

**A new architecture as transparent electrodes for solar and IR applications based on
photonic structures via soft lithography**

by

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A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

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Iowa State University
Ames, Iowa
2011
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ACKNOWLEDGEMENTS

I would like to use this occasion to give my most sincere gratitude to my major professor Dr. Kristen Constant, who has been consistently helping me and giving me invaluable advice on the research project and my academics. I am especially grateful to Professor Kai-Ming Ho, who provides this research opportunity to me and continues to give me strong support. I also want to thank Professor Sumit Chaudhary for his advice and help on the project and organic solar cell fabrication. I appreciate Professor Zhiqun Lin and Professor Steve Martin for being on my committee and a part of this process. I would also like to express my appreciation to my group members Dr. Joong-Mok Park and Dr. Wai Leung, who have been patiently helping me in my research and from whom I had learned so much.

I want to express my thankfulness to my parents, Dehuai Kuang and Cuifeng Chen, my uncle Yihuai Kuang, my brother Zhong Kuang, and other family members. Without them I wouldn't have made this far and they continue to be my strongest support.

ABSTRACT

Transparent conducting electrodes with the combination of high optical transmission and good electrical conductivity are essential for solar energy harvesting and electric lighting devices. Currently, indium tin oxide (ITO) is used because ITO offers relatively high transparency ($>80\%$) to visible light and low sheet resistance ($R_s = 10 \text{ ohms/square } (\Omega/\square)$) for electrical conduction. However, ITO is costly due to limited indium reserves, and it is brittle. These disadvantages have motivated the search for other conducting electrodes with similar or better properties. There has been research on a variety of electrode structures involving carbon nanotube networks, graphene films, nanowire and nanopatterned meshes and grids. Due to their novel characteristics in light manipulation and collection, photonic crystal structures show promise for further improvement. Here, we report on a new architecture consisting of nanoscale high aspect ratio metallic photonic structures as transparent electrodes fabricated via a combination of processes. For (Au) and silver (Ag) structures, the visible light transmission can reach as high as 80% , and the sheet resistance of the structure can be as low as $3.2\Omega/\square$. The optical transparency of the high aspect ratio metal structures at visible wavelength range is comparable to that of ITO glass, while their sheet resistance is more than 3 times lower, which indicates a much higher electrical conductivity of the metal structures. Furthermore, the high aspect ratio metal structures have very high infrared (IR) reflection (90%) for the transverse magnetic (TM) mode, which can lead to the development of fabrication of metallic structures as IR filters for heat control applications. Investigations of interdigitated structures based on the high aspect ratio metal electrodes are ongoing to study the feasibility in smart window applications in light transmission modulation.

INTRODUCTION

Transparent conducting electrodes with the combination of high optical transmission and high electrical conductivity are essential and desirable in solar energy harvesting and optoelectronic applications. Transparent conducting oxides (TCOs) are wide bandgap materials that offer high transparency for visible light and relatively good electronic conduction. [1] Indium tin oxide (ITO) and Zinc oxide (ZnO) are typical oxide materials used for such purposes. [2] ITO is widely used in the flat panel displays and solar cells. [3,4] It is also found in heat mirrors and smart windows applications due to its excellent infrared reflection properties. [5] However, there are several drawbacks in using ITO. It is costly due to limited indium resources. [6] The brittle nature of the oxide has also limited its potential use in various novel devices such as flexible solar cells and flexible displays. [7] There are trade-off between the optical and electrical properties of ITO depending the film thickness. [8] These disadvantages have motivated the search for alternative conducting electrodes with similar or better performance. In recent research efforts, carbon nanotube networks, graphene films, silver nanowire meshes and nanopatterned metal grids have been evaluated as potential replacements for ITO based electrodes. [9-12] In particular, nanopatterned metal grids made by nano-imprinting techniques are showing promise because of the straightforward and effective process and its amenability to roll-to-roll printing for large area fabrication. [12-15] Different microscale or nanoscale patterning techniques can be examined to investigate other possible fabrication processes for patterned structures as transparent electrodes.

Aim and objectives

Due to their functionality of light manipulation, photonic crystal structures show promise in solar radiation collection and absorption for photovoltaic devices and outcoupling efficiency enhancement in solid-state lighting. Various patterning and fabrication techniques to make such photonic structures and their optical properties have been investigated. One simple and cost-effective method is by utilizing soft lithography. Here, we report on a new architecture consisting of transparent nanoscale high aspect ratio metallic photonic structures fabricated via a combination of processes, including

soft lithography, oblique angle metal deposition, argon plasma ion etching. The optical and electrical properties of the structures are characterized and evaluated to determine their applicability as transparent electrodes. Different metals, including gold (Au) and silver (Ag), were studied. Furthermore, the optical properties in the infrared region are characterized for the high aspect ratio metal structures for heat control applications. Investigations in the interdigitated structures based on the high aspect ratio metal electrodes are ongoing to study the feasibility in smart window applications in light transmission modulations.

Organization and layout of the thesis

This thesis is divided into the following sections. Literature reviews on ITO transparent electrodes and recent achievements in finding the replacements for ITO with various fabrication techniques are presented. The concept of photonic crystals is also introduced in the subsequent section with emphasis on woodpile structures and their fabrication methods. A brief discussion on the research work in the layer-by-layer woodpile structures by soft lithography technique is also given and recent results are discussed. The focus of the thesis will be on the experimental approach in making a photonic structure based architecture using soft lithography, oblique angle metal deposition, and argon ion milling. The optical and electrical properties of the structures are characterized and the results are discussed in detail. Furthermore, scale-up process is explained for large area sample fabrication as a promising route for commercialization. The large area samples are also characterized. Finally, future plans on interdigitated structures and reducing the periodicity of the structure are briefly discussed.

CHAPTER 1. LITERATURE REVIEW ON TRANSPARENT ELECTRODES

1. Indium tin oxide (ITO)

ITO is widely used in the flat panel display industry and it can be found in liquid crystal displays (LCDs) in computer monitors, televisions, and touch screens. (Figure 1(a)) [16] In addition, ITO can be found in conventional silicon solar cells and emerging compound photovoltaics such as copper indium gallium selenide (CIGS) and cadmium telluride (CdTe). [17] Furthermore, the emergence and development in organic semiconducting materials have enabled novel solar devices such as organic solar cells and organic LEDs. [18,19] (Figure 1(b)) ITO is highly reflective for the thermal infrared (IR) radiation and is a key component in IR-reflecting coatings on windows in automotive and architectural applications, and it is used as conducting electrodes for smart window and smart display applications with transmission intensity modulations.



Figure 1: Use of ITO as transparent conducting electrodes in (a) high-definition LCD TV by Sony and (b) organic solar cell panels by Konarka [20]

Since the turn of this century, the search for clean energy, and the need for utilizing energy more efficiently have been primary topics for both industry and academic research. Such interests have spurred developments in organic solar cells (OSCs), organic light emitting diodes (OLEDs). [21, 22] The advancements in organic solar cells and OLEDs are largely processing advantages including lower production costs, and simple fabrication methods when compared to their inorganic counterparts. Furthermore, they

offer the possibility of device fabrication on flexible substrates over large areas, which could greatly improve their functionality. [23-26] (Figure 2)

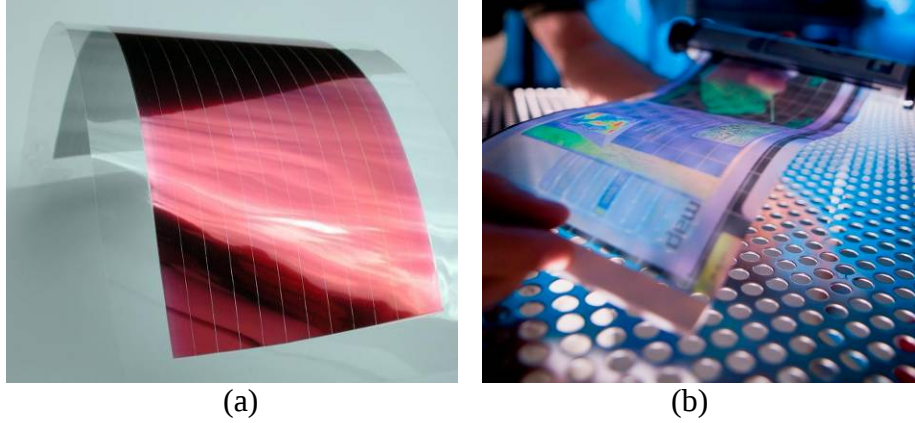


Figure 2: Examples of (a) flexible organic solar cells and (b) flexible displays [25,26]

Currently, most OSCs and OLEDs employ indium tin oxide (ITO) coated substrates as their anode electrodes at the front side of the devices because ITO offers relatively high transparency for visible light and low sheet resistance for electrical current conduction. However, the optical transmission of ITO decreases with increasing thickness (Figure 3(a)). [19] This means that thinner ITO is desirable to have sufficient optical transmission for visible light harvesting. On the other hand, the sheet resistance of ITO is higher if thinner ITO is used. (Figure 3(b)) Therefore, an optimal thickness of ITO needs to be chosen as compromise between the best optical and electrical properties.

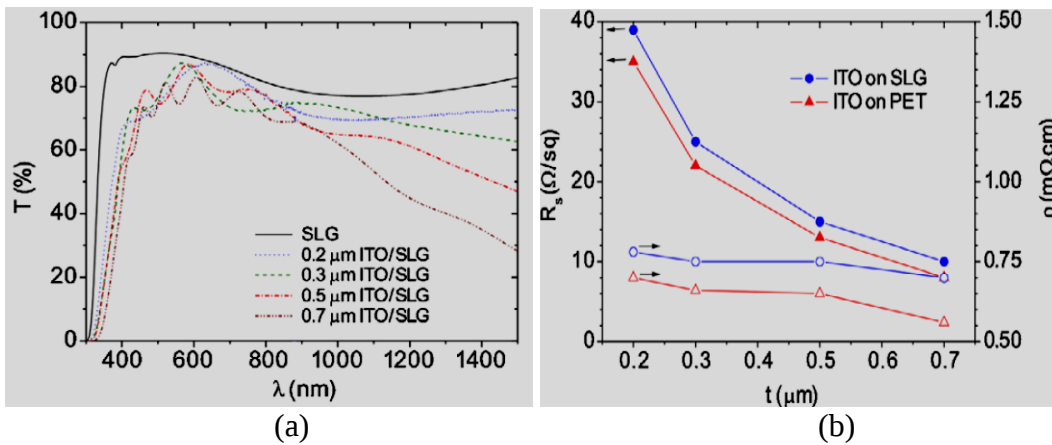


Figure 3: (a) The optical transmission of ITO on soda lime glass (SLG) with different thickness and (b) the sheet resistance and electrical resistivity of ITO on SLG and polyethylene terephthalate (PET) polymer films at different thickness [8]

Furthermore, ITO is very brittle [7] and has poor mechanical stability, in addition to indium's high cost as a limited resource. Figure 4 shows a 100nm thick ITO under different tensile loading along the horizontal direction. It shows that at 1.28% strain point defects start to form. At 1.43% strain, the point defects start to initiate line defects (Figure 4(c)). As the strain increases further to 3.42%, many line defects form on the ITO surface and this results in cracking and ultimately sample failure due to electrical path disruptions.

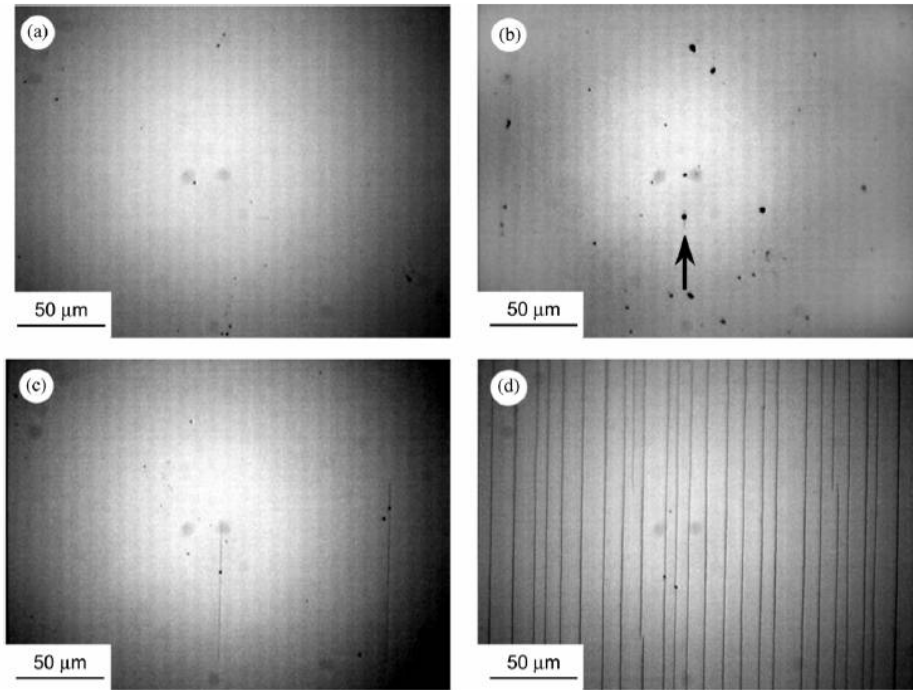


Figure 4: SEM images of ITO surface (a) without mechanical load, (b) with 1.28% strain, (c) with 1.42% strain, and (d) with 3.42% strain [7]

These disadvantages in ITO have motivated the search for conducting electrodes with the same or better optical and electrical properties, which could achieve equivalent or superior device performance. It is intuitive to consider metallic materials such as gold or copper as the replacements for the ITO electrodes since they possess outstanding electrical properties, i.e. very high electrical conductivities, which are crucial because they could enhance the performance of the transparent electrodes significantly. However, because of their extremely shallow skin depths, metallic materials are highly reflective in the visible spectrum regime, which will prevent visible lights transmission. Figure 5 shows the sheet resistance and optical transmission at 400nm wavelength of an ultrathin

gold film prepared by sputtering with different film thickness. [27] It shows that at a thickness thinner than 6nm, the gold film has a visible transmission already less than 20%. A thickness around 1nm would give a 70% transmission, but the sheet resistance would be increased significantly to $70\Omega/\square$.

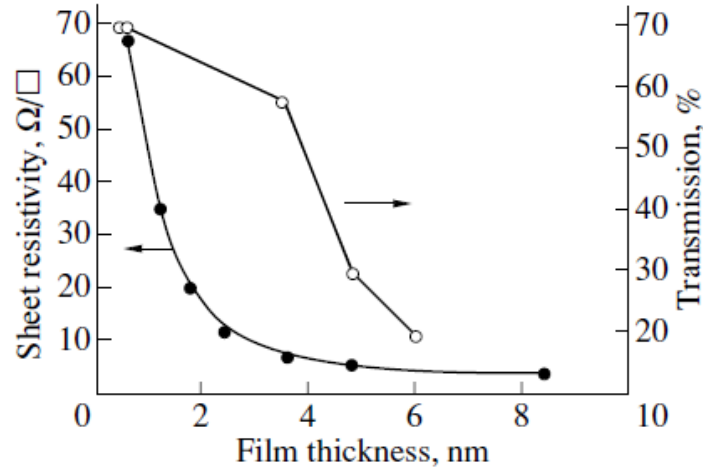


Figure 5: The sheet resistance and optical transmission of ultrathin gold films [27]

Therefore, many studies have been performed on various metallic structures that can permit high visible light transmission but also retain relatively high electrical conductivities. In recent investigations, carbon nanotube networks, random silver metal nanowire meshes and patterned metal nanowire grids (fabricated using nano-imprint lithography techniques) have been evaluated as potential replacements for ITO.

2. Graphene and carbon nanotube based transparent films as electrodes

i. Large area, continuous, few-layered graphene

Graphene has been extensively studied due to its unique electronic and mechanical properties. Graphene film is formed with a single-layer, atomic-thickness sheet with carbon atoms that are densely packed in a honeycomb crystal lattice. It possesses outstanding properties such as high conductivity, transparency, mechanical strength, and flexibility. [28] Graphene has been one of the more intriguing materials in recent research in different applications and many efforts are ongoing to utilize it as a better transparent

electrode (compared to ITO). [29, 30] Graphene films with multiple layers are also being investigated to improve their electrical properties.

One research group has reported a recent progress in the large area, few-layered graphene as anodes for organic photovoltaic devices. The graphene film was synthesized on a Ni film-coated SiO₂/Si wafer using chemical vapor deposition (CVD) process. [31] To transfer the graphene films, the Ni film was etched using FeCl₃ and HCl solution. A dry-transfer technique with a polydimethylsiloxane (PDMS) stamp was used to transfer the graphene film to another substrate. Graphene films with different thicknesses were fabricated. For 6–30 nm thick graphene films, the average sheet resistance varies from 1350 to 210Ω/□ with an optical transparency from 91% to 72% in the visible light wavelength range. (Figure 6(a))

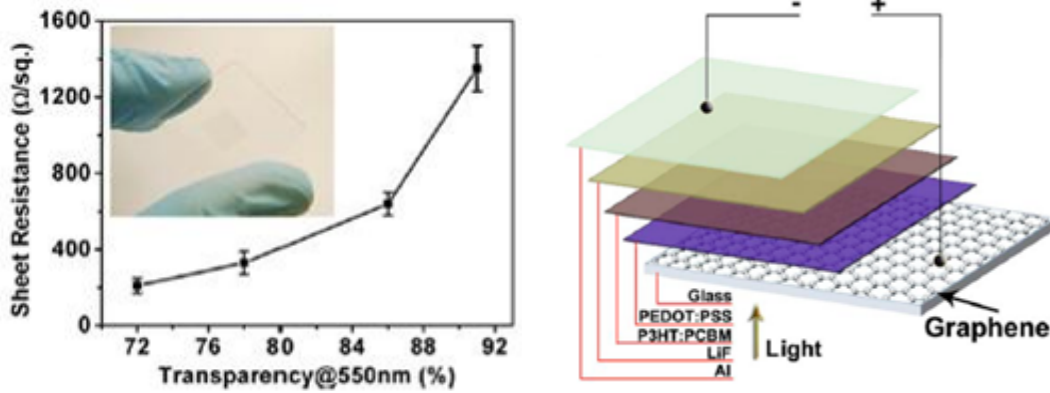


Figure 6: (a) Transmission and sheet resistance of the graphene films and (b) the schematic of the photovoltaic device based on the graphene film [31]

Figure 6(b) shows the schematic of the photovoltaic device structure based on the graphene films as transparent electrodes. Poly(3,4-ethylenedioxythiophene): (polystyrenesulfonate) (PEDOT:PSS) was spin coated on the films to improve the hole collection. Poly(3-hexyl) thiophene and phenyl-C₆₁-butyric acid methyl ester (P3HT:PCBM) blend with 160nm thickness was the active layer for light absorption. Lithium fluoride (LiF) and aluminum were thermally evaporated to form the cathode. The performance of the devices is listed in Table 1.

Table 1: Short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE) of various photovoltaic devices [31]

Cell devices	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
Pristine graphene	2.39	0.32	27	0.21
Graphene treated by UV	5.56	0.55	24.3	0.74
Graphene modified by PBASE	6.05	0.55	51.3	1.71
ITO	9.03	0.56	61.1	3.10

For photovoltaic cells based on pristine graphene films, the performance (PCE) is very low at only 0.21%. The poor performance was attributed to the hydrophobic property of graphene which makes uniform coating of PEDOT:PSS impossible. To improve the surface wettability, the graphene anode was modified by UV/ozone treatment. This increased the PCE to 0.74%. Although the cell efficiency was improved, the reduction in FF has a negative effect on the device results the decrease in FF reflects the increase in series resistance of the cell. This is due to the disruption of the aromatic bonding between the carbon atoms by the oxygen groups produced by the UV/ozone. Instead of UV/ozone, self-assembled pyrene buanoic acid succidymidyl ester (PBASE) was used to improve the wettability of the graphene film without disrupting the carbon covalent bonding in the graphene. The results show a much better efficiency at 1.71%. However, this is still inferior to ITO based photovoltaic devices. Nevertheless, the group has recently reported the layer-by-layer stacked graphene based device that has similar performance as the ITO. [32]

ii. Carbon nanotube networks

Carbon nanotubes are molecular-scale cylindrical structures of graphitic carbon. Most single-walled nanotubes (SWNT) have a diameter of close to 1nm, with a tube length that can be much longer. [33] The structure of a SWNT can be thought as wrapping a single layer of graphene into a seamless cylinder. The strength of the carbon-carbon bonds gives carbon nanotubes amazing mechanical properties. The electronic properties of carbon nanotubes are also extraordinary. [34] Especially notable is the fact that nanotubes can be metallic or semiconducting depending on their structure. [35] Many studies have been

done where carbon nanotubes were investigated as a potential replacement for ITO due to their superior electrical properties. [36]

Barnes' group recently reported a carbon nanotube network as transparent electrodes for organic solar cells without a hole transport layer. [37] The SWNT electrodes (inset of Figure 7(a)) were produced using an ultrasonic spray method that yields the extremely smooth film. First, aqueous SWNT dispersions were prepared using a high-molecular-weight polymeric derivative of cellulose (sodium carboxymethyl cellulose (CMC)). CMC has been previously reported as an excellent agent for dispersing SWNTs in water. [38] Use of ultrasonic spraying combined with the CMC-based dispersions, permits precise amounts of SWNTs to be uniformly dispensed over large areas. Samples were then soaked in nitric acid to remove the CMC and produce conducting films.

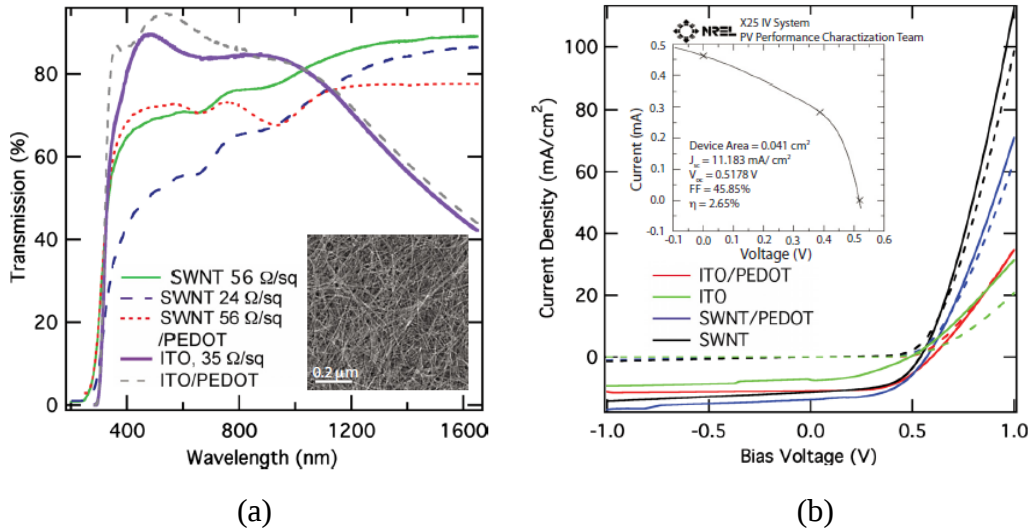


Figure 7: (a) Transmission spectra of ITO and SWCNT transparent electrodes with and without PEDOT:PSS and (b) their respective I-V characteristics [37]

Figure 7(a) shows the transmission spectra of different transparent electrodes. ITO with or without PEDOT:PSS layer still has superior optical transmission in the visible wavelength range. The 56 $\Omega/\square$ SWNT with or without PEDOT:PSS has about 70% in the same wavelength region. The organic photovoltaic devices were fabricated with P3HT:PCBM blend solutions as the active layer with or without the PEDOT:PSS as the hole transfer layer (HTL). Figure 7(b) inset shows the NREL-certified I-V curve for a device made on a 60 $\Omega/\square$ SWNT electrode without a HTL. This device has a power conversion efficiency of 2.65%. For an ITO-based device fabricated in the group without

the HTL, the efficiency was shown only at 1.44% for the same active layer thickness. This indicates SWNT electrode without PEDOT:PSS outperforms the ITO electrode. Figure 7(b) shows data not from NREL-certified device measurements, but were obtained on a well-characterized solar simulator with NREL calibrated reference diodes. It showed that, for a $24\Omega/\square$ SWNT electrode, the device efficiency could be as high as 3.37%, much better than ITO electrode without a HTL and similar to that of ITO with a HTL. Therefore, carbon nanotube network electrodes are promising for high efficiency organic photovoltaic devices.

3. Solution-processed metal nanowire mesh transparent electrodes

Peumans [11] recently reported the fabrication of silver (Ag) nanowire mesh as transparent electrodes for organic solar cells. The Ag nanowires were first synthesized by the reduction of Ag nitrate in the presence of poly(vinyl pyrrolidone) (PVP) in ethylene glycol by the Langmuir-Blodgett (LB) assembly technique [39], which can be used to assemble a large-area monolayer of anisotropic building blocks. The Ag nanowires are $8.7\mu\text{m}$ long and have a diameter of around 103nm. Then, a volume of the nanowire suspension is dropped on a glass substrate and agitated by a shaker. The resulting films are random meshes of Ag nanowires without significant bundling of wires that are uniform over the area of the substrate, as seen in Figure 8(a). After annealing at 200 °C for 20min to remove the PVP surfactant layer on the nanowires and to fuse the crossings between the meshed Ag nanowires, a sheet resistance of $100\Omega/\square$ was achieved. The nanowire meshes with higher nanowire aerial density could achieve a sheet resistance as low as $10\Omega/\text{sq}$, which is at the same order of ITO glass. However, as shown in Figure 8(b), as the nanowire density increases, the solar transmissivity decreases. This is because nanowire mesh blocks more light when there is more material on the substrate and smaller open spaces between the nanowires. Nevertheless, the author had achieved a high solar transmittance of 84-88% with the sheet resistance of about $10\text{-}22\Omega/\square$.

To evaluate the potential use of a metal nanowire mesh as transparent electrodes, small molecular weight organic solar cells were fabricated on the Ag nanowire meshes with a solar transmittance of 86% and a sheet resistance of $16\Omega/\square$. The Ag nanowire mesh was spin-coated with a layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)

(PEDOT:PSS). The presence of the transparent, conductive PEDOT:PSS layer was used to improve the holes collection efficiency.

An organic solar cell composed of 45nm of copper phthalocyanine (CuPc), 45nm of 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI)/10 nm of bathocuproine (BCP) was deposited by vacuum sublimation onto the Ag nanowires with 100nm Ag back electrode. However, when comparing the performance to the device with ITO as the transparent electrode (65mW/cm^2 , AM1.5 illumination), the Ag nanowire mesh device does not show any noticeable improvement. Though the short circuit current density (J_{SC}) is larger than the ITO based device, the open-circuit voltage (V_{OC}) is still lower, and the cell efficiency is inferior to that of ITO based device.

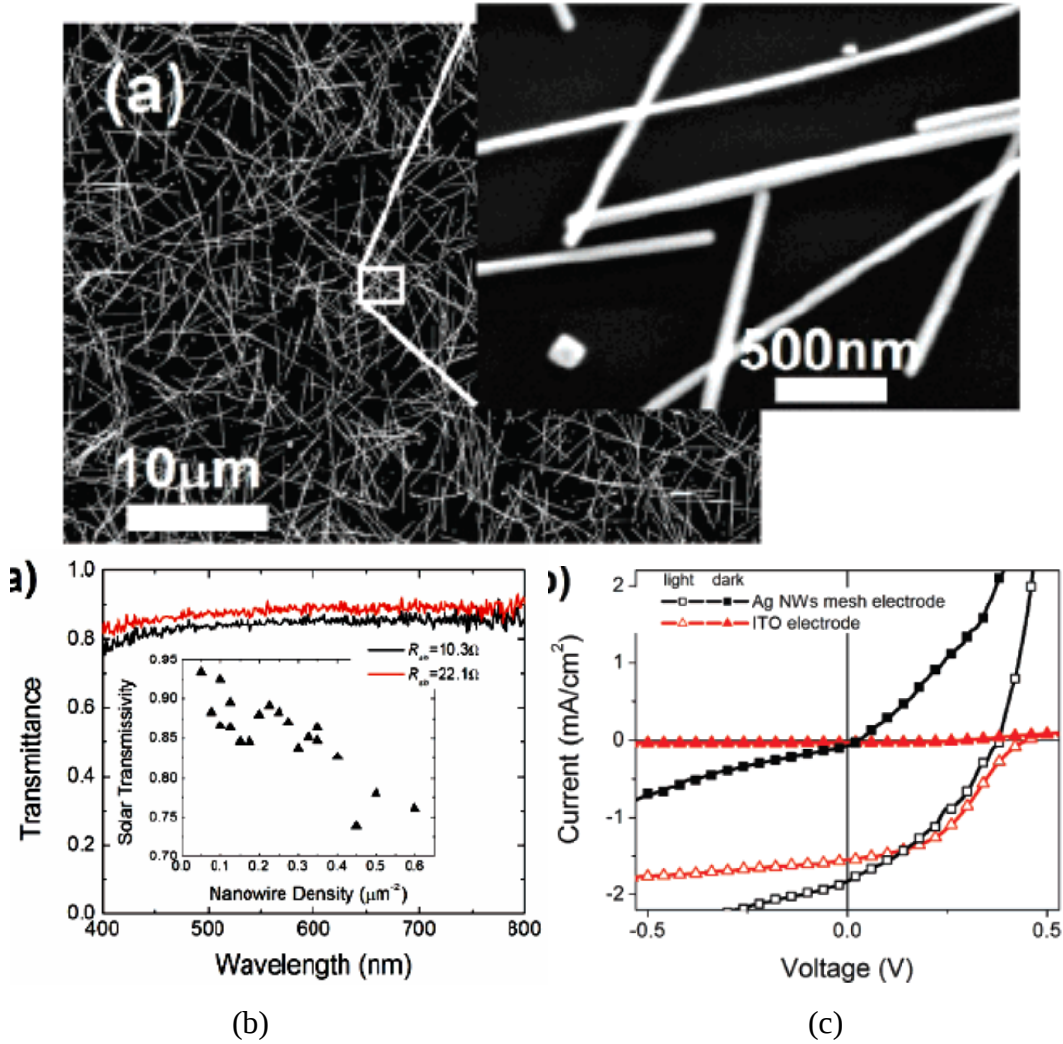


Figure 8: (a) SEM images of the Ag nanowire mesh, (b) its optical transmission and (c) solar cell device performance [11]

While the silver metal nanowire meshes have very good optical transparencies compared to ITO substrates, their electrical conductivities are equivalent to that the ITO substrates, but their solar cell device performances are still inferior to ITO based devices. Furthermore, they suffer from current shunting due to the random nature of nanowire networks. Therefore, patterned structures are investigated to eliminate such disadvantages.

4. Patterned silver grid structure for organic solar cells

Tvingstedt and Inganäs reported on a patterned silver structure as transparent electrodes and their use for organic solar cell devices. [40] They utilized a simple soft lithographic metal deposition method for the patterning of the silver grids. The fluidic channel patterns in an elastomeric polydimethylsiloxane (PDMS) mold are filled with an electroless silvering solution to generate Ag grids of widths down to 20 μm and heights of about 100nm, on both glass and plastic substrates. The electroless silvering solution mixture is prepared and added at the open ends of the PDMS channels. The capillary force and lower pressure at the other end of the channels provides the driving force for the silvering solution flow. Figure 9(a) shows the actual sample with 600 μm spacing, 40 μm silver bar width, and 100nm height. The resistance over a length of 8mm is 86 Ω for each individual line. The transmission of the structure is shown in Figure 9(b) with comparison to that of ITO. The structure has a similar transmission as ITO in the visible wavelength range, and it is higher in the near IR regime due to the large spacing between the silver lines and, therefore, lower absorption and reflection.

