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Review

A Review of Conductive Metal Nanomaterials as Conductive, Transparent, and Flexible Coatings, Thin Films, and Conductive Fillers: Different Deposition Methods and Applications

Samira Naghdi [1], Kyong Yop Rhee [1,*], David Hui [2] and Soo Jin Park [3,*]

1 Department of Mechanical Engineering, College of Engineering, Kyung Hee University, Yongin 446-701, Korea; samira.naghdi@gmail.com
2 Department of Mechanical Engineering, University of New Orleans, New Orleans, LA 70148, USA; dhui@uno.edu
3 Department of Chemistry, College of Natural Science, Inha University, Incheon 402-751, Korea
* Correspondence: rheeky@khu.ac.kr (K.Y.R.); sjpark@inha.ac.kr (S.J.P.); Tel.: +82-31-201-2565 (K.Y.R.); +82-32-876-7234 (S.J.P.); Fax: +82-31-202-6693 (K.Y.R.); +82-32-860-8438 (S.J.P.)

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Abstract: With ever-increasing demand for lightweight, small, and portable devices, the rate of production of electronic and optoelectronic devices is constantly increasing, and alternatives to the current heavy, voluminous, fragile, conductive and transparent materials will inevitably be needed in the future. Conductive metal nanomaterials (such as silver, gold, copper, zinc oxide, aluminum, and tin) and carbon-based conductive materials (carbon nanotubes and graphene) exhibit great promise as alternatives to conventional conductive materials. Successfully incorporating conductive nanomaterials into thin films would combine their excellent electrical and optical properties with versatile mechanical characteristics superior to those of conventional conductive materials. In this review, the different conductive metal nanomaterials are introduced, and the challenges facing methods of thin film deposition and applications of thin films as conductive coatings are investigated.

Keywords: optoelectronic; transparency; flexibility; stretchability; ITO; conductive nanomaterial; conductive filler

1. Introduction

Functional coatings can be applied to substrates in order to modify their surface properties, such as corrosion resistance or wettability, or to add a new property, such as electrical conductivity or optical reflection, to the final product. Conductive coatings or conductive thin films are frequently used to cover dielectric substrates or substrates that are less conductive than the coating. Depositing such a sensitive coating requires a finely tuned method that does not alter the electrical, optical, and mechanical properties of the coating. Recently, use of conductive nanomaterials such as conductive metal nanomaterials and carbon-based nanomaterials (carbon nanotubes and graphene) has opened new opportunities for electronic and optoelectronic devices. Valuable characteristics such as transparency allow conductive coatings to be used for optoelectronic devices such as liquid crystal displays (LCDs), touch screens, solar cells, organic light-emitting diodes (OLEDs), and electrochromic devices. Moreover, adding flexibility to conductive nanomaterials improves their application in the fields of wearable electronics, electromagnetic interference (EMI) shielding, and wearable antennas, as well as acting as interconnections in textile-integrated devices such as health monitoring sensors. Finally, to provide corrosion protection to key conducting components, such as conductors and electrodes in devices, using a corrosion resistant conductive coating is vital. Therefore, finding the best-suited conductive nanomaterials that have the desired properties (e.g., flexibility, transparency, and chemical stability) and selecting a cost effective and scalable deposition method are vital.

1.1. Why Are Conductive Nanomaterials Used in Coatings and Thin Films?

Conductive nanomaterials have been the focus of research for a long time and can be used in the future as alternatives to traditional conductive and transparent metal oxides in the electronic and optoelectronic industries. Using conductive metal nanomaterials as a thin film or coating instead of traditional conductive metal foils or metal coatings would have a tremendous impact on the cost, volume, weight, and mechanical properties of electronic, optoelectronic, and photovoltaic devices. These materials could be incorporated easily into thin films by simple, inexpensive, solution-based deposition techniques, such as spin coating, spray coating, and ink-jet printing. Conductive metal nanomaterials (which are limited in at least one dimension) play a key role in fabricating stretchable conductive thin films and coatings, since their mechanical properties include greater flexibility (and, in some designed structures, stretchability) than in conventional conductive materials.

1.2. Why Is Flexibility Needed in Some Cases and Transparency in Others?

As mentioned above, depending on the device performance and application of conductive metal nanomaterials, they can be used to form a transparent conductive film and/or a flexible (stretchable) one. The specifications vary based on the type of device. Optical transparency is beneficial for some applications, whereas it is crucial for others (e.g., displays). Moreover, flexibility and good mechanical properties are vital for thin film electrodes on plastic substrates, whereas they are not important for electrodes on rigid substrates.

In spite of the vast applications of the conventional transparent conductive metal oxides, why is there a demand for replacing them with alternatives? Indium tin oxide (ITO), fluorine tin oxide (FTO), and Al-doped zinc oxide (AZO) are some of the conventional transparent conductive metal oxides that possess high electrical conductivity and optical transparency, and that are used as transparent conductive electrodes in optoelectronic and photovoltaic devices. Among the different metal oxides, ITO offers over 85% transparency in the visible range of the electromagnetic spectrum as well as very low resistivity of 7.5×10^{-4} Ω cm [1]. Compared to other transparent conductive metal oxides, ITO can be deposited at relatively low temperatures. Moreover, if there is a demand to make a pattern of transparent conductive coatings, ITO can be etched more easily than FTO and AZO. Additionally, the sputtering deposition technique that is commonly used to deposit ITO thin film is an easier method compared to the deposition methods of FTO and AZO. Therefore, the reasons for replacing ITO with conductive metal nanomaterials need to be made clear.

As mentioned previously, conductive transparent metal oxides exhibit excellent conductivity and transparency, which is needed for industrial applications. However, some obstacles limit their application and motivate scientists to search for other alternatives for these materials. Some of the disadvantages of conventional transparent conductive materials (especially ITO) are described below.

1.2.1. Cost

The limited supply of these materials, coupled with rapidly increasing demand, could make it difficult to fabricate a cost-effective, large-scale, transparent conductive coating. Moreover, the sputtering method (as the common method for deposition of metal oxide coatings) is an expensive method which also would limit the vast deposition of these materials to produce large area solar cells and light emitting diodes (LEDs) for lighting applications.

1.2.2. Brittleness

In applications involving flexible substrates such as flexible optoelectronic devices, the poor mechanical stability of these materials could cause cracks to form during bending or stretching of the substrate, leading to device failure. These cracks diminish the electrical properties of the transparent conductive thin film.

1.2.3. Poor Choice for Use as a Conductive Coating (Electrode) on Organic Substrates

In applications of metal oxides as electrodes on organic active layers (such as OLEDs, organic photovoltaic cells (OPVs) and organic transistors), the sputtering deposition method would cause defects and damage to the organic substrate, leading to device failure. Moreover, these metal oxides exhibit poor electrical contact with organic substrates.

1.2.4. Limited Chemical Stability

The chemical instability of these metal oxides in an acid or base environment (i.e., a corrosive situation) limits their application.

1.2.5. Poor Choice for Use as an Electrode in Solar Cells

When used as an electrode in solar cells, the filled valence band structure of ITO does not contribute to the charge separation process, which results in decreasing its photocurrent generation [2,3].

1.2.6. Lack of an Easy and Cost-Effective Deposition Technique

The most common technique for deposition of these materials is the vacuum sputtering method, which requires vacuum conditions and high temperature. Moreover, depositing an expensive material such as ITO on the substrate via this method wastes 70% of the coating materials (ITO) due to ejection from the target substrate [4]. Therefore, increased prices due to increased demand for these materials makes the sputtering technique an impractical deposition option.

1.3. Solution

Highlighting the ineffectiveness of conventional transparent conductive materials may motivate researchers to find alternatives for these methods. Therefore, synthesizing conductive transparent nanomaterials (from cheaper, more abundant raw materials) and investigating their efficiency in electronic and optoelectronic industries can significantly decrease the obstacles to development of cost-effective flexible solar cells, displays, etc.

1.4. Application of Conductive Nanomaterials as Nanofiller and Percolation Threshold

As mentioned above, conductive metal nanomaterials could be used as alternatives to conventional conductive metals and transparent conductive metal oxides. Research results have offered two different approaches for taking advantage of their impressive properties. These nanomaterials can be directly deposited on different substrates via simple solution-based deposition methods to form a conductive coating and thin film. The second approach for using these materials is as fillers in conductive polymers (to increase their conductivity) and in insulator polymers (to make them conductive). These fillers not only modify the electrical properties of the host polymer but can also enhance its mechanical properties. Because of their small size [5], nanomaterials possess a huge specific surface area [6,7], which leads to their unique properties; placing these specific materials within polymer networks would result in nanocomposites with noble properties. A number of factors affect the quality and the physical and mechanical properties of the nanocomposite, including the type, purity, aspect ratio (length-to-diameter ratio for 1D nanomaterials, diameter (lateral size or mean width)-to-thickness for 2D nanomaterials), and alignment of conductive metal nanomaterials. The major challenge in producing nanocomposites is achieving uniform dispersion of the fillers into the polymer networks. Different methods of producing conductive nanomaterial/polymer nanocomposite have been investigated, including melt blending, solution mixing, in situ, and latex blending methods.

For using a different method of preparing a nanocomposite it must be considered that there is a threshold (the percolation threshold) in the optimal amount of fillers; above this value, the fillers agglomerate into the host polymer matrix, leading to dramatic degradation of the electrical and mechanical properties of the nanocomposite.

