All-Solution-Processed Transparent Conductive Electrodes with Crackle Templates:

Author: Chaobin Yang

Persistent link: http://hdl.handle.net/2345/bc-ir:108648

This work is posted on eScholarship@BC, Boston College University Libraries.

Boston College Electronic Thesis or Dissertation, 2019

Copyright is held by the author. This work is licensed under a Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0).

ALL-SOLUTION-PROCESSED TRANSPARENT CONDUCTIVE ELECTRODES WITH CRACKLE TEMPLATES

Chaobin Yang

A dissertation

submitted to the Faculty of

the department of Physics

in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy

Boston College Morrissey College of Arts and Sciences Graduate School

December 2019

© Copyright 2019 Chaobin Yang

ALL-SOLUTION-PROCESSED TRANSPARENT CONDUCTIVE ELECTRODES WITH CRACKLE TEMPLATES

Chaobin Yang

Advisor: Michael J. Naughton, Ph.D.

In this dissertation, I first discuss many different kinds of transparent conductors in Chapter one. In Chapter two, I focus on transparent conductors based on crackle temples. I and my colleagues developed three (one sputter-free and two fully all-solution) methods to fabricate metallic networks as transparent conductors. The first kind of all-solution process is based on crackle photolithography and the resulting silver networks outperform all reported experimental values, including having sheet resistance more than an order of magnitude lower than ITO, yet with comparable transmittance. The second kind of all-solution proceed transparent conductor is obtained by integrating crackle photolithography-based microwires with nanowires and electroplate welding. This combination results in scalable film structures that are flexible, indium-free, vacuum-free, lithographic-facility-free, metallic-mask-free, with small domain size, high optical transmittance, and low sheet resistance (one order of magnitude smaller than conventional nanowire-based transparent conductors).

TABLE OF CONTENTS

Table of (Contents	iv
List of Fig	gures	vi
Acknowle	edgement	ix
Table of A	Abbreviations	xi
Introduct	tion	1
1.0 Int	roduction	2
1.1 (Characterization	3
1.1.1	Transmittance	3
1.1.2	Sheet resistance	.10
1.1.3	Figure of merit	.15
1.2 I	TO and ITO Alternatives	16
1.2.1	ITO and its drawbacks	.16
1.2.2	ITO alternatives	.16
1.3	Fransparent Conductive Oxide	18
1.3.1	Materials	.18
1.3.2	Fabrication	.20
1.3.	2.1 Sputtering/Sputter deposition	20
1.3.	2.2 Chemical vapor deposition	20
1.3.	2.3 Pulsed laser deposition	20
1.3.3	Limitations TCO	.22
1.4 (Carbon-based TCE	23
1.4.1	Graphene	.23
1.4.2	Carbon nanotube	.26
1.5 I	Metallic Networks	28
1.5.1	Lithographic made networks	.28
1.5.2	Metallic nanowire networks	.28
1.5.3	Networks based on crackle templates	.31
2.0 Mi	crodomain Networks Based on Crackle Templates with Vacuum	
Metal Dep	position	33
2.1	Microdomain Networks Based on Crackle Templates with Vacuum Metal	
Deposit	ion	34
2.1.1	Processes and results	.34
2.1.2	Advantages and disadvantages	.39
2.2	Microdomain Networks Based on Crackle Templates with Vacuum Metal	
Deposit	ion and Electroplating	40

	2.2.1	Processes and results	40
3.0	Z.Z.Z	rodomain Networks Based on Crackle Templates with Solution	40
Met	al Der	nosition	42
3.	1 S	putter-free Microdomain Networks Based on Crackle Templates	
	3.1.1	Introduction	43
	3.1.2	Results and discussion	45
	3.1.3	Experimental details	66
	3.1.4	Conclusion	68
3.	2 A	Ill-solution-processed Microdomain Networks Based on Crackle	
Pl	notolit	hography	70
	3.2.1	Introduction	70
	3.2.2	Results and discussion	72
	3.2.3	Experimental details	88
	3.2.4	Conclusion	90
4.0	Nat	nodomain Networks Based on Crackle Templates with Solution M	etal
Dep	ositio	n	91
p 4.	1 4		hv
ar	nd Elec	troplating	
	4.1.1	Introduction	
	4.1.2	Results and discussion	94
	4.1.3	Experimental details	.108
	4.1.4	Conclusion	110
5.0	Sui	nmary	111
6.0	Re	ferences	112

LIST OF FIGURES

Figure 1. Set up of transmittance measurement.	6
Figure 2. A schematic of an integrating sphere.	7
Figure 3. A schematic of an optical spectrometer.	
Figure 4. Haze measurement requires four scans using the integration	1g sphere
configurations shown in figure.	9
Figure 5. Geometry for defining bulk resistance (left) and sheet resistance ((right). 12
Figure 6. Contact arrangements for Van der Pauw resistance measuremen	ts. 13
Figure 7. Correction factor based on the ratio of the two Van der Pauw	resistance
measurements.	14
Figure 8. Typical TCOs and related dopants.	19
Figure 9. Schematic of a sputtering system.	
Figure 10. A transparent ultra large-area graphene film transferred on a	~1 m PET
sheet.	
Figure 11. Transmittance curve of roll-to-roll layer-by-layer transferred	graphene
films on quartz substrates.	
Figure 12. Structural and optoelectronic properties of carbon nanotube tra	ansparent
conducting films.	
Figure 13. Fabrication processes of metallic nanowires.	

Figure 14. Images of self-cracking templates and the corresponding crack
nanonetworks (CNN)
Figure 15. Fabrication processes of metallic networks based on crackle templates
with vacuum metal deposition
Figure 16. Optical transmittance versus the corresponding sheet resistance for CNN
Ag network samples on glass at 550 nm
Figure 17. Demonstration of metallic networks' mechanical flexibility and
application to touch screen
Figure 18. Fabrication processes of metallic networks based on crackle templates
with vacuum metal deposition and electroplating
Figure 19. Details of the sputtering/evaporation-free CNN process
Figure 20. Characterization of Ag network on PET
Figure 21. Morphologies of plated metallic networks depend on different surface
properties of CYTOP
Figure 22. Morphologies and XRD spectra of the sputtering/evaporation-free CNN.
Figure 23. Optoelectronic properties of metallic networks
Figure 24. Metal coverage and thickness. 54
Figure 25. Haze of a typical Ag nanonetwork
Figure 26. Flexibility and stability of the sputtering/evaporation-free CNN
Figure 27. Sheet resistance variation versus bending times for Ag-plated network. 58
Figure 28. Details of the variation of the resistance
Figure 29. Air stability of sputtering/evaporation-free Cu network

Figure 30. Examples of applications of the sputtering/evaporation-free CNN	62
Figure 31. Durability of transparent heater.	63
Figure 32. IR image of transparent heater while bending.	64
Figure 33. All solution-processed TCE fabrication process.	73
Figure 34. Optical microscope images of three stages of preparation of ci	racked
silver networks	74
Figure 35. Microscope images of completed TCEs made by the nail polish proc	cess.77
Figure 36. Transmittance of all-solution-processed TCEs as a functi	on of
wavelength obtained with samples in Figure 35.	78
Figure 37. AFM images of a representative nail polish-based sample	81
Figure 38. Transmittance and sheet resistance of a typical low-resistance s	ample
before and after electroplating.	83
Figure 39. Photography and SEM images of samples.	84
Figure 40. Transmittance vs. sheet resistance of completed nail polish-based	TCEs
before (red circles) and after (red squares) electroplating Ag	87
Figure 41. Two different micro/nanowire-based TCE fabrication processes	96
Figure 42. Optical and SEM images of micro/nanowire-based TCEs.	98
Figure 43. Optical transmittance T and sheet resistance Rs of samples prepa	red by
NF (blue) and MF (red) vs. electroplate welding time	101
Figure 44. TCEs made by MF and NF, and their performance.	103
Figure 45. Optical images of micro/nanowire-based TCEs made by MF	104
Figure 46. Sheet resistance of MF sample measured while bending	107

ACKNOWLEDGEMENT

First, I would like to thank my advisor Prof. Naughton for his patient instructions and all kinds of support during my Ph.D. study. I could have accomplished nothing without the wisdom and super power he kindly shared to me. During our first meeting, he asked me whether I know what is "common sense". I didn't understand the language and said no. He was surprised that I don't have common sense but he did not fire me. Happily, I got my first assignment which is to google what "common sense" means. This story clearly shows Prof. Naughton is nice to work with and I made a smart choice. After some years of "re-search", magically, I am close to get Ph.D. now. A little sadly, I still cannot confidently say I have a lot common sense. Everything can make sense, because there is hardly anything that makes no sense to anyone. This may be the reason why we still don't have a peaceful world and people aren't significantly happier than before after human beings have achieved so many technologies. Common sense may not exist at all because everyone chooses to see different "common".

I would also like to thank my committee members, Prof. K. Kempa, Prof. J. Gao and Prof. D. Broido for insightful suggestions, beneficial discussions, generous supports in many aspects and friendly personal interactions during my Ph.D. study. I would also thank Dr. Burns for his huge amount of help in simulation and experiments. I would like to thank all our group members that I have the privilege to work with. I would like to do this in a chronological order. I started my experimental training under the guidance of Dr. Ye Fan, who was patient and strict enough to explain everything to me and very helpful in my everyday life. I have been working closely with Dr. Binod Rizal, Dr. Jeff Naughton, Dr. Aaron Rose, Dr. Nathan Nesbitt, Dr. Yitzi Calm, Dr. Luke D'Imperio, Dr. Juan M. Merlo, Victoria Gabriele, Mark Schiller and Linden Hayes. I would also like to thank the helpful interactions with them. I owe my special thanks to Svet Simidjiysky, who has been helping me constantly on machining.

I would like to thank the Boston College Integrated Sciences Cleanroom and Nanofabrication Facility for providing the cleanroom facilities. The research leading to these results has received partial funding from the Guangdong Innovative and Entrepreneurial Team Program titled "Plasmonic Nanomaterials and Quantum Dots for Light Management in Optoelectronic Devices". I am grateful to Steve Shepard for his tremendous help with all the training, characterization and fabrication. I also owe my gratitude to Dr. Dezhi Wang for his training of the SEM and TEM systems for me. I would also like to thank Dr. Gregory McMahon, who patiently trained me on the FIB system.

Lastly I thank my parents and family for their encouragement, help and love during my PhD and throughout my life. It usually takes five years to Ph.D. study in my home country, so they had a hard time to understand why I didn't finish after five years. I easily solved the problem by telling them I am doing postdoc. Right now, my second term of postdoc is very close to the end so hope everything can come to a happy ending.

TABLE OF ABBREVIATIONS

(in order of appearance)

TC	Transparent conductor
TCE	Transparent conductive electrode
OLED	Organic light-emitting diode
ТСО	Transparent conductive oxide
ITO	Indium tin oxide
AZO	Aluminum-doped zinc oxide
MNN	Metallic nanowire networks
AgNW	Ag nanowire
Т	Transmittance
R _s	Sheet resistance
FoM	Figure of merit
F_{TCE}	Figure of merit using optical and electronic conductivity
ϕ	Figure of merit using T^{10}/R_s
CVD	Chemical vapor deposition
PLD	Pulsed laser deposition
FTO	Fluorine-doped tin oxide

CNT	Carbon nanotube
R2R	Roll-to-roll
SEM	Scanning electron microscope
XRD	X-ray powder diffraction
AFM	Atomic force microscopy
CNN	Crack nanonetworks
PET	polyethylene terephthalate
BOE	buffered oxide etch
HMDS	bis(trimethylsilyl)amine
IPA	isopropyl alcohol
CPL	crackle photolithography
MF	microwires first
NF	nanowires first

INTRODUCTION

In this thesis, in Chapter 1, I will first introduce how to characterize transparent conductors. With this knowledge we can compare the performance of different kinds of transparent conductors. Due to all the drawbacks of ITO, people are investigating on its alternatives. ITO and its alternatives (*e.g.* transparent conductive oxide, graphene, carbon nanotubes and metallic networks) are discussed in Chapter I. Among all the metallic networks, metallic networks based on crackle templates stand out.

In Chapter 2 and 3, microdomain-sized metallic networks based on crackle templates are introduced in more details. In Chapter 2, two kinds of microdomain networks with vacuum metal deposition are discussed. Then, in Chapter 3, two kinds of microdomain networks with solution metal deposition discovered by me and my colleagues are introduced. Among them, the second kind networks are made by all-solution processes.

In Chapter 4, nanodomain networks are made by integrating cracklephotolithography-made networks with nanowires and electroplating. Very good performance is observed and the resulting network is a great candidate for ITO alternative.

1.0 INTRODUCTION

Transparent conductors (TCs), which combine high electrical conductivity with high optical transmittance, play a crucial role in numerous modern devices, such as thin film solar cells, flat panel displays, touch screen displays, smart windows, energy harvesters, transparent memory, electromagnetic shielding, heaters, sensors, supercapacitors, and organic light-emitting diodes (OLEDs)^[1–12] The touch screen market itself is believed to reach \$4.8 billion by 2019.^[13]

Cadmium oxide (CdO) was the first kind of transparent conductive oxide (TCO) discovered,^[14] and was produced as a thin film by oxidizing a sputtered Cd film.^[15] The most successful TCO, indium tin oxide (ITO), was developed by Corning Glass Works as early as 1951.^[16] ITO has become the dominating material in the TC industry and continues to be until today. Drawbacks of ITO and several kinds of ITO alternatives are going to be discussed in this Chapter.

1.1 CHARACTERIZATION

Optical transmittance (T) and electrical sheet resistance (R_s) are typically used in characterization of TCs. Several different kinds of figure of merit (as functions of transmittance and sheet resistance) have been proposed to compare performance between various TCs. In this Chapter, we will discuss these features and terms.

1.1.1 Transmittance

Transmittance is the ratio of the electromagnetic power of transmitted light to the power of the incident light. For monochromatic light, every photon has the same energy, so one can use the number of photons to represent the intensity of light. Experimentally, the numbers of incident and transmitted photons are measured over the same length of time by a spectrometer. One can assume the same number of background photons (noise) is collected during a measurement of incident and transmitted light, and this number should be subtracted. The number of background photons can be measured by turning a light source off in an otherwise dark laboratory. Thus, the transmittance of a sample (T_{sample}) is given by:

$$T_{sample} = \frac{Transmitted \ photons \ through \ sample - Background \ photons}{Incident \ photons - Background \ photons} \tag{1}$$

Similarly, the transmittance of a substrate in which a sample may rest is given by:

$$T_{substrate} = \frac{Transmitted \ photons \ through \ substrate-Background \ photons}{Incident \ photons-Background \ photons}$$
(2)

Because different researchers use different substrates during their experiments, T_{sample} should always be normalized by $T_{substrate}$, and a so-normalized T_{sample} can be calculated by

Normalized
$$T_{sample} = \frac{T_{sample}}{T_{substrate}}$$

= $\frac{Transmitted photons through sample-Background photons}{Transmitted photons through substrate-Background photons}$ (3)

One usually multiplies T by 100% to obtain the percent transmittance (%T), which ranges from 0% to 100%. A transmittance curve is the normalized transmittance of a sample versus wavelength of incident light. The setup of our transmittance measurement is shown in

Figure 1. Optical transmittance is measured by using an integrating sphere system (Ocean Optics Spectroclip-TR), a halogen light source (Ocean Optics HL-2000-FHSA) and a spectrometer (Ocean Optics Maya 2000 Pro). In this dissertation, all transmittance data presented are normalized to their substrate. In Figure 1, light comes from the Ocean Optics halogen light source (blue cylinder in figure) and enter the integrating sphere system (black clip). An ITO-coated plastic film is placed between the two spheres in the integrating sphere system. The Maya spectrometer collects light that passes through the sample under test.