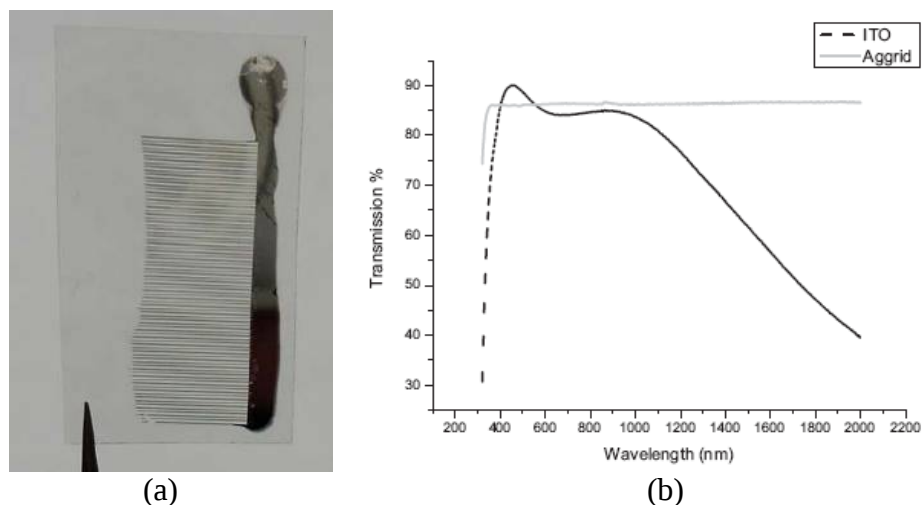


Figure 9: (a) Still image of the silver patterned electrode and (b) its transmission comparison with ITO [40]

A proof-of-principle organic solar cell device was fabricated based on the silver patterned electrode. The active bulk heterojunction layer in the organic photovoltaic cell here comprise a blend of a low bandgap polyfluorene (APFO-Green 5) as electron donor, and the methanofullerene [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) is utilized as the electron acceptor. PEDOT:PSS with diethylene glycol (DEG) was used to enhance the hole collection. And aluminum is evaporated on top as the counter electrode. (Figure 10)

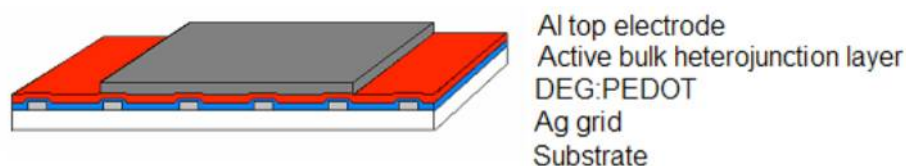


Figure 10: Schematic of the organic solar cell with the silver grid as anode [40]

Different devices were made to compare their performance and the results are list in Table 2. It shows that a PEDOT-based device without ITO or Ag grid has the lowest efficiency at around 0.63%. The device with ITO plus PEDOT has higher efficiency at 0.83%. With the Ag grid plus PEDOT as the anode, the efficiency is further increased to 1.00%. For the grid-based solar device, the FF is improved from 0.36 to 0.47. This is attributed to the significantly smaller series resistance in cells using the high conductive metal grids. The author also indicated better conductivity of the grid structure could be obtained with smaller periodicity of the pattern.

Table 2: Photovoltaic performance of cells with DEG:PEDOT anode with and without current collecting Ag grids compared to an ordinary ITO based device [40]

Cell exploiting:	J_{sc} [mA/cm ²]	V_{oc} [V]	FF	PCE [%]
PEDOTwithout grid	3.05	0.58	0.36	0.63
ITO with PEDOT	3.63	0.58	0.43	0.83
PEDOTwith Ag grid (W=40μm, S=600μm)	3.67	0.58	0.47	1.00

5. Nano-imprinted transparent metal electrodes in organic light-emitting diodes and organic solar cells

Jay Guo *et al.* [12-14] report on utilizing nano-imprinting lithography (NIL) technique for making transparent metal electrodes for organic devices. This NIL technique can produce metal electrodes with patterns of controlled metal thickness and line-width, which pose great advantages over random metallic nanowire meshes. The design for the patterned metal electrode is a 2D rectangular grid structure with two grating parts. One has a 700 nm period as the main part of the electrode, and the second one has a period of 10 μm, which is aligned orthogonally with respect to the 700nm period and is used to ensure the electrical continuity of the 700 nm period grating lines, because some lines are broken because of defects.

In order to obtain the desired metallic patterns, it is crucial to fabricate a NIL mold with narrow line-width grid patterns. To achieve this, two 1D grating SiO₂ molds are used to make the 2D grid mold by doing the NIL twice. One 1D grating mold has a periodicity of 700 nm with a depth of 500 nm and a duty cycle of 50%. The duty cycle is the ratio of the line-width to the periodicity of the grating. The second 1D grating mold has a periodicity of 10μm and a line-width of 850 nm. Buffered HF solution was used to etch both silica molds to reduce their line-widths to 70 nm and 400 nm, respectively, so the resultant 2D grid mold would have narrow line-widths for high optical transparency. After the buffered HF etching, the 10 μm 1D mold was first used to imprint a 140 nm thick nano-imprint resist spin-coated on a SiO₂ substrate. (Figure 11(a)) After demolding and anisotropic oxygen plasma etching to remove the residual resist from the imprinted

area, a 20 nm-thick chromium (Cr) was deposited as mask for the exposed SiO_2 area. After the resist lift-off in acetone, a 20 nm thick Cr grating was formed on the SiO_2 substrate with 10 μm periodicity and a 400 nm line-width. (Figure 11(b)) After this, another 140 nm thick nano imprint resist was deposited onto this SiO_2 substrate, which already contained the first very thin Cr grating, and another imprinting step was repeated on the resist with the 700 nm period, 70 nm line-width 1D mold, with the grating direction oriented orthogonally with respect to the first one. After another metallization and lift-off, the substrate has two 20 nm thin Cr gratings on top to form a rectangular grid pattern with 700 nm and 10 μm periodicities. Then, reactive ion etching (RIE) was performed to transfer the grid pattern from the 2D Cr mask on the SiO_2 substrate, also forming a 2D rectangular grid pattern (140 nm deep) after Cr removal. (Figure 11(c))

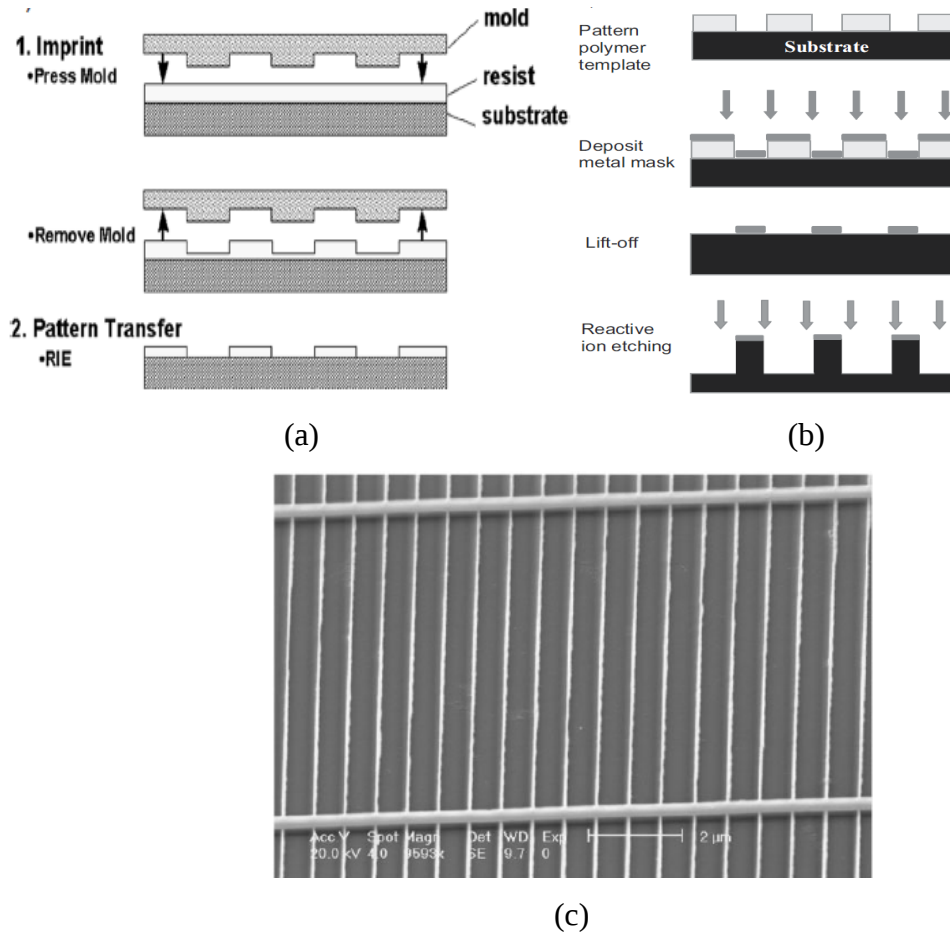
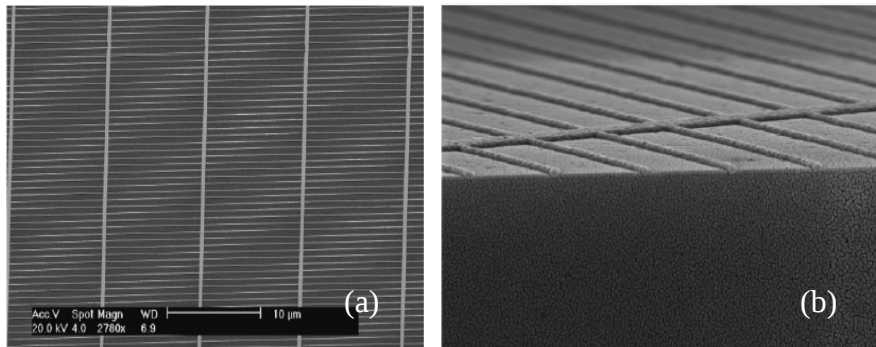


Figure 11: (a) NIL technique for resist patterning on substrate and (b) metallization of the patterned resist for pattern transfer in the substrate by using the metal mask, and (c) the SEM image of the 2D grid pattern on the SiO_2 substrate after the NIL applied twice [12]

After the 2D pattern on the SiO₂ substrate was fabricated, it was used as an imprint mold to make 2D metal patterns. The functionalities of these metal patterns were tested as metallic transparent electrodes. To do this, another NIL technique was performed on an imprint resist-coated glass substrate. This time, only one imprint step was needed since the 2D imprint mold was used and a 2D pattern would form onto the resist at once. After demolding and excess resist removal in the imprinted area, different metals were deposited onto the substrate at a thickness of 40nm. After lift-off of the resist, a smooth and homogeneous 2D metallic grid pattern was formed on the glass substrate with two periodicities, one is 700 nm with 70 nm line-width and another is 10 μ m with 400 nm line-width. (Figure 12(a)) Different metals such as Au, Cu, and Ag were used to fabricate the 2D patterns and the optical transmission of Au and Cu in the visible spectrum range (Figure 12(b)) is over 80%, and the average transmission of Ag is also about 78%. This is attributed to the narrow line-width (70nm) of the 700nm grating, while the 10 μ m period grating (400 nm wide) only served to ensure the electrical connections of the smaller grating without affecting its optical properties. A four-point probe method was used to measure the sheet resistances of these metal electrodes. It was found that the sheet resistance for Au, Cu, and Ag electrodes were 24 Ω /sq, 28 Ω /sq, and 23 Ω /sq, respectively, which are all higher than that of ITO (12 Ω /sq). This is due to the narrow line-width and small thickness of the metals (resulting in a small cross-sectional area). When the thickness of the Au electrode was increased from 40 nm to 80 nm, the sheet resistance was decreased from 24 Ω /sq to 8 Ω /sq. However, the average transmittance of Au electrode was reduced from 84% to 78%.



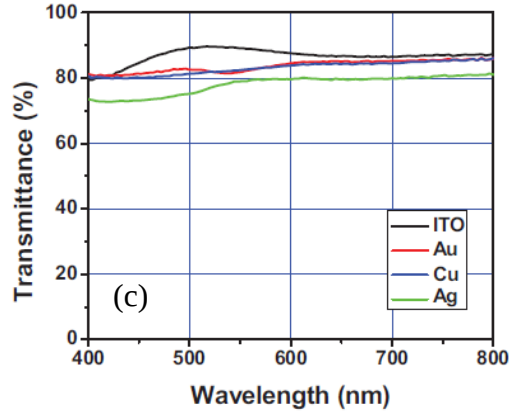


Figure 12: The SEM images of the 2D metallic grids from (a) topview and (b) sideview and (c) their optical transmittance in the visible spectrum. [13]

To demonstrate its feasibility, organic solar cells (OSCs) were fabricated using these metallic patterns as the front-side electrode. Firstly, an imprint resist was prepared using the 2D SiO_2 grid imprint mold by NIL, and a flexible composite PDMS stamp was made using the patterned resist as master. Then a 40 nm thick metal layer was deposited on the PDMS stamp, and the metal pattern on top of the PDMS was transferred to a PEDOT:PSS coated glass or PET substrate. (Figure 13(a)) Then, another conducting PEDOT:PSS layer, light absorbing P3HT:PCBM blend (1:1 wt/wt) (in N_2 purged glove box), and LiF/Al cathode were deposited onto the substrate to complete the organic solar cell device.

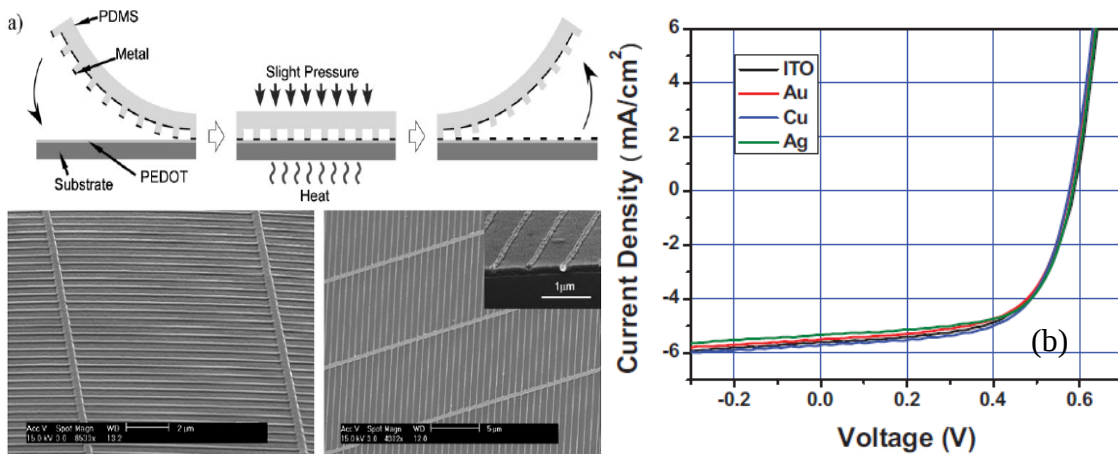


Figure 13: (a) Schematic of nano-imprinting of metals on PEDOT thin film with flexible PDMS stamp for solar cell fabrication and (b) its performance [13]

The fabricated solar cells had an area of approximately 0.1 cm^2 . Current versus voltage characteristics were measured in air by illuminating the OSC devices with AM 1.5G at $100 \text{ mW} \cdot \text{cm}^{-2}$ (Figure 13(b)) and were compared to a device fabricated with conventional ITO electrode, and the characteristic parameters for different electrode materials are listed in Table 3.

Table 3: Device characteristics of solar cells fabricated using nanopatterned Au, Cu, and Ag and conventional ITO electrodes [13]

Transparent Electrode	$J_{sc} [\text{mA} \cdot \text{cm}^{-2}]$	$V_{oc} [\text{V}]$	FF [%]	Efficiency [%]
ITO	5.59	0.59	0.61	2.00
Au	5.50	0.57	0.62	1.96
Cu	5.71	0.57	0.63	2.06
Ag	5.34	0.58	0.65	2.00

It was shown that the devices with metallic nanopatterned electrodes have similar characteristics as those with an ITO electrode, and the power conversion efficiencies are all at around 2%. It was worth noting that the device with the Cu electrode showed a slightly increased photocurrent and power conversion efficiency (2.06%) as compared to those with the Au or ITO electrodes. The optical transmission of Cu and Au are very similar, which led the authors to reason that it is because Cu (4.65 eV) has a lower work function than Au (5.22 eV). Therefore, Cu has better hole collection efficiency between the electrode and PEDOT:PSS layer. Thus, it is expected that improvements in device performance through efficient hole collection by using metals with lower work functions than PEDOT:PSS.

The patterned metal grids show good visible transparency, which was achieved by choosing small line-widths and thickness for the patterned metals. Though their sheet resistance is on the same order as the ITO substrates, it is still significantly higher than that of bulk metals. However, it is desirable to obtain the electrical conductivity of patterned metallic structure close to that of bulk metals, thus resulting in better device performance. This has motivated a new area of investigation in improving the optical and electrical properties in patterned metallic structures and hence improving organic solar cell device performances. Furthermore, the nano-imprint lithography (NIL) technique at

present is still costly compared to other standard nano-patterning fabrication techniques. For economic viability, it is crucial to find new ways to utilize commonly available processing methods in order to reduce the cost for mass production.

CHAPTER 2. CONTROLLING THE LIGHT WITH PHOTONIC CRYSTAL STRUCTURES

1. Photonic crystals in nature

Although the concept of synthetic photonic crystal was introduced not too long ago, its existence has long been evident in nature. [41, 42] The wings of a butterfly consist of small scales, which have microscale periodic patterns. (Figure 14(a)) These patterns can selectively reflect certain wavelength of the visible light and a structural color is seen in the butterfly wings. Another example is the Australian opal gemstone. In opal, spherical silica beads with nanoscale sizes are arranged in a periodic fashion. Visible light is diffracted and reflected from the surface of opal, and distinct colors can be observed. (Figure 14(b))

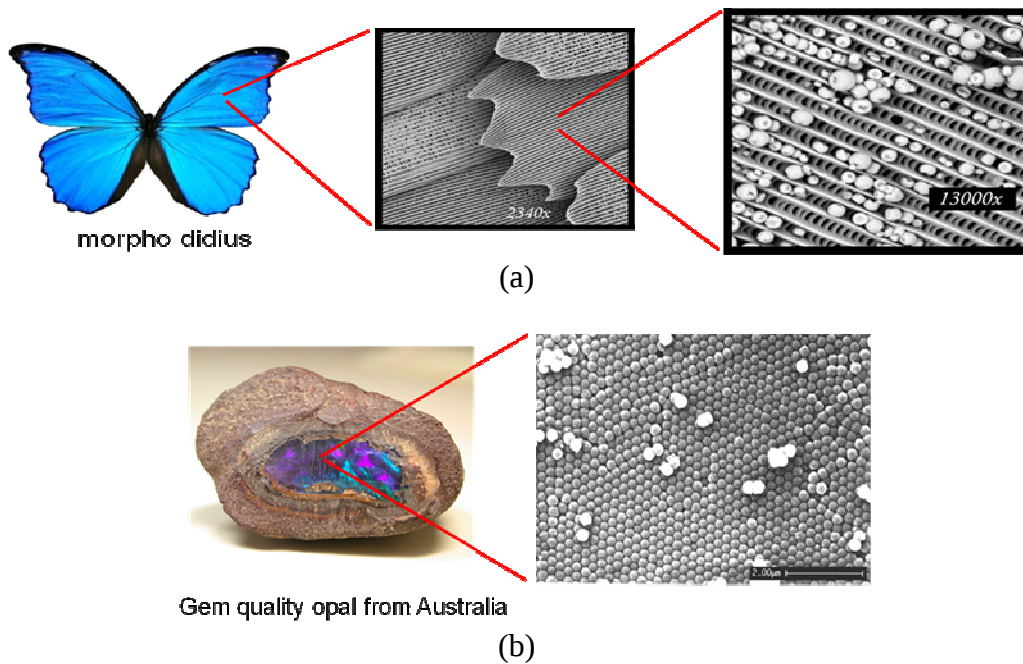


Figure 14: (a) Periodic patterns in the scales of the butterfly wings, and (b) periodically arranged SiO_2 spheres in an opal gemstone. [41,42]

2. Definition of photonic (bandgap) crystals

Since the concept of photonic band-gap (PBG) crystals, or photonic crystals, was introduced by Eli Yablonovitch over two decades ago, significant progress in understanding and fabrication has been made by many theorists and experimentalists [43].

Unlike naturally existing crystals, PBG crystals are synthetically fabricated periodic structures that manipulate electromagnetic (EM) waves. Within these designed media, though the majority of the EM waves are able to propagate freely, there are EM waves of a certain frequency range that cannot propagate in one or all directions depending on the configuration and dimensionality of the structure. Therefore, PBG crystals can be categorized into three groups with respect to the dimensionalities of the crystals.

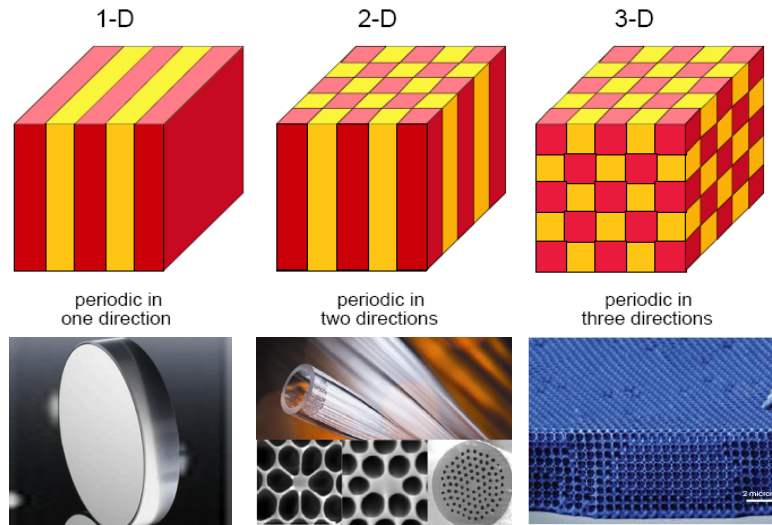


Figure 15: Schematics of one, two, and three dimensional photonic crystals [44]

One-dimensional (1D) PBG crystals are the simplest photonic crystals. In general, a 1D photonic crystal is in the form of a multilayer film made of alternating layers of two materials with different dielectric constants (or indices of refraction) so that the structure is only periodic in one direction. (Figure 15) They are usually known as a Bragg mirrors or multilayer reflectors. [44] The propagation of EM waves in a one-dimensional periodic structure was first studied by Lord Rayleigh in 1887 and the optical properties of multilayer films have been widely studied and utilized for decades, but it was not until recently that they are regarded as a sub-category of photonic crystals. The most used 1D

photonic crystal structure is the dielectric mirrors. A dielectric mirror is a type of a mirror composed of multiple thin layers of dielectric material, typically deposited on a substrate of glass or some other optical material. By careful choice of the type and thickness of the dielectric layers, an optical coating with specified reflectivity at different wavelengths of light can be designed. Dielectric mirrors are also used to produce ultra-high reflectivity mirrors of 99.999% or better over a narrow range of wavelengths.

A 2D photonic crystal is constructed so that it is periodic in two directions and homogenous in the third. Therefore, band gaps can exist for the plane that contains the periodicity. Introducing defects into 2D photonic crystals has also been investigated. Strong confinement and control of photons is possible by utilizing these 2D photonic structures, and they have found applications in waveguiding in the optical domain as photonic crystal fibers with performance superior to ordinary optical fibers. Photonic-crystal fibers (PCF) are a new class of optical fiber based on the properties of photonic crystals. Because of its ability to confine light in hollow cores or with confinement characteristics not possible in conventional optical fiber, PCFs are now finding applications in fiber-optic communications, fiber lasers, nonlinear devices, high-power transmission, highly sensitive gas sensors, and other areas. [45]

Three dimensional (3D) photonic crystals have full photonic band gaps in all three directions in space. The parameters that influence the band gap structure, thus the optical properties of a 3D photonic crystal, are the symmetry of the structure, the dielectric constant contrast, the filling ratio, the structural topology, and the shape of the scattering centers. In order to have a complete band gap, the Brillouin Zone (BZ) in reciprocal space should be constructed to be as close as possible to the shape of a sphere to allow frequency overlapping in all directions in space. [46] The first-order BZ of a face-centered cubic (FCC) structure has the closest resemblance to a sphere. If the requirements of parameters above are fulfilled, such as a high enough dielectric contrast ($\epsilon_1/\epsilon_2 \geq 2$), a full photonic band gap can exist in the band structure. A typical first-order BZ of a FCC structure and its band structure is illustrated in Figure 16.

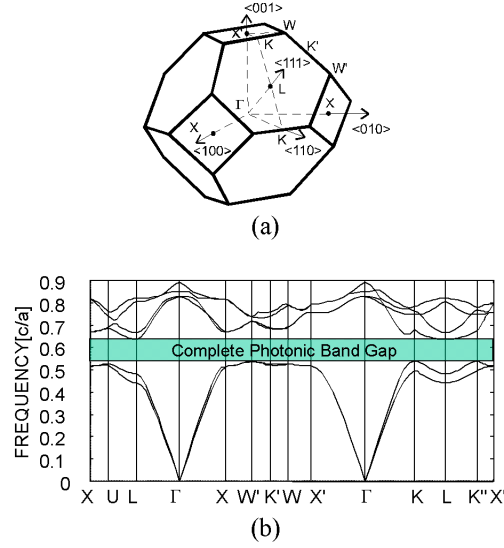


Figure 16: (a) First-order BZ of a FCC structure and (b) its corresponding band structure, most applications will require at least a 10% gap/mid-gap ratio [47]

The first periodic dielectric structure to possess a full 3-D photonic band gap was the diamond structure with the tetrahedral symmetry and was theoretically discovered by Ho *et al.* in Iowa State University. [48] However, the diamond structure is not easy to fabricate experimentally, especially at the micron and submicron length scales for infrared and optical applications. Modified forms of the diamond structure were developed in order to facilitate the fabrication of 3D photonic crystals. The first successfully experimentally fabricated 3D photonic crystal was constructed by Yablonovitch *et al.* in 1991 and was given the name Yablonovite. (Figure 17) [49]

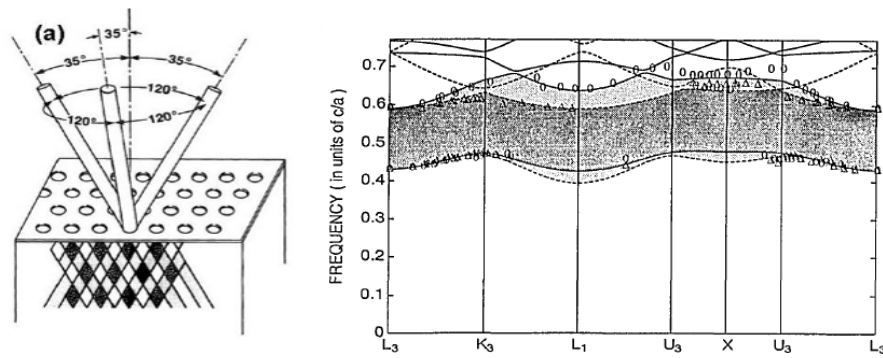


Figure 17: Schematic of the Yablonovite 3-D PBG crystal construction. A slab of dielectric material is covered by a mask containing a triangular array of holes. Each hole is drilled through three times at a 35.26° angle away from normal and spread out at 120° on the azimuth with respect to each other. The resulting structure below the slab is a fully 3-D periodic FCC structure with the band gap in microwave region. The removed volume fraction is 78%. [49]

3. Layer-by-layer 3D PBG structures

A layer-by-layer (LBL) structure, which is also named the woodpile structure, that could exhibit a full 3D photonic band gap was first proposed by Ho *et al.* [50] In designing the LBL structure, layers of dielectric rods are stacked in a sequence such that every four layers repeats with a distance, c . Within each layer, the rods are parallel to each other and separated by a periodic distance, a . The adjacent layers are arranged so that they are oriented 90° to the first layer and the subsequent layers are shifted by half period ($0.5a$) in the direction perpendicular to the rod axes. A schematic of the woodpile structure with rectangular cross-sections is shown in Figure 18. Furthermore, changing the rods to circular or elliptical cross-sectional shapes does not critically affect the performance of the crystals even if the aspect ratio is changed. Thus, it was concluded that the photonic band gap is insensitive to such structural details. It was also pointed out that for $c/a = \sqrt{2}$, the structure can be considered as an FCC structure with a basis of two rods; otherwise the symmetry is face-centered-tetragonal (FCT). However, Ho *et al.* state that the c/a ratio can be varied but an optimized full band gap can still result with a relatively high gap/mid-gap ratio, provided that the dielectric contrast of the material to that of air is greater than 1.9 and the filling ratio of the solid material in the structure is at its optimum. [50]

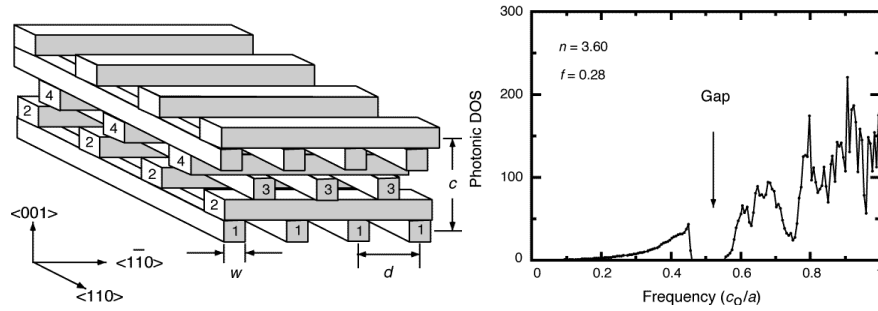


Figure 18: Woodpile LBL photonic crystal structure and its photonic DOS diagram [51]

The first woodpile structure was built by Ozbay in the microwave range by stacking alumina cylindrical rods (refractive index = 3.1) and in far-infrared range by silicon micromachining on (110)-oriented silicon wafers. (Figure 19) Transmission

characteristics of these crystals showed a good agreement with the calculated theoretical predictions. [52]

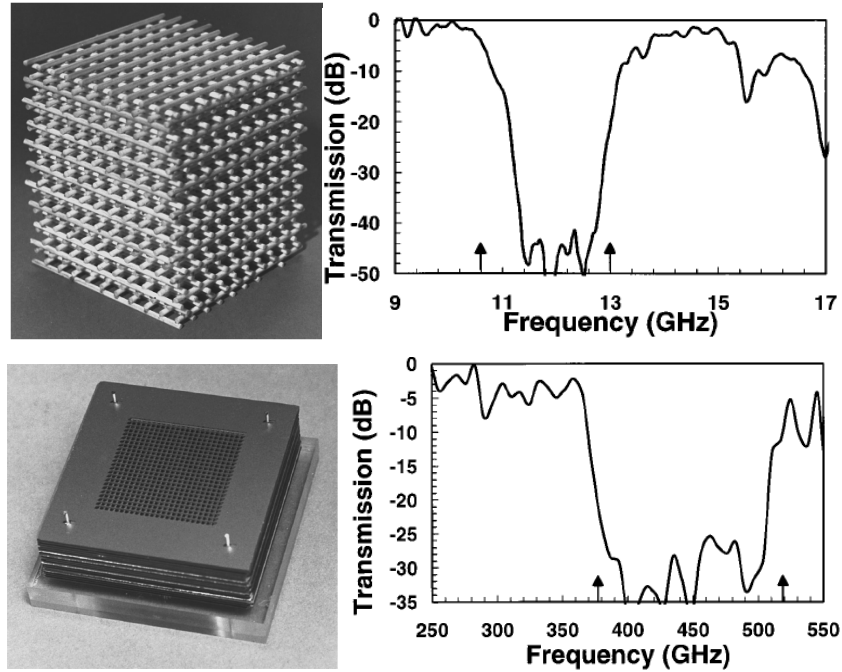


Figure 19: First woodpile photonic crystal structures and their transmissions in GHz range [52]

Lin *et al.* later utilized microelectronics fabrication techniques to build infrared-range-wavelength LBL photonic crystals, which are made of polycrystalline silicon (refractive index = 3.6). (Figure 20(a), (b)) [53] It was found that when the EM waves propagate along the stacking direction, the Fourier-transform infrared (FTIR) transmission spectrum shows a strong dip in 10-14 μm , indicating the existence of the 3D photonic band gap in this range, and the dip becomes more evident as the number of layers is increased from 2 to 5. (Figure 20(c)) The gap/mid-gap ratio of 40% is large. With such a large 3D bandgap, detailed manipulation of photonic defect states is plausible for many practical applications.