1.5. Percolation Theory

Percolation theory explains the electrical properties of nanocomposites reinforced with conductive metal nanomaterials. When filler is added gradually to the polymer, the polymer resistivity decreases. At the critical filler concentration, called the percolation threshold, the resistivity of the polymer decreases dramatically due to the formation of a continuous conducting three-dimensional network. Increasing the amount of filler above the percolation threshold saturates the conductivity of the nanocomposite due to the multiple electrons networks, whereas electrons paths do not exist below the percolation threshold. The factors that determine the percolation threshold include the aspect ratio, dispersion, alignment, and functionalization of the filler, as well as the type of polymer. Theoretically and experimentally, it has been shown that increasing the aspect ratio dramatically decreases the percolation threshold, which is important from an economical point of view. Moreover, in composites formed from the combination of a conductive metal nanomaterial and polymer, the polymer provides mechanical stability and the conductive metal nanomaterial is responsible for electrical conductivity. Therefore, to preserve the mechanical properties of the polymer, using a conductive metal nanomaterial with a high aspect ratio (low percolation threshold) as filler must be considered. In this regard, high aspect ratio fillers such as conductive metal nanowires (NWs) have been the focus of research.

2. Conductive Metal Nanomaterials

2.1. Sintering of Metal Nanoparticles (NPs)

Before introducing the different types of conductive metal nanomaterials, it is important to understand the sintering process. Generally, after deposition of conductive metal nanomaterials on a substrate via the solution-based deposition method, sintering is a vital step for evaporation and removal of the carrier solution, control and curing of the thin film microstructure, and production of a continuous layer by fusing the individual NPs and NWs together through heating or another form of energy input. Because of the high surface area of metal NPs and NWs, their melting points are much lower than that of the corresponding bulk metal, and they need a lower temperature during melting and sintering compared to the bulk metal. Different methods of sintering are available; depending on the application of printed film and type of substrate, the sintering method could vary, though selective heating of the conducting layers with minimal heat transfer to the substrate is highly desirable. Traditional sintering (in an oven or heating chamber) based on convection heating is one method of sintering; in the case of plastic substrates, heating would deform the substrate before completely sintering the NPs and NWs. Electrical sintering, heating by microwaves, laser sintering, plasma sintering, and chemical sintering are alternative methods to the traditional convection method. Among these techniques, laser sintering has emerged as a method that could concentrate a high power in a small area with accurate control of beam power and location, although this method is expensive and complicated.

2.2. Silver Nanoparticles and Silver Nanowires (Ag NPs and Ag NWs)

New functional materials, Ag NPs and Ag NWs, are widely used in fields such as chemical engineering, aerospace, medicine, and electronics. These materials have attracted attention due to their electrical, optical, and thermal properties. Among metals, Ag has the highest electrical conductivity (6.3×10^7 S/m). Ag NWs are considered to be a promising candidate for use in highly conductive, transparent, and flexible electronics and could even replace ITO [8,9]. Ag NWs and Ag NPs have low material and processing costs compared to ITO. Moreover, the easy deposition method of Ag NWs and Ag NPs from the liquid phase is attractive to scientists. Chou et al. reported that Ag NPs deposited on a glass substrate as a thin film by the spin coating method would exhibit low resistance of 2.4×10^{-5} Ω cm after sintering at 250 °C for 30 min [10]. Increasing the temperature above 400 °C led to decreased conductivity due to the growth of pores in the film (Figure 1), which cause discontinuities in the conducting lines. They found that smaller Ag NPs had a similar reaction, but at lower temperature.

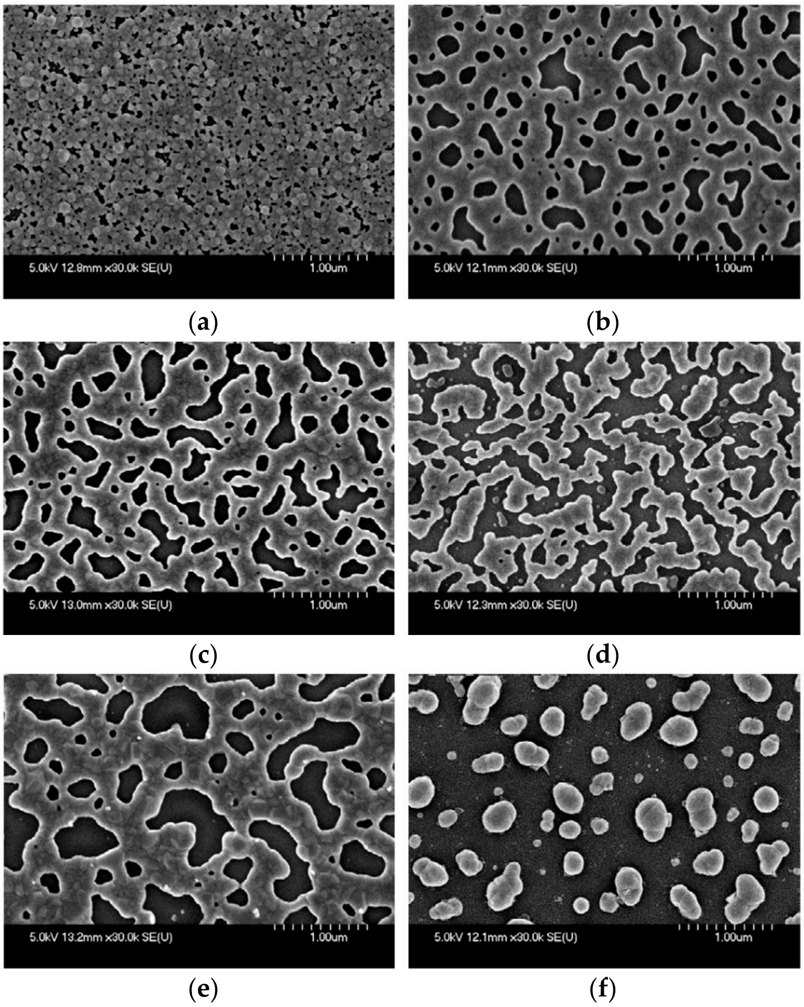

Figure 1. Scanning electron microscopy (SEM) images of Ag nanoparticles (NPs) at different temperatures and of changes in pores' morphology by increasing the sintering temperature: (**a**) 100 °C, (**b**) 200 °C, (**c**) 250 °C, (**d**) 300 °C, (**e**) 350 °C, and (**f**) 400 °C. Reproduced with permission from [10]. Copyright 2005 IOP Publishing.

Li et al. synthesized stable Ag NPs with a particle size less than 10 nm [11]. The Ag NPs showed high conductivity at low sintering temperature and promising application as printed source/drain in organic thin film transistors (OTFTs). Lee et al. described an application of Ag NPs in printable circuits [12], where Ag NPs (50 nm size) in solution were printed on a glass substrate using the ink-jet printing method and an ordinary commercial printer. After deposition of a water-based solution of Ag NPs on glass substrate (thickness 530 nm) and heat treatment at 260 °C for 3 min, the thin film exhibited resistivity of 1.6×10^{-5} Ω cm, close to the bulk resistivity of Ag. Kim et al. directly printed different sizes of Ag NPs on plastic substrate [13]. They showed that inter-particle necks form during sintering, with size increasing with temperature, leading to increased conductivity (Figures 2 and 3).

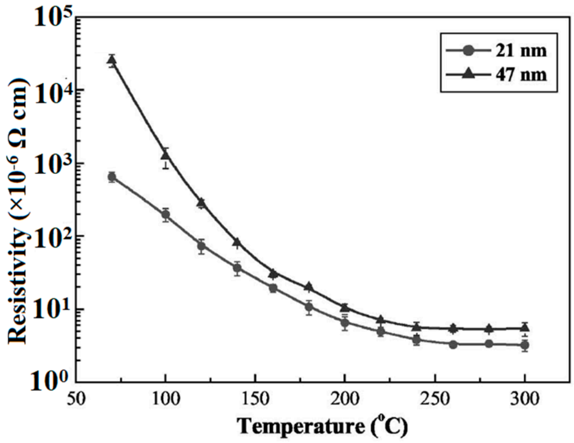

Figure 2. Decreasing the resistivity of the thin film composed of Ag NPs (with different size of 21 and 47 nm) by increasing the sintering temperature. Reproduced with permission from [13]. Copyright 2005 ECS Publishing.

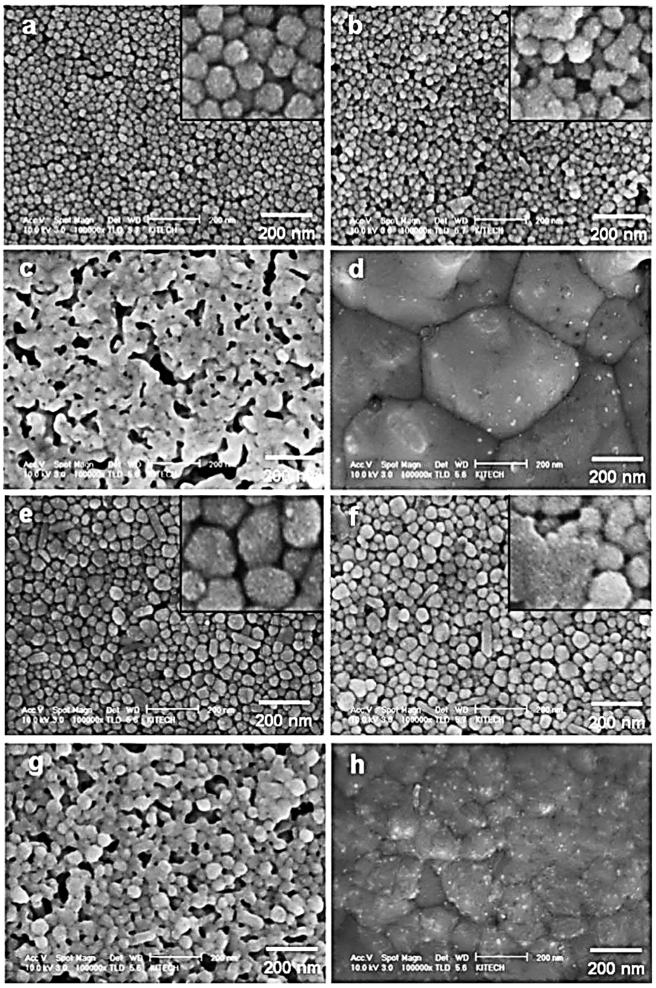

Figure 3. Increasing the Ag NPs size by increasing the sintering temperature: heat treatment of the thin film composed of 21 nm size NPs at (**a**) 100, (**b**) 140, (**c**) 200, and (**d**) 300 °C; heat treatment of the thin film composed of 47 nm size NPs at (**e**) 100, (**f**) 160, (**g**) 200, and (**h**) 300 °C. Reproduced with permission from [13]. Copyright 2005 ECS Publishing.

