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Ultrathin Metal Films as the Transparent Electrode in ITO-Free Organic Optoelectronic Devices

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Transparent conductive electrodes, as transmission windows of photons and electrons, play important roles in high-performance organic optoelectronic devices. The replacement of widely used indium tin oxide (ITO) electrodes has been attempted due to the increasing cost and intrinsically brittle characteristics of ITO. Ultrathin metal films, with excellent optoelectrical features, high flexibility, and sufficient mechanical stability, have been considered a potential candidate for the use as transparent conductive electrodes. However, ultrathin metal films follow the Volmer-Weber mechanism, resulting in a rough and discontinuous morphology with poor optoelectrical properties due to the bad adhesion to substrates. This review summarizes the progress in strategies for preparing ultrathin and ultrasmooth metal films with superior transmittance and conductivity by successfully suppressing the Volmer-Weber mechanism. The electrical and optical performances of the ultrathin metal films based on improved nucleation processes, as well as applications in ITO-free organic optoelectronic devices, are also described and discussed in detail.

1. Introduction

Great improvements have been developed in organic optoelectronic devices owing to their unique advantages of light weight, flexibility, transparency, low-cost, and solution-process compatibility with roll-to-roll manufacturing.^[1] Organic optoelectronic devices have demonstrated their wide applications in smart,

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wearable, and portable equipment.^[2] Transparent conductive films, simultaneously with high conductivity and transmittance, are increasingly important elements as the optical and electrical windows to transform photons and charges in organic optoelectronic devices. Furthermore, stretchable and wearable devices, which represent the development tendency of modern electronic technologies, require the electrodes with the ability to be bent, compressed, twisted, stretched, and deformed into arbitrary shapes.^[3] Indium tin oxide (ITO) is still the most commonly and widely used transparent conductive film, since it provides a relatively high and broadband transmittance of over 80% in the whole visible wavelength region and a particularly low sheet resistance of $\approx 10 \ \Omega \ sq^{-1}$ with a thickness of $\approx 100 \text{ nm.}^{[4]}$ Despite the excellent optoelectronic properties, the use of ITO as the

transparent electrode for organic optoelectronic devices is still suffering from several challenges. First, with fast developments in modern electronic equipment, the demand of ITO has increased rapidly, which is in contradiction with the lacking of the indium reserve in the earth, and the price of indium has risen over approx. \$600 kg^{-1.[5]} In addition, the inevitable material waste in the vapor-phase sputtering ITO process dramatically increases the cost. The typical cost of ITO with 10 Ω sq⁻¹ has been up to \$26 m⁻².^[6] Second, the intrinsically brittle ITO induces the risk of a catastrophic decrease in device performance owing to the formation of microscopic cracks, which damage the conductivity and surface morphology of the transparent electrode in mechanically flexible organic optoelectronic devices.^[7] Third, the ion invasion and the waveguide mode induced by the high refractive index of ITO also impact the performance of optoelectronic devices.^[8]

Owing to the disadvantages of ITO, various research efforts have been conducted to develop desirable alternative transparent conductive electrodes, which can be fabricated by lowcost process with reasonable optoelectrical characteristics and robust structural durability for flexible and stretchable applications. Up to now, ITO-free optoelectronic devices with superior performance based on novel transparent electrodes, such as graphene,^[9] carbon nanotubes,^[10] conductive polymers,^[11] metal nanowires,^[12] metal meshes,^[13] and ultrathin metal films,^[14] have been within sight.



Carbon-based transparent conductive materials have been considered as replacements for ITO in optoelectronic devices.^[15] An individual carbon nanotube (CNT) possesses high electrical conductivity and electron mobility.^[16] Individual CNTs have been found to have mobilities in excess of 100 000 cm² V⁻¹ s⁻¹.^[17] However, the transparent conductive films based on CNT meshes show unsatisfactory optoelectronic properties owing to the random distribution of CNTs.^[18] The junction resistances induced by the tube-tube contacts in the CNT network decrease the conductivity, and the current preparation technology for CNT films still needs to be improved for application in large-scale devices based on roll-to-roll processing. Graphene, a 2D material based on close-packed carbon atoms, features high optical transparency, electrical mobility, and flexibility, and has been prepared as a new-generation transparent electrode.^[19] A roll-to-roll fabricated monolayer 30-inch graphene film has been reported with a sheet resistances as low as $\approx 125 \Omega \text{ sq}^{-1}$ with 97.4% optical transmittance, and a doped four-layer graphene film has also been prepared with the sheet resistance at a value as low as $\approx 30 \Omega \text{ sg}^{-1}$ at $\approx 90\%$ transparency, which is superior to commercial ITO films.^[20] The transparent and conductive graphene electrodes in optoelectronic devices are normally obtained from reduced graphene oxide and chemical vapor deposition (CVD) technology.[21] Solution-processed reduced graphene oxide is an easy and cheap method for graphene but suffers from the poor optical and electrical performance owing to the partial separation of the oxygen-containing groups.^[22] CVD-prepared graphene provides extremely good film quality, but the high fabrication cost and complex process to transfer graphene film from metal foil to a target rigid or flexible substrate limit its further applications. Polymeric transparent electrodes, such as PEDOT:PSS, are prepared by solution processes and are suitable for roll-to-roll technology. Although the transparency, flexibility, and thermal stability of PEDOT:PSS are remarkable, the conductivity is still not high compared to that of ITO.^[23] Prof. Zhennan Bao has reported a transparent PEDOT:PSS electrode with high flexibility and stretchability, and a fluorosurfactant was applied as an additive to improve its conductivity, corresponding to a sheet resistance of 46 Ω sg⁻¹ with a transmittance of 82% at 550 nm. The PEDOT:PSS film demonstrated stable properties during the course of over 5000 stretch cycles of 0 to 10% strain.^[24] In addition, the wet chemical processes of the polymeric tranparent conductive film are not easily applied to the top electrode in devices without damaging the organic functional materials.

Metal films with strong capacities of charge-carrier collection and transport have been widely applied as electrodes by simple thermal deposition and sputtering. However, the high absorption and reflection of thick metal films exclude their potential consideration for use as transparent conductive electrodes. To improve their optical properties, network-structured metal films, such as the metal nanowire network electrodes as well as metal mesh electrodes with various periodic or random microstructured holes, are promising strategies.^[25] Metal nanowire network films, such as Ag^[26] and Cu^[27] nanowires, synthesized by a simple solution process have demonstrated high transmittance as well as mechanical stability in ITO-free organic optoelectronic devices. To further improve the properties of metal nanowire network films, various novel hybrid flexible metal





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nanowire electrodes have been proposed as well. For example, Ag nanowire/CNT nanocomposite transparent conductors,^[28] Ag nanowire/PEDOT flexible electrodes,^[29] Ag nanowire/nanoparticle hybrid transparent electrodes,^[30] and core–shell metal nanowire flexible electrodes^[31] have exhibited excellent opto-electronic performances. Nevertheless, the junction resistance,



long-term stability, poor chemical stability, and rough surface still need to be solved before their wide replacement of ITO.^[32] Introducing meshes within metal films directly can effectively eliminate the junction resistance of random nanowire networks.^[33] Recently, mask-free fabrication strategies by lowtemperature laser processing for flexible metal grid transparent electrode have been reported.^[34] Unfortunately, the clear shadowing loss and large roughness of the metal grids challenge their application as transparent conductive electrodes. Furthermore, the complex fabrication processes for metal grids are also incompatible with transparent top electrodes in organic optoelectronic devices.

A transparent ultrathin metal film, simultaneously with reasonable conductivity and mechanical robustness, is a promising candidate for transparent conductive electrodes in ITO-free organic optoelectronic devices. The thermal deposition of a metal layer follows the Volmer-Weber nucleation mode due to its bad adhesion with the substrate, resulting in a noncontinuous film with discrete islands and random crevices.^[35] The rough morphology of an ultrathin metal film decreases the optical transparency and deteriorates its electrical conductivity. Recent research efforts have been focused on the improvement of metal nucleation to produce uniform and continuous ultrathin metal films with desirable ultrasmooth surfaces and excellent optoelectrical properties as alternative transparent electrodes in ITO-free devices. It has been demonstrated that the Volmer-Weber mechanism could be suppressed effectively by physical and chemical modification of the substrate. Moreover, stretchable transparent electrodes are substantially more challenging to achieve than normal transparent electrodes^[36] As one of the most promising candidates of electrodes, ultrathin and ultrasmooth metal films have been demonstrated with the capacity to absorb and oppose strains without clear variations in optoelectronic performance.^[37] An ultrasmooth and thin metal electrode has shown its mechanical reliability after 20 000 stretch cycles under a 20% tensile strain.^[38]

This review aims to systematically summarize the strategies to prepare ultrathin metal films and their applications in the state-of-the-art ITO-free organic optoelectronic devices. In this review, we will start from a discussion of the growth kinetics of metal films, followed by a survey of recent updates in the developments of ultrathin metal films with improved nucleation based on seed layers with various wetting inducers, as well as doping effect, template-stripping process, and chemisorption strategies. Then, we will discuss the properties of ultrathin metal films with improved surface features. Finally, we will provide an overview of the applications of desirable ultrathin metal films as transparent conductive electrodes in ITO-free organic optoelectronic devices based on various recently reported works.