An integrating sphere has white interior that can scatter or diffuse light equally to all direction. After multiple scattering reflections, only light that has been diffused in the sphere hits the port or detectors is used for probing the light. A schematic of an integrating sphere is shown in **Figure 2**. The baffle is positioned to prevent first reflections from entering the field-of-view for photodetector. In this way, only incident flux which has undergone at least two reflections can enter the optical system.

Figure 3 shows a schematic of an optical spectrometer which can take in light, break it into its spectral components, digitize the signal as a function of wavelength. The first step is to direct light through a slit. The slit vignettes the light as it enters the spectrometer. The divergent light is then collimated by a concave mirror and directed onto a grating. The grating then disperses the spectral components of the light at slightly varying angles, which is then focused by a second concave mirror and imaged onto the detector.

Optical transmission haze is another term often used to characterize TCs. When light goes through a transparent material, interactions can happen due to reflection of two surfaces and irregularities on the surfaces. Two types of scattering are typically considered: Wide Angle Scattering which causes haze due to loss of transmissive contrast and Narrow Angle Scattering which results in reduction of sharpness. **Figure 4** shows configurations to measure T_1 , T_2 , T_3 and T_4 . Haze = $(T_4/T_2 - T_3/T_1) \cdot 100\%$ is used to calculate haze.



Figure 1. Set up of transmittance measurement.

Light comes from Ocean Optics Halogen light source (blue cylinder) and entered integrating sphere system (black clip). ITO coated plastic film is placed between the two spheres in integrating sphere system. Maya spectrometer collects light that goes through ITO coated film.



Figure 2. A schematic of an integrating sphere. The integrating sphere's interior is covered with a diffusive white reflective coating. After multiple reflection on the coating, light distributes uniformly to all directions.



Figure 3. A schematic of an optical spectrometer. This optical spectrometer consists of a slit, a mirror, a grating, a collector lens and a detector.



Figure 4. Haze measurement requires four scans using the integrating sphere configurations shown in figure. From Ref. [17]

1.1.2 Sheet resistance

In a three-dimensional conductor, the bulk resistance (current in *L* direction shown in **Figure 5** left) is defined as $R = \frac{\rho L}{A}$, where ρ is the resistivity, *L* is the length, and *A* (A=Wt) is cross-sectional area of the conductor. Sheet resistance is a term used for twodimensional thin film systems in which electrons travel through the film (current in L direction shown in **Figure 5** right) rather than pass through a bulk conductor. With A=Wt, resistance in a thin film can be written as $R = \frac{\rho}{t} \frac{L}{W} = R_s \frac{L}{W}$. Here, R_s is the sheet resistance. Because $R_s = \frac{\rho}{t}$ and the unit of ρ is $\Omega \cdot cm$, the unit of R_s is ohm per square (denoted $\Omega \Box^{-1}$ or Ω sq⁻¹).

The Van der Pauw resistance measurement^[18] is the most commonly used resistance technique. It assumes 1) the sample is isotropic 2) it is homogeneous 3) it is twodimensional (thickness small compared to breadth & width) and 4) its boundary is sharply defined. Violation of any of these four requirements will invalidate a Van der Pauw resistance measurement.

Once four electrical contacts to a sample are established, two resistance measurements $R_{ab-cd} (=V_{ab}/I_{cd})$ and $R_{ad-bc} (=V_{ad}/I_{bc})$ (shown in **Figure 6**) are taken, with the difference being that one each of adjacent current and voltage contacts are switched. The sheet resistance of the sample can then be computed using these two resistances, along with a correction factor based on their ratio.

$$R_s = \frac{\pi}{\ln 2} \frac{R_{ab-cd} + R_{ad-bc}}{2} f \tag{4}$$

where ln2 is the natural logarithm of 2 (~0.693147...) and π is 3.141593.... The ratio $\pi/ln2$ is ~4.5. The correction factor *f* is shown in **Figure 7** as a function of the ratio of R_{ab} _{cd} and R_{ad-bc} .^[18]



Figure 5. Geometry for defining bulk resistance (left) and sheet resistance (right).



Figure 6. Contact arrangements for Van der Pauw resistance measurements. With reading from V divided by I, one can get resistance measurements $R_{V-I} = R_{ab-cd}$ and R_{ad-bc} from the set ups on the left and right, respectively.



Figure 7. Correction factor based on the ratio of the two Van der Pauw resistance measurements.

1.1.3 Figure of merit

A figure of merit (FoM) is often used to compare the relative performance of TCEs prepared by various methods. Ideally, a FoM should be a function of *T* and *R*_s and increase with *T* but decrease with *R*_s. Haacke^[19] proposed to use a FoM they called $\phi = T^{10}/R_s$, which puts heavy weight on transmittance *T* and has units of Ω^{-1} . Another popular FoM is the ratio of electrical conductance to optical conductance, $F_{TCE} = \sigma_{dc}/\sigma_{op}$, which can be written as $F_{TCE} = Z_0 / \{2R_s(T^{-1/2} - 1)\}$, where $Z_0 = \sqrt{\mu_0/\varepsilon_0} \approx 377 \ \Omega$ is the impedance of free space, R_s is sheet resistance and *T* is transmittance at 550 nm for incident light wavelength.^[20-23] As we will show, FoM values computed by these arbitrary formulas have limited scientific merits, nonetheless, to compare our results with literature values, we will employ both ϕ and F_{TCE} FoM analyses.

1.2 ITO AND ITO ALTERNATIVES

1.2.1 ITO and its drawbacks

As stated, ITO is the most successful TC. ITO has optical transmittance higher than 80% in the visible range and sheet resistance R_s of about 10 Ω . An ITO transmittance curve is shown in **Figure 23**. In spite of its near ubiquity, ITO suffers from several major drawbacks. First, the demand for ITO has increased dramatically after flat panel displays were invented, and ITO requires indium, which is a rare earth element in short supply on earth. Second, ITO is mechanically brittle and therefore not suitable for foldable and stretchable devices. The next generation of TC material need to be free of rare earth metals, only contain elements which have sufficient resources on earth, and capable of being produced at a low cost.

1.2.2 ITO alternatives

Global efforts are underway to seek a replacement for ITO, with intensive investigations of materials such as aluminum-doped zinc oxide (AZO)^[24,25], graphene^[26], carbon nanotubes, reduced graphene oxide^[27,28], metal nanowires (MNWs)^[29,30], and continuous metallic networks^[31–33]. More details will be discussed in this chapter. Transmittance and sheet resistance are used to compare their performance. Also, it is ultimately crucial to consider the cost of materials and the facilities needed for fabrication, and whether vacuum processes are required. Solution processes are preferable to vacuum-based processes for three reasons: (1) Solution processes have lower facilities cost.

Glass/plastic containers are much cheaper to build and maintain than vacuum chambers and pumps. (2) Solution processes have higher efficiency of material usage. In a vacuum deposition, the whole inner wall of a vacuum chamber will be covered by metal and these materials on inner wall are very hard to recycle. However, materials in a beaker after a solution reaction will be much easier to recycle. (3) Solution processes have better scalability. To deposit metal on a substrate, one always need a vacuum chamber larger than the substrate. A larger glass/plastic container is easier to access than a larger vacuum chamber.

1.3 TRANSPARENT CONDUCTIVE OXIDE

Transparent conducting oxides (TCO) have both high optical transparency in the visible range and high electrical conductivity. Normally, high conductive materials (*e.g.* copper, silver and gold) are not optically transparent. Researchers have found metal elements such as In, Sn, Zn, Ga and Cd are able to be used in the formation of transparent conductive oxides.^[34]

1.3.1 Materials

TCOs usually requires the following properties: (i) transmittance larger than 80% in the visible range (400 nm-700 nm); (ii) low resistivity after doping $(10^{-5}-10^{-4} \Omega \cdot \text{cm})$; and (iii) a large electronic band gap (> 3 eV).^[2,35–37] Oxides of metals as In, Sn, Zn, Ga and Cd can satisfy the conditions above, and thus have been most often used in TCO fabrication. In **Figure 8**, we show the most often used compounds and their dopants.

Materials	Dopant or compounds	
SnO ₂	Sb, F, As, Nb, Ta	
In_2O_3	Sn, Ge, Mo, F, Ti, Zr, Mo, Hf, Nb,	
Ta, W, Te		
ZnO	Al, Ga, B, In, Y, Sc, F, V, S, Ge,	
Ti, Zr, Hf		
CdO	In, Sn	
Ga ₂ O ₃		
ZnO-SnO ₂	Zn ₂ SnO ₄ , ZnSnO ₃	
ZnO-In ₂ O ₃	$Zn_2In_2O_5$, $Zn_3In_2O_6$	
In ₂ O ₃ -SnO ₂	In ₄ Sn ₃ O ₁₂	
CdO-SnO ₂	Cd ₂ SnO ₄ , CdSnO ₃	
CdO-In ₂ O ₃	CdIn ₂ O ₄	
MgIn ₂ O ₄		
GaInO ₃ ,(Ga, In) ₂ O ₃	Sn, Ge	
CdSb ₂ O ₆	Y	
Zn-In ₂ O ₃ -SnO ₂	$Zn_2In_2O_5-In_4Sn_3O_{12}$	
CdO-In2O3-SnO2	CdIn2O4-Cd2SnO4	
ZnO-CdO-In2O3-SnO2		

Figure 8. Typical TCOs and related dopants. From Ref. [2]

1.3.2 Fabrication

The first kind of transparent conductive oxide fabricated was CdO by thermal oxidation of Cd in 1907. After that, more vacuum based methods (*e.g.* sputtering, evaporation, and pulsed laser deposition) and solution-based methods were introduced, none of which were used to fabricate a TC for current work.

1.3.2.1 Sputtering/Sputter deposition

Sputtering is the most commonly used technique when depositing TCO films. In a sputtering system, a gas molecule (e.g. Ar) is usually ionized by a plasma and an ion beam (e.g. Ar^+) is created to impinge upon a target of a material to be deposited. Then, sputtered material leaves the target surface and deposits on a substrate. **Figure 9** show a typical schematic of sputtering system.

1.3.2.2 Chemical vapor deposition

Chemical vapor deposition (CVD) is a method to coat a material with vapor precursors that are caused to react by heating. It involves heterogeneous chemical reactions happening on or near the substrate surface.^[38]

1.3.2.3 Pulsed laser deposition

Pulsed laser deposition (PLD) utilizes a high-power pulsed laser beam that is focused on the target in a vacuum chamber to evaporate and deposit target material onto a substrate.^[39,40] PLD is very effective and excellent for depositing epitaxial films under moderate vacuum.^[2]



Figure 9. Schematic of a sputtering system. From <u>https://en.wikipedia.org/wiki/Sputter_deposition</u>, downloaded on 11th Nov 2019.

1.3.3 Limitations TCO

There are four major disadvantages of TCO (including ITO) that can limit the applications of them.^[2] (i) More and more modern electronics require mechanical flexibility and TCOs are usually metallic ceramic-like oxides, which crack at relatively low strains of 2-3%.^[41] For example, such mechanical strain can cause degradation of solar cell devices.^[42] (ii) TCOs are also relatively not very chemically stable. They can corrode or react when exposed to some salts and acids in the environment. (iii) TCOs are relatively expensive because of vacuum-based deposition. It is expensive to build and maintain a vacuum chamber and materials deposited onto the inner wall of vacuum chambers are wasted and hard to recycle. Vacuum chambers also limit the scalability of a fabrication process because a vacuum chamber also needs to be significantly larger than the sample. (iv) Another issue that makes TCOs expensive is the material cost. ITO consumes about 75% of the global indium production, with global indium supplies dwindling and price likely to increase in the future. Indium-free TCO alternatives are under development, including AZO and fluorine-doped tin oxide (FTO)^[43]. However, all these materials remain brittle, like ITO.

1.4 CARBON-BASED TCE

Carbon-based TCEs include graphene^[26], carbon nanotubes (CNT)^[44–46], and reduced graphene oxide ^[27,28]. Graphene films deposited in vacuum can be uniform, but carbon nanotube and reduced graphene oxide films are not uniform because solution processes are used in their fabrication.

1.4.1 Graphene

Graphene is a single layer of carbon atoms in the form of a honeycomb lattice, and it has conduction and valence bands touching at the K-point in the phase space.^[47,48] Its Dirac-like dispersion of electronic states leads to novel properties, including high electron mobility and high carrier concentration.^[49] Its atomically thin (0.34 nm) structure results in very high transparency (~97%). These properties make it an excellent candidate for a TC.^[27,50]

CVD and plasma-enhanced CVD are used to produce uniform graphene films without small flakes.^[51] High uniformity is required to make practical devices with graphene. In CVD processes, camphor is used as a precursor to synthesize graphene, and a metal (e.g. Ni and Cu) is used as a catalyst for the reaction.^[52,53] The resulting few-layer graphene can be of large area.^[52] Roll-to-roll (R2R) transfer techniques need to be used to produce practical electronics.^[26,54] **Figure 10** shows a transparent ultra large-area graphene film transferred on a 35-inch PET sheet.^[26] **Figure 11** shows transmittance curve of roll-to-roll layer-by-layer transferred graphene films on quartz substrates.^[26]


Figure 10. A transparent ultra large-area graphene film transferred on a ~1 m PET **sheet.** From Ref. [26].



Figure 11. Transmittance curve of roll-to-roll layer-by-layer transferred graphene films on quartz substrates. From Ref. [26].

1.4.2 Carbon nanotube

Carbon nanotubes (CNTs) are nanometer sized fibers with extremely high aspect ratio (>10⁶), current carrying ability (10⁹ A/cm²), and thermal conductivity (3500 W m⁻¹ K⁻¹).^[46,55] These features make CNTs a rational candidate for the fabrication of highly transparent and stretchable electrodes. ^[56,57]

There exist several methods to fabricate CNT networks: filtration^[58], drying from solvent^[59], spin coating^[60], air brush technique^[61] and Langmuir–Blodgett^[62] deposition. In **Figure 12**, a SEM image of CNT-based transparent conductive film and transmittance of such films are shown.^[63]



Figure 12. Structural and optoelectronic properties of carbon nanotube transparent conducting films.