Another approach for increasing the conductivity of deposited thin film is avoiding the coffee ring effect. The coffee ring effect is usually observed in dried sessile droplets. Deposition of metal NP ink on a substrate causes particles to segregate around the droplet edge boundary (Figure 4), leading to non-uniform deposition of the ink, which affects the conductivity of the printed film. Choosing a carrier solution with a high boiling point and low surface tension for Ag NPs (such as ethylene glycol) improves the quality of the printed film and its conductivity (Figure 5) [14].

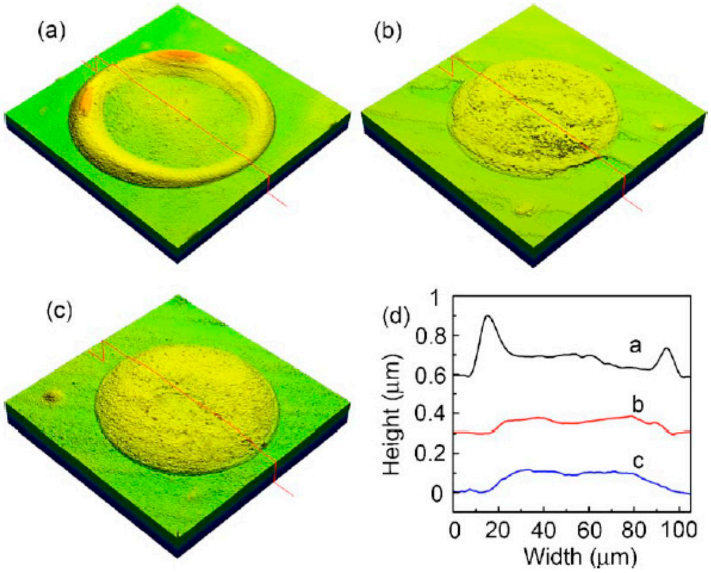

Figure 4. 3D images of ink-jet printed single dots of Ag NPs with different ethylene glycol as carrier solutions: (**a**) 0 wt.%; (**b**) 16 wt.%; (**c**) 32 wt.%; and (**d**) corresponding 2D profile. (Reproduced with permission from [14]. Copyright 2006 AIP Publishing.

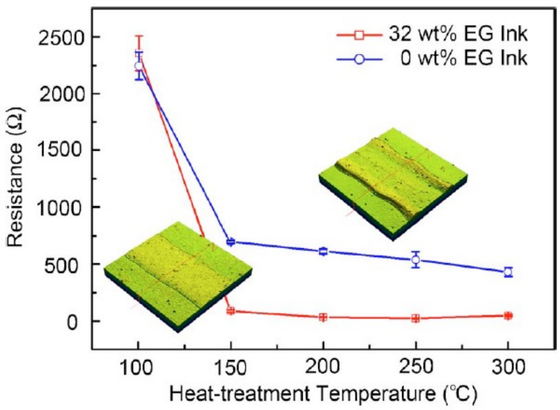

Figure 5. Decreasing the resistance of ink-jet printed Ag NPs thin film by increasing the sintering temperature (0 and 32 wt.% ethylene glycol as carrier solution). Reproduced with permission from [14]. Copyright 2006 AIP Publishing.

Kim et al. reported on use of transparent Ag NW electrodes as an alternative to ITO. They showed that printed thin film from Ag NW solution on a flexible substrate, which had greater than 85% transparency and sheet resistance around 10 Ω/sq, had great potential to be used as a transparent flexible electrode in optoelectronic devices. The electrode had the ability to bend at a radius of 4 mm without altering the sheet resistance. In addition, their easy, solution-based deposition method only needed a low-temperature annealing step (180 °C), which was compatible with a variety of plastic substrates [3]. Ag NPs also showed great potential as source/drain electrodes for organic transistor devices. The Ag NP ink (stabilized with poly(vinyl pyrrolidone) (PVP)) could be used with ink-jet printing methods to produce a source/drain electrode with enhanced field-effect transistor characteristics relative to transistors with vacuum-evaporated Ag electrodes. The results revealed that the presence of oxygen atoms on the electrode surface, as a result of the presence of a PVP-derived chemical modifier, induces an interface dipole, which increases the work function of the ink-jet printed electrodes, thereby enabling the injection of charge carriers into the organic semiconductor [15]. In another study, Ag NWs with length and diameter of 6.5 µm and 85 nm, respectively, were shown to have the capability to be used as transparent, flexible, conducting thin film [16]. The results demonstrated a connection among film thickness, optical transparency, and sheet resistance (Figures 6 and 7). With increasing film thickness, optical transparency at 550 nm decreased, while the direct current (DC) onductivity of the film increased. The maximum optical transparency was 92% at very low thickness. The DC conductivity ranged from 2×10^5 S/m (very thin film) to saturation at 5×10^6 S/m (thick film). Sheet resistance of the film reached its lowest value of 1 Ω/sq at thicknesses above 300 nm. In terms of flexibility, even the thinnest film showed excellent sheet resistance stability after 1000 bending cycles. The σ_{DC}/σ_{Op} (DC to optical conductivity ratio) increased from 25 for the thinnest film and saturated at 500 at a thickness of 200 nm; the increase in conductivity ratio with thickness (from 25 to 500) indicates that this thin film holds great promise as an alternative to doped metal oxide films and a replacement for ITO as transparent electrodes (since the best amount of σ_{DC}/σ_{Op} for ITO is 350 [16]).

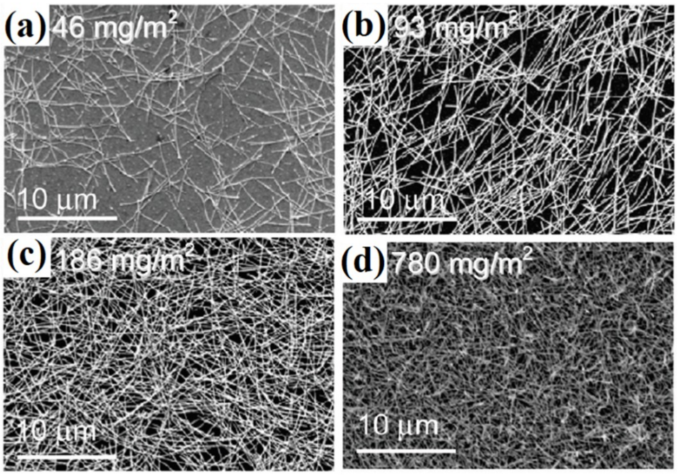

Figure 6. SEM images of the Ag (nanowire) NW thin film with different thicknesses shows increasing the film uniformity by increasing the film thickness. Different thicknesses are realized by varying different deposited mass per unit area: (**a**) 46 mg/m^2, (**b**) 93 mg/m^2, (**c**) 186 mg/m^2, and (**d**) 780 mg/m^2. Reproduced with permission from [16]. Copyright 2009 ACS Publishing.

As mentioned above, solution-based deposition methods such as ink-jet printing need to overcome the coffee ring effect, which negatively affects the thin film properties [14]. By taking advantage of the 2D structure of these metallic rings, a transparent conductive pattern better than that of conventional transparent conductive metal oxides, such as ITO, was obtained (optical transparency 95% and sheet resistance of 0.5 cm^2 was 4 Ω/sq) [17]. Layani et al. demonstrated that, in addition to the great potential of Ag NW thin film as a flexible transparent structure, burying this film at the surface of transparent polymers such as poly(vinyl alcohol) (PVA), polyethylene terephthalate (PET), and polyimide matrix could produce the same response [18]. An obstacle to the application of Ag NWs as a thin film is oxidation of the NWs during the coating process, which negatively affects the conductivity of the thin film. A solution proposed by Zeng and his co-workers was incubation of the Ag NWs in hydrogen chloride (HCl) vapor. HCl treatment not only avoided oxidation of Ag NWs, but also decreased the NW diameter, resulting in decreased resistance of the Ag NW thin film. The film deposited using the rod-coating method achieved 75% transmittance and a sheet resistance of 175 Ω/sq, with outstanding mechanical flexibility and stability of conductivity that only decreased 2% after 100 bending cycles (Figure 8) [19].

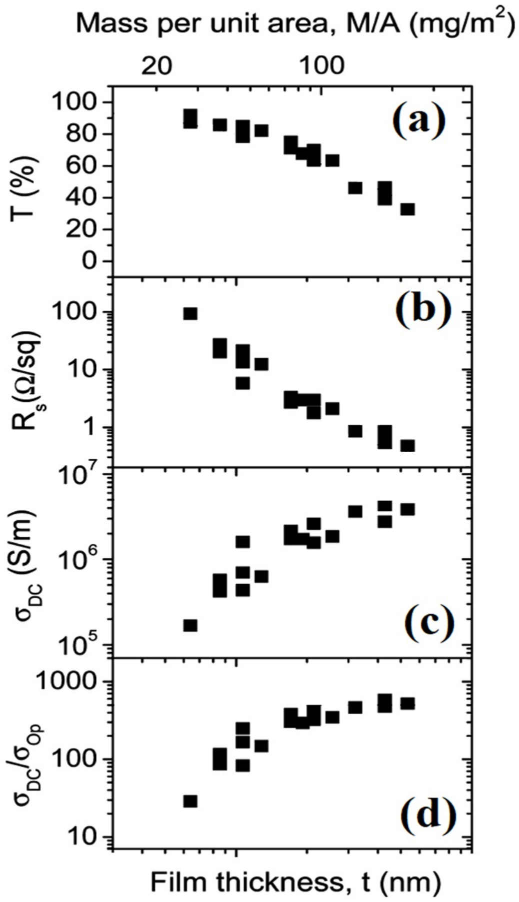

Figure 7. Changing the different characteristic of Ag NW thin film by increasing the film thickness: (**a**) optical transmittance (at 550 nm); (**b**) sheet resistance; (**c**) DC conductivity; and (**d**) σ_{DC}/σ_{Op}. Reproduced with permission from [16]. Copyright 2009 ACS Publishing.

