiconducting material once stress is applied.

Lillemose et al. reported piezoresistive effects of the conductive polymer polyaniline. In their paper, the polyaniline had an intrinsically negative gauge factor. In addition, according to the report by Nambiar and Yeow, some conducting polymers can be used as sensors interacting with biological samples, since some conducting polymers have biocompatibility. To prove their argument, they demonstrated conducting polymers based on tactile sensors. Pan et al. demonstrated ultrasensitive pressure sensors through elastic microstructured conducting polymers. They showed a new material design concept to develop sensitive pressure sensors. Further improvement of sensitivity was realized by patterning elastic microstructured conducting polymers (Figure 10). A giant piezoresistance effect in silicon nanowires was discovered. He and Yang revealed that silicon nanowires have unusually large piezoresistance effects compared to bulk silicon. Cao et al. first studied the principle calculations of giant piezoresistance in silicon nanowires. According to their study, the unusual phenomenon originates from the presence of two surface states and an unusual surface relaxation of nanowires.

Carbon-based materials, such as carbon nanotubes and graphene, have drawn attention as piezoresistive sensors. Yamada et al. developed resistance-changing sensors capable of inducing 280% strain with high durability. Although the sensitivity was not as high as for those based on semiconductors, they designed reliable and highly stretchable strain sensors by using thin films of aligned single-walled carbon nanotubes (Figure 11). In addition, Bae et al. demonstrated wearable piezoresistive sensors based on graphene films. Their rosette type sensors allowed for the detection of the direction of the principal strain.

In addition, the unique mechanical properties of CNTs have been used in composite materials to enhance stretchability. Different types of sensors based on different principles have been introduced in the literature. Timsit suggested that the contact resistance changes under stress, which can be used in other types of sensors, although the principle is slightly different from the piezoresistive effect. In addition, Park et al. suggested a highly sensitive CNT–composite elastomer sensor based on a tunneling piezoresistance effect. Through

<table>
<thead>
<tr>
<th>Material</th>
<th>Gauge Factor</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>1.6–2</td>
<td>[173]</td>
</tr>
<tr>
<td>Single-crystalline Si</td>
<td>85.5</td>
<td>[174]</td>
</tr>
<tr>
<td>Poly-Si</td>
<td>43</td>
<td>[175]</td>
</tr>
<tr>
<td>a-SiC</td>
<td>–35</td>
<td>[176]</td>
</tr>
<tr>
<td>Poly-SiC</td>
<td>6</td>
<td>[177]</td>
</tr>
<tr>
<td>Metallic CNTs</td>
<td>0.06–0.082</td>
<td>[178]</td>
</tr>
<tr>
<td>Semiconducting CNTs</td>
<td>400–850</td>
<td>[179]</td>
</tr>
<tr>
<td>C-diamond</td>
<td>2000–3836</td>
<td>[180]</td>
</tr>
<tr>
<td>Polydiamond</td>
<td>10–100</td>
<td>[180]</td>
</tr>
<tr>
<td>Graphene</td>
<td>2.4–14</td>
<td>[181]</td>
</tr>
</tbody>
</table>

Figure 10. Pressure-sensor demonstration for a chessboard. a) Some chess pieces on a real chess board incorporated in the pressure sensor b) Mapping results from the pressure sensor. a,b) Reproduced with permission. Copyright 2014, Macmillan Publishers Ltd.
unique structure properties, the CNT–composite elastomer has a much higher resistance change in response to external stress. They explained that the large resistance changes are attributed to the tunneling current flow under the stress. Using these much more sensitive sensors, they succeeded in demonstrating medical diagnostic tools.

