

## *Supporting Information*

### **Evidence and Influence of Copper Vacancies in p-Type CuGaO<sub>2</sub> Mesoporous Films**

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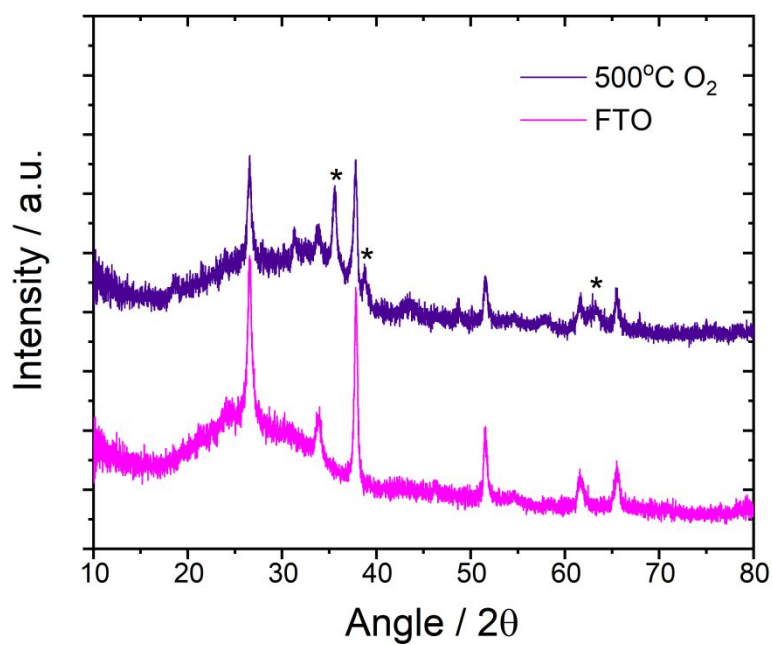
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**Table S1. EDS Measurements**

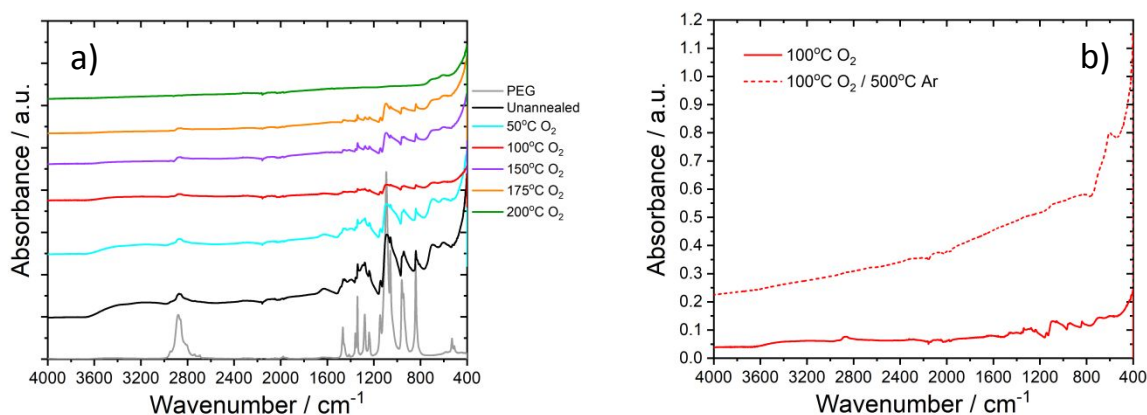
| Annealing Condition      | Atomic%  |          |          | Cu/Ga Ratio |
|--------------------------|----------|----------|----------|-------------|
|                          | O        | Cu       | Ga       |             |
| 100°C O <sub>2</sub>     | 59.3±1.4 | 19.9±0.7 | 20.8±0.7 | 0.96±0.05   |
| 200°C O <sub>2</sub>     | 49.9±0.2 | 24.3±0.1 | 25.7±0.3 | 0.95±0.01   |
| 300°C O <sub>2</sub>     | 49.0±0.5 | 24.9±0.3 | 25.8±0.3 | 0.97±0.02   |
| 100°C O <sub>2</sub> /Ar | 49.3±0.3 | 25.1±0.4 | 25.9±0.1 | 0.97±0.02   |
| 200°C O <sub>2</sub> /Ar | 49.0±0.4 | 24.8±0.1 | 26.1±0.3 | 0.95±0.01   |
| 300°C O <sub>2</sub> /Ar | 48.8±0.3 | 25.2±0.4 | 26.3±0.2 | 0.96±0.02   |
| All Samples <sup>a</sup> | 49.2±0.5 | 24.9±0.4 | 26.0±0.3 | 0.96±0.02   |

<sup>a</sup>All samples excluding 100°C O<sub>2</sub> because values are skewed by the presence of polymer in the sample