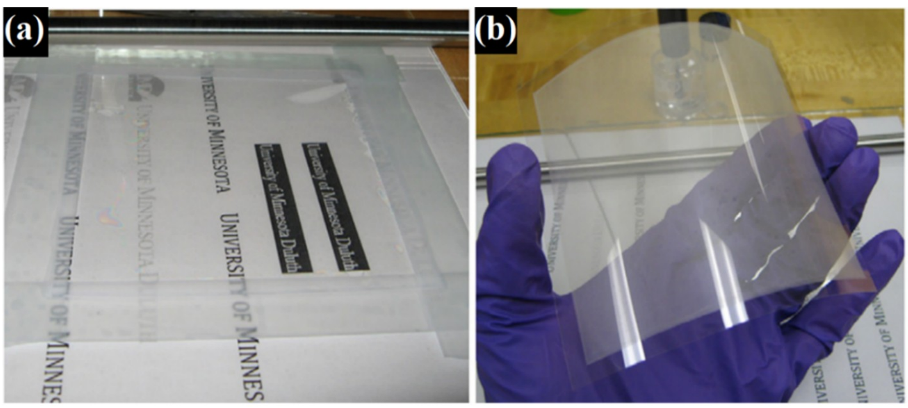

Figure 8. (**a**) Fabricating the Ag NW thin film via rod-coating method; and (**b**) a large, uniform, and flexible Ag NW thin film deposited on PET substrate. Reproduced with permission from [19]. Copyright 2011 Springer Publishing.

Liu et al. proposed using Ag NW with different diameters (5.1 to 12.2 nm) mixed with hexadecane solvent to prepare ink (30 wt.% of Ag particles) to test the effect of Ag NW diameter on the resistance of the produced thin film [20]. A 100-nm-thick thin film was obtained by printing Ag NW ink, followed by sintering at a temperature much lower than the melting point of bulk Ag. Their results showed that the electrical resistance of the ink-jet printed film was not affected by Ag NW size, and that increasing the sintering temperature decreased the resistance of the thin film. They showed that using a hexamethyldisilazane (HMDS) surface treatment followed by dipping the films into methanol could enhance the electrical properties of the thin film. Depositing patterned film of Ag NW on the surface of PET using a simple spray coating showed great promise in application of these conductive nanomaterials as next-generation transparent conductive coatings. Integration of a poly(dimethylsiloxane) (PDMS)-assisted contact transfer technique with spray coating resulted in large-scale, high-quality patterned films. The σ_{DC}/σ_{Op} for various films fabricated in this work was in the range 75–350, which is comparable to that of ITO on flexible substrates. Moreover, the excellent mechanical properties of the film are promising for applications as flexible electrodes in touch panels [21]. Adhesion between the substrate and the thin film is a challenge during thin film deposition. If the adhesion is not strong enough, it will create problems during stretching or bending of the film. To address this issue during fabrication of a transparent Ag NW thin film on stretchable elastomeric substrate, researchers used polydopamine to modify the wettability of the substrate. This modification changed the substrate to a hydrophilic surface to facilitate solution-based deposition of Ag NWs. Akter et al. demonstrated that spray deposition of Ag NWs on the surface of a polydopamine-modified elastomeric substrate resulted in good adhesion, high optical transparency (80%), and low sheet resistance (35 Ω/sq) [22]. After stretching the sample up to 20%, its sheet resistance remained stable. Another key factor that enhances the mechanical, optical, and electrical properties of a conductive thin film is spatial uniformity of the conductive metal nanomaterials networks. Exfoliated clay platelets are one element that could facilitate uniform spatial deposition of Ag NWs [23]. The Ag NWs in the deposited ink were efficiently interconnected with great spatial uniformity that improved the optical and electrical properties close to ITO (conductivity ratio of 300). Length of the Ag NW (unlike its diameter) is another important factor in determining electrical and optical conductivity and even its mechanical properties. Lee and his coworkers showed that very long Ag NWs sintered via laser radiation showed high optical transparency and high electrical conductivity as a flexible electrode [24]. Zhu et al. also demonstrated that very long Ag NWs had the potential to be applied as a transparent electrode (transmittance 91% and sheet resistance of 1313 Ω/sq) [25]. They employed room-temperature plasma for sintering and enhancing the electrical conductivity of the Ag NW network (welding the junctions tightly). They believed that their deposition method (rod coating) facilitated direct deposition of the Ag NW network on different substrates, which could increase the range of applications of these transparent conductive films. In another study, it was revealed that deposition of Ag NWs on PDMS exhibits a great electrical conductivity of ~8130 S/cm (sheet resistance of 0.24 Ω/sq) [26]. Moreover, this conductive combination (Ag NW/PDMS) showed excellent mechanical properties. After some stretching/releasing cycles, its conductivity reached a high value of 5285 S/cm and was stable thereafter. Mixing Ag NW with mesoscale Ag NW (1–5 mm in diameter) is another approach that has been proposed for enhancing the electrical properties of transparent electrodes composed of Ag NW [27]. A previous study demonstrated that a hybrid of nanoscale and mesoscale Ag NWs yields a high transmittance of 92% and sheet resistance of 0.36 Ω/sq, which is one order of magnitude lower than the sheet resistance of Ag NW electrodes. In addition to the length and sintering method used with Ag NW thin films, the deposition method is another factor that affects the electrical, optical, and mechanical properties of the film. The ease of use, scalability, and applicability to deposit the conductive nanomaterials on different substrate types (rigid and flexible) are other factors that contribute to its appeal as a deposition method. Researchers have shown that, using a vacuum filtration method followed by PDMS-assisted transfer printing, Ag NW thin film can be deposited on flexible and rigid substrates with adhesion to the substrate (Figure 9) [28]. PDMS-assisted transfer printing allowed rapid deposition of patterned thin films on different substrates. Moreover, using anodized aluminum oxide as a membrane during the transfer process, the Ag NW film could easily be heated to a high temperature. Using a high temperature for sintering of the film resulted in good optical transparency and high electrical conductivity. Deposition of the Ag NW thin film on a flexible PET substrate via this method resulted in a low sheet resistance of 10 Ω/sq and transparency of 85%.

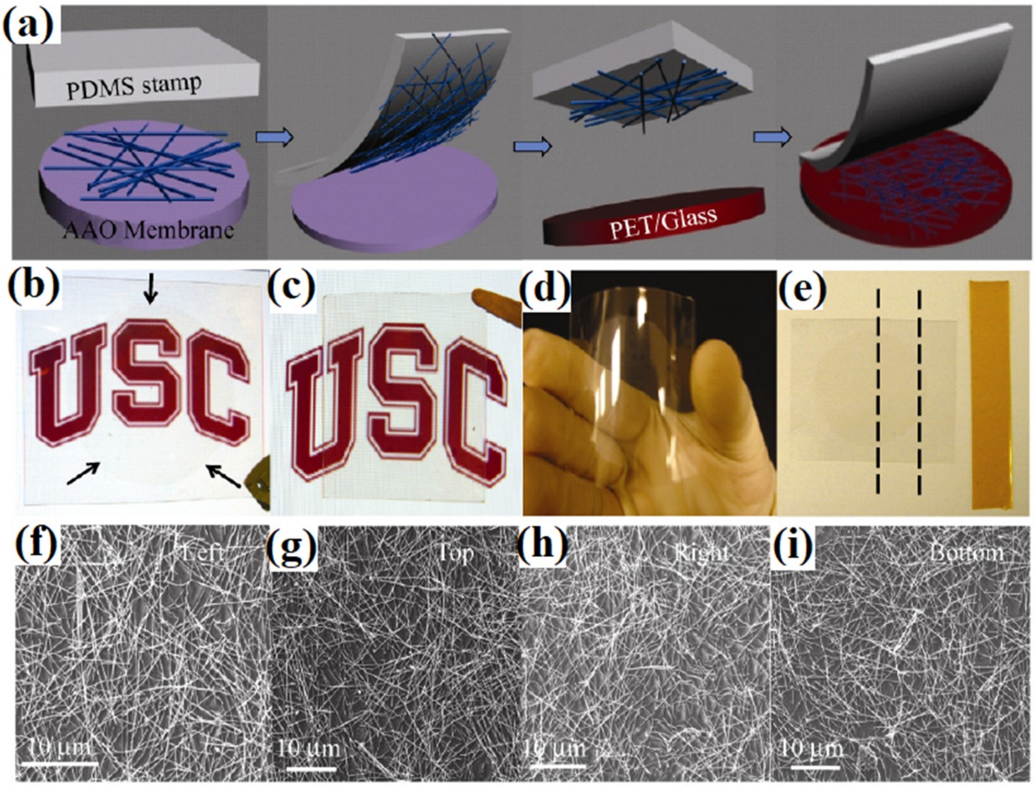

Figure 9. (**a**) Schematic transfer process of Ag NWs from anodized aluminum oxide membrane to PET substrate by using Poly(dimethylsiloxane) (PDMS) stamp; (**b**) Ag NW thin film on PET substrate; (**c**) Ag NW thin film on glass substrate; (**d**) flexibility of the Ag NW thin film on PET substrate; (**e**) adhesion test shows remaining Ag NWs on PET after peeling off the sticky tape from the area between dotted line. SEM images of the (**f**) left, (**g**) top, (**h**) right, and (**i**) bottom regions of the thin film to show the uniformity of the film across the entire area. Reproduced with permission from [28]. Copyright 2010 Springer Publishing.

