Atomic Layer Deposition



Conformal Physical Vapor Deposition Assisted by Atomic Layer Deposition and Its Application for Stretchable Conductors

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Physical vapor deposition (PVD) is a versatile thin-film coating technique that can deposit a wide selection of inorganic materials at low cost. However, the process is based on line-of-sight transfer, which can lead to shadowing effects and limit film uniformity over nonplanar topographies. This work describes improving conformal PVD coating on polymer nanostructures by increasing surface energy using a thin oxide interlayer deposited by atomic layer deposition (ALD). The proposed ALD-assisted PVD process allows conformal coating at low cost, and can be adopted for a wide variety of materials compatible with tradition PVD. Conformal gold films over nanostructures with 500 nm half-pitch and aspect ratio up to 1.5 are demonstrated. The film uniformity is characterized using cross-sectional electron microscopy, energy-dispersive X-ray spectroscopy, and electrical measurements, showing a clear improvement in coating uniformity with the oxide interlayer. This PVD process is then used to fabricate metallic nano-accordion structures, which can be used for stretchable conductors. The demonstrated process can improve material selection and reduce process cost of conformal coating, which can find applications in integrated circuit manufacturing, stretchable electronics, and wearable sensors.

1. Introduction

There has been significant research interest in materials that combines mechanical compliance, electrical conductivity, and optical transparency.^[1–25] Such stretchable, transparent conductors would break the mold of existing hard electronics and lead to new applications such as wearable sensors, stretchable devices, and flexible display. One approach to realize

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stretchable conductor is to disperse conductive 0D, 1D, and 2D nanomaterials onto soft elastomeric substrates. These include nanoparticles,^[6–8] carbon nanotubes,^[9–11] silver nanowires,^[12-14] and graphene,^[15-19] all of which have demonstrated high conductivity and large stretchability. Another method is based on geometry, where thin conductive layers with micro/nanoscale corrugated structure maintain conductivity by unbending during stretching. These structures can be induced by surface buckling^[19-22] or self-assembled patterns.^[23] Our recent work has demonstrated that interference lithography and atomic layer deposition (ALD) can be used to create a freestanding nano-accordion structure,^[24,25] which can be simultaneously stretchable, conductive, and transparent. This approach allows precise control of the structure period, height, and thickness to allow independent design of material properties. However, this approach relies on ALD of the conductive film, which has high cost

and long deposition time. The ability to obtain conformal thinfilm coating using a low-cost process can facilitate scale-up manufacturing and broad implementation of flexible electronics.

ALD is a widely employed vapor phase technique, where two gas precursors are introduced in alternating cycles to create a self-limited surface reaction.^[26,27] Each cycle result in a single monolayer coating, allowing precise control of film thickness by using discrete cycles. Since the gas precursors can permeate within rough topography and deep pores, ALD has demonstrated conformal coating in high-aspect-ratio grating structures,^[24,25] high-density nanoscale features,^[28,29] and 3D porous lattice.^[30–34] However, ALD also has a number of drawbacks, such as long reaction time and expensive precursor gases, contributing to high process cost. Compared with physical vapor deposition (PVD), the selection of deposition material is also limited. Furthermore, metal ALD generally requires high synthesis temperature, which can be problematic for polymer surfaces or template structures.

A more established alternative is PVD, which is one of the most widely used technique for precise deposition of thin films, including metals and a diverse range of organic/inorganic materials. Representing a class of techniques where the





deposition material is transformed to the vapor phase before condensing on the target surface, PVD plays an important role in microelectronics, microelectromechanical systems (MEMS), and photonics.^[35] It has many key advantages, including wide material selection, high composition purity, and low process cost. However, the process is limited by line-of-sight material transfer, which can lead to shadowing effects during deposition. This results in poor conformal coating and nonuniform film thickness over surface topography and in deep trenches, especially for structures with sub-micrometer features and high aspect ratio (AR). Several advanced PVD techniques have been introduced to mitigate the shadowing effects, such as ionized PVD,^[36-39] where the deposition materials are ionized in high electric field to direct deposition in deep trenches. However, the coating on the vertical sidewalls can still be porous and rough, resulting in poor film properties. Another approach to improve step coverage is oblique angle PVD,^[40-42] where the substrate is obliquely tilted and rotated in the coating chamber. However, the deposition is still limited by line-of-sight effects, and the coating uniformity is sensitive to the aspect ratio of surface topography. Though these advanced PVD techniques showed improved conformal film coating, they still have limitations for complex nanostructures with high AR.