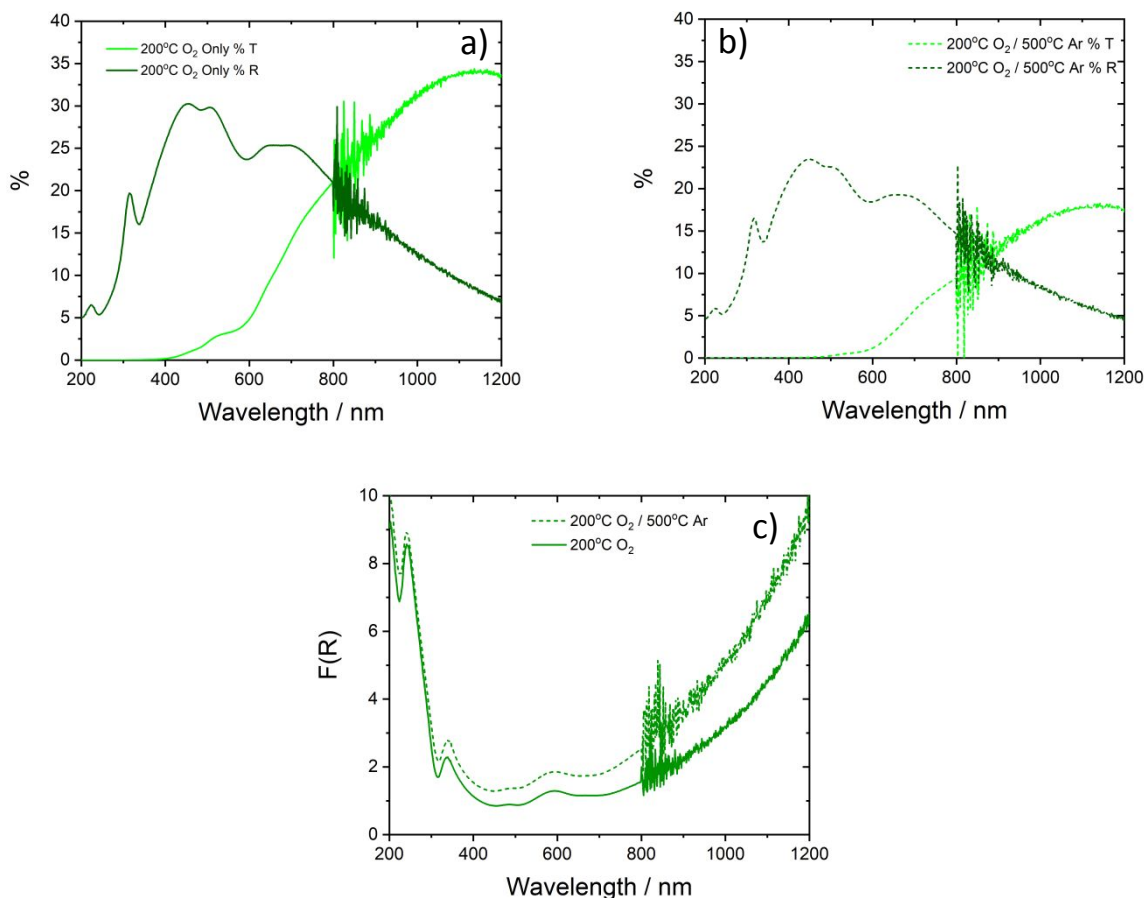


**Figure S1.** Powder XRD at 500 °C showing formation of CuGa<sub>2</sub>O<sub>4</sub> spinel (\*peaks)

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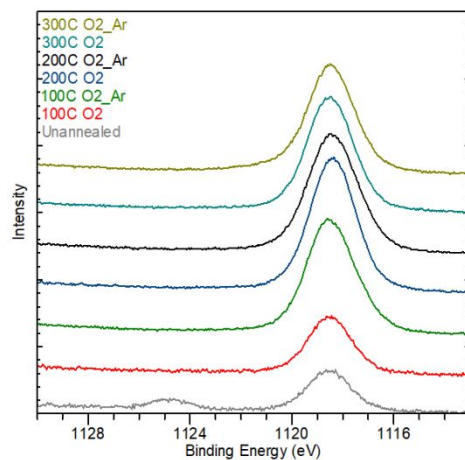


**Figure S2.** FTIR spectra of a) CuGaO<sub>2</sub> films annealed under O<sub>2</sub> from 50-200 °C and b) CuGaO<sub>2</sub> films annealed at 100°C under O<sub>2</sub> and with a subsequent Ar step.

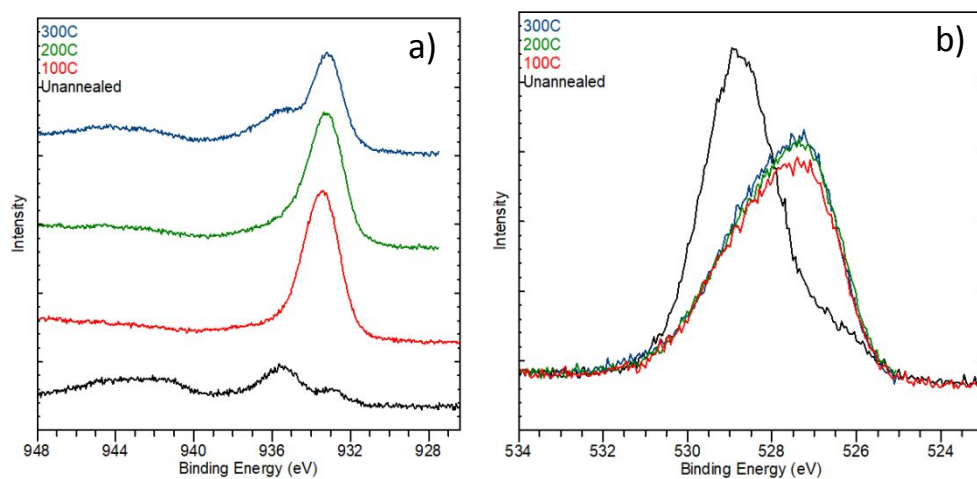


**Figure S3.** UV-Vis-NIR transmittance (T) and reflectance (R) data collected for CuGaO<sub>2</sub> films annealed at 200 °C/O<sub>2</sub> (a) and 200 °C/O<sub>2</sub> followed by 500 °C/Ar (b). (c) Kubelka-Munk plot calculated from reflectance data.

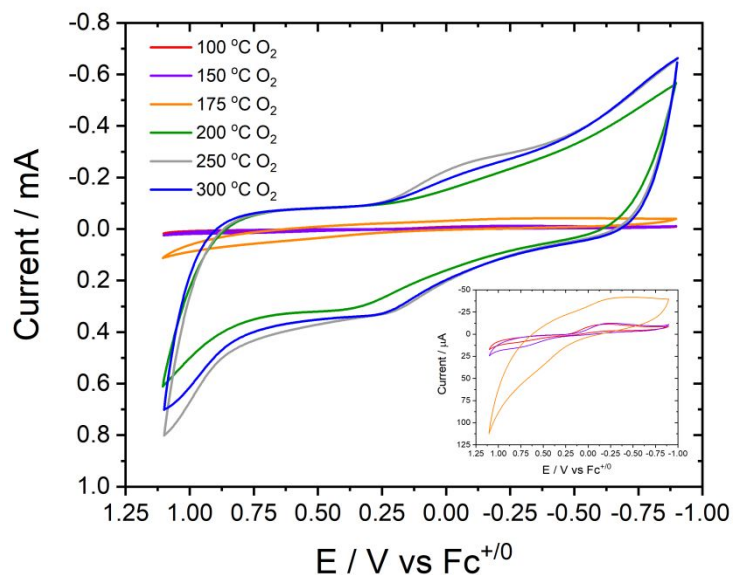
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**Figure S4.** XPS of Ga2p<sub>3/2</sub> peak over all annealing conditions



**Figure S5.** XPS of a) Cu 2p<sub>3/2</sub> and b) O 1s peaks for Ar annealed films



**Figure S6.** CV at all temperatures under O<sub>2</sub>

### EIS Fitting Analysis

Analysis of EIS data was achieved by fitting with the equivalent circuit model shown in Figure 7a and Figures S7. Equations for the impedance of particular circuit elements are presented below. All data and fitting constants are presented thereafter as figures and tables.

#### Resistors

$$Z_R = R$$

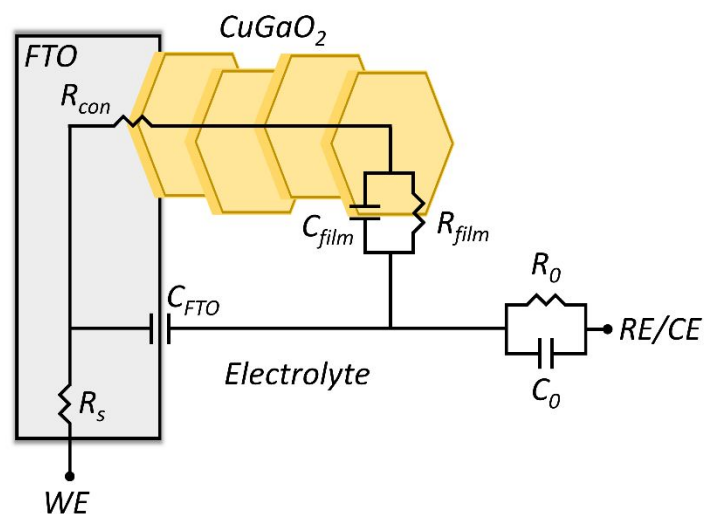
#### Capacitors (Constant Phase Elements)