In cases of Ag NPs and NWs, solution-based methods are more popular with researchers, so a method for preparing a suitable solution (ink) composed of Ag NWs or Ag NPs with highly stable dispersion is needed. Ag-conductive ink is a mixture of Ag particles, solvents, surfactants, etc. During the sintering process that follows thin film deposition, the additive to the Ag ink must be removed, but high boiling points impede this removal at low sintering temperatures. A sintering temperature higher than 200 °C is usually needed for this reason, which restricts the use of flexible substrates for Ag thin film. Cao and his co-workers used low boiling point additives to facilitate ink-jet printing of Ag NP (40 nm) ink on Lucky porous high glossy photo paper, which showed 5.1×10^{-3} Ω cm resistivity after low temperature sintering [29]. They found that a combination of polyethylene glycol and ethylene glycol (ratio was 1:2, respectively) mixed with OP-10 as a dispersing agent could be removed easily from the thin film after heating the deposited film at 100 °C for 2 h.

2.3. Ag NPs and Ag NWs as Filler

Surface functionalized Ag NPs (with diacide) were used as conductive filler in polymer. Results showed that using an appropriate amount of diacids led to sintering of Ag NPs that resulted in reducing the resistivity of the composite to as low as 5×10^{-6} Ω cm, which was considered stable [30]. Researchers showed that the diameter of Ag NWs does not affect their electrical properties [20], whereas their length does affect their application in optoelectronic devices, as mentioned above. Madaria et al. demonstrated that using Ag NWs with different lengths as a conductive network in polymer matrix and their application as electrodes in polymer solar cells influenced their performance. Short Ag NWs (4–10 μm) have higher coverage than longer ones, which results in a high fill factor, whereas the high coverage of short Ag NWs leads to low transparency of the deposited film, resulting in low photocurrent. Using long Ag NWs had the reverse effect on fill factor and photocurrent. To overcome this issue, they mixed different long and short Ag NWs to achieve simultaneous high fill factor and photocurrent [31]. Application of Ag NWs as filler in poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) successfully increased the electrical conductivity of the polymer and had excellent transparency and flexibility (Figure 10) [32]. The presence of Ag NWs in the composite enhanced the electrical properties, while PEDOT:PSS improved the adhesion of the thin film to different substrates. Increasing the concentrations of Ag NW in the composite film showed a decrease in optical transmittance from 82.3% to 74.1% at 550 nm and a decrease in resistance of the composite film.

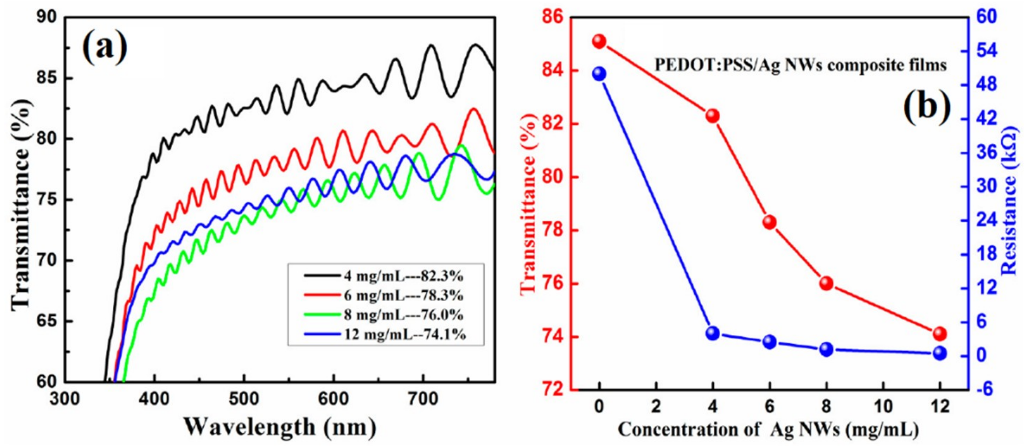

Figure 10. (**a**) Optical transmittance and (**b**) variation of the transmittance (at 550 nm) and resistance of PEDOT:PSS/Ag NW composite by increasing the concentration of Ag NWs filler from 4 to 12 mg/mL. Reproduced with permission from [32]. Copyright 2017 MDPI Publishing.

Based on the papers reviewed in this section, Ag NPs and Ag NWs have attracted increasing attention as conductive metal nanomaterials that could be promising alternatives to ITO in transparent conductive electrodes (Table 1). Although Ag has many advantages, some obstacles remain. Ag NW thin film on bare substrate is very rough, and the thin film can be removed easily by friction; two solutions are using it as filler [20,30–32] or burying Ag NW under the surface of a polymer matrix [18]. Ag NW or Ag NP thin films can be easily oxidized in air and need either a protective layer to prevent oxidation or strong acid treatment to remove the oxidized layer. After deposition of Ag NP or Ag NW thin film, a sintering step is needed, which can increase the cost of production and in some cases negatively affect the substrate. Finally, the cost of manufacturing Ag products may be an obstacle; Ag is expensive and is too scarce to be used extensively in industry.

Table 1. Summary of different deposition methods and properties of the Ag NW and Ag NP coatings and thin films.

Ref.	Material	Coating Method	Coating Thickness (nm)	Transparency (%)	Electronic Factor	Flexibility
[10]	Ag NPs	Spin coating	82	Not available	2.4×10^{-5} Ω cm	Not available
[12]	Ag NPs	Ink-jet printing	530	Not available	1.6×10^{-5} Ω cm	Not available
[14]	Ag NPs	Ink-jet printing	100	Not available	3.5×10^{-6} Ω cm	Not available
[3]	Ag NWs	Solution-processed	100	85 (solar)	10 Ω/sq	Flexible
[16]	Ag NWs	Vacuum filtration (transfer)	107	85	13 Ω/sq	Flexible
[17]	Ag NPs	Ink-jet printing	300	95	4 ± 0.5 Ω/sq	Flexible
[19]	Ag NWs	Rod-coating	Not available	75	175 Ω/sq	Flexible
[21]	Ag NWs	Spray deposition	Not available	85	33 Ω/sq	Flexible
[22]	Ag NWs	Spray deposition	Not available	80	35 Ω/sq	Flexible Stretchable
[24]	Ag NWs	Vacuum filtration	Not available	89 95	9 Ω/sq 69 Ω/sq	Flexible
[25]	Ag NWs	Rod-coating	Not available	91	13 Ω/sq	Flexible
[28]	Ag NWs	Vacuum filtration	Not available	85	10 Ω/sq	Flexible
[33]	Ag NWs	Spray deposition	Not available	90	50 Ω/sq	Not available

2.4. Gold Nanoparticles (Au NP)

As a noble metal, Au has a high electrical conductivity (~10^4–10^5 S/cm) and resistance to corrosion or oxidation; using Au as a thin film requires deposition at high temperature and under high vacuum. Therefore, the low sintering temperatures and simple, solution-based deposition methods of Au NP are advantages of Au NPs over bulk Au (with melting temperature of 1063 °C). A thin film of Au NPs can be printed easily on a substrate via drop-on-demand ink-jet technology (solution-based method) [34]. Argon-ion laser radiation is employed for sintering the Au NPs after deposition, providing localized heating, as required for printing on temperature-sensitive substrates. After the sintering process, the molten Au NPs were agglomerated and formed a continuous film with a specific electrical resistivity of 1.4×10^{-7} Ω m. Controlling the size of the Au NPs was one of the factors that can control the sintering temperature of the Au NP conductive thin film. Huang et al. reported a plastic-compatible ink-jet printing deposition method of organic-encapsulated Au NPs and showed a low sintering temperature of 150 °C for highly conductive Au film [35]. As common plastic substrates deform by heat treatment at 150–200 °C, achieving sintering temperatures of 150 °C or lower is highly desirable. They found that by controlling the size and length of the organic-encapsulated Au NPs, they were able to lower the sintering temperature of the Au thin film and produce a conductive film of Au NPs with a sheet resistance less than 0.03 Ω/sq. A solution-based ink-jet printing method was used for deposition of Au NPs (2–5 nm) dispersed in toluene (as carrier solution) on plastic substrate, followed by laser sintering [36]. The sintering process resulted in solvent evaporation and melting of the Au NPs to form a continuous, electrically conductive pattern on plastic substrate. Researchers reported that curvature and surface effects of Au NPs could successfully lower the melting temperature of particles. Other researchers also have reported dramatic decreases in Au NP sintering temperature (~300 °C) as a result of using very small Au NPs (5–20 nm) in the deposition process, producing a pattern, thin film, or circuit of NPs on temperature-sensitive substrates [37–39]. Although applications of Au NPs as a thin film on plastic substrates have resulted in high-conductivity films or patterns, the cost of this material and its rarity in the Earth's crust are obstacles that limit the use of this valuable material.

2.5. Copper Nanoparticles and Nanowires (Cu NPs and NWs)

As conductive nanomaterials, Cu NPs and Cu NWs could be attractive alternatives to traditional transparent conductive materials (Table 2). Two different types of metal NPs were introduced above, Ag NPs and Au NPs, both of which have shown great electrical, optical, and mechanical properties. However, Ag NPs and Au NPs cannot compete with Cu NP in terms of cost and abundance. Cu is several times more abundant than Ag and Au, as well as being much cheaper and having electrical conductivity comparable to Ag. Cu is insensitive to oxygen and moisture, indicating that solution-based deposition methods are well-suited for preparation of Cu NP and Cu NW thin films. Moreover, in a range of applications of these nanomaterials, particularly in corrosive conditions, using Cu NPs and Cu NWs is advantageous. Production methods for these nanomaterials include chemical reduction, sonochemical reduction, thermal reduction, and microemulsion techniques. In one study, a conductive ink of Cu NPs (45 ± 8 nm) was deposited on glass substrate by the ink-jet printing method [40]. The printed pattern became highly conductive after sintering at 325 °C for 1 h under vacuum, with a low resistivity of 17.2 μΩ cm, and showed highly stable electrical properties after prolonged storage at ambient conditions (Figure 11).