2. Growth Kinetics of Ultrathin Metal Films

The physical deposition of ultrathin films is a nonequilibrium and complex process, which is a serious constraint to the surface geometry as well as the optoelectrical properties of ultrathin films. Ultrathin-film growth on substrates follows nucleation, coalescence, and subsequent thickness growth. In the nucleation process, three growth mechanisms can occur according to the interaction between substrate atoms and deposited atoms, as shown in Figure 1a: 1) the Frank-van der Merwe mechanism, the deposited materials are produced layer by layer when the interaction between deposited atoms and the substrate is stronger than the attraction of adjacent deposited atoms; 2) the Volmer-Weber mechanism, individual 3D islands form on the surface of the substrate which requires the attraction from an adjacent deposited atom to be larger than that from the substrate atoms; 3) the Stranski-Krastanov mechanism, a few monolayers grow first, followed by separated 3D island-like growth owing to the interface energy increasing with the thickness of the deposited film.^[39] The following process of ultrathin

a)	Θ < 1ML	1ML < O < 2ML	Θ > 2ML
Volmer-Weber	-	-	
Frank-van der Merwe		7777777	77777777
Stranski-Krastanov	··· ··································		

(b) Au (3 nm)/glass	Au (5 nm)/glass	Au (10 nm)/glass	Au (15 nm)/glass
50nm	50nm	50nm	50nm

Figure 1. a) The nucleation of deposited film at the initial states. Θ is monolayer (ML) covered on substrates. Reproduced with permission.^[39] Copyright 2002, Optical Society of America. b) SEM images of Au film deposited directly on bare substrates with the thickness of 3, 5, 10, and 15 nm, respectively. Reproduced with permission.^[45] Copyright 2016, The Royal Society of Chemistry.

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film growth, namely the coalescence process, is the extension of islands to form a continuous network through the surface and bulk transport of deposited materials. The coalescence process from islanded nanoclusters to a continuous network can be featured by a percolation threshold thickness.^[40] Further material deposition results in the thickness growth after the percolation threshold. During the complex film growth processes, the surface energy, supersaturation, substrate temperature, impurities, and vacuum conditions also control and affect the real structures and geometrical morphologies of the deposited films.

At room temperature, the nucleation and subsequent growth of ultrathin metal films is not at thermodynamic equilibrium, owing to the kinetic limitations,^[41] and is driven by a comparison of the interfacial free energy (γ_{inter}) with the mismatch between the surface free energies of the clean metal (γ_m) and the substrate (γ_s) .^[42] Because the interfacial free energy is usually larger than the difference of the surface free energies $(\gamma_{inter} > \gamma_s - \gamma_m)$, the metal phases do not wet the substrate.^[43] As a result, the growth of an ultrathin metal film typically follows the Volmer-Weber mechanism and starts with isolated metal islands.^[44] Figure 1b shows the growth processes of a Au film on a bare glass substrate. The 3D separated islands can be observed first, and as the deposition continues, the islands extend and eventually converge into a continuous and conductive film after the percolation threshold thickness, which is typically 10-20 nm.^[45] Unfortunately, the transmittance in visible wavelength region of such thick metal films is too low for transparent electrodes in optoelectronic devices. Although a high transmittance can be realized for an ultrathin metal film, the Volmer-Weber growth mechanism of metal films results in a noncontinuous and rough film with poor electrical conductivity. As a consequence, it is exceptionally important to obtain an ultrathin and ultrasmooth continuous metal film for the application in ITO-free optoelectronic devices as a transparent electrode via an improved nucleation process by suppressing the 3D island growth. The goal to minimize the thickness of a continuous metal film can be realized by reducing the interfacial free energy and surface energy of metals. A reduction in the interfacial free energy can be reached by an enhancement in the interfacial adhesion, and the strong adhesion leads to a reduction in the surface diffusion of metal atoms on the substrate surface.^[46]

3. Improvement of Metal Nucleation

A large number of theoretical and experimental works have been conducted to optimize the growth characteristics of metal films with ultrathin thickness, pursuing the aim to suppress the isolated 3D island formation and achieve the Frank–van der Merwe growth mode of metal films. Deposition rates and temperatures have noticeable effects on the nucleation process of deposited metal films.^[47] Rapidly deposited metal atoms tend to aggregate with sufficient nucleation sites and grow out over the substrate before the film grows thicker. A low-temperature substrate can also reduce the surface sliding of metal atoms and avoid the formation of large metal islands. Rand and co-workers have investigated the function of the evaporation parameters on the nucleation of deposited metal films, and demonstrated

the optimized deposition rate of 0.55-0.6 nm s⁻¹ and substrate temperature of -5 °C for the minimized percolation threshold of ultrathin deposited Ag films.^[48] The origin of the Volmer-Weber mechanism of deposited ultrathin metal is the mismatched surface energies which results in a rough metal film with various crevices, large gain sizes and fluctuations. Apart from the optimization of the evaporation parameters, modifying the wetting behaviors of the metal on the substrate and underlying dielectric layers is also a key and effective strategy to minimize the percolation threshold and reduce the surface roughness.^[49] Ultrathin and ultrasmooth metal films with significantly reduced root-mean-square surface roughness, lowered grain-size distribution, and narrowed peak-to-valley surface topological height distribution have been reported by introducing seed layers, modification layers, doping materials, striping templates and so on.^[50] In this section, we will discuss the physical and chemical strategies to reinforce the nucleation of ultrathin metal film and suppress the Volmer-Weber mechanism.

3.1. Physisorption for Ultrathin Metal Films

3.1.1. Seed Layer

A seed layer with a thickness of 1-2 nm has been reported to modify the growth mechanism of a metal film.^[51] The most commonly used seed material is a metal, such as Ge, Ca, Sn, Ag, Al, Ni, Ti, and Cu.^[52] Figure 2 shows the representative morphologies of Ag films deposited on a bare SiO₂/Si substrate and SiO₂/Si substrate covered by a Ge seed layer (Ge/SiO₂/Si). Surface morphologies with significant differences can be observed from the atomic force microscopy (AFM) images of Ag films with and without the seed layer. The roughness of the ultrathin Ag film is dramatically improved from 6 nm (Ag/SiO₂/Si) to 0.6 nm (Ag/Ge/SiO₂/Si), a factor of 10, by a 1 nm Ge seed layer. The deposited 1 nm Ge, as the seed layer, follows the Volmer-Weber mechanism, however, the islands of Ge are significantly smaller than those of Ag corresponding to a significantly larger nucleus density, which provides an elevated density of nucleation sites for Ag atoms. As a result, the Ge seed layer guarantees the production of an ultrasmooth and homogeneous Ag film.^[53]

Transition metal oxides have also been applied as seed materials for deposited ultrathin metal films, especially in transparent multilayers with a dielectric/metal/dielectric (D/M/D) configuration.^[48,52h,54] Ghosh and co-workers reported a TiO₂/ Ag/Al-doped ZnO transparent electrode in which TiO₂ acted as a seed layer for the ultrathin Ag film.^[55] The TiO₂ intermediate layer improved the smoothness and continuity of the Ag film by reducing the percolation threshold thickness. V2O5, WO₃, and MoO₃ have also been reported as seed layers to vary the surface topography of subsequently deposited metal films by modifying the wetting behavior.^[56] In D/M/D transparent multilayers, transition metal oxides can normally improve the metal nucleation as well as the thermal and chemical stabilities of the ultrathin metal film, and more importantly, can be applied as optical spacers to increase and broaden the transparency of the ultrathin multilayer and spatially redistribute the optical field in ITO-free optoelectronic devices.[57]



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Figure 2. a-c) AFM images and d-f) height histograms of the Ag/SiO₂/Si, Ag/Ge/SiO₂/Si, and Ge/SiO₂/Si samples, respectively. The roughness of Ag/SiO₂/Si sample is ≈ 6 nm on average corresponding to a peak-to-valley height difference of 34 nm. The roughness of Ag/Ge/SiO₂/Si sample is ≈ 0.6 nm corresponding to a peak-to-valley height difference of 6 nm. The peak-to-valley height difference of Ge/SiO₂/Si sample is ≈ 0.6 nm. Reproduced with permission.^[53] Copyright 2009, American Chemical Society.