$$Z_{CPE} = \frac{1}{Q(i\omega)^\beta}$$

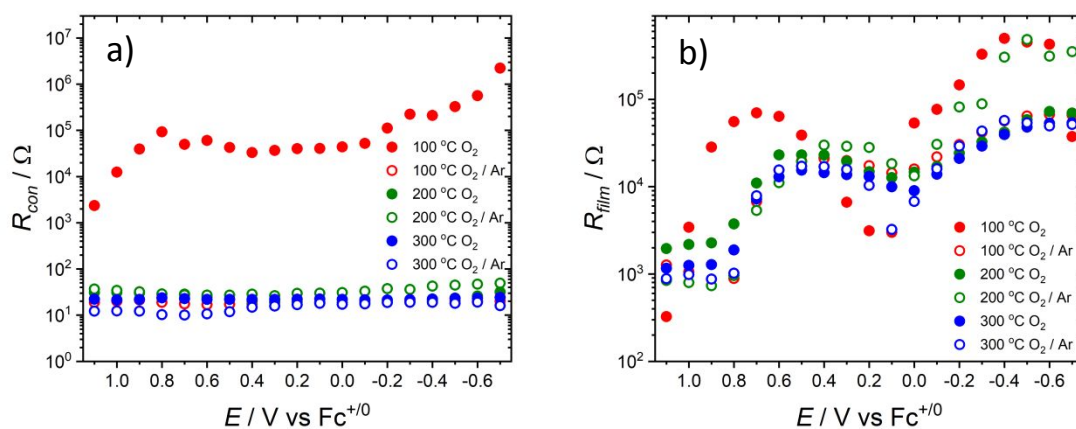
#### Transmission Line

$$Z_{TL} = \left( \frac{R_d R_{film}}{1 + R_{film} C_{film} (i\omega)^\beta} \right)^{1/2} \coth \left[ (R_{film} / R_d) (1 + R_{film} C_{film} (i\omega)^\beta)^{1/2} \right]$$

# Supporting Information

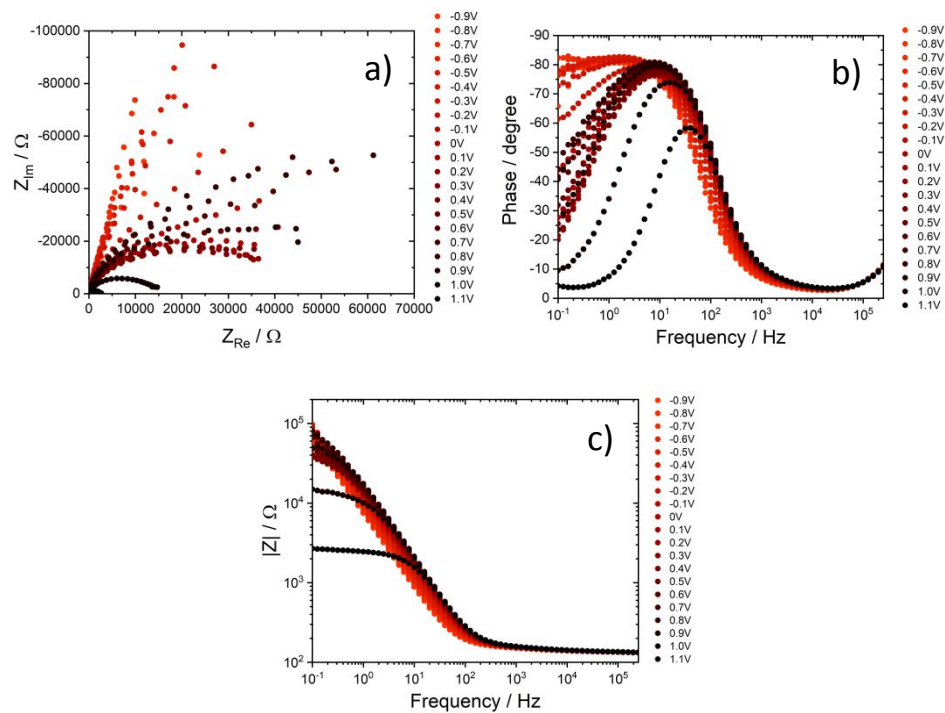


**Figure S7.** Equivalent circuit used to model 100 °C  $\text{O}_2$  data.

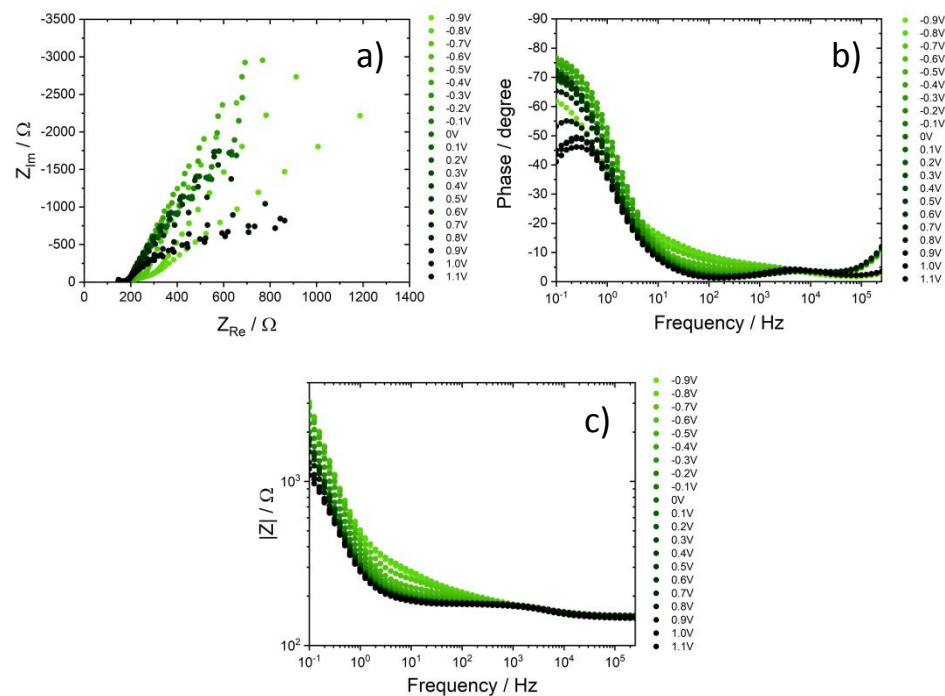


**Figure S8.**  $R_{con}$  measurements of films at each annealing condition (a) and  $R_{film}$  measurements for films at each annealing condition (b)