(a) SEM image of a CNT transparent conducting film. (b) Transmittance dependence on the wavelength from 300 nm to 1100 nm of four different single-walled carbon nanotube films. This figure is reproduced from Ref. [63].

1.5 METALLIC NETWORKS

Metallic networks are viable candidates for ITO alternatives due to the flexibility of metals. There are patterned metallic networks made by lithographic processes and random metallic networks made by either welding metallic nanowires or made from self-cracking templates. Lithographic made networks are relatively expensive because of the high lithographic facility cost and metallic mask cost.

1.5.1 Lithographic made networks

Photolithography, nanoimprint lithography and electron-beam lithography have been used for fabrication of metallic networks.^[20,31,64] The average domain sizes made by these three techniques become smaller from the former to latter. The sheet resistances of resulting networks are relatively smaller because continuous metallic networks do not require a welding step. Both vacuum-based metal deposition^[20,64] and solution-based metal deposition^[31] can be used.

1.5.2 Metallic nanowire networks

Metallic nanowire networks (MNN) are the most commonly used ITO alternative.^[2,65] Different MNN fabrication processes have been developed with several kinds of metal, which include Ag^[66], Cu^[67] and Au^[68]. Comparing to processes that need a vacuum chamber, MNNs are very inexpensive to make, because their fabrication processes involve only chemical reactions in solution. However, their sheet resistances are limited

by contact resistance between nanowires. This problem can be partially solved by either welding^[65] or reducing the number of contacts. The second method can be achieved with ultra-long nanowires. **Figure 13** shows the general fabrication processes for MNNs: nanowire synthesis, nanowire purification, nanowire ink fabrication, and ink deposition. In future Chapter, we will show results from other groups' WNNs.



Figure 13. Fabrication processes of metallic nanowires. The figure uses silver as example. From Ref. [2].

1.5.3 Networks based on crackle templates

The natural phenomenon of stress-induced self-cracking of brittle materials is used by this process.^[69,70] The general idea is borrowed from nature, *e.g.* mud cracking in dried-out river bed. **Figure 14** shows some examples of such self-cracked films. After used as masks for metal deposition, the masks will be removed in the end, leaving behind ribbons of metal.^[65] The resulting crack nanonetworks (CNN) are a kind of nanoribbon networks, with metal thickness (\approx 100 nm) much smaller than the ribbon width (approximately several µm), and inter-ribbon distance of the order of 50 µm. Because of the large open window between the ribbons, these networks can be plated with metal without significantly reducing light transmission.^[71,72] We will discuss all our networks based on crackle templates in detail in next Chapter.



Figure 14. Images of self-cracking templates and the corresponding crack nanonetworks (CNN).

Photograph of self-cracked (a) TiO2, (b) egg-white and (c) nail polish.^[70] (d) SEM image of CNN based on egg-white mask, with sputtered Ag lines. The inset shows SEM image of a fragment of this network, clearly showing the ribbon-nature of the network lines. The arrow points to a small fragment of egg-white mask that has not been removed.^[32] (e) SEM image of an Ag-plated egg-white CNN. The inset shows a side-view metallic network.^[71] (f) Vacuum-less Ag-based CNN, with the inset showing small section of the network.^[33]

2.0 MICRODOMAIN NETWORKS BASED ON CRACKLE TEMPLATES WITH VACUUM METAL DEPOSITION

Han, *et al.*^[32] proposed to make metallic networks with random self-cracking films as masks followed by vacuum-based metal deposition. That work is discussed in Section 2.1. Peng, *et al.* improved Han's process by electroplating on the vacuum-deposited metal and achieved metallic networks with lower sheet resistance.^[71] That work is discussed in Section 2.2. Vacuum-based metal deposition is used because self-cracking materials used in these two works do not survive solution-based metal deposition.

2.1 MICRODOMAIN NETWORKS BASED ON CRACKLE TEMPLATES WITH VACUUM METAL DEPOSITION

Han et. al.^[32] proposed an approach to fabricate crack-nanonetworks (CNN) based on "cracked" gel film. The cracked gel film is used as a mask for vacuum metal deposition. This cracked gel mask can eliminate expensive metal masks used in typical photolithography, and therefore offers an inexpensive way to fabricate metallic networks.

2.1.1 Processes and results

The CNN fabrication process is shown in **Figure 15**, which includes four steps: gel film deposition, self-cracking of gel film (as a mask for metal deposition), metal deposition, and lift-off of gel film templates. Images of the gel film, cracks, and the resulted metallic networks are also in Figure 15. In that work, TiO_2 was used as the gel film and either glass or polyethylene terephthalate (PET) was used as a substrate.

Figure 16 plots the optical transmittance at 550 nm versus the sheet resistance of this work and several other works. *F* here refers to F_{TCE} . Ag network samples in this work have good electro-optical properties, with transmittance ranging from 82% (with sheet resistance $\approx 4.2 \ \Omega \ \Box^{-1}$) to 45% (with sheet resistance $\approx 0.5 \ \Omega \ \Box^{-1}$), and very high F_{TCE} ranging from 300 to 700.



Figure 15. Fabrication processes of metallic networks based on crackle templates with vacuum metal deposition.

Gel film deposition, self-cracking of gel film (as a mask for metal deposition), metal deposition, and lift-off of gel film templates are shown on the left side. The images of the gel film, cracks, and the resulted metallic networks are also shown on the right side.^[32]





Results of various metallic networks and ITO are shown. F here refers to F_{TCE} .^[32]

Figure 17a shows the sheet resistance of this Ag network on PET as a function of the bending angle.^[32] The measurement setup is shown in the inset. When the bending angle varies from -120° to 120° , a slight chance in the resistance is observed and this chance is however reversible, even after multiple bending cycles. Also, the Ag network is used for touch screen application. Figure 17b and Figure 17**Figure 16**c show a working prototype of a mechanically flexible touch screen display based on this Ag network ("SCNU" were written on this touch screen).



Figure 17. Demonstration of metallic networks' mechanical flexibility and application to touch screen.

a) Sheet resistance of Ag network as a function of the bending angle. Inset shows the photograph of the experimental setup of the two-probe electrical measurement. b,c) Working prototype of a mechanically flexible touch-screen display based on the metallic network, with the written letters visible on the display behind (the letters "SCNU" were written).^[32]

2.1.2 Advantages and disadvantages

There are two major advantages of this CNN compared to conventional TCs such as ITO. First, the self-formed template is inexpensive and can create random but very uniform networks of cracks. Second, continuous networks produced with this method do not need "welding", and thus have good mechanical flexibility. Here, welding refers to make adjacent nanowires to be joined, thus creating better mechanical properties of nanowires. Researchers have developed various welding methods such as thermal heating^[73], mechanical pressing^[74], chemical welding^[75], plasmonic treatment^[76,77] and nano-joining by conductive polymers^[78], conductive nanoparticles^[79] or carbon nanomaterials^[80,81].

One disadvantage is that a vacuum chamber (with its high capital cost) is needed to deposit the metal because the template in this work cannot survive in solution metal deposition. Also, the domain size of the resulting metallic networks is more than about 10 μ m, thus make it difficult to use in applications where submicron domain size is needed.

2.2 MICRODOMAIN NETWORKS BASED ON CRACKLE TEMPLATES WITH VACUUM METAL DEPOSITION AND ELECTROPLATING

Peng et. al.^[71] further electroplated metallic networks made by the method in Section 2.1 to increase their conductivity. The seed metal is still deposited in vacuum, since they used the same approaches in Section 2.1, but the electroplating metal was deposited in solution.

2.2.1 Processes and results

Figure 18a shows fabrication processes of the work.^[71] Processes that are the same as 2.1 (formation of self-cracking templates, vacuum metal deposition and lift-off) are first used to make metallic network and this network is used as seed layer for electroplating. Up to 10 μ m metal is electroplated onto seed layer. Figure 18b shows diagram of electroplating on seed layer.

2.2.2 Advantages and disadvantages

After electroplating, the sheet resistance of final product is about one order of magnitude smaller than itself before electroplating. Small sheet resistance is achieved at the cost of smaller transmittance which is unwanted. Because the process of making seed layer is the same as that in Section 2.1, this process also inherit all those advantages and disadvantages mentioned in Section 2.1.



Figure 18. Fabrication processes of metallic networks based on crackle templates with vacuum metal deposition and electroplating.

Schematic diagram of a) the metallic network fabrication and b) electroplating of metal layers.^[71]

3.0 MICRODOMAIN NETWORKS BASED ON CRACKLE TEMPLATES WITH SOLUTION METAL DEPOSITION

In both Section 2.1 and Section 2.2, metal is deposited in a vacuum chamber. The cost of building vacuum chambers is high (\$50k – \$500k on USD) and a large portion of depositing material is wasted in the chamber and is hard to recycle. A fabrication process made with a vacuum chamber also lacks scalability because the size of the samples is limited by size of the sample holder in the vacuum chamber. For these reasons, solution deposition of metal would be preferred. Following from those works, we developed two approaches that can replace vacuum metal deposition by solution metal deposition. The first approach is discussed in Section 3.1, in which solution metal deposition is used but it still needs vacuum chamber for plasma etch.^[33] The second approach in Section 3.2 is a fully vacuum-free process.^[72]

3.1 SPUTTER-FREE MICRODOMAIN NETWORKS BASED ON CRACKLE TEMPLATES

Here, we describe a method in which metal is deposited in solution but vacuum chamber is still needed for plasma etching, as described in "A Practical ITO Replacement Strategy: Sputtering-Free Processing of a Metallic Nanonetwork", published in *Advanced Materials Technologies* in 2017.^[33] In this paper, a high performance metallic CNN was demonstrated by employing a sputtering/evaporation-free process, which combines advantages of the standard CNN processing with electroless plating, enabled by unique properties of the commercial amorphous fluoropolymer CYTOP. This network shows outstanding optoelectronic performance, with FoM (defined in Section 1.1.3) $F_{TCE} \approx 20000$ (at T $\approx 86.4\%$ and Rs $\approx 0.13 \Omega$ sq⁻¹), as well as excellent mechanical flexibility and stability. This network outperforms the current industry standard, ITO, in performance and likely in cost, as a result of the elimination of the sputtering/evaporation step. This is therefore a dramatic step toward replacing ITO with a metallic cracking nanonetwork.

3.1.1 Introduction

Crack-nanonetworks (CNN) have been proposed as an ITO replacement for many applications.^[2,32,71,82] These are metallic networks that can be made highly transparent, with low haze, and simultaneously very conductive and mechanically flexible. However, while these networks outperform ITO in many aspects, the need for vacuum sputtering/evaporation processing of this initial type of CNN, and the likely associated

manufacturing costs, may outweigh their performance gains over ITO. Therefore, elimination of vacuum processing in general, and sputtering/evaporation in particular, is a key to turn the CNN method into a more viable ITO replacement. Here, we propose and demonstrate such a new sputtering/evaporation-free process. This is a dramatic step towards replacing ITO with a CNN.

In earlier studies, we investigated various methods of making CNNs.^[32,71] The basic idea is to cover a substrate with a self-cracking material template, which forms a thin film which, when properly processed, self-cracks, forming a dense network of micro-scale cracks. After deposition of a metal (via e.g. vacuum chamber-based sputtering or evaporation), and subsequent wash-removal of the template, the corresponding network of metallic microwires forms in place of the crack network. We have explored various self-cracking templates (e.g. TiO₂,^[32] polymer sol-gel CA600,^[32] egg white,^[71] etc.), but none of those could survive vacuum-free, wet-deposition of a metal. Other groups have conducted electroplating and electroless metal plating by using SiO₂ and resin sacrificial layers, but the process for metal-seed deposition is still based on a sputtering process, or a complicated solution process (more than 30 min to nucleate catalyst particles)^[83,84]. Here, we present a new solution process which eliminates the need for sputtering or evaporation. It combines advantages of the standard CNN processing with electroless plating, enabled by unique properties of the commercial amorphous fluoropolymer CYTOP, which has been widely used as a dielectric and hydrophobic layer in electronic devices.^[85]

3.1.2 Results and discussion

Figure 19a illustrates schematically the major steps of the process. First, a layer of CYTOP is deposited on a polished surface of crystal Si (step 1), followed by deposition of the sacrificial material (we investigated two separate materials for this sacrificial layer step, egg white (albumin) and CA600) (step 2), which self-cracks upon drying (step 3). In step 4, a plasma etch transfers the template crack pattern into the corresponding pattern of etched grooves in CYTOP, and the remains of the template film are removed by washing. In step 5, electroless plating is used to selectively deposit metal into the grooves. In step 6, CYTOP is removed by plasma etching. Steps 7 and 8 represent an example of the network transfer process. First, the network is coated with UV-curable glue, and then a flexible substrate (e.g. polyethylene terephthalate, PET) is attached to it (step 7). After the glue is cross-linked under UV radiation, the PET substrate is peeled off, with the network attached to it (step 8). The network remains embedded in the UV glue, which reduces the surface roughness (**Figure 20**).



Figure 19. Details of the sputtering/evaporation-free CNN process.

a) Processing steps (follow the arrows). b) Optical images illustrating control of wetting properties of CYTOP via plasma treatment: before treatment (left image), after plasma treatment for 30 s (middle image), and after follow-up thermal sintering treatment (right image). c) Schematic diagram of the electroless deposition process ("M" represents Ag or Cu).^[33]



Figure 20. Characterization of Ag network on PET. a) 3D morphology via AFM. and b) SEM image of sputtering/evaporation-free Ag network on PET substrate after peel-off.^[33]

There are additional treatments of the CYTOP layer, which involve control of the wetting properties. Images in Figure 19b show the reversible hydrophobic property of CYTOP under plasma and thermal treatments. The initial surface is hydrophobic, with contact angle as high as 115° (left image). Here, contact angle is the angle between the surface of liquid and the outline of the contact surface. After a short (< 1 min) plasma treatment, the surface becomes hydrophilic (contact angle about 45°, middle image). Such plasma treatment is used before step 2, to facilitate the template deposition. The hydrophobic property can be recovered by thermal treatment, as demonstrated in the right panel of Figure 19b. This process is used before step 5, to selectively deposit metal in the etched grooves. The surface property of CYTOP strongly affects the morphology of the plated metallic network (Figure 21). Because the hydrophobic material is prepared on an initially hydrophilic substrate, the larger the contrast in chemical affinity between the two regions, the better the morphology of the metallic network (smaller metal particles). Metal particles are likely to grow in hydrophilic regions because metal particles are in liquids.