3.1.2. Piezoelectric-Type Sensors

Piezoelectricity is a term used to explain materials that generate an electrical potential in response to an applied stress. Piezoelectricity was first studied in 1880 by the brothers Pierre and Jacques Curie, with underlying physics in a pyroelectric effect.\(^\text{[191]}\)

The pyroelectric effect means that materials produce an electrical potential induced by a temperature change. Later, Gabriel Lippmann, in 1881, theoretically suggested the converse (or indirect) piezoelectric effect, which indicates the phenomenon that materials feel mechanical strain when they are subjected to an electrical field.\(^\text{[192]}\)

Based on further studies, Woldemar Voigt described 20 crystal classes having piezoelectricity.\(^\text{[193]}\)

Piezoelectricity originates from the changes of ion arrangement in dielectric materials. Once piezoelectric materials are subjected to stress, the neutrality of the charge in the crystals starts breaking, which induces an electric field across the material boundary. The electricity induced by stress can be expressed by the following equations:

\[
D = \varepsilon_E E_i + d_i \sigma_j \tag{17a}
\]

\[
\delta = S_E \sigma_j + d_i E_i \tag{17b}
\]

\(D, E, \sigma, \varepsilon, d, S_E\) represent the electric displacement, the electric field, the stress, the strain, the free-space electric permittivity, the piezoelectric coefficient, the electric relative permittivity, and the mechanical compliance matrix. \(i, j, i, i\) are indices. \(D\) and \(E\) are \((3 \times 1)\) tensors for directional coordination, and \(\sigma\) and \(\delta\) are \((6 \times 1)\) tensors for stresses or strains. Since \(d_{11}\) and \(d_{33}\) are generally strong among piezoelectric coefficients, they are the most common elements to explain piezoelectric phenomena. The \(d_{33}\) is known as the longitudinal piezoelectric coefficient, which means that the electric polarization is aligned in the direction of the applied stress. The \(d_{11}\) is known as the transverse coefficient, which means that the electric polarization is aligned in the direction perpendicular to the applied stress. Because of the strain-dependent charge change, piezoelectric materials have typically been used for sensor applications.

One of the most popular materials is ZnO. Applied stress breaks the ionic neutrality of the tetrahedral ZnO, inducing a change in its dipole moment. Due to this response, ZnO has been used as a common material for piezoelectric-type strain sensors.\(^\text{[194–198]}\) In addition, it has been widely studied in the fields of nanogenerators to produce electricity by using dipole alignment under the stress.

Other materials such as PbZr\(_x\)Ti\(_{1-x}\)O\(_3\) (PZT), BaTiO\(_3\) (BTO), and Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbTiO\(_3\) (PMN-PT) have been studied as piezoelectric materials. In fact, these materials have an even higher piezoelectric coefficient than that of ZnO.\(^\text{[199]}\) Although only the possibility of nanogenerators has been described, previously reported devices can be useful as strain sensors as well because they have strain-dependent properties—piezoelectricity. However, the process is accompanied by an exfoliation process because inorganic materials that possess piezoelectricity are basically rigid and brittle. Park et al. reported a BTO-based nanogenerator in 2010.\(^\text{[200]}\) They first fabricated BTO-based devices on a rigid Si substrate and exfoliated them by etching away the Si layers. Similarly, Kwon et al. successfully demonstrated PZT-based devices in 2012.\(^\text{[201]}\) By using an exfoliation process, PZT ribbons were transferred onto plastic substrates and could be used as the nanogenerator. Later, a PMN-PT-based nanogenerator was introduced.\(^\text{[202]}\) The exfoliation process to transfer PMN-PT film was employed on target substrates. Since the piezoelectric
coefficient of PMN-PT was much higher than those previously reported, PMT-PT based devices showed many sensitive results. In addition, PMN-PT based sensors have been demonstrated on the heart of a living rat for biological stimuli detection.

There are polymer-based piezoelectric materials such as poly(vinylidene fluoride) (PVDF) and its copolymers (Figure 12) that can work as piezoelectric-type sensors. In the case of polymer-based piezoelectric materials, more stress is allowed due to the intrinsic flexible material properties. However, the piezoelectric coefficient is not high compared with that of piezoelectric inorganic materials.[187,203,204] Thus, the performance of the PVDF-based sensors and copolymers is not that high compared with those based on inorganic piezoelectric materials. To overcome this limitation, Cauda et al. revealed that the dimensional confinement and oriented crystallization of PVDF are key factors to determine the piezoelectricity.[205] In addition, some composites such as PVDF/multiwall carbon nanotubes, PVDF/ZnO, and PVDF/PZT were developed to improve performance.[206,207]

Piezoelectricity was discovered in 2D materials in 2014.[208] Wu et al. revealed that MoS₂ has strong piezoelectricity, which disappears in the bulk because of opposite orientations of the dipole moments in adjacent atomic layers. Specifically, MoS₂ flakes with odd numbers of atomic layers produce electricity under stress while those with even numbers do not. Based on this approaches, the potential of piezoelectricity in MoS₂ was investigated for sensor applications. Moreover, Zhu et al. also reported a similar result from monolayer MoS₂.[209] Due to its broken inversion symmetry, the MoS₂ could have piezoelectricity and its coefficient was $2.9 \times 10^{-10} \text{ cm}^{-1}$.

