

Optical and Electrical Properties of ITO Coated Willow Glass for Upscaling Perovskite Solar Cell Manufacturing Using Photonic Curing

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Abstract—Indium tin oxide (ITO) coated Willow glass is an excellent substrate for roll-to-roll manufacturing of perovskite solar cells (PSCs) but can have large variability in its optical and electrical properties. Photonic curing uses intense light pulses instead of heat to process materials and has the potential to facilitate faster processing speeds in roll-to-roll manufacturing to upscale the production of PSCs. The substrate materials' properties play an integral role in the photonic curing outcome. Here, we present the effect of ITO transmission on the photonic curing of NiO sol-gel precursors into metal oxide and consequently the PSC performance.

Keywords—Willow glass, ITO, perovskite solar cells, photonic curing, large area, high throughput, roll-to-roll

I. INTRODUCTION

Perovskite solar cells (PSCs) have shown significant progress compared to other photovoltaic technologies, with efficiencies reaching 17.9% for module sizes between 800 – 6,500 cm² [1]. Halide perovskites have the advantage of solution processibility with excellent optoelectronic properties. Using a single roll-to-roll production line with a 1.5 m web width at 30 m/min web speed, a yield of up to 4 GW/year is forecast [2]. To drive down the cost of PSC manufacturing, improvements must be made towards higher throughput by increasing the processing speed and area. One promising approach to meet these goals is adapting intense pulsed light annealing, also known as photonic curing, instead of thermal annealing for materials processing. Thermal annealing requires large-size annealing tools or a slow web speed due to the long time required (tens of minutes). Photonic curing takes milliseconds, thereby increasing roll-to-roll web speed by orders of magnitude [3]–[6].

Photonic curing uses short, microsecond or millisecond, pulses of broadband light (200 – 1500 nm) from a xenon flash lamp to deliver low energy (< 100 J/cm²) and high power (up to 50 kW/cm²) to the sample. The current understanding of the photonic curing mechanism is that the light pulse is absorbed by any light-absorbing component in the sample, upon which the photons are converted to heat and drive the transformation (oxide calcination, crystallization, phase change, etc.). Photonic curing has been applied to several materials in PSCs: halide perovskite active layers [3]–[8]; NiO sol-gel films [3]; SnO₂ nanoparticles and sol-gel films [8], [9]; and mesoporous and compact TiO₂ [10]–[12]. In addition, photonic curing has been used to anneal ITO films on Corning Willow® glass after DC magnetron sputtering, producing similar optical and electrical

properties as thermally annealed ITO films but with a much shorter time [13]. ITO coated Willow® glass (WG) is an excellent substrate candidate for flexible PSCs because of its compatibility with large-area, roll-to-roll manufacturing.

For films that are not strongly light-absorbing, e.g., wide-bandgap metal oxides, having light-absorbing substrate materials when using photonic curing can aid the materials processing. Reference [14] demonstrated that ZrO₂ films on Al can be converted at lower radiant energy than on PEN. Conducting oxide (e.g., ITO) or metal (e.g., Al) layers on the substrate can act as the light-absorbing layer that generates heat to convert the non-light-absorbing sol-gel precursors into metal oxide films. We previously applied photonic curing to process NiO hole transport layer (HTL) and methylammonium lead iodide (MAPbI₃) active layers and achieved a power conversion efficiency of 12% with *p-i-n* PSCs on WG/ITO without any thermal annealing [3]. However, we noticed that the optical and electrical properties of WG/ITO sheets vary greatly. We find that the optical transmission of the WG/ITO determines the extent of NiO metal oxide conversion during photonic curing and has a high impact on PSC performance. Here we characterize the optical transmission and sheet resistance for a variety of ITO (150 nm) coated WG (100 µm, Fraunhofer FEP) substrates and compare how their properties affect the performance of PSC devices with photonic cured NiO HTLs.

II. EXPERIMENTAL RESULTS

WG/ITO substrates were characterized with UV-vis spectroscopy, bolometry measurements, and linear four-point sheet resistance measurements to determine their optical and electrical properties. Photonic curing and bolometry measurements were done using a NovaCentrix PulseForge® Invent. The photonic curing conditions for processing NiO sol-gel precursor films were 500 V lamp voltage, 3.5 ms pulse length, and 10 pulses at a repetition rate of 0.35 Hz [3]. The light absorption is determined by using a bolometer to measure the radiant energy of pulsed light passing through the sample and referencing to the full radiant energy with no sample, as described in [3].

