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Review

Review of the Versatile Patterning Methods of Ag Nanowire Electrodes

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Abstract: To use Ag nanowires for various industries, it is crucial to develop an appropriate patterning method. There are various types of patterning methods, but there has been no comprehensive review discussing and summarizing them. This review paper provides an overview of the various patterning techniques of Ag nanowire electrodes, including photolithography, nanoimprint lithography, inkjet printing, electrohydrodynamic jet printing, and other emerging methods. These transparent electrodes have received significant attention due to their high transparency, low sheet resistance, and flexibility, making them ideal for applications such as flexible electronics, touch screens, and solar cells. Each patterning technique has its benefits and limitations, and its suitability depends on specific application requirements. Photolithography is a well-established technique that can achieve high-resolution patterns, while nanoimprint lithography is a low-cost and versatile method for large-area patterning. Inkjet printing and E-jet printing provide the advantages of high throughput, precise control, and the ability to print on different substrates. Stencil printing, laser direct writing, and electrospinning are emerging techniques that showing high potential for patterning Ag nanowire electrodes. The choice of patterning technique ultimately depends on various factors, such as resolution requirements, cost, substrate compatibility, and throughput.

Keywords: Ag nanowire; patterning; electrode; flexible; application

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1. Introduction

The development of technology for flexible and wearable devices has led to increased interest in mechanically and chemically reliable transparent electrode materials [1–10]. Among the most commonly used materials for transparent electrodes is indium tin oxide (ITO), which has the advantages of high transparency, conductivity, and chemical stability [11,12]. However, ITO is intrinsically brittle, which makes its use challenging in flexible or wearable devices. As alternatives to ITO, therefore, carbon-based materials such as graphene or carbon nanotubes (CNTs), or metal-based networks such as metal meshes or metal nanowires, are actively being studied for transparent electrodes [13–15]. In particular, Ag nanowire networks have shown superior properties, especially in optical transmittance and electrical conductivity [16–21]. In addition, the synthesis of Ag nanowires is easy and mass-producible, which is suitable for industry. Ag nanowires have also shown the potential for large-area coating using a roll-to-roll process. Therefore, intensive research has been conducted on the application of Ag nanowires to various futuristic devices (Figure 1) [22]. Despite the various advantages of Ag nanowires for transparent electrodes, the progress of the development of commercial devices using Ag nanowires is limited because there are several critical issues to be solved, including low stability to chemical and mechanical damages. More importantly, facile and easy patterning methods are required, especially for the application of touch panels and various sensors [23–25]. This review aims to provide an overview of the available Ag nanowire electrode patterning technologies, discussing the pros and cons of different methods, their performance and optimization requested.

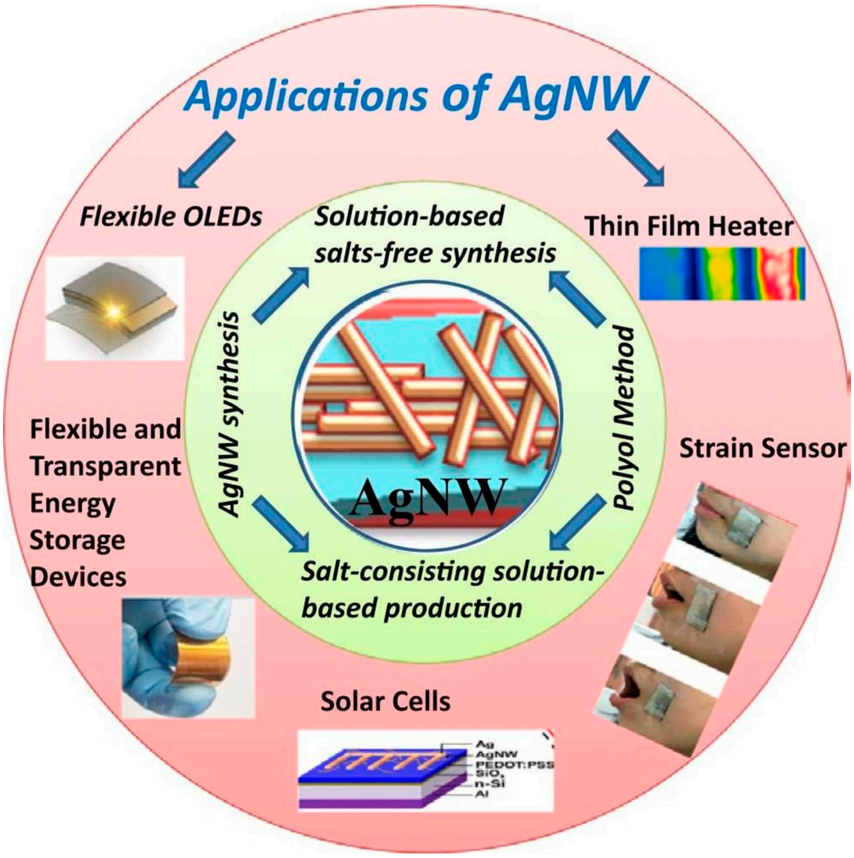

Figure 1. Schematic of various application areas of Ag nanowires. Reproduced with permission from Ref. [22]. Copyright 2022, Elsevier.

2. Various Patterning Technologies of Ag Nanowire Electrodes

2.1. Photolithography

Photolithography patterning of Ag nanowire electrodes is a crucial process in the fabrication of electronic and optoelectronic devices [26–29]. The process involves the use of photosensitive solutions, such as photoresists, which can be selectively exposed and developed to create intricate patterns of Ag nanowire electrodes on a variety of substrates (Figure 2) [28].