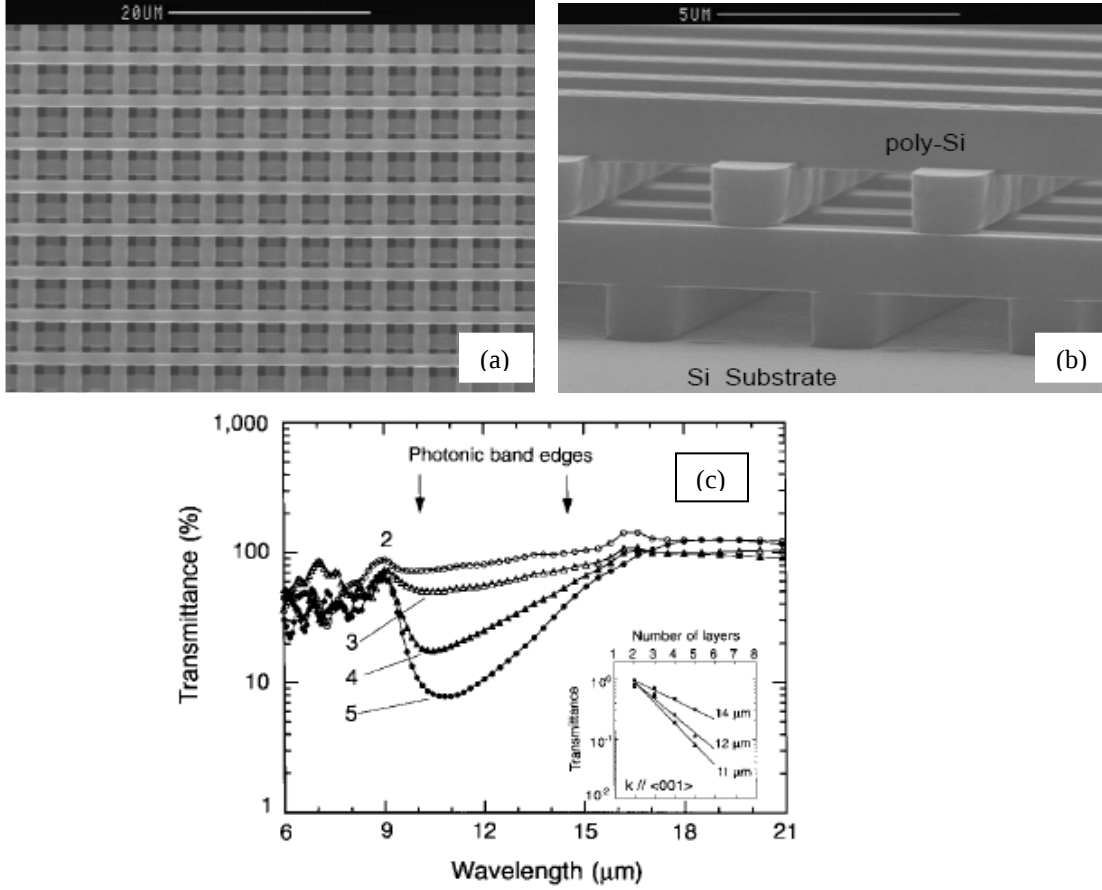


Figure 20: SEM micrographs of the poly-Si photonic crystal (a) viewed along the stacking direction (b) and viewed from cross-section, the spacing between adjacent rods is $4.2\mu\text{m}$, rod width is $1.2\mu\text{m}$, and the layer thickness is $1.6\mu\text{m}$, (c) the transmission spectrum is also shown for light propagating along the stacking direction. [53]

Lin *et al.* [54] also reported on a three-dimensional tungsten woodpile photonic crystal, which experimentally shows IR radiation enhancement at the near-infrared (NIR) range. The 3D tungsten photonic crystal is fabricated using a modified silicon semiconductor fabrication process. A layer of silicon dioxide is first deposited and patterned on a silicon wafer. Then a 500nm thick tungsten film is deposited onto the silicon dioxide pattern to fill the channels. The overlayer metal was then removed by a chemical mechanical polishing process. Another layer of silicon dioxide is deposited and patterned on the first polished layer. The process is repeated several times to produce consecutive tungsten gratings with the adjacent layers aligned perpendicularly to each other. At the end of the process, the silicon dioxide is chemically etched, resulting in a free-standing thin film

photonic crystal structure. (Figure 21(a)) The periodicity of the structure is $1.5\mu\text{m}$, and the tungsten rod width and height are $0.5\mu\text{m}$ and $0.75\mu\text{m}$, respectively.

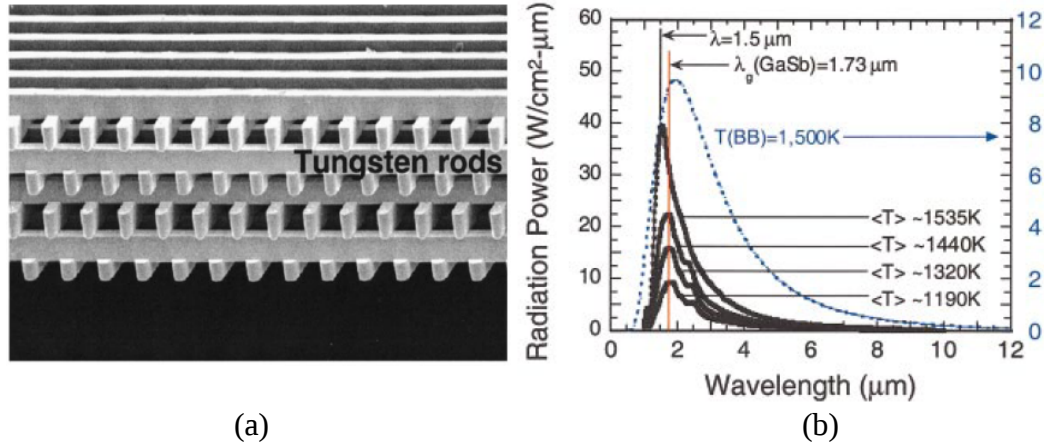


Figure 21: (a) SEM image of a 3D tungsten woodpile photonic crystal and (b) its emission spectra when electrically heated to different temperatures [54]

The 3D tungsten woodpile structure is biased by applying a voltage across the sample area and is heated via joule heating. The emission spectrum (Figure 21(b)) measured by an FTIR spectrometer shows the radiation power of the sample at different temperatures. The blue curve is the radiation power of a blackbody at 1500 Kelvin (K). As the temperature of the sample increases, the radiation power also increases at the main peak region, which is located at around $1.5\mu\text{m}$ wavelength, which is at the bandgap energy of GaSb of $1.73\mu\text{m}$, while the radiation beyond $3\mu\text{m}$ wavelength is significantly suppressed. The radiation peak also becomes narrower and slightly shifted to smaller wavelength when the temperature is increased.

4. Layer-by-layer fabrication of polymeric molds by soft lithographical techniques

i. Conventional soft lithography

Soft lithography was first introduced by Xia and Whitesides as a non-photolithographic method of micro- and nanofabrication. [55] In this technique, a

patterned elastomeric stamp, which can be made of poly(dimethylsiloxane) (PDMS), is first prepared by cast molding, in which a prepolymer of the elastomer is poured over a master having a relief structure. After thermally curing, the rigid PDMS mold is peeled off and ready for further use. The master can be fabricated by ultra-violet (UV) photolithography with a photoresist structure patterned on a solid support such as silicon a wafer. Therefore, the pattern on the PDMS stamp has the negative profile and topography of the master.

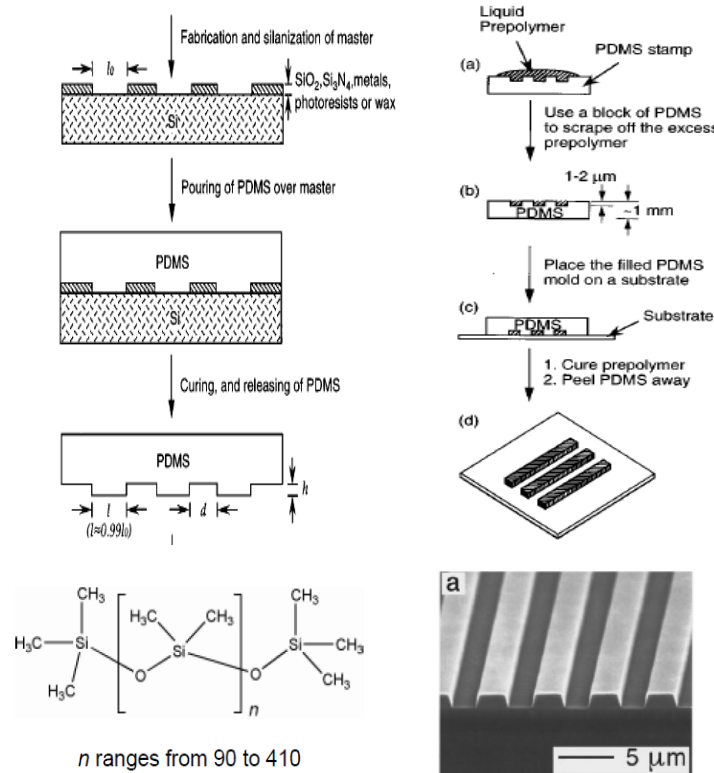


Figure 22: Procedure of making the PDMS stamp and the steps of microtransfer molding (μTM) technique [55]

In the microtransfer molding (μTM) technique of soft lithography, a thin layer of liquid prepolymer (organic polymers or sol-gel precursors) is applied to fill the patterned surface area (usually in micro-scale) of a PDMS mold. The excess prepolymer is removed from the top of mold. The PDMS mold, filled with prepolymer in the patterned area, is placed in contact with a substrate and then converted to solid by UV-curing or thermal curing. When the PDMS mold is carefully peeled off the substrate, a patterned structure remains.

ii. Two-polymer microtransfer molding (2P- μ TM)

For the purpose of making LBL polymeric structures, the photoresist structure on the solid support of the master is a series of parallel bars, and the resultant PDMS stamp is patterned in the form of parallel troughs. By using the μ TM technique, a one-layer parallel polymeric bar structure in micro-scale is formed. In order to make 3D layer-by-layer structures, Jae-Hwang Lee *et al* from Iowa State University (ISU) demonstrated an improved microtransfer molding method called two-polymer microtransfer molding (2P- μ TM) by which precise LBL polymeric structures can be made. [56] In 2P- μ TM, two prepolymers are used, one as the filler in the PDMS troughs, and the other as the adhesive to enhance bonding between the first layer and the substrate and also between adjacent layers. The filler is UV-curable polyurethane (PU) and the adhesive is polymethacrylate (PA). A wet-and-drag (WAD) infilling method is used to apply both prepolymers. After UV curing of the prepolymers, a single-layer PU parallel bar structure is formed with a thin layer of PA on top of each PU bar. The dimensions of the bars are 1.4 μ m in width and 1.1 μ m in height. A two-layer woodpile PU structure can be made by simply stacking the second layer on to the first one with the bar direction arranged so they are 90° to each other. (Figure 23) LBL structures with higher number of layers can be fabricated using the same process. The 2P- μ TM technique is residue-free and has a higher transfer yield for each layer than the conventional μ TM technique. A 12-layered PU mold was successfully built using this technique. (Figure 24)

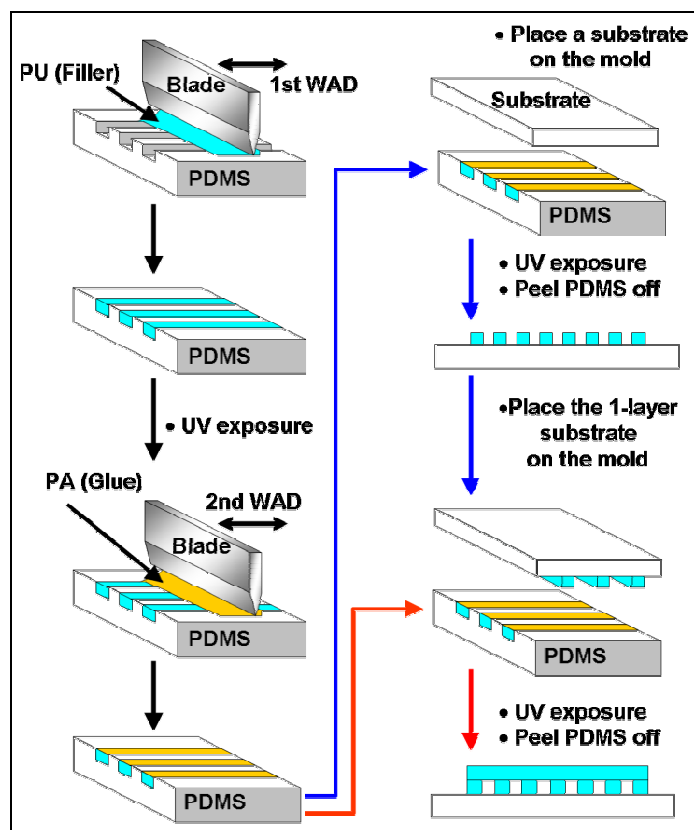


Figure 23: Schematic of the two-polymer microtransfer molding process [56]

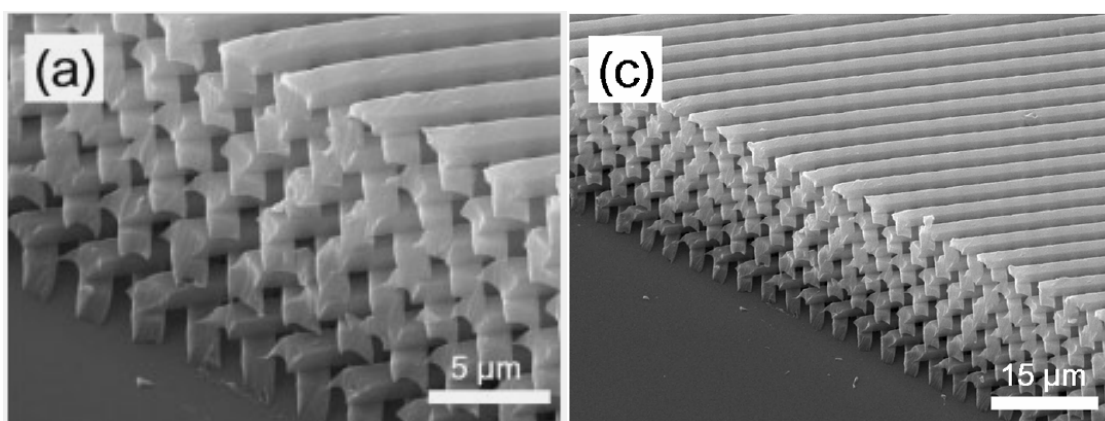


Figure 24: SEM image of a 12-layer LBL PU mold built by 2-P μ TM technique [56]

5. *Soft-lithographical fabrication of titania woodpile photonic crystals*

The multilayer woodpile PU structure demonstrates a simple and economical fabrication process of 3D microscale patterning. However, PU has a refractive index similar to glass at around 1.5. This indicates low dielectric contrast to show the photonic bandgap effect. Nevertheless, the PU mold provides a high quality template for further fabrication to make 3D structures of materials with high dielectric constant to illustrate the photonic bandgap effect. The photonic systems group in ISU also has successfully used the PU mold as template to fabricate ceramic 3D woodpile structures with a relatively high refractive index material. [57] Titanium dioxide (TiO_2) with optical wavelength refractive index of around 2.3 was used to form the 3D woodpile structure using the PU mold as template. In order to successfully transport the ceramic titania material into the micro-sized polymeric mold, titania slurry was prepared by mixing nanosized titania particles in aqueous solution. The infiltration of the slurry was done by the vacuum-assisted pressure-driven microfluidic flow. The as-received titania nanoparticles (NanoTek® Titanium Dioxide, Nanophase Technologies Corp.) had nearly-spherical shape and an average size of 34 nm. The particles contain both anatase and rutile phases with the majority phase being anatase. The concentration of the slurry was 20%wt. of solid particles in DI (de-ionized) water. After the slurry was prepared, it was agitated in an ultrasonic bath for at least 1 hour to disperse the nanoparticles in the aqueous solution.

The slurry was extracted with a needle syringe, and the needle was then removed and replaced with a 0.22 μm syringe filter before placing solution droplets on the PU mold. After placing ~ 5 drops of the titania slurry on the PU mold, the mold was totally submerged in the slurry and was put into a vacuum chamber. Then, a vacuum was applied to extract air trapped within the mold structure allowing the slurry to be drawn in. After this step, more titania was spin-coated onto the PU mold until homogenous ceramic surface was achieved. After infiltration, the sample was dried in air for one day. The final stage was to transfer the structure to another substrate to expose the portion of the structure in contact with the original substrate. A silicon substrate of a comparable size to the PU mold structure was placed on the dried sample using an adhesive (PU). The sample was then placed in a point-contact mounting stage and put into a low intensity UV

chamber to cure the liquid PU for 3 hours to form the second backplane. After curing, the sample was placed in an isopropanol solution to dissolve the photoresist, and glass substrate was carefully removed from the sample, leaving the sample on the silicon substrate. The whole procedures are illustrated in Figure 25.

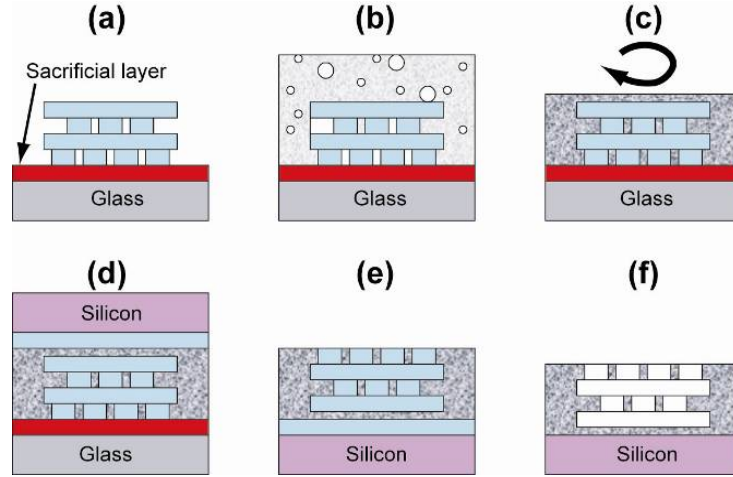


Figure 25: Schematic illustration of the titania woodpile structure fabrication procedure. (a) Template fabrication on a sacrificial-layer-coated glass plate; (b) Vacuum-assisted wetting of titania slurry; (c) Multiple spin-coating and drying; (d) Silicon wafer bonding with a photo-curable prepolymer; (e) Separation of glass plate by dissolving the sacrificial layer; (f) Firing [57]

Our group fabricate woodpile structures having two to twelve layers, where 4-, 8- and 12-layer structures are semi-crystalline. A 12-layer sample is shown in Figure 26 as an example of the results of infiltration. The structure has a total thickness of over $14\mu\text{m}$ and is $3.5 \times 3.5\text{mm}^2$ in lateral dimensions. Each rectangular rod is $0.9\mu\text{m}$ wide and $1.0\mu\text{m}$ high and the center-to-center spacing is $2.5\mu\text{m}$, which corresponding to a filling ratio of 36%. A low-magnification SEM image (tilt angle of 60° to the surface normal) shows a well-defined large-area structure (Figure 26(a)). In a closer view (Figure 26(b)), all 12 layers are clearly visible with an underlying layer, (which was once the over-layer). The quality of the resulting structure is very high and edges of each bar are sharp.

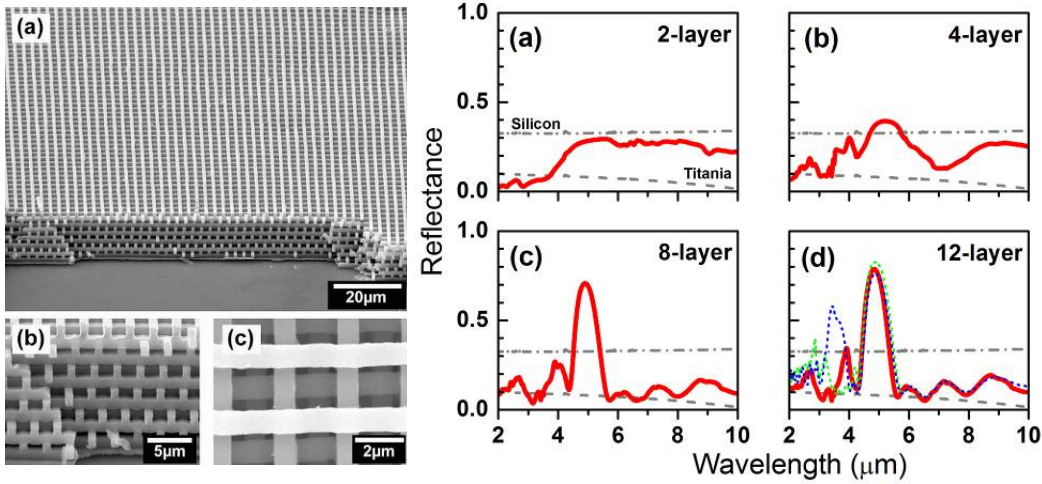


Figure 26: SEM micrographs of a 12-layer titania woodpile structure and the reflectance spectra of 2-layer, 4-layer, 8-layer, and 12-layer samples with comparison to silicon and titania [57]

The reflectance spectra of titania woodpile structures on silicon wafers having different numbers of layers are measured by a Fourier-transform spectrometer with a microscope (Bruker Hyperion 1000) with a sampling area of approximately $100 \times 100 \mu\text{m}^2$. In Figure 26, the reflectance spectra are shown with the reflectance spectra of a bare silicon substrate and a bare titania plate from the same slurry. For a 2-layer structure, the reflectance spectrum shows no distinctive peak and follows that of silicon in the longer wavelength region. The reflectivity is slightly lower as the 2-layer sample scatters light rather than reflects coherently due to its incomplete half unit-cell. We also see an absorption feature of titania in that region. The reflectance at wavelengths shorter than $4.5 \mu\text{m}$ drops considerably because of diffraction from the PC structure and additional scattering from structural roughness. However, for 4-, 8- and 12-layer structures, the reflectance at the main bandgap around $5 \mu\text{m}$ consistently increases as a function of the number of layers over that of silicon in contrast to other peaks. For thicker samples, the baseline of reflectance is closer to bare titania rather than to bare silicon because optical effects from the silicon substrate are shielded by the multiple layers. The peak reflectance of the 12-layer sample is about 0.8, which is almost 10-fold higher than that of titania film at the same wavelength. The theoretical reflectance spectra of the 12-layer structure were calculated. The calculated reflectance spectra are in very good agreement with the measured spectrum in the frequency region of the main band gap and at longer wavelengths. The discrepancy between the calculation and the experiment is obvious at

shorter wavelengths because the optical effects from diffraction and alignment are considerable. It is worth emphasizing that the semi-crystalline woodpile structures with only 90°-alignment could be very advantageous for applications utilizing its main PBG because its optical functionality is comparable to that of a perfectly aligned crystal. [57]

6. Woodpile structures with 1 μ m periodicity

Further experiments were carried out to examine the feasibility of the 2P- μ TM technique for the fabrication of layer-by-layer structures with smaller feature sizes. Firstly, a silica master with parallel grating bars was used to prepare PDMS molds. The grating bar dimensions are 400nm x 400nm x 4mm (width x height x length) with a line-to-line spacing (periodicity) of 1 μ m. The patterned area was 4mm x 4mm, which contains 4000 grating bars. The PDMS molds are prepared in the same manner as the 2.5 μ m pitch masters. However, due to the elastomeric nature of the soft PDMS molds, the features of the molds with 1 μ m periodicity or less sometimes deform and distort, and channel collapse may result after peeling off the PDMS from the master and leaving it in air for even only a few hours. This could ultimately reduce the final transfer yield greatly for the polyurethane patterns during the 2P- μ TM. To avoid such process complications, the PDMS molds are used for the 2P- μ TM immediately after they are freshly peeled off of the grating master, when the PDMS features are still intact. During the 2P- μ TM, it was found that PU is over-cured after 4min high UV exposure. This is due to the reduction of the feature size of the PU bars in the PDMS molds. The smaller dimensions of each PU bar in the PDMS channel require that the amount of PU material is much less than that of 2.5 μ m period samples. Therefore, the high UV exposure time needed to partially cure the PU before placing the adhesive must be reduced to avoid over-curing of the PU, which would reduce the PU transfer yield significantly. The optimal time for the high UV exposure was found to be 65 seconds instead of 4 minutes. Furthermore, it was also found that at 1 μ m feature size, pure PA did not provide sufficient adhesion for the PU to transfer from the PDMS channels onto a substrate. To improve the transfer yield, a mixture of PU and PA prepolymers was used. The adherence of PU is greater than PA, but it is also much more viscous making it difficult to form a thin glue layer on the orders of nanometers between the PU bar and the substrate. Therefore, mixtures of PU and PA

were chosen so that it has sufficient adhesion and relatively low viscosity. The optimal mixture ratio of PU to PA is 3:7. The PU+PA mixture was thoroughly mixed by ultrasonication for at least one hour before use. The SEM images (Figure 27) show that with the improved parameters, 1 μ m period woodpile PU structures can be made with high yield of 4mm x 4mm area.

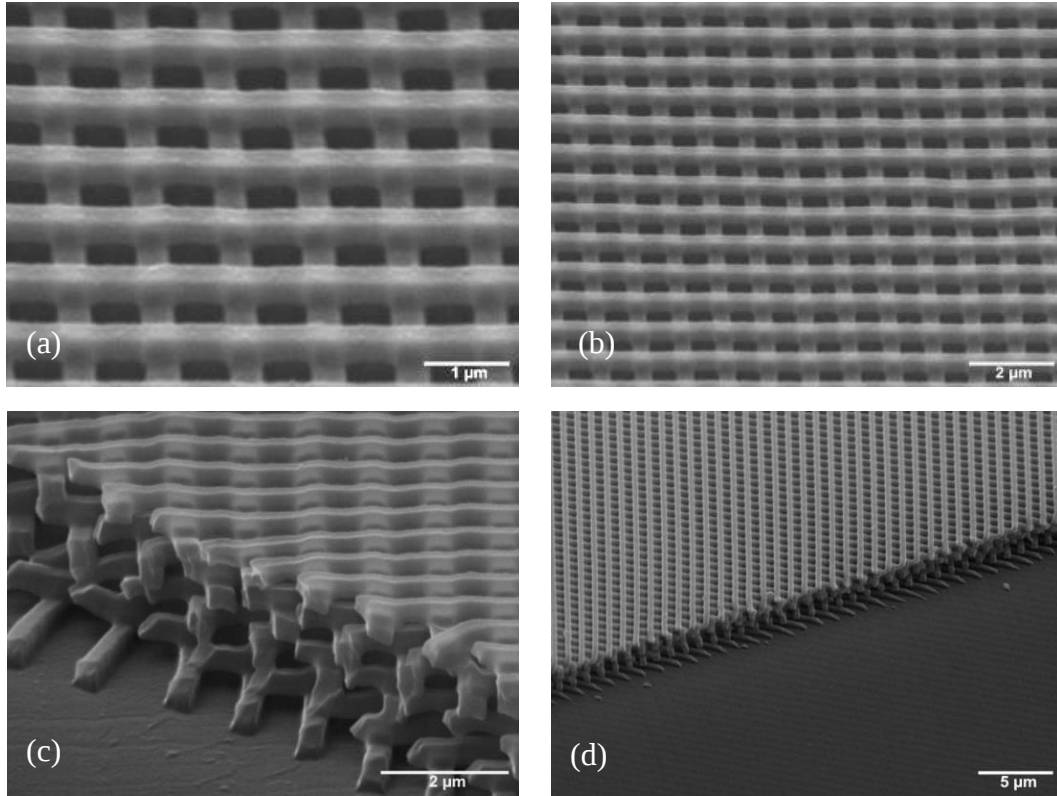


Figure 27: SEM images of 2L and 8L PU woodpile structures with 1 μ m periodicity

The optical properties of the 1 μ m periodicity structures were characterized. The specular reflection of 2L and 8L samples was measured using a FTIR spectrometer (Magna 760) in the near IR region. (Figure 28) The light source was polarized to see the effect of different polarizations. The results show that for a 2L structure, the reflection is quite low and is below 15% for both polarizations. For the 8L structure, both polarizations produced reflection peaks at around 1.2 μ m and 1.7 μ m wavelengths. For the 1.2 μ m peak, there were two sub-peaks. Both polarizations have similar reflection around 30-32%. For the 1.7 μ m peak, one polarization has reflection intensity around 25%, but

the other has reflection around 37%. These interesting features of polymer based woodpile structure are worth of further investigations.

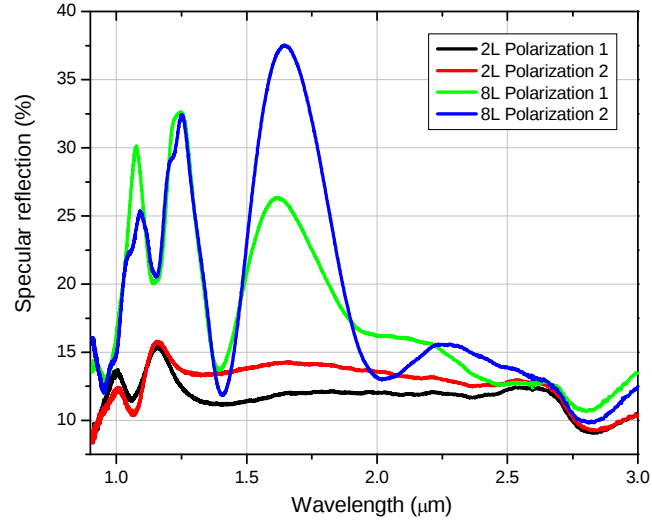


Figure 28: specular reflection spectra of 1μm periodicity woodpile structures with 2L and 8L

CHAPTER 3. EXPERIMENTAL APPROACH AND SAMPLE CHARACTERIZATION

1. Fabrication process of high aspect ratio structures

i. Introduction of the fabrication process

The structure is fabricated in a multi-stage process. First, a polyurethane (PU) grating structure with a periodicity of $2.5\mu\text{m}$ is fabricated on glass substrate by two-polymer microtransfer molding (2-P μTM). [56] (Fig. 29a) Metal films such as gold and silver are deposited onto the grating structure by e-beam evaporation. The sample is tilted 45° to the normal direction of the source so the PU bar itself will act as shadow mask to block the metal from being deposited on the bottom of the trench. In order to achieve high transmission, the metal on top of the PU bars is removed. We employ argon ion milling, a physical etching technique, to physically remove the metal by ion bombardment.

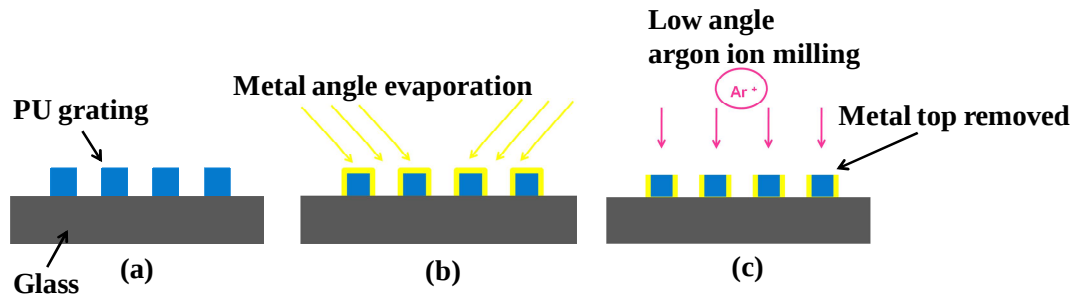


Figure 29: Schematics of the fabrication process (a) PU one-layer grating by 2-P μTM on glass substrate, (b) angle depositions of metal films on PU grating, (c) directional low angle argon ion milling to remove the metal from the top.

ii. 2P- μTM for one-layer (1L) PU grating fabrication

A PU polymeric grating structure was first fabricated using the two-polymer microtransfer molding (2P- μTM) technique on a transparent substrate such as glass or sapphire. [56] Using an existing PR master for making 3D woodpile photonic crystals, a one-layer PU grating structure with $2.5\mu\text{m}$ periodicity was fabricated. [56] The PU bar

height is around $1.2\mu\text{m}$, and the top and bottom widths are $0.85\mu\text{m}$ and $1.35\mu\text{m}$, respectively. Therefore, the profile of the PU bars was isosceles-trapezoidal and has a base angle around 80° .