This work reports a hybrid method where both PVD and ALD are employed to improve conformal coating of a metal film on a nanostructured polymer template. In this approach, illustrated in Figure 1, a thin layer of metal oxide film is deposited using ALD as an interlayer to increase surface energy and promote particle adhesion for subsequent metal deposition. Au PVD coating on an untreated polymer nanostructure is shown in Figure 1a, illustrating discontinuous and nonuniform coating on the sidewalls. This can be attributed to poor binding of deposited Au particles to the polymer surface, which can then migrate and form large aggregates.^[43-45] The PVD coating can be improved by using a thin conformal oxide layer deposited using ALD, as shown in Figure 1b, serving as an interlayer. The oxide has high surface energy compared with polymer,^[46-48] which can enhance the binding and adhesion of deposited Au particles.^[34] The interlayer is also believed to limit the migration of gold grains, reducing film roughness and nonuniformity.

This approach has a number of advantages. First, only a thin oxide interlayer is required using ALD, a cost and time-intensive process, while the thicker metal film is deposited using conventional PVD. Second, ALD coating of oxide requires lower process temperature (\approx 90 °C) than metals (\approx 200 °C),^[26,32–34]





which enables the use of polymer templates. Third, the use of PVD enables a wide range of metals and other organic and inorganic materials that are not available through ALD. A number of interlayer thickness and materials, including Al_2O_3 , ZnO, and TiO₂ were examined. The uniformity of conformal Au PVD was characterized using electron microscopy, energy-dispersive X-ray spectroscopy (EDS), and measurement of electrical conductivity of the fabricated films. The conformal metal PVD approach was used to fabricate Au nano-accordion structures for stretchable conductors, and the electrical, mechanical, and optical properties of these structures are reported.

2. Results and Discussion

Several nanostructure templates were prepared to investigate the thickness uniformity of Au PVD film over polymer surface topography. Initially, silicon substrates were spin-coated with SU-8 photoresist and patterned with 1D periodic structures using interference lithography.^[49,50] A uniform SU-8 buffer layer with 250 nm thickness was used for adhesion. To study film uniformity in structures with the same density, the structure period was kept constant at 1 µm period for all the experiments. The structure height was determined by the initial resist thickness, and the width was controlled by the exposure dose. Different oxide interlayers, including, Al₂O₃, ZnO, and TiO₂, were then deposited at low temperature ≈ 90 °C. The interlayer thickness was controlled by the number of ALD cycles and ranges from 5 to 15 nm. Au PVD films with 30 nm thickness are then coated using thermal evaporation (Kurt J. Lesker Company). The deposition rates were varied from 0.2 to 1 Å s⁻¹ to investigate the quality of the Au PVD film. Different nanostructure AR, oxide ALD species and thickness, deposition rates to investigate the uniformity of the proposed conformal PVD film. The detailed description of the fabrication process can be found in Section SA (Supporting Information).

To investigate the effect of surface topography, we fabricated periodic nanostructures with constant width of 600 nm and heights of 400, 600, 900, and 1200 nm, yielding AR of 0.67, 1.0, 1.5, and 2.0, respectively. In these experiments, 5 nm of Al_2O_3 interlayer was coated using ALD, and 30 nm of Au film was deposited using PVD at a rate of 0.2 Å s⁻¹. The effect of interlayer thickness was also examined but had little effect on Au film quality, as described in Section SB (Supporting Information). The cross-sectional scanning electron microscopy (SEM) images of the fabricated nanostructure samples are shown

in **Figure 2.** Low thickness variation and smooth surface morphology can be observed in the structure ridge and valley for all the samples. It can be noted that the uniformity of the Au film on the sidewalls degrades as structure AR is increased. However, this is a significant improvement on samples fabricated without the interlayer, which would result in discontinuous and rough sidewall coating. The sidewall film uniformity can be better observed in cross-section SEM in the perpendicular direction, as described in Section SB (Supporting Information).





Figure 2. a–d) Cross-section SEM images of 30 nm Au PVD film coating with 0.2 Å s⁻¹ deposition rate on nanostructures with AR of 0.67, 1.0, 1.5, and 2.0. A 5 nm Al_2O_3 ALD interlayer is used in all the samples.