## Supporting Information

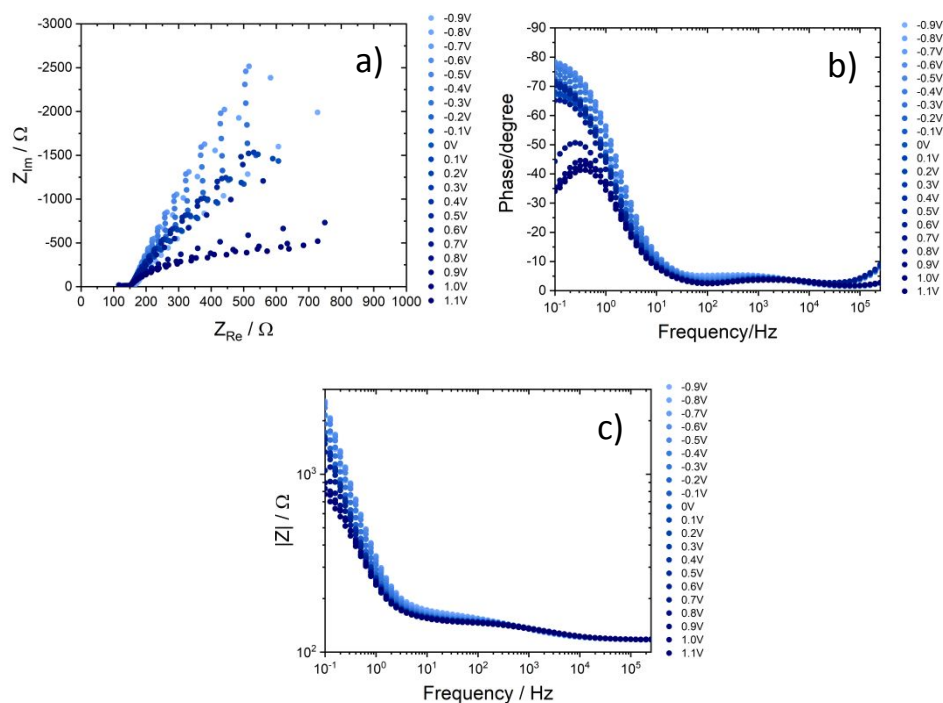


**Figure S9.** EIS data for a CuGaO<sub>2</sub> film annealed at 100 °C under O<sub>2</sub>. a) Nyquist, b) Bode – Phase, c) Bode – Z

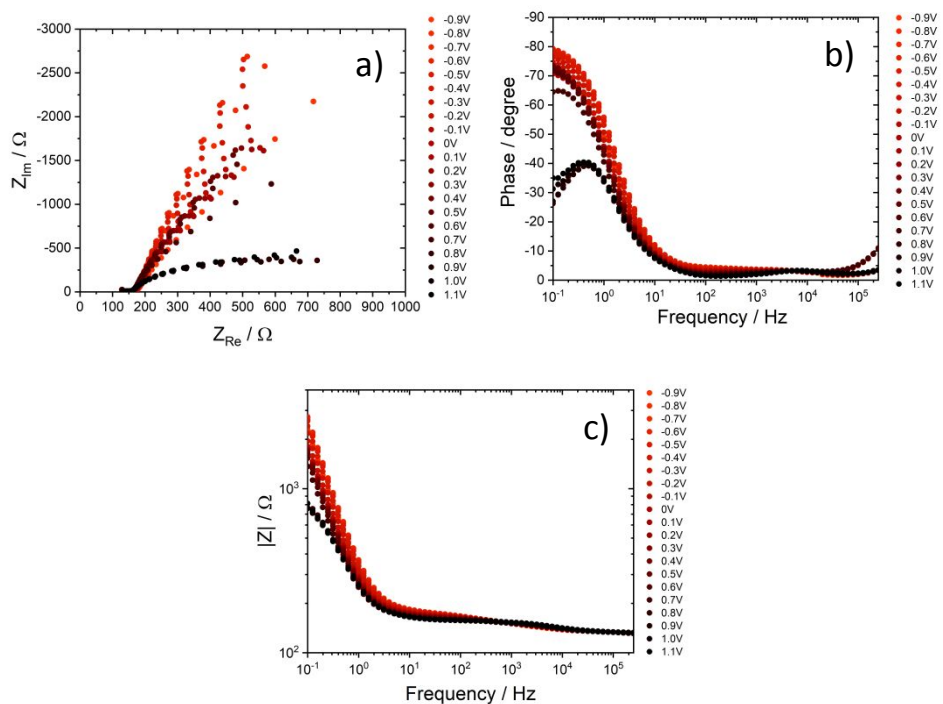


**Figure S10.** EIS data for a CuGaO<sub>2</sub> film annealed at 200 °C under O<sub>2</sub>. a) Nyquist, b) Bode – Phase, c) Bode – Z

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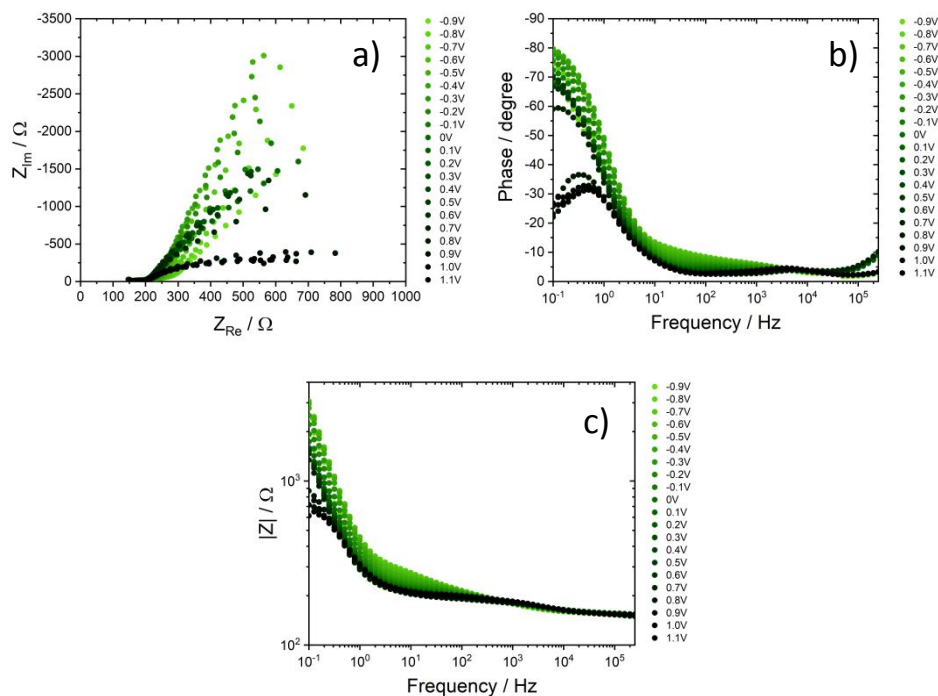


**Figure S11.** EIS data for a CuGaO<sub>2</sub> film annealed at 300 °C under O<sub>2</sub>. a) Nyquist, b) Bode – Phase, c) Bode – Z