3.1.3. Capacitive-Type Sensors

To understand capacitor-type strain sensors, we need to start with the definition of capacitance given by Maxwell in 1873.[210] Capacitance is the ability to store an electrical charge in a body, which is expressed by the following equation:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$  \hspace{1cm} (18)

where $\varepsilon_0$, $\varepsilon_r$, $A$, and $d$ represent the free-space permittivity, the relative permittivity, the area, and the distance between conductors, respectively. That is to say, capacitance is a function of the relative permittivity, the area, and the distance. Since the underlying parameters that determine capacitance are simple, it is one of the most widely used types of sensors.[211] Recently, simple PDMS-dielectric-based, highly sensitive capacitor-type sensors were reported using PEDOT:PSS or CNTs as electrodes.[212,213] To apply stretchable functions, highly stretchable capacitive sensors with nanowire electrodes were also studied.[214,215] It was found that the compressibility of the capacitive sensor could be enhanced due to the air gaps between the silver nanowires. However, further patterning processes are required for air gaps to consider a change in capacitance.[216,217] To overcome these issues, high-definition structuring of thin elastomeric films was applied to fabricate highly sensitive capacitive sensors.[218] The silicon mold induced micropatterns onto PDMS, which led to unprecedented sensitivity and very short response times.

3.2. Photonic Sensors

The photosensitivity of electrical devices is a crucial technology for remote control, biological health monitoring, and automotive systems.[55,219] Various materials, device structures, and morphologies of photosensing devices have been used as photodiodes and phototransistors, such as nanofilms, nanowires,
nanoparticles, quantum dots, polymers, and organic/inorganic hybrid structures.

Recently, developing printable and flexible platforms with new materials and structures has been required. To achieve a broad bandwidth and fast response, low-bandgap materials are considered, such as Si, CdS, and polymers. Light-sensitive polymers are highly desirable as simple printing processes and low-temperature annealing are available for flexible photosensing applications. Most recently, hybrid types, such as quantum-dot/graphene, organic–inorganic perovskite, and organic-dye/inorganic films have been developed to enhance photosensitivity. These sensors are transparent, lightweight, and bendable in sensor platforms and have attracted attention owing to their high potential for use in future human-friendly applications. In this section, we will introduce the recent progress of printable photosensing technologies.

3.2.1. Inorganic Photodetectors

The key figure-of-merit parameters of photodetectors must be considered by using the responsivity \( (R) \), the detective \( (D^*) \), the noise-equivalent power \( (\text{NEP}) \), the linear dynamic range \( (\text{LDR}) \), and the response speed. \( R \) is the ratio of the photocurrent to the incident light intensity, which indicates the magnitude of the efficiency of the photodetector for the optical signal. \( R \) is given as \( R = \frac{J_{\text{ph}}}{L_{\text{light}}} \) where \( J_{\text{ph}} \) is the photocurrent and \( L_{\text{light}} \) is the incident light power density. It is an important parameter to determine a high conversion rate between photons and carriers. \( D^* \) is given by \( (\frac{A\Delta f}{R})^{1/2} \) where \( A \) is the effective area of the detector, \( \Delta f \) is the electrical bandwidth, and \( R \) is the responsivity, and \( i_n \) is the noise current at the same conditions. The NEP is another figure-of-merit for photodetectors. It represents the minimum impinging optical power that a detector can distinguish from the noise current \( (i_n) \). It is given by \( \frac{(A\Delta f)^{1/2}}{R} \) or \( \frac{i_n}{R} \). The LDR is the photosensitivity linearity. It is given by \( 20\log(\frac{J_{\text{ph}}}{J_{\text{dark}}}) \), where \( J_{\text{dark}} \) is the dark current of the devices.