The PVD deposition rate can also affect film uniformity. For comparison, the deposition rate is increased fivefold to 1 Å s⁻¹ for the same template geometry examined previously. The cross-section SEM images for structure with AR of 0.67 and 2.0 are shown in **Figure 3**. Difference of film uniformity on sidewalls can be observed and is especially pronounced for the 2.0 AR structure. This can be attributed to the grain migrations, with a slower deposition rate allowing the gold clusters to adhere more uniformly on the sidewalls. These cross-section SEM allows a qualitative inspection of the important role the oxide interlayer can play on the Au film uniformity.

The uniformity of the conformal Au PVD film was further investigated using transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS). For reference, the scanning transmission electron microscope (STEM) image and corresponding Au EDS signal of the 30 nm Au PVD sample without interlayer are shown in **Figure 4**. Here, the polymer template has a width of 400 nm and height of 600 nm, yielding a structure AR of 0.67. As expected, the Au



Figure 3. a,b) Cross-section SEM images of 30 nm Au PVD film coating with 1 Å s⁻¹ deposition rate on nanostructures with AR of 0.67 and 2.0. A 5 nm Al_2O_3 ALD interlayer is used in all the samples.



film is discontinuous and highly porous on the sidewalls. The film thickness on valleys and trenches is much higher than the sidewalls, illustrating the main drawback of PVD due to line-of-sight transfer. EDS mapping data for Au are shown in Figure 4b, and are nearly identical to the STEM image. This indicates that coated film contains only Au, and there are no other chemical reactions to consider. It is also important to note that significant thickness deviation can be observed, resulting in high roughness in the Au film.

To investigate the interlayer effect, we examine the Au PVD film on polymer nanostructure with Al_2O_3 ALD interlayer using TEM and EDS, as shown in **Figure 5**. Similar to the sample without the interlayer, the template structure also has height of 400 nm, width 600 nm, and AR of 0.67. The deposited Au film is 30 nm thick using 0.2 Å s⁻¹ deposition rate, and the Al_2O_3 ALD interlayer is 5 nm thick. The STEM image in Figure 5a shows the Au film is conformal and covers the polymer template completely, a significant improvement compared with the results

without the Al₂O₃ interlayer shown in Figure 4. This result is confirmed by the Au EDS map as shown in Figure 5b, where the Au film closely follows the underlying Al₂O₃ ALD film. Note the interlayer film conforms perfectly to the template surface, as illustrated in the Al and O EDS maps shown in Figure 5c,d. While the Au film is not as uniform as the Al₂O₃ film on the sidewalls, the film discontinuity and roughness has been greatly mitigated. This can be attributed to the high surface energy of Al_2O_3 , reported to be greater than 500 mJ m⁻²,^[46,47] which promotes the adhesion of Au grains over the nanostructure topography during PVD. In comparison, the surface energies of SU-8 with and without O2 plasma treatment are 45 and 79 mJ m⁻², respectively.^[48] The Au grains, also with high surface energy over 1 [m⁻², therefore favor forming aggregates as opposed to adhering on the polymer surface. The EDS analysis of higher AR template structures does indicate Au film degradation, as described in Section SC (Supporting Information). However, the results indicate a significant improvement over PVD coating without using interlayers, shown previously

in Figure 4. Therefore, the film quality has been improved by introducing a thin Al_2O_3 ALD interlayer, which can have a dominant effect in determining the film electrical and mechanical properties.

To further investigate the effect of the oxide interlayer and compare the quality of the Au films deposited using PVD, we characterized the film sheet resistances using a four-point probe system. Using this method, any film discontinuity or porosity along the sidewalls that are not readily observable in SEM and EDS images can be quantitatively examined. The sheet resistance measurements reported in this work are all measured





Figure 4. a) Cross-sectional STEM images and b) EDS of Au PVD coating on polymer nano-structures with poor film uniformity.