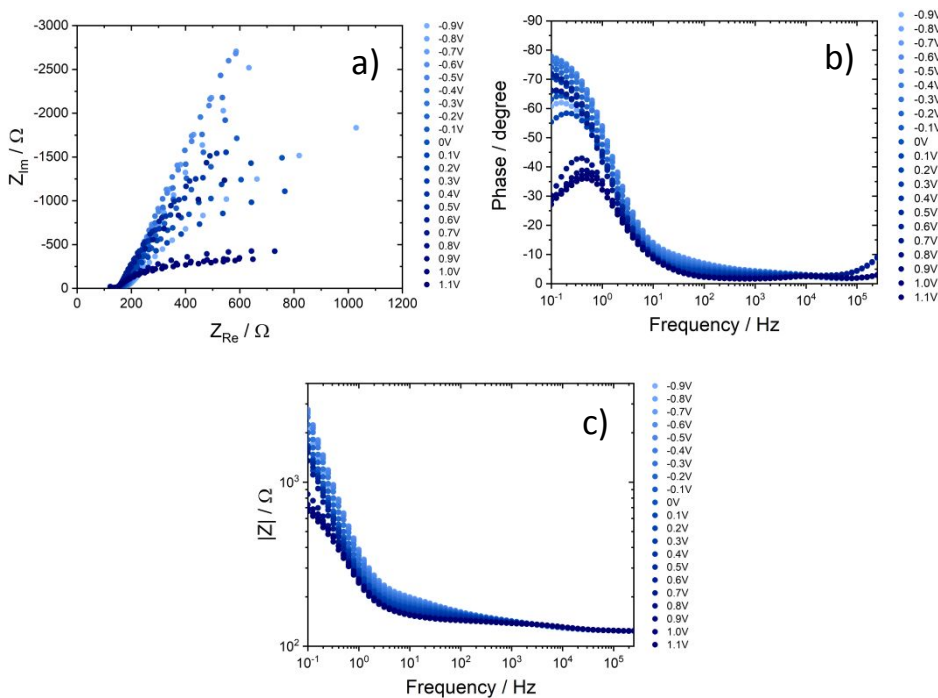


**Figure S12.** EIS data for a CuGaO<sub>2</sub> film annealed at 100 °C under O<sub>2</sub> followed by 500 °C under Ar. a) Nyquist, b) Bode – Phase, c) Bode – Z

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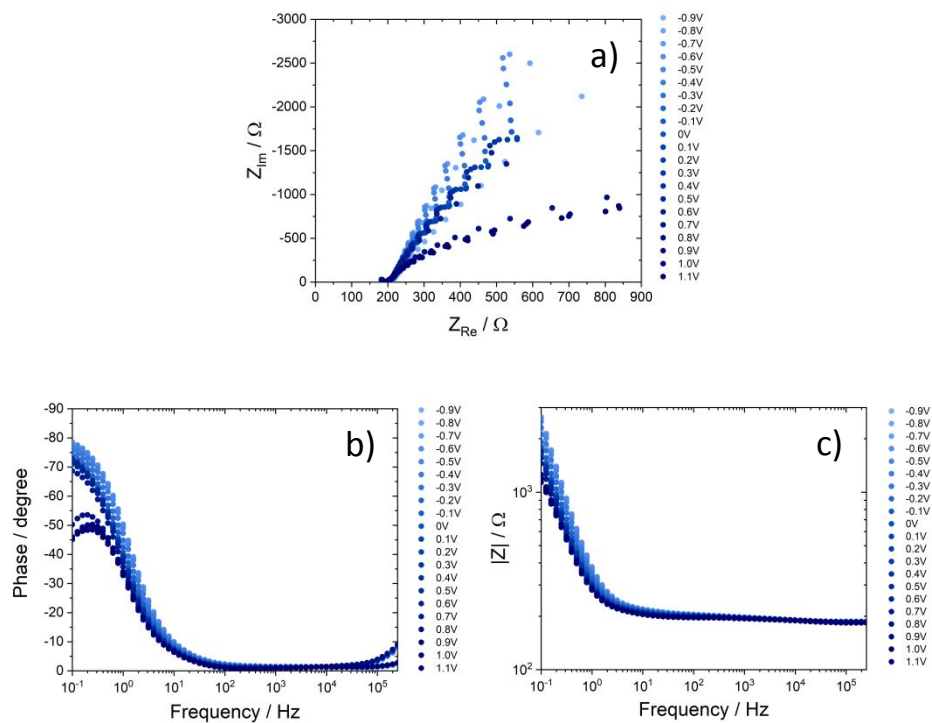


**Figure S13.** EIS data for a CuGaO<sub>2</sub> film annealed at 200 °C under O<sub>2</sub> followed by 500 °C under Ar. a) Nyquist, b) Bode – Phase, c) Bode – Z



**Figure S14.** EIS data for a CuGaO<sub>2</sub> film annealed at 300 °C under O<sub>2</sub> followed by 500 °C under Ar. a) Nyquist, b) Bode – Phase, c) Bode – Z

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**Figure S15.** EIS data for a  $\text{CuGaO}_2$  film annealed at  $500\text{ }^\circ\text{C}$  under Ar. a) Nyquist, b) Bode – Phase, c) Bode –  $Z$

## Supporting Information

**Table S2: Impedance fit for 100°C O<sub>2</sub> Annealed Film<sup>a</sup>**

| Potential | R <sub>s</sub> | R <sub>0</sub> | C <sub>0</sub> | β <sub>0</sub> | R <sub>con</sub> | R <sub>film</sub> | C <sub>film</sub> | β <sub>film</sub> | C <sub>FTO</sub> | β <sub>FTO</sub> |
|-----------|----------------|----------------|----------------|----------------|------------------|-------------------|-------------------|-------------------|------------------|------------------|
| -0.9      | 1.00           | 129.60         | 1.03E-09       | 0.99           | 2.01E+05         | 8.45E+03          | 2.00E-05          | 0.90              | 2.41E-05         | 0.95             |
| -0.8      | 1.00           | 129.60         | 1.03E-09       | 0.99           | 1.25E+07         | 1.55E+04          | 2.00E-05          | 0.90              | 2.23E-05         | 0.92             |
| -0.7      | 1.00           | 129.60         | 1.03E-09       | 0.99           | 2.24E+06         | 3.74E+04          | 2.00E-05          | 1.00              | 2.09E-05         | 0.92             |
| -0.6      | 1.00           | 129.60         | 1.03E-09       | 0.99           | 5.63E+05         | 4.26E+05          | 7.24E-05          | 1.00              | 1.95E-05         | 0.93             |
| -0.5      | 1.00           | 129.60         | 1.03E-09       | 0.99           | 3.26E+05         | 4.51E+05          | 2.87E-06          | 1.00              | 1.65E-05         | 0.94             |
| -0.4      | 1.00           | 129.60         | 1.03E-09       | 0.99           | 2.10E+05         | 4.98E+05          | 3.23E-06          | 1.00              | 1.46E-05         | 0.96             |
| -0.3      | 1.00           | 129.60         | 1.03E-09       | 0.99           | 2.22E+05         | 3.27E+05          | 6.18E-06          | 1.00              | 1.47E-05         | 0.94             |
| -0.2      | 1.00           | 129.60         | 1.03E-09       | 0.99           | 1.12E+05         | 1.46E+05          | 1.64E-05          | 1.00              | 1.51E-05         | 0.92             |
| -0.1      | 1.00           | 129.60         | 1.03E-09       | 0.99           | 5.24E+04         | 7.67E+04          | 4.35E-05          | 0.85              | 1.42E-05         | 0.92             |
| 0         | 1.00           | 129.60         | 1.03E-09       | 0.99           | 4.37E+04         | 5.36E+04          | 1.87E-04          | 0.85              | 1.34E-05         | 0.93             |
| 0.1       | 1.00           | 129.60         | 1.03E-09       | 0.99           | 4.06E+04         | 3.00E+03          | 4.50E-04          | 0.85              | 1.27E-05         | 0.93             |
| 0.2       | 1.00           | 129.60         | 1.03E-09       | 0.99           | 4.03E+04         | 3.13E+03          | 2.75E-04          | 1.00              | 1.26E-05         | 0.91             |
| 0.3       | 1.00           | 129.60         | 1.03E-09       | 0.99           | 3.68E+04         | 6.64E+03          | 1.67E-04          | 1.00              | 1.22E-05         | 0.90             |
| 0.4       | 1.00           | 129.60         | 1.03E-09       | 0.99           | 3.32E+04         | 2.15E+04          | 7.15E-05          | 0.79              | 1.09E-05         | 0.92             |
| 0.5       | 1.00           | 129.60         | 1.03E-09       | 0.99           | 4.27E+04         | 3.89E+04          | 5.51E-05          | 0.80              | 1.11E-05         | 0.91             |
| 0.6       | 1.00           | 129.60         | 1.03E-09       | 0.99           | 6.07E+04         | 6.38E+04          | 3.31E-05          | 1.00              | 1.06E-05         | 0.91             |
| 0.7       | 1.00           | 129.60         | 1.03E-09       | 0.99           | 5.00E+04         | 7.00E+04          | 1.06E-05          | 0.90              | 8.74E-06         | 0.95             |
| 0.8       | 1.00           | 129.60         | 1.03E-09       | 0.99           | 9.33E+04         | 5.55E+04          | 3.59E-05          | 0.78              | 1.04E-05         | 0.91             |
| 0.9       | 1.00           | 129.60         | 1.03E-09       | 0.99           | 3.93E+04         | 2.83E+04          | 3.04E-05          | 0.63              | 9.05E-06         | 0.95             |
| 1         | 1.00           | 129.60         | 1.03E-09       | 0.99           | 1.25E+04         | 3.42E+03          | 2.63E-04          | 0.74              | 9.33E-06         | 0.95             |
| 1.1       | 1.00           | 129.60         | 1.03E-09       | 0.99           | 2.36E+03         | 3.26E+02          | 3.89E-03          | 0.80              | 1.01E-05         | 0.94             |