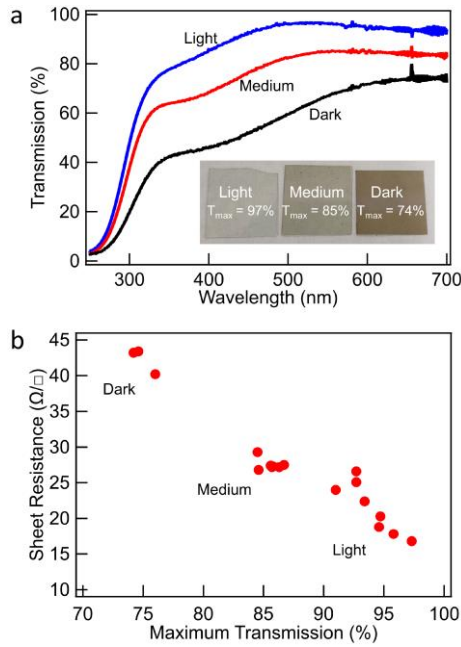


Fig. 1 (a) UV-vis transmission of light (blue), medium (red), and dark (black) ITO on WG substrates, referenced to uncoated WG. The inset shows an image of the light, medium, and dark WG/ITO substrates. (b) Sheet resistance as a function of maximum UV-vis transmission found in WG/ITO substrates.

Fig. 1a shows representative UV-vis spectra for WG/ITO samples we classify as light, medium, and dark categories. Spectroscopic ellipsometry data for the ITO on WG reveal non-uniformity in the optical constants as a function of depth into the ITO layer. To achieve a good fit to the ellipsometry data, the ITO on WG must be modeled as five layers with distinct indices of refraction and extinction coefficients for each layer [3]. Fig. 1b shows that the sheet resistance decreases as the UV-vis maximum transmission—referenced to uncoated WG—of the ITO increases. Note that this is not the typical conductivity-transmission relationship for transparent conducting materials, which normally show lower resistance (higher conductivity) for less transparent films due to increased thickness. Here we observe the opposite trend, which also indicate materials variation in agreement with ellipsometry results.

For PSCs with thermally annealed NiO HTLs, ITO films with high transmission are desirable to maximize the light intensity reaching the perovskite absorber layer. However, processing with photonic curing requires a light-absorbing layer to convert the incoming photons from the light pulse into heat because NiO sol-gel precursor is mostly transparent and very thin (~ 30 nm), hence not able to absorb enough light to effectively convert to metal oxide on its own. Bolometry measurements show that the ITO layer absorbs between 8 to 30% of the incoming light. Therefore, ITO layers with different transmissions absorb different amounts of light and heat the NiO sol-gel precursor to different temperatures for the conversion. Consequently, there is a tradeoff between high transmission for solar cell performance and light absorption required for photonic curing to be effective.

Next, we compare how the maximum ITO optical transmission ($T_{\max}$) affects PSC performance. Fig. 2a shows

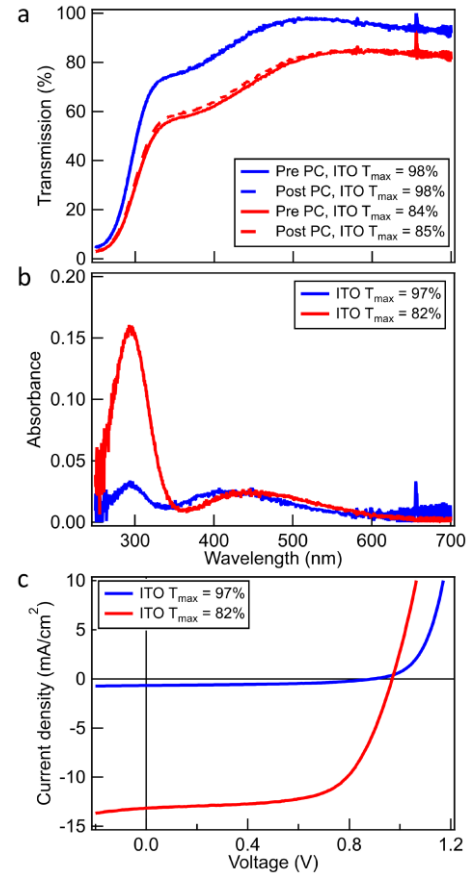


Fig. 2 (a) UV-vis transmission, referenced to uncoated WG, of light ITO ($T_{\max} = 98\%$, blue) and medium ITO ($T_{\max} = 84\%$, red) on WG before (solid) and after (dashed) photonic curing. (b) UV-vis absorbance, referenced to WG/ITO, of photonic cured NiO films processed on light WG/ITO ($T_{\max} = 97\%$, blue) and medium WG/ITO ($T_{\max} = 82\%$, red). (c) Average reverse-scan $J-V$ curves for PSCs with photonic cured NiO and MAPbI₃ made on light WG/ITO ($T_{\max} = 97\%$, blue) and medium WG/ITO ($T_{\max} = 82\%$, red).