in the direction perpendicular to the structure ridge, which can be 10% higher than the parallel direction.^[25] The sheet resistances for the fabricated samples with and without Al₂O₃ ALD interlayers are plotted versus the structure aspect ratio on a semilog scale, as shown in Figure 6. The measurement for different Au PVD deposition rates, 0.2 and 1 Å s⁻¹, are also plotted. The plots include a 30% error bar, which is the estimated uncertainty in the measurements. For a planar resist surface, or AR = 0, the sheet resistances for 0.2 Å s^{-1} PVD deposition rate are 1.92 and 1.94 Ω sq^{-1} with and without Al_2O_3 interlayer, respectively. At higher deposition rate of 1 Å s⁻¹, the sheet resistances are slightly lower at 1.83 Ω sq^-1 with and without Al₂O₃ interlayer. This can serve as the reference measurements for Au film in the absence of topography, where there is no line-of-sight limitations and the interlayer has no effect on film quality as expected. As the AR is increased to 0.5, the resistances for the Au film without Al₂O₃ interlayer increase roughly by an order of magnitude to 23.53 and 25.17 Ω sq⁻¹ for deposition rates of 0.2 and 1 Å s⁻¹, respectively. The resistances for the Au film with Al₂O₃ interlayer, however, are roughly the



Figure 5. a) Cross-sectional STEM images and b–d) EDS of Au PVD coating on polymer nanostructures (AR = 0.67) with Al_2O_3 ALD interlayer. b–d) The EDS signals for Au, Al, and O.



same at 1.93 and 2.05 Ω sq^{-1} for deposition rates of 0.2 and 1 Å s^{-1}, respectively. This indicates the significant improvement in film uniformity for structures with low AR ratio, where the samples with Al₂O₃ interlayers exhibit little to no degradation in electrical properties.

The effect of the Al_2O_3 interlayer is even more pronounced at higher structure AR. The resistances with interlayer (solid and dashed blue lines) increase more gradually, while those without (solid and dashed black lines) more dramatically at high AR. A significant increase in the measured resistances can be observed for all the samples at

AR = 0.67, after which the sheet resistance increases exponentially with similar degradation in electrical properties. However, the resistances for the film with interlayer are generally about an order of magnitude lower than those without. The PVD deposition rate also has an effect on the electrical properties of the Au film, albeit to a lesser degree. In general, the higher deposition rate has little effect at low AR up to 0.5, and can increase resistance by up to twofold at higher AR. The degradation of film quality at higher rate can be attributed to aggregation of abundant Au particles during deposition, leading to porous films. The raw resistance data can be found in Section SD (Supporting Information).

Beyond Al_2O_3 , other metal oxides including TiO_2 and ZnO were also evaluated as the interlayer material to improve conformal coating of PVD film. The interlayers were deposited using ALD, with 5 nm thickness on the photoresist template prior to 30 nm Au PVD coating. The resulting Au films also exhibit more continuous and smooth morphology, as illustrated in the STEM and EDS images shown in **Figure 7**. The periodic polymer templates used have feature width and height of

600 nm, yielding an aspect ratio of 1.0. The STEM images of the TiO₂ and ZnO interlayer samples are shown in Figure 7a,b, respectively. For both TiO₂ and ZnO, it can be observed that the Au PVD films conform well to the topography and have relatively uniform thickness on the sidewalls. The conformal profiles were confirmed by the Au EDS signals, as shown in Figure 7c,d for TiO₂ and ZnO interlayers, respectively. The thickness of the Au film is thinner and slightly porous at the sidewalls, but appears uniform and smooth. A clear example of the porous Au along the sidewalls can be observed in Figure S5 (Supporting Information). In both cases, the Au films conform well to the interlayers, as the EDS images indicate in Figure 7e,f for TiO₂ and ZnO, respectively. These results report similar improvement in conformal coating when compared with the Al₂O₃ interlayer, with TiO₂ appearing to have a slightly more uniform profile.

The electrical properties of the conformal Au PVD film on different oxide interlayer

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Figure 6. Measured sheet resistance versus structure aspect ratio for 0.2 and 1 Å s^{-1} Au PVD deposition rate, with and without Al_2O_3 ALD interlayers.