<sup>a</sup>This data set fit with impedance model shown in Figure S7; Units- R<sub>s</sub>, R<sub>0</sub>, R<sub>con</sub>, R<sub>film</sub> (Ω)

C<sub>0</sub>, C<sub>film</sub>, C<sub>FTO</sub> (F)

# Supporting Information

**Table S3: Impedance fit for 100°C O<sub>2</sub> / 500°C Ar Annealed Film<sup>a</sup>**

| Potential | R <sub>s</sub> | R <sub>0</sub> | C <sub>0</sub> | β <sub>0</sub> | R <sub>con</sub> | R <sub>D</sub> | R <sub>film</sub> | C <sub>film</sub> | β <sub>film</sub> | C <sub>FTO</sub> | β <sub>FTO</sub> |
|-----------|----------------|----------------|----------------|----------------|------------------|----------------|-------------------|-------------------|-------------------|------------------|------------------|
| -0.9      | 2.21           | 132.30         | 5.85E-10       | 0.96           | 15.92            | 113.40         | 1.59E+04          | 6.83E-04          | 0.93              | 2.85E-06         | 0.98             |
| -0.8      | 1.77           | 133.40         | 2.00E-09       | 0.95           | 19.17            | 84.42          | 4.28E+04          | 5.87E-04          | 0.94              | 8.15E-06         | 0.89             |
| -0.7      | 1.67           | 133.40         | 1.94E-09       | 0.95           | 20.04            | 76.55          | 6.59E+04          | 5.65E-04          | 0.95              | 9.86E-06         | 0.87             |
| -0.6      | 1.62           | 133.40         | 1.98E-09       | 0.95           | 20.02            | 72.42          | 6.69E+04          | 5.73E-04          | 0.95              | 9.54E-06         | 0.87             |
| -0.5      | 1.10           | 133.50         | 1.61E-09       | 0.96           | 20.26            | 69.98          | 6.43E+04          | 5.96E-04          | 0.94              | 1.04E-05         | 0.85             |
| -0.4      | 0.97           | 133.40         | 1.55E-09       | 0.96           | 20.39            | 65.26          | 5.67E+04          | 6.42E-04          | 0.94              | 1.10E-05         | 0.84             |
| -0.3      | 0.96           | 133.40         | 1.55E-09       | 0.96           | 20.08            | 62.87          | 4.20E+04          | 7.10E-04          | 0.93              | 1.12E-05         | 0.84             |
| -0.2      | 0.96           | 133.40         | 1.47E-09       | 0.97           | 19.68            | 61.37          | 3.04E+04          | 7.91E-04          | 0.92              | 1.05E-05         | 0.84             |
| -0.1      | 0.87           | 133.50         | 1.44E-09       | 0.97           | 19.11            | 61.45          | 2.19E+04          | 8.58E-04          | 0.92              | 9.03E-06         | 0.85             |
| 0         | 0.79           | 133.50         | 1.44E-09       | 0.97           | 18.82            | 59.02          | 1.59E+04          | 8.92E-04          | 0.92              | 9.13E-06         | 0.85             |
| 0.1       | 0.80           | 133.40         | 1.49E-09       | 0.97           | 18.9             | 52.74          | 1.44E+04          | 9.04E-04          | 0.92              | 8.94E-06         | 0.84             |
| 0.2       | 0.54           | 133.50         | 1.46E-09       | 0.97           | 19.3             | 47.83          | 1.74E+04          | 9.05E-04          | 0.92              | 9.55E-06         | 0.83             |
| 0.3       | 1.15           | 132.60         | 1.19E-09       | 0.98           | 18.63            | 50.00          | 1.98E+04          | 9.09E-04          | 0.92              | 7.31E-06         | 0.85             |
| 0.4       | 0.89           | 133.20         | 1.49E-09       | 0.97           | 17.57            | 48.88          | 2.09E+04          | 9.27E-04          | 0.93              | 5.56E-06         | 0.88             |
| 0.5       | 0.70           | 133.30         | 1.54E-09       | 0.96           | 17.18            | 46.90          | 1.97E+04          | 9.58E-04          | 0.93              | 5.55E-06         | 0.88             |
| 0.6       | 0.91           | 133.10         | 1.55E-09       | 0.96           | 16.87            | 43.30          | 1.55E+04          | 1.02E-03          | 0.92              | 4.95E-06         | 0.89             |
| 0.7       | 0.93           | 132.90         | 1.57E-09       | 0.96           | 17.57            | 35.39          | 6.74E+03          | 1.12E-03          | 0.91              | 6.60E-06         | 0.86             |
| 0.8       | 0.40           | 133.20         | 2.02E-09       | 0.86           | 18.99            | 23.56          | 8.88E+02          | 1.20E-03          | 0.89              | 1.07E-05         | 0.81             |
| 0.9       | 0.31           | 132.90         | 1.87E-09       | 0.86           | 21.34            | 6.32           | 8.76E+02          | 1.27E-03          | 0.85              | 1.40E-05         | 0.78             |
| 1         | 0.54           | 133.10         | 1.83E-09       | 0.87           | 20.13            | 0.55           | 1.06E+03          | 1.33E-03          | 0.81              | 7.22E-06         | 0.83             |
| 1.1       | 1.50           | 132.60         | 1.13E-09       | 0.91           | 19.02            | 3.18           | 1.27E+03          | 1.40E-03          | 0.79              | 3.49E-06         | 0.90             |