Figure 19c schematically depicts the chemistry of the electroless plating. Electroless plating is mainly different from electroplating by not using external electrical power. It involves simultaneous chemical reactions in an aqueous solution, which occur without the use of external electrical power. The process is very efficient and fast (a few seconds), controlled by adjusting the concentrations of the AgNO₃ and HF reactants. The chemical reaction involved has been widely used in silicon nanowire array fabrication and solar cells.^[86–90]



Figure 21. Morphologies of plated metallic networks depend on different surface properties of CYTOP.

a) Without recovering hydrophobic property before electroless plating; b) recovered hydrophobic property through a simple thermal sintering before electroless plating. Metal particles in b) are smaller than those in a).^[33]

Figure 22a-f show SEM images of resulting CNNs, made of different metals (silver and copper) and sacrificial materials (both egg white and CA600). One can control the morphology of the networks by varying the template material, thickness, cracking temperature, etc., as discussed in our published work.^[32] Figure 22g shows a photograph of a silver network (egg white template) on a PET substrate, demonstrating its good transparency and mechanical flexibility. The crystallinity of the plated metal is excellent, comparable to that obtained by vacuum processing, as demonstrated in Figure 22h and Figure 22i.



Figure 22. Morphologies and XRD spectra of the sputtering/evaporation-free CNN.

a, b) SEM images of silver network based on the CA600 template. c, d) SEM images of silver network based on the egg white template. e, f) SEM images of copper network based on the egg white template. g) Photograph of the silver network on a PET substrate, demonstrating its flexibility and transparency. h, i) XRD spectra of silver and copper networks, respectively. h) and i) show that crystallinity of the plated metal is excellent.^[33]

Figure 23 demonstrates optoelectronic properties of various transparent conductors. Figure 23 plots the relationship between the optical transmittance (*T*) and the sheet resistance (R_s). FoM (F_{TCE}) defined in Section 1.1.3, is used to evaluate the optoelectronic performance.^[91] Our sputtering/evaporation-free Ag networks have good performance with low sheet resistance (~1 Ω sq⁻¹) and high transmittance (~85%), with $F_{TCE} \sim 2,000$. Much better performance is achieved with the corresponding Cu networks: $F_{TCE} \sim 20,000$ (T = 86.4% and $R_s \sim 0.13 \Omega$ sq⁻¹), with a thickness of ~ 3 µm and metal wires coverage ~ 14% (**Figure 24**). This excellent performance is likely due to the high crystallinity and compact morphology of the plated copper, as evidenced by Figure 22f and Figure 22i. Figure 23b shows a comparison of optical transmittance spectra in the visible regime between these metallic networks ($R_s(Cu) \sim 0.159 \Omega$ sq⁻¹, $R_s(Ag) \sim 3.1 \Omega$ sq⁻¹) and a conventional sputtered ITO film (thickness ~ 150 nm, $R_s \sim 14 \Omega$ sq⁻¹).^[32] The haze of the Ag metal nanonetwork is small (~ 7%) after transferring to PET/UV substrate (**Figure 25**).





a) Optical transmittance of metallic networks as a function of sheet resistance (As comparison to Crack Cu NWs,^[83] Plating Ag mesh,^[92] Ag NWs,^[23] Electro-spun Ag NWs,^[93] Graphene,^[94] Dry transfer Ag NWs,^[73] PEDOT : PSS,^[95] Sputter Ag mesh,^[96] Cu mesh^[97] and ITO). The solid lines represent Equation (1) for the given values of *F*. *F* here refers to F_{TCE} . b) Transmittance versus wavelength for our two networks, as compared with ITO.^[33]



Figure 24. Metal coverage and thickness.

a) Optical image of a plated Cu network which is used to calculate the surface coverage, with the area coverage of ~14% (Red: metal wires; Black: substrate). b) Thickness measurement shows the typical wire thickness of ~3 μ m.^[33]



Figure 25. Haze of a typical Ag nanonetwork.

Specular transmittance, diffusive transmittance and haze of a sample transferred to PET/UV substrate are shown.^[33]

Mechanical and thermal stability are important for some device applications, such as touch screen and wearable electronics. Figure 26a shows that the stability under bending of our Ag plated CNN is excellent, and as expected, it outperforms the commercial ITO film. 700 cycles are measured as shown in Figure 27 and Figure 28. In the test, the bending radius was chosen to be about 4 mm. Figure 26b shows that our Ag-plated CNN is very stable under sonication, and in fact it outperforms even the Ag-evaporated CNN. A tape test was also conducted to evaluate adhesion of the networks to the PET substrate, as summarized in Figure 26c. In each cycle, 3M "Scotch" tape was pressed to the sample and subsequently peeled-off, with the resistance monitored in real-time. As in the test, the stability of the Ag plated CNN is very good, and again outperforms the Ag-evaporated CNN. The thermal stability of these networks (on silicon substrates) was evaluated by using a hot plate in a gradient of 50°C. As shown in Figure 26d, the resistance of the Ag networks decreases slightly as temperature increases; this is expected because resistivity increases with temperature.^[98,99] The Cu networks are less stable in air at high temperature, likely due to oxidation. This can be prevented with protective coatings. However, even without any such coating, our Cu networks remained stable at room temperature for more than 90 days (Figure 29).



Figure 26. Flexibility and stability of the sputtering/evaporation-free CNN.

a) Sheet resistance variation with bending (bending radius ~ 4 mm). ITO film is shown as the control. b) Sheet resistance variation with sonication time for the plated and the evaporated CNN. c) Tape test for the plated and the evaporated CNN. Morphologies of evaporated CNN in the early (left inset), and late (right inset) stage of the test. d) Thermal stability of the Ag and Cu plated CNN on silicon substrate.^[33]



Figure 27. Sheet resistance variation versus bending times for Ag-plated network. Sheet resistance of Ag-plated network is measured for 700 cycles and the set-up of the measurement is shown in the insert.^[33] These data are plotted on the scale shown to emphasize that the was negligible variation in R_s with bending compared to what occurs in ITO (see Figure 26).



Figure 28. Details of the variation of the resistance.

Variation of resistance of ITO film and our sputtering/evaporation-free Ag network are shown.^[33]


Figure 29. Air stability of sputtering/evaporation-free Cu network. Sheet resistance of Cu network in first 100 days is shown.^[33]

Figure 30 shows examples of applications of our sputtering/evaporation-free CNN. First is as an optically-transparent heater, with the CNN on PET substrate and two narrow silver paste lines along edges as contacts. The heater has a resistance of $R_s \sim 3 \Omega \text{ sq}^{-1}$, and it is subjected to three voltage pulses 1.5 V, 2.5 V and 3.5 V. The corresponding temperature variations are shown in Figure 30a. The durability of the transparent heater is also tested with a pulse voltage for 200 s (Figure 31). Thermographic IR camera images demonstrate high temperature uniformity of this heater (Figure 30b), even under bending strain (Figure 32). Figure 30c shows photographs of the heater, with a star shaped area painted with thermochromic paint (star) (with a transition temperature of ~ 37°), and subjected to a single voltage pulse (3 V) for 200 s. As the heater temperature increases, the image of the star gradually disappears. This illustrates the principle of the thermochromic signage.



Figure 30. Examples of applications of the sputtering/evaporation-free CNN.

a) Plots of temperature vs time for a transparent heater, for three square voltage pulses, and b) thermographic IR camera image of the heater (heated area size: $30 \text{ mm} \times 30 \text{ mm}$). c) A sequence of photographs of our CNN on PET with a star-painted using the thermochromic paint, and subjected to a single voltage pulse (3V). The painted star is shown fading away after 2 seconds, and completely disappearing after 4 seconds.^[33]



Figure 31. Durability of transparent heater.

Temperature vs time is shown while transparent heater is tested with a pulse voltage of 200 s.^[33]



Figure 32. IR image of transparent heater while bending. High temperature uniformity of this heater under bending strain is demonstrated by Thermographic IR camera image.^[33]

A rough cost estimation of traditional sputtered ITO and our sputtering/evaporationfree metallic networks is showed in **Table 1**. The sample size is set to be 10 cm \times 10 cm. We list the cost of metal source in the table. Silicon wafer (or amorphous silicon film) is used as the substrate during the process. The silicon element is consumed in the metal deposition reaction, but it is negligible. So the silicon wafer could be reused, at least hundreds of times if properly handled. Of course one could use a flexible amorphous silicon substrate, which would reduce the cost. For ITO, the expensive sputtering equipment, maintenance charge, and vacuum electricity consumption definitely increase the cost. For a solution process, the cost of equipment is almost 1/10 of a sputtering equipment, also without expensive maintenance and electricity usage.

NO.	Chemicals used	Price[\$/g]	Quantity used	Cost/sample
			[mg]	[\$]
1	ITO target	1.41	71	0.1
2	AgNO ₃ (Sinopharm	0.94	75	0.07
	chemical reagent, 99.8%)			
3	Cu(NO ₃) ₂ ·3H ₂ O(Aladdin,	0.43	154	0.066
	99.99%)			

Table 1. Cost comparison (only metal source) between ITO and current sputtering/evaporation-free metallic networks.

3.1.3 Experimental details

Preparation of the sacrificial layer materials: Egg white was diluted with distilled water and centrifuged at a 3500-5000rpm for 5min. Polymer sol-gel CA600 (Sheng Hu Manicure Co., Dongguan, China) was used as received without further purification.

Preparation of the patterned hydrophobic substrate: P-type polished crystal silicon (Sheng Shun electronic Co., Shenzhen, China) was thoroughly cleaned by supersonic treatment with the following solvents in sequence: acetone, ethanol and distilled water, each for 20 minutes, following by drying with N₂ flow. CYTOP (CYTOPTM, Asahi Glass Company, Japan), was chosen as a hydrophobic coating material. It was diluted with a fluorocarbon solvent (CT-solv180) at a volume ratio of 1:1. Spin coating was conducted to form a uniform hydrophobic membrane on silicon with a two-stage process: 500 rpm for 15 s and 3000 rpm for 30 s. Before spinning egg white, the CYTOP layer was treated by a simple plasma-flash (20-35 s), to render it less hydrophobic (contact angle $\sim 70^{\circ}$) and make sacrificial layer coating easier. The sacrificial layer (egg white or CA600) was coated by a Mayer bar method (BEVS Industrial Co., Ltd, Guangzhou). Cracking occurs spontaneously under ambient conditions. We could roughly control the cracking process by changing the concentration of the sacrificial materials, the thickness, and the temperature, etc., details of which can be found in our previous paper.^[32] After cracking, CYTOP under the cracks was exposed and removed by plasma etching for 200-300 s. The cracked mask layer on top was washed away with distilled water. To recover the hydrophobic property and selectively deposit metal, the cracked CYTOP layer was thermally annealed in air at 180°C for a few minutes. The resulting contact angle of the final CYTOP layer was ~110°. A patterned hydrophobic layer on silicon substrate was formed.

Ag electroless deposition: Metallic networks were deposited through an electroless plating solution process. The patterned substrate was immersed into a mixture of AgNO₃ (7.7 wt%), H₂O (69.2 wt%) and HF (23.1 wt%). The metal network thickness can be controlled by the concentration of solution and the plating time. After drying with N₂ flow, UV-curable glue was dipped onto the sample. A cleaned flexible PET film (thickness: 50 μ m) was covered onto the UV glue and irradiated by ultraviolet light (365 nm) for ten seconds. The metallic networks were then transferred to the PET substrate after peeling off. Essentially, one can transfer the networks to any comparable substrate.

Cu electroless deposition: The aqueous solution for Cu electroless deposition contained $Cu(NO_3)_2(0.02 \text{ M})$ and HF(5 M). The reaction apparatus was place onto a hot plate, keeping a constant temperature at 50°C. The patterned substrate was immersed into the solution until the desired thickness was reached. Subsequent steps were the same as for Ag electroless deposition.

Ag mesh and ITO deposition: A home-made thermal evaporation vacuum system was used to deposit Ag mesh according to our previous study, while ITO was deposited by sputtering from an ITO target (AJA International. ATC Orion 8, USA). The thickness of the ITO was about 150nm.We have used the ITO in our previous paper.^[32]

Characterization: An SEM (JEOL JCM-5700, Tokyo, Japan) and an optical microscope (MA 2002, Chongqing Optical & Electrical Instrument Co., Ltd) were used to characterize the morphologies of samples. The crystallinity and phase information of the metal particles were determined by an X-ray diffraction system (X'Pert-Pro MPD PW

67

3040/60XRD with Cu-K α 1 radiation, PAN Analytical, Netherlands). Contact angles were measured on an OCA 15 Procontact-angle system (Dataphysics, Germany) using a 2 µL droplets at room temperature. Sheet resistance of samples was measured by two methods: the Van der Pauw method, with four silver paste contacts deposited at the corners of the sample, and recorded by a Keithley 2400 Sourcemeter (Keithley, USA); and with two silver pastes at the edges of a square sample when conducting bending and adhesive testing. Optical transmittance was measured using an integrating sphere system (Ocean Optics, USA). All of the transmittance data presented here are normalized to the substrate. *Fabrication of flexible heater:* Two silver paste lines were brushed at the edges of a square sample as contacts. DC voltage was supplied to the heater through a source-meter (PPS3003T-3S, ATTEN, China) and a Keithley 2400 Source-meter (Keithley, USA) coupled with a thermal resistance was used to monitor the temperature of the heater. The infrared image was recorded by an infrared thermal imager (NEC San-ei Instruments, Ltd, Japan).

Fabrication of thermochromic device: A commercial thermochromic paint was painted onto the sputtering-free Ag network transparent electrode by screen printing. Silver paste was brushed on the two edges of the sample as contacts.

3.1.4 Conclusion

In summary, we have developed a low-cost replacement for ITO, a metallic crack nanonetwork (CNN), which requires no sputtering or evaporation. The network is not only potentially much less expensive than ITO (Table 1), but also outperforms ITO in electro-optic performance, mechanical strength and flexibility. In fact, the figure of merit of this network based on Cu is a very high $F_{\text{TCE}} \sim 20,000$, corresponding to T = 86.4% (at 550 nm) and $R_s \sim 0.13 \ \Omega \ \text{sq}^{-1}$. For the Ag based network, it is still very high, $F_{\text{TCE}} \sim 2,000$, corresponding to $R_s \sim 1.13 \ \Omega \ \text{sq}^{-1}$ and transmittance $T \sim 84.8\%$. We have performed comparative studies with other networks, and also provided examples of two applications: a transparent heater and a thermochromic display/signage. Even with vacuum-based plasma etching still employed in our process, our sputtering/evaporation-free CNN networks represent a practical ITO replacement for many applications including, in addition to those proposed here, LED lighting and photovoltaics.