One commonly used positive-tone photoresist in the photolithography patterning of Ag nanowire electrodes is AZ5214E [28]. This photoresist has a high sensitivity to UV light, which makes it an ideal choice for patterning Ag nanowires. After the photoresist is applied to the Ag nanowires, it is exposed to UV light through a photomask, which causes the photoresist to become cross-linked and hardened in the exposed areas. The unexposed areas of the photoresist are then removed using a developer solution, leaving behind a patterned photoresist layer on the Ag nanowires. The exposed Ag nanowires can then be etched away using a suitable etchant solution, leaving behind the desired pattern of Ag nanowire electrodes. In contrast, negative-tone photoresists such as SU-8 are used to create patterns where the exposed areas are not cross-linked and remain unhardened [30]. The unexposed areas of the photoresist are then developed away, leaving behind the desired pattern. In the case of Ag nanowire patterning, a negative-tone photoresist can be used to create a patterned photoresist layer on the Ag nanowires, which can then be used as a template for subsequent etching steps. The choice of photoresist and developer used in the process depends on the specific requirements of the device and the desired pattern. For example, a high-resolution pattern with a small feature size may require the use of a photoresist with a high sensitivity to UV light, such as AZ5214E. In contrast, a pattern with larger feature sizes may require the use of a photoresist with a lower sensitivity to UV light to ensure that the pattern is not overexposed. The developer solution used in the photolithography patterning process is an essential component in the removal of the unexposed areas of the photoresist. In the case of AZ5214E, a developer solution consisting of a 1:1 mixture of AZ 726 MIF and AZ 726 MIF Developer is commonly used. The developer solution dissolves the unexposed areas of the photoresist, leaving behind the desired photoresist pattern on the Ag nanowires.

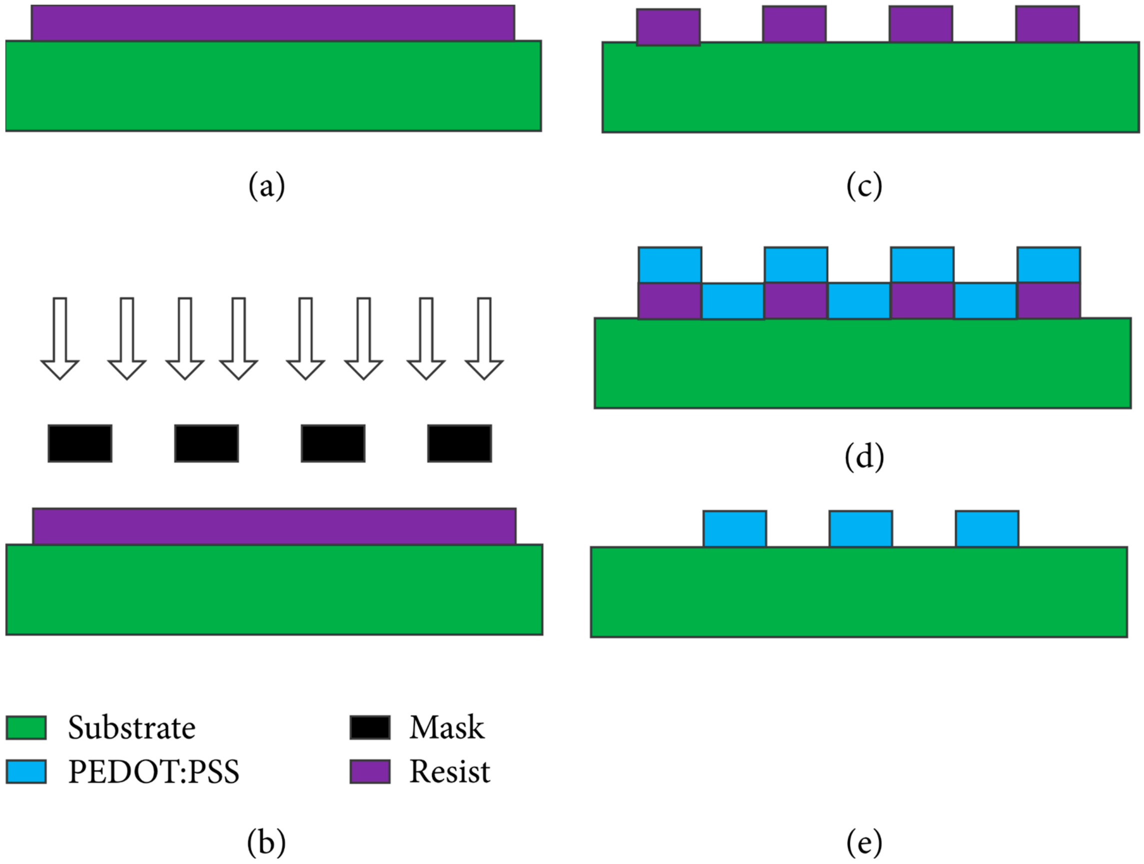

Figure 2. Schematic processes of photolithographic patterning of PEDOT:PSS. Photoresist was first spin-coated (**a**) and patterned (**b**), (**c**) on a substrate. Then, PEDOT:PSS was subsequently deposited (**d**). After lift-off of left resist, PEDOT:PSS patterns were left on the substrate (**e**). Reproduced from Ref. [28] under the Creative Commons Attribution 4.0 International (CC BY 4.0) License).