<sup>a</sup>This data set fit with impedance model shown in Figure7a; Units- R<sub>s</sub>, R<sub>0</sub>, R<sub>con</sub>, R<sub>d</sub>, R<sub>film</sub> (Ω)

C<sub>0</sub>, C<sub>film</sub>, C<sub>FTO</sub> (F)

# Supporting Information

**Table S4: Impedance fit for 200°C O<sub>2</sub> Annealed Film<sup>a</sup>**

| Potential | R <sub>s</sub> | R <sub>0</sub> | C <sub>0</sub> | β <sub>0</sub> | R <sub>con</sub> | R <sub>D</sub> | R <sub>film</sub> | C <sub>film</sub> | β <sub>film</sub> | C <sub>FTO</sub> | β <sub>FTO</sub> |
|-----------|----------------|----------------|----------------|----------------|------------------|----------------|-------------------|-------------------|-------------------|------------------|------------------|
| -0.9      | 1.00           | 125.00         | 3.81E-09       | 0.90           | 1.13E+03         | 3.07E+04       | 3.36E+04          | 5.59E-05          | 1.00              | 1.78E-05         | 0.86             |
| -0.8      | 1.00           | 125.00         | 3.81E-09       | 0.90           | 7.67E+03         | 4.84E+04       | 3.90E+04          | 6.58E-05          | 1.00              | 2.29E-05         | 0.85             |
| -0.7      | 1.00           | 125.00         | 3.81E-09       | 0.90           | 9.70E+03         | 5.08E+04       | 3.90E+04          | 7.73E-05          | 1.00              | 2.49E-05         | 0.84             |
| -0.6      | 1.00           | 125.00         | 3.81E-09       | 0.90           | 8.73E+03         | 4.41E+04       | 3.52E+04          | 9.75E-05          | 1.00              | 2.87E-05         | 0.82             |
| -0.5      | 1.00           | 125.00         | 3.81E-09       | 0.90           | 6.86E+03         | 3.47E+04       | 2.94E+04          | 1.17E-04          | 1.00              | 3.59E-05         | 0.78             |
| -0.4      | 1.00           | 125.00         | 3.81E-09       | 0.90           | 5.34E+03         | 2.67E+04       | 2.32E+04          | 1.40E-04          | 1.00              | 4.59E-05         | 0.75             |
| -0.3      | 1.00           | 125.00         | 3.81E-09       | 0.90           | 4.10E+03         | 2.08E+04       | 1.77E+04          | 1.76E-04          | 1.00              | 5.65E-05         | 0.72             |
| -0.2      | 1.00           | 125.00         | 3.81E-09       | 0.90           | 3.08E+03         | 1.53E+04       | 1.29E+04          | 2.24E-04          | 1.00              | 6.52E-05         | 0.70             |
| -0.1      | 1.00           | 125.00         | 3.81E-09       | 0.90           | 2.15E+03         | 1.13E+04       | 9.00E+03          | 2.99E-04          | 1.00              | 6.62E-05         | 0.70             |
| 0         | 1.00           | 125.00         | 3.81E-09       | 0.90           | 1.74E+03         | 8.52E+03       | 6.21E+03          | 3.85E-04          | 1.00              | 6.62E-05         | 0.69             |
| 0.1       | 1.00           | 125.00         | 3.81E-09       | 0.90           | 1.43E+03         | 6.81E+03       | 4.73E+03          | 5.32E-04          | 1.00              | 6.05E-05         | 0.70             |
| 0.2       | 1.00           | 125.00         | 3.81E-09       | 0.90           | 1.25E+03         | 5.65E+03       | 4.02E+03          | 7.94E-04          | 1.00              | 5.70E-05         | 0.70             |
| 0.3       | 1.00           | 125.00         | 3.81E-09       | 0.90           | 9.98E+02         | 4.66E+03       | 5.81E+03          | 1.27E-03          | 0.94              | 5.01E-05         | 0.71             |
| 0.4       | 1.00           | 125.00         | 3.81E-09       | 0.90           | 7.78E+02         | 2.87E+03       | 1.14E+04          | 1.52E-03          | 0.92              | 4.07E-05         | 0.74             |
| 0.5       | 1.00           | 125.00         | 3.81E-09       | 0.90           | 6.14E+02         | 1.68E+03       | 1.13E+04          | 1.67E-03          | 0.94              | 3.16E-05         | 0.77             |
| 0.6       | 1.00           | 125.00         | 2.49E-09       | 0.90           | 4.93E+02         | 1.03E+03       | 7.37E+03          | 1.80E-03          | 0.93              | 2.36E-05         | 0.80             |
| 0.7       | 1.00           | 125.00         | 1.89E-09       | 0.90           | 4.29E+02         | 6.95E+02       | 3.17E+03          | 1.95E-03          | 0.92              | 1.90E-05         | 0.82             |
| 0.8       | 1.00           | 125.00         | 1.33E-09       | 0.90           | 4.23E+02         | 6.16E+02       | 9.61E+02          | 2.17E-03          | 1.00              | 1.79E-05         | 0.83             |
| 0.9       | 1.00           | 125.00         | 1.28E-09       | 0.90           | 4.61E+02         | 6.86E+02       | 5.71E+02          | 2.11E-03          | 1.00              | 1.76E-05         | 0.83             |
| 1         | 1.00           | 125.00         | 1.28E-09       | 0.90           | 5.62E+02         | 7.67E+02       | 4.70E+02          | 2.17E-03          | 1.00              | 1.87E-05         | 0.82             |
| 1.1       | 1.00           | 125.00         | 1.28E-09       | 0.90           | 6.28E+02         | 8.57E+02       | 4.02E+02          | 2.53E-03          | 0.96              | 1.99E-05         | 0.81             |

<sup>a</sup>This data set fit with impedance model shown in Figure7a; Units- R<sub>s</sub>, R<sub>0</sub>, R<sub>con</sub>, R<sub>D</sub>, R<sub>film</sub> (Ω)

C<sub>0</sub>, C<sub>film</sub>, C<sub>FTO</sub> (F)