Solution-based photodetectors offer advantages of low cost, simplicity, and flexibility over large-area fabrication, as compared to conventional semiconductor devices requiring lattice matching and complex growth. Several groups have reported the breakthrough of printable photodetectors.

3.2.2. Colloidal-Quantum-Dot Photodetectors

Colloidal quantum dots are of interest as an optoelectronic material because of their solution processability, high durability post-processing, and tunable optical absorption and emission spectra through quantum size effects (Figure 13).[226,227] As a representative achievement, Konstantatos et al. reported an interesting result about ultrasensitive quantum-dot photodetectors using a solution process.\(^\text{[222]}\) A single spin-coating of PbS colloidal-quantum-dot nanocrystals was performed at an electrode array (Figure 14a). The devices showed large photoconductive gains with responsivities (A W\(^{-1}\)) of over \( 10^3 \) A W\(^{-1}\) and exhibited a detectivity \( (D^*) \) of \( 1.8 \times 10^{13} \) Jones at a wavelength of 1300 nm. To enhance the electrical properties and the packing of PbS nanocrystals, a post-synthetic ligand exchange was used to reduce the length of the ligand (oleic acid to n-butylamine). The length of the ligand was reduced from ca. 2.5 nm to ca. 0.6 nm and the dark-current density was measurable. Finally, the removal of n-butylamine was performed in methanol and the dark-current density significantly increased. For the noise current versus the dark current, the best device (neck-then-oxidize) approached the shot noise limit within 3 dB (Figure 14b).

Figure 13. The absorption properties of PbS colloidal quantum dots through the quantum-size effect. The dot size can be adjusted from 3 to 10 nm in diameter. Reproduced with permission.\(^\text{[227]}\) Copyright 2009, IEEE.

Figure 14. a) Structure of PbS colloidal-quantum-dot photodetector. b) Measured noise current as a function of measured dark current. The lowest noise current is reached within 3 dB of the shot noise limit. c) Detectivity and responsivity of the devices show \( 1.8 \times 10^{13} \) Jones and over \( 10^3 \) A W\(^{-1}\) at 1300 nm. Reproduced with permission.\(^\text{[226,227]}\) Copyright 2006, Macmillan Publishers.
The responsivity and detectivity of devices showed that they are close to the absorption spectrum of PbS nanocrystals.

### 3.2.3. 2D Photodetectors

Two-dimensional (2D) materials such as graphene and transition-metal dichalcogenides have extraordinary optoelectronic properties for single or few-layer formation.\cite{224,228,229-230} Photodetectors based on these materials enable ultrafast and ultrasensitive photodetection in a broad wavelength range from ultraviolet to terahertz frequencies.\cite{230} However, the fabrication of the devices usually requires complex E-beam lithography processes.

Manga et al. reported a hybrid of titanium dioxide (TiO$_2$) with graphene composites to improve the photoconductivity.\cite{231} Typically, graphene oxide (GO) nanosheets are dispersed in aqueous solution. However, typical titanium alkoxide can precipitate in an aqueous solution due to rapid hydrolysis. In order to overcome the low yield of TiO$_2$–graphene composites, titanium (IV) bis(ammonium lactate) dihydroxide (TBA) was used and dark solutions were prepared due to the photocatalytic behavior of TiO$_2$ from the photoreduction of GO to graphene.\cite{231} As shown in the top of Figure 15a, graphene sheets were distributed in a TiO$_2$ matrix and a percolation network was formed. The graphene–TiO$_2$ composites created an injection barrier to the flow of the photoexcited electrons. As shown in the middle and bottom of Figure 15a, the spin-coating of graphene–TiO$_2$-composite-based photodetectors showed photoconductive behavior under light in air, and under vacuum. The photodetectors exhibited $D^*$ and LDR of over $10^{12}$ Jones and 58 dB under UV region, respectively.