Zhou et al. demonstrated a patterning of Ag nanowires through photolithography (Figure 3a–i) [31]. A positive-tone photoresist, RZJ-390PG (Ruihong Electronic Chemical Co., Ltd., Suzhou, China), was applied to a substrate. The photoresist was exposed to UV light through a photomask to create a patterned layer on top of the Ag nanowires. The unexposed areas of the photoresist were then developed away using a developer solution, leaving behind a patterned photoresist layer on the Ag nanowires. The exposed Ag nanowires were then etched away using a suitable etchant solution to create the desired pattern of Ag nanowire electrodes. In the work by Jeon et al. [30], a photoresist (SU-8) was used to create a patterned layer on top of the Ag nanowires (Figure 3j–l). The insulating line consisting of patterned SU-8 provided the insulating bridges that could form the patterned Ag nanowire electrodes for the fabrication of transparent touch panels.

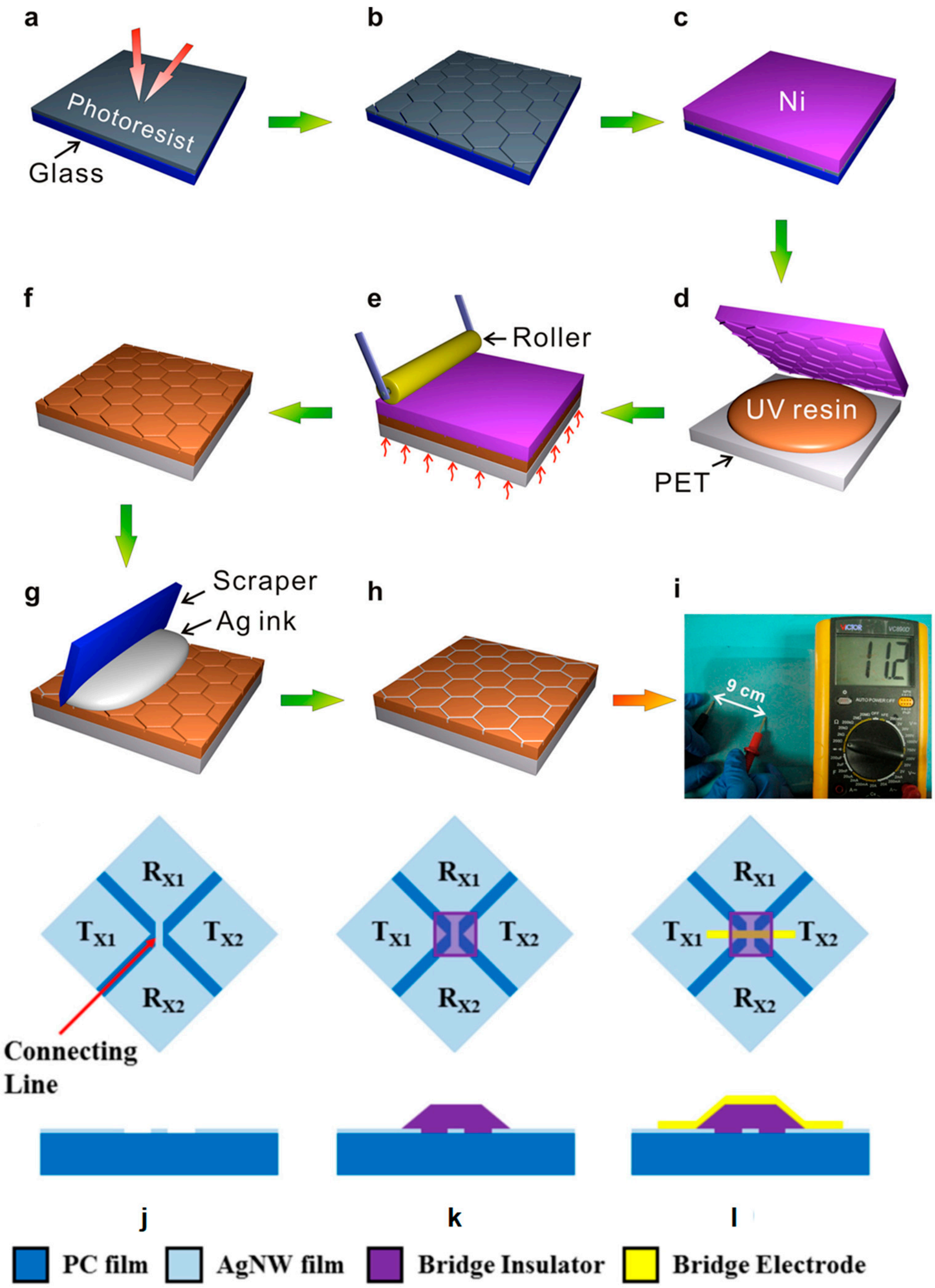

Figure 3. (**a**–**i**) Schematic illustration of the fabrication steps of an embedded Ag network on PET substrate. (**a**) Fabrication of a hexagonal pattern on the photoresist on a glass substrate using photolithography. (**b**) Development of hexagonal photoresist mold. (**c**) Pattern transfer to a Ni mold using electroforming. (**d**) Dispersing UV resin on a PET substrate. (**e**) Mold transfer with UV nanoimprinting lithography. (**f**) Hexagonal pattern formation with plasma treating. (**g**) Dispersing the nanostructured Ag ink and scratching by Ag paste scratch technology. (**h**) Sintering and cleaning of the embedded Ag networks. (**i**) Resistance value of the patterned Ag networks. Reproduced with permission from Ref. [31]. Copyright 2014, American Chemical Society. (**j**–**l**) All processes of fabricating a flexible and transparent patterned Ag nanowire electrode-based touch panel. (**a**) Patterning Ag nanowire electrode, (**b**) forming a transparent bridge insulator (SU-8), and (**c**) forming a bridge electrode (AZO) over the bridge insulator. Reproduced from Ref. [30] under the Creative Commons Attribution 4.0 International (CC BY 4.0) License).