The surface action of an ultrathin metal film with a seed layer has been described by a kinetic approach and a thermodynamic approach. From the kinetic viewpoint, the seed layer may improve the activation energy barrier for the surface diffusion of deposited metal atoms owing to the strong cohesion from the seed materials, and small clusters of metal with a high density are induced on the seed layer at very beginning of metal film growth. The kinetic discussion related to surface mobility has been normally applied to describe the working principle of metallic seed layer. In a thermodynamic scenario, the seed layer is related to modulate surface free energies and the interfacial free energy between the substrate and metal, and reduce the energy difference between the substrate and deposited metal film. Schubert et al. reported metallic seed layers to improve the surface morphology of an ultrathin Ag film, based on the thermodynamic scenario, by reducing the mismatch of surface energy (γ) between the substrate (MoO₃ with $\gamma = 0.06$ J m⁻²) and Ag (γ_{Ag} = 1.25 J m⁻²). Ca, Al, and Au, with the surface energy of 0.5, 1.15, and 1.5 J m⁻², respectively, demonstrated a positive contribution to improve the qualities of ultrathin Ag films, as shown in Figure 3, and the Au seed layer exhibited the best

improvement due to the highest surface energy.^[58] However, many contradictory experimental results indicated that MoO₃ could directly act as a seed layer to modify the wetting behavior of Ag and Au ultrathin films. For instance, Jasieniak and coworkers demonstrated that MoO₃ as the seed layer provided a good nucleation surface for an ultrathin and uniform Au film.^[59] The different surface morphologies of deposited metal films on MoO₃ may generate owing to the various substrate temperatures, impurities, vacuum conditions, and deposition rates.

3.1.2. Doping Effect

During the deposition process, the presence of gases as dopants can influence the thermodynamics and kinetics by modifying free energies of wetting.^[42] The coadsorbed dopants demonstrate different adsorption energies of the metal on various substrates. When the mismatch in adsorption energies is large enough, the thermodynamic driving force of the metal can be accordingly eliminated, and the coalescence process becomes thermodynamically preferred.^[44a] On the other hand, the





Figure 3. SEM images of 7 nm Ag film deposited a) without seed layer, b) with Ca seed layer, c) with Al seed layer, and d) with Au seed layer. The scale bar is 200 nm. γ refers to the surface energy. Reproduced with permission.^[58] Copyright 2013, Wiley-VCH.

coadsorbed dopants also alter the thickening kinetics by reducing diffusion barriers and altering the energetics for the upstepping of metal atoms.^[42] An oxygen-doped ultrathin metal film with partial oxidation has been demonstrated with improved wettability, and a 6 nm oxygen-doped Ag film with the uniform and completely continuous surface has been reported.^[60] However, the oxygen concentration should be under special precise control owing to the oxidative activity of metals, which may cause a dramatic destruction of the electrical conductivity of the metal film under a relatively high oxygen surrounding. To avoid the negative roles of oxygen doping, a nitrogen-doped Cu film has been reported, as shown in Figure 4a. With a minimal nitrogen dose during the incipient growth stages of Cu, the Volmer-Weber mode was suppressed through the nitrogen-doping effect, which induced a limited surface diffusion of metal clusters and a positive modification of the cluster coalescence behavior.^[61]

Except for doping by the surrounding atmosphere, codeposition with a small quantity of an additional metal can also improve the nucleation process of ultrathin metal films. A Ag film with Cu additions has demonstrated an altered surface topography compared to that of the pure Ag film deposited on an ITO substrate owning to the surface-diffusion and grain-boundary-grooving mechanism.^[62] Guo and co-workers



Figure 4. a) The different growth progress of ultrathin Cu and nitrogen-doped Cu ultrathin film (top part), and SEM images of the 6.5 nm Cu and nitrogen-doped Cu film with the scale bar of 20 nm (bottom). Reproduced with permission.^[61] Copyright 2016, Wiley-VCH. b) Al-doped ultrathin Ag film by codeposition of Al during Ag deposition. SEM images of 9 nm pure Ag and Al-doped Ag film demonstrate obvious different surface morphologies. The corresponding AFM images are inset in the SEM images. The roughnesses of 9 nm pure Ag and Al-doped Ag film are 10.8 and 0.86 nm, respectively. Reproduced with permission.^[63a] Copyright 2014, Wiley-VCH.

have reported an ultrathin and ultrasmooth Ag film based on Al doping with a sub-nanometer surface roughness, as shown in Figure 4b.^[63] The codeposited small amount of Al decreased the diffusion rate of metal atoms, resulting in an increased nucleus density with a small particle size for the Ag film. By introducing Ta_2O_5 as a seed layer, the percolation threshold of a uniform ultrathin Al-doped Ag film is further decreased, and the 4 nm Ta_2O_5 /Al-doped Ag film was electrically continuous with a uniform and ultrasmooth morphology.^[64]

3.1.3. Template-Stripping Process

Based on the bad adhesion and wettability of metal films on substrates, template-stripping technology can prepare ultrasmooth metal films of high quality over a large region.^[65] Templates with angstrom roughness, such as silicon, mica and polished glass, can transfer their natural flatness to the metal films which are peeled off from the templates. As shown in Figure 5a, a Ag film is deposited on the pre-cleaned ultrasmooth Si substrate, and then a photopolymer film is coated on the Ag film as the backing film.^[66] After the photopolymer solidifies, the photopolymer-metal bilayer is peeled off from the substrate due to the weak adhesion. The template-stripped Ag film demonstrates an ultrasmooth and homogeneous surface maintaining the roughness of the Si template, as shown in Figure 5b.^[67] Mica prepared by cleavage provides an excellent smooth surface, however, often introduces mica sheets on the surface of the metal film during the separating process. Polished glass and Si with similar flat surfaces to that of mica have been commonly used as templates, and a superhydrophobic coating is often applied before depositing metal films to further decrease the adhesion to the templates.^[68] Apart from the epoxy, metal foils have also been reported as an adhesion layer to transfer the metal film from the template.^[69] More interestingly, the glass and Si templates can be prepatterned, and ultrasmooth metal film with complex surface structures can be realized by the template-stripping technology.^[70] Norris and co-workers have reported ultrasmooth metal films with highquality and high-throughput multipatterns, including holes, grooves, bumps, ridges, and pyramids, by applying the template-stripping process on precisely patterned Si substrates.^[69]

3.2. Chemisorption for Ultrathin Metal Films

An alternative approach to improve the nucleation process of deposited ultrathin metal has been developed based on an adhesion layer with functional groups to strongly increase the interactions between metals and substrates.^[71] The additional adhesion layer provides densely distributed metal-nucleation sites to reduce the percolation threshold and prepare a continuous and homogeneous film via the formation of strong chemical bonds between metal atoms and the modification material coated on the substrate. The morphology of commonly used metal electrodes, such as Au, Ag, and Cu, have been significantly altered by the chemically functionalized adhesion materials with sulfur-containing groups.^[72] Hatton et al. have used 3-mercaptopropyl(methyl)dimethoxysilane (MPMS) as the adhesion promoter to prepare ultrathin Au films.^[73] As shown in Figure 6a, the thiol moiety of MPMS covalently bonds to Au atoms via the S-Au linkage, whilst the MPMS molecule is fixed to the glass surface via the strong siloxane bond. We employed a photoresist polymer (SU-8) with sulfur-containing groups as the adhesion layer to suppress the discrete islands of the deposited Au film by chemical bonds, and the flexible SU-8 adhesion layer was separated from glass, as the new substrate, to realize an ultrathin Au electrode with high flexibility and mechanical stability.^[45] By engaging the SU-8 modification layer and a Ag seed layer, a 4.4 nm ultrathin and ultrasmooth Au transparent conductive flexible electrode has been realized recently.^[74] Jen et al. applied a self-assembled monolayer of 11-mercapto-undecanoic acid (MUA) between an ultrathin Ag film and ZnO layer as a molecular binder to covalently attach Ag and ZnO together by the thiol group bonding with Ag and the hydroxyl group bonding with ZnO.^[75] Yoo and co-workers demonstrated ZnS as the substrate modification layer to promote the nucleation of uniform and ultrathin Cu films with few grain boundaries.^[76]

Amine groups are also adapted to suppress the surface diffusion of metal and therefore improve the growth of continuous metal films with ultrathin thickness.^[77] Kang et al. reported an amine-containing nonconjugated polyelectrolyte (polyethyleneimine, PEI) as the molecular adhesive for an ultrathin Ag film. As shown in Figure 6b, the deposited Ag atom accepted an electron pair from the functional amine group of PEI to form a coordinate covalent bond, therefore, the initially



Figure 5. a) Scheme of template-stripping technology. b) AFM images of Ag film before (left) and after (right) template-stripping process with scan area of 5 and 1 μm, respectively. Reproduced with permission.^[67] Copyright 2013, The Royal Society of Chemistry.