![Figure 15. a) Inkjet-printed TiO$_2$–graphene heterojunction photodetectors. The charge injection and separation occurs at the interface between the TiO$_2$ and the graphene. The photocurrent of TiO$_2$–graphene photodetectors in vacuum showed better sensitivity than those in air because of the trap sites of adsorbed oxygen on the TiO$_2$ surface. The optimum ratio of the TiO$_2$–graphene composite can lead to photocurrent generation by photoinjection of electrons into the graphene. Optical images of all-inkjet-printed graphene and TiO$_2$–graphene devices. Reproduced with permission.\cite{231} Copyright 2010, John Wiley & Sons, Inc. b) Solution-processed-graphene- and quantum-dot-composite-based deep-UV photodetectors. Reproduced with permission.\cite{232} Copyright 2015, American Chemical Society. c) Photodetectors based on inkjet-printed liquid-exfoliated graphene and MoS$_2$ nanosheets. Inkjet-printed graphene interdigitizing electrode are shown in black and MoS$_2$ in yellow. Photocurrent characteristics of graphene–MoS$_2$ photodetectors in the dark and under illumination at 532 nm. The photoconductivity shows supralinear behavior due to the defects. Reproduced with permission.\cite{233} Copyright 2014, Royal Society of Chemistry.](image-url)
Zhang et al. reported deep UV photodetectors with the hybrid structure of monodispersed graphene and quantum-dot (GQDs) mixed solutions.\textsuperscript{232} The authors focused on deep-UV (DUV) photodetectors. This range covers diverse applications such as the detection of the chemical evolution, remote control, and communication.\textsuperscript{234} GQDs were tunable in the UV to DUV range due to quantum-confinement and edge effects. Spin-coated GQDs on Ag–Au electrodes are shown at the top of Figure 15b. Different band alignments of the GQDs with the Ag (cathode) and the Au (anode) allow a drift of the electrons and holes. This structure can easily separate electron–hole pairs under light and produce high photocurrents under wavelengths of 254 and 302 nm, as shown in the top and bottom of Figure 15b. Asymmetric Ag–Au-based GQD photodetectors exhibited good photodetectivity with a $D^*$ of $9.59 \times 10^{11}$ Jones. This approach reveals that low-cost photodetectors open up new opportunities in using nanomaterial-based solution processes.

Another approach of photodetectors based on liquid-exfoliated graphene and MoS$_2$ nanosheets is shown in Figure 15c. Finn et al. demonstrated the inkjet printing of graphene and MoS$_2$-based photodetectors.\textsuperscript{233} In order to improve the ability of continuous electrode film formation, high and low centrifugation, coupled with a resuspension of sediment, was applied, and the flake size of the graphene has shown a broad distribution from 350 to 600 nm.\textsuperscript{233} Exfoliated MoS$_2$ has photoconductive properties, where inkjet-printed MoS$_2$ was employed to the active region. Inkjet-printed graphene and MoS$_2$ photodetectors showed uniform films, as shown in the top of Figure 15c. The photocurrent of the inkjet-printed graphene–MoS$_2$ photodetectors is shown in the bottom of Figure 15c. A supralinearity of the changing conductance was observed with increasing light intensity due to photocurrent quenching and the negative photoconductivity.\textsuperscript{233}

### 3.2.4. Organic–Inorganic Perovskite Photodetectors

Organic–inorganic metal halide perovskites have emerged in the photovoltaic society with a high power conversion efficiency (PCE) because of the long charge-carrier lifetime and diffusion length. These advantages indicate a high potential of optoelectronic devices for photodetector applications. Typically, perovskite materials with high external quantum efficiency (EQE) are observed in the spectral range from 300 to 800 nm.\textsuperscript{223,235} In order to evaluate the figure-of-merit in such photodetectors, a low saturation current ($J_0$) is very important regarding the density of defects and traps within the bandgap. Perovskite materials naturally have very low defects and traps, which is a highly desirable feature for photodetectors.