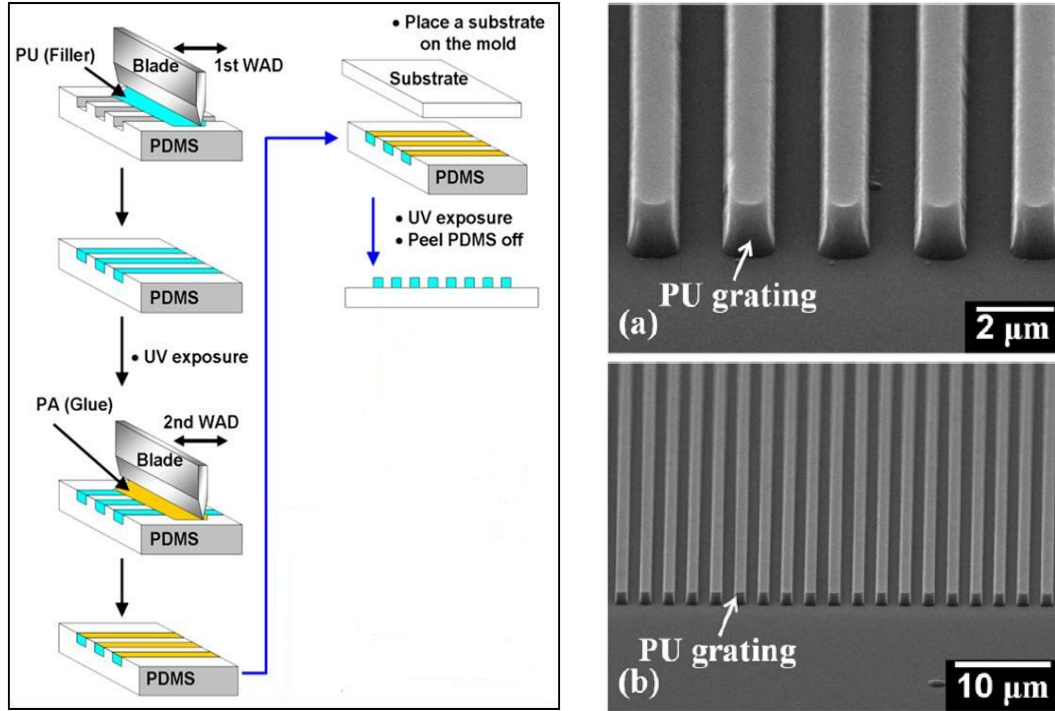


Figure 30: Schematic for making one-layer PU grating structure with 2P- μTM and the SEM images of the PU grating structure at (a) high and (b) low resolutions

Figure 30a and 30b show scanning electron microscope (SEM) images of the PU grating structure on a $200\mu\text{m}$ thick glass substrate at both high and low magnifications. Typical samples have an area of $4 \times 4 \text{ mm}^2$. Therefore, a single continuous PU bar has a length of 4mm . There are a total of 1600 microbars in one sample and it is possible some bars could have breakage along the length. Nevertheless, a transfer yield of 99% PU bars is achievable and desired for the subsequent fabrication process steps.

iii. Oblique angle metal deposition

Karabacak and Lu [58] showed a patterned structure could be coated with a homogenous metal layer using the oblique angle deposition at various angles. (Figure 31) A dc magnetron sputtering system was used to deposit ruthenium (Ru) onto the substrates

with heights 400 nm and width 200 nm, which gives an aspect ratio (AR) 2:1. The substrates are attached to a stepper motor and rotated at a fixed speed, and they are tilted at 15° and 30° for sidewall coverage. It was shown that at 30° tilted angle the growth rate at the sidewalls is approximately the same as that at the bottom. Such technique of sidewall coverage of metals could provide potential applications for fabricating high aspect ratio metal nanopatterns.

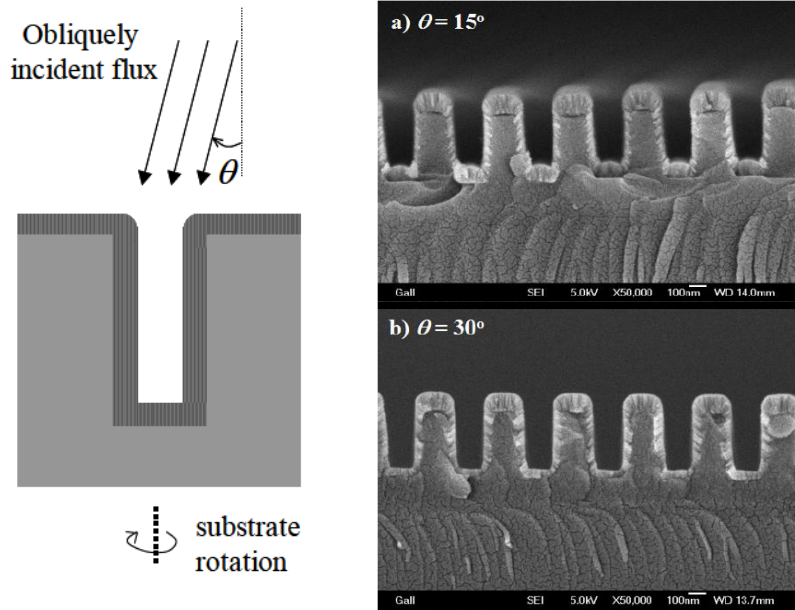


Figure 31: Oblique angle deposition on patterned substrates [58]

For the purpose of transparent electrodes, it is necessary to eliminate the metal coating in the channels between adjacent bars and on the top of PU bars. By choosing a tilted angle of 45° or higher with PU bars of 1:1 aspect ratio, the metal deposition is blocked by the PU bars so that during the thermal evaporation they only coat the sidewalls and tops of PU bars but not the spaces in between the bars. The same steps can be repeated from the other side of the PU bars to coat the other sidewall of the PU bars. (Figure 32(a), (b), (c)) Different metals such as gold (Au), copper (Cu), silver (Ag), and aluminum (Al) can be deposited. The deposition rate for the metals was maintained at 0.1nm/sec to ensure homogeneous metal coating. The e-beam evaporator pressure was maintained at 10^{-6} Torr during deposition. The metal thickness was chosen to be between 20nm and

80nm so that the sidewalls have narrow line-widths to allow optical transmission for visible light.

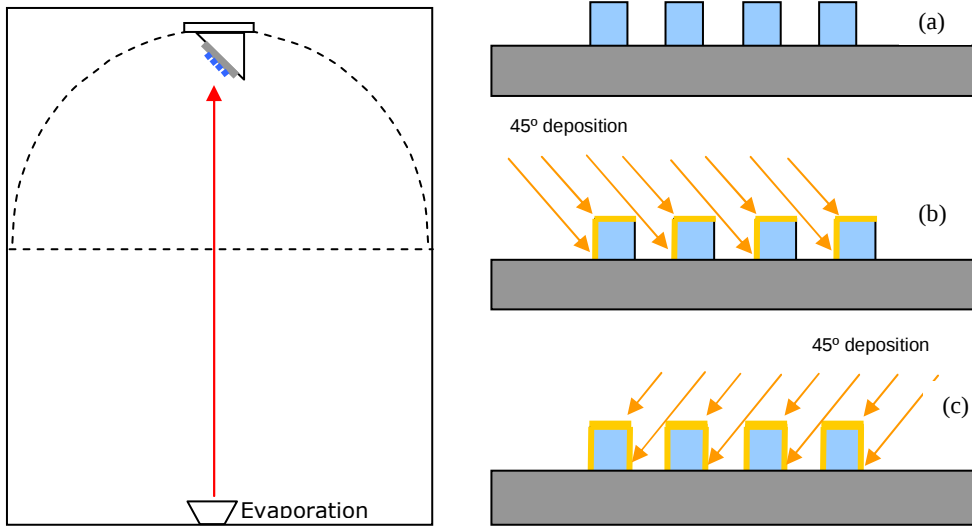


Figure 32: Schematics of oblique angle deposition of metallic materials. (a) Starting PU grating structure on glass substrate, (b) 45° angle deposition of metal from one side of the PU grating, and (c) 45° angle deposition of metal from the other side of the PU grating

Figure 33(a) shows SEM image of a one-layer 2.5 μm period PU grating on a glass substrate after angled thermal evaporation of 40nm gold on each side of the PU bars. The images show good coverage of gold on the top and sidewalls of the PU bars, while the space between the bars are not coated. Because the PU bars have a trapezoidal shape, the structure after metal deposition also has the same shape, which is best illustrated by the SEM image of the sample with PU removed by KOH etching. (Figure 33(b))

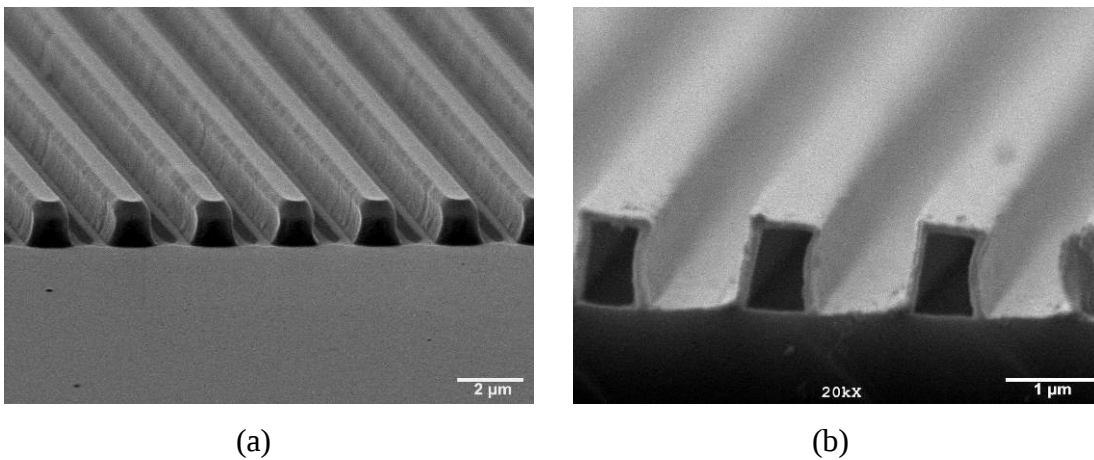


Figure 33: (a) Angle deposited gold 40nm on PU grating and (b) PU removed by KOH etching revealing the metal profile

The metal film thickness was chosen to be larger than 20nm with the consideration of the growth mechanism of metal films. [59] (Figure 34) A metal film is considered to form nuclei by the evaporated atoms in the beginning step and slowly aggregate into islands. The islands will coalesce at about 10nm thickness and then create a non-uniform film first. A continuous metal is formed when the thickness is reached at 20nm. Therefore, in order to obtain a uniform continuous metal film, a thickness above 20nm is needed. It should be noted that in reality metal films form nanoscale grains not single crystals.

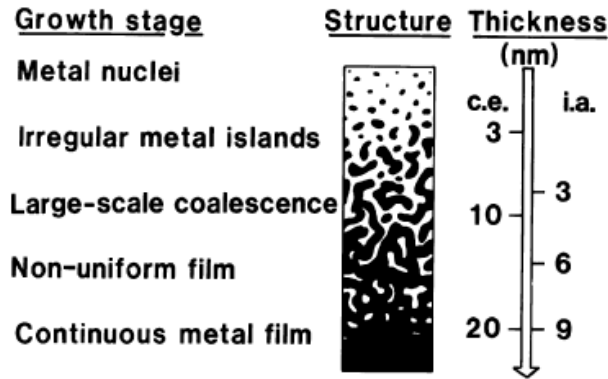


Figure 34: Gold metal film growth by conventional evaporation (c.e.) and ion-assisted evaporation (i.e.) [59]

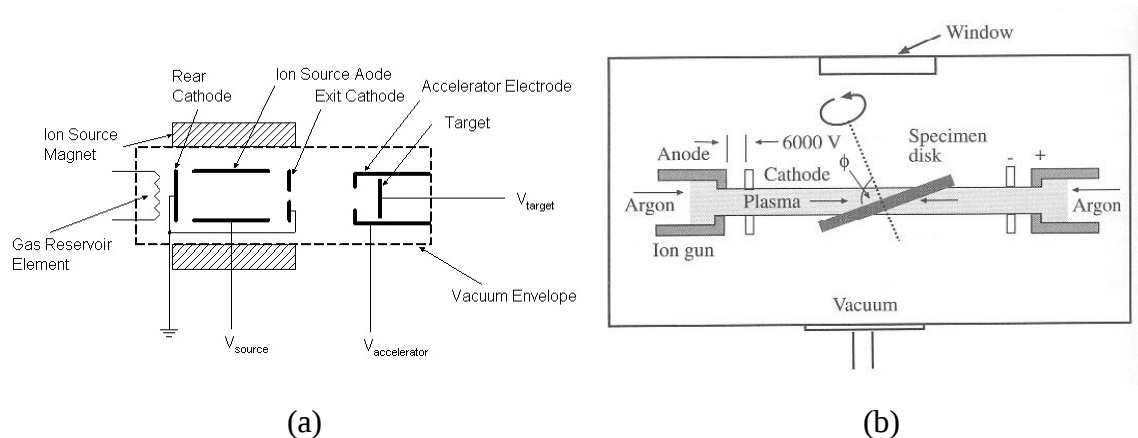
iv. Removal of metal top layers by low angle argon ion milling (etching)

With the metal on top of the PU bars, the optical transmission cannot be sufficiently high for transparent electrode applications. Indeed, as discussed in the next section, the optical transmittance of visible light for a $2.5\mu\text{m}$ pitch metal coated PU grating is only about 40% with the metal on top of the PU bars. Therefore, it is crucial to remove the metal top layers for higher transmission. It is also necessary to ensure the sidewalls are intact during the metal top layer removal so their electric properties are not affected. Argon ion milling was found to be a very effective and cost-effective method for such purpose.

Argon ion milling is a conventional technique widely used for sample preparation in transmission electron microscopy (TEM) in which ultra-thin samples are required for characterization. Unlike the more popular focused ion beam (FIB) etching technique, which works at very high resolution at nanometer scale, argon ion milling is much less

focused and can process samples with much larger areas. [60] This is an advantage for sample fabrication with high throughput and large area. Although there are several options for instruments that are designed to accommodate different ion source materials and various milling conditions, we focus here on an argon ion source for metal top layer removal for the current process. It has been shown that argon ion milling is capable of etching metals such as gold and silver, and it can even be used to remove oxide for nanostructure fabrication. [61, 62]

The two most important parameters for argon ion milling are plasma generation and ion extraction. The ion source used in this study is a Penning ion source [63]. The instrumental setup of the Penning ion source is schematically presented in Figure 35(a). The ion source has a gas inlet for argon to flow at a controlled rate into the chamber. The argon gas is then ionized by electron impact at the rear cold cathode and a plasma discharge is created. The plasma chamber is designed specifically such that, along with the ion source magnet, electrons are contained inside the chamber by the cathode and anode. The magnetic field created causes the electrons to be reflected backwards and forwards many times so that they are efficiently re-used. When the gas flow rate and the applied bias potentials are adjusted to a working range, some of the ionized argon can escape the plasma source and are accelerated by the accelerator electrode towards the vacuum chamber in the form of an ion beam. By controlling the accelerator electrode voltage at an appropriate level, the sample target in the vacuum chamber can be milled (sputtered) by the argon ion beams. Furthermore, the ion beam can be adjusted to a lower angle so that the etching rate can also be controlled, which also results in a smoother than when the ion beam is incoming at a high angle. [64,65] (Figure 35(b) and (c))



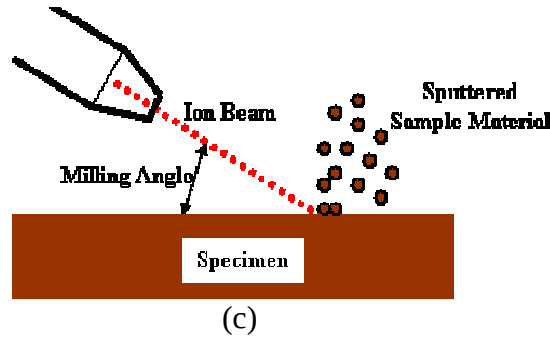


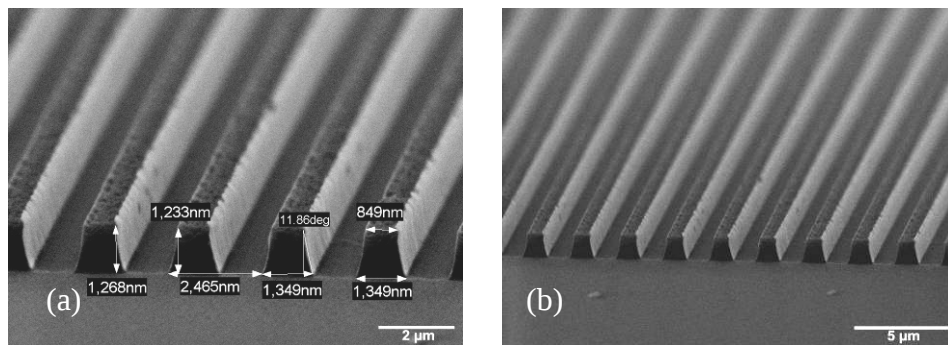
Figure 35: (a) Schematics of the Penning ion source, (b) the chamber of the ion milling machine, and (c) the argon ion milling (sputtering) process [63, 64]

A Gatan dual mill (model 600) was used to perform the metal top layer etching for the metal coated 1-layer PU grating structures shown in the previous section. PU gratings with a periodicity of $2.5\mu\text{m}$ were used for the angled thermal evaporation with gold and silver. The ion milling was carried out at a voltage of 3kV and a gun current of 1mA. The high voltage ensures that the argon ions have enough energy to bombard the metals on top of the PU bars for removal. The current was chosen at 1mA so that the ion beam would have a sufficient beam size ($\sim 3\text{-}4\text{mm}$) to cover the sample. The vacuum pressure was maintained at around 10^{-4} Torr during the milling. In addition, a low milling angle (10°) was used so the ion beam is etching the metal top surface at a controllable rate and the ion beam covers a larger area. The ion beam direction was aligned parallel to the PU bar direction so that only the metal on top of PU bars is removed but the metal on the sidewalls is not. (Figure 36(a)). The milling time varies between 3 to 5 min depending on the top metal layer thickness. After ion milling, the top metal layers on the PU bars are etched off, leaving the PU bars and the metal sidewalls intact. (Figure 36(b))



Figure 36: Schematics of structure (a) before and (c) after low angle argon ion milling

Figure 37 shows the SEM images from edge and top view of the one-layer PU grating of $2.5\mu\text{m}$ periodicity coated with 40nm gold after argon ion milling. The sample has a trapezoidal shape, with a slated angle of about 10° , and the bar height are $1.2\mu\text{m}$. They show that the top metal layers on PU bars of the sample were completely removed by the argon etching. The etching is very homogenous over the entire sample area ($4\text{mm} \times 4\text{mm}$). Because the mechanical integrity of PU bars is not altered during the milling process, the metal layers on both PU sidewalls remain intact without defect or breakage from the ion milling. The heights of the gold sidewalls are estimated to be the same as that of the PU bars. Therefore, the gold sidewalls can be defined as high aspect ratio nanowires with 40 nm line-widths with 30:1 aspect ratio. Since gold was deposited on both sidewalls, the periodicities of the gold nanowire patterns are reduced by half to around $1.2\text{-}1.3\mu\text{m}$. It was observed that the top of PU bars is slightly roughened, which indicates some over-etching by the argon ions. Such imperfections can be avoided if a lower voltage or a shorter milling time was used. However, as shown in the next section, this slight roughness does not significantly affect the optical and electrical properties of the samples. As the SEM images show, our metallic structures leave most of the substrate area available for transmission of light, except the nanoscale cross section that the thickness of metallic sidewalls occupy. Furthermore, a structure with periods larger than optical wavelength is useful to improve optical properties (higher transmission and reduced diffraction), and the polarization effect does not take place in the visible wavelength range.



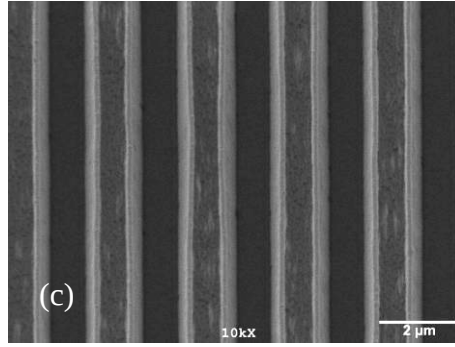


Figure 37: Scanning electron microscope (SEM) images of argon ion milled 40nm gold sidewalls on a 2.5 μ m period polymeric grating structure from the edge view in (a) and (b) and top view in (c).

2. Sample characterization

After the metallic patterned structures were prepared, they were characterized to examine the feasibility of the structures as transparent electrodes for organic solar cell devices. For use as transparent electrodes, optical transmission in the visible range and sheet resistance must match or improve upon those of ITO.

i. Optical measurements

Visible light comprises a large portion of the electromagnetic radiation from the sun that reaches earth surface. Therefore, it is of profound importance that the visible light be efficiently harvested for solar cell applications, therefore, one of the most important parameters for transparent electrodes is the optical transmission in the visible range.

a. PU transmission in visible wavelengths

Because the PU remains in the final structure, it is necessary to study the optical properties of the PU materials used to make the grating patterns. The transmission of PU films on glass in visible wavelength range (Figure 38) shows similar spectra as the glass substrate ($\sim 92\%$), which indicates that PU is highly transparent for visible light. It should be noted that the PU prepolymer is UV-curable. Therefore, it can be highly absorptive for

UV light. This is clearly shown in a transmission dip around 365nm wavelength when the transmission is measured for a thick PU film. Nevertheless, if the PU material used is thin ($\sim 10\text{-}20\mu\text{m}$), no such absorption dip is evident and it is suitable for use as the matrix for transparent electrode structures.

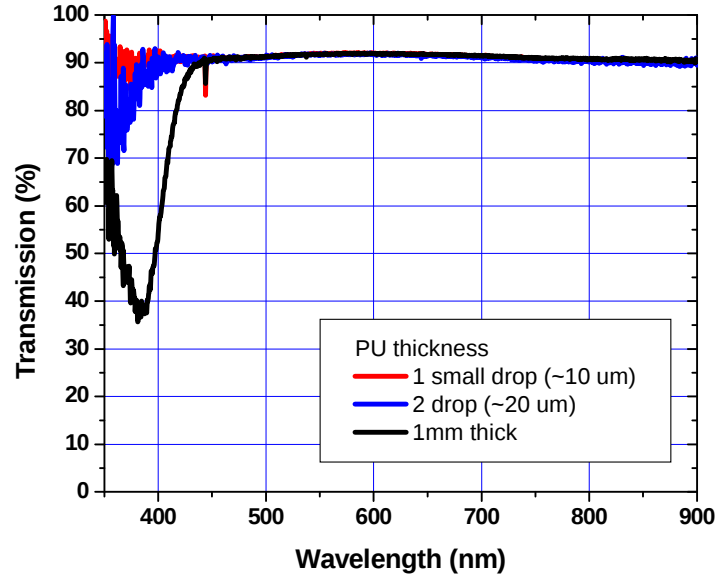


Figure 38: Optical transmission of PU in visible wavelength range

b. Visible transmission utilizing integrating spheres

Because the one-layer PU structures made by the 2P- μTM technique are microscale grating patterns, there is diffraction of the visible light, and the transmission at normal incidence is only one portion of the total light transmission. (Figure 39)

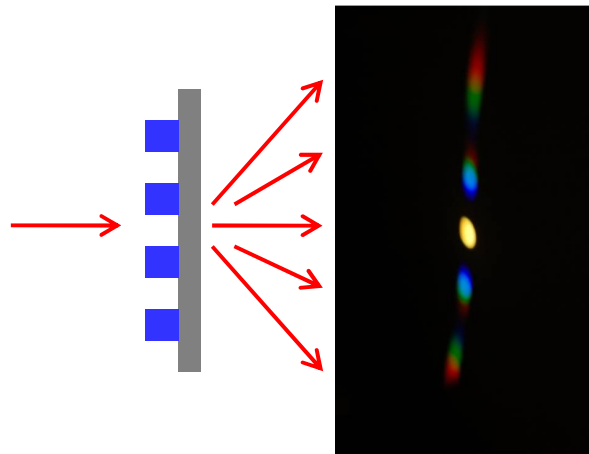


Figure 39: diffraction of the PU grating

Therefore, it is necessary to collect all the light transmitted through the sample. To accomplish this, an integrating sphere was used for the optical measurement. [66] In the integrating sphere setup (Figure 40(a)), the sample is placed on a sample holder at the opening of the integrating sphere. A visible light source (Ocean 2000 spectrometer) is used to illuminate the sample. The light transmitted through the sample propagates in a diffuse manner. The inside wall of the integrating sphere is coated with a highly reflective paint, and all the diffuse light is eventually reflected to the detector, where the total diffuse light is collected and the total diffuse transmission is measured. The samples were measured with air as the reference.

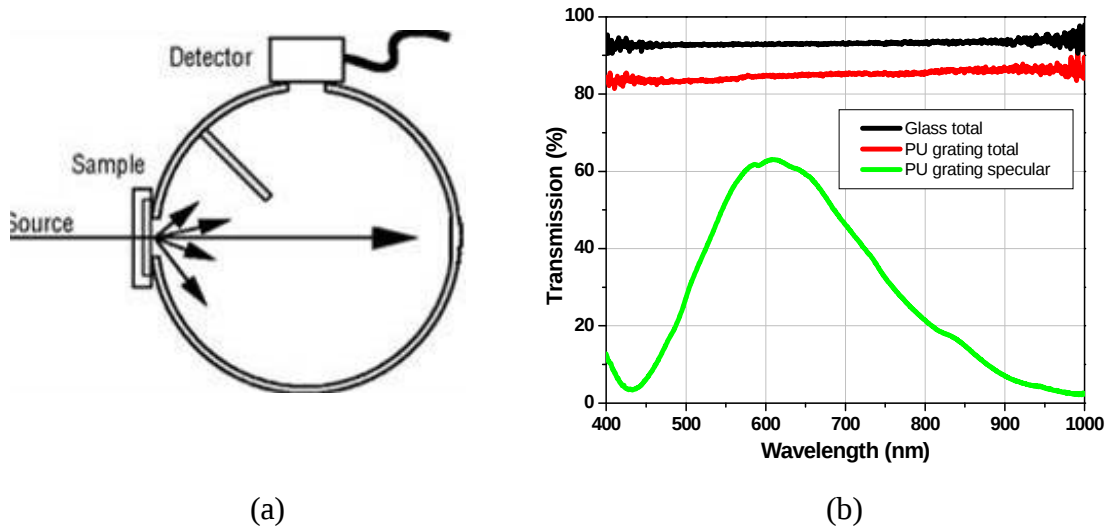


Figure 40: (a) The schematic of an integrating sphere [66] and (b) comparison of diffused and specular transmission of a 1-layer $2.5\mu\text{m}$ period PU grating on glass substrate as well as the transmission of a glass substrate

Figure 40(b) shows the diffuse and specular transmission of a 1-layer $2.5\mu\text{m}$ period PU grating on glass substrate. The specular transmission has a peak with the maximum at around 650 nm wavelength of about 62%. However, light intensities below and above this peak wavelength decrease. When an integrating sphere is used, the measured transmission is significantly increased for all the wavelengths in the visible range. The diffuse transmission spectrum is generally flat with no peaks. The structural effects of the sample on the optical measurement are eliminated. The average intensity is about 85%. For comparison, the transmission of a glass substrate was also measured and was about 92%, which is consistent with the theoretical value. The transmission of the PU grating structure is about 7% lower than that of both glass substrate and PU film on glass sample.

This is due to additional reflective diffraction from the grating structure, as we observed similar diffraction pattern in reflection but at much lower intensity. Nevertheless, the transmission of PU grating structure is sufficiently high for use as transparent electrode.

c. Transmission of grating structure after metal deposition

After the PU grating structure was fabricated, oblique angle evaporation was done to deposit metals on the PU surface and the transmission of the metal-deposited structures was also measured with the integrating sphere setup. Figure 41 shows the total transmission of the PU grating structure with 20nm and 40nm gold deposited on the PU bars. Both spectra show low transmission in the visible regime due to the metal on the top of PU bars as well as the sidewalls. The width of the PU bars is around $1.2\mu\text{m}$ and is about half of the periodicity of $2.5\mu\text{m}$, which means the transmission should be reduced by half with respect to the transmission of PU grating structure without metal.

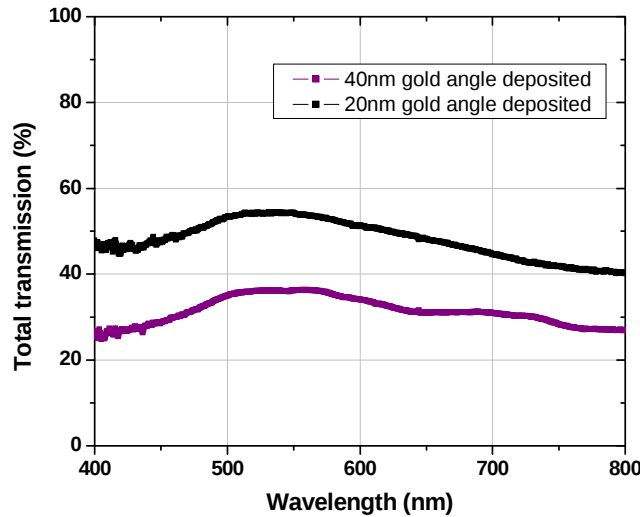


Figure 41: Total transmission of one-layer PU grating structure with gold deposition

As seen for the 40nm gold spectra in Figure 41, the transmission is reduced to about 37% at the peak of 550nm wavelength. The transmission of PU grating structure is about 85%. Covering the PU bars should reduce the transmission to half. In addition, the metal thickness of 40nm on both sidewalls accounts for 3% more transmission reduction. So, with metal deposition the total transmission is theoretically reduced to about 40%. The

actual transmission value of 37% is close to the theoretical value of 40%. The lower transmission could be caused by slight over-coverage of gold on the glass substrate at the bottom of the PU bars, as seen in the SEM image in Figure 37(a). The lower transmission at wavelength below 500nm is due to absorption of gold and lower transmission above 600nm wavelength is possibly caused by higher reflective diffraction of the structure at longer wavelength. The 20nm gold deposited sample has higher transmission than that of 40nm gold with the peak value at 550nm wavelength more than 50%. The reason for such high transmission is that 20nm thickness is close to the skin depth of the gold, which can allow some light transmission through the metal coating. Also, at 20nm thickness, the metal film may not continuous and could have cracks on the metal surface, which could also lead to increased transmission. However, the discontinuity in metal films has negative impact on the electrical conductivity, which will be discussed later.

d. Transmission of argon ion milled structures

We then performed optical transmission measurements on these structures after the argon ion milling step for structures with two metal sidewalls, gold and silver, at 40nm thickness. For comparison, the transmission of a standard commercially available ITO coated glass was also measured. The ITO coated glass has peak transmission of 88% at around 600 nm wavelength and an average transmission of 82% over the entire optical wavelength range (400 nm – 800 nm). For the ion milled patterned structures with metallic sidewalls, gold and silver showed similar transmission spectra. For gold, the peak total transmission was 82% at around 650 nm and the average total transmission was close to 80%. For silver, the peak transmission was also around 82% at around 650 nm, and the average is about 78%. A slightly lower transmission at wavelength below 550nm is still observed, and it is possibly caused by the absorption of a small amount of redeposited metals in the channels of the grating structure during the ion milling process. For two sidewalls of 40nm thick metal over the periodicity of 2.5 μm , the reduction in transmission due to the metals is theoretically about 3%. Therefore, with the metallic sidewalls, the measured transmission is dropped by an additional 2-3%. Additional

reduction in transmission may be caused by some PU top surface roughness, which results in diffuse scattering backwards. Even though the transmission is not as high as that of ITO coated glass, it is sufficient to demonstrate the feasibility of the structure for transparent electrode applications. Figure 42 inset shows an ion milled sample with 40nm gold sidewalls. The logo underneath the sample can be clearly viewed because the average transmission is around 80%.

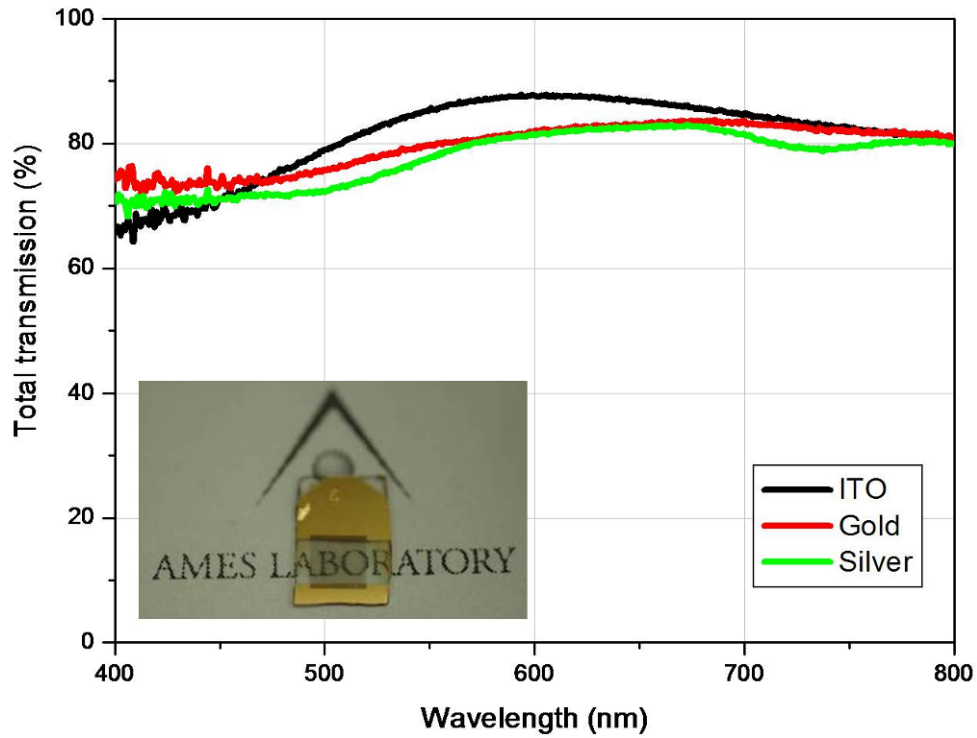


Figure 42: Total transmissions of ITO glass and one-layer 2.5 μ m period PU grating structures on glass with 40nm gold and silver sidewalls after argon ion milling

e. Metal thickness effect on the transmission

Further studies were done to characterize the metal thickness effect on the transmission of the ion milled structures. The transmission spectra of ion milled samples with different thickness were plotted in Figure 43.