The use of photolithography patterning has enabled the creation of flexible, high-performance electronic and optoelectronic devices that have the potential to revolutionize various fields, including displays, sensors, and wearable electronics. The use of photolithography patterning of Ag nanowire electrodes has several advantages. One of the most significant advantages is the ability to pattern Ag nanowires on a variety of substrates, including glass, plastic, and flexible materials. This versatility makes it possible to fabricate electronic and optoelectronic devices for a range of applications, from flexible displays to wearable electronics. Furthermore, the use of photolithography patterning enables the creation of intricate patterns with feature sizes down to a few hundred nanometers. This high resolution makes it possible to create complex electronic devices with small feature sizes, such as sensors and transistors.

Consequently, photolithography patterning of Ag nanowire electrodes is a versatile and widely used technique for the fabrication of electronic and optoelectronic devices. The choice of photoresist and developer used in the process depends on the specific requirements of the device and the desired pattern. The ability to pattern Ag nanowires on a variety of substrates and create intricate patterns with high resolution makes photolithography patterning an essential process for the development of the next generation of electronics.

2.2. Laser Patterning

Laser patterning has proven to be a highly effective method for patterning Ag nanowire electrodes due to its capacity to produce fine patterns in a single process [32,33]. Typically, the laser patterning process uses a high-power laser beam to ablate the Ag nanowires to have the desired pattern [34]. There are two different types of laser patterning methods including direct and indirect ablation processes. In the direct ablation process, the Ag nanowires are removed by the directly focused laser beam, which evaporates the Ag nanowires. Various laser types of laser sources, including excimer lasers, femtosecond lasers, and picosecond lasers [32–34] can be used where the choice of laser type determines pattern resolution, substrate material, and laser processing speed. In the indirect ablation method, the laser beam is focused on a sacrificial layer, such as a photoresist layer, which is coated on top of the Ag nanowires. The sacrificial layer absorbs the laser beam, heats up, and evaporates, and consequently, the underlying Ag nanowires are ablated and removed from the substrate. The laser patterning process involves several steps, including substrate preparation, Ag nanowire deposition, sacrificial layer coating (in the case of indirect ablation), and laser patterning [35]. For direct ablation, the laser patterning step can be performed directly on the Ag nanowire layer. In contrast, for indirect ablation, the sacrificial layer is first patterned using photolithography, and then the laser patterning step is performed on the sacrificial layer to remove the unwanted Ag nanowires. In addition to its ability to produce fine patterns in a single process, laser patterning offers several other advantages. It can pattern Ag nanowires on a variety of substrates, including flexible substrates, without damaging the substrate material. Moreover, it can create complex patterns and shapes that may not be possible with photolithography.

Song et al. demonstrated a patterning of Ag nanowire by using a laser patterning technology (Figure 4a) [35]. A layer of Ag nanowires was deposited on a flexible substrate, and a laser was used to ablate the Ag nanowires in the desired pattern. The resulting patterned Ag nanowire electrodes exhibited high transparency and low sheet resistance, making them suitable for use in flexible and transparent electronic devices. In the work by Oh et al., invisible Ag nanowire electrodes were patterned by laser-induced Rayleigh instability (Figure 4b–d) [36]. Ag nanowires were selectively disconnected by laser irradiation, which made the conductive patterns on the non-irradiated area. The resulting patterned Ag nanowire electrodes exhibited high transparency and low sheet resistance, making them suitable for use in organic light-emitting diode (OLED) applications.

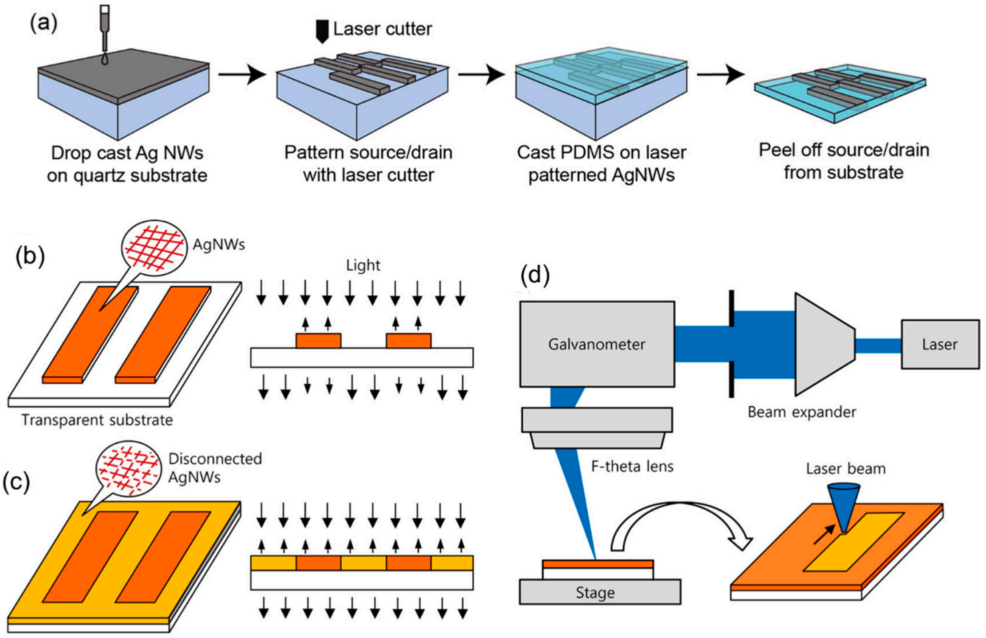

Figure 4. (**a**) Schematic of the fabrication of the source/drain composite electrode. Reproduced with permission from Ref. [35]. Copyright 2020, American Chemical Society. (**b**–**d**) (**b**) Origin of the electrode pattern visibility. (**c**) Scheme used to overcome the electrode visibility issue. (**d**) Schematic of the optics setup used for patterning. Reproduced with permission from Ref. [36]. Copyright 2016, American Chemical Society.