3.2 ALL-SOLUTION-PROCESSED MICRODOMAIN NETWORKS BASED ON CRACKLE PHOTOLITHOGRAPHY

In Section 3.1, metal was deposited in solution but a vacuum chamber was still used for plasma etching. For this reason, the fabrication process in Section 3.1 is sputtering/evaporation free but not an all-solution process. In this section, an all-solution method conceived in this thesis work is described. A paper entitled "All-Solution-Processed, Scalable, Self-Cracking Ag Network Transparent Conductor" was published on *physica status solidi (a)* in 2017.^[72]

In this work, we developed a scalable and fully solution-based method to produce environmentally stable Ag micro/nanowire networks for transparent conductors. By applying a self-cracking, water-soluble acrylate copolymer film as a photoresist mask, we obviate the need for formal photomask fabrication and costly vacuum and lithographic facilities. We also increase adhesion and decrease roughness of the metal networks by depositing metal into the regions created by a glass etch step. As a result, the networks can potentially be inexpensively scaled to large areas, as well as be flexible after removal from the substrate. They also exhibit record values of figures of merit that have been employed in the literature, offering a possibly excellent replacement for ITO.

3.2.1 Introduction

Previously existing indium-free, all-solution processed TCEs include metal nanowires^[29,66], chemically-derived graphene oxide^[27,100] and lithography-processed metallic networks^[31,101]. Among these, the latter exhibits the best performance, but its

production is costly and not generally scalable. Although the lithographic process makes highly controllable periodic patterns, such an aspect is not necessary for most applications of TCEs. With random patterns, a self-cracking method^[32,71] avoids lithographic processes but, to date, the metal must be deposited under vacuum because self-cracking templates (*e.g.* $TiO_2^{[32]}$, CA600^[32], albumin^[71], acrylics, *etc.*) that survive conventional wet processes have not been available. Vacuum-based deposition has higher facility costs and makes less efficient use of metal than solution-based deposition. Xian, *et al.*^[33] and Gupta, *et al.*^[84] have introduced electroless plating with self-cracking templates using Si as reducer or catalyst, but such a substrate is nontransparent.

Here, we present a method to produce scalable Ag metal networks on glass substrates which avoids both lithographic processes and vacuum metal deposition, and the network is continuous, such that its performance as a TCE is not impeded by thermally-annealed junctions/contacts between individual nanowires. Silver is chosen because of its good electrical conductivity and chemical stability. Our process starts with photoresist-coated glass, soft-baked but not yet UV exposed. A water-based, self-cracking solution (*e.g.* nail polish) is then spin-coated. This solution self-cracks upon drying, yielding a cracked film that functions as a photomask for the underlying resist. After UV exposure and development of the resist, a non-water-soluble random pattern of gaps/crackles in the resist under the cracked nail polish film remains. We then use buffered oxide etch (BOE) to etch the exposed glass under the gaps, thus creating channels in the substrate and increasing the adhesion^[102] of metal in the subsequent step, electroless deposition of Ag. The photoresist is then removed by lift-off in acetone, yielding a connected network of Ag wires on glass. The thickness of the Ag wires can be increased by electroplating,

which also both increases conductivity and reduces sample roughness by filling in the etched glass channels.

3.2.2 Results and discussion

Figure 33 is a schematic of our fabrication process for an all-solution-processed TCE. First, bis(trimethylsilyl)amine (HMDS) and then Shipley S1805 photoresist are spin coated onto a glass substrate, and soft-baked to dry. A water-based nail polish (e.g. Qian Zhi Xiu Co., Shenzhen, China) solution is then spin coated over the photoresist, and allowed to dry. This nail polish self-cracks as it dries in air, but does not adhere to the underlying photoresist to such an extent as to crack that as well. Figure 34a shows an optical microscope image of cracked nail polish on photoresist on glass. Another important property of this nail polish is that it blocks UV light, which makes it an appropriate photoresist mask. After 405 nm UV illumination for 2 seconds, only the photoresist not covered by the nail polish (i.e. in the gaps created by the cracking) is exposed and decross-linked, and thus becomes soluble in resist developer (MF319). As the nail polish mask also dissolves in that water-based developer, it is also removed in this step. After developing for 1 minute and drying with nitrogen gas, one is left with a random network of cracks in the photoresist over the glass, the crack pattern having been transferred from the self-cracking nail polish. An example photoresist pattern is shown in Figure 34b.



Figure 33. All solution-processed TCE fabrication process.

(a) spin coat photoresist and soft bake; (b) spin coat self-cracking material; (c) material self-cracks upon drying in air; (d) UV expose photoresist (PR); (e) develop photoresist; (f) etch glass; (g) electrolessly deposit silver; (h) lift off photoresist; (i) electroplate silver.



Figure 34. Optical microscope images of three stages of preparation of cracked silver networks.

(a) Self-cracked material (nail polish) on photoresist on glass. (b) Cracked photoresist (after removal of cracked nail polish) on glass. (c) Silver network on glass, made by nail polish process. (d) Silver network on glass, made by egg white process. Scale bar in (a), pertaining to all four images, is 500 μ m.

The intermediate photoresist pattern is stable in both acidic and alkaline solutions, and so can act as a mask for subsequent BOE etch and Ag electroless deposition processes. To protect the back and sides of the glass substrate from the BOE and Ag electroless deposition processes, they are covered with tape. Notably, though we only present Ag networks in this work, the chemical stability of our cracked photoresist patterns suggests they can be used as masks for electroless deposition of other metals, and so this technique should be applicable to producing networks composed of a broad set of materials. In our implementation of the process, the substrates are placed in a BOE solution for 2 minutes, which etches channels into the substrate ~1 μ m deep. The resulting etched channels' surfaces also facilitate increased adhesion of the subsequent electrolessly-deposited Ag, as compared to non-etched surfaces, because of increased roughness and silanol groups created on the glass^[102]. The electroless Ag deposition process utilizes Tollens' reagent^[103]. This deposition method involves three reactions.

First, the aqueous salt AgNO₃ is converted to silver oxide (Ag₂O) by OH⁻ ions and a brown precipitate forms. Second, aqueous ammonia is added which dissolves the brown silver oxide and forms aqueous $[Ag(NH_3)_2]^+$. Third, the $[Ag(NH_3)_2]^+$ complex is reduced by adding a solution which contains aldehyde groups, usually a sugar like glucose or dextrose. We used a dextrose solution which was added to the beaker containing the sample and Tollens' reagent, under continuous stirring. After about 2 minutes, about 100 nm-thick silver deposits on all surfaces in contact with the solution, including both photoresist and exposed glass on the top side of the substrate, as well as the tape on the protected back and sides of the substrate. The stripping of the photoresist to lift off the unwanted silver is performed by placing the substrate in acetone for 5 minutes, leaving behind a silver network at the bottom of the etched channels on a glass substrate, as shown in Figure 34c. The tape is also removed from the substrate back at this time. The fabrication process thus described is all-solution based.

The thickness of the silver in the etch channel bottoms can be increased by electroplating, with the existing silver network as the cathode facing a silver plating anode in silver electroplating solution. The thickness of the electroplated silver can be controlled by plating time, and can be built up to fill the entire depth of the etched channels as depicted in Figure 33i, without broadening the line widths. Also, using different spin speeds for the diluted nail polish ("crack material" in Figure 33b) allows one to control the thickness of the polish and, as a result, the average domain size of the nail polish crack pattern. The higher the spin speed, the thinner the nail polish and smaller the domain size. In Figure 35, we show optical microscope images of completed TCEs made using various spin speeds. By increasing the speed from 1,000 to 6,000 rpm in 1,000 rpm increments, we observe the average domain size decreases from $\sim 200 \ \mu m$ to \sim 50 µm and metal coverage ratio increases from \sim 20% to \sim 25%. In Figure 36, we also show how optical transmittance changes with spin speed. Higher speed yields smaller domain sizes and higher metal coverage ratio, thus lowering transmittance. This observation is consistent with our previous cracking work^[32].



Figure 35. Microscope images of completed TCEs made by the nail polish process.

The differences in domain size result from various nail polish solution spin speeds. Spin speed, nominal domain size and metal coverage ratio, respectively, are: (a) 1,000 rpm, 197 μ m, 20.5%; (b) 2,000 rpm, 117 μ m, 21.5%; (c) 3,000 rpm, 95 μ m, 22.0%; (d) 4,000 rpm, 73 μ m, 22.4%; (e) 5,000 rpm, 68 μ m, 24.5%; (f) 6,000 rpm, 49 μ m, 25.6%. Scale bar in (a), pertaining to all four images, is 500 μ m.



Figure 36. Transmittance of all-solution-processed TCEs as a function of wavelength obtained with samples in Figure 35.

In an alternative process, the diluted nail polish can be replaced by 0.6 g mL⁻¹ egg white/water solution. However, the smallest domain size we have been able to obtain from an egg white process is larger than 500 μ m (Figure 34d). This large domain size is not suitable for applications that need fine features (*e.g.* displays). All samples presented in this paper are made by the nail polish process except that in Figure 34d.

Electroplating processes have been used previously^[71] to increase conductivity of already completed metallic networks, but there were two main drawbacks. First, although thick electroplating of metal decreases sheet resistance dramatically, it also increases the sample surface roughness. Second, because electroplating deposits metal in all directions, the widths of the metallic wires will increase along with their thickness. For samples having a high ratio of metallic wire width to domain size, increasing the wire width will increase the metal coverage ratio of the sample and thus decrease the optical transmittance. Our method solves both of these problems by electroplating the silver within the etched channels, which largely constrains the wire widths to the channel widths for thicknesses equal to the depth of the channels. In Figure 37, we show atomic force microscope (AFM) images of a representative sample before electroless deposition, after electroless deposition and after two stages of electroplating. We also show a crosssection view indicating the contributions of Ag at the various deposition stages, Figure 37d. One can see that electroless deposition provides a thin, nearly conformal coating of the exposed surfaces in the glass trench, and that electroplating walls fills the trench, nearly always with some degree of 'dog ears' protruding above the top edges. Once the trench is filled at its middle, further plating forms a smoother wire, as shown. The

surface roughness of such samples is generally less than those prepared without etched substrates because silver deposits from the negative height relative to the glass surface.



Figure 37. AFM images of a representative nail polish-based sample.

(a) Pre-electroless deposition, (b) Post-electroless deposition, (c) Post-electroplated, all for the same area; (d) Profiles along the cut lines indicated in the AFMs, showing the contributions to Ag thickness by electroless deposition (red), partial electrodeposition (yellow), and overfilled electrodeposition (gray).

Figure 38 shows optical transmittance and sheet resistance before and after electroplating ~1 µm thick silver. After electroplating, we were able to achieve sheet resistances below 0.01 Ω \Box^{-1} with only a slight (~1%) reduction in transmittance. The electroplating time for the sample shown in Figure 38 is 380 s. Our best value of 0.008 Ω \Box^{-1} is the lowest sheet resistance for a TCE we have found in the literature. Error! Reference source not found is a photograph of a 100 mm-diameter glass substrate coated by our completed 0.01 Ω \Box^{-1} TCE, placed in front of a building, illustrating both the scalability of our process and the high transparency. In addition, the resistance and transmittance of samples with low R_s changed little (~1% and 2%, respectively) after 8 months in ambient air.

Some applications (*e.g.* wearable devices) of TCEs desire mechanical flexibility. As an optional step, by placing our post-electroplating sample in BOE for 5 minutes, we can etch the glass undercutting the silver network and release the silver network from the substrate, making it free-standing and/or transferrable to a flexible substrate. **Error! Reference source not found.**b is a photograph of a piece of a free-standing silver TCE $(0.01 \ \Omega \ \Box^{-1})$ about 1 cm² in area, with resistance-measurement electrodes attached, placed above the digital readout of a resistance meter, showing high conductance (*i.e.*, low resistance of 0.3 Ω) and high optical transparency. Side view and top view SEM images at various magnifications of a free-standing silver network on a stainless steel support are also shown in **Error! Reference source not found.**.





Sheet resistance change from about 3 $\Omega \square^{-1}$ to below 0.01 $\Omega \square^{-1}$ by electroplating with only 1% transmittance reduce.



Figure 39. Photography and SEM images of samples.

(a) Photograph of a 100 mm-diameter glass substrate coated by completed TCE (sheet resistance 2.2 $\Omega \Box^{-1}$) placed in front of a building (red dash outline added for guidance).



Figure 40. Photography and SEM images of samples (cont).

(b) Photograph of a ~1 cm² piece of a free-standing Ag network TCE (0.01 $\Omega \Box^{-1}$), with electrodes attached, placed above the readout of a resistance meter (blue outline added for guidance). Side view (c) and top view (d), (e) SEM images at various magnifications of the free-standing silver network in (b). Scale bars: (c) 10 µm; (d) 50 µm; (e) 10 µm.

Our results, shown in Figure 41, compare favorably, in fact superior, in all FoM schemes with those of various silver TCEs from the literature; we use F_{TCE} and ϕ here to illustrate this. Our pre-electroplated results shown as red circles (F_{TCE} up to 1,000; $\phi \sim$ 0.09) are slightly better than almost all previous preparations, including those that use vacuum silver deposition (self-cracking template: right triangles, $F_{\text{TCE}} = 504$, $\phi = 0.03^{[77]}$; nanotrough: crosses, $F_{\text{TCE}} = 327$, $\phi = 0.03^{[104]}$) and solution silver deposition (silver nanowires: down triangles, $F_{\text{TCE}} = 212$, $\phi = 0.02^{[29]}$; lithography template: diamonds, $F_{\text{TCE}} = 376$, $\phi = 0.01^{[31]}$). The F_{TCE} of our post-electroplated samples (red squares, F_{TCE} up to 208,000, $\phi \sim 14$) is also higher than that of an electroless-based process that requires Si as a substrate (up triangles, $F_{\text{TCE}} = 1,341$, $\phi = 0.13$)^[33] and an electroplatingbased process that needs vacuum silver as a seed layer (left triangles)^[71], which appeared to have the previous record FoM values ($F_{\text{TCE}} \sim 20,000, \phi = 1.3$). For reference, commercial ITO (blue star) has an $F_{\text{TCE}} \sim 350$, $\phi \sim 0.03^{[105]}$. It should be noted, however, that this and all FOMs are most useful when comparing TCEs at the same or comparable transmittance or sheet resistance levels. In addition to the physical performance and solution-based fabrication advantages of the Ag network presented herein, the conductor material cost compares favorably to that of extant emerging and legacy TCE technologies^[106], with a calculated consumed Ag cost of under \$1.00 m⁻².





Results from other approaches using silver, including commercial ITO (blue star), are included for comparison.

3.2.3 Experimental details

<u>Preparation of substrates</u>: We demonstrated our process with two types of glass substrates. The first were $\sim 25 \times 25 \text{ mm}^2$, 1.1 mm thick glass substrates cut from $\sim 25 \times 75 \text{ mm}^2$ microscope slides. The second were 100 mm diameter soda lime glass wafers (University Wafer no. 1631). Both substrates were first sonicated in acetone (J.T. Baker Chemicals) for 10 minutes, followed by another 10 minute sonication in isopropyl alcohol (IPA) (J.T. Baker), and then dried by blowing nitrogen gas.