UV-vis transmission spectra for two different WG/ITO substrates before and after photonic curing. Optical transmission increases slightly for the medium ($T_{\max} = 84\%$) WG/ITO substrate and remains constant for the light ($T_{\max} = 98\%$) WG/ITO substrate. ITO sheet resistance decreases by 12% for the medium WG/ITO substrate but remains constant for the light WG/ITO substrate. Fig. 2b shows NiO film UV-vis absorbance after photonic curing NiO sol-gel precursor films on two WG/ITO substrates with different transmissions. The NiO film processed on the medium ($T_{\max} = 82\%$) WG/ITO substrate shows a much larger absorbance peak (OD = 0.15) at 300 nm than that on the light ($T_{\max} = 97\%$) WG/ITO substrate (OD = 0.03), indicating that the NiO is converted to a greater extent on the medium WG/ITO substrate. Furthermore, Fig. 2c shows the average reverse-scan $J-V$ plot for $p-i-n$ PSCs made on the two substrates. The PSC device structure is WG/ITO/NiO/MAPbI₃/Phenyl-C₆₁-butyric acid methyl ester/bathocuproine/Al, listed from bottom to top. Both NiO HTLs and MAPbI₃ absorber layers were photonic cured, i.e., thermal annealing was not used to process these devices. Devices made on the medium WG/ITO substrate have significantly better PSC performance than on the light WG/ITO,

with $V_{OC} = 0.967$ V, $J_{SC} = 13.2$ mA/cm², FF = 0.65, and efficiency = 8.3%. In contrast, devices made on the light WG/ITO substrate have $V_{OC} = 0.892$ V, $J_{SC} = 0.67$ mA/cm², FF = 0.47 and efficiency = 0.3%. This shows that the optical transmission of the substrate has a great impact on the photonic curing process, and consequently device performance.

III. DISCUSSION

To understand these observations, we perform SimPulse® simulations to obtain temperature versus time profiles during photonic curing for light ($T_{max} = 97\%$) and medium ($T_{max} = 85\%$) WG/ITO substrates (Fig. 3). The results show that the maximum temperature reached is 197°C and 353°C for light and medium WG/ITO substrates, respectively. This large difference in processing temperature explains the NiO photonic curing outcome shown in Fig. 2b. Because the light absorption of the light WG/ITO substrate is small, the NiO sol-gel precursor is not completely converted to NiO by photonic curing. The medium WG/ITO substrate absorbs more light and reaches a higher temperature, enabling the NiO sol-gel precursor to convert to metal oxide. In addition, the sheet resistance of the medium WG/ITO substrate decreases after photonic curing, which could be due to annealing effects similar to those reported in [13].

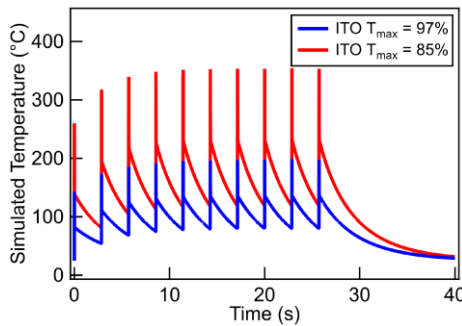


Fig. 3 SimPulse® simulated top film temperature versus time for light WG/ITO (red) and dark WG/ITO (blue) during the photonic curing process.

The variability in WG/ITO optical transmission can lead to drastically different PSC performance (Fig. 2c) when photonic curing is used for materials processing. We expect there to be an optimal point in substrate optical transmission where the light absorption is just high enough to enable conversion of NiO sol-gel precursor without reducing the amount of light that reaches the MAPbI₃ absorber layer too much. Therefore, the light absorption and optical transmission of the substrate and conducting oxide are important considerations when fabricating PSCs using photonic curing.