Figure 6. a) Growth mechanism of deposited ultrathin Au film based on MPMS as the adhesion promoter. Reproduced with permission.^[73] Copyright 2003, The Royal Society of Chemistry. b) Growth mechanism of Ag deposited on PEI adhesion layer. Reproduced under the terms of a Creative Commons Attribution 4.0 International License.^[78] Copyright 2015, Macmillan Publishers Limited. c) Growth mechanism of Au deposited on APTMS:MPTMS adhesion layer. Reproduced with permission.^[80] Copyright 2011, Wiley-VCH.

deposited Ag atom was fixed on the surface of PEI, which was precoated on the substrate. As a result, the coordination reaction provided dense nucleation sites and improved the flatness and homogeneousness of the ultrathin Ag film with the suppression of random Ag migration and aggregation.^[78] Amine-containing adhesives have been applied for Au deposition as well.^[79] As reported by Hatton and co-workers, in Figure 6c, a mixed mono-layer of 3-mercaptopropyl(trimethoxysilane) (APTMS) with an amine group and 3-aminopropyl(trimethoxysilane) (MPTMS) with a thiol group was used as a molecular adhesive to prepare ultrathin Au transparent conductive films.^[80] It has been reported that the coordinate covalent bond Au–N is weaker than Au–S.^[81]

4. Material Selection and Properties of Ultrathin Metal Films

For an ultrathin metal transparent electrode in an organic optoelectronic device, material selection is focused on the properties of the ultrathin metal film. From the point of practical application, the metal films must be cheap to produce. The most commonly used metal candidates for ultrathin electrodes are coinage metals, such as Ag, Au, and Cu. For the application of wearable and portable equipment, the metal electrode should be mechanically reliable with a high flexibility. Considering the physical point of view, the films should exhibit optimized optoelectronic performance by overcoming the deleterious tradeoff between the optical transmittance and electrical conductance. The material type and the film thickness are key factors to

achieve high electrical conductance. Table 1 provides the electrical resistivity values of several bulk materials.^[82] Ag and Cu are most commonly used electrode materials owing to their lower electrical resistivities. Cu has better strength than Ag but offers inferior oxidation resistance. As is known to all, the sheet resistance of a metal film decreases with increasing film thickness, but the transparent performance decreases accordingly due to the absorption and reflection of the thick metal film. On the other hand, the optoelectronic properties of ultrathin metal films are also strongly governed by the quality of the metal films such as film continuity, surface roughness, and grain size, which depend on the growth kinetics and nucleation process of the metal film. In addition, as the transmission window of electrons and holes in the organic optoelectronic devise, the work function (Table 2) of a metal electrode should be evaluated to achieve a low potential barrier.^[83] In some cases, 1–3 nm alkali metals, transition metals and oxides have been applied as the electrode modification layer to reduce the mismatched energy levels between the metal electrode and organic functional laver and to improve the efficiency of charge transmission.^[84] In Table 3, the major performances of ITO and ultrathin metal transparent electrodes are listed. The ultrathin metal films demonstrate ultrasmooth surfaces with roughness values less than 1 nm. The optical transparencies and sheet resistances of the ultrathin metal electrodes are comparable with those of ITO electrodes, and the flexibilities and mechanical reliabilities of the ultrathin metal films are substantially better than those of ITO. In the following section, we will discuss the optoelectronic properties as well as the mechanical reliability of deposited

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Table 1. Electrical resistivity values of bulk metals.^[82]

Matal	Projetivity at 20 %C (v.O. and	
wetai	Resistivity at 20 °C [µs2 cm]	
Ag	1.6	A
Cu	1.7	
Au	2.4	^
Al	2.8	A
Mg	4.6	
W	5.6	A
Мо	5.7	
Zn	5.8	6
Ni	7.8	C
In	8.0	C
Pt	10.0	
Pd	11.0	
Sn	11.5	F
Cr	12.6	_
Та	15.5	G.
Ti	39.0	lr

ultrathin metal films and summarize the improvements in the performance of ultrathin metal films with satisfactory film morphologies based on various novel strategies.

4.1. Electrical Conductivity

Ultrathin metal films deposited directly on untreated substrates are electrically discontinuous at the initial step of film growth owing to the Volmer–Weber mode. After the thickness increases past over the percolation threshold, discrete metal clusters grow and then converge to form a conducting channel, and the ultrathin metal films become conductive.^[85] The resistivity (ρ) of an ultrathin metal film is dramatically affected by the electron scattering from the grain boundaries and surfaces.^[86] As described by Juan M. Camacho, the resistivity (ρ) value can be determined by Equation (1)^[87]

$$\rho = \rho_{\rm FS} + \rho_{\rm MS} - \rho_0 \tag{1}$$

in which, ρ_0 is the bulk resistivity. The resistivity associated with film surfaces (ρ_{FS}) can be described by the Fuchs and Sondheimer (FS) model with consideration of the statistic distribution of λ values and the function of the film surfaces in Equation (2),^[88] and the resistivity associated with grain boundaries (ρ_{MS}) is given by the Mayadas and Shatzkes (MS) model including the grain boundaries, as shown in Equation (3)^[89]

$$\frac{\rho_{\rm FS}}{\rho_0} = \left[\frac{3}{2k^2} \int_1^\infty dt \left(\frac{1}{t^3} - \frac{1}{t^5}\right) \frac{(1-p)(1-e^{-kt})}{1-pe^{-kt}}\right]^{-1} \text{ with } k = t/\lambda_0 \qquad (2)$$

$$\frac{\rho_0}{\rho_{\rm MS}} = \left[1 - \frac{2}{3}\alpha + 3\alpha^2 - 3\alpha^3 \ln(1 + 1/\alpha)\right]^{-1} \text{ with } \alpha = \frac{\lambda_0}{D} \left(\frac{R}{1 - R}\right) \quad (3)$$

Table 2. Electron work function values of metals.^[83a]

Metal	Plane	Work function [eV]	Method
Ag	100	4.64	PE ^{a)}
	110	4.52	PE
	111	4.74	PE
Al	100	4.20	PE
	110	4.06	PE
	111	4.26	PE
Au	100	5.47	PE
	110	5.37	PE
	111	5.31	PE
Ca	Polycrystalline	2.87	PE
Cu	100	5.10	PE
	110	4.48	PE
	111	4.94	PE
	112	4.53	PE
Fe	100	4.67	PE
	111	4.81	PE
Ge	Polycrystalline	5.0	CPD ^{b)}
In	Polycrystalline	4.09	PE
Li	Polycrystalline	2.93	FE ^{c)}
Mg	Polycrystalline	3.66	PE
Mn	Polycrystalline	4.1	PE
Mo	100	4.53	PE
	110	4.95	PE
	111	4.55	PE
	112	4.36	PE
	114	4.50	PE
	332	4.55	PE
Na	Polycrystalline	2.36	PE
Ni	100	5.22	PE
	110	5.04	PE
	111	5.35	PE
Pb	Polycrystalline	4.25	PE
Pt	Polycrystalline	5.64	PE
	110	5.84	FE
	111	5.93	FE
	320	5.22	FE
	331	5.12	FE
Si	Ν	4.85	CPD
	P 100	4.91	CPD
	P 111	4.60	PE
W	Polycrystalline	4.55	
	100	4.63	
	110	5.22	
	111	4.45	
	113	4.46	
	116	4.32	
Zn	Polycrystalline	3.63	PE
	Polycrystalline	(4.9)	CPD

^{a)}PE, photoelectric effect; ^{b)}CPD, contact potential difference; ^{c)}FE, field emission.

where *t* is the thickness of film, *p* is the fraction of elastically dispersed electrons by the thin film surfaces, λ_0 refers to the mean free path, *D* refers to the mean grain size, and *R* refers to the reflection coefficient of the grain boundaries.

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 Table 3. Characteristics of ITO and ultrathin metal electrodes.