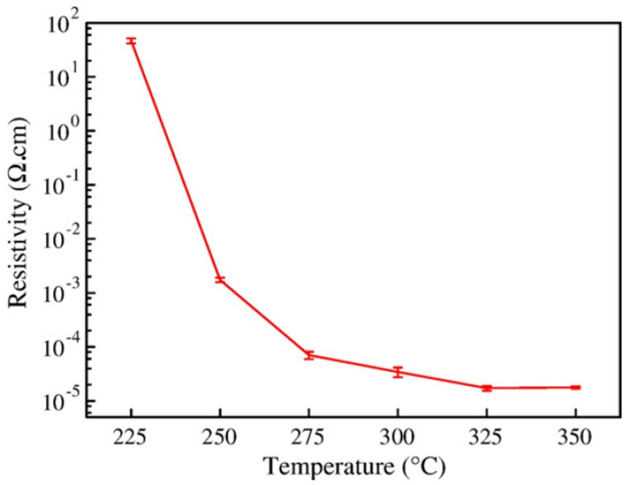

Figure 11. Decreasing the resistivity of a thin film compose of Cu NPs by increasing the sintering temperature. Reproduced with permission from [40]. Copyright 2006 Elsevier Publishing.

However, Cu NPs exhibit great oxidation resistance in the presence of oxygen; during synthesis, a surface oxide layer can form on the particles due to the higher thermodynamic stability of the oxide phases. Jeong and his co-workers used poly(*N*-vinylpyrrolidone) as a capping agent to protect Cu NPs from oxidation [41]. They printed a conductive pattern of Cu NP ink on plastic by the ink-jet printing method and showed that increasing the thickness of the surface oxide layer on Cu NPs would increase the sintering temperature and resistance of the deposited Cu NP thin film. To address this issue, they increased the molecular weight of the polymer used as a capping agent to reduce the thickness of the surface oxide layer. As mentioned earlier, one of the obstacles that limits the application of conventional transparent conductive materials is their fragile structures; Cu NPs and NWs have highly flexible structures with constant electrical properties even after bending [4]. Another research group reported Cu NW thin films as electrodes in an organic solar cell application [42]. A Cu NW thin film was fabricated using transfer printing from a flexible PDMS stamp on PET substrate. The Cu NW thin film electrode had high optical transparency and electrical conductivity combined with a highly flexible structure (bending to a 3 mm radius of curvature with no effect on electrical conductivity) (Figure 12).

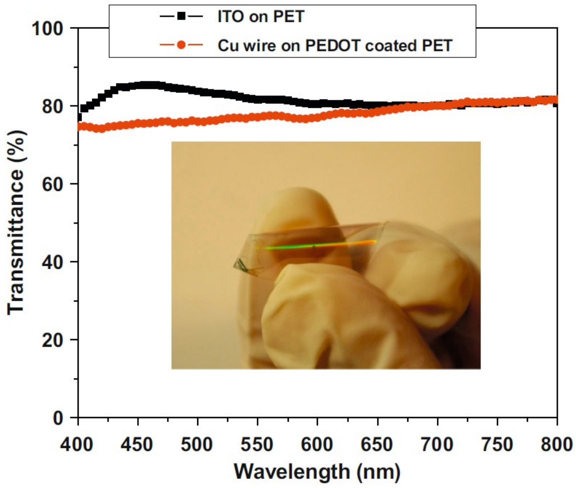

Figure 12. Optical transmittance of Cu NW thin film on PEDOT-coated PET substrate and commercial ITO thin film on PET substrate (inset photo shows the flexibility of the Cu NW thin film on PEDOT-coated PET substrate). Reproduced with permission from [42]. Copyright 2010 Elsevier Publishing.

Table 2. Summary of different deposition methods and properties of Cu NW coatings and thin films.

Ref.	Material	Coating Method	Coating Thickness (nm)	Transparency (%)	Sheet Resistance (Ω/sq)	Flexibility
[43]	Cu NW	Rod coating	Not available	85	30	Flexible
[44]	Cu NW	Rod coating	Not available	95	100	Not available

Rathmell et al. also reported on the same type of research, using well-dispersed Cu NWs in a solution as ink [43]. The thin film deposited on a plastic substrate using Cu NW ink presented low sheet resistance of 30 Ω/sq at a transmittance of 85%, which is comparable to ITO (a traditional transparent conductive material); however, unlike ITO, the Cu NW thin film remained highly conductive even after severe mechanical deformation. The results of these studies showed that the photoelectric performance of Cu NWs can be increased using the aspect ratio of the NWs; increasing the aspect ratio of Cu NWs requires a profound understanding of the process procedure (Figure 13) [44].

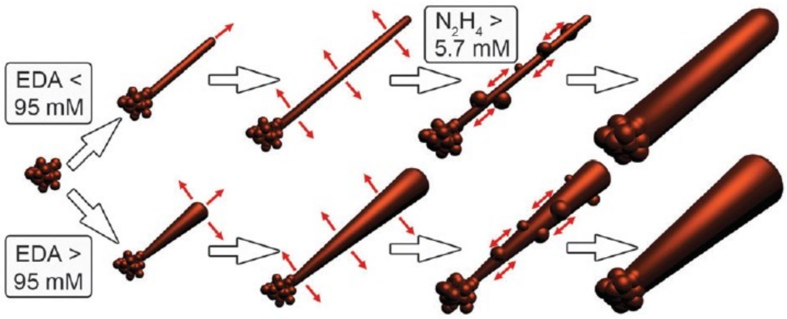

Figure 13. The process of tapering and thickening of Cu NWs in the direction of the red arrows. Reproduced with permission from [44]. Copyright 2014 RSC Publishing.

The alkylamine-mediated method is one of the proposed methods for synthesizing high-aspect-ratio Cu NWs (diameter of 18 nm and length up to 40 mm) [45]. Results suggest that the high aspect ratio of NWs provides a long pathway for transferring electrons with a large space for optical transmittance. The thin film deposited from the mentioned Cu NWs presented a low sheet resistance of 100 Ω/sq at high transmittance (95%). Moreover, such a thin film showed a low sheet resistance (102 Ω/sq) at tensile strains up to 60%, which was stable even after 200 strain/stretch cycles [46]. A thin film of helical Cu NWs showed reversible stretchability up to 700% strain [47]. The characteristics of Cu NPs and NWs make them outstanding candidates in different device manufacturing applications that require high electrical conductivity, optical transparency, flexibility, and great oxidation stability [48].

2.6. Cu NPs and NWs as filler

Use of Cu NPs and NWs is not limited to ink; they have been also used as filler in conductive composites. Using Cu NWs as conductive filler in a polystyrene matrix by the dry mixing method produced a highly conductive network, which successfully demonstrated EMI shielding capabilities [49]. Moreover, the composite prepared using Cu NW as filler not only presented high conductivity, great optical transparency, and excellent flexibility, but also exhibited oxidation resistance [50]. Application of Cu NW as filler in AZO is also promising for producing a composite with low sheet resistance (35.9 Ω/sq) and high optical transparency (83.9% at 550 nm), and the Cu NW/AZO composite maintained its performance even after 1280 bending cycles with a bending radius of 2.5 mm (Figure 14) [51]. From the results above, it can be concluded that Cu NPs and NWs could be good candidates for industrial-scale production of conductive metal nanomaterials, with the one obstacle of a low aspect ratio.

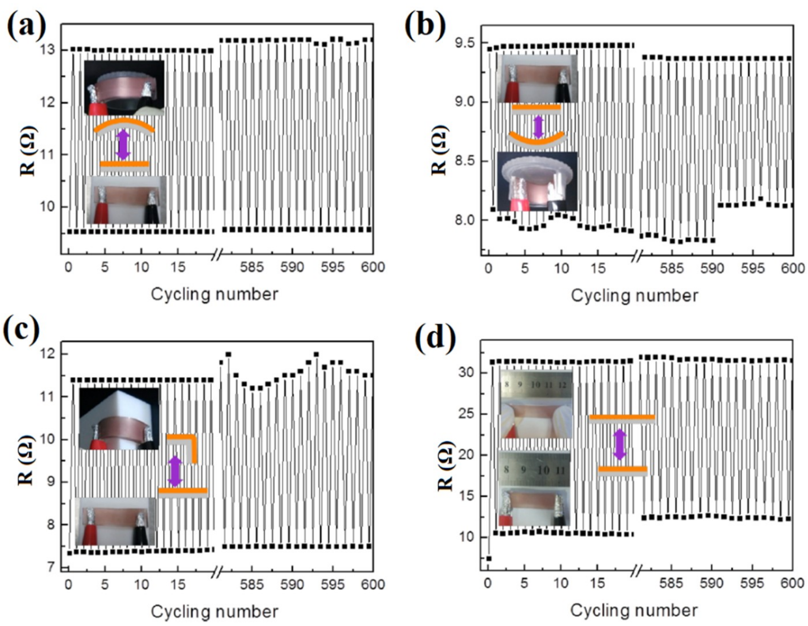

Figure 14. Changing the resistance of the composite film of Cu NW/AZO: (**a**) tensile bending with curvature radius of 25 mm; (**b**) compressive bending with curvature radius of 23 mm; (**c**) vertical bending; and (**d**) 20% stretching-releasing process. Reproduced with permission from [51]. Copyright 2014 ACS Publishing.