Figure 16a shows the first hybrid perovskite photodetector using a solution process. Excluding the electrodes, all the materials were fabricated using a spin-coating process. Interestingly, a very low dark current ($J_d$) of $1.5 \times 10^{-11}$ mA cm$^{-2}$, a good rectification ratio of ca. $10^5$, and a very high detectivity of $4 \times 10^{14}$ Jones were observed. The dark-current density of hybrid perovskite photodetectors is much lower than some conventional solution-processed photodetectors, such as CdTe, and Cu(In,Ga)Se$_2$ (CIGS).\textsuperscript{223,236} Such high performances can be attributed to the excellent intrinsic optical and electronic properties of the hybrid perovskite, as well as the careful interface design. Figure 16b shows flexible perovskite photodetectors with broadband wavelength from UV to visible light.\textsuperscript{237}

![Figure 16.](https://example.com/figure16.png)

**Figure 16.** a) (Left) The structure of a hybrid perovskite photodetector. (middle) The $J$–$V$ curves of the photodetectors. The photodetector based on poly[(9,9-bis(30-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) as a hole-blocking layer (PD3, blue line) showed the best performance compared with the non-hole blocking layer (PD1, black line) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, PD2, red line). (Right) The EQE and detectivity of perovskite photodetectors. Reproduced with permission.\textsuperscript{[223]} Copyright 2014, Macmillan Publishers Ltd. b) (Left) The current–time curves of a flexible hybrid perovskite photodetector with different curvatures at 365 and 780 nm, respectively. (Right) Band diagram of the photodetector. There is no electrical current flowing under equilibrium conditions and no illumination due to the Schottky barriers. The Schottky barrier was lower, leading to photogenerated holes migrating to the surface and being trapped under illumination. Reproduced with permission.\textsuperscript{[237]} Copyright 2014, John Wiley & Sons.
These photodetectors showed photoresponsivities of 3.49 and 0.0367 A W$^{-1}$ and EQEs of 1190% and 5.84% at 365 and 780 nm. The photodetectors exhibited excellent flexibility of photocurrent during bending tests, as shown in the left of Figure 16b. Indium-tin-oxide (ITO) electrodes formed a Schottky contact with the perovskite layer and the current was blocked by the barrier height under the dark. On the other hand, the photocurrent occurred from hole migration on the surface. Research on hybrid perovskite photodetectors is still at an early stage, but shows much promise. Materials, interfaces, and structures of hybrid perovskite photodetectors must be considered to improve the sensitivity and broad spectral detectivity.

3.2.5. Medical Applications using Optoelectronics

Conventional medical monitoring systems such as pulse oximeters and electrocardiograms (ECGs) have been used widely to check the vitality of the human body. In particular, human pulse rates and blood oxygen concentration are measured by using two components of light-emitting diodes (LEDs) with two peak-emission wavelengths and one photodiode. A clip-like device can evaluate the light-absorption characteristics of hemoglobin and the pulsating blood flow. It should be noted that this device occupies a large piece over the finger and links to an electrical wire to monitor the patient vital signs, which can cause discomfort and restricted movement for a person. In order to overcome these issues, Lochner et al. reported an organic light-emitting diode (OLED)-based emission system as shown in Figure 17a. OLEDs can be fabricated in various shapes, and in thin and flexible structures compared with conventional LEDs. Organic optoelectronic material-based sensor systems can detect acquired pulse rates and oxygenation. Measured values are highly accurate and compatible with conventional electronics as shown in Figure 17b. They are expected to form shapes freely, such as rings and/or patches, with which patients will be more comfortable.

3.3. Chemical and Biological Applications

In this Section, we will review various approaches of chemically modified surfaces and their applications to the field of biological sensors. The chemically modified surface of the sensor acts as the binding sites and catalysts through the recognition of target molecules and the amplitude in the selectivity to reduce the interference from non-specific bindings. Approaches of surface modification including compounds containing enzymes, deoxyribonucleic acid (DNA), proteins, peptides, carbohydrates, and diols have been proposed. Several approaches have been considered by non-specific chemical modification of the surface. For example, the capacitance change in response to humidity, pressure, dipole moments, and temperature can be tracked using dielectric materials. Here, we will discuss some of the work on biosensors, including biomolecules and multimodal detection.
3.3.1. Chemical- and Bio-Detecting Sensors