materials were also examined, as shown in Figure 8. Here, the sheet resistances for Au PVD film with Al₂O₃, ZnO, and TiO₂ interlayers are plotted. The values for direct PVD coating on bare photoresist template without interlayer are also plotted for comparison. The Au deposition rate is 0.2 Å s⁻¹ for these experiments to promote uniform film thickness. In comparison to Al₂O₃, ZnO interlayer results in similar resistance values as structure AR is increased. However, the TiO₂ interlayer yields the most beneficial effects on promoting conformal Au coating. The change in sheet resistance of gold film on TiO2 was less dramatic than other oxide interlayers, suggesting better binding and less migration of the Au grains during deposition. Its sheet resistance at the highest structure AR of 1.5 was around 100 Ω sq⁻¹, which is 14 times smaller than the case without any interlayers. This compares well to 12.3 Ω sq^-1 for platinum ALD coating on nanostructures with similar geometry,^[25] which is highly conformal but fabricated using the more expensive process. It is also interesting to note that the sheet resistance of Au film on TiO₂ interlayers is always about ten times lower than the coating with no interlayer. Thus, TiO2 ALD interlayer is suitable and effective in improving conformal PVD coating on polymer nanostructures with high AR. While this work is limited to investigating conformal Au films, conformal coating of other inorganic materials deposited using PVD can potentially also benefit from an oxide interlayer.

3. Applications in Stretchable Conductors

The reported ALD-assisted conformal metal PVD film can find applications in stretchable conductors. Using the periodic polymer nanostructure as a template, the Au film forms a corrugated film resembling a nanoscale accordion. In prior work, we introduced such nano-accordion structures using ZnO^[24] and Pt films^[25] using ALD, and here we demonstrate that such a stretchable conductor can be achieved using conformal ALDassisted PVD coating. This process can greatly reduce fabrication cost by reducing ALD process time and enable a greater variety of metals such as gold. To demonstrate this principle, the conformal Au PVD film is transferred to a flexible polydimethylsiloxane substrate (PDMS) substrate, as described in more details in Section SA (Supporting Information). The resulting structure is freestanding, with one side of the accordion fold ridge in contact and bonded to the PDMS substrate. The thin oxide interlayer remains on the top, exposed Au surface, which can serve as a passivation layer. The demonstrated process can transfer the nano-accordion structure a flexible substrate and can enable mechanical and optical testing.



Figure 7. a,b) Cross-sectional STEM images for Au PVD film on polymer nanostructures (AR = 1) with TiO₂ and ZnO ALD interlayers. c,d) EDS signals for Au on TiO₂ and ZnO samples. e,f) EDS signals for Ti and Zn for their respective samples.

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Figure 8. Measured sheet resistance versus structure aspect ratio for Au PVD with 0.2 Å s⁻¹ deposition rate for samples with Al₂O₃, ZnO, TiO₂, and no ALD interlayers.

The uniaxial stretchability of the fabricated Au nano-accordion structures was tested along the fold direction. Here, a mechanical testing module with two clamps was installed within a SEM chamber for in situ imaging of the stretched structures. The Au nano-accordion structures tested has period of 1 μ m, width of 600 nm, and height of 300 nm, yielding a structure AR of 0.5. Note this is the smallest AR structure fabricated and has measured sheet resistance close to a planar film. The stretch test is summarized by the top-view SEM images shown in **Figure 9**. Here, the strain in percentage is measured by marking ten structure periods, with 0% indicating the initial unstrained state shown in Figure 9a. The Au nano-accordions are then stretched from the free side of PDMS substrate against the fixed side on the test module, and Figure 9b–f depicts 18, 26, 30, 34, and 41% strain, respectively. It can be observed that



the fold geometry is maintained without structural degradation in all samples. At larger strain when the structures do collapse, the failure mechanism originates from the unbending of the curved section on top of the structure ridge.^[24] The onset of such failure would lead to systematic structure collapse, which was not observed in the Au PVD samples. In this experiment, the structure collapsed at 45% strain due to the failure of the PDMS substrate.

The maximum stretchability of 41% for the Au nano-accordion structure is promising, since it is achieved with a relatively low AR of 0.5. In prior work using AZO nano-accordion structures using ALD, similar AR structures suffered systematic structure collapse at 10% strain.^[24] The maximum strain in such nano-accordion structure can be calculated by^[24]

$$\varepsilon_{\max} = \frac{4\sigma_{FS}}{3E\Lambda r} \left(\frac{h^3}{t}\right) \tag{1}$$

where σ_{FS} is the failure stress, *E* is the film's modulus, *r* is the radius of curvature for the ridge, and Λ , *h*, and *t* are the structure period, height, and thickness, respectively. As described by this equation, nano-accordion structures with higher AR and lower thickness will have more stretchability. Therefore, it is expected that the metallic nano-accordion structures with higher AR are expected to show stretchability of more than 100%. More flexible substrates, such as Ecoflex (Smooth-On, Inc.), will be more suitable for mechanical characterizations, and is the subject of future research. It is also expected that higher strain can result in plastic deformation in the Au nano-accordion structures, and dynamic testing using cyclic loads will be investigated.