Preparation of the cracked photoresist on glass: HDMS (Ultra Pure Solutions, Inc) and positive photoresist (Microposit[™] S1805, Dow Chemical Co.) were both spin-coated (Laurell Technologies Corp.) at 1,000 rpm for 15 s and then 4,000 rpm for 45 s. The coated substrates were baked on a hot plate (Barnstead Thermolyne) at 110 C for 1 min. Nail polish (Qian Zhi Xiu Co., Shenzhen, China) and deionized (DI) water were mixed with volume ratio 5:1. The diluted nail polish was spin coated for 15 s at 500 rpm and for 45 s at speeds between 1,000 rpm and 6,000 rpm, depending of the desired domain size. The samples were then allowed to air dry for 5 min after the nail polish. They were then UV flood exposed (USHIO USH-350DS) and developed (in Microposit[™] MF-319, Dow Chemical Co.), and rinsed in water for 5 minutes and dried by blowing nitrogen gas.

<u>Silver electroless deposition</u>: A buffered oxide etch (BOE) solution (7:1 volume ratio of 40% NH₄F in water to 49% HF in water) from J.T. Baker Chemicals was employed. Samples were placed in the BOE for 2 minutes. After BOE etch, the samples were immersed in DI water for 5 minutes. The Tollens' reagent process used a solution made by mixing a 60 mL of 0.1 M L⁻¹ silver nitrate (Sigma-Aldrich Corp.) solution with a 30 mL, 0.8 M L⁻¹ potassium hydroxide (J.T. Baker) solution. A brown silver oxide

precipitate forms, which is then dissolved by adding ammonia hydroxide (J.T. Baker) dropwise, with stirring. A 6 mL, 0.25 M L⁻¹ dextrose solution (Fisher Scientific) is added to this solution. The etched sample is then dropped into the mixed solution for two minutes with stirring. The volume of solution above is suitable for electroless deposition of a 25×25 mm² sample. One can increase the volumes of all solution proportionally for larger samples.

<u>Silver electroplating</u>: Constant 5 mA current (Gamry Instruments, Inc., Interface 1000 system) was applied across silver plating anode (Esslinger & Co.) and Ag network, both placing in ready-to-use silver plating solution (Krohn Industries, Inc.). The silver anode was sonicated in acetone and IPA for 10 minutes before use.

<u>Characterization</u>: A scanning electron microscope (JEOL JCM-6000), optical microscope (Olympus BX61) and AFM (Vecco Dimension 3100) were used to characterize the samples. Sheet resistances were measured by the van der Pauw method. A current source (Keithley 224) and voltage meter (Keithley 175A) were connected to samples using silver paste and gold wires. Optical transmittance was measured by using an integrating sphere system (Ocean Optics Spectroclip-TR) with a halogen light source (Ocean Optics HL-2000-FHSA) and spectrometer (Ocean Optics Maya 2000 Pro). All transmittance data presented are normalized to that of a clean, glass substrate. The performance of aluminosilicate glass coated by 175 nm ITO (Delta Technologies, LTD., No. CB-40IN-0107) was compared with all other TCEs.

3.2.4 Conclusion

We have demonstrated an all-solution processed transparent conductor that can be scalable and inexpensively produced, via two innovations. First, we used a self-cracking material as a UV mask to avoid high cost lithography and vacuum processes, and second, we etched the glass substrate to create channels which are filled by subsequent electroplating. Moreover, using Ag as the metal material, the network films are chemically and environmentally stable, and compatible with other soft processes, offering them as a possible cost-effective, smart transparent conductor for *e.g.* OLEDs, thin film solar cells, and electromagnetic shielding.

4.0 NANODOMAIN NETWORKS BASED ON CRACKLE TEMPLATES WITH SOLUTION METAL DEPOSITION

In this Chapter, we further improved the process in Section 3.2 by integrating metallic networks with metallic nanowires to decrease domain size of networks, so the resulting networks can be used in applications that require small domain size.^[65]

4.1 ALL-SOLUTION-PROCESSED MICRO/NANO NETWORKS BY CRACKLE PHOTOLITHOGRAPHY AND ELECTROPLATING

In Section 3.2, we introduced an all-solution process to produce metallic networks, but one problem is that the domain sizes of patterns are in 1000 μ m² scale. In this Chapter, we introduce another all-solution method that integrate microwires with nanowires to reduce domain size. This work was published on *physica status solidi (RRL)* in 2019, with the title "All-Solution-Processed, Micro/Nanowires with Electroplate Welding as Transparent Conducting Electrodes".^[65]

In this work, we developed an all-solution processed transparent conductive electrode with sheet resistance one order of magnitude smaller than other approaches to nanowire-based transparent conductors. This is achieved by integrating all-solution produced microwires with a nanowire solution and electroplating and electrowelding. Advantages of the resulting transparent conductor are: indium-free, vacuum-free, lithographic-facility-free, metallic-mask-free, small domain size ($\approx 10 \ \mu m^2$), low sheet resistance ($R_s < 1 \ \Omega \ \Box^{-1}$), high optical transmittance (T > 80%), mechanical flexibility, and scalability, thus making it a potentially excellent replacement for ITO.

4.1.1 Introduction

As described in prior sections, efforts are underway to seek a replacement for ITO and among the alternatives for ITO, metallic (*e.g.* silver^[29], gold^[107], copper^[108]) nanowires stand out because they are indium-free, vacuum-free by growing from solution^[66], and can be flexible, thus overcoming most of ITO's drawbacks. Although metals have excellent bulk electrical conductivity, the contact resistance between nanowires dominates the resistivity of TCEs made by MNWs; therefore, nanowire-to-nanowire "welding" is a necessary step after MNW coating (via *e.g.*, drop coating^[29,74], spin coating, spraying^[30], Mayer rod coating^[109], and vacuum-filtering. Good welding between nanowires is also essential for mechanical properties of nanowires, and required for foldable and stretchable electronics.^[75,79,110,111] Researchers have developed various welding methods such as thermal heating^[73], mechanical pressing^[74], chemical welding^[75], plasmonic treatment^[76,77] and nano-joining by conductive polymers^[78], conductive nanoparticles^[79] or carbon nanomaterials^[80,81].

There are several approaches in the literature for preparing continuous metallic networks that do not require such a welding step: (i) lithographically-made patterns followed by vacuum-based metal deposition^[20,64]; (ii) lithographically-made patterns followed by solution-based metal deposition^[31]; and (iii) random self-cracking films as

mask followed by vacuum-based metal deposition^[32,82]. It is necessary to mention, however, that self-cracking materials used at room temperature and pressure reported to date do not survive solution-based metal deposition. Suh *et al.* reported Si₃N₄ can crack with tensile stress in Si₃N₄ / Si systems but (low pressure and high temperature) chemical vapor deposition is used for Si₃N₄ deposition and TCEs made by this method must be transferred to flexible substrates, because Si is not transparent.^[112,113] To eliminate both costly lithographic facilities and costly vacuum-based metal deposition, some of the current authors previously reported a maskless photolithographic process called crackle photolithography (CPL)^[72,114] by replacing a conventional metallic mask with UV-stable self-cracking films. Random photoresist patterns produced by CPL survive solutionbased metal deposition and CPL-based TCEs are fully solution-processed and do not require hard lithographic or mask writing facilities.^[72] Although continuous metal networks can achieve extremely low sheet resistance (< 0.1 Ω \Box^{-1}), lower than MNWs by electroplating^[71,72], the domain sizes in all the aforementioned continuous metallic network examples are limited by mask domain size or crackle size, and therefore are larger than for MNWs. For this reason, these metallic networks may be difficult to apply to display products, where there is a drive toward smaller pixel dimensions.

Here, we report the integration of Ag nanowires (AgNWs) with microscale continuous Ag networks made by CPL^[72,114]. This combination maintains the qualities of both MNWs and continuous metallic networks, and results in scalable film structures that are flexible, indium-free, vacuum-free, lithographic-facility-free, and metallic-mask-free, with small domain size and high electrical conductivity. Here, silver is chosen because of its chemical stability and excellent conductivity. One can either spin coat Ag nanowires

first (NF), then fabricate a microwire network, or reverse the process by fabricating a microwire network first (MF) and then depositing nanowires. One can also solder nanowires to microwires by electrowelding/plating to improve mechanical contact and further lower sheet resistance.

4.1.2 Results and discussion

Figure 42 is a schematic of the two different approaches to obtain micro/nanowire TCEs. Panel 1 shows the NF process. A AgNW / isopropyl alcohol (IPA) solution is first spin coated onto a glass substrate and annealed in air at 200 °C. Annealing can provide better contact between AgNWs, and thus lower contact resistance.^[73] Next, microwires are produced via CPL (Figure 42.1b to Figure 42.1e).^[72,114] Bis(trimethylsilyl)amine (HMDS) and Shipley S1805 photoresist are spin coated and soft baked to evaporate photoresist solvent. A self-cracking material solution (e.g. nail polish / water solution^[72,82,114]) is then spin coated which, upon drying in air at room temperature, selfcracks. TiO₂ nanoparticles^[32], CA600 (an acrylic resin water-based dispersion)^[32], CYTOP^[33] and albumin^[71] are also known to crack spontaneously upon drying. To our knowledge, however, none of these self-cracking materials can survive conventional wet processes, so many previous works required vacuum-based metal deposition. Nail polish is particularly useful as a cracking template in CPL because it can block UV light, which makes it an appropriate photoresist mask and, therefore, CPL can avoid the fabrication of a conventional metal mask. After 2 s exposure to 405 nm UV light, only the photoresist not covered by the nail polish gets exposed. Exposed photoresist and nail polish mask will subsequently dissolve in the water-based photoresist developer MF319 and leave randomly cracked photoresist patterns over AgNW-coated glass (Figure 42.1c). These photoresist patterns are transferred from nail polish; however, they will survive both acidic and alkaline solutions during conventional wet processes, and so can be used as masks for subsequent buffered oxide etch (BOE) and electroless Ag deposition processes. BOE will create $\approx 1 \,\mu$ m deep channels. The purpose of BOE here is to activate the glass surface by creating silanol groups,^[102] thus increasing adhesion of electrolessly-deposited Ag. Using Tollen's electroless reaction^[103], about 100 nm thick Ag is deposited onto all surfaces. Using lift-off in acetone, the photoresist together with unwanted silver are removed, leaving the Ag microwire network. If desired, additional Ag can be electroplated to increase contact between micro/nanowires and as a result the sheet resistance of the whole sample can be further decreased.

Panel 2 in Figure 42 is the MF process. Microwires are made by the same CPL process above: spin coat and soft bake photoresist, spin coat nail polish which then cracks, UV expose and develop photoresist, BOE etch glass, electrolessly deposit Ag and lift off. Different from the NF process, one extra electroplating step can be done to increase the thickness of microwires before spin coating the nanowires. The electroplated Ag will fill the etched channels first without significantly increasing the microwires' width, thus making the sheet resistance decrease faster than the transmittance decrease. After spin coating Ag nanowires, a second electroplating can also be done for micro/nanowire welding.


Figure 42. Two different micro/nanowire-based TCE fabrication processes.

Method NF, nanowires first: (1a) spin coat AgNWs and bake; (1b) spin coat photoresist and soft bake; spin coat self-cracking material; material self-cracks upon drying in air; (1c) UV expose photoresist (PR); develop photoresist; (1d) etch glass; (1e) electrolessly deposit silver; lift off photoresist; (1f) electroplate silver. Method MF, microwires first: (2a) spin coat and soft bake photoresist followed by spin coat self-cracking material; material self-cracks upon drying in air; (2b) UV expose photoresist; develop photoresist; (2c) etch glass; electrolessly deposit silver; lift off photoresist; (2d) electroplate silver; (2e) spin coat AgNWs; (2f) electroplate silver again. **Figure 43** (a) and (b) show optical images of TCEs on glass substrates made by the NF and MF methods. Corresponding SEM images by the two methods are shown in (c) and (d). One can clearly see nanowires cover the open space between the microwires in both methods. As a result, domain size drops significantly, to $\approx 10 \ \mu m^2$ in micro/nanowires samples. In Figure 43f, a nanowire junction after electroplating (see Figure 42.1f) is compared with junctions before electroplating (Figure 43e). Electroplating increases the width of the nanowires and makes two wires embedded into each other, rather than merely touching. This benefits the sheet resistance and only slightly decreases the transmittance. Figure 43g is a photograph of a 100 mm diameter glass substrate coated by micro/nanowires, placed in front of a building, demonstrating both the high transparency and the wafer-scalability of our process.



Figure 43. Optical and SEM images of micro/nanowire-based TCEs.

(a),(c) Optical and SEM images of silver micro/nanowires made by NF (Figure 42.1f). (b),(d) Corresponding images made by MF (Figure 42.2f). Dashed lines indicate edges of microwires. (e) SEM of junctions between nanowires before eletroplating. (f) SEM of a junction between two nanowires after eletroplating.



Figure 44. Optical and SEM images of micro/nanowire-based TCEs (cont.).

(g) Photograph of a 100 mm-diameter glass sample (inside dashed circle) made by MF (Figure 42.2f), held in front of a building. Scale bars: (b) 100 μ m, pertaining also to (a); (d) 10 μ m, pertaining also to (c); (f) 200 nm, pertaining also to (e). SEM images taken at 60 degree tilt.

Electroplating is used in both the NF and MF methods for micro/nanowire welding (see Figure 42.1f and Figure 42.2f). **Figure 45** demonstrates how the transmittance and sheet resistance of micro/nanowires change by varying electroplate welding time. Transmittance is measured at 550 nm and averaged over five different spots. Both transmittance and sheet resistance are scaled to the same sample before electroplate welding. Electroplate welding decreases transmittance and sheet resistance because micro/nanowire width increases. It is interesting to note that in the first 20 seconds, sheet resistance drops fastest. The reason is that nanowire junctions change from "touching" to "embedded" in this timeframe, as shown in Figure 43f. Because longer electroplating time can decrease transmittance and the decrease of sheet resistance saturates after 20 seconds, we chose 20 seconds for the electroplate welding time for both NF and MF micro/nanowires.





T (hollow) and Rs (filled) are relative to the same sample before electroplating. Rs is measured by the 4-probe van der Pauw method. Lines are guides to the eye.

Particularly for the MF method, electroplating is used to increase Ag microwire thickness (Figure 42.2d). Previous work has used electroplating to increase the conductivity of TCEs and has achieved good results,^[71] but there remains one drawback: electroplated Ag grows in all directions, so the increasing widths of Ag metallic wires will decrease transmittance. The CPL process solves this problem by electroplating the silver within the etched channels, which largely constrain the microwire widths to the channel widths.^[72,114] Thus, one can use relative longer electroplating time (*e.g.* 50 s) to increase the microwire thickness and reduce the sheet resistance by one order of magnitude without appreciably changing optical transmittance.