Material	Thickness [nm]	Modification ^{a)}	Roughness [nm]	7 ^{b)} [%]	$R_{\rm s}^{\rm c)}$ [Ω sq ⁻¹]	Flexibility	Ref.
ITO	100	_	1.2	92(@550 nm)	≈10	-	[4]
ITO	-	-	-	>90	50–60	Available	[6]
ITO	100-300	_	-	>80	20	_	[8]
ITO	-	-	2.52	82	38	Bending cycles < 200	[54c]
Ag	15	Ge seed layer	0.6–0.8	_	20	_	[53]
Ag	7	Au seed layer	-	83(@580 nm)	19	-	[58]
Cu	7	Al seed layer	<0.6	75(@600 nm)	4.5	-	[52g]
Au	10	Cr seed layer	-	60	27.9	-	[52f]
Ag	7	Ni seed layer	3.9	75	11	Bending cycles > 10000	[50d]
Ag	8	TiO ₂ seed layer TiO ₂ /Ag/AZO	-	86	6	Bending radius 3-6 cm Bending cycles 400	[55]
Ag	11	NiO/Ag/NiO	1.73	82	7.6	Bending cycles > 2000	[54c]
Au	15	PEDOT:PSS/Au/PEDOT:PSS	-	82.6	20.9	Bending cycles 2000	[95e]
Ag	10	WO ₃ /Ag/WO ₃	0.72	≈90	9	Bending cycles ≈2000	[57a]
Cu	8	Oxygen-doped ZnO/Cu/ZnO	≈0.3	83	9	Bending radius 1–10 mm	[54d]
Cu	12	ZnS/Cu/WO ₃	-	≈60	12	-	[76]
Au	10	MoO _x /Au/MoO _x	-	85	7–8	-	[57d]
Au	11	AZO/Au/AZO	-	≈90	7	Available	[54e]
Ag	7	Al doped	0.78	80(@550 nm)	28	-	[63a]
Ag	4	Ta ₂ O ₅ seed layer Al doped	0.76	75	46.8	Available	[64]
Cu	6.5	N doped	-	84	20	Bending radius 1–12 mm	[61]
Ag	6	O doped ZnO/AgO _x /ZnO	_	91	20	Bending radius 1–10 mm	[60a]
Ag	9	PEI/Ag/PEDOT:PSS	0.23	>95	<10	Bending radius < 1 mm	[78]
Au	8	MPTMS:APTMS	0.4	77	11	-	[80]
Cu	12	ZnS	-	≈60	13	-	[76]
Au	7	SU-8	0.35	72(@550 nm)	24	Bending cycles > 1000	[45]
Au	4.4	Ag seed layer SU-8	0.365	78.4(@550 nm)	70.4	Bending cycles > 2000	[74]
Ag	10	ZnO/MUA/Ag/ZnO	0.95	>80	8.61	Bending cycles 200	[75]
Ag	6	O ₂ plasma	-	85.6	9.3	-	[109]
Ag	7 8	ZnS Cs ₂ CO ₃		74(@550 nm) Device	9.75 8.38	Available	[110]
Ag	4	Al seed layer	-	87(@550 nm)	19.5	-	[103b]
Ca:Ag alloy	8	MoO ₃ /Ca:Ag/MoO ₃	-	95(@550 nm)	27.1	Bending cycles 800	[104]
Ag	15	MoO_3 and Au seed layer	-	76(@425 nm)	3.9	-	[105b]
Ag	7	MoO ₃ /Au/Ag/MoO ₃	_	89.65	16	Bending radius 4–10 mm Bending cycles 1000	[123]
Au	7	SU-8/MoO ₃ /Au	0.575	≈75	19	Bending cycles 2000	[125]
Ag	8	MPTMS/Ag/MUTAB	0.5	78	6	Bending cycles 1200	[124]
Ag	10	Cu seed layer Cu/Ag/ MoO ₃	_	≈90	18	Bending radius 5 mm Bending cycles 1000	[126]
Au	15	MoO ₃ /Au/Ag/MoO ₃ /Alq ₃	-	88.67	7	Bending cycles 1000	[128]
Au	7	Cu seed layer	-	≈70	22	-	[131]
Ag	10	Au seed layer MoO3/Au/Ag/MoO3	_	85(@550 nm)	16	-	[130]

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Table 3. Continued.

Material	Thickness [nm]	Modification ^{a)}	Roughness [nm]	T ^{b)} [%]	$R_{\rm s}^{\rm c)}$ [Ω sq ⁻¹]	Flexibility	Ref.
Au	10	MoO ₃ seed layer MoO ₃ /Au/MoO ₃	_	≈90	11.5	-	[59]
Cu	5	ZnO seed layer ZnO/Cu/ZnO	-	83	10	-	[132]
Cu	6	ZnO seed layer ZnO/Cu/ZnO	_	88	10	Available	[133]
Cu	8	AZO seed layer AZO/Cu/AZO	1.916	84	9	-	[133]
Au	12	IZO seed layer IZO/Au/IZO	_	81	5.5	-	[134]
Au	9	AZO seed layer AZO/Au/AZO	2.1	83	12	-	[135]
Au	10	ITO/Au/ITO	_	72	5.6	-	[136]
Ag	10	TiO ₂ /Ag/TiO ₂	_	82	8	-	[137]
Au	9	TiO _x seed layer TiO _x /Au/AZO	0.95	88	14	-	[138]
Ag	7	SnO _x seed layer SnO _x /Ag/SnO _x	-	82	9	Bending radius 20 mm	[139]
Ag	7	FTO seed layer FTO/Ag/FTO	-	95.5	8	-	[140]
Ag	8	ZTO seed layer ZTO/Ag/ZTO	2–3	82	8.8	-	[141]
Ag	10	ZTO seed layer ZTO/Ag/ZTO	-	≈85	8–10	-	[142]
Ag	10	WoO ₃ seed layer WoO ₃ /Ag/WoO ₃	1.3	80	12.2	Bending cycles 3000	[143]
Ag	10	MoO ₃ seed layer MoO ₃ /Ag/MoO ₃	-	70	1.4	-	[144]
Ag	13	MoO ₃ /Ag/MoO ₃	_	80(@550 nm)	5	-	[145]
Ag	10	Au seed layer	_	80	16	-	[130]
Cu	18	Al seed layer	_	70	66	-	[52h]
Ag	8	TeO ₂ seed layer	_	77.1	5	_	[146]
Ag	12	MoO ₃ seed layer	-	85(@550 nm)	8.5	-	[147]
Ag	7	ZnS		83(@550 nm)	9.6	Bending cycles 1000 Bending radius 2 mm	[148]
Ag	12	PVK	_	69	10	Bending cycles 1000	[149]
Ag	12	MoO ₃ seed layer	_	-	12.3	-	[150]
Ag	10	Fullerene-containing surfactant	-	>85	24.59	-	[151]
Ag	6	Ag(O) seed layer	0.6	94	12.5	Bending cycles 1000 Bending radius 6 mm	[152]
Ag	12	PFN	1.3	54.3	9.4	-	[153]
Ag	9	TiO ₂ /PEI	<1	69.7(@550)	6.3	Bending cycles 200	[154]
Ag	8	TiO ₂	2.2	87.7	6.8	Bending cycles 400 Bending radius 2 cm	[155]
Au	12	AZO/Au/AZO	_	81.7	5	Bending cycles 900	[156]
Ag	6	Au/MoO _x	_	80.02(@450)	2.62	-	[157]
Ag	15	Au seed layer	_	70(@400)	7.8	-	[158]
Cu	10	ALD at low temperature	0.62	74(@550)	10.2	Bending radius 1 mm	[159]

^{a)}Strategies to improve the nucleation of ultrathin metal films; ^{b)}Transmittance; ^{c)}Sheet resistance.





From the equations provided above, we can conclude that the resistivity value of an ultrathin metal film can be varied by the surface appearance and cluster sizes induced during the film growth processes. Thus, the conductivity of an ultrathin metal film can be improved effectively by modifying the nucleation process of the deposited metal with a uniform and continous surface morphology. For instance, a 4 nm Au film deposited on a bare glass substrate is not conductive, while the sheet resistance of a 4 nm Au film deposited on a modified glass substrate based on a molecular adhesive is ~83 K\Omega sq⁻¹ owing to the improved growth mechanism with a reduced percolation threshold thickness. The conductivity of 6 nm Au on the modified glass substrate, with the sheet resistance of 87.6 Ω sq⁻¹, is two orders of magnitude lower than that of the Au film on the untreated substrate, with an average sheet resistance of 4.7 K\Omega sq⁻¹.^[45]

4.2. Optical Transparency

As a window to transport photons, the transmittance of an ultrathin metal electrode plays an important role for ITO-free organic optoelectronic devices. When a metal is deposited

on an untreated substrate, discontinuous islands are formed owing to the Volmer-Weber mechanism, and the islands grow and agglomerate with continued deposition to finally form a continuous film. The ultrathin metal film with a thickness beneath the percolation threshold can be assumed as a collection of particles that are small with respect to the wavelengths of light in visible wavelength region.^[90] When a light beam is applied to the rough metal film, the particles induce localized surface plasmon resonance (LSPR) absorption and light scattering, which dramatically decrease the optical transparency of the ultrathin metal film. Figure 7b shows the optical transmission spectra of deposited ultrathin Au films on substrates with untreated and activated surfaces, and the transmission spectra of ideal Au films theoretically simulated by the transfer-matrix method are also provided as reference.^[91] Decreasing transparency with increasing deposition thickness of the film can normally be observed, however, a substantial difference in the optical characteristics of the Au film based on various substrate conditions can also be immediately found. The ultrathin Au film on the untreated substrate exhibits an apparent dip in the spectra that redshifts and widens with increasing Au thickness. The dip feature of the dip is characteristic of LSPR-induced



Figure 7. a) SEM images of ultrathin Au films deposited on substrates with activated surface and untreated surface. b) Optical transmittance spectra of Au films deposited on substrates with activated surface and untreated surface. Simulated transmittance spectra of ideal ultrathin Au film is also provided in (b) as reference. Reproduced with permission.^[91] Copyright 2014, Wiley-VCH.

absorption in a rough and discontinuous film, and the particles and clusters in the film act as subwavelength antennas to concentrate the optical field by LSPR.^[92] After the substrate is modified by a molecular adhesive with thiol groups, the deposited Au atoms are fixed by chemical bounding, and the undesired particles are effectively suppressed, as shown in Figure 7a. As a result, the LSPR absorption is significantly reduced, and the optical spectra exhibit the corresponding features of the simulated spectra of the ideal films. We can conclude from the above discussions that the improved nucleation of an ultrathin metal film not only optimizes the surface morphology features but also increases the optoelectronic properties of the film by suppressing the Volmer–Weber mechanism.