Despite these advantages, there are also some limitations to the use of laser patterning for patterning Ag nanowire electrodes. One limitation is the cost of the laser system, which may be prohibitive for small-scale production processes. Another limitation is the slow processing speed, which may be a challenge for high-volume production. Finally, the laser patterning process may also require specialized expertise and equipment, which can limit its use in certain applications.

Consequently, one limitation of the laser patterning process is the cost associated with laser equipment and the complexity of the process, which may require specialized expertise. Another limitation is the potential for damage to the Ag nanowires and substrate material during the laser patterning process, particularly when using direct ablation methods. Additionally, the resolution of laser patterning may not be as high as that achievable with photolithography, particularly for features with sizes smaller than the wavelength of the laser beam. Overall, the choice of patterning method for Ag nanowire electrodes will depend on various factors, including the desired pattern resolution, substrate material, and cost considerations.

2.3. Nanoimprint Lithography (NIL)

NIL has emerged as a promising alternative to conventional photolithography processes for patterning Ag nanowire transparent electrodes [37–40]. The technique is a cost-effective and versatile patterning method that can create complex patterns with high resolution and accuracy. Shi et al. demonstrated a periodic Ag nanowire with microscale mold by NIL technology (Figure 5a) [38]. They used NIL to fabricate Ag nanowire-based transparent electrodes with a mesh pattern for use in flexible and stretchable devices. The pattern had a feature size of sub-100 nm, where the different widths and heights were generated through the different imprinting parameters in identical imprinting stamps. The patterned Ag nanowires were demonstrated for an ammonia sensor. Sciacca et al. demonstrated a Ag nanowire transparent electrode patterned by combining a soft solution process (Tollens' reaction) and nanoimprint lithography (Figure 5b) [39]. They used four steps of the patterning process, including: (1) substrate-conformal imprint lithography

(SCIL) for imprinting nanosized trenches in a PMMA template, (2) nucleation and growth of crystalline Ag on the substrate surface through the Tollens' reaction, (3) achieving a patterned Ag nanowire electrode by removing the PMMA templates, (4) flattening the rough surface through annealing by using a rapid thermal annealing (RTA). Crystallized Ag nanowires (Figure 4d) were successfully patterned, as shown in Figure 4c.

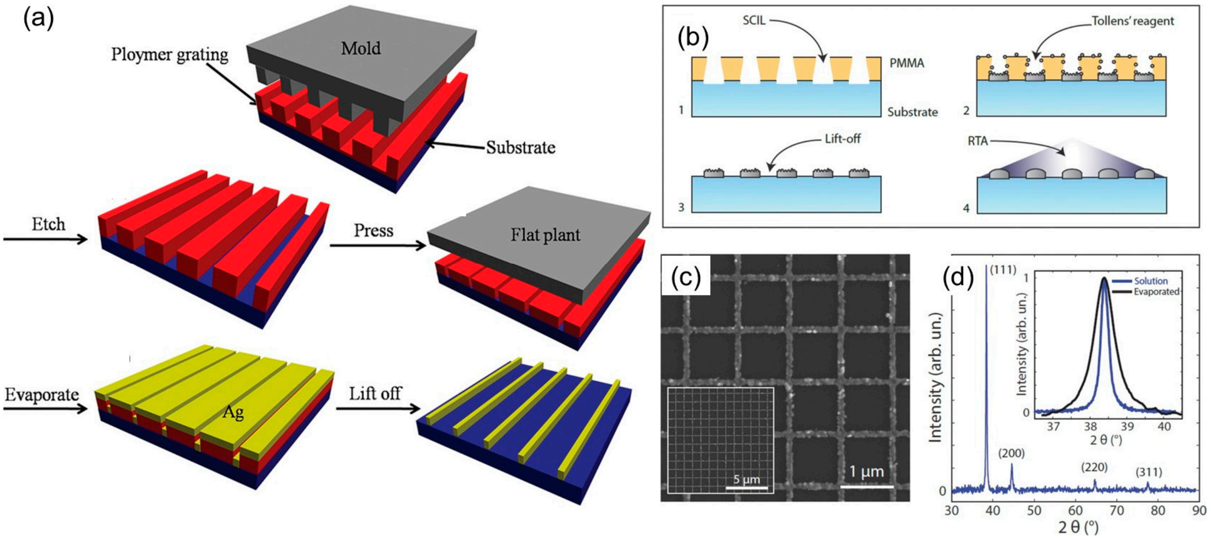

Figure 5. (**a**) Schematic illustration of the fabrication process of the metal nanowires. Reproduced with permission from Ref. [38]. Copyright 2011, American Chemical Society. (**b**) Schematic of the solution-grown nanowire network fabrication process: (1) SCIL to produce a grid nanopattern in PMMA, (2) solution phase growth of Ag nanowires in the trenches defined by the template via the Tollens' reaction, (3) lift-off, and (4) RTA to smooth the nanowire surface. (**c**) SEM images of a freshly grown nanowire network before RTA treatment, showing the confinement of the growth over a large area. (**d**) XRD before RTA treatment of solution-grown nanowire network measured in the range 30°–90° with the θ–2θ configuration, showing the crystalline nature of the nanowire; inset: comparison of the (111) Ag reflection peak for solution-grown and evaporated Ag, indicating the larger average grain size in the former. Reproduced with permission from Ref. [39]. Copyright 2016, Wiley.