The domain size of the nail polish crack pattern can be controlled by spin speeds of the nail polish solution. In **Figure 47**, we show optical microscope images of micro/nanowires made by the MF method using spin speeds from 2,000 to 5,000 rpm. The performance of samples made by all speeds is shown in **Figure 46**a, indicated by different colors. Each color has four points and from right to left they are: before the first electroplating (Figure 42.2c); after the first electroplating (Figure 42.2c); after the second electroplating, Figure 42.2e); after the second electroplating (Figure 42.2f). First, one can see lower nail polish spin speed yields larger domain sizes and lower microwire metal coverage, and thus higher transmittance, which is consistent with our previous CPL work.^[72] Second, among all steps adding Ag to samples, the first electroplating, which the NF process does not have, decreases sheet resistance the most and this electroplating step turns out to be the reason that MF samples outperform NF samples.



Figure 46. TCEs made by MF and NF, and their performance.

(a) T and Rs of MF samples made by spin coating nail polish solution at speeds from 2,000 to 5,000 rpm. For each set of data, points from right to left represent performance before first electroplating (Figure 42.2c), after first electroplating (Figure 42.2d), after spin coating AgNWs (Figure 42.2e) and after second electroplating (Figure 42.2f). (b) T vs. Rs for TCEs made by the current NF (circles) and MF (squares) methods. Results from other silver nanowire approaches, as well as commercial ITO (star), are included for comparison.



Figure 47. Optical images of micro/nanowire-based TCEs made by MF.

(a) - (d) optical microscope images of MF samples made by spin coating nail polish solution at speeds from 2,000 to 5,000 rpm. Scale bar for 500 μ m in (d) pertains to all four images.

A figure of merit (FoM) is often used to compare the performance of TCEs prepared by various methods. We use both ϕ and F_{TCE} here (both defined in Section 1.1.3) to compare our result in Figure 46b with various AgNWs from other work. Our NF results shown as red circles (F_{TCE} up to 404, $\phi = 0.03$) are slightly better than almost all previous works, including those that deposit AgNWs by drop coating (crosses, $F_{TCE} = 211$, $\phi =$ 0.02)^[29] and by Mayer rod coating (down triangles, $F_{TCE} = 100$, $\phi = 0.0046$)^[109]. They are also superior to those that weld AgNWs by solution methods (mechanical pressing: up triangles, $F_{TCE} = 186$, $\phi = 0.012$;^[74] thermal heating: left triangles, $F_{TCE} = 223$, $\phi =$ $0.02^{[73]}$) and even lithography-made nanogrids (right triangles, $F_{TCE} = 164$, $\phi = 0.016$)^[20]. The FoM of our MF samples (red squares, F_{TCE} up to 2016, $\phi = 0.153$) is also higher than that of a micro/nanowires process made by photolithography (diamonds, $F_{TCE} = 579$, $\phi =$ 0.026)^[101]. For reference, commercial ITO (blue star) has an $F_{TCE} = 350$ and $\phi = 0.03$.

Many applications of TCEs require mechanical flexibility. Our micro/nanowires can be transferred to flexible substrates, such as polyethylene terephthalate (PET). **Figure 48** shows results from bending tests of the MF micro/nanowires on PET substrates. Figure 48a shows how sheet resistance changes in the first 1,000 bending cycles. Each point in the figure is the average of the measured sheet resistance data over 50 cycles, scaled to the initial, unbent value R_{si} . After 1,000 of these \approx 90 degree bends, the resistance was about 30% higher than the initial value, indicating some chronic changes to the network. Figure 48b shows how sheet resistance changes in each cycle, wherein the scaled R_s increases by up to 300% at maximum bend but, at least for these first few bends (inset), largely recovers when unbent. We plot the data in Figure 48b against radius of curvature, indicating the ability of these flexible films to be bent to a few centimeters radius. The data in Figure 48 were measured by the 4-probe van der Pauw method.



Figure 48. Sheet resistance of MF sample measured while bending.

(a) R_s over the first 1,000 bending cycles, scaled to initial, unbent value. Each point is an average from 50 bending cycles divided by sheet resistance before bending. (b) Scaled R_s vs. inverse radius of curvature for two bending cycles. Inset: Scaled R_s during first six bending cycles.

4.1.3 Experimental details

<u>Preparation of substrates</u>: Glass substrates in two types of sizes are used. One were $25 \times 25 \text{ mm}^2$, 1.1 mm thick glass substrates and the other were 100 mm diameter, 0.6 mm thick soda lime glass wafers (University Wafer No. 1631). Polyethylene terephthalate (PET) substrates cut into $40 \times 40 \text{ mm}^2$ were used for flexible sample. All substrates were first sonicated in acetone for 10 minutes, followed by another 10 minute sonication in isopropyl alcohol (IPA), and then dried by blowing nitrogen gas.

<u>Preparation of AgNW films</u>: A 20 mg ml⁻¹ AgNW-IPA solution (ACS Material no. Agnw-L70) was first diluted 10 times by IPA to 2 mg ml⁻¹. AgNWs have \approx 70 nm diameter and 100 - 200 µm length. The AgNW-IPA solution was spin coated on glass at 500 rpm for 10 s and then 3,000 rpm for 30 s. The coated substrates were baked on a hot plate at 200 °C for 5 minutes.

Preparation of the cracked photoresist on glass: HDMS (Ultra Pure Solutions, Inc) and positive photoresist Microposit[™] S1805 (Dow Chemical Co.) were both spin-coated at 1,000 rpm for 15 s and then 4,000 rpm for 45 s. The coated substrates were baked on a hot plate at 110 °C for 1 min. Nail polish (Qian Zhi Xiu Co., Shenzhen, China) and deionized (DI) water were mixed with volume ratio 5:1. The diluted nail polish was spin coated for 15 s at 500 rpm and for 45 s at speeds between 2,000 rpm and 5,000 rpm, depending of the domain size desired. The samples were then allowed to dry in air for 5 minutes after the nail polish. They were then UV flood exposed (USHIO USH-350DS) for 2 s and developed in Microposit[™] MF-319 (Dow Chemical Co.) for 1 minute. Samples were rinsed in DI water for 5 minutes and dried with nitrogen gas.

Silver electroless deposition: The backs of the glass substrates were covered with tape to protect them from the buffered oxide etch (BOE) and Ag electroless deposition processes. Samples were placed in BOE solution (7:1 volume ratio of 40% NH₄F in water to 49% HF in water, J.T. Baker Chemicals) for 2 minutes. After BOE, the samples were rinsed in water for 5 minutes. The Tollens' reagent process used a solution made by mixing a 60 mL of 0.1 M silver nitrate (Sigma-Aldrich Corp.) solution with a 30 mL, 0.8 M potassium hydroxide (J.T. Baker) solution. The aqueous salt AgNO₃ was converted to silver oxide (Ag₂O) by OH⁻ ions and a brown precipitate formed. Ag₂O was then dissolved by adding ammonium hydroxide (J.T. Baker) dropwise, with stirring and aqueous $[Ag(NH_3)_2]^+$ formed. The $[Ag(NH_3)_2]^+$ complex was reduced by adding a 6 mL, 0.25 M dextrose solution (Fisher Scientific), which contained aldehyde groups. The etched glass samples were placed at the same time with the dextrose solution into a beaker for two minutes, under continuous stirring. The above volumes of solution were suitable for electroless deposition of a 25×25 mm² sample. One can increase the volumes of all solutions proportionally for larger samples. The tape was removed from the substrate back before lifting off photoresist and unwanted silver in acetone for 5 minutes. Silver electroplating: A constant current of 5 mA (Gamry Instruments, Inc., Interface 1000 system) was applied across the silver network cathode and silver plating anode (Esslinger & Co.), placed face-to-face in ready-to-use silver plating solution (Krohn Industries, Inc.). The silver anode was sonicated in acetone and IPA for 10 minutes before use.

<u>Preparation of flexible samples</u>: UV glue (optically clear liquid adhesive by Octopus Glue) was dropped to the surfaces of micro/nanowire-coated glass samples. PET

substrates were used to cover the UV glue and then samples were UV exposed for 10 minutes to solidify the glue. These samples were then etched in BOE for 8 hours to remove the glass substrates, leaving the micro/nanowires on UV glue-coated PET substrates.

<u>Characterization</u>: An optical microscope (Olympus BX61) and scanning electron microscope (JEOL JCM-6000) were used to characterize the samples. Sheet resistances were measured by the van der Pauw method. A current source (Keithley 224) and volt meter (Keithley 175A) were connected to samples using silver paste to four corners. Optical transmittance was measured by using an integrating sphere system (Ocean Optics Spectroclip-TR) with a halogen light source (Ocean Optics HL-2000-FHSA) and spectrometer (Ocean Optics Maya 2000 Pro). All transmittance data presented are normalized to that of a clean, glass substrate. The performance of aluminosilicate glass coated by 175 nm ITO (Delta Technologies, LTD., No. CB-40IN-0107) was compared with all other TCEs.

4.1.4 Conclusion

In conclusion, we have demonstrated two variants of an all-solution method to produce Ag micro/nanowire films as transparent conductors. By integrating crackle photolithography-based microwires with nanowires and electroplate welding, we obtain transparent conductors with $R_{\rm s} < 1 \ \Omega \ \Box^{-1}$, T > 80%, and domain size $\approx 10 \ \mu m^2$ We also showed that samples can be transferred to flexible substrates, making a possible cost-effective candidate for flexible applications.

5.0 SUMMARY

We have demonstrated a nanodomain all-solution processed transparent conductor that can be scalable and inexpensively produced, via two innovations. First, we used a self-cracking material as a UV mask to avoid high cost lithography and vacuum processes, and second, we integrated crackle photolithography-based microwires with nanowires and electroplate welding. Moreover, using Ag as the metal material, the network films are chemically and environmentally stable, and compatible with other soft processes, offering them as a possible cost-effective candidate for ITO alternatives.

Works in this thesis need a transferring process to get metallic networks onto flexible substrates. Future research of this project will focus on investigating how to fabricate directly on flexible substrates. We are working on a PDMS and tape free all solution process. By eliminating the transferring process and fabricating directly onto flexible substrates, existing all-solution R2R processes can be simplified.

6.0 **REFERENCES**

- B. Han, Q. Peng, R. Li, Q. Rong, Y. Ding, E. M. Akinoglu, X. Wu, X. Wang, X. Lu, Q. Wang, G. Zhou, J.-M. Liu, Z. Ren, M. Giersig, A. Herczynski, K. Kempa, J. Gao, *Nat. Commun.* 2016, *7*, 12825.
- [2] J. Gao, K. Kempa, M. Giersig, E. M. Akinoglu, B. Han, R. Li, Adv. Phys. 2016, 65, 553.
- [3] K. K. Kim, S. Hong, H. M. Cho, J. Lee, Y. D. Suh, J. Ham, S. H. Ko, *Nano Lett.* 2015, 15, 5240.
- [4] H. Lee, S. Hong, J. Lee, Y. D. Suh, J. Kwon, H. Moon, H. Kim, J. Yeo, S. H. Ko, ACS Appl. Mater. Interfaces 2016, 8, 15449.
- [5] T. Sannicolo, M. Lagrange, A. Cabos, C. Celle, J.-P. Simonato, D. Bellet, *Small*2016, *12*, 6052.
- [6] V. Oddone, M. Giersig, *Phys. Status Solidi RRL* 2017, *11*, 1700005.
- [7] J. Xiong, S. Li, Y. Ye, J. Wang, K. Qian, P. Cui, D. Gao, M.-F. Lin, T. Chen, P. S. Lee, *Adv. Mater.* 2018, *30*, 1802803.
- [8] H. Lu, X. Ren, D. Ouyang, W. C. H. Choy, Small 2018, 14, 1703140.
- C. K. Jeong, J. Lee, S. Han, J. Ryu, G.-T. Hwang, D. Y. Park, J. H. Park, S. S. Lee,
 M. Byun, S. H. Ko, K. J. Lee, *Adv. Mater.* 2015, *27*, 2866.
- [10] J. H. Park, S. Han, D. Kim, B. K. You, D. J. Joe, S. Hong, J. Seo, J. Kwon, C. K.

Jeong, H. -J. Park, T. -S. Kim, S. H. Ko, K. J. Lee, *Adv. Funct. Mater.* **2017**, *27*, 1701138.

- [11] J. Jung, H. Lee, I. Ha, H. Cho, K. K. Kim, J. Kwon, P. Won, S. Hong, S. H. Ko, ACS Appl. Mater. Interfaces 2017, 9, 44609.
- [12] S. Hong, H. Lee, J. Lee, J. Kwon, S. Han, Y. D. Suh, H. Cho, J. Shin, J. Yeo, S. H.
 Ko, Adv. Mater. 2015, 27, 4744.
- [13] ReportsnReports, "Transparent Conductive Coatings: Technologies and Global Markets," can be found under http://www.reportsnreports.com, 2015.
- [14] F. Streintz, Ann. Phys. 1902, 314, 854.
- [15] K. Bädeker, Ann. Phys. 1907, 327, 749.
- [16] J. M. Mochel, *Electrically Conducting Coatings on Glass and Other Ceramic Bodies*, **1951**, US2564707A.
- [17] F. Galeotti, W. Mróz, M. Catellani, B. Kutrzeba-Kotowska, E. Kozma, J. Mater. Chem. C 2016, 5407.
- [18] L. J. Van der Pauw, *Philips Tech. Rev.* **1958**, *20*, 220.
- [19] G. Haacke, J. Appl. Phys. 1976, 47, 4086.
- [20] J. van de Groep, P. Spinelli, A. Polman, *Nano Lett.* **2012**, *12*, 3138.
- [21] M. Dressel, G. Grüner, *Electrodynamics of Solids: Optical Properties of Electrons in Matter*, Cambridge University Press, Cambridge, UK, 2002.
- [22] L. Hu, D. S. Hecht, G. Grüner, *Nano Lett.* **2004**, *4*, 2513.
- [23] S. De, T. M. Higgins, P. E. Lyons, E. M. Doherty, P. N. Nirmalray, W. J. Blau, J. J. Boland, J. N. Coleman, *ACS Nano* 2009, *3*, 1767.
- [24] T. Minami, H. Nanto, S. Takata, Jpn. J. Appl. Phys. 1984, 23, L280.