In a transparent metal film system, the kinetic process of the molecular adhesive and nucleation-inducing seed layer is not the only factor to focus on. The material properties, such as the dielectric constant, also have to be taken into consideration for high-performance transparent films. The surface plasmon (SP) mode is the collective oscillation of electrons excited at the interface between a dielectric material and a metal film.^[93] The wave vector $k_{\rm sp}$ can be described as Equation (4) by solving Maxwell's equation^[93d]

$$k_{\rm sp} = k_0 \sqrt{\frac{\varepsilon_{\rm m} \varepsilon_{\rm d}}{\varepsilon_{\rm m} + \varepsilon_{\rm d}}} \tag{4}$$

where \mathcal{E}_{m} and \mathcal{E}_{d} refer to dielectric constants of the metal and dielectric material, respectively. Because the wave vector k_{sp} of the planar SP mode is normally smaller than the wave vector k_{0} in free space, the SP is a nonradiative mode. Incident photons are trapped by the SP mode at the interface between the dielectric material and metal film owing to the optical mismatch. As shown in the dielectric-seed-layer/Ag system in **Figure 8**a, considerable incident light is trapped and persists at the interface if the dielectric constant of the seed layer is lower than that of Ag. According to Equation (4), the SP mode can be suppressed by using seed materials with a large E_d , which offers the possibility of increasing optical transmittance through the dielectric seed layer/Ag system (Figure 8b).^[94] Actually, the SP mode can be

ignored when the thicknesses of the seed layer and metal film are ultrathin enough.

In ultrathin metal electrodes with multilayers, the thickness and refractive index should also be evaluated, especially in a system with an antireflective layer. The antireflective layer is commonly used in D/M/D system in which one dielectric film acts as the nucleation-inducing seed layer to guarantee the production of an ultrathin metal film with high conductivity and the other dielectric film serves as the antireflective layer to enhance the optical transmittance.^[95] As shown in Figure 8c, after depositing an ultrathin Ag film on the PEI modification layer, a PEDOT:PSS layer was spin-coated on top of the PEI/Ag electrode.^[78] The PEDOT:PSS layer, with a high refractive index (≈1.44 at 550 nm) and a suitable thickness, induced destructive interference, and thus reduced the reflection of the Ag film. The optical transmittance of the ultrathin PEI/Ag electrode was enhanced and broadened by the PEDOT:PSS antireflective layer to a visible-range transmittance of over 95%, which was a value comparable to that of the traditional ITO film.

In a desirable transparent conductive electrode, both the optical transparency and electrical conductivity should be optimized with values as large as possible. The figure of merit (Φ) has been engaged as a tool to access the performance of transparent conductive electrodes. The figure of merit is defined as a criterion by the quantified combination of the transmittance (T) and sheet resistance ($R_{\rm s}$)^[96]

$$\Phi = \frac{T}{R_{\rm s}} = T\sigma d \tag{5}$$

where *d* is the thickness of the transparent conductive film and σ is the electrical conductivity. Figure 9 compares the figure of merit of different transparent conductive films as a function of film thickness, as provided by Prof. Kalus Ellmer.^[97] Ultrathin metal films demonstrate a lower figure of merit than transparent conductive oxide electrodes, owing to the tradeoff between transparency and conductivity associated with ultrathin metal thickness. However, transparent ultrathin metal films based on D/M/D systems give high experimental values of the figure of merit, which are comparable to that of ITO films.



Figure 8. a,b) Conceptual diagram of optical properties of a dielectric/Ag system associated with SP modes. a) $E_d < E_{Ag}$ and b) $E_d > E_{Ag}$. Reproduced with permission.^[94] Copyright 2012, The Royal Society of Chemistry. c) Schematic explanation of the antireflective function of the PEDOT:PSS layer on the PEI/Ag film, and PEN is the substrate. Reproduced under the terms of a Creative Commons Attribution 4.0 International License.^[78] Copyright 2015, Macmillan Publishers Limited.

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Figure 9. Theoretical curves of figure of merit (Φ) as a function of film thickness d for metals (dotted lines, left) and transparent conductive oxide (TCO) layers (solid lines, right). Experimental Φ of ITO, Au, Ni, ZnO/Au/ZnO, and Bi₂O₃/Au/Bi₂O₃ films are also dotted. Reproduced with permission.^[97] Copyright 2012, Springer Nature.

4.3. Mechanical Reliability

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Owing to the technological developments toward flexible electronics for wearable and portable equipment, it is very important for the transparent electrodes to maintain their performances under bending. Undesirable changes of the transparent conductive films would lead to devices with a shorter lifetime and a lower efficiency or to complete failure. Analyzing the characteristics of ultrathin metal films under stress provides information about the degree of the mechanical reliability of the films. The bending strain (*S*) in a metal film deposited on a polymer substrate can be given by Equation (6)^[98]

$$S = \left(\frac{d_{\rm m} + d_{\rm s}}{2R'}\right) \left(\frac{1 + 2\eta + \chi\eta}{(1 + \eta)(1 + \chi\eta)}\right) \tag{6}$$

where $d_{\rm m}$ and $d_{\rm s}$ refer to the thickness of deposited metal film and substrate, respectively; $\eta = d_m/d_s$; *R*' is the bending radius; and $\chi = E_{\rm m}/E_{\rm s}$, $E_{\rm m}$ and $E_{\rm s}$ are the Young's modulus of the metal film and polymer substrate, respectively. The bending strain is reduced by decreasing the thickness of the metal film. As a result, a lower bending radius can be expected in the ultrathin metal film, corresponding to a higher flexibility. An ultrathin and ultrasmooth Ag transparent electrode prepared by the template-stripping process, which was designed on an ultrathin photopolymer substrate, demonstrated an extremely small bending radius of 30 µm without performance degradation.^[99] In addition, the strain can be further reduced when a capping layer with suitable thickness (d_c) and the Young's modulus (E_c) is applied over the ultrathin metal film, such as with the D/M/D configuration. When the equation $d_s^2 E_s = d_s^2 E_c$ is satisfied, the sandwiched metal film becomes a neutral surface, and the bending curvature is only limited by the substrate and capping layers.^[98] In this case, with dielectric layers of low modulus and small thickness, the ultrathin metal electrode with multilayers can be bent to super small radii.

Interface properties related to the interfacial adhesion are critical parameters in controlling the mechanical reliability and long-term stability of thin flexible films.^[100] For the application of flexible electrodes, the interfacial delamination should be taken into consideration owing to the poor adhesion of metal deposited on substrates. In ultrathin metal electrodes, seeding layers or adhesion layers are applied to the substrate to improve the nucleation of the metal film, in consequence, the interactions associated with the interfaces are reinforced. Delamination failures were also found at the interfaces between substrates and modification layers. Generally, plasma or ion-beam treatments can effectively improve adhesion levels.^[41] As shown in Figure 6, the modification layers exhibited robust chemical bonds with the ultrathin metal films as well as the substrates and can effectively suppress interfacial delamination.

The robustness of an ultrathin metal film against mechanical deformation is usually verified by the bending test, in which the electrical properties are compared as functions of the bending radius and number of bending cycles, as shown in Figure 10.^[78] The ultrathin Ag electrode sandwiched between PEI and PEDOT:PSS (PAP electrode) under bending to radii of ≈0.7-3 mm demonstrated uniform electrical performance. Meanwhile, the ITO electrode showed catastrophic electrical failure with dramatic increase in resistances due to cracks, which were formed and propagated perpendicularly to the direction of the applied stress, as shown in the inset of Figure 10a. Under the protection of PEI and PEDOT:PSS supporting layers, no evident microscopic cracks were observed in the ultrathin Ag film. As shown in Figure 10b, the PAP electrode indicated excellent flexibility and mechanical reliability after repeated bending cycles with a nearly constant resistance.