In NIL, a mold with a patterned relief structure is pressed onto a thin film of thermoplastic resist coated on the substrate [37–40]. The resist can be made from a variety of materials, including polystyrene, polymethylmethacrylate, and cyclic olefin copolymer. Upon heating, the resist flows and fills the relief structures of the mold, resulting in a replica of the mold pattern on the substrate. After the resist is cooled and hardened, the mold is removed, leaving a patterned surface. One of the major advantages of NIL is its high-resolution capability, with the ability to achieve features on the sub-50 nm scale [37–40]. This is due to the fact that the pattern is defined by the mold, which can be fabricated using advanced techniques such as electron beam lithography or focused ion beam milling. This makes NIL particularly well suited for the fabrication of high-resolution patterns such as those required for advanced electronic devices. Additionally, NIL is a low-cost process, as it does not require the use of expensive photomasks or other specialized equipment. Another advantage of NIL is its compatibility with various substrates, including polymer substrates [37–40]. This makes it well suited for the fabrication of flexible electronic devices, which require the use of flexible substrates. The use of flexible substrates is particularly important for applications such as wearable electronics and flexible displays [37–40]. Furthermore, NIL can be used for large-area patterning, making it a promising technique for the production of large-scale electronic devices. There are also several challenges associated with the use of NIL for patterning Ag nanowire electrodes. One of the main challenges is the selection of a suitable resist material that is compatible with the Ag nanowire ink and can withstand the high-temperature and pressure conditions of the imprinting process.

In addition, the residual layer left after the imprinting process can affect the electrical properties of the Ag nanowire electrode, and therefore needs to be carefully controlled. However, with ongoing research and development, these challenges are expected to be overcome, making NIL a promising patterning technique for the fabrication of Ag nanowire transparent electrodes.

2.4. Patterning with Intense Pulsed Light (IPL) Followed by Wiping or Cleaning Process

Patterning using IPL treatment is also an attractive method to pattern Ag nanowires due to its easy and fast patterning process [9,16,41,42]. Ag nanowire pattern was formed by locally irradiating intense pulsed light (IPL) on Ag nanowire electrodes, causing the IPL-treated parts of the Ag nanowires to strongly adhere to the polymer substrate and removing the non-treated parts by wiping or cleaning (Figure 6a) [16]. The Ag nanowires on the non-irradiated region were removed during the cleaning process, while the Ag nanowires on the irradiated region were merged with the polyimide substrates and became intact, which formed the patterning. In the work by Jun et al., the Ag nanowires were patterned by using an IPL system on the stretchable thermoplastic urethane (TPU) film (Figure 6b) [41]. They achieved 300 μm of pattern widths on the large-scale substrate with a dimension of 125 mm × 125 mm (Figure 6c,d). Although this patterning method using IPL is facile and fast, the patterning resolution and selectivity of the substrates are limited. Thus, the IPL-based patterning methods can be used for limited applications requiring large pattern width such as touch panels.

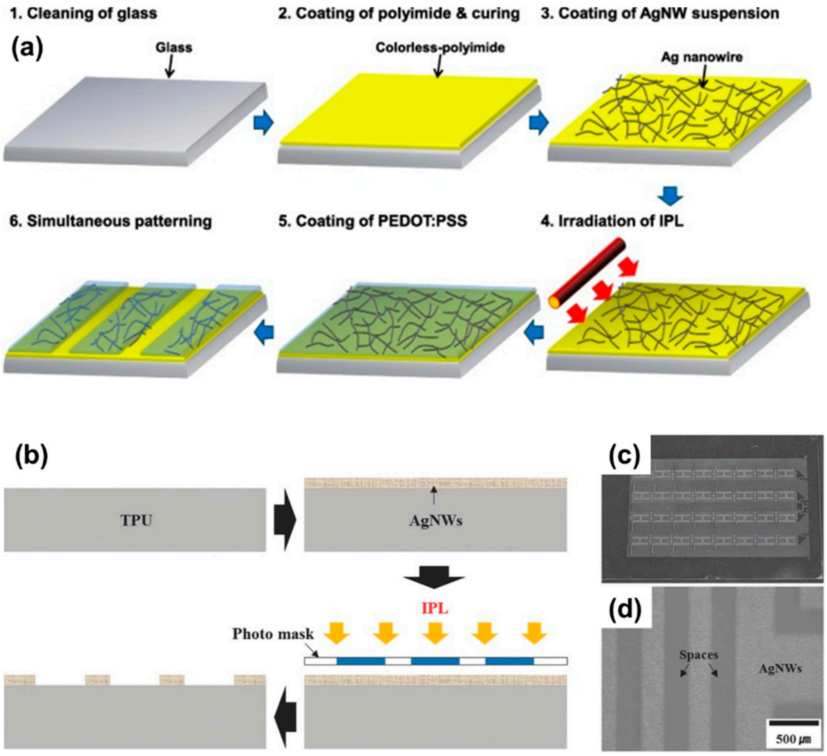

Figure 6. (**a**) A schematic description of the fabrication process for AgNW/PEDOT:PSS-based electrode on cPI substrate. Reproduced with permission from Ref. [16]. Copyright 2015, Elsevier. (**b**) Schematic illustration of the procedure for patterning AgNWs on a stretchable polymer, (**c**) a fabricated capacitive sensor (diagonal length of the panel was 125 mm), and (**d**) fabricated AgNW patterns on the stretchable polymer. Reproduced with permission from Ref. [41]. Copyright 2016, Wiley.