- [25] H. Kim, C. M. Gilmore, Appl. Phys. Lett. 2000, 76, 259.
- [26] S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. Özyilmaz, J.-H. Ahn, B. H. Hong, S. Lijima, *Nat. Nanotechnol.* 2010, *5*, 574.
- [27] G. Eda, G. Fanchini, M. Chhowalla, Nat. Nanotechnol. 2008, 3, 270.
- [28] Z. Yin, S. Wu, X. Zhou, X. Huang, Q. Zhang, F. Boey, H. Zhang, *Small* 2010, 6, 307.
- [29] J.-Y. Lee, S. T. Connor, Y. Cui, P. Peumans, *Nano Lett.* 2008, *8*, 689.
- [30] V. Scardaci, R. Coull, P. E. Lyons, D. Rickard, J. N. Coleman, *Small* 2011, 7, 2621.
- [31] B. Sciacca, J. van de Groep, A. Polman, E. C. Garnett, Adv. Mater. 2016, 28, 905.
- [32] B. Han, K. Pei, Y. Huang, X. Zhang, Q. Rong, Q. Lin, Y. Guo, T. Sun, C. Guo, D. Carnahan, M. Giersig, Y. Wang, J. Gao, Z. Ren, K. Kempa, *Adv. Mater.* 2014, 26, 873.
- [33] Z. Xian, B. Han, S. Li, C. Yang, S. Wu, X. Lu, X. Gao, M. Zeng, Q. Wang, P. Bai,
 M. J. Naughton, G. Zhou, J.-M. Liu, K. Kempa, J. Gao, *Adv. Mater. Technol.* 2017, 2, 1700061.
- [34] H. Mizoguchi, T. Kamiya, S. Matsuishi, H. Hosono, *Nat. Commun.* 2011, 470.
- [35] R. G. Gordon, *MRS Bull.* **2000**, 52.
- [36] H. Hosono, H. Ohta, M. Orita, K. Ueda, M. Hirano, *Vacuum* 2002, 419.
- [37] K. L. Chopra, S. Major, D. K. Pandya, *Thin Solid Films* 1983, 1.
- [38] Q. Wei, Ed., Surface Modification of Textiles, Woodhead Publishing, 2009.
- [39] Y. Furubayashi, T. Hitosugi, Y. Yamamoto, Y. Hirose, G. Kinoda, K. Inaba, T.

Shimada, T. Hasegawa, Thin Solid Films 2006, 157.

- [40] K. Matsubara, P. Fons, K. Iwata, A. Yamada, S. Niki, *Thin Solid Films* **2002**, 176.
- [41] J.-W. Park, G. Kim, S.-H. Lee, E.-H. Kim, G.-H. Leeb, *Surf. Coatings Technol.* 2010, 915.
- [42] M. Sibiński, K. Znajdek, Opto-Electronics Rev. 2017, 33.
- [43] E. Kuantama, D.-W. Han, Y.-M. Sung, J.-E. Song, C.-H. Han, *Thin Solid Films* 2009, 4211.
- [44] M. Kaempgen, G. S. Duesberg, S. Rotha, Appl. Surf. Sci. 2005, 425.
- [45] L. Xiao, Z. Chen, C. Feng, L. Liu, Z.-Q. Bai, Y. Wang, L. Qian, Y. Zhang, Q. Li,
 K. Jiang, S. Fan, *Nano Lett.* 2008, 4539.
- [46] L. Cai, L. Song, P. Luan, Q. Zhang, N. Zhang, Q. Gao, D. Zhao, X. Zhang, M. Tu,
 F. Yang, W. Zhou, Q. Fan, J. Luo, W. Zhou, P. M. Ajayan, S. Xie, *Sci. Rep.* 2013, 3048.
- [47] C. N. R. Rao, K. Biswas, K. S. Subrahmanyam, A. Govindaraj, *J. Mater. Chem.* 2009, 2457.
- [48] B. Partoens, F. M. Peeters, *Phys. Rev. B* 2006.
- [49] D. N. Matsukevich, *Science (80-.).* **2004**, 663.
- [50] K. Rana, J. Singh, J.-H. Ahn, J. Mater. Chem. C 2014, 2646.
- [51] P. R. Somani, S. P. Somani, M. Umeno, Chem. Phys. Lett. 2006, 56.
- [52] S. Bhaviripudi, X. Jia, M. S. Dresselhaus, J. Kong, *Nano Lett.* **2010**, 4128.
- [53] A. N. Obraztsov, E. A. Obraztsova, A. V. Tyurnina, A. A. Zolotukhin, *Carbon N. Y.* 2007, 2017.
- [54] J. W. Suk, A. Kitt, C. W. Magnuson, Y. Hao, S. Ahmed, J. An, A. K. Swan, B. B.

Goldberg, R. S. Ruoff, ACS Nano 2011, 6916.

- [55] M. F. L. De Volder, S. H. Tawfick, R. H. Baughman, A. J. Hart, *Science (80-.)*.
 2013, 535.
- [56] L. Cai, J. Li, P. Luan, H. Dong, D. Zhao, Q. Zhang, X. Zhang, M. Tu, Q. Zeng, W. Zhou, S. Xie, Adv. Funct. Mater. 2012, 5238.
- [57] D. J. Lipomi, M. Vosgueritchian, B. C.-K. Tee, S. L. Hellstrom, J. A. Lee, C. H. Fox, Z. Bao, *Nat. Nanotechnol.* 2011, 788.
- [58] N. Kouklin, M. Tzolov, D. Straus, A. Yin, J. M. Xua, *Appl. Phys. Lett.* 2004, 4463.
- [59] T. V. Sreekumar, T. Liu, S. Kumar, L. M. Ericson, R. H. Hauge, R. E. Smalley, *Chem. Mater.* 2003, 175.
- [60] M. A. Meitl, Y. Zhou, A. Gaur, S. Jeon, M. L. Usrey, M. S. Strano, J. A. Rogers, *Nano Lett.* 2004, 1643.
- [61] N. Ferrer-Anglada, M. Kaempgen, V. Skákalová, U. Dettlaf-Weglikowska, S. Roth, *Diam. Rel. Mater.* 2004, 256.
- [62] Y. Kim, N. Minami, W. Zhu, S. Kazaoui, R. Azumi, M. Matsumoto, Jpn. J. Appl. Phys. 2003, 12.
- [63] C. Niu, MRS Bull. 2011, 766.
- [64] J. van de Groep, D. Gupta, M. A. Verschuuren, M. M. Wienk, R. A. J. Janssen, A. Polman, *Sci. Rep.* 2015, *5*, 11414.
- [65] C. Yang, J. M. Merlo, L. A. D'Imperio, A. H. Rose, Y. M. Calm, B. Han, J. Gao,
 G. Zhou, M. J. Burns, K. Kempa, M. J. Naughton, *Phys. Status Solidi RRL* 2019, 1900010.
- [66] Y. Sun, B. Gates, B. Mayers, Y. Xia, *Nano Lett.* **2002**, *2*, 165.

- [67] M. Jin, G. He, H. Zhang, J. Zeng, Z. Xie, Y. Xia, *Angew. Chem. Int. Ed.* 2011, 10560.
- [68] X. Lu, M. S. Yavuz, H.-Y. Tuan, B. A. Korgel, Y. Xia, J. Am. Chem. Soc. 2008, 8900.
- [69] A. Lucantonio, G. Noselli, X. Trepat, A. Desimone, M. Arroyo, *Phys. Rev. Lett.*2015, 188105.
- [70] J. Gao, Z. Xian, G. Zhou, J.-M. Liu, K. Kempa, Adv. Funct. Mater. 2018, 1705023.
- [71] Q. Peng, S. Li, B. Han, Q. Rong, X. Lu, Q. Wang, M. Zeng, G. Zhou, J.-M. Liu, K. Kempa, J. Gao, *Adv. Mater. Technol.* 2016, *1*, 1600095.
- [72] C. Yang, J. M. Merlo, J. Kong, Z. Xian, B. Han, G. Zhou, J. Gao, M. J. Burns, K. Kempa, M. J. Naughton, *Phys. Status Solidi A* 2017, 215, 1700504.
- [73] A. Madaria, A. Kumar, F. Ishikawa, C. Zhou, *Nano Res.* 2010, *3*, 564.
- [74] T. Tokuno, M. Nogi, M. Karakawa, J. Jiu, T. T. Nge, Y. Aso, K. Suganuma, *Nano Res.* 2011, *4*, 1215.
- S. J. Lee, Y.-H. Kim, J. K. Kim, H. Baik, J. H. Park, J. Lee, J. Nam, J. H. Park, T. W. Lee, G.-R. Yi, J. H. Cho, *Nanoscale* 2014, *6*, 11828.
- [76] E. C. Garnett, W. S. Cai, J. J. Cha, F. Mahmood, S. T. Connor, M. G. Christoforo,
 Y. Cui, M. D. McGehee, M. L. Brongersma, *Nat. Mater.* 2012, *11*, 241.
- [77] S. Han, S. Hong, J. Ham, J. Yeo, J. Lee, B. Kang, P. Lee, J. Kwon, S. S. Lee, M. Y. Yang, S. H. Ko, *Adv. Mater.* 2014, *26*, 5808.
- [78] J. Lee, P. Lee, H. B. Lee, S. Hong, I. Lee, J. Yeo, S. S. Lee, T.-S. Kim, D. Lee, S. H. Ko, *Adv. Funct. Mater.* 2013, 23, 4171.

- [79] S.-P. Chen, Y.-C. Liao, Phys. Chem. Chem. Phys. 2014, 16, 19856.
- [80] S.-T. Hsiao, H.-W. Tien, W.-H. Liao, Y.-S. Wang, S.-M. Li, C.-C. MMa, Y.-H.
 Yub, W.-P. Chuang, J. Mater. Chem. C 2014, 2, 7284.
- [81] P. Lee, J. Ham, J. Lee, S. Hong, S. Han, Y. D. Suh, S. E. Lee, J. Yeo, S. S. Lee, D. Lee, S. H. Ko, Adv. Funct. Mater. 2014, 24, 5671.
- [82] K. D. M. Rao, R. Gupta, G. U. Kulkarni, Adv. Mater. Interfaces 2014, 1, 1400090.
- [83] S. Kiruthika, R. Gupta, K. D. M. Rao, S. Chakraborty, N. Padmavathy, G. U. Kulkarni, J. Mater. Chem. C 2014, 2089.
- [84] N. Gupta, K. D. M. Rao, R. Gupta, F. C. Krebs, G. U. Kulkarni, ACS Appl. Mater. Interfaces 2017, 8634.
- [85] B. B. W. L. Kalb, T. Mathis, S. Haas, A. F. Stassen, *Appl. Phys. Lett.* 2007, 92104.
- [86] R. Douani, T. Hadjersi, R. Boukherroub, L. Adour, A. Manseri, *Appl. Surf. Sci.* 2008, 7219.
- [87] K. Peng, Y. Yan, S. Gao, J. Zhu, Adv. Funct. Mater. 2003, 127.
- [88] N. Megouda, R. Douani, T. Hadjersi, R. Boukherroub, J. Lumin. 2009, 1750.
- [89] Y. Ogata, K. Kobayashi, M. Motoyama, *Curr. Opin. Solid State Mater. Sci.* 2006, 163.
- [90] T. Qiu, P. K. Chu, Mater. Sci. Eng. R 2008, 59.
- [91] D. S. Hecht, L. Hu, G. Irvin, Adv. Mater. 2011, 1482.
- [92] A. Khan, S. Lee, T. Jang, Z. Xiong, C. Zhang, J. Tang, L. J. Guo, L. Wen-Di, Small 2016, 3021.
- [93] P. C. Hsu, D. Kong, S. Wang, H. Wang, A. J. Welch, H. Wu, Y. Cui, J. Am. Chem. Soc. 2014, 10593.

- [94] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim,
 J. Y. Choi, B. H. Hong, *Nature* 2009, 706.
- [95] M. Vosgueritchian, D. J. Lipomi, Z. Bao, Adv. Funct. Mater. 2012, 421.
- [96] K. D. Rao, C. Hunger, R. Gupta, G. U. Kulkarni, M. Thelakkat, *Phys. Chem. Chem. Phys.* 2014, 15107.
- [97] W. K. Kim, S. Lee, D. H. Lee, I. H. Park, J. S. Bae, T. W. Lee, J. Y. Kim, J. H. Park, Y. C. Cho, C. R. Cho, S. Y. Jeong, *Sci. Rep.* 2015, 10715.
- [98] S. Hong, J. Yeo, G. Kim, D. Kim, H. Lee, J. Kwon, H. Lee, P. Lee, S. H. Ko, ACS Nano 2013, 5024.
- [99] M. S. Miller, J. C. O'Kane, A. Niec, R. S. Carmichael, T. B. Carmichael, ACS Appl. Mater. Interfaces 2013, 10165.
- [100] J. Wan, F. Gu, W. Bao, J. Dai, F. Shen, W. Luo, X. Han, D. Urban, L. Hu, Nano Lett. 2015, 3763.
- [101] J. Jang, H.-G. Im, J. Jin, J. Lee, J.-Y. Lee, B.-S. Bae, ACS Appl. Mater. Interfaces
 2016, 8, 27035.
- [102] N. Chitvoranund, S. Jiemsirilers, D. P. Kashima, J. Aust. Ceram. Soc. 2013, 49, 62.
- [103] W. M. Haynes, Ed., CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, USA, 2016.
- [104] H. Wu, D. Kong, Z. Ruan, P.-C. Hsu, S. Wang, Z. Yu, T. J. Carney, L. Hu, S. Fan,
 Y. Cui, *Nat. Nanotechnol.* 2013, 421.
- [105] N.d., ITO coated glass substrate from Delta Technologies.
- [106] B. Azzopardi, C. J. M. Emmott, A. Urbina, F. C. Krebs, J. Mutale, J. Nelson,

Energy Environ. Sci. 2011, 3741.

- [107] P. E. Lyons, S. De, J. Elias, M. Schamel, L. Philippe, A. T. Bellew, J. J. Boland, J. N. Coleman, J. Phys. Chem. Lett. 2011, 2, 3058.
- [108] A. R. Rathmell, S. M. Bergin, Y.-L. Hua, Z.-Y. Li, B. J. Wiley, Adv. Mater. 2010, 22, 3558.
- [109] L. Hu, H. S. Kim, J.-Y. Lee, P. Peumans, Y. Cui, ACS Nano 2010, 4, 2955.
- [110] Y. Won, A. Kim, W. Yang, S. Jeong, J. Moon, NPG Asia Mater. 2014, 6, e132.
- [111] P. Lee, J. Lee, H. Lee, J. Yeo, S. Hong, K. H. Nam, D. Lee, S. S. Lee, S. H. Ko, *Adv. Mater.* 2012, 24, 3326.
- [112] Y. D. Suh, J. Kwon, J. Lee, H. Lee, S. Jeong, D. Kim, H. Cho, S. H. Ko, Adv. Electron. Mater. 2016, 2, 1600277.
- [113] Y. D. Suh, S. Hong, J. Lee, H. Lee, S. Jung, J. Kwon, H. Moon, P. Won, J. Shin, J. Yeo, S. H. Ko, *RSC Adv.* 2016, 6, 57434.
- [114] M. J. Naughton, C. Yang, K. Kempa, M. J. Burns, *All Solution-Process and Product for Transparent Conducting Film*, 2017, U.S. Patent Application No. 15/455,762.