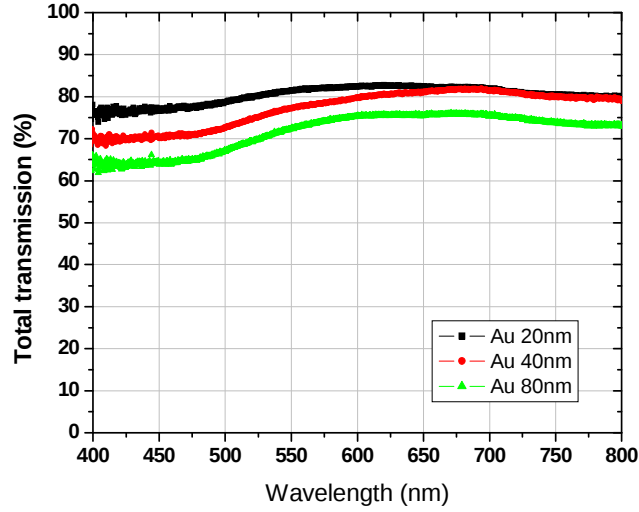


Figure 43: Total transmission spectra of the ion milled structures with different metal thickness

The spectra show that as the gold thickness increases from 20nm to 80nm, the overall transmission decreases. The spectra have similar profile with small decline at wavelengths below 550nm due to metal absorption. The average transmission of the structures is decreased from 80.3% to 71.7% when the gold thickness is increased from 20nm to 80nm. (Table 4) The reduction of transmission is mostly due to the increased thickness of metal as well as the trapezoidal profile of the PU bars to block the light transmission. The transmission for 40nm gold thickness is 77.3% with some samples close to 80%. A similar trend is observed for silver samples, where the average transmission is increased from around 78% at 40nm thickness to 83% at 20nm thickness.

Table 4: Total transmission of gold and silver metals with different sidewall thicknesses

	20nm (Avg.)	20nm (Max.)	40nm (Avg.)	40nm (Max.)	80nm (Avg.)	80nm (Max.)
Gold	80.3%	82.8%	77.3%	82.0%	71.7%	76.1%
Silver	83.1%	85.5%	77.9%	83.0%	N/A	N/A

f. Polarization effects in the visible range

We also studied the polarization effect of our structures in visible wavelength range. In this experiment, a polarizer was used to polarize the incident light in front of the samples. The samples are aligned either parallel (transverse magnetic (TM) mode) or

perpendicular (transverse electric (TE) mode) to the electric field of the light. For comparison, the transmission results with unpolarized light was also plotted. (Figure 44)

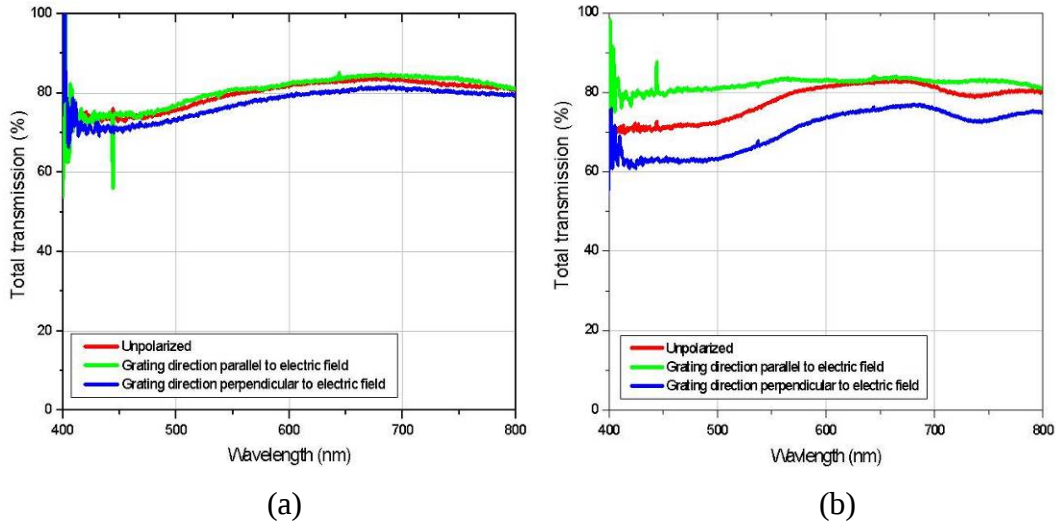


Figure 44: Transmission of the (a) gold and (b) silver structure with polarized light

For sample with gold sidewalls, the average total transmissions of the TM mode and TE mode are 81% and 78%, respectively. This shows only about 3% of difference for different polarizations. For the silver sample, the TM and TE mode transmissions are 82% and 70%, respectively. The transmission difference is about 12%. The TE mode has much lower transmission in silver possible due to higher reflection in the TE mode for silver. Nevertheless, the polarization effect is not severe for either sample since the periodicity is $2.5\mu\text{m}$, which would show great polarization contrast in the infrared wavelength regime. Further studies were done in the infrared range in a later section.

ii. Electrical measurements

To characterize the electrical conductivity, two-wire electrical measurements were performed to measure the resistance of the argon ion milled high aspect ratio metallic structures. The electrical resistance was measured with Fluke 8840A multimeter.

a. 2-wire Resistance of ITO

For comparison, the resistance of a 100nm ITO coated glass was also measured. First, the theoretical resistance value was estimated using the sheet resistance (R_s) of the ITO coated glass. The sheet resistance of a thin film is defined as:

$$R_s = \frac{\rho}{t} \quad (1)$$

where ρ is the resistivity and t is the thickness of the film. The sheet resistance of the ITO coated glass is measured to be $10\Omega/\square$ using a standard four-point probe for the most commonly used ITO for transparent electrode applications. For 2-wire resistance, a 4mm wide ITO coated glass area is confined by two metal contacts and ends with a 3mm separation. (Figure 45) Therefore, the theoretical value of the 2-wire resistance can be calculated by:

$$R = \frac{\rho}{t} \frac{L}{W} = R_s \frac{L}{W} \quad (2)$$

where L is the separation of the metal contacts and W is the width. The 2-wire resistance therefore was calculated to be 7.5Ω . The measured resistance for the ITO coated glass is about 7Ω with 200nm gold metal contacts deposited at two ends of the ITO coated glass, which is very close to the estimated value of 7.5Ω .

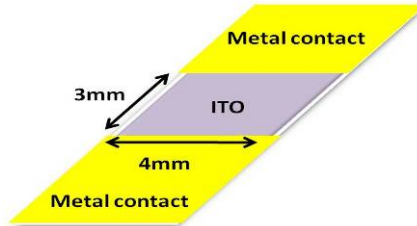


Figure 45: Design of the ITO coated glass sample for 2-wire resistance measurement

b. 2-wire resistance of ion milled samples

The same process was carried to deposit 200nm gold metal contacts at both ends of the ion milled samples. (Figure 46) The separation of the metal contacts is 3mm. The width of the sample is 4mm. Therefore, we can compare the measured resistance of the ion milled samples with the measured resistance of ITO coated glass. Conductive silver paste can also be used as contacts for such purpose.

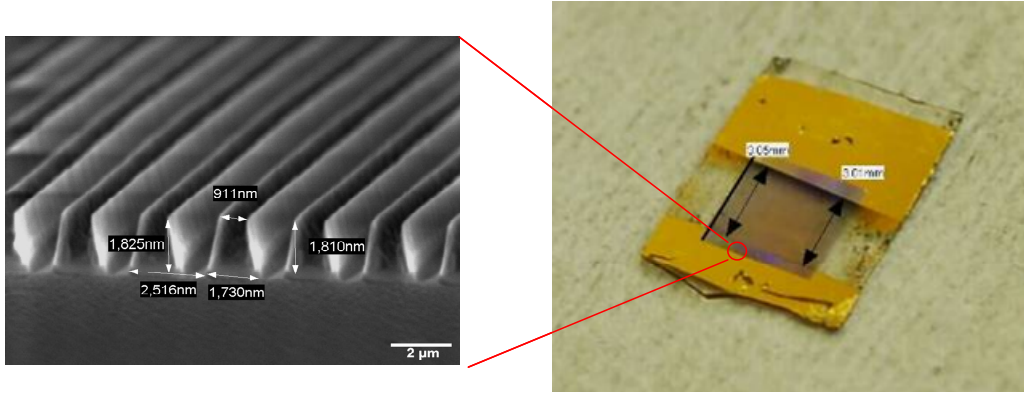


Figure 46: SEM and still images show the depositions of metal contacts on the sample for the 2-wire resistance measurement.

The measured 2-wire resistance of the ion milled gold and silver samples with different thickness is listed in Table 5. For 20nm thickness, the gold and silver samples have an average resistance of 38.5Ω and 21.8Ω , respectively. Both are higher than that of 100nm ITO coated glass. However, as the thickness was doubled to 40nm for both metals, the resistance was drastically reduced to 7.3Ω and 2.4Ω , respectively, for gold and silver. The 40nm gold sample is virtually the same as the ITO coated glass, and the silver structure is three times less than that of ITO coated glass. Therefore, when considering the electrical conductivity, the 40nm samples are similar or better than the ITO coated glass. Moreover, at such thickness, the optical transmission in visible is still sufficiently high in the range of 78-80%. As the thickness increased to 80nm for the gold structure, the resistance is reduced further to 4.4Ω . However, the optical transmission for the ion milled sample is too low ($\sim 71\%$) to be used as transparent electrodes. Therefore, we chose the optimal metal thickness of 40nm with both high optical transmission and electrical conductivity for further experiments and characterization.

Table 5: Average resistance (Ω) of the gold and silver samples with different thickness

	20nm (Avg.)	40nm (Avg.)	80nm (Avg.)
Gold	38.5	7.3	4.4
Silver	21.8	2.4	N/A

It should be noted that as the metal thickness is increased from 20nm to 40nm, the thickness is doubled, but the resistance is lowered by more than 5 times for the gold samples and almost 10 times for the silver samples. This is because metal films of very small thickness are likely to be discontinuous. (Figure 34) As the film thickness is grown beyond 20nm, continuous and uniform metal film forms and the electrical conductivity of the film scales with thickness. This is seen when the gold thickness is increased from 40nm to 80nm, the resistance is reduced from 7.3Ω to around half at 4.4Ω.

c. Sheet resistance calculation

Catrysse and Fan [67] established a method for calculating the sheet resistance of nanopatterned metallic structures. Specifically for a 1D metallic grating structure, the sheet resistance can be calculated by:

$$R_s = \left(\frac{\rho}{h} \right) * \left(\frac{a}{w} \right) \quad (3)$$

where ρ is the bulk resistivity of metal, h is the height, a is the periodicity, and w is the width. Figure 47 shows the theoretical sheet resistance of a 1D metallic pattern with fixed periodicity of 400nm and width of 80nm, while varying the height of the structure. At height smaller than 20nm, the non-linear increase in the sheet resistance is also observed due to the discontinuity and coalescence in the metal. At thickness greater than 20nm, the sheet resistance shows a linear decrease as the height increases.

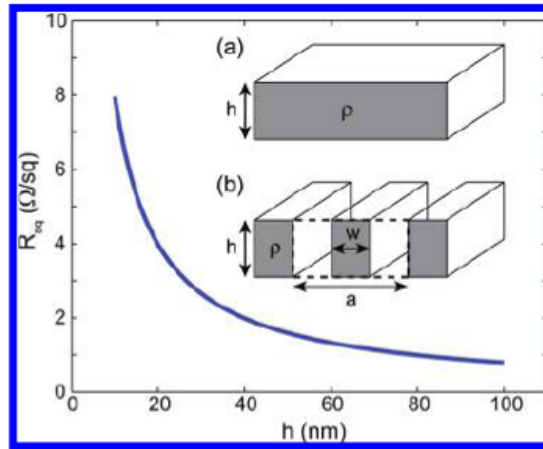


Figure 47: Electrical sheet resistance of a 1D metallic grating structure with $a = 400\text{nm}$, $w = 80\text{nm}$, and varying height [67]

Based on their method, we can estimate the theoretical sheet resistance of our ion milled structures. The ion milled structures have the periodicity at $2.5\mu\text{m}$, height around $1.2\mu\text{m}$, and the width of the metals at 80nm (two sidewalls with 40nm). The bulk resistivities of gold and silver are $2.20 \times 10^{-8} \Omega\cdot\text{m}$ and $1.59 \times 10^{-8} \Omega\cdot\text{m}$, respectively.[68] The calculated values of sheet resistance from the equation are $0.57 \Omega/\square$ and $0.41 \Omega/\square$ for our gold and silver structure, respectively, based on Equation 3. Both are at around 20 times better than that of ITO and such high aspect ratio metallic structure is very promising for very low resistivity transparent electrode applications if we could achieve similar sheet resistance values.

To find the actual sheet resistance value of our structures, a variation of Equation 2 was used. The sheet resistance R_s can be calculated by $R_s = R \cdot (W/L)$, where R is the measured 2-wire resistance, W is the sample width and L is the separation between the contacts. With those values measured and known, from the equation we find the sheet resistance of the ion milled samples with 40nm gold and silver are $9.7 \Omega/\square$ and $3.2 \Omega/\square$, respectively. Both values are less than the ITO sheet resistance typically used for organic LEDs and solar cells. However, they are still about 10-20 times higher than the theoretical values. Possible reason for the higher sheet resistance is breakage in some PU bars during the grating structure fabrication. In such a case, the metal deposited on these PU bars will also be broken and does not contribute to the electrical conduction. This will severely reduce the conductivity of the sample. The other possible reason is over-etching of the metal on the top by ion milling, and the height of the metal is less than the original height of PU ($1.2\mu\text{m}$), which would also increase the sheet resistance. In addition, the argon ion milling may also attack the metal sidewalls slightly and reduce the width of the metals, which could also result in increased sheet resistance. Therefore, it is crucial to prepare the PU grating structures with the best yield. Furthermore, better etching methods should be investigated. It is also beneficial to fill the channels to protect the sidewalls during the etching process.

3. Organic photovoltaic device based on the transparent electrodes

i. Structure inversion fabrication process

To fabricate devices such as organic or inorganic solar cells or LEDs on our transparent electrode platform, it is necessary to fill the open trenches with a transparent material to provide a flat area for the active layer deposition. We achieved this as shown in Figure 48.

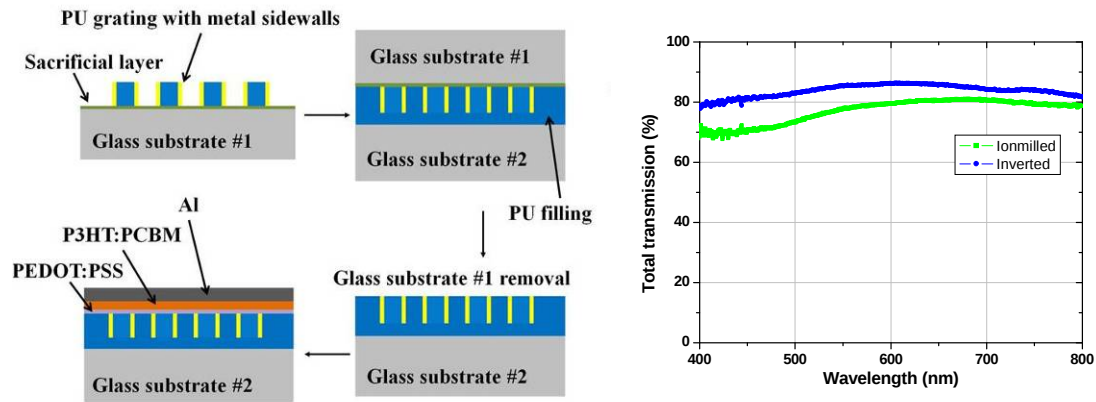


Figure 48: (a) Schematics for sample inversion and organic active layer depositions and (b) the comparison of transmission of the ion milled sample before and after inversion.

We first made the PU grating on a water-soluble sacrificial layer coated glass substrate. After metal deposition and argon ion milling, a small drop of PU prepolymer was placed on the sample to fill in the trenches of the grating structure. The PU prepolymer also served to glue a second glass substrate onto the sample. After the PU filling was ultraviolet cured and solidified, the sample was submerged in distilled water to dissolve the sacrificial layer, and the original glass substrate was detached. Upon the separation of the original glass substrate, the bottom part of the structure was exposed and the sample was inverted. The inverted structure has an average total diffused transmission about 84%, which is about 4% higher than the ion milled structure before inversion. This is because the filling of PU in the air gaps reduces backscattering of the light from the grating structure; in addition, a smoother PU bottom surface is exposed. The resistance of the inverted structure is about 30 Ω . The fact that the inverted sample has higher resistance than before inversion is probably due to over-filling of PU at the two ends of the sample,

which would block the connections of metal contacts to some of the metallic sidewalls during two-wire electrical measurements.

ii. Organic photovoltaic device fabrication with inverted structure

As a proof-of-concept for applicability of our transparent electrodes, we fabricated a bulk-heterojunction polythiophene:fullerene based solar cell on our inverted structures. The fabrication is a solution-based spin coating process. A conducting film of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS, Clevios P VP Al 4083) was first spin coated at 3000 rpm for 60 seconds on the inverted structure followed by annealing at 60°C for 5 minutes. The PEDOT:PSS layer is used to improve the hole collection between the electrode and the light absorbing layer. The light absorbing active layer, poly(3-hexylthiophene) and [6,6]-phenyl C61-butyric acid methylester (P3HT:PCBM) blend solution (17 mg/ml in dichlorobenzene), was spin coated at 600 rpm for 30 seconds on the PEDOT:PSS coated structure. The P3HT absorbs photons and creates excitons, which are loosely bound electron-hole pairs and may recombine if they are not separated quickly. The excitons then diffuse to the P3HT/PCBM interface and dissociates. At the interface, the electron travels through PCBM to the cathode, and the hole travels through P3HT to the anode. An Al (200 nm) electrode (area= 3.14 mm²) was deposited by thermal evaporation on top. I-V measurements were done using an ELH Quartzline lamp with intensity calibrated using a standard Si photodiode.

iii. I-V characteristics and discussions

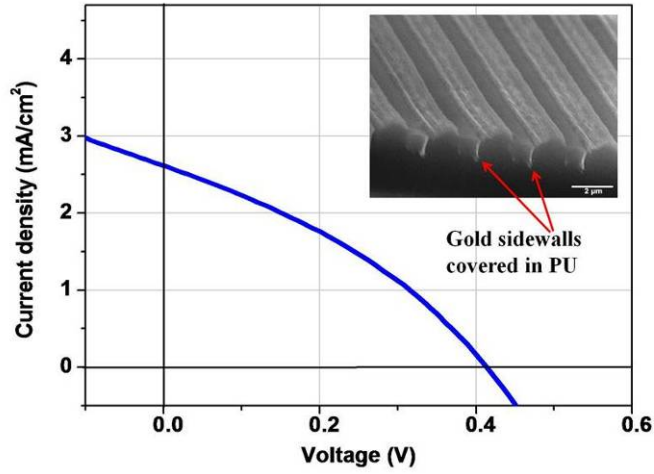


Figure 49: Current density versus voltage characteristics of organic solar cells with the gold structure as the transparent electrode

The optical to electrical power conversion efficiency (η) of the device can be calculated with the following equation:

$$\eta = \frac{FF \cdot I_{sc} \cdot V_{oc}}{P_s} \quad (4)$$

Where FF is the fill factor, I_{sc} is the short circuit current, V_{oc} is the open circuit voltage, and P_s is the illumination intensity (typically at $100\text{mW}/\text{cm}^2$). From Figure 49, we found the short circuit current of our sample to be about $2.5\text{mA}/\text{cm}^2$, the open circuit voltage about 0.42V , and the fill factor about 34% . Therefore, the power conversion efficiency of the device is about 0.36% .

The device successfully showed photovoltaic characteristics. However, the performance was still inferior to typical ITO electrode-based solar cells (usually short-circuit current $\sim 8\text{-}10\text{ mA}/\text{cm}^2$). Since the conductivity and transmittance of our transparent electrode was in fact comparable to ITO, we believe that the performance of our solar cell is not similar to ITO based devices because in some regions the top exposed regions of the gold sidewalls was partially covered by PU due to imperfect material processing prior to PEDOT:PSS deposition. SEM in Figure 48 inset shows some evidence of such imperfections. Some contribution to poorer performance can also be ascribed to resistive losses due to horizontal transport of holes through PEDOT:PSS layer, before they are

collected by metal nanoribbons. However, this issue can be easily resolved by using highly conducting formulations of PEDOT:PSS such as PH500. It has been shown that PH500 is able to efficiently transport holes over distances greater than 100 microns. [69] The image shows that some metallic ribbons are embedded inside the polymer, and they are not exposed at the top. As a result, they may not be in contact with PEDOT:PSS for charge transfer. However, this issue can be resolved by slight etching of the unnecessary polymer covering the metal electrode edges. In addition, the field enhancement at the interfacial contact between active layers and the electrodes may be a more vital issue than the optical improvement of the electrodes for achieving better performance efficiency of the device.

iv. Uneven surface during sample inversion

Another possible reason the solar cell device with low efficiency is the poor contact between the organic layers with the gold electrodes embedded in the PU matrix. The sacrificial layer used on the first substrate is organic based glue material and it can be easily etched by the argon ion milling too. (Figure 50) This will create additional air space in the channels and on the substrate. When PU is used to fill the channels in the grating structure, this additional space will be filled with additional PU and after the detachment of the first substrate, an uneven surface will be revealed. The unevenness will depend on the original thickness of the sacrificial layer, and it is in the range of 300nm. Therefore, in order to improve the contact between the metal and the active layers, a thinner sacrificial layer should be used. Another way is to use slight oxygen etching to remove some of the PU on the surface to expose the metal completely.

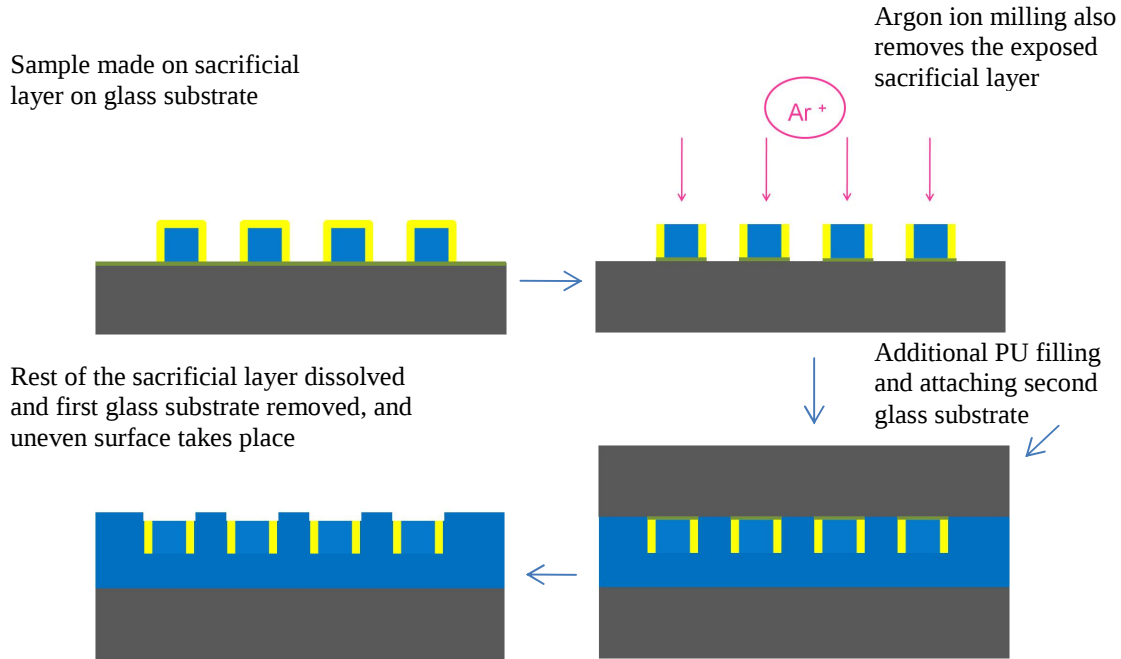


Figure 50: The inversion process with uneven surface

4. IR reflection for heat mirror applications

i. Introduction

In addition to the visible light diffuse transmission measurements, the optical properties of the ion milled metal structures in the near and mid infrared wavelength region were also examined. The purpose of this is to study whether the metal structures which have high visible light transparency can also act as an infrared radiation filter, in which IR is blocked by the metal structures and reflected backwards. At present, commercially available IR filters are hot mirrors, which are composed of multilayer dielectric thin films of thickness on the nanometer scales. (Figure 51(a) and (b)) [70] Even though they have high visible light transmission and can block the radiation in the near IR range, they are still costly and too mechanically rigid for many potential applications.

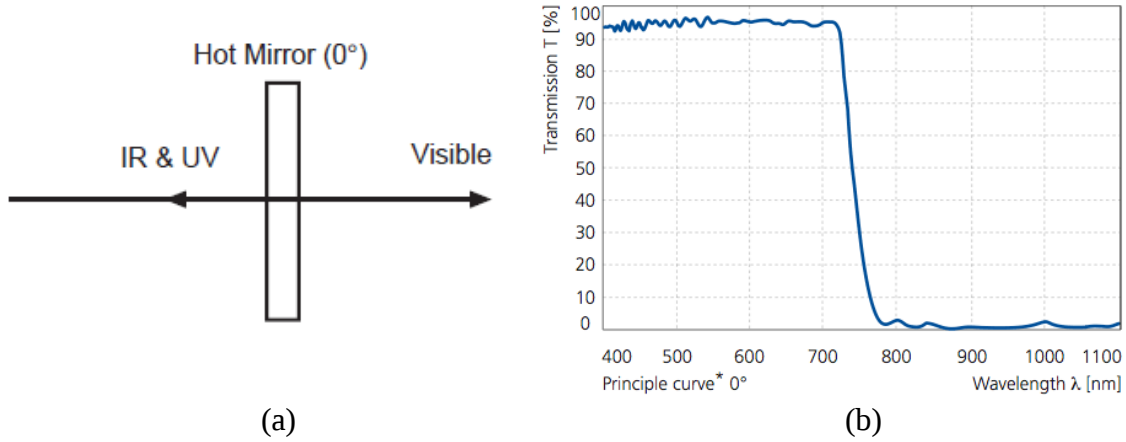


Figure 51: (a) The hot mirror IR filter and (b) its transmission in the visible and near IR range [70]

ii. Photon recycling using high aspect ratio metallic photonic crystals

K.M. Ho *et al.* [71] proposed a metallic structure design which can serve as an IR filter with high visible light transmission as a replacement for the hot mirrors for many potential IR applications. In this design, a free-standing 2D metallic grid made of silver is used. (Figure 52(a)) The periodicity of the grid is 500 nm. The line-width of the silver wire is 100 nm, and the duty cycle is 10% for high visible light transmission. The height of the nanowire is 500 nm, which ensures complete IR reflection, and the aspect ratio of the silver nanowire is 5:1. The calculated optical properties of the 2D grid structure shows very high visible transmission ($\sim 90\%$) and almost no transmission in the IR range. The reflection in the visible range is very low, but a steep cutoff starts at about 800 nm and the reflection reaches about 90% at around $1\mu\text{m}$ wavelength. The IR reflection remains higher than 90% at longer wavelengths in the IR range, forming a plateau. This shows the designed structure can be used as highly visible transparent IR filters.

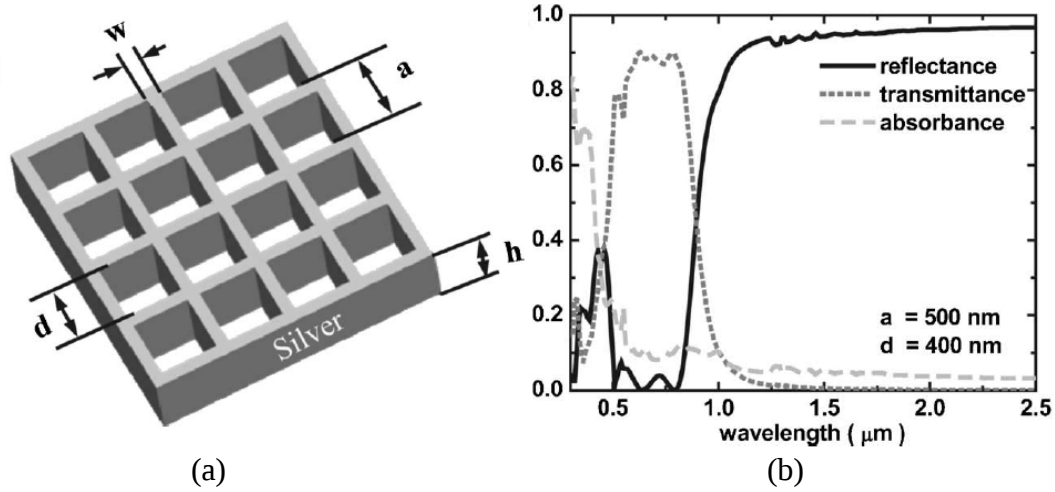


Figure 52: (a) the 2D photonic crystal structure design and (b) the theoretical values of the optical properties of the structure [71]

iii. Theoretical calculations based on 1D grating structures

We performed theoretical calculations based on our 1D high aspect ratio metal structures using a transfer-matrix method (TMM) simulation package. [72] The infrared reflections were plotted and characterized. The structure is designed so that it has similar dimensions as the ion milled samples. The periodicity is set at $2.5\mu\text{m}$, and the width is $1.2\mu\text{m}$. As illustrated in Figure 53, when the polarization angle is set at 90 degree, the electric field of the incident light is perpendicular to the grating direction, and the light is transmitted through the structure. When the polarization angle is set at zero degree in the program, the electric field of the incident light is parallel to the grating direction, and the light is absorbed and reflected from the metal on the sidewalls of the grating structure, which results in high reflection.

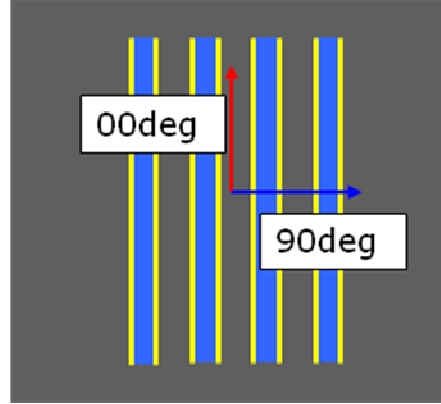


Figure 53: The design of the 1D grating structure and the two polarizations of the incident light

In Figure 54 (a), the height of the structure varied from $0.2\mu\text{m}$ to $1.4\mu\text{m}$ to study the effect of the structure height on the IR reflection characteristics of the structure. The gold thickness on the PU sidewalls is set at constant 50nm for all heights. The specular reflection for both polarizations of different heights was then calculated. The spectra show that for 90 degree polarization, the incident light is mostly transmitted through the structure and the reflection is at a minimum below 10%. For the zero degree polarization, the reflection starts to increase at the cutoff wavelength around 2000nm , which is correspondent to the periodicity of the metallic grating structure. The reflection for $0.2\mu\text{m}$ height slowly increases to around 60% from the cutoff wavelength to longer wavelength. As the height increases, the reflection intensity keeps increasing. For heights above $0.8\mu\text{m}$, a plateau forms at an intensity approaching 90% above 4000nm wavelength. Therefore, we can anticipate that for the real structure with $1.2\mu\text{m}$ height, the IR reflection for zero degrees will be high as well. In Figure 54(b), we chose the dimensions of the PU grating structure with the height fixed at $1.2\mu\text{m}$ and varied the metal thickness from 25nm to 75nm . The spectra show that even at 25nm thickness the reflection intensity is still high and close to around 90% for the zero degree polarization. The cutoff frequency remains around 2000nm wavelength, while the plateau is form at around 4000nm wavelength.