2.5. Inkjet Printing

Inkjet printing has emerged as a promising method for patterning Ag nanowire transparent electrodes due to its high throughput and precise control of pattern geometry and placement [43–45]. Wang et al. used a commercial inkjet printer to deposit Ag nanowire ink onto a polyethylene terephthalate (PET) substrate (Figure 7a) [43]. The substrate was pre-treated with UV ozone to improve the wettability of the substrate surface, allowing for better adhesion of the Ag nanowires. By controlling the printing parameters such as the printing speed and number of printing passes, they were able to produce highly conductive patterns with good uniformity and resolution. In the work by Finn et al., Ag nanowire networks were patterned by using a piezoelectric inkjet printer (Figure 7b,c) [46]. They achieved uniform Ag nanowire networks with a length of 2 mm with a sharp edge (Figure 7d,e).

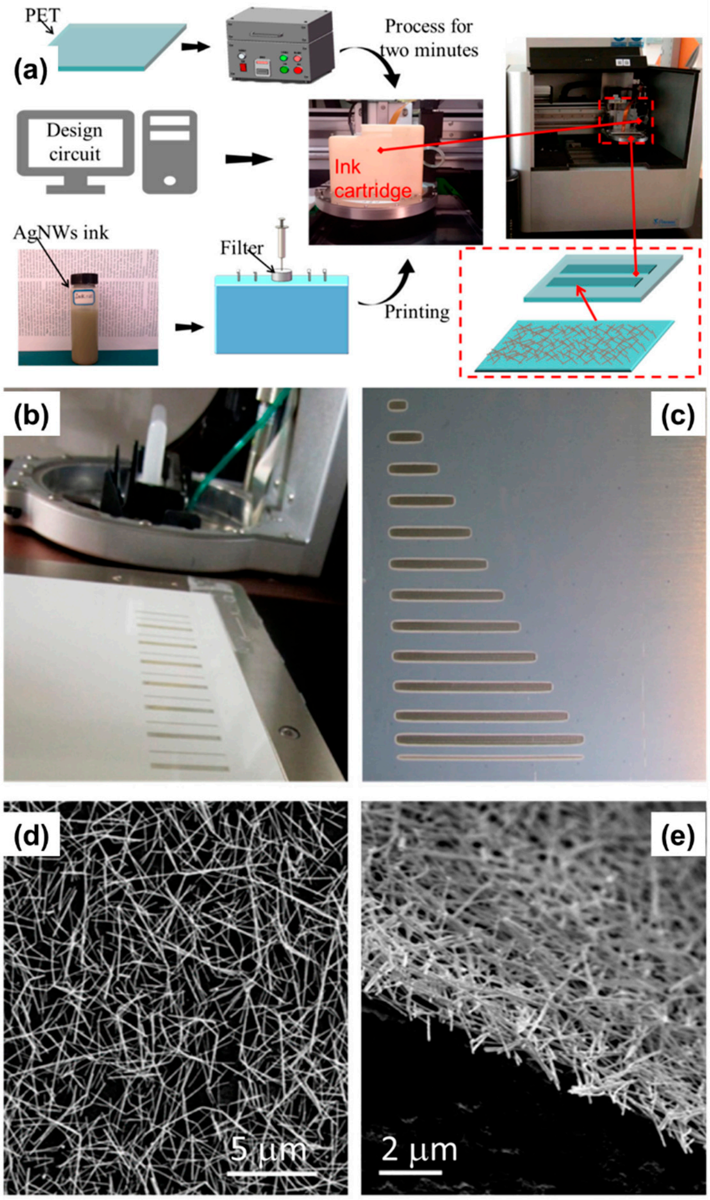

Figure 7. (**a**) Schematic diagram of the fabrication process of AgNWs-FTCE pattern by inkjet printing. Reproduced from Ref. [43] under the Creative Commons Attribution 4.0 International (CC BY 4.0) License). (**b**–**e**) Inkjet-printed Ag nanowire networks. (**b**) Inkjet printing of Ag nanowire lines on a coated PET substrate, which was aligned with index pins on the printer's heated platen. (**c**) Printed lines of different lengths (w = 2 mm, N = 20). (**d**) SEM image of a relatively thin Ag nanowire network (N = 12 passes). (**e**) SEM images of the edges of thick nanowire networks (N = 80 passes). Reproduced with permission from Ref. [46]. Copyright 2015, American Chemical Society.

Despite its advantages, there are also some challenges associated with the use of inkjet printing for patterning Ag nanowire electrodes [43–45]. One of the main challenges is the clogging of the print head, which can occur due to the presence of agglomerated Ag nanowires or other impurities in the ink. In addition, the drying of the ink on the substrate can also affect the uniformity and conductivity of the resulting pattern. Continuous research to overcome the limitations of inkjet printing is required to make inkjet printing a more promising method for the fabrication of patterned Ag nanowire transparent electrodes in large-scale substrates.

2.6. Electrohydrodynamic Jet (E-Jet) Printing

E-jet printing is an emerging technique for the patterning of Ag nanowire transparent electrodes that offers several advantages over conventional patterning methods [23,47]. In E-jet printing, a high electric field is applied to a liquid meniscus, which generates a fine jet that is directed onto the substrate to form the pattern (Figure 8a) [47]. This method allows for precise control over the size and shape of the pattern, as well as high aspect ratio features with sub-micron resolution (Figure 8b,c) [47].