5. Applications of Ultrathin Metal Electrodes

With the global developments in organic optoelectronic devices, high-quality transparent electrodes that meet certain requirements are increasingly desired. Ultrathin metal films, with superior optical transparency and electrical conductivity, demonstrate their distinct advantages of high compatibility with flexible devices as well as low-cost materials and fabrication processes. Ultrathin metal films have been considered as an excellent replacement for the traditional ITO transparent electrode in organic optoelectronic devices. In this section, we will summarize the integration and application of ultrathin metal films as the optical and electrical windows in optoelectronic devices including organic light-emitting devices (OLEDs), organic solar cells (OSCs), and perovskite solar cells (Per-SCs).

5.1. Organic Light-Emitting Devices

In OLEDs, the organic emitting layers and functional layers are sandwiched between a transparent electrode and a reflective electrode, and the transparent electrode, functioning as the window to extract photons generated by exciton decay,





Figure 10. Changes in resistance of the flexible ITO and PEI/Ag/PEDOT:PSS (PAP) electrodes on the PEN substrates as the function of the a) bending radius and b) number of bends. The inset shows the photograph of bending test machine, ITO and PAP electrodes after bending with scale bar of 100 mm. Reproduced under the terms of a Creative Commons Attribution 4.0 International License.^[78] Copyright 2015, Macmillan Publishers Limited.

is crucial to the performance of OLEDs.[101] According to the direction of light, the OLEDs are classified as bottom-emitting OLEDs, top-emitting OLEDs, and transparent or semitransparent OLEDs.^[102] In bottom-emitting OLEDs, in which light outcouples from the substrate side, ultrathin metal electrodes with high optical and electrical properties have demonstrated to be desirable replacement bottom transparent electrodes to overcome the deficiencies of the traditional ITO.^[103] For example, we applied an ultrathin Au electrode based on an SU-8 substrate modification layer to replace ITO in OLEDs, and a current efficiency with a 17% enhancement was obtained in the ultrathin-Au-electrode-based OLEDs compared to that of ITO-based reference.^[45] Although the transmittance of the ultrathin Au electrode was lower than that of ITO, the improved performance arises from the suppressed waveguide mode and the optimized optical field distribution. Tang and co-workers designed a bottom electrode based on a nanostructured ultrathin transparent metal for high-efficiency OLEDs with improved broadband light outcoupling performance.[104] They used Ca as the doping material and MoO₃ as the seed to prepare ultrathin Ag electrodes, and a quasi-random outcoupling structure was also introduced by soft nanoimprint lithography for angle-independent and broadband light outcoupling. Owing to the eliminated microcavity effect and minimized surface plasmon loss, the white OLEDs based on designed ultrathin transparent Ag electrodes realized a power efficiency of 112.4 $\rm lm~W^{-1}$ and an external quantum efficiency of 47.2%.

Top-emitting OLEDs, in which the light is emitted away from the carrier substrate, provide the possibility to integrate the backplane driver electronic circuit on the opaque substrate for display applications.^[105] However, owing to the microcavity induced by the reflective metal electrodes, narrowed spectra and angular-dependent emission characteristics are inevitable.^[106] Optimizing the transparency of top electrode is the most effective approach to eliminate the microcavity effect in top-emitting OLEDs, especially for white OLEDs with broadband emitting properties. ITO is not applicable as the top transparent electrode due to the high-temperature process. In recent research, ultrathin metal electrodes with antireflective layers have been considered as potential top electrodes for topemitting OLEDs.^[107] Schwab et al. fabricated an ultrathin electrode with a stack architecture of Au/Ag/NPB, in which 2 nm Au acted as the wetting seed layer and NPB as the antireflective layer as well as capping layer.^[107] Benefiting from the increased transmittance of the multilayer ultrathin Ag electrode, highperformance top-emitting white OLEDs with broadband emission and angular color stability were achieved.

Transparent OLEDs, as the particular case with two transparent electrodes, will be desired in future display equipment.^[108] Ultrathin metal films with favorable optoelectronic properties and a compatible fabrication process are a popular electrode candidate for transparent OLEDs.^[109] Choi et al. reported transparent OLEDs based on transparent ultrathin metal electrodes with optimized structures.^[110] They used ZnS/ Ag/MoO₃ and ZnS/Cs₂CO₃/Ag/ZnS as the anode and cathode, respectively. ZnS and Cs₂CO₃ functioned as the nucleation-promoting layers to prepare ultrathin Ag films with uniform and continuous morphologies. In addition, ZnS and MoO₃, with high refractive indexes, improved the transmittances of both the anode and cathode. The resultant OLEDs obtained a high transmittance of 74.22% at 550 nm with a nearly Lambertian emission property.

OLEDs with ultrathin and ultrasmooth metal electrodes based on various preparation strategies have also demonstrated high flexibility, stretchability and mechanical stability.^[111] As shown in Figure 11a, the green OLEDs based on templatestripped ultra-smooth metal electrodes kept uniform and stable light-emitting properties without any dark spots or cracks after bending and even completely folding, and no evident deterioration in device performance was observed after repeated bending cycles, as shown in Figure 11b.^[112] We also applied ultrathin and ultrasmooth Ag electrodes to stretchable OLEDs resulting in highly mechanically robust characteristics with mechanical stability (Figure 11c). The stretchable OLEDs prepared by a laser-programmable buckling process achieved a luminous efficiency of 70 cd A⁻¹ under 70% strain and accommodated over 100% strain while exhibiting only small fluctuations in performance over 15 000 stretch-release cycles.[113]







Figure 11. a) Photographs of the flexible OLEDs based on template-stripped metal electrodes with various bending radius, and b) the changes in luminance and efficiency of flexible OLEDs as the function of bending cycles, and the inset shows the EL spectra and current density under different bending cycles. Reproduced with permission.^[112] Copyright 2012, Optical Society of America. c) Photographs of the stretchable OLEDs with various strain values as well as on an extended and bent finger joint. Reproduced under the terms of a Creative Commons Attribution 4.0 International License.^[113] Copyright 2016, Macmillan Publishers Limited.

5.2. Organic Solar Cells and Perovskite Solar Cells

OSCs with similar device structures to those of OLEDs have potential applications in the field of clean and renewable energy by converting sunlight to electricity on a large scale.^[114] Ultrathin metal films prepared by suppressing the Volmer-Weber growth mode have been emerging as a novel viable class of transparent electrodes for OSCs with improved far-field transmittance and flexibility. Hatton and co-workers reported OSCs based on widely applicable ultrathin metal films as the bottom window electrode.^[115] The ultrathin Cu, Ag, Au, and Cu/ Ag films were prepared by chemical coordination via their lone pairs between metal atoms and substrate modification layers, and the performances in the ultrathin-metal-electrode-based OSCs were comparable to those of ITO-based cells. Flexible OSCs with a template-stripped ultrathin and ultrasmooth metal electrode were also fabricated, exhibiting an increased power conversion efficiency (PCE) due to the improved charge extraction at the ultrasmooth metal electrode interface.^[116] Ultrathin metal electrodes have also been applied as the transparent top electrode for high-performance OSCs.^[58] In the top-illuminated OSCs with a transparent ultrathin metal electrodes, a capping layer is commonly used out cell to improve the light incidence.

In OSCs, the PCE is limited by incomplete light absorption due to the low charge mobility and short exciton diffusion

length of organic materials.^[117] Incorporating out-of-cell antireflective microstructures and in-cell plasmonic microstructures can optically enhance incident light inside OSCs by increasing the light path and trapping photons associated with plasmon resonance effects, however, the complex fabrication processes of microstructures increase the cost and may damage the performance of active materials in OSCs owing to the use of water and organic solvents.^[118] To improve the light absorption in OSCs, the most simple and direct method is to design an optical microcavity to trap the incident light in active layers.^[119] Ultrathin metal electrodes with semitransparent properties are the best choice to achieve a resonant microcavity in OSCs. By optimizing the refractive index and optical thickness in the constructed microcavity, we can modify the spatial distribution of optical fields inside OSCs to enhance the trapping and collection of photons, resulting in an improved device performance. Jen and co-workers reported a microcavity-based OSCs with an ultrathin Ag electrode and a TeO₂ inset layer.^[120] A microcavity was formed associated with the semitransparent TeO₂/ Ag anode and the back reflecting cathode, and the interference of coherent reflected and transmitted light determined the spatial distribution of optical fields and the generation of charge in the cells. The TeO₂ inset layer, on the one hand, played the role of a seed layer to prepare a uniform and continuous ultrathin Ag film with superior optical and electrical properties, and on





Figure 12. a) Simulated electric field intensity inside OSCs with and without TeO_2 layer. The incident light is on the left with the wavelength of 600 nm, and the maximized field intensity is located within active layer of OSCs with TeO₂. b) Simulated distribution of electric field as the function of the wavelength of incident light. Reproduced with permission.^[120] Copyright 2012, Wiley-VCH.