To investigate the suitability of the Au nano-accordion structure for stretchable conductors, the strain-dependent electrical properties were characterized. The sheet resistance of the structure after transfer to PDMS substrate is measured to be 9.03 Ω sq⁻¹, indicating that some structure collapsed during transfer and leading to a fivefold increase in resistance. The resistances from 0 to 25%



Figure 9. a-f) Top-view SEM images of Au nano-accordion structures with 0, 18, 26, 30, 34, and f) 41% strain.

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Figure 10. Measured sheet resistance versus applied strain in Au nano-accordion structure on PDMS substrate. A linear best-fit line is plotted.

strain are illustrated in Figure 10. The measured data are fairly uniform and varies from 9.03 to 10.91 Ω sq⁻¹, well within the standard deviation of the measurement plotted as the error bar. A linear fit of the data is also shown, having an equation of $R_{\rm s} = 0.22\varepsilon + 9.17$. At larger strain the resistance increases significantly, indicating that the nano-accordion structure is failing through buckling in the direction perpendicular to the strain axis. This can be attributed to the substrate contracting along this direction, which has been observed in previous work.^[23] These data indicate that the electrical behavior is strain independent up to 25% strain, which is desirable for stretchable conductors. The accordion geometry demonstrated in this work has 1D corrugation, which allows stretching along a single direction. However, more complex corrugation in orthogonal directions is also possible by using a 2D array photoresist template, which can lead to biaxial stretching and bending.

The fabricated Au nano-accordion structure is highly conductive, but it is also optically opaque due to high material absorption of metals. To improve optical transparency, portions of the Au film can be removed using an additional lithography and etching step, yielding a microstructured nano-accordion. This process is described in more details in Section SA (Supporting Information). Two samples with different ratios of

opening to structure areas were fabricated to demonstrate this process. The first sample has 70% opening ratio, with 7 and 3 μ m for open and closed structure areas, respectively, and the second sample has 95% opening ratio, with 19 and 1 μ m for open and closed areas, respectively. The SEM images of the microstructured Au nano-accordions on PDMS with 70% opening are shown in **Figure 11**. Here, it can be observed that the accordion structures maintain high profile fidelity through wet etching and transfer processes. This process allows the selective removal of nano-accordion structure using windowing patterns that can be independently designed.



The broadband transmittance of the microstructured nano-accordions is characterized using spectrophotometer (Cary 5000 UV-vis-NIR, Agilent Technologies) to investigate the optical effects of the microstructured openings. The measured transmittance from 400 to 2000 nm wavelength for 0, 70, and 95% opening ratios are depicted in Figure 12. As expected, the solid Au nano-accordions, or 0% opening ratio, exhibits low optical transmission. This is similar to a planar Au film with 30 nm thickness, with an absorption peak at 500 nm wavelength. However, the microstructured nano-accordions with 70% opening have around 60% in most of the UV-NIR wavelength range. The structures with 95% opening ratio have even higher transmission, more than 80% in the same ranges, and are comparable to the 90% transmission for a bare PDMS substrate. The transmittance is dominated by the PDMS due to the high opening area ratio, and the transmission peak at 500 nm attributed to the Au film can no longer be observed. The optical transmittance of Au nano-accordions when stretched is also measured, as shown in Figure 12. Here, the samples are stretched to 40% strain, and optical transmission increases slightly across all wavelength. The improvement is around 5% and can be attributed to the period of the accordion increasing under strain. Since the film thickness does not change, the metal volume fraction for one unit period decreases, increasing optical transmission. A photograph image of the 70 and 95% opening nano-accordion structures on PDMS substrates is shown in the inset diagram, where the sample transparency can be visually observed.