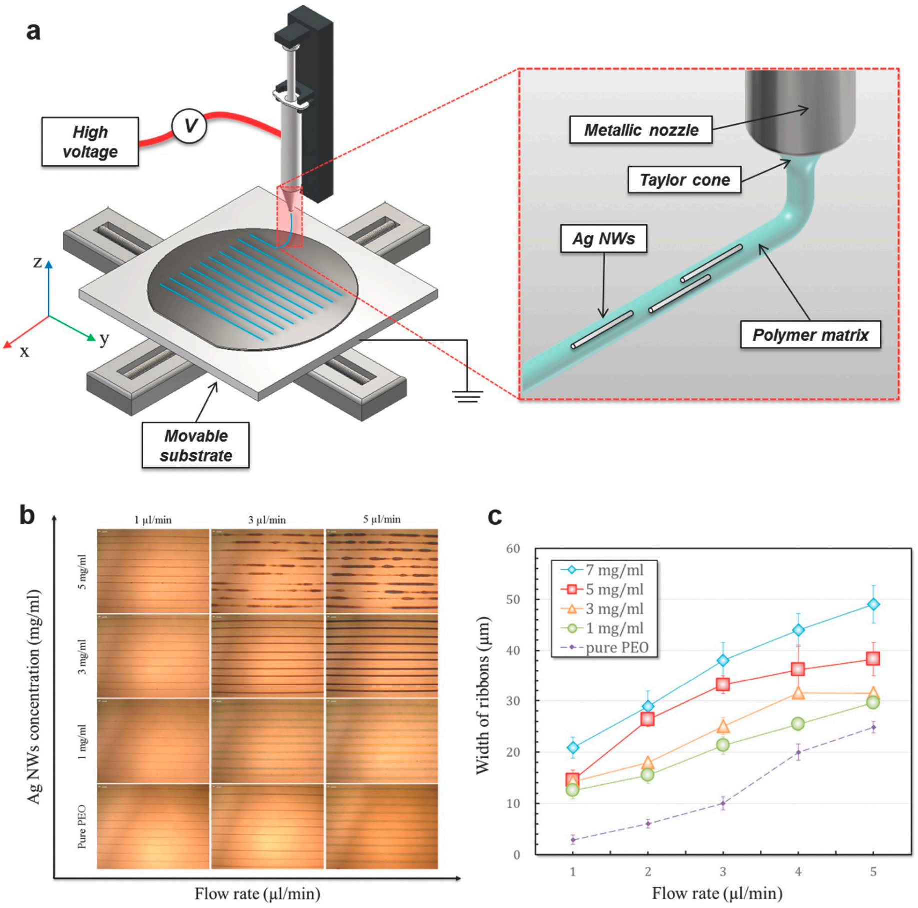

Figure 8. (**a**) Schematic of experimental setup for electrohydrodynamic jet printing system; (**b**) EHD jet printed ribbons with various concentrations and flow rates; (**c**) correlation between width of ribbons and the flow rate. Reproduced with permission from Ref. [47]. Copyright 2014, Wiley.

One of the main advantages of E-jet printing is its versatility in terms of the materials that can be used as the ink [23,47]. Unlike other printing techniques that require the ink to be in a specific viscosity range, E-jet printing can use inks with a wide range of viscosities and even suspensions of nanoparticles. This means that Ag nanowire ink can be used for the E-jet printing of transparent electrodes with high conductivity and low sheet resistance. E-jet printing also offers the advantage of being able to print on a variety of substrates, including rigid and flexible substrates. This makes it a promising technique for the fabrication of flexible electronic devices, such as wearable sensors and displays. Furthermore, E-jet printing can be used for the patterning of a wide range of materials, including metals, polymers, and ceramics, making it a versatile technique for the fabrication of complex devices with multiple components [48]. However, there are still some challenges associated with the use of E-jet printing for the patterning of Ag nanowire transparent electrodes [23,47]. One point requiring further investigation is the optimization of the printing parameters, such as the electric field strength and the ink concentration, to achieve the desired pattern quality and resolution. Another aspect is the development of suitable inks that are compatible with the E-jet printing process and can provide high conductivity and low sheet resistance. Nonetheless, with continuous research and development, E-jet printing is expected to become an important technique for the patterning of Ag nanowire transparent electrodes in various electronic applications.

3. Summary and Perspective

In conclusion, Ag nanowire transparent electrodes offer a promising alternative to conventional ITO thin films in optoelectronic devices. However, the challenges lie in developing reliable and cost-effective patterning methods for large-scale fabrication. In this review, several patterning techniques for Ag nanowire electrodes were discussed, including photolithography, NIL, inkjet printing, and E-jet printing. Each technique has its advantages and limitations (Table 1), and the choice depends on factors such as resolution, throughput, and substrate compatibility. Photolithography remains the most widely used technique due to its high precision and reproducibility, but it is not suitable for large-scale production. NIL offers high resolution and substrate compatibility, while inkjet printing and E-jet printing are well suited for large-scale production and the fabrication of flexible devices. Although each fabrication patterning method has its own weaknesses, ongoing research and development are expected to improve their reliability and effectiveness in view of an increasingly widespread adoption of Ag nanowire transparent electrodes in optoelectronic devices.

Table 1. A summary of the various types of patterning technologies.

Methods	Merits	Demerits
Photolithography	• High compatibility with industry • Fine patterning • Fast patterning speed	• Complex processing step • High cost for materials • Using toxic etchant
Laser patterning	• Fine patterning • Easy to control pattern shape	• Slow patterning speed • Using dangerous laser source • Possibility to substrate damage
NIL	• Large-scale patterning • Low-cost process • Excellent compatibility with polymeric substrate	• Difficult to find resist materials • Side effect by residual layer
IPL/wiping	• Easy and fast process • Large-scale patterning	• Limited patterning size • Limited selectivity of substrate materials
Inkjet printing	• Easy to control pattern shape	• Limited patterning size • High cost for ink formulation • Nozzle head clogging
E-jet printing	• Easy to control pattern shape • High compatibility with various substrates	• Limited patterning size • Difficult to control parameter • High cost for ink formulation

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