The surface of graphene oxide has the capability to sense water molecules and chemisorbed functional groups that produce a decrease in the electrical impedance. This interaction of GO is capable of humidity detection.\(^{249}\) Figure 18a shows spray-coated GO-based humidity flexible sensors.\(^{250}\) The fast response of GO sensors with a GO thicknesses of 15 nm resulted in highly sensitive nanoporous GO structures. Simple processing of GO sensors is highly expected with various chemical detections, low cost, and flexible sensor fabrication. Recently, degenerative disorders – Alzheimer’s, Huntington’s, and Parkinson’s disease – have been addressed. Kim et al. developed ultrathin In\(_2\)O\(_3\) film via a solution process with a film thickness of ca. 4 nm (Figure 18b).\(^{53}\) The In\(_2\)O\(_3\) film was immobilized using a specific aptamer to detect dopamine. Dopamine sensors showed high sensitivity with sub-nanomolar-concentration dopamine detection. Moreover, the sensors had high selectivity upon exposure to several molecules. Figure 18c shows the demonstration of smart contact lenses with glucose detectors and wireless communication systems. Typically, type-II diabetes frequently tests blood sugar levels by piercing the finger to draw blood for diabetes prediction. However, this method provides a one-time result and often causes pain or trauma.\(^{251}\) To overcome this issue, Yao et al. developed a new type of glucose-monitoring system that consisted of contact lenses, glucose sensors, and telecommunication circuits.\(^{252}\) Glucose sensors covered the range of glucose concentration from 0.05 to 2 \times 10^{-3} \text{ M}, which permitted glucose levels within tears to be detected. The read-out/telecommunication circuit did not require an extra power system and full wireless power/data operation.\(^{251,252}\) This sensor has a high potential to be applied to daily glucose monitoring. Conformal-film-based pH and glucose biosensors with ultrathin In\(_2\)O\(_3\) semiconductor films on artificial skins having highly rough surface and eyes were also demonstrated under the detection ranges of human tears.\(^{253}\) Most recently, Kim et al. reported multifunctional biological
sensors using CNT microyarns to compose the capacitive sensors, as shown in Figure 18d.[54] Multifunctional sensors have been an emerging technology due to electronic-skin (E-skin) applications.[20] The authors demonstrated CNT fabric-based piezocapacitive stretchable devices. This sensor was capable of multi-detection such as touch, temperature, humidity, and chemical species.

3.3.2. Epidermal and Artificial-Skin Sensors

Epidermal sensing with lightweight, durability, and conformal contact with the skin has been in demand for wearable technology.[20,254,255] Epidermal sensors provide intimate biological contact with electrical and/or chemical monitors. Recently, vital signs of the heart rate, temperature, blood pressure, electroencephalography, and lactate have been investigated for realizing epidermal sensing.[254,256–259] Here, we will focus on the latest research on printed conformal sensors.

Jia et al. reported tattoo-like electrochemical biosensors that exhibited chemical selectivity upon lactate concentrations during physical exercise, as shown in Figure 19a.[258] Lactate is one of the biomarkers for tissue oxygenation and can be monitored for exercise to check physical performance. A tattoo lactate sensor was applied on the forearm to assess the real-time lactate concentration profile and the variation of lactate levels was detected through the oxidation of lactate by the enzymatic reaction of lactate oxidase. Recently, Harada et al. demonstrated a fully printed multifunctional artificial skin sensor.[260] Typically, force sensors are incapable of identifying touch and slip/friction forces, or require complex structures. Thus, much research has focused on high sensitivity and mechanical flexibility for such sensors. To detect various force situations, the authors proposed three-axis tactile-force-detecting structures, using a full printing process, as shown in Figure 19b. This work demonstrated the functionality of human-skin-like multi-points, slip-force detection, and temperature recognition on a flexible substrate. When two directions of the force are applied to this sensor, different strain distributions occurred. In particular, applying a force from the top left (slipping situation) resulted in different stress distributions. As a result, different stress distributions of touch and slip could be tracked. The authors also demonstrated multi tracking of the force and temperature as shown in the right of Figure 19b.