2.7. Other Conductive Metal Nanoparticles

It has been shown that metal NPs such as Ag (NWs and NPs), Au (NPs), and Cu (NWs and NPs) can be used as conductive coatings and conductive fillers; moreover, as alternatives to transparent metal oxides, these nanomaterials exhibit high optical transparency and flexibility. Several metal NPs have been investigated by researchers for use as conductive nanomaterials. Zinc oxide (ZnO) NPs were introduced by Izumi and his co-workers as a conductive nanomaterial [52]. In terms of cost and safety, ZnO NPs are a promising alternative to ITO. Tin (Sn) NP is another metal nanomaterial; the low cost of production of this NP as ink favors its use with the ink-jet printing method [53,54]. A sintering step follows deposition of Sn NPs; as is the case with other metal NPs, the sintering temperature of

Sn NPs is size-dependent and it is totally different than the bulk Sn. A modified polyol method in the presence of PVP was applied to produce Sn NP of different sizes ranging from 35.1 to 11.3 nm. Melting temperature ranged from 234.1 °C for bulk material to 177.3 °C for 11.3 nm NPs. Moreover, hydrogen treatment followed by plasma ashing of the Sn thin film decreased its sheet resistance from 1 kΩ/sq to 50 Ω/sq. Aluminum (Al) NPs also have been introduced as conductive nanomaterials that could be used in the form of ink and could replace expensive NP inks such as Au and Ag [55]. One challenge for using Al NP is oxidation. Research results have revealed that catalytic decomposition and an oleic acid coating method could lead to synthesis of oxide-free Al NPs. Using oleic acid in the synthesis of Al NPs could control the size of the NP by forming a self-assembled monolayer, protecting it from oxidation. The printed conductive thin film of Al NPs on substrate exhibited good electrical conductivity after sintering at 300 °C.

3. Deposition Methods

The special characteristics of nanomaterials have made them an integral part of modern life. Taking advantage of such revolutionary materials demands appropriate methods for incorporating them in devices. As a thin film, conductive metal nanomaterials could be useful alternatives to metal foils and films, and transparent metal oxides, if the chosen deposition method is appropriate and does not alter their positive characteristics. In this regard, uniform distribution of nanomaterials on a substrate with precise control of density is required. This issue is more challenging when the substrate is flexible or has an anisotropic shape. Deposition methods of nanomaterials can be divided into two groups: dry and wet (solution-based) methods. Dry methods derive the thin film of nanomaterials directly from a precursor (such as chemical vapor deposition). Wet methods disperse the nanomaterials in solvent and subsequently fabricate a film from the solution. In wet deposition methods, there are some important factors in producing a solution or ink from conductive metal nanomaterials. The chemistry and formulation of the solution have great impact on the quality of the produced thin film. The viscosity of the solution, the stability of the nanomaterials in solution (or ink), and the size of nanomaterials (in the case of ink-jet printing) are important factors. The difficulty of the wet deposition methods is the need for functionalization of nanomaterials or the use of surfactants and sonication to improve the stability of the solution; using such additives degrades the electrical properties of the thin film. In addition, sonication of the solution to stabilize the surfactant shortens the metal NWs, which leads to diminished electrical properties of the thin film. Furthermore, after thin film deposition, surfactants that are not removed from the film leave a residue that increases the sheet resistance of the film. Here, the different deposition methods of conductive thin films are introduced.

3.1. Ink-Jet Printing

The ink-jet printing method is a fast, simple, and cost-effective method that could be a great alternative to the expensive, complicated, and time-consuming conventional lithography method. Printing different conductive patterns, thin films, and lines (circuits) in a single step at low temperature (compatible with plastic substrate) on different types of substrate (flexible and rigid) is simplified. This method also is suitable for large-area and roll-to-roll production of films. There are many reports on producing ink from Ag NPs [13,14,29,56], Au NPs [34,38,57], Cu NPs [40,41], Al NPs [55], and Sn NPs [53], and subsequent deposition of conductive thin films and circuits from these nanomaterials by ink-jet printing methods [12,17,20,58,59].

3.2. Spin Coating

Spin coating is one of the most popular and convenient solution-based deposition methods for fabricating a uniform thin film on a flat substrate. In this method, the substrate is rotated at high speed, and centrifugal force is used to spread the solution on the entire substrate surface; excess material is cast away from the surface of the flat substrate. The thickness of the deposited thin film varies depending on rotation speed, rotation time, and solution viscosity. There are some reports on spin coating deposition of metal NWs [10] via this method.

3.3. Rod Coating

Rod coating is a scalable, cost-effective, and simple method for deposition of conductive thin film on a substrate in a continuous and controlled manner. The rod size, solvents, viscosity or concentration of the nanomaterials in the solvent, and wetting properties of the solution are important factors that affect the quality and uniformity of deposited thin film via this method. The size of grooves in the wire-wound rod controls the thickness of the thin film and is dependent on rod diameter. A portion of the solution flows through the grooves in the wire-wound rod, resulting in deposition of a thin film at room temperature. Use of the rod coating method to deposit a conductive thin film of Ag NWs [19,23,25] and Cu NWs [43,44] has been reported.

3.4. Spray Coating

Spray coating is a simple, fast, compatible, inexpensive, and scalable deposition method to obtain a conductive thin film directly on the substrate at room temperature and uses a spraying device (based on forced air, such as with an airbrush or spray gun) to deposit the materials on the substrate through the air. This method is a major coating technique used in industry; any type of substrate (rigid or flexible) with any type of geometry (not only flat substrate) can be coated via this method. The uniformity of the deposited thin film by spray coating is dependent on spray pressure, which must be optimized. Heating the substrate during spray deposition can help to accelerate the drying of deposited materials. After deposition, washing the thin film with water or acid treatment is recommended to remove the residual solvents. Reports on spray deposition of Ag NWs [21,22,33,60,61] have demonstrated the workability of this method [62,63].

3.5. Vacuum Filtration or Transfer Printing Method

The vacuum filtration method (so-called transfer printing) is a thin film production method that needs a subsequent transferring process to deposit the produced thin film on the target substrate. First, the thin film is produced on a filter membrane via vacuum filtration; subsequently, part or all of the deposited film is transferred to the target substrate. Usually, the thin film produced with this method is homogenous, and the thickness of the film can be controlled via solution concentration and volume of the filtered suspension. A limitation of this method is the film size (it is not a scalable method), which is restricted to the size of the filter membrane. Experiments showed that Ag NWs [16,18,24] and Cu NWs [42] could be used for producing a conductive thin film (in some cases, transparent) via the vacuum filtration method.

3.6. Dip Coating

Dip coating is another conductive thin film deposition technique, which is typically used when the coating material does not respond to electric or magnetic fields. Pre-treatment (for example, chemical functionalization) of the substrate could enhance the applicability of this method. To produce a thin film via dip coating, the substrate is immersed in a container (filled with the coating material solution), removed from the tank, and subsequently drained. Changing the duration of these steps controls the thickness of the film. Studies have reported that dip coating was used effectively to produce Ag NWs [64,65] conductive thin films.

3.7. Other Deposition Methods

Other deposition methods for producing a conductive thin film from conductive metal nanomaterials are used less regularly than the methods introduced above; these include solution casting [66,67], the Langmuir-Blodgett deposition method [68,69], screen printing [32], stamp printing [70], electrophoretic deposition [71–73], and printing via laser ablation [74]. Among the methods introduced above, only some are scalable and feasible for industrial/commercial production (rod, spray, and dip coating), and more research is needed to increase compatibility with industrial demands.

4. Application of Conductive Thin Films and Coatings

Application of conductive metal nanomaterials as thin films and coatings is critical for electronic and optoelectronic devices and components [75]. In particular, their application as electrodes in different devices such as LCDs, touch panels, flat panels or plasma displays, OLEDs, and solar cells is revolutionary in terms of weight, volume, cost, and mechanical properties of the new products [21,76]. Their high conductivity makes them good candidates for antistatic and antiglare coatings, printable electronics, and EMI shielding material, while their mechanical properties (stretchability and flexibility) make them potential candidates for flexible displays [22]; loudspeakers; and artificial eyes, skin, noses, and muscles [26,77,78]. Using conductive metal nanomaterials in the form of thin films requires high electrical conductivity even under strain, stretch, and bending, as well as no mechanical degradation or deformation of the film even after several bending cycles [79]. Other applications of conductive metal nanomaterials consist of corrosion resistance coatings for electrical/electronic components [80], antireflection coatings [65], and field emission displays [81]. Conductive metal nanomaterials can be used in inks and printed directly on substrates to form a conductive thin film, or they can be reinforced into polymer networks, resulting in a conductive composite. When conductive metal nanomaterials are used as filler, their properties are added to those of the polymers, forming an outstanding composite with exceptional structural, mechanical, electrical, and optical properties with a vast range of applications.

4.1. Solar Cells

A solar cell (a type of photovoltaic device) is used to convert the energy of photons directly into electricity. In the manufacture of organic and thin film solar cells, transparent conductive electrodes are very important [82]. Ag NW and Cu NW thin films are two alternatives to conventional metal oxide thin films [3,42,83,84] and have been used as transparent conductive electrodes, exhibiting 19% higher photocurrent compared to organic solar cells based on an ITO electrode [3,83,84]. Conductive metal nanomaterials also have been applied as transparent conductive composites. A combination of Ag NWs and polymethacrylate exhibited great potential as an electrode for polymer solar cells [31] and counter electrodes of dye-sensitized solar cells [85].

4.2. OLED

An OLED is a type of LED that uses a thin film of organic compound as its emissive electroluminescent layer to emit light in response to an electric current. The film of organic compound is placed between two electrodes, of which at least one is transparent. OLEDs are very light and can be produced with a very thin and flexible structure. ITO as a conventional material used to fabricate transparent electrodes of OLEDs; however, it does not produce good mechanical properties or flexibility, decreases the performance and mechanical stability of OLEDs, and its deposition is limited to a small range of substrates [29]. The sputtering deposition of ITO (the most common method for ITO deposition) on flexible substrates results in a thin film with high sheet resistance due to the low-temperature thermal treatment that is required by the substrate. Furthermore, low mechanical resistance and cost of producing ITO limit its application as a transparent electrode for OLEDs [86]. Metal NWs show great potential to be used as transparent conductive electrodes (as both anode and cathode) for OLEDs. The OLEDs produced using these materials exhibited high optical transparency and did not show any failure after bending or mechanical deformation [87–89].