These results indicate it is possible to enhance the optical transmission by removing the structured film in selected area. This results in a hierarchical structure, with microstructured opening area and nano-accordion geometry. It is expected that higher optical transmission can be acquired by increasing the opening-to-structure ratio, but the electrical performance suffers as a result. For the fabricated 70 and 95% opening nano-accordion structures, the conductivities degrade rapidly upon stretching due to isolated crack formation in the thin Au nano-accordion lines. While the failure is not systematic, the samples quickly become nonconductive. Therefore, there is a competition between achieving high conductivity or optical transmission in these current samples. The electrical and optical properties using more complex 2D windowing micropatterns to ensure multiple Au line connections are the subject of future research.



Figure 11. SEM images of microstructured Au nano-accordion structures with AR of 0.5 and 70% opening ratio on PDMS substrate.





Figure 12. Measured transmittance for Au nano-accordion (NA) structures with 0, 70, and 95% openings. The visual images of the samples with 70 and 95% openings are shown in the inset diagram.

4. Conclusion

We present an alternative approach to deposit conformal metal layer on nanostructured polymer topography using ALDassisted PVD. We demonstrate that the film uniformity, roughness, and morphology of Au PVD coating at the sidewalls can be improved by using a thin metal oxide layer deposited using ALD. Au films deposited on different nanostructure aspect ratio from 0.5 to 1.5 and interlayer materials were investigated using TEM, EDS, and electrical conductivity measurements. The results indicate that for all AR, oxide interlayers as thin as 5 nm thickness can improve the uniformity of Au PVD film. The oxide ALD process requires relatively low temperature and short process time for the interlayer, while coating the Au film using PVD can reduce process cost and enable more materials. This process can potentially be applied to other conformal metal coatings using PVD. The process was used to demonstrate Au nano-accordion structures that are conductive and can be stretchable up to 41%. The structure can also demonstrate broadband optical transparency by patterning microstructured opening areas, resulting in a hierarchical nano-accordion structure. The demonstrated stretchable, transparent conductor can find applications in wearable display and devices for augmented reality.

5. Experimental Section

Template Fabrication: The polymer template was fabricated using negative photoresist SU-8 (Microchem, Corp.). An antireflection layer (ARC i-CON-16, Brewer Science, Inc.) was used under the resist to reduce back reflection. A buffer layer of fully cross-linked SU-8 was used to improve adhesion to the template structure. A Lloyd's mirror interference lithography using HeCd laser with 325 nm wavelength was used to expose period nanostructure with 1 μ m period. The exposure dose was varied from 3 to 6 mJ cm⁻² to control the template feature width. After postexposure bake at 65 °C for 5 min, the samples were developed in propylene glycol monomethyl ether acetate (PGMEA), rinsed in isopropyl alcohol (IPA), and then hard baked at 210–220 °C.



Conformal Film Deposition: The photoresist nanostructure templates were subsequently coated with oxide interlayer using ALD in a custom made viscous-flow. hot- walled, vacuum reactor described previously.^[32-34] Trimethyl aluminum (TMA, Strem Chemicals, min 98% pure) was used as a precursor and coreacted with deionized water to deposit Al₂O₃. The ALD recipe used for these experiments was 1/30/1/60 (TMA dose/nitrogen purge/water dose/nitrogen purge, in seconds) at 550 mTorr and 90 °C with a typical growth rate of 1.3 Å cycle⁻¹, and 40 cycles were conducted to deposit around 5 nm of Al₂O₃. Titanium (IV) chloride (TiCl4, 99%, STREM Chemical) was used as a precursor and coreacted with deionized water to deposit TiO₂. The ALD recipe used for these experiments was 1/40/1/60 (TiCl4 dose/nitrogen purge/water dose/nitrogen purge, in seconds) at \approx 1.8 Torr and 90 °C with a typical growth rate of 0.4 Å cycle⁻¹, and 130 cycles were conducted to deposit around 5 nm of TiO2. Diethyl zinc (DEZ, Strem Chemicals, min 98% pure) was used as a precursor as the metal-containing precursor with deionized water to deposit ZnO. The ALD recipe used for these experiments was 2/60/2/60

(DEZ dose/nitrogen purge/water dose/nitrogen purge, in seconds) at 1.8 Torr and 90 °C with a typical growth rate of 0.7 Å cycle⁻¹, and 70 cycles were conducted to deposit around 5 nm of ZnO. The Au PVD coating was then deposited using thermal evaporation (Kurt J. Lesker Company).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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