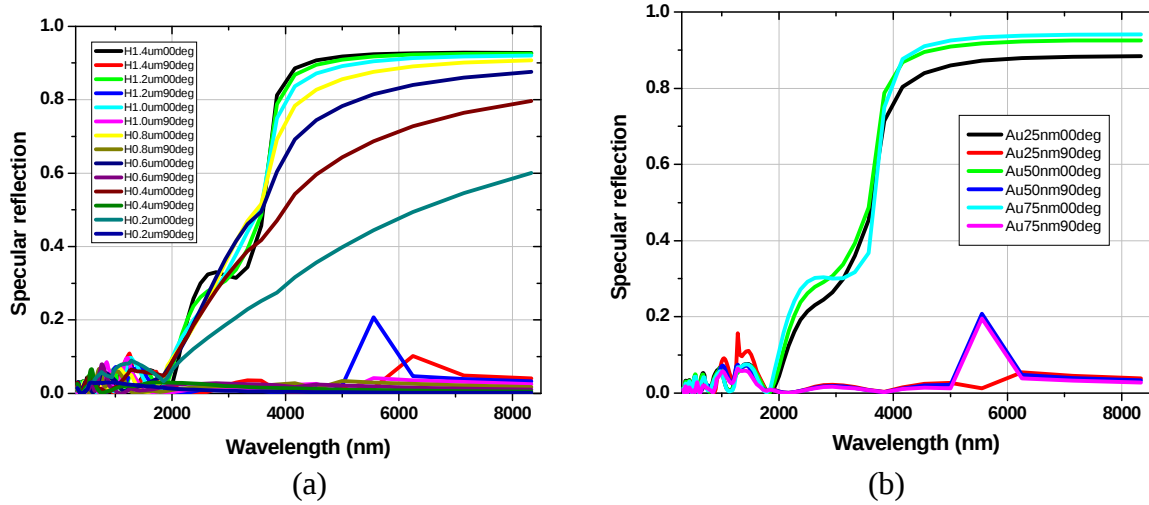


Figure 54: (a) PU one-layer on glass pitch = $2.5\mu\text{m}$, width = $1.2\mu\text{m}$, Gold sidewalls 50nm thickness, with varying heights and (b) PU one-layer on glass pitch = $2.5\mu\text{m}$, width = $1.2\mu\text{m}$, height = $1.2\mu\text{m}$, with varying thickness of gold sidewalls

We also carried out the calculations for $1\mu\text{m}$ periodicity.. The width is also reduced to 400nm. The reflection characteristics are similar to that of the $2.5\mu\text{m}$ periodicity one but the cutoff frequency is around 900nm wavelength, which is at the edge of the near infrared regime and it is of great interest for heat mirror applications. In Figure 55 (a), the periodicity and width is fixed at $1\mu\text{m}$ and 400nm, respectively, while the height is varied from 200nm to 800nm. The gold thickness is also held constant at 65nm. The spectra show that for 90 degree polarized light, the reflection intensity in infrared regime is very low and close to almost zero. The large reflection peak for 800nm at around 1500nm wavelength is possible due to enhanced plasmonic effect of the metal structure. Such effect is also shown in 600nm height at smaller peak intensity. For the zero degree polarization, the reflection intensity starts to increase at around 900nm wavelength. The reflection is already very high, approaching 90% for 200nm height. At 400nm height and beyond, the flat plateau is clearly shown at around 1500nm wavelength. This indicates high reflection for such dimensions in the near IR range.

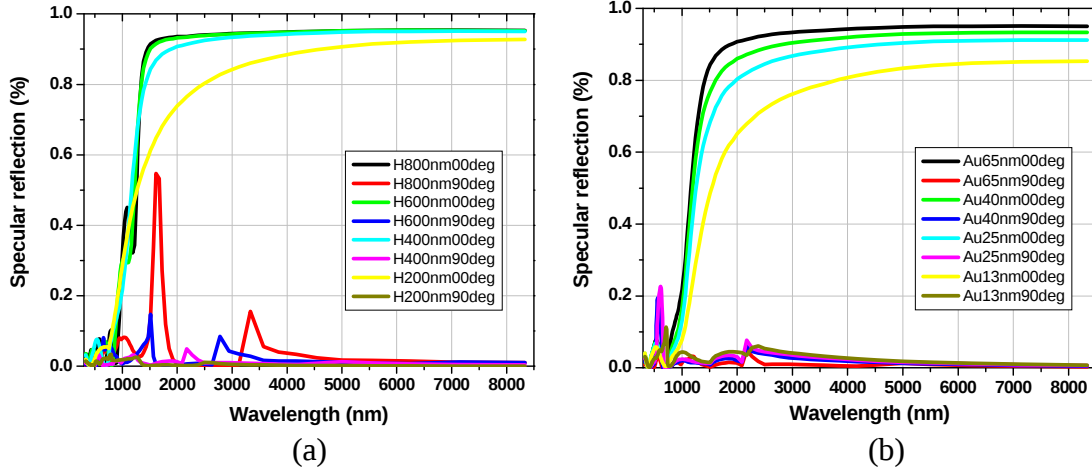


Figure 55: (a) PU one-layer on glass pitch = $1\mu\text{m}$, width = 400nm, Gold sidewalls 65nm thickness, with varying heights and (b) PU one-layer on glass pitch = $1\mu\text{m}$, width = 400nm, height = 400nm, with Gold sidewalls varying thickness of gold sidewalls

In Figure 55 (b), the height of the structure is fixed at 400nm, and the gold thickness is varied from 13nm to 65nm. For the 90 degree polarization, the reflection is low for all the thickness from 13nm to 65nm. For the other polarization, the cutoff wavelength also starts at around 900nm wavelength, and even at 13nm gold thickness the specular reflection is above 80% at the plateau area. The plateau moves closer to around 1500nm wavelength when the gold thickness is increased from 25nm to 65nm. This shows at very small thickness the IR reflection is already high for the zero polarization.

iv. Experimental results of the ion milled structures

An FTIR spectrometer (Nicolet 760) was used to measure the specular infrared reflection of the ion milled samples. In Figure 56 (a) and (b), the specular reflection from 450 nm to 5000 nm wavelength is plotted for both theoretical and measured 1D grating structures with 40nm silver sidewalls. The PU grating dimensions are also the same with the periodicity of $2.5\mu\text{m}$, height of $1.2\mu\text{m}$, and width of $1.2\mu\text{m}$. For this measurement, IR polarizers were used to separate the light source into transverse electric (TE) mode and transverse magnetic (TM) mode. In TE mode, the electric field is perpendicular to the grating structure (90 degree polarization), and in TM mode, the electric field is parallel to the grating structure (zero degree polarization), and reflections of both modes were measured.

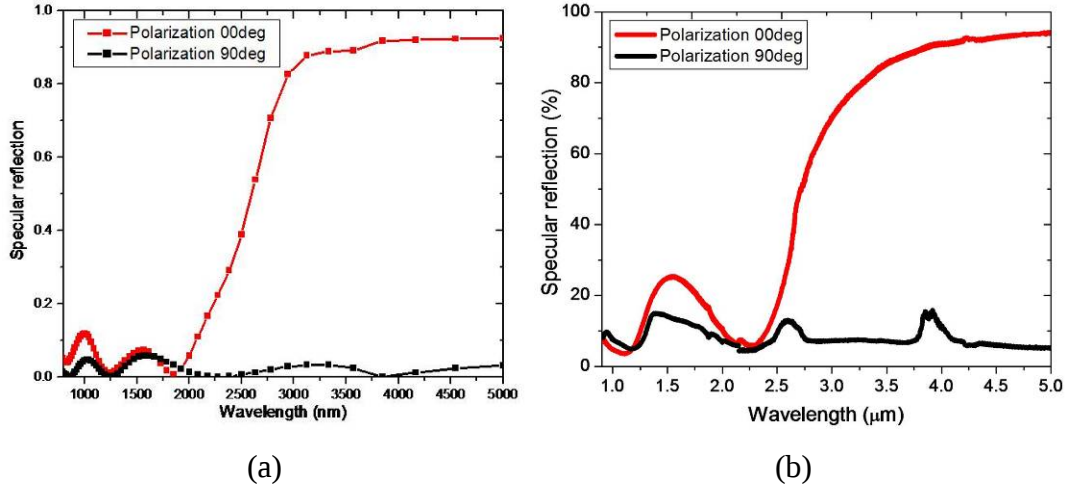


Figure 56: (a) Calculated and (b) measured specular reflection of a one-layer PU grating structure (periodicity = $2.5\ \mu\text{m}$, width = $1.2\ \mu\text{m}$, height = $1.2\ \mu\text{m}$) on glass substrate with 40nm silver sidewalls

For both calculated and measured spectra, the results show very similar IR reflection for both modes. For TE mode, the reflection is close to zero. This is because the electric field of the incident light is aligned perpendicular to the metal coated PU grating and the light sees minimal amount of metal in this direction. Therefore, most IR light is transmitted, resulting in a very low reflection. In the contrary, the TM mode has electric field aligned parallel to the direction of the metal grating. The reflection in the near IR range is also very low. A cutoff starts at around 2000nm wavelength for the calculated spectrum, and a plateau is formed at 3000nm wavelength and the reflection intensity can reach above 90%. Similarly, a cutoff at about 2200 nm wavelength is formed for the measured spectra, and the reflection is increased substantially to more than 80% at about 3000nm wavelength. A plateau is formed with average reflection intensity near 90%. The high reflection in this range results from the electric field of the TM mode light source interacts with the metal along the grating direction, and most of the light is absorbed and reflected back. Therefore, the experimental result shows our structure is highly reflective for infrared light in one polarization and can be used as an IR polarizer, and the average of both polarizations will have about 45% reflection. This indicates our structure is feasible for IR reflection in hot mirror applications.

v. Quasi-2D structure with high mid-IR reflection

To realize high IR reflection in both polarizations, the first intuition would be to make a second layer of PU grating structure on the one-layer ion milled structure and aligned perpendicularly to the first layer, and repeat the angle deposition and argon ion milling to form metallic sidewalls on the second layer. However, as shown in Appendix A, the ion milling process will be perpendicular to the first layer PU and remove the PU and metal sidewalls, which are exposed to the ion beam during the milling, altogether. Therefore, the first layer would not be a continuous grating structure and would not be effective.

As an alternative solution and to test the feasibility of our structures as IR reflector for both polarizations, we fabricated the 1D grating structures on two sides of a substrate to form a quasi-2D structure. Because glass substrates have some absorption in the mid-IR range, we chose a 400 μm sapphire as the substrate. In this scheme, two one-layer PU grating structures were fabricated on both sides of the substrate, with them aligned orthogonally to each other at around 90°. The dimensions of the PU grating structure is the same as for prior samples. The periodicity is 2.5 μm , the width is 1.2 μm , and the height is 1.2 μm . Silver was deposited using the angle evaporation technique to coat the sidewalls as well as the top of the PU bars, and the metal on the PU top surface is removed by the argon ion milling. The schematic of the quasi-2D structure is shown in Figure 56 (a). When a white light source was passed through the structure, the transmitted light forms a 2D diffraction pattern. (Figure 57 (b)) The measured total transmission is still around 60% for the visible light.

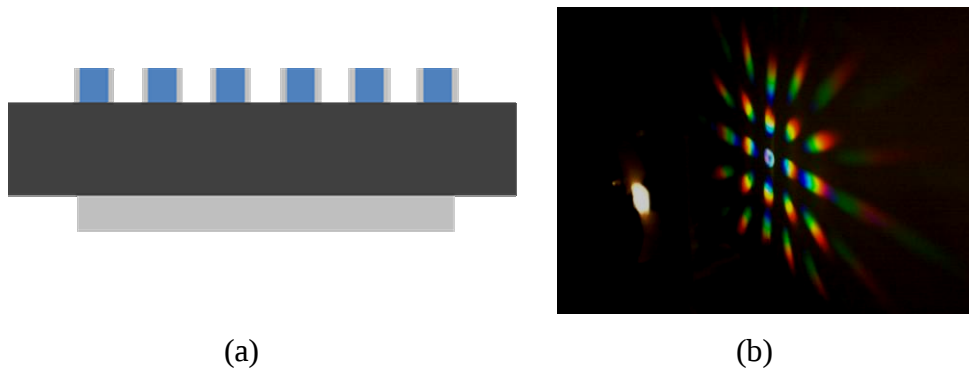


Figure 57: (a) Schematic of the quasi-2D structure and (b) the 2D diffraction pattern form with a visible light source transmitted through the structure

The infrared optical properties of the structure were also measured with an FTIR spectrometer and IR polarizer. The reflection in mid-IR range is shown in Figure 58. When the polarizer was aligned parallel to the top layer grating structure (Alignment 2), the reflection has a cutoff at around 2200nm wavelength, and the intensity increased quickly to above 80% at 3000nm. A plateau appears from 3500nm to 4000nm and the intensity saturates above 90%. When the polarizer was aligned orthogonally to the top layer grating (Alignment 1), the cutoff wavelength also started at around 2250nm, and the reflection intensity gradually increased to above 70-80% at around 4000nm. Small absorption dips appear around 3400nm and 4200nm wavelengths, which are due to the absorption by the PU polymer in those wavelengths. The average reflection intensity of both polarizations is about 80%. This shows our structure is suitable to be used as hot mirrors in IR reflecting applications.

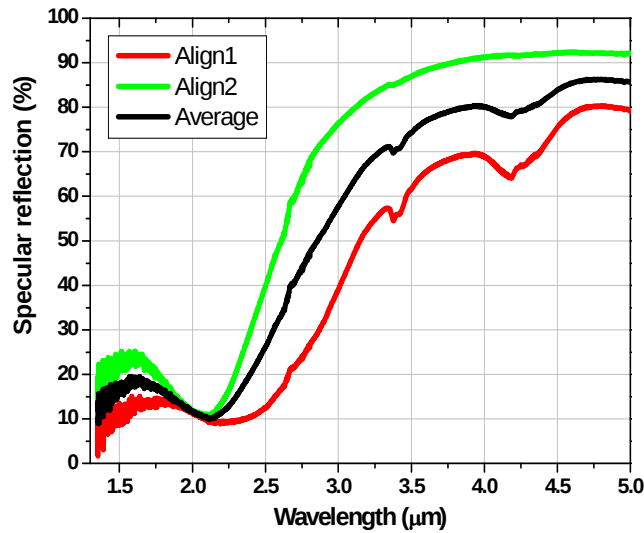


Figure 58: Specular reflection of the structure at two polarizations and the average

vi. Design of 2D LBL structure

It is imperative to achieve the actual 2D structure (rather than the quasi 2D structure) for high IR reflection in both polarizations. Such structure should be fabricated with a different experimental approach using a top-down process such as reactive ion etching

(RIE) to remove the metal on the PU top surface without removing the PU. The design of such structure is shown in Figure 59 (a) in top view and (b) in perspective view. Therefore, the structure would have high reflection in the infrared range in both polarizations.

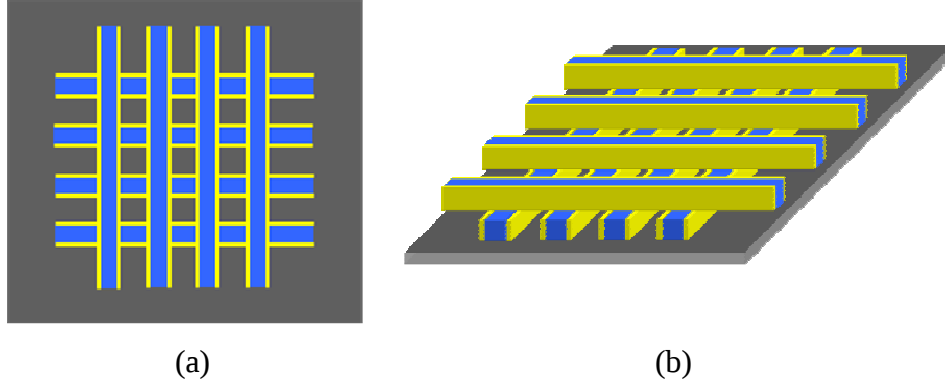


Figure 59: schematics of the real 2L structure from (a) top view and (b) perspective view

The theoretical value of the specular IR reflection was calculated and plotted in Figure 60. The spectra show the cutoff also starts at about 2000nm wavelength for both polarizations. There are also some dips in the range between 2000-4000nm wavelengths. Nevertheless, at wavelengths above 4000nm, the reflection intensity of both polarizations quickly rises to above 90% and then plateaus. Therefore, the structure is a very good spectral reflector in the mid-IR range. However, it is necessary to reduce the periodicity to $1\mu\text{m}$ in order to use such structure for near-IR reflection.

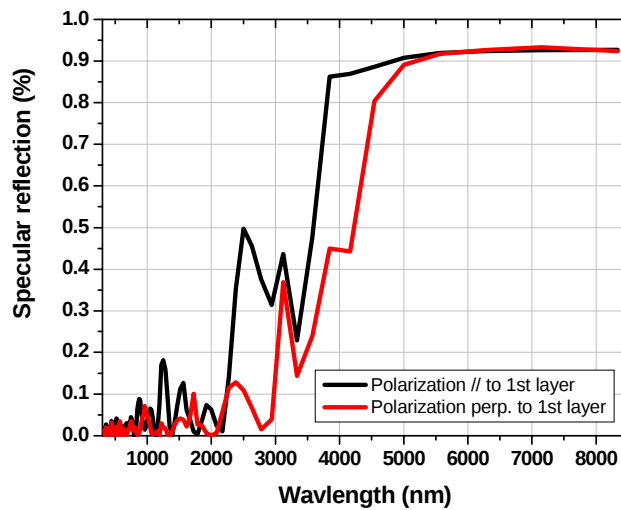


Figure 60: Specular reflection of the 2L structure with $2.5\mu\text{m}$ periodicity, $1.2\mu\text{m}$ width, $1.2\mu\text{m}$ height, and with 50nm Au on both sidewalls

5. Lower aspect ratio structure

i. PU grating structure

We also fabricated structures with the same periodicity but at a smaller height and studied optical and electrical properties. A photoresist master with $2.5\mu\text{m}$ periodicity, $1.2\mu\text{m}$ width, and 300nm height was first fabricated on a silicon wafer. PDMS molds were made using the master, and 2P- μTM was used to make one-layer PU grating structures on a glass or sapphire substrates. The SEM images of the PU grating structure show the periodicity is around 2400nm and the height is around 300nm . (Figure 61 (a)) The total area is as before at 4mm^2 . The yield is also very high at above 99%.

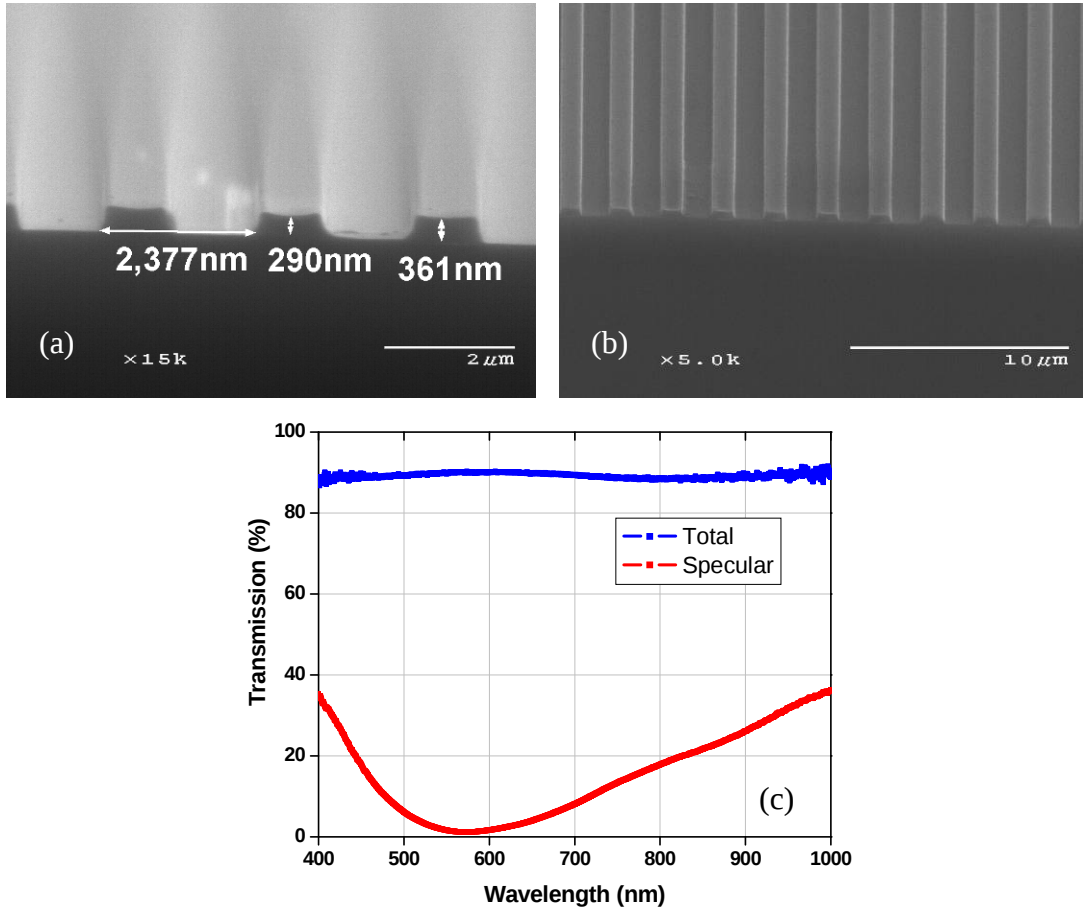


Figure 61: SEM images of PU one-layer grating with $2.5\mu\text{m}$ periodicity, $1.2\mu\text{m}$ width and 300nm height at (a) $\times 15000$ resolution and (b) $\times 5000$ resolution, and (c) the total and specular transmission of the grating structure on glass substrate

The specular and total transmission for these structures were measured. (Figure 61 (c)) The measured specular transmission in visible range shows a dip at around 550nm almost approaching 0%. At shorter or longer wavelengths, the specular transmission reaches around 40%, which is not high enough for the transparent electrode applications. However, the total transmission measured with the integrating sphere is much higher in the entire wavelength range. The transmission intensity is almost flat and is above 90% from 400nm to 1000nm wavelength, which is only 2% lower than the glass substrate but about 5% more than the similar grating structure with 1.2 μ m height. Therefore, we can anticipate the structure would also have higher transmission with metal deposited on the PU sidewalls.

ii. Lower angle deposition for metal evaporation process

Since the height of the structure is decreased from 1.2 μ m to 300nm while the width is the same at 1.2 μ m, the aspect ratio of the PU bars is also changed from 1:1 to 1:4. If the angle of the metal evaporation was still kept at 45°, the channels between adjacent PU bars would be coated with metals. This would greatly reduce the optical transmission since the additional metal coating in the channels could block additional light transmitted through the structure. It was found that, when the deposition angle was 14° with respect to the sample surface, the metal was deposited only on the sidewalls and top of the PU bars. (Figure 62) Therefore, we used the 14° deposition angle for the samples with 300nm height. The samples were also ion milled after the metal deposition and optical and electrical measurements were done for characterization.



Figure 62: Schematic for the lower angle metal deposition at 14°

iii. Optical transmission and electrical resistance results

The optical transmission of the structure was also measured using the integrating sphere for the total transmission. The measurements were done for gold and silver samples with two different thickness, 30nm and 60nm, before and after the argon ion milling step. In Figure 63(a), the spectra show that, the transmission for gold samples with 30nm sidewall thickness can reach over 60% before ion milling. This is because at lower angle evaporation, the metal deposited on the PU top surface ($\sim 15\text{nm}$) is much thinner than the metal deposited on the sidewalls and is also below the skin depth for visible light. Therefore, some light can transmit through the metal on the PU top surface along with the light transmitted through the channels without metal coating. After the sample is ion milled, the average total transmission increases to more than 86%. Such transmission is almost as high as an ITO coated glass. Therefore, our structure can also have equivalent optical performance as the standard transparent electrode when the structure dimensions are optimized. Similarly, for the 60nm thick gold samples, the total transmission before ion milling is also around 60%, and after ion milling the transmission is increased to around 82%, which is also relatively high.

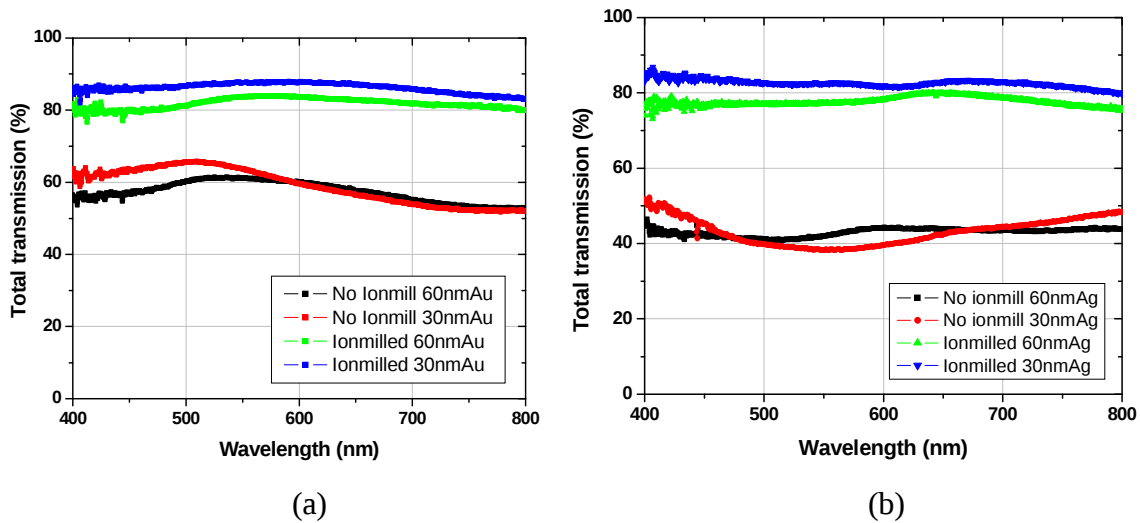


Figure 63: (a) Total transmission of the 300nm height structures with 30nm and 60nm gold sidewall thickness before and after argon ion milling (b) Total transmission of the 300nm height structures with 30nm and 60nm silver sidewall thickness before and after argon ion milling

For the silver samples, the total transmission before ion milling for both thicknesses was around 40%, possibly due to higher reflection of silver. After ion milling, the transmission was increased to around 78% for the 60nm Ag sidewalls and 83% for the 30nm Ag sidewalls. Both are also high and suitable to be used as transparent electrodes if their conductivities are also good.

We used the same scheme as for the high aspect ratio samples to measure the electrical resistance of the 300nm samples. Nevertheless, with 300nm height, these samples should not be regarded as low aspect ratio structures since the metal sidewalls are still tall with respect to their thickness. The aspect ratio is also high at 10:1 for the 30nm metal sidewalls and 5:1 for the 60nm metal sidewalls. It is anticipated that with lower volume of metal material coated on the sidewall due to the lower height, the resistance of the 300nm height structures would be higher. With metal contacts or silver paste deposited on the two ends of the sample with around 3mm separation, the resistance was measured and the results are listed in Table 6.

Table 6: Average resistance (Ω) of gold and silver samples with different thickness

	30nm (Avg.)	60nm (Avg.)
Gold	190.2	27.8
Silver	42.5	7.1

We noticed a significant change in resistance for the gold samples when the thickness is reduced from 60nm to 30nm. For 60nm thick gold, the resistance is 27.8 Ω , but the resistance is increased to about 190 Ω at 30nm, which is more than 6 times of increase when the thickness only reduced by half. A similar increase also was observed in silver samples, where the resistance was increased from 7.1 Ω to 42.5 Ω , also a 6 times increase when the thickness is reduced from 60nm to 30nm. It is possible that at 30nm thickness at smaller height, the metal film is not as homogeneous or continuous and the resistance could increase exponentially in such a thickness range. Other metal thickness should be studied to understand this issue fully. Nevertheless, at 60nm thickness, the resistance is

sufficiently low and the optical transmission is high enough to test its performance as transparent electrodes.

iv. Solar cell device fabrication

We fabricated an organic solar cell device using the 300nm height sample after ion milling to test its performance as a transparent electrode. PEDOT:PSS and P3HT:PCBM blends were spin coated onto the structure and aluminum contact electrode was evaporated on the top, following the same parameters for making the solar cell device with the inverted structure. The SEM images in Figure 64 show the device at different magnifications for a 300nm height structure with 60nm silver sidewalls after the argon ion milling.

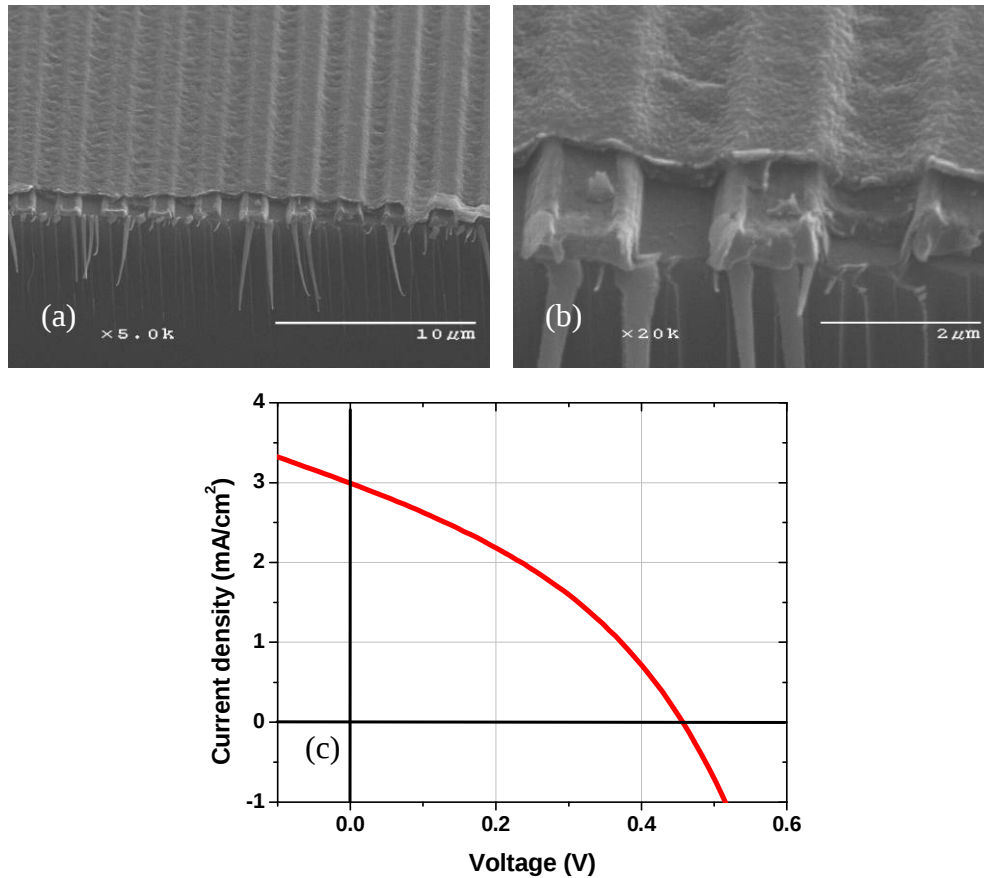


Figure 64: SEM images of the solar cell device fabricated on a 300nm height structure after ion milling with 60nm silver sidewalls at (a) x5000 magnification and (b) x20000 magnification, and the I-V characteristics of the device

The SEM images show the organic layers were conformally coated on the grating structure and the corrugated surface is still observed after aluminum contact deposition. The grating structure underneath shows the metal sidewalls are in contact with the active layers. The device has a short circuit current density of $2.92\text{mA}/\text{cm}^2$, an open circuit voltage of 0.4553V , and the fill factor is estimated at about 35%. The power conversion efficiency is calculated to be about 0.47% using Equation 4. Textured surface could be used to improve the efficiency of ITO-based organic solar cells with similar grating dimensions. [73] However, this structure still has lower efficiency than one based on ITO-coated substrate. Possible reasons are shorting between the aluminum counter electrode and the silver metal sidewalls at the top of the PU bar corner edge due to very thin or no organic layer coating at the edge. A PEDOT:PSS layer was used to improve the hole collection and conduction from the active layer to the metal grating electrode underneath. It is also possible that the PEDOT:PSS spin coating on the grating structure could raise issues for the performance. To illustrate this, we spin coated only PEDOT:PSS layer on a 300nm height PU grating sample to check the coating uniformity on the corrugated surface.