4.3. Supercapacitor

Supercapacitors are appropriate for use in applications that require very fast charge/discharge cycles (compared to long-term compact energy storage), providing higher power and capacitance than other capacitors and accepting/delivering charge much faster than batteries, while they can tolerate more charge/discharge cycles compared to rechargeable batteries. This kind of short-term energy storage has applications in computers, cars, trains, buses, and elevators. Using conductive nanomaterials with high electrical conductivity, large specific surface area, and great mechanical strength as both the current collector and active electrode in supercapacitors changes the mechanical and electrochemical performance of supercapacitors, maintaining the structural properties even after several stretching cycles. Furthermore, the high conductivity of these materials would accelerate the supercapacitor charge-transfer during the discharging process.

4.4. Circuitry

Electrical circuits are inseparable parts of almost all electronic and optoelectronic devices [11,40], with applications in radio frequency identification tags, transistors, wearable electronics, smart labels, LEDs, and LCDs. Production of conductive ink using conductive nanomaterials was a valuable achievement, since these materials have the ability to be printed as a conductive thin film by simple deposition methods on different types of substrates (rigid or flexible). Producing these conductive inks dramatically reduced the cost of manufacturing electrical circuits, since these advanced inks do not require conventional lithography, vacuum processing, or costly substrates [16].

4.5. Transistor

A transistor is a device for amplifying or switching electrical power and electronic signals. By increasing the controlled output relative to the input power, a transistor can amplify a signal. Moreover, it is a fundamental part of modern electronic devices. Transistors are semiconductor devices usually made of Si or Ge. If the active semiconductor layer is deposited as a thin film, it is called thin film transistor (TFT). If the semiconductor thin film and the electrodes are transparent (such as ITO), the transistor is called a transparent thin film transistor (TTFT); the main challenge regarding these devices is that the deposition temperature of the transparent thin film must be compatible with those of conventional substrates. Therefore, there is a need for an alternative to ITO (which needs a high temperature during deposition) to form a thin film without affecting the substrate and in which the electrical and optical properties are comparable to those of ITO. Metal NPs [57] have shown great potential to be used as source and drain in a TTFT, dramatically decreasing the cost of production and compatible with deposition on different types of substrate (flexible and rigid). Moreover, the combination of these nanomaterials with polymers (composites) is another promising alternative for brittle and costly conventional transparent conductive metal oxides (such as ITO) [67,74,90].

4.6. Electromagnetic Interference (EMI) Shielding

Electromagnetic radiation, which freely passes through the air, can interfere with electrical circuits and limit or interrupt their performance. EMI usually is caused by electromagnetic radiation originating from an external source. When designing a circuit, it is important to minimize the amount of electromagnetic radiation (interference) generated and provide sufficient electromagnetic shielding to tolerate EMI from the environment. EMI shielding uses conductive or magnetic materials to reduce the EMI by blocking the electromagnetic radiation. If the design of a circuit cannot protect itself against excessive electromagnetic radiation, it can be protected by electromagnetic shielding. The electrical conductivity of the shielding materials is an important factor in its EMI shielding effectiveness. The materials conventionally used to make EMI shielding are metal sheets (Al, Cu, and steel); recently, nanocomposites (polymer reinforced with highly conductive fillers) are becoming popular due to their low weight, low cost, and great mechanical properties. In selecting the conductive filler, high aspect ratio nanomaterials such as metal NWs [49], which require very low filler loading, make the product economically feasible and retain the mechanical properties of the polymers [91,92].

4.7. Transparent Film Heaters

A thin and flexible polymer film coated with a transparent conductive film that converts electric energy into thermal energy while maintaining transparency is called a transparent film heater. The input voltage controls the temperature of the heater. This type of material is usually used in heating outdoor displays, defogging vehicle windows, and thermal therapies [23]. The material used most commonly in manufacturing transparent film heaters is ITO; however, its scarcity, cost, and poor mechanical properties limit its future application. Moreover, the intrinsic slow temperature response of ITO affects its applicability as a film heater. Metal NWs [32] and composites (combinations of conductive metal nanomaterials and polymers) [32,93] were introduced as alternatives for ITO in transparent film heaters.

4.8. Dielectric

One application of conductive metal nanomaterials is as conductive filler for polymers, resulting in dielectric property. The dielectric constant of the polymers exhibited a great increase after addition of a small amount of conductive filler [94,95]. In particular, conductive nanomaterials with high aspect ratios, such as metal NWs, could dramatically increase the dielectric constant of the polymers with very low percolation threshold.

4.9. Conductive Thread

Incorporating conductive metal nanomaterials in the form of conductive threads introduced a novel application of these materials in the form of wearable electronics [96], wearable antennas, health monitoring sensors, etc. Common types of thread, such as cotton, polyester, and nylon, are electrical insulators, whereas conductive threads made of solid metal wires (Cu or stainless steel) or an insulator thread covered by a thin layer of conductive material such as Ag, are expensive, heavy, rigid and brittle, and would break down or be damaged by bending. Conductive metal nanomaterials such as Ag NWs and Au NWs could be manufactured as a thread and used as an alternative to conventional conductive threads. Moreover, using metal NPs as a coating on insulator thread (instead of continuous metal coating or a solid metal wire) would decrease the cost of conductive thread and result in production of lighter conductive thread. Furthermore, the produced conductive thread would be thinner, with improved mechanical properties [64].

4.10. Aerospace Industry

Lightweight composites composed of conductive metal nanomaterials as filler in polymer matrices have been of great interest for the aerospace industry. Use of heavy metal meshes, such as Cu mesh, to protect the outer surface of aircraft against lightning strike by providing a conductive path needs to be replaced with lighter conductive materials whose properties are comparable to or better than those of the conventional materials. In order to fabricate new types of materials as an alternative to conventional materials in aerospace, there are some issues that need to be addressed such as high conductivity, low weight, eco-friendliness, flexible manufacturability, high mechanical strength, and ease of repair [60].

4.11. Medical Applications

Applications in electronic implants have some limitations, one of which is the difference between living tissue and the materials used in the implant. The materials (metal and semiconductor) used in the electronic implant are brittle, while most tissues are soft and flexible. One of the key parameters for choosing a proper electronic implant is flexibility and stretchability. Generation of cracks in the electronic implant as a result of bending and stretching causes failure and isolation of conductive pathways. Using conductive materials with high aspect ratios such as metal NWs would help to bridge the cracks under stretching, allowing the material to remain conductive [97].

4.12. Lithium-Ion Batteries (LIB)

LIBs are a variety of rechargeable batteries in which Li ions move from the negative electrode to the positive electrode during discharge and back during charging. LIBs are one of the most popular types of rechargeable batteries in home and portable electronics. Because of their low self-discharge and high energy density, there is an increasing demand for use of LIBs in aerospace and military applications, as well as in electric vehicles. One benefit of using LIBs in new applications is using new materials as an alternative to conventional heavy metal current collectors, which could efficiently decrease the weight of the final product. Using conductive metal nanomaterials as conductive thin films or as conductive filler for a highly conductive current collector for both the anode and the cathode of LIBs has been reported. Using these conductive metal nanomaterials not only makes LIBs lighter, but also enhances their mechanical properties [98].

5. Conclusions and Outlook

This paper introduced conductive metal nanomaterials and reviewed their methods of deposition and application. Obstacles and limitations facing their use in the electronic and optoelectronic industry were reported, and the challenges faced with enhancing the electrical properties of conductive metal nanomaterials were revealed. In this review, it was clear that one challenge regarding application of conductive metal nanomaterials is the sintering process that follows their deposition as a thin film and that is needed to increase their conductivity. The sintering process limits the choice of substrate for these nanomaterials. At the proper temperature, the sintering process results in increased conductivity of the film due to formation of inter-particle necks. The sizes of the inter-particle necks increase with increasing temperature, which leads to increased conductivity, although increasing the sintering temperature above a certain amount leads to decreased conductivity due to growth of pores in the film and subsequent discontinuity of the conducting films. A method for lowering the sintering temperature of these nanomaterials is needed, since it could widen the options of substrates available for these materials. One proposed solution for lowering the sintering temperature is decreasing the size of the nanomaterials. During production of a conductive thin film composed of conductive metal nanomaterials, the thickness of the film has implications for its optical transparency and electrical conductivity: increasing the thickness of the film increases the electrical conductivity and decreases the optical transparency. Furthermore, in producing a conductive thin film or coating from conductive metal nanomaterials or conductive composite (conductive metal nanomaterials as filler), the aspect ratio of the nanomaterials affects their electrical properties. In forming a composite, increasing the aspect ratio decreases the percolation threshold, which is an important step in lowering the cost of production while maintaining the mechanical properties of the host polymer. In some applications (e.g., OLEDs, touchscreens), conductive metal nanomaterials result in improved flexibility of the produced device, in addition to economic advantages. Nevertheless, the priority of the conductive metal nanomaterials industry is finding the best method of producing cost-effective, high quality conductive metal nanomaterials at an industrial scale. The immediate objectives of future research should be to scale up production of conductive metal nanomaterials and improve their quality. Using conductive metal nanomaterials in everyday applications is still at an early stage of research and development, but the prospects and application opportunities in smart optoelectronics make it an attractive topic for research. Moreover, using conductive metal nanomaterials as filler in polymers or producing conductive hybrids by mixing different types of conductive metal nanomaterials together will broaden the potential applications of these conductive nanomaterials.

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Nomenclature

AZO	Al-doped zinc oxide	Al	Aluminum
Cu	Copper	EMI	Electromagnetic interference
FTO	Fluorine tin oxide	Au	Gold
HMDS	Hexamethyldisilazane	HCl	Hydrogen chloride
ITO	Indium tin oxide	LED	Light emitting diode
LCD	Liquid crystal display	LIB	Lithium-ion batterie
NP	Nanoparticle	OLED	Organic light-emitting diode
OPV	Organic photovoltaic cell	PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)
PDMS	Poly(dimethylsiloxane)	PVP	Poly(vinyl pyrrolidone)
PET	Polyethylene terephthalate	Ag	Silver
NW	Nanowire	TFT	Thin film transistor
Sn	Tin	ZnO	Zinc oxide

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