IV. SUMMARY

To achieve large area, roll-to-roll manufacturing using photonic curing, it is critical to have tight control of the substrate quality (i.e., low variability in optical transmission and light absorption) to have a consistent process. Any variations in these properties will have a large impact on photonic curing, particularly when the ITO layer is the primary light-absorbing component in the sample stack. Here we demonstrate that high transmission WG/ITO substrates do not absorb enough light in the photonic curing process to convert NiO sol-gel precursor

into metal oxide. In contrast, medium transmission WG/ITO substrates could be used to process NiO metal oxide films with photonic curing to fabricate functioning PSCs. Furthermore, the medium WG/ITO substrates showed a 12% improvement in sheet resistance after photonic curing. To optimize photonic curing for processing a particular material system, it is important to consider the optical properties of the substrate materials as this can dramatically affect the photonic curing process parameters and the manufacturing yield.

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REFERENCES

- [1] National Renewable Energy Laboratory (NREL), “Champion photovoltaic module efficiency chart,” 2020. <https://www.nrel.gov/pv/module-efficiency.html> (accessed Apr. 16, 2021).
- [2] EMC, “High speed inline roll-to-roll module production – EMC,” 2020. <https://enmatcorp.com/high-speed-inline-roll-to-roll-module-production/> (accessed Nov. 15, 2020).
- [3] R. T. Piper, T. B. Daunis, W. Xu, K. A. Schroder, and J. W. P. Hsu, “Photonic curing of nickel oxide transport layer and perovskite active layer for flexible perovskite solar cells: a path towards high-throughput manufacturing,” *Front. Energy Res.*, vol. 9, p. 76, 2021.
- [4] W. Xu, T. B. Daunis, R. T. Piper, and J. W. P. Hsu, “Effects of photonic curing processing conditions on MAPbI₃ film properties and solar cell performance,” *ACS Appl. Energy Mater.*, vol. 3, no. 9, pp. 8636–8645, 2020.
- [5] A. H. Ghahremani, S. Pishgar, J. Bahadur, and T. Druffel, “Intense pulse light annealing of perovskite photovoltaics using gradient flashes,” *ACS Appl. Energy Mater.*, vol. 3, no. 12, pp. 11641–11654, 2020.
- [6] J. Troughton *et al.*, “Photonic flash-annealing of lead halide perovskite solar cells in 1 ms,” *J. Mater. Chem. A*, vol. 4, no. 9, pp. 3471–3476, 2016.
- [7] B. W. Lavery, S. Kumari, H. Konermann, G. L. Draper, J. Spurgeon, and T. Druffel, “Intense pulsed light sintering of CH₃NH₃PbI₃ solar cells,” *ACS Appl. Mater. Interfaces*, vol. 8, no. 13, pp. 8419–8426, 2016.
- [8] A. H. Ghahremani, B. Martin, A. Gupta, J. Bahadur, K. Ankireddy, and T. Druffel, “Rapid fabrication of perovskite solar cells through intense pulse light annealing of SnO₂ and triple cation perovskite thin films,” *Mater. Des.*, vol. 185, p. 108237, 2020.
- [9] M. Zhu *et al.*, “Millisecond-pulsed photonic-annealed tin oxide electron transport layers for efficient perovskite solar cells,” *J. Mater. Chem. A*, vol. 5, no. 46, pp. 24110–24115, 2017.
- [10] S. Das *et al.*, “Low thermal budget, photonic-cured compact TiO₂ layers for high-efficiency perovskite solar cells,” *J. Mater. Chem. A*, vol. 4, no. 24, pp. 9685–9690, 2016.
- [11] B. Feleki, G. Bex, R. Andriessen, Y. Galagan, and F. Di Giacomo, “Rapid and low temperature processing of mesoporous TiO₂ for perovskite solar cells on flexible and rigid substrates,” *Mater. Today Commun.*, vol. 13, pp. 232–240, 2017.
- [12] S. Luo *et al.*, “Instantaneous photoinitiated synthesis and rapid pulsed photothermal treatment of three-dimensional nanostructured TiO₂ thin films through pulsed light irradiation,” *J. Mater. Res.*, vol. 32, no. 9, pp. 1701–1709, 2017.
- [13] M. Junghänel, S. Weller, and T. Gebel, “P-65: Advanced Processing of ITO and IZO Thin Films on Flexible Glass,” in *SID Symposium Digest of Technical Papers*, vol. 46, no. 1, pp. 1378–1381, 2015.
- [14] T. B. Daunis, K. A. Schroder, and J. W. P. Hsu, “Photonic curing of solution-deposited ZrO₂ dielectric on PEN: a path towards high-throughput processing of oxide electronics,” *npj Flex. Electron.*, vol. 4, no. 1, p. 7, 2020.