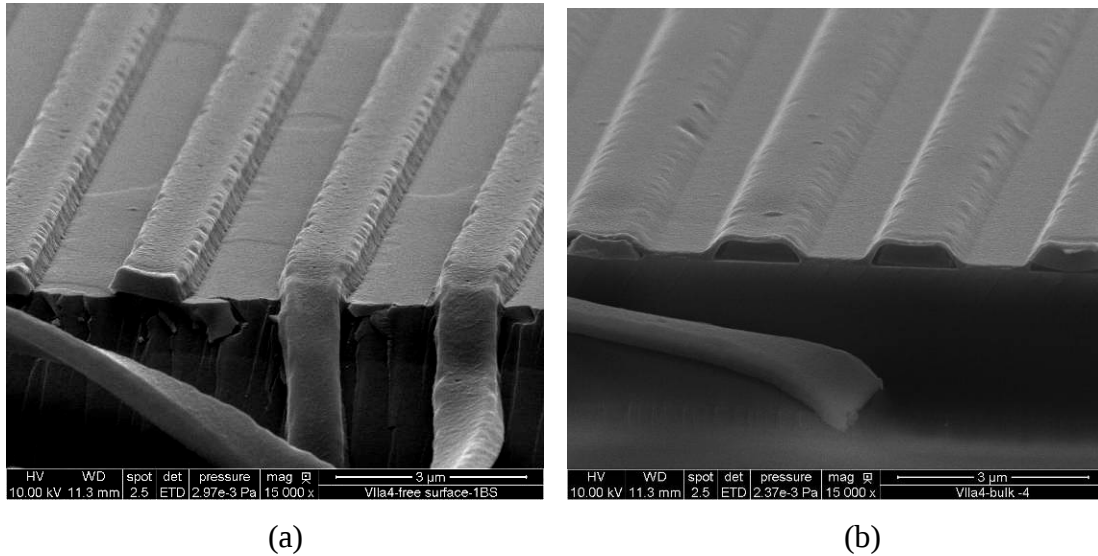


Figure 65: Spin coating of PEDOT:PSS on a 300nm height PU grating sample at different areas with (a) minimal coating on the PU top surface and in the channels, (b) and continuous conformal coating

In Figure 65 (a), we observed the PEDOT:PSS was not conformally coated on the grating structure. Some disconnected PEDOT:PSS layers can be seen in the channels of

the grating, while some PEDOT:PSS may have deposited on the PU top surface. On the other hand, we observed a continuous conformal coating of PEDOT:PSS in some areas of the sample. (Figure 65 (b)) We believe these areas provide the best conduction between the PEDOT:PSS and the metal grating structure below, and no sharp edges of the metal would be exposed through the active layers to short with aluminum counter electrodes. Therefore, it is crucial to optimize the spin coating process to create a better PEDOT:PSS layer on top of the grating surface in order to improve the efficiency of our structure as transparent electrodes.

CHAPTER 4. SCALE-UP PROCESS FOR LARGE AREA SAMPLES

1. Introduction

To realize these transparent electrode structures for possible commercialization, it is necessary to increase the sample area to an industrially applicable size. We used a standard photolithography process to fabricate 2x2 in² 1D grating photoresist (PR) patterns as masters to make PDMS molds, and PU grating structures were made by direct printing of PDMS on PU prepolymer. The angle metal deposition was again used to coat the PU grating structure on the sidewalls as well as the top. Because the available argon ion milling machine cannot accommodate large area samples for etching, an argon plasma etcher was first used to etch the metal on the top PU surface. The optical and electrical properties of the structures were characterized. To reduce the diffraction effects for display and light applications, we applied encapsulation to the etched structures and we studied the optical properties of the encapsulated structure. Finally, the top metal was removed by argon ion milling carried out at the University of Minnesota. This shows that much better etching is achievable and should be investigated further for large area sample fabrication in the future.

2. Large area photoresist pattern by photolithography

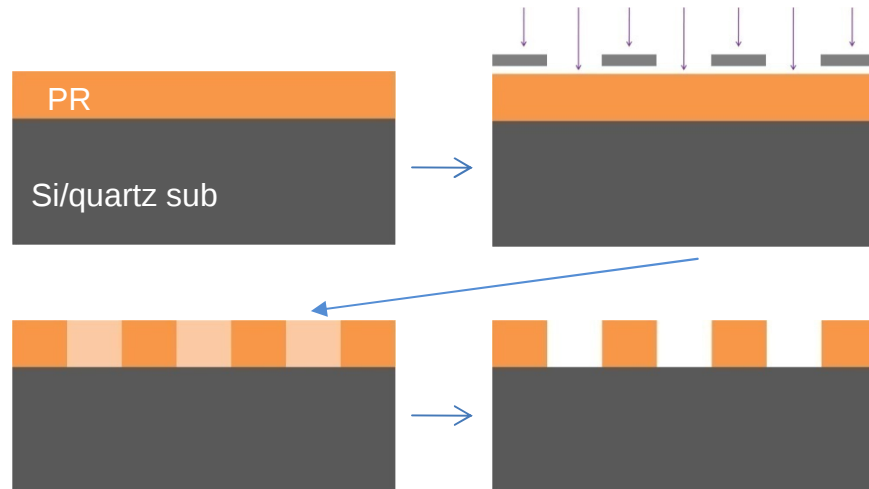


Figure 66: Schematics for photoresist pattern fabrication

One dimensional PR grating patterns were made by standard photolithography. Photoresist solutions are dispensed and spin-coated onto a substrate, typically 3 inch silicon wafers. Different photoresist, AZ5214 or HiR 1075, was used to vary the thickness creating PR patterns with two different heights, 1400nm and 300nm. A chrome mask with a $2 \times 2 \text{ in}^2$ area was used during the contact UV exposure to remove unwanted areas on the PR film. After the exposed PR was dissolved away by the developer, a grating pattern is formed. (Figure 66)

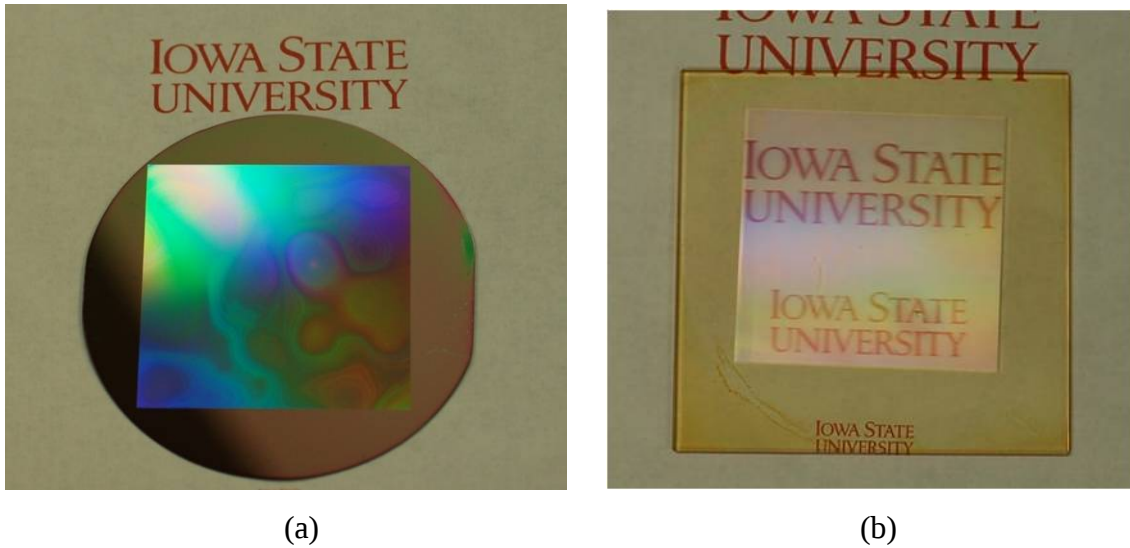


Figure 67: Digital images of (a) $2 \times 2 \text{ inch}^2$ photoresist grating pattern on a silicon substrate and (b) $2 \times 2 \text{ inch}^2$ PR on a quartz substrate

Figure 67 (a) shows the photoresist grating pattern fabricated on a 3 inch silicon wafer. The overall quality of the pattern is good with some visible newtonian rings created during the UV exposure, where the chrome mask was pressed mechanically against the photoresist and pressure differentials were induced at different areas. The PR grating pattern can also be made on a transparent substrate such as glass or quartz. (Figure 67(b)) The grating pattern shows a rainbow color due to the diffraction, and the image shows high transparency and that the ISU logo underneath can be clearly seen.

3. PU one-layer grating fabrication by direct printing

The 1D PR grating pattern was used to make the PDMS following the same soft lithography process. Then the PDMS mold was used to replicate the grating pattern onto the PU. The PU prepolymer was first dispensed on a transparent substrate, then the PDMS mold was brought into contact and mechanically pressed onto the prepolymer. The PU was solidified by UV curing. The PDMS mold was then peeled off from the PU and the 1D grating pattern was transferred to the PU. (Figure 68) During the printing process, excess PU could not be squeezed completely at the bottom, an underlayer PU is formed. This process is not suitable for structure inversion. Nevertheless, in many cases that don't require inversion, this approach is simple and cost-effective for some applications.

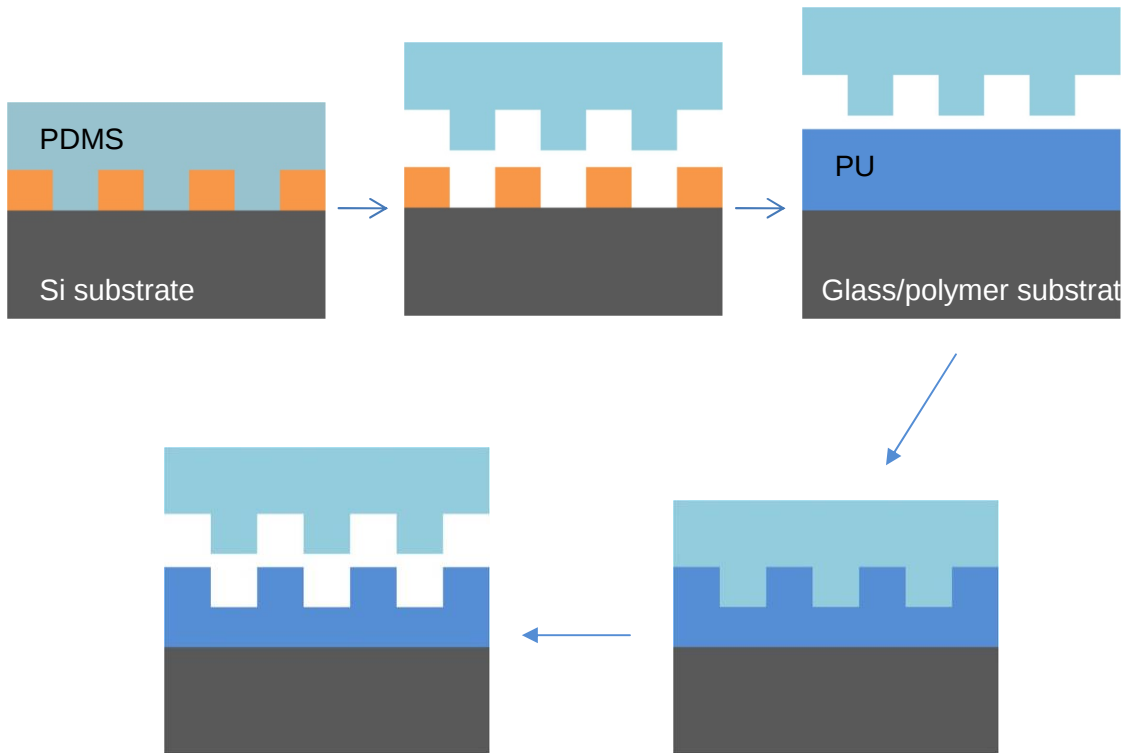


Figure 68: Schematics for PU one-layer grating pattern fabrication

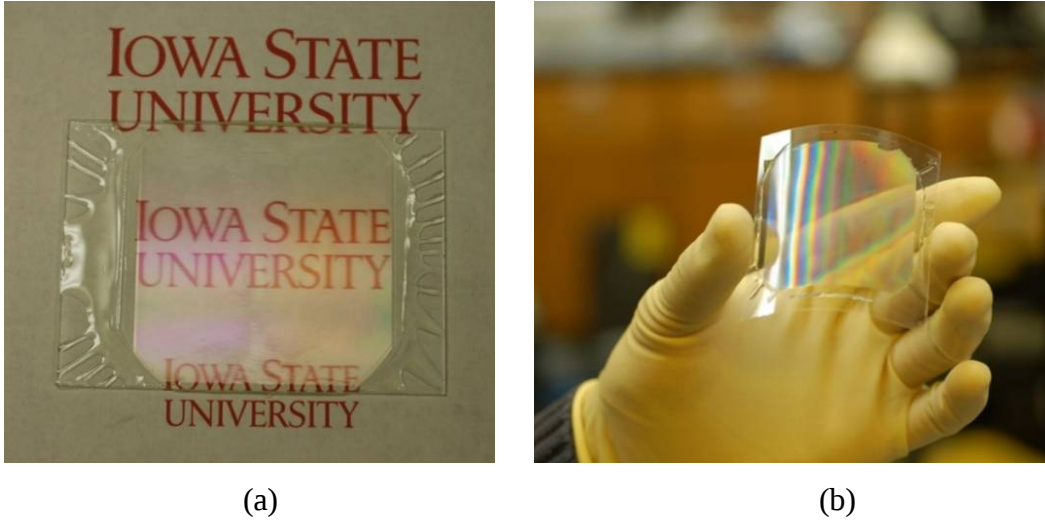


Figure 69: Digital images of (a) 2x2 inch² PU one-layer grating pattern on glass substrate and (b) on flexible PET substrate to show the flexibility of the sample

Figure 69 shows the PU one-layer grating structure on different substrates. The PU grating on the glass substrate also shows rainbow color from the reflection, and the logo underneath can be clearly seen without distortion. The measured total transmission is also high and the same as the smaller area samples, around 85-86% over the entire visible wavelengths. The PU grating structure can also be fabricated on a flexible substrate such as PET films. (Figure 69 (b)) This shows our structures can be utilized for more novel device applications. Further studies on this should be pursued.

4. Metal depositions (angle and conformal depositions)

After the PU grating structure is made, metal depositions are carried out to form metallic coatings on the PU surface. Both sputtering and angle evaporation can be applied for the metallization step. Then argon plasma etching is performed to remove the metal on PU top surface or in the channels of the grating structure. The etching process is highly anisotropic, so only the metal on top and in the channels is etched but the metal sidewalls are intact. (Figure 70)

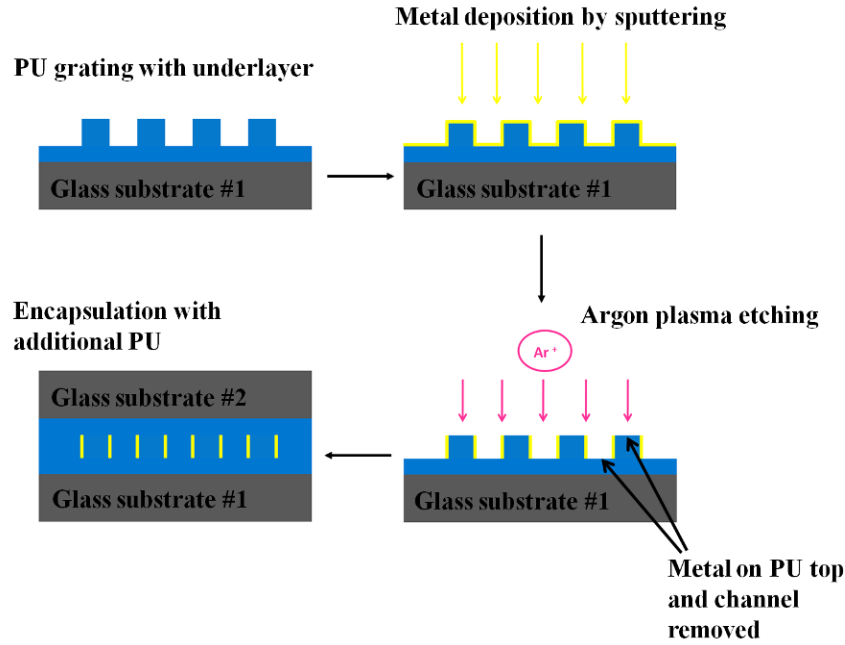


Figure 70: Schematics for large area metal deposition, argon plasma etching, and encapsulation process

For applications such as solid-state lighting and smart windows, the diffraction effect from the grating structure must be reduced. This can be done through an encapsulation process. (Figure 70 (d)) In this case, additional PU liquid prepolymer is placed on top of the etched structure and UV cured, with a second glass substrate enclosing the entire structure. The additional PU fills the air channels between the metal sidewalls to reduce the diffraction effect from the grating pattern.

5. Argon plasma etching

i. Background

Plasma etching, or dry etching, is one of the most widely used techniques in semiconductor processing. It has a wide range of applications from removing organic contaminants to patterning silicon wafers. It is also used to etch metallic films and it is a suitable method to remove unwanted metal layers in our large area structures. In plasma etching, argon or other reactive gas is introduced into the vacuum chamber at low pressure. The radiofrequency (RF) generator is connected to the cathode is used to

energize the electrons and ionize gas atoms to form a plasma. Some of the argon ions escape from the plasma and physically bombard the sample placed on top of the sample stage. (Figure 71) The argon plasma etching process is affected by factors including the argon pressure level and the RF power. In this research we only used argon gas for the etching. [74]

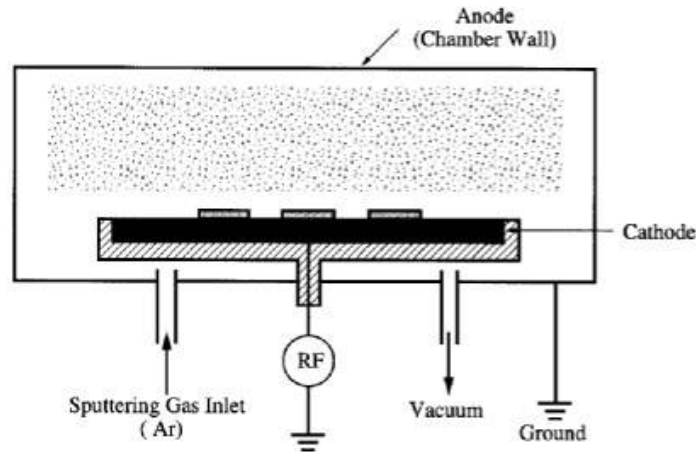


Figure 71: the argon plasma etching process [74]

ii. Argon plasma etching of thin metal films

We first investigated the argon plasma etching on large area metal thin films deposited on glass substrates. It was found that the etching was not complete or homogeneous, and much of the metal remained especially in the center of the sample. The possible cause is that the glass substrate is an insulator and does not conduct between the metal film and the sample stage (cathode). Therefore, the argon ions created in the plasma are only weakly attracted to the cathode and do not gain sufficient energy to effectively bombard the metal film especially in the center of the sample. Therefore, the setup was modified to improve the etching. A copper mesh was placed on top of the metal film sample, and it was also connected to the cathode. (Figure 72)

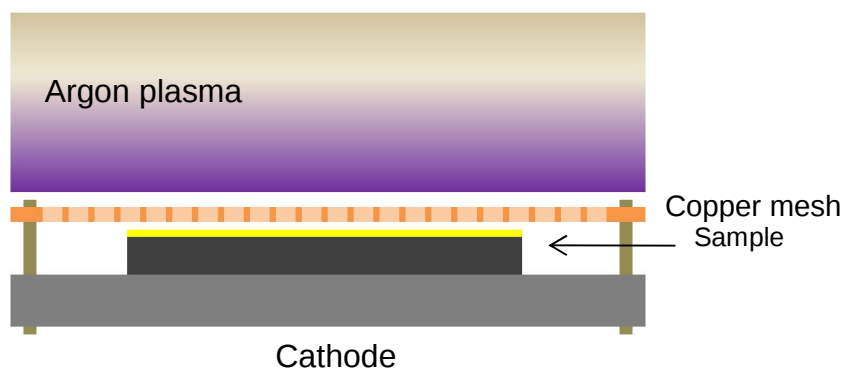
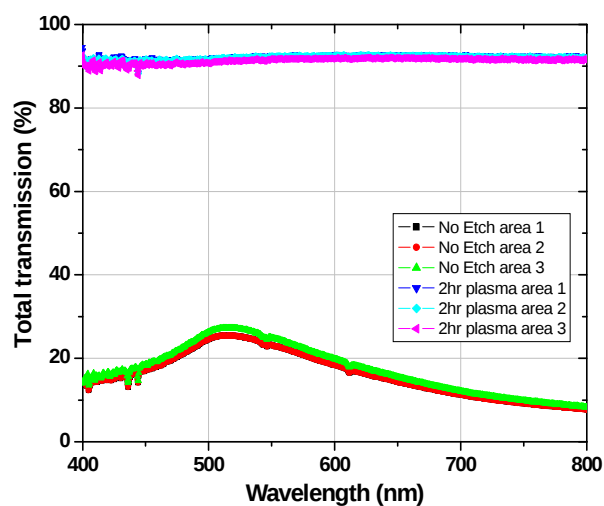


Figure 72: Modified argon plasma set up with copper mesh

In the modified configuration, the argon ions are attracted to and accelerated by the mesh, and some of the argon ions can pass through the mesh and bombard the metal film underneath. It is also likely that the copper mesh gets etched at the same time during the process. The mesh was adjusted during each etching interval to expose the non-etched areas. When the process is complete, the etching is much more uniform and all the areas were etched homogeneously.



(a)



(c)

Figure 73: (a) Comparison of 50nm gold films on glass before and after plasma etching (b) measured transmission spectra of the 50nm Au film before and after plasma etching

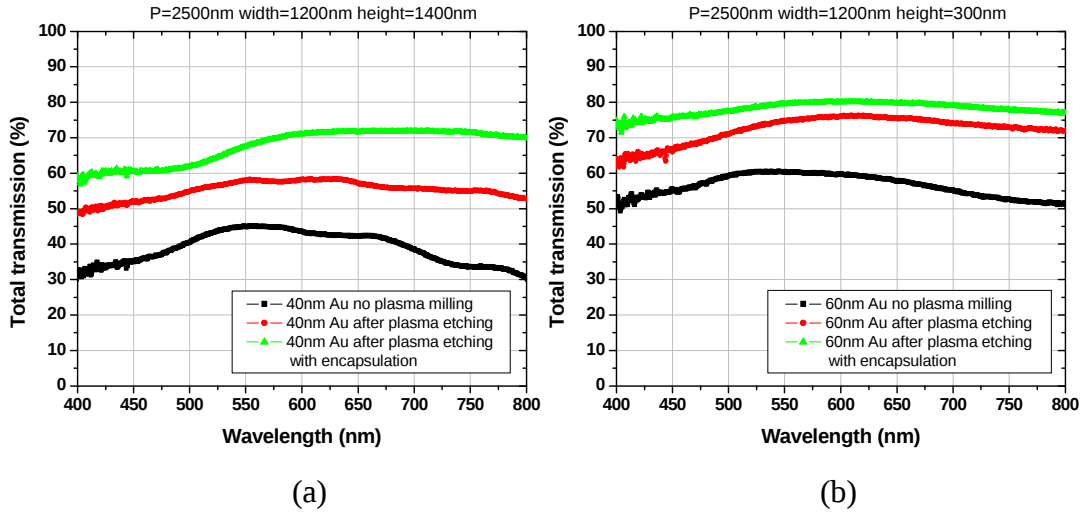
Figure 73 (a) shows the still image of a 50nm gold film on glass before and after argon plasma etching. Before plasma etching, the 50nm gold film shows the typical golden color, while the logo underneath is somewhat visible because the metal thickness is in the

range of the skin depth. The spectra in Figure 73 (b) show that before the plasma etch, the transmission is about 15-20% with a transmission peak at around 550nm wavelength. After plasma etching, all the metal underneath the copper mesh was removed completely, showing clearly the logo image underneath (Figure 72 (a)). The total transmission is increased to around 92%, the same transmission as the glass substrate. Therefore, the argon plasma is a viable technique for removing metal thin films and it was used to etch thin metal coatings on the large area PU grating structures.

iii. Plasma etching for 1D grating structure

a. Total transmission of the structure

We then tried the argon plasma etching on metal coated grating structures. Angle depositions were done to coat the sidewalls and the top of the PU grating structures with different heights. Then the samples were wrapped in aluminum foils and copper meshes were placed on top of the patterned area to perform the argon plasma etching.





(c)

Figure 74: The measured transmission spectra for structures (a) with 1400nm height (v) and with 300nm height with gold sidewalls before and after plasma etching, (c) and the image of a 300nm height structure with gold sidewalls after plasma etching

Figure 74 (a) shows the transmission spectra of a 1400nm height sample before plasma etching, after plasma etching, and after encapsulation. Before etching, the transmission is similar to that of the high aspect ratio structure with smaller area at around 40-45%. With argon plasma etching, the maximum transmission obtained was only around 60%. This is because while the metal on top of PU bars are being etched, the PU underlayer in the channels is also exposed to argon ions and it is more easily etched by the argon ions. This will create a much deeper trough in the channels and enhance the diffraction effect of the grating structure. Furthermore, for the PU grating where the metal top is removed, the PU material in between the two metal sidewalls could also be etched if the process is not stopped. However, when the structure is encapsulated, PU prepolymer fills inside the channels and significantly reduces the diffraction effect. In this case, the measured total transmission is improved to above 70% for wavelengths beyond 600nm. For the 300nm height structure, the transmission is already 60% before etching, similar to that of the smaller area samples. After plasma etching, the total transmission is increased to about 77%. With encapsulation, the transmission intensity was further increased to 80%. Figure 74(c) shows a 300nm height sample after the argon plasma etching. It shows the transmission is much higher than non-etched areas outside the pattern, and the logo underneath is clearly seen without distortion. However, some areas are not completely etched and they show the grid of the copper mesh. For the taller structure, the total transmission is 10% less than ion milled smaller samples, and the shorter structure has

also a 2-3% decrease. Therefore, the plasma etching is not as good as the argon ion milling. The SEM images show that after the plasma etching, the gold coating on top of the grating edge may not be completely etched off, and there are many particulates on top of the grating as well as in the channels. It is possible that there is some redeposition of gold or copper from the mesh onto the structure. These additional defects may lower the transmission of the samples. (Figure 75)

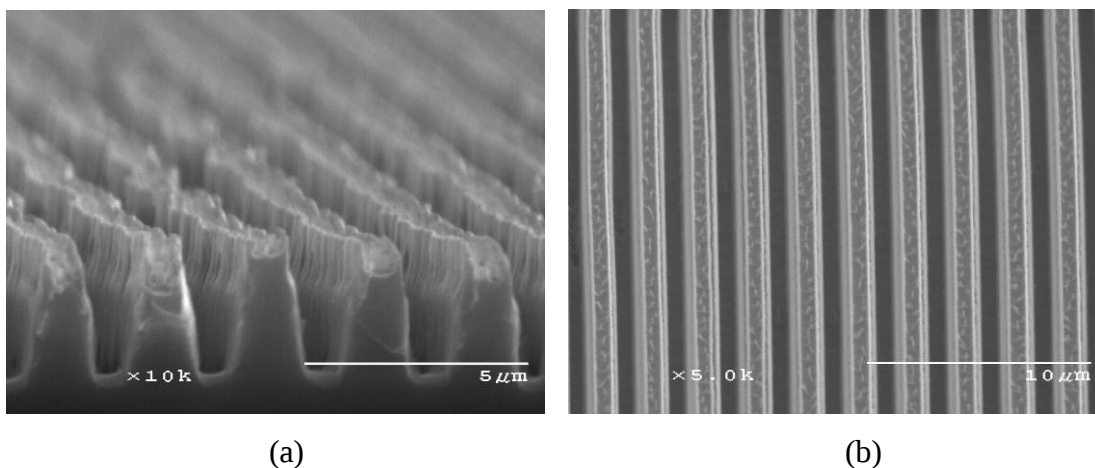


Figure 75: SEM images of a 300nm height structure after plasma etching (a) at tilt view and (b) top view

b. Total transmission of encapsulated structure - Reduction of diffraction

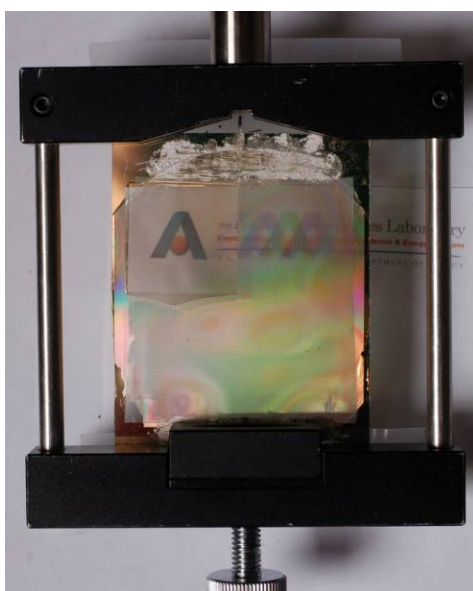


Figure 76: Image of a 1400nm height structure after argon plasma etching with a corner of the structure encapsulated

To show the optical property differences between the unencapsulated and encapsulated structure, a plasma etched sample was only partially encapsulated at the corner. Two identical logos are placed beneath and about 3cm away from the sample. (Figure 76) For the unencapsulated area on the right, we can see the double image of the logo due to the diffraction of the grating structure. For the encapsulated area, the logo can be clearly seen without distortion. The diffraction effect is vastly reduced. This approach demonstrates that the structure, when encapsulated, is suitable for transparent electrode applications in solid-state lighting and smart windows.

c. Transmission of the encapsulated structure - Different incident angles

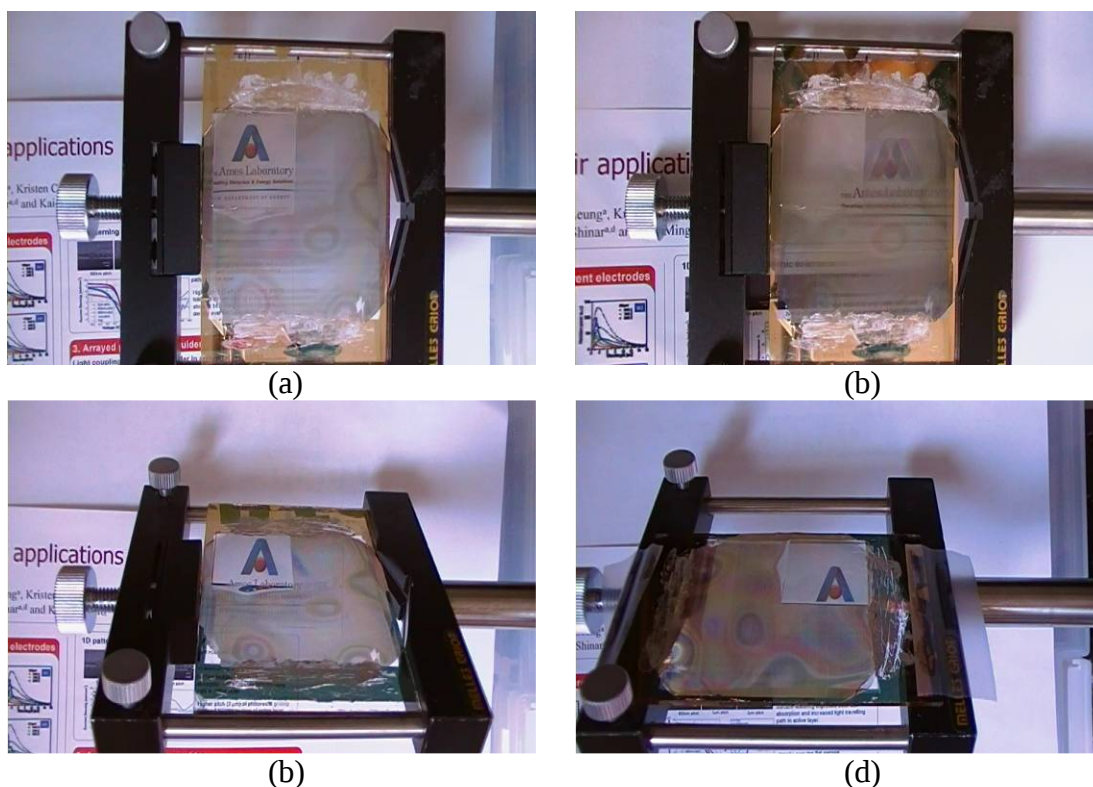


Figure 77: Still images from the movie clip when the “Ames Laboratory” logo is (a) under the encapsulated area, (b) unencapsulated area showing double imaging with vertical grating direction, (c) encapsulated area with sample tilted 60° and (d) with sample tilted 60° but also rotated 90°. (Unencapsulated PU grating structure dimensions: periodicity = 2.5 μm , height $\approx$ 1.2 μm , width $\approx$ 1.2 μm .)