3.4. 3D-Printing Technology

Three-dimensional (3D) printing technology has attracted tremendous attention to directly realize complex objects such as wearable sensors, robotics, and medical devices.[21,261,262] A simple, low-cost, and free shape creation from bottom-up printing enables desired functional objects. The development of functional sensor-based E-skin applications has been actively studied. Muth et al. reported the development of 3D-printed strain sensors within stretchable elastomers.[21] Low-cost conductive carbon grease with low viscosity was used in patterning sensing elements and it was capped by a filler fluid as shown in the bottom of Figure 20a. Highly stretchable sensors based on carbon resistive ink within an elastomeric matrix were designed and the resistance was significantly changed by different gestures using fingers. Unlike monitoring sensors such as strain, temperature, and electrochemical response, it is challenging to construct devices such as FETs, lasers, photovoltaics, and light-emitting devices using the 3D-printing technique. Kong et al. demonstrated 3D-printing-based fully integrated quantum-dot-based light-emitting diodes (QD-LEDs) as shown in Figure 20b.[263] Interestingly, five different materials based on inks, including emissive QD materials, elastomeric matrices, organic polymers as interlayers, electrodes, and transparent

![Figure 19.](image-url)
substrates were employed using a 3D printer. The authors successfully demonstrated green, and orange–red QD-LEDs, and constructed a 3D-printed multidimensional array of embedded QD-LEDs. This approach has a high potential of being applied to new multifunctional devices with optoelectronic functionality.

4. Issues and Challenges

Nowadays, printable semiconductors, insulators,[264,265] and conductors[266–268] have been developed for sensor applications with active and passive components such as resistors, capacitors, antennas, and various transducers. However, most research has focused on partial printing processes, where parts of the devices are fabricated using traditional vacuum deposition and photolithography processes.[3] The integration of each component is a large challenge to realize fully printed electronics[269] and should address the following issues: i) the chemical compatibility and environments of sequential depositions for ink materials, ii) optimizing the processing temperatures to minimize the degradation of each layer and to provide the best sensing performance together, and iii) developing fine-patterning and high-resolution technologies based on control over the ink properties of the coating and film formation.

As we discussed several issues, entirely printable processing of electronic devices is still limited and complex due to the
lack of processing platforms for inorganic and organic combinations, desired performance, processing temperatures, and methods. Recently, some approaches, such as organic–carbon nanohybrid heterojunction structures,[270] polymer-based digital mechanoreceptors,[271] and metal-free, single-polymer memory,[272] have been demonstrated for high-performance and simple processing. The best strategy is to approach new platform developments that take into account all of these issues together with a fundamental understanding of the chemical, mechanical, and electrical properties of printable materials. However, most research on printing technologies has still been considered using traditional semiconductor processing methods, such as photolithography and vacuum deposition. These approaches are only related to optimizing and improving performance of each printable material, but lack a deep fundamental understanding of combined processing of organic, inorganic, and hybrid materials. These aspects should be addressed to enable flexible and fully printable processes.

5. Conclusions and Outlook

In the past few years, breakthroughs in technological advancements of new processing methods, materials, and platforms have accelerated the realization of flexible and stretchable electronics for various functions via printing technologies. Based on this progress (Figure 1), new expectations for highly functional, economical, fashionable, and practical sensor devices have been developed. Printable sensors have especially received attention so as to potentially alleviate several of the challenges in: i) developing new sensing materials based on nanomaterials, hybrid composites, and simplified thin-film processing methods; ii) considering biological contact between the substrate and the human body; iii) enabling the recognition of multimodal sensing environments; and iv) developing new methods and architectures via 3D printing technology. Many types of sensors have already been proposed for new conceptual human-friendly systems in the past decade.

Despite the significant progress in printable sensor technologies, there is still much to be developed for feasible printing process techniques entailing the integration of sensors, large-areas, low-cost, and reproducibility.

To realize such developments, it is important to understand the underlying mechanics in devices. Detection of how much strain can occur in devices should be considered in design, in order to minimize device wear and maximize performance. In addition, conformal devices, which are an extreme case of flexible devices, require numerical modeling to ensure sufficient conformal contact with the target environment.

Advances in wearable technologies have further enhanced interest in electromechanical sensors. Different types of electromechanical sensors have different advantages and disadvantages. Thus, we should continue to develop all types of transducers and integrate them for multiple functionalities.

Beyond conventional methods of printing technology, we have discussed many issues that should be considered in developing new processing platforms. To ultimately overcome these challenges beyond the current status in printable processes, the fundamental understanding of chemical, mechanical, and electrical properties of printable materials in tandem with processing effects should be required.

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