the other hand, acted as the optical spacer, with a high refractive index and suitable thickness, to confine the local electromagnetic field inside the photoactive region of OSCs as shown in **Figure 12**. As a result, the microcavity-based OSCs with the ultrathin metal electrode demonstrated a higher PCE compared with that of the ITO-based devices, owing to the electromagnetic field within the cell being amplified by the microcavity resonance. Guo and co-workers also reported an Al-doped Ag ultrathin electrode with a Ta₂O₅ seed layer as the optical spacer to realize resonant light absorption in OSCs.^[64] D/M/D ultrathin transparent electrodes, such as MoO₃/Ag/MoO₃, have also been applied for resonant-microcavity-improved light harvesting in OSCs.^[48]

Organic-inorganic hybrid metal halide Per-SCs, exhibiting the characteristics of a large carrier mobility, adjustable bandgap, long carrier life, and low-cost manufacturing process, have generated great research interest.^[121] Through academic research, the PCEs of Per-SCs have increased from 3% to over 22% in just a few years.^[122] Most of the high-performance Per-SCs are based on ITO and fluorine-doped SnO₂ (FTO) as transparent electrodes, however, ITO/FTO-free Per-SCs with both metal anodes and metal cathodes have already emerged in academia and have been developed quickly in recent years.^[123] Chang et al. fabricated large-area ITO-free Per-SCs with ultrathin Ag films as the transparent bottom electrode, as illustrated in Figure 13a.^[124] The ultrathin large-area Ag electrode were sandwiched between two thiol-functionalized self-assembled monolayers; 3-mercaptopropyltrimethoxysilane (MPTMS) beneath the Ag film acted as an adhesive layer, and (11-mercaptoundecyl)trimethylammonium bromide (MUTAB) above the Ag electrode was employed as a buffer layer. The reported largearea ITO-free Per-SCs demonstrated a PCE up to 16.2% with good ambient stability as well. We also designed an ultrathin Au film, based on an SU-8/MoO₃ hybrid nucleation-inducing laver, as the transparent bottom electrode for flexible ITO-free Per-SCs.^[125] Ultrathin metal films have also been employed as transparent top electrodes for Per-SCs, and a top illuminated Per-SC incorporating an optical microcavity and by using an



Figure 13. a) Schematic illustration of Per-SC architecture based on MPTMS/Ag/MUTAB transparent electrode. The chemical bonds in the MPTMS/ Ag/MUTAB transparent electrode are also illuminated. Reproduced with permission.^[124] Copyright 2016, The Royal Society of Chemistry. b) Photographs of semitransparent flexible Per-SC, which is based on ultrathin metal bottom and top electrodes, with various thickness of Au top electrodes. Photograph of the bending Per-SC is shown in the bottom right corner of (b). Reproduced with permission.^[128] Copyright 2016, Elsevier B.V.



ultrathin Ag electrode based on a Cu seed layer as the window of light illumination was recently reported.^[126] In addition, a thermostable semitransparent Per-SC with self-encapsulating properties was prepared.^[127] The Per-SC consisted of an ITO transparent bottom electrode and a semitransparent metal top electrode, in which an ultrathin Ag film was sandwiched between an SnO_x seed layer and an SnO_x capping layer. The SnO_x protected the metal against corrosive halide compounds in the perovskite and shielded the device from the detrimental impact of moisture. The semitransparent Per-SC obtained an average transmittance of 29% for the wavelength region from 400 to 900 nm. Figure 13b shows the photographs of semitransparent ITO-free flexible Per-SCs based on an ultrathin Au anode and an ultrathin Ag cathode, and the semitransparent Per-SCs exhibited an average light transmittance of 15.94% for 500-2000 nm.^[128] Moreover, the semitransparent ITO-free flexible Per-SCs demonstrated a high mechanical robustness with a sustained PCE after 1000 bending cycles.

As the theoretical limitation of PCE is approaching in Per-SCs, a tandem junction solar cell has been proposed to break the limitation in performance. The tandem solar cell consists of a bottom cell based on prevailing solar cells, such as Si-based cells, and a top cell based on Per-SCs with higher bandgaps.^[129] The ultrathin metal electrodes provide the possibility to combine semitransparent Per-SCs in tandem constructions. Yang et al. reported solution-processed perovskite/Cu(In,Ga)(Se,S)₂ four-terminal tandem solar cells, and an ultrathin Ag film based on a Au seed layer was applied as the top transparent electrode for the upper cell in the tandem device.^[130] Huang and coworkers also designed perovskite/Si tandem solar cells based on an ultrathin Au electrode resulting in a 23% combined PCE for the tandem cell.^[131]

6. Conclusion and Outlook

Transparent ultrathin metal conductive films have attracted intense research interests as alternative transparent conductive electrodes in rigid and flexible ITO-free organic optoelectronic devices. The performance of organic optoelectronic devices is dominated by the deleterious tradeoff between the optical transmittance and the electrical conductivity of ultrathin metal electrodes associated with the metal thickness and nucleation process. This review provides the recent progress in the use of ultrathin metal electrodes in ITO-free organic optoelectronic devices that possess the advantages of an ultrasmooth surface with atomic roughness, high transparency and conductivity, low processing cost, and compatibility with heat-sensitive polymer substrates. According to the interactions between substrate atoms and deposited atoms, the growth of a film follows the Frank-van der Merwe mechanism, Volmer-Weber mechanism, or Stranski-Krastanov mechanism. Unfortunately, the ultrathin metal film demonstrates the Volmer-Weber growth mode due to the mismatched surface energies, resulting in a discontinuous and rough surface with poor optoelectronic properties. Efforts to improve metal nucleation with a significantly lowered percolation threshold thickness by suppressing the Volmer-Weber mechanism are summarized and discussed. The wetting behavior of substrates is improved by introducing a

seed layer with 1–2 nm of metal or metal oxide, and continuous and ultrasmooth metal films are also realized based on doping effects as well as the template-stripping technologies. The quality of an ultrathin metal film can also be modified by the chemical trapping of the metal atoms owing to the formation of chemical covalent bonds between the deposited metal atoms and modification layers on the substrate. The successful balance and improvement of the optical transmittance and the electrical conductivity with desirable values is achieved by the optimized metal nucleation of the deposited ultrathin metal films. As a result, ITO-free organic optoelectronic devices based on ultrathin transparent metal electrodes have demonstrated remarkable performance with superior efficiency, flexibility, stretchability, and mechanical stability.

Based on the developing materials and processing techniques, ultrathin metal films have achieved different levels of success as alternative transparent electrodes in organic optoelectronic devices. However, the current strategies for improving the quality of ultrathin metal films still face challenges, and not all of them demonstrate competitive advantages over ITO for commercial applications. Despite the balanced tradeoff in the optoelectrical properties of ultrathin metal electrodes, high optical transparency with broadband spectra is still a problem, compared with the properties of ITO films. The semitransparent-metal-electrode-induced microcavity is of benefit to trap photons in solar cells and to improve the light absorption, but it is deleterious to realize high-quality lightemitting equipment, especially the white-light-emitting devices with broadband spectra. Antireflective coatings and capping layers have been applied to improve the optical characteristics of ultrathin metal electrodes. For example, ultrathin Ag films with high and broadband optical transmittance in the visible wavelength region (with an average transparency > 95%) have been reported based on a PEDOT:PSS optical capping layer with suitable thickness and refractive index.^[78] However, more effective and economical methods are still desired. In addition. the chemical and thermal stabilities in some cases are unsatisfactory, and the transparency and conductivity are damaged by the reconstituted metal particles from the ultrathin metal film owing to thermal and chemical corrosions, which may lead to a shorter lifetime of devices based on ultrathin metal electrodes. Currently, introducing D/M/D constructions for ultrathin metal electrodes and encapsulation are the main strategies to guarantee the device stability and lifetime. The insufficiently understood principles of improved wetting behavior in current strategies limit further enhancements in the performance of ultrathin metal films. Universally applicable principles of dynamic and kinetic nucleation are needed to deduce based on experimental and theoretical phenomena, and can aim to guide the design and choice of improvement methods to turn the film growth from the Volmer-Weber mode toward the Frank-van der Merwe mode. By realizing the strong interaction between the metal atoms and substrates, the percolation threshold will be decreased properly to atomic thickness, corresponding to an ultrathin and ultrasmooth metal film with sufficient mechanical, thermal and chemical stabilities. Furthermore, the technical breakthroughs for roll-to-roll processing ultrathin metal films with low-cost, low-temperature and high-speed are still desired. Therefore, applying ultrathin metal films to totally

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replace the expensive and brittle ITO in organic optoelectronic devices is calling for stringent fundamental research and technological improvements. The development of ultrathin metal electrodes will open up a pathway for the commercialization of ITO-free organic optoelectronic devices.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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