For better comparison, we made a sample with only a small area encapsulated, leaving the remainder only plasma etched, and we recorded a movie clip of the sample showing

its transmission and diffraction properties of different areas. (which can be viewed here <http://home.engineering.iastate.edu/~sumitc/documents/electrodes>) The movie shows the transmission mode of the sample as well as its dependence on the incident angle by viewing the “Ames Laboratory” logo from the top. We observed that, when the sample is at a distance but parallel to the logo, the encapsulated area (top left corner of the sample) still clearly shows the image below without any visible distortion. (Figure 77 (a)) For the plasma etched, unencapsulated area, however, we observe that the image is indistinct. When the sample is moved closer to the logo, we see double imaging due to the diffracting nature of the grating, which causes the blur for the unencapsulated area. (Figure 77 (b)) In contrast, the double image effect was not seen for the encapsulated area when the sample was moved up and down with respect to the logo. Furthermore and more importantly, when the sample was tilted (up to 70°) with respect to the logo plane, with the tilting direction either parallel to or perpendicular to the grating direction, the image below still can be seen clearly without any noticeable decrease in transmission intensity through the sample, nor did the sample induce a diffraction effect. (Figure 77 (c) and (d))

We also studied the diffraction phenomenon of the structure in which we shine a green laser through the sample and observed the diffraction pattern projected on a piece of white paper. For the plasma etched area, the transmitted light formed a diffraction pattern due to the grating structure, and the light intensity was distributed accordingly at different diffraction orders. When the laser was directed on to the encapsulated area, the intensity of the zeroth order was noticeably increased while the light intensities of other orders were very significantly reduced. This indicates the incident light was concentrated on the direct beam with minimal diffraction effects.

In order to quantitatively characterize the effect of encapsulation, we measured the total transmission of the structure at different incident angles. Figure 78 illustrate how the incident angle is changed with respect to the grating direction. The sample is rotated as a venetian blind in the direction orthogonally to the grating direction.

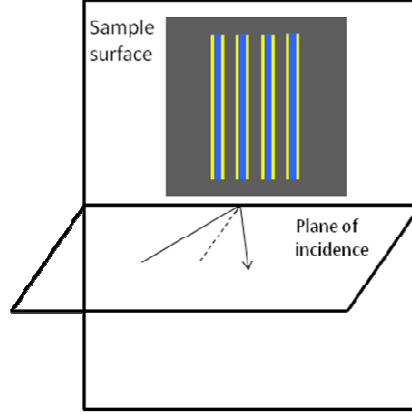


Figure 78: schematic for the transmission measurement at different incident angles

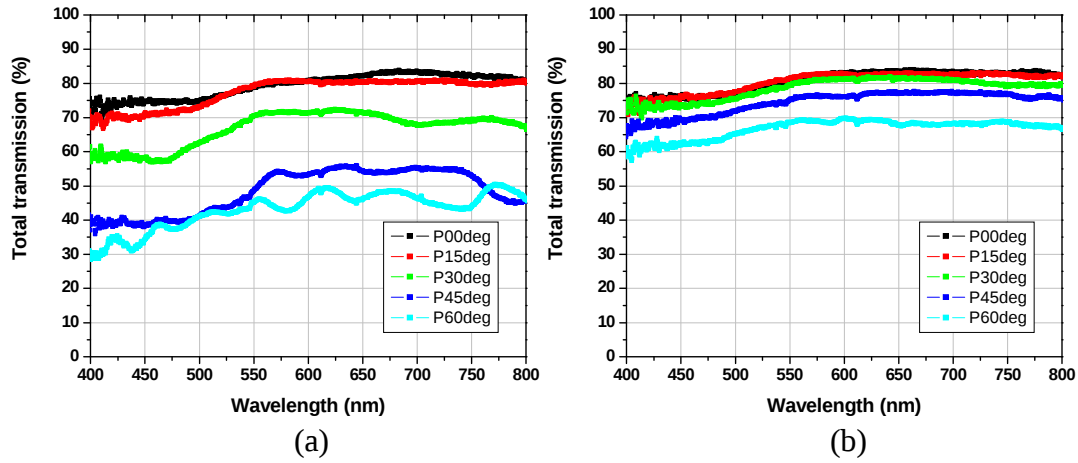


Figure 79: The measured total transmission spectra of (a) an unencapsulated sample and (b) an encapsulated sample. The grating sample dimensions are $2.5\mu\text{m}$ periodicity, $1.2\mu\text{m}$ width, and $1.2\mu\text{m}$ height with 40nm gold sidewalls

A 4mm^2 one-layer grating sample of $2.5\mu\text{m}$ periodicity, $1.2\mu\text{m}$ width, and $1.2\mu\text{m}$ height with 40nm gold sidewalls after ion milling was used to measure its transmission at different incident angles. Another sample with the same dimensions was used to examine the encapsulation effect on the transmission by applying a PU overlayer on top with the PU filling inside the channels of the grating structure. (Figure 79) An unpolarized light source is used. For the unencapsulated sample, the transmission is still around 80% when it is tilted 15° from the normal. When the angle is increased to 40° , the transmission intensity is dropped to around 70%. At 45° , it is dropped even further to 55%. And at 60° , the total transmission is below 50%. Therefore, without encapsulation, there is a significant reduction in transmission when the light incident angle is large. In contrast,

for the encapsulated sample, the transmission intensity stays above 80% even at 30° incident angle. At 45°, the transmission is only reduced a little to around 76-77%. At 60° angle, the intensity is still at around 70%. Additionally, the glass slide itself has a transmission reduced from 92% to 87% when it is tilted at 60°, and for an ITO coated glass it is decreased to below 80% at 60° incident angle. This indicates our encapsulated structures still have relative high transmission intensity at large incident angles.

In summary, for applications such as solid-state lighting and smart windows, we have successfully made the structure with a larger sample area (5 x 5 cm²), while other dimensions are the same. Additional PU prepolymer was used to fill the air channels between the metal sidewalls to reduce the diffraction effect from the grating pattern, and another glass substrate was bonded on top of the structure with the additional PU to form an encapsulated structure. It is likely that most applications would require such encapsulation to protect the structure. It is demonstrated that, with the open trenches filled, our structure does not suffer reduction in optical transmission even at very high incident angles (>70°), and the diffraction is at an insignificant minimum. High transmission at steep incident angles is attributed to the higher refractive index of PU ($n \approx 1.5$) which replaces the low index air gap as well as to the PU overlayer which effectively removes the roughness left by etching. The application of additional PU for encapsulation effectively removes the original PU grating structure, which was the primary cause for the diffraction effect, resulting in thin vertically standing high aspect ratio metal bars with a periodicity of around 1.2 -1.3 μm . Furthermore, at the air/PU interface, if the incident angle of light is 60°, it is reduced to about 35° by refraction thereby guiding the light through the structure. The transmission of encapsulated structures can be further improved by the adoption of various anti-reflection treatments at the encapsulation/air interface.

iv. Large area structures by argon ion milling

Utilizing the argon ion milling equipment, which is capable of large area sample processing, at the Nano Fabrication Center in the University of Minnesota, [75] we demonstrated that argon ion milling is a more effective process to remove metal on PU

top surface without any noticeable over-etching of the PU underlayer. The etching is much more uniform and homogeneous and has a controllable rate compared to argon plasma etching. The large area samples also have $2.5\mu\text{m}$ periodicity, $1.2\mu\text{m}$ width, and the heights are 300nm or 1400nm . Figure 80 (a) shows the still image of the 300nm height sample after ion milling. The entire area has very high transmission and the logo underneath is clearly seen. There is a rainbow color due to the grating structure. The SEM image of a 1400nm height sample at a tilted angle shows the gold on the sidewalls are intact. The metal layers on top of the PU bars have been cleanly removed. This suggests that the argon ion milling technique the more effective process remove the metal layers on top of PU bars for the transparent electrode fabrication.

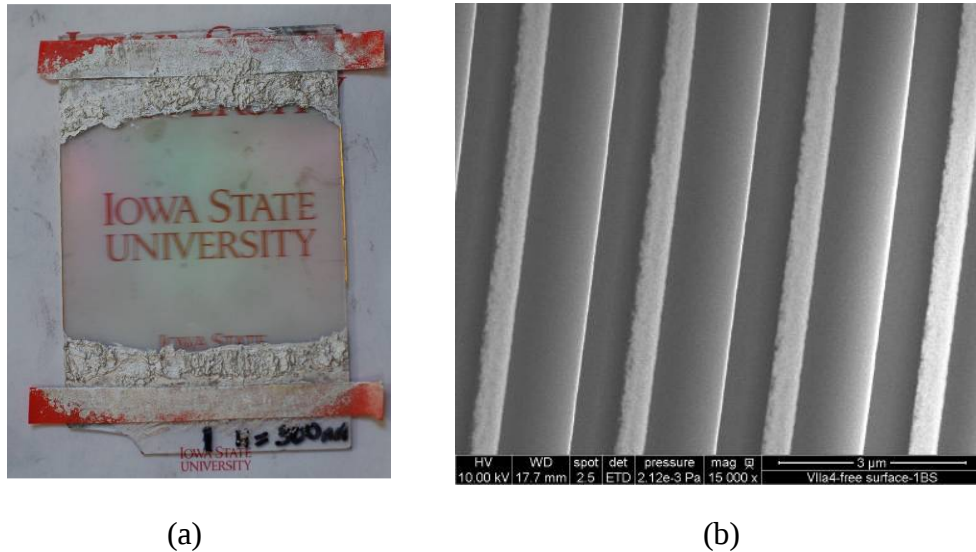


Figure 80: (a) An ion milled sample with 300nm height (b) SEM image of an ion milled sample with 1400nm height at tilted angle

The transmissions of the samples were measured and shown in Figure 81. Before ion milling, the metal-coated PU grating structures have similar transmission intensities as prior samples. After argon ion milling, the transmission intensity for the 1400nm height sample is about 76%. This is a 16% increase from the plasma etched sample. As we seen in the SEM image, the etching of the PU is minimized and the surface is smooth. The structure is in tact and no over-etching is observed in the channels.. For the 300nm height sample, the transmission is also higher than the plasma etched one. The transmission intensity is increased to about 86%, which is also an 8-9% improvement from the plasma

etched sample. Transmission measurements confirm that argon ion milling is the preferred technique.

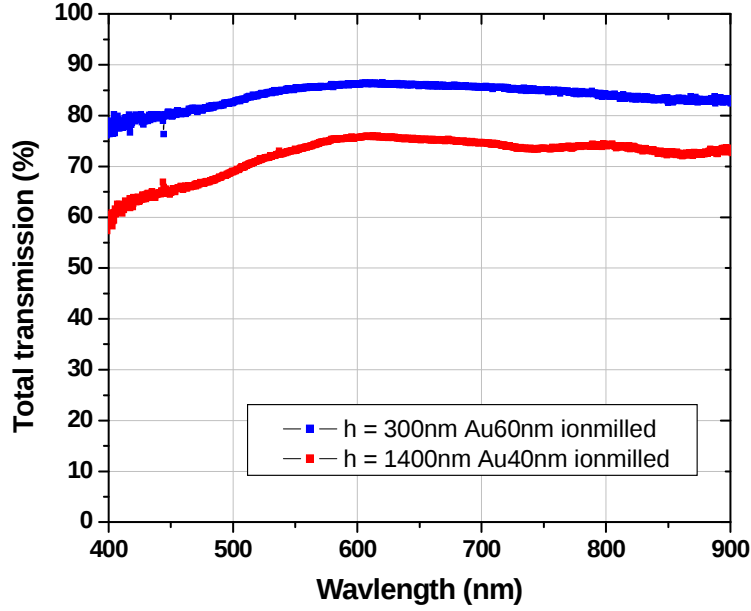


Figure 81: Total transmission of the 1D PU grating structures with gold sidewalls after ion milling for two samples with 300nm height and 1400nm height

We deposited silver paste at two ends of the structures with a separation of about 4.5cm, and measured the 2-wire resistance of the structures. For the 1400nm height sample, the resistance is as low as 12-18 Ω , and for the 300nm sample, the resistance is also low at 52 Ω . This demonstrates that our structures are highly conductive even over large areas suggesting the few, if any, of the metal bars are broken.

CHAPTER 5. FUTURE RESEARCH PLANS

The high aspect ratio metallic transparent electrodes have numerous potential applications including smart windows and solid-state lighting devices. Two different areas should be investigated further to evaluate the feasibility of our structures in these applications. First, interdigitated structures infilled with active materials could be used to manipulate the transmission intensity through the sample. Secondly, there is a need for the reduction of periodicity for high reflection for near IR applications.

1. Interdigitated structure

One of the more fascinating properties of transparent electrodes is its potential in switching the light transmission from high intensity to low in smart window applications. One good example of smart windows is using electrochromism to regulate the transmission of light through the device with changing color in a reversible fashion by applying a dc voltage. [76]

In our design, an interdigitated structure based on the high aspect ratio metallic structure can be utilized as electrodes to apply voltages on active materials to manipulate their optical properties similar to that of electrochromic devices. (Figure 82) From the top view, we illustrate that the adjacent metallic ribbons are disconnected from each other to form the interdigitated structure. Polarizing voltages can therefore be applied for the adjacent metallic ribbons.

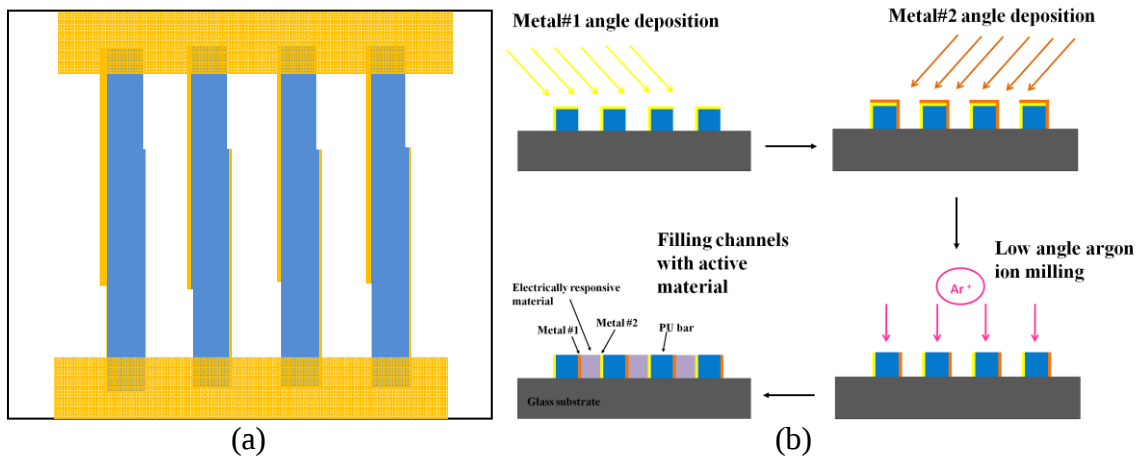


Figure 82: (a) The designed interdigitated structure and (b) the schematics for interdigitated structure process

The fabrication process for the interdigitated structure is similar to that of argon ion milled small area transparent electrode structures. As shown in Figure 82 (b), a metal is first angle deposited from one side of the PU grating. One end of the grating structure is covered by a mask before the metal deposition. This is done to intentionally leave a small part of the grating without metal coating on the sidewall to separate the two adjacent metal sidewalls to the contacts. The same metal material or a different metal is then deposited from the other side to coat both sidewalls of the PU bars. The other end of the grating structure is also block to separate the adjacent metal sidewalls at the other end. The metals on top of PU bars can be physically removed by argon ion milling. At last, the empty channels are filled with active materials which can respond to the applied voltage and the optical properties of the structure can be characterized.

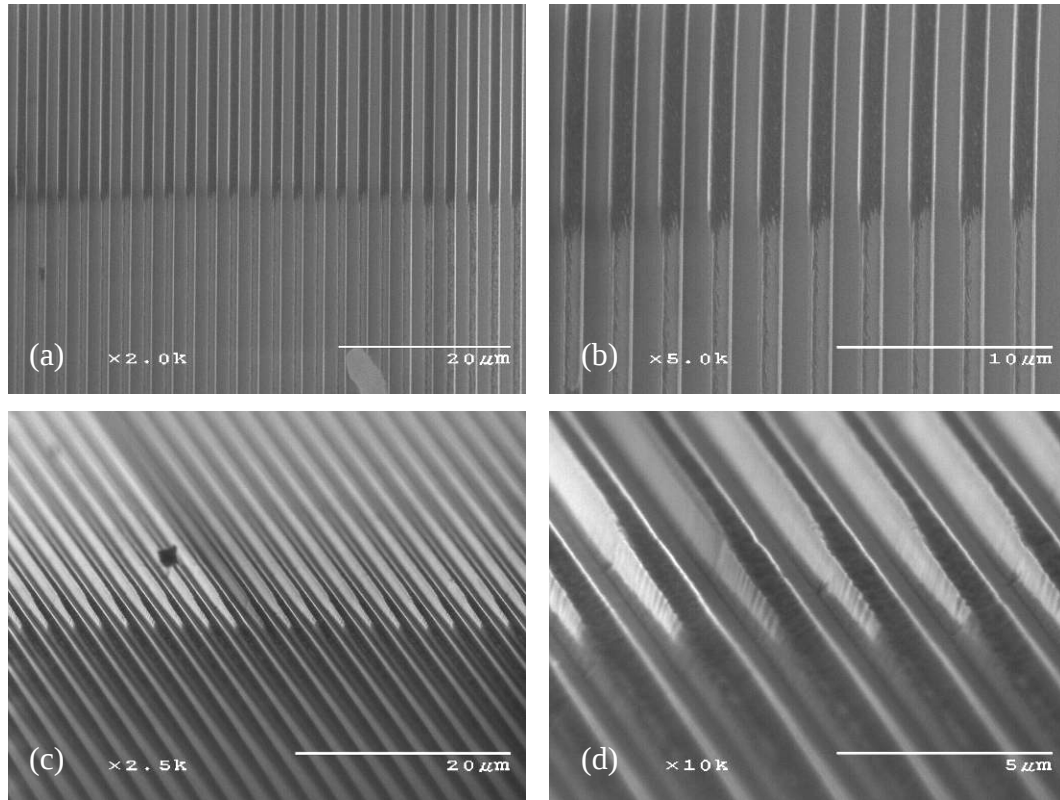


Figure 83: SEM images of the interdigitated structure with Ag sidewalls

Figure 83 shows the SEM images of the interdigitated structure after argon ion milling at one end of the electrode. In the top view, it is observed that the metal coating on top of

the PU grating is completely removed by the argon ion milling. The interdigitated structure has one end of the metal ribbons on one sidewalls is terminated while the adjacent metal ribbons are still continuous along the PU bars. From the tilted angle view, we observed that there was indeed no metal coating on the PU sidewalls where the ribbons terminate.

There are other emerging applications with the interdigitated structure. One of them is to incorporate such high aspect ratio wall shaped interdigitated electrodes in blue phase liquid crystal displays (BPLCDs). [77] BPLCDs have drawn great interest due to their submillisecond response time, wide view and simple fabrication process. (Figure 84)

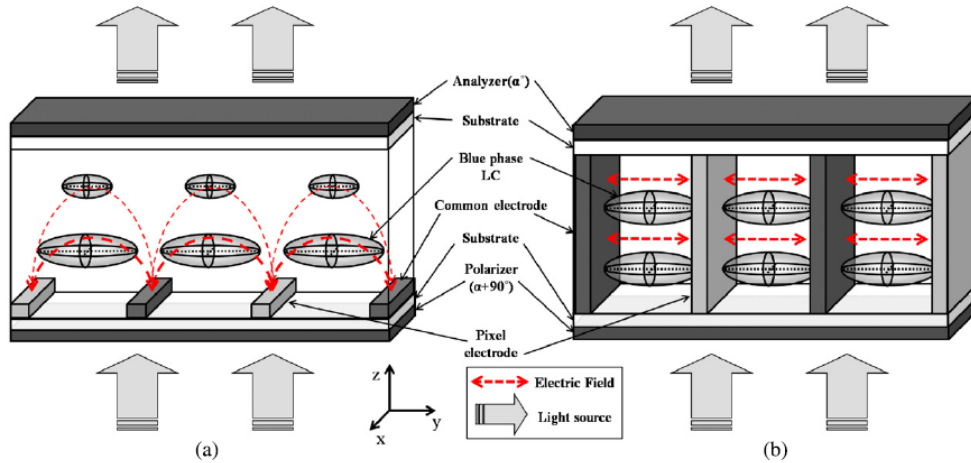


Figure 84: schematic of (a) a conventional interdigitated electrode structure and (b) a wall-shaped electrode structure with high aspect ratio metal electrodes [77]

However, the conventional device requires a relatively high operating voltage because the electric fields are restricted near the electrode surface. To overcome this technical barrier, a wall-shaped electrode configuration is chosen so that the induced birefringence is uniform between electrodes throughout the entire cell gap. Consequently, the operating voltage is reduced by about 2.8 times. Therefore, our interdigitated structure would serve this purpose very well. In addition, development of organic light emitting transistors (OLETs) has become another interesting research topic in display and lighting. [78] Such wall-shaped electrode configuration could also be used to improve the efficiency and performance.

2. $1\mu\text{m}$ periodicity one-layer structure

To utilize the high aspect ratio metallic transparent electrodes for high reflection in the near-IR region, the periodicity of the grating structure needs to be reduced. One-layer PU grating structure with $1\mu\text{m}$ periodicity, 400nm width, and 400nm height was fabricated using the 2P- μTM technique. The grating structure was subsequently used to make the metallic transparent electrodes. Angle metal depositions of 40nm gold were carried out for the metal coatings on the PU surface and argon ion milling was done to remove excess metal on top of the PU grating. After ion milling, the structure shows metallic ribbons on the sidewalls of the PU bars stayed intact while the metal on top was completely removed. (Figure 85) There may be some over-etching in the PU bars if the ion milling step is done longer than it is needed.

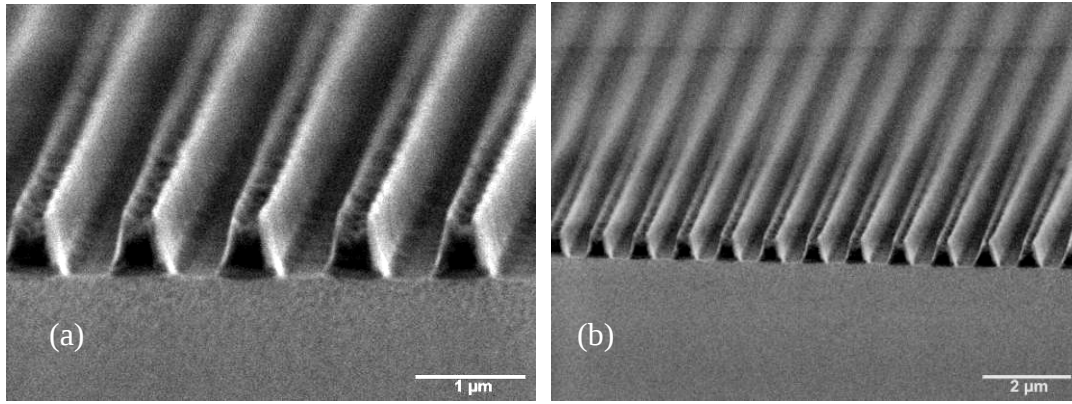


Figure 85: Scanning electron microscope (SEM) images of argon ion milled gold sample. The original polymeric gratings have a $1\mu\text{m}$ periodicity and 400nm width and 400nm height. The gold sidewall thickness is 40nm

The optical properties of the structure were characterized. The total transmission was measured before and after ion milling process. It showed that the transmission intensity is less than 30%. Such low transmission may be caused by excess gold deposition in the channels of the grating structure. After ion milling, the total transmission of the sample is significantly increased to above 80%. (Figure 86 (a)) Transmission intensity is dropped below 550nm wavelength due to the absorption of gold possibly redeposited as a very thin layer in the channels.

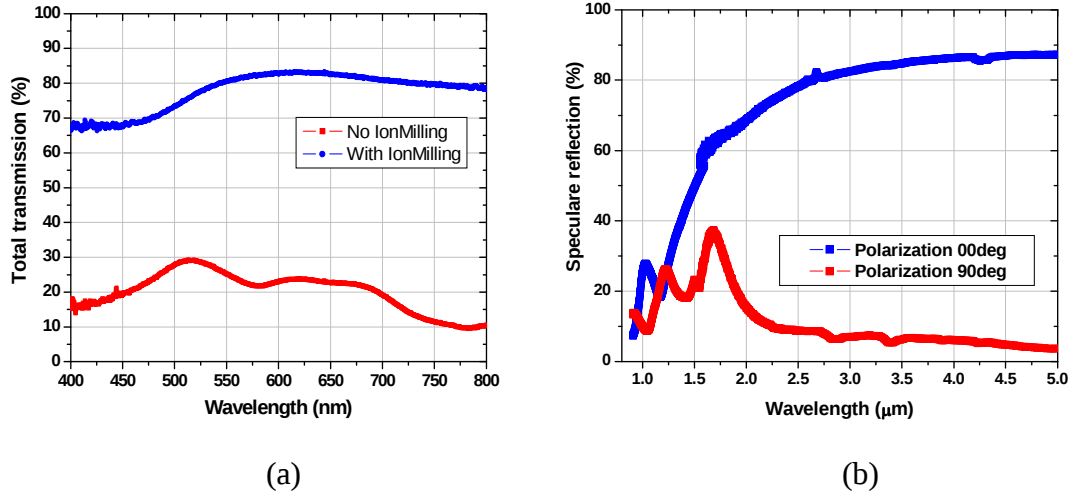


Figure 86: (a) Total transmission of visible light before and after ion milling (b) specular reflection of the structure at two different polarizations

The specular reflection of the sample in near and mid IR region was also measured using the FTIR spectrometer. Similarly to the $2.5\mu\text{m}$ periodicity grating structure, the $1\mu\text{m}$ periodicity sample has a near zero reflection for the TE mode (90 degree polarization) at wavelengths beyond 2000nm . A cutoff is formed at around 1200 nm wavelength for the TM mode, and the reflection intensity keeps increasing and reaches around 90% in the plateau area. Optimization of the structural dimensions is still needed to further study the $1\mu\text{m}$ periodicity samples. In addition, successful large area sample fabrication process is crucial for commercialization in the near future. Moreover, the feasibility of incorporating roll-to-roll printing process for both $2.5\mu\text{m}$ and $1\mu\text{m}$ large area structures is of particular interest and importance.

CHAPTER 6. CONCLUSIONS

In summary, we have fabricated novel patterned nanoscale metallic structures for use as transparent electrodes by a combination of two-polymer microtransfer molding, oblique metal deposition and argon ion milling techniques. Such structures have high optical transparency in the range of 80% for visible light and low sheet resistance ($3.2\Omega/\square$). Different metallic materials were deposited to show the feasibility of such a process to accommodate the requirements for various device applications. A working proof-of-principle organic solar cell device was fabricated. Furthermore, such transparent electrodes can be fabricated in large area and have other important applications in smart windows and solid state lighting, and roll-to-roll processing can be realized for such structures in the foreseeable future.

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APPENDIX A: ARGON ION MILLING FROM PERPENDICULAR DIRECTION

The argon ion milling step is carried out from the direction perpendicular to that of the grating structure. It was found that as the milling process progressed, the PU bars as well as the metal on their surface would be etched off from top to the bottom without maintaining the original structural integrity or the original PU grating dimensions. Figure A1 (a) illustrates the etching on the grating structure at different areas. The etching started from the corner of the PU bars which got removed by the argon ion bombardment first. (Figure A1 (d)) Then the metal on the other side of PU was etched, and the PU bars was etched more uniformly to the middle of the height. (Figure A1 (c)) As the ion milling continued, the PU bars closest to the ion gun were almost completely removed leaving only a thin layer of the PU bars. (Figure (b)) Therefore, the argon ion milling process should be done parallel to the grating direction.

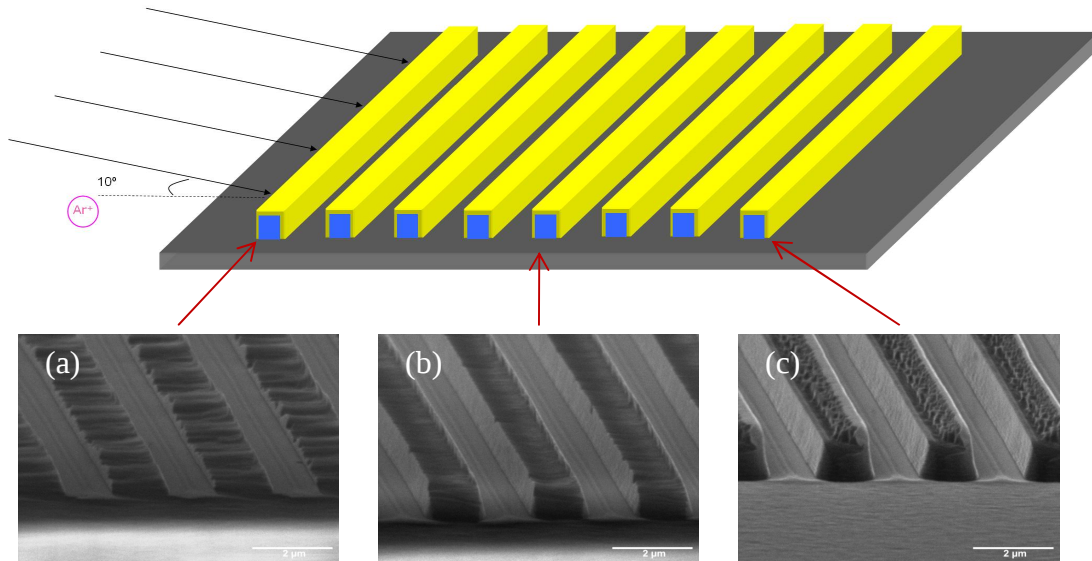


Figure A1: (a) Schematic of argon ion milling for the angle deposited grating structure from the perpendicular direction and the SEM images of the structure was (b) mostly etched, (c) etched to the middle of the PU bars, and (d) etched starting from one corner

APPENDIX B: ABSORPTION ENHANCEMENT IN SOLAR CELLS WITH METAL GRATING STRUCTURE

Theoretical studies have shown that with optimized periodicity, height, and thickness of the metal grating structure, the electric field in the active layers could be immensely enhanced. This would improve the light absorption in the organic layers and in turn increase the power conversion efficiency of the device.

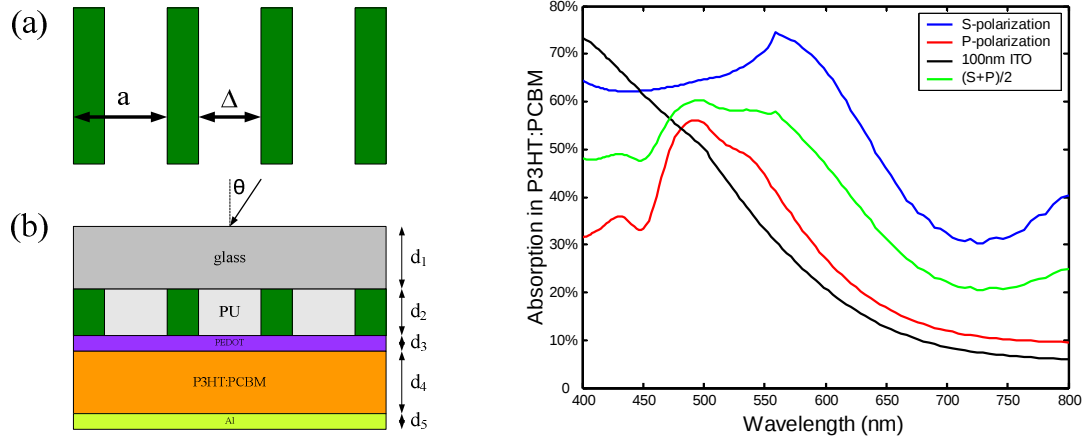


Figure B1: (a) The schematic design of the metal grating structure with smaller periodicity, and (b) the design of the solar cell structure with optimized thickness of each layer, and (c) the absorption enhancement improvement in P3HT:PCBM with respect to a standard 100nm thick ITO on glass

In the design for the simulation, the PEDOT:PSS film is neglected ($d_3 = 0$), The thickness of glass substrate is set to be infinite ($d_1 = +\infty$). That is, the whole structure is deposited on a semi-infinite thick glass substrate, and light is incident from the glass (see Figure B1 (b)). The parameters are set for the periodicity of the silver grating $a = 360 \text{ nm}$, fill factor of the metal $f = 0.12$, height is $d_2 = 300 \text{ nm}$, for the P3HT:PCBM layer $d_4 = 160 \text{ nm}$, the aluminum counter electrode $d_5 = 800 \text{ nm}$. As a comparison, the absorption spectrum is also plotted with a 100 nm thick ITO coated glass as the electrode with other parameters same. In the interested wavelength range of $480 \sim 620 \text{ nm}$, the enhancement for two polarizations ranges from 7% to 137%. Averaging two polarizations these two peaks give a plateau from 470 nm to 570 nm (green line in Figure B1 (c)). This shows, with optimization, our structure can be used for field enhancement to improve the solar cell efficiency considerably.