# Supporting Information

**Table S5: Impedance fit for 200°C O<sub>2</sub> / 500°C Ar Annealed Film<sup>a</sup>**

| Potential | R <sub>s</sub> | R <sub>0</sub> | C <sub>0</sub> | β <sub>0</sub> | R <sub>con</sub> | R <sub>D</sub> | R <sub>film</sub> | C <sub>film</sub> | β <sub>film</sub> | C <sub>FTO</sub> | β <sub>FTO</sub> |
|-----------|----------------|----------------|----------------|----------------|------------------|----------------|-------------------|-------------------|-------------------|------------------|------------------|
| -0.9      | 52.71          | 104.20         | 1.58E-07       | 0.61           | 47.27            | 283.2          | 1.48E+04          | 8.27E-04          | 0.92              | 3.55E-05         | 0.74             |
| -0.8      | 55.39          | 101.50         | 1.48E-08       | 0.85           | 47.21            | 304.1          | 5.86E+04          | 6.33E-04          | 0.93              | 2.84E-05         | 0.76             |
| -0.7      | 49.84          | 107.00         | 9.46E-09       | 0.87           | 49.02            | 255            | 3.50E+05          | 5.17E-04          | 0.94              | 3.13E-05         | 0.75             |
| -0.6      | 61.34          | 95.11          | 8.14E-09       | 0.90           | 46.75            | 220.7          | 3.12E+05          | 4.91E-04          | 0.95              | 2.89E-05         | 0.75             |
| -0.5      | 50.25          | 106.30         | 1.16E-08       | 0.86           | 44.81            | 181.6          | 4.84E+05          | 5.08E-04          | 0.95              | 2.80E-05         | 0.75             |
| -0.4      | 57.92          | 98.26          | 8.35E-09       | 0.90           | 42.37            | 149.1          | 3.04E+05          | 5.49E-04          | 0.95              | 2.30E-05         | 0.76             |
| -0.3      | 65.35          | 92.56          | 1.96E-08       | 0.85           | 36               | 131.3          | 8.86E+04          | 6.18E-04          | 0.94              | 1.43E-05         | 0.81             |
| -0.2      | 63.43          | 92.25          | 7.45E-09       | 0.91           | 37.62            | 111.9          | 8.14E+04          | 6.94E-04          | 0.93              | 2.73E-05         | 0.73             |
| -0.1      | 71.14          | 84.33          | 4.47E-09       | 0.96           | 33.09            | 103.8          | 3.06E+04          | 8.12E-04          | 0.91              | 1.28E-05         | 0.79             |
| 0         | 66.85          | 89.32          | 4.54E-09       | 0.95           | 30.95            | 94.75          | 1.33E+04          | 8.99E-04          | 0.90              | 1.14E-05         | 0.80             |
| 0.1       | 71.29          | 85.58          | 2.58E-09       | 0.99           | 29.82            | 83.94          | 1.83E+04          | 9.80E-04          | 0.88              | 1.10E-05         | 0.80             |
| 0.2       | 62.03          | 93.92          | 2.41E-09       | 0.98           | 29.58            | 79.65          | 2.81E+04          | 9.93E-04          | 0.89              | 1.41E-05         | 0.76             |
| 0.3       | 67.66          | 87.73          | 5.55E-09       | 0.94           | 26.3             | 79.51          | 2.90E+04          | 1.03E-03          | 0.89              | 8.76E-06         | 0.81             |
| 0.4       | 71.12          | 81.68          | 2.61E-09       | 1.00           | 28.41            | 75.11          | 2.99E+04          | 1.05E-03          | 0.89              | 1.14E-05         | 0.76             |
| 0.5       | 70.65          | 82.28          | 2.60E-09       | 1.00           | 27.27            | 75.55          | 1.93E+04          | 1.07E-03          | 0.90              | 8.78E-06         | 0.78             |
| 0.6       | 71.28          | 81.70          | 2.67E-09       | 1.00           | 27.03            | 74.39          | 1.11E+04          | 1.09E-03          | 0.90              | 7.01E-06         | 0.80             |
| 0.7       | 70.00          | 83.14          | 2.66E-09       | 1.00           | 27.55            | 68.74          | 5.33E+03          | 1.16E-03          | 0.89              | 6.13E-06         | 0.82             |
| 0.8       | 71.32          | 82.82          | 3.06E-09       | 0.90           | 28.85            | 56.59          | 9.62E+02          | 1.22E-03          | 0.87              | 7.72E-06         | 0.81             |
| 0.9       | 72.12          | 81.96          | 4.33E-09       | 0.88           | 31.94            | 40.88          | 7.34E+02          | 1.27E-03          | 0.84              | 1.04E-05         | 0.78             |
| 1         | 76.26          | 77.99          | 4.06E-09       | 0.89           | 34.22            | 33.49          | 7.97E+02          | 1.28E-03          | 0.81              | 1.07E-05         | 0.78             |
| 1.1       | 80.24          | 73.81          | 5.45E-09       | 0.88           | 36.74            | 29.06          | 8.42E+02          | 1.37E-03          | 0.78              | 1.26E-05         | 0.77             |

<sup>a</sup>This data set fit with impedance model shown in Figure7a; Units- R<sub>s</sub>, R<sub>0</sub>, R<sub>con</sub>, R<sub>d</sub>, R<sub>film</sub> (Ω)

C<sub>0</sub>, C<sub>film</sub>, C<sub>FTO</sub> (F)

# Supporting Information

**Table S6: Impedance fit for 300°C O<sub>2</sub> Annealed Film<sup>a</sup>**

| Potential | R <sub>s</sub> | R <sub>0</sub> | C <sub>0</sub> | β <sub>0</sub> | R <sub>con</sub> | R <sub>D</sub> | R <sub>film</sub> | C <sub>film</sub> | β <sub>film</sub> | C <sub>FTO</sub> | β <sub>FTO</sub> |
|-----------|----------------|----------------|----------------|----------------|------------------|----------------|-------------------|-------------------|-------------------|------------------|------------------|
| -0.9      | 0.02           | 118.70         | 4.25E-10       | 0.96           | 21.79            | 124.80         | 1.28E+04          | 7.31E-04          | 0.92              | 7.67E-06         | 0.91             |
| -0.8      | 0.12           | 119.30         | 1.83E-09       | 0.94           | 25.14            | 69.40          | 3.61E+04          | 6.24E-04          | 0.93              | 1.17E-05         | 0.88             |
| -0.7      | 0.25           | 119.10         | 1.78E-09       | 0.94           | 24.12            | 62.12          | 5.38E+04          | 5.99E-04          | 0.94              | 1.12E-05         | 0.88             |
| -0.6      | 0.38           | 118.90         | 1.64E-09       | 0.95           | 23.16            | 54.80          | 5.31E+04          | 6.14E-04          | 0.94              | 1.01E-05         | 0.89             |
| -0.5      | 0.91           | 118.00         | 1.25E-09       | 0.97           | 23.09            | 50.25          | 4.81E+04          | 6.50E-04          | 0.93              | 1.15E-05         | 0.87             |
| -0.4      | 1.01           | 117.80         | 1.19E-09       | 0.97           | 22.45            | 48.41          | 3.95E+04          | 7.13E-04          | 0.93              | 1.14E-05         | 0.86             |
| -0.3      | 4.10           | 114.80         | 1.45E-09       | 0.96           | 21.65            | 48.44          | 2.91E+04          | 8.03E-04          | 0.92              | 1.03E-05         | 0.87             |
| -0.2      | 1.86           | 117.00         | 1.23E-09       | 0.97           | 21.26            | 49.14          | 2.10E+04          | 9.00E-04          | 0.91              | 8.89E-06         | 0.88             |
| -0.1      | 4.02           | 114.90         | 1.26E-09       | 0.97           | 21.47            | 49.83          | 1.38E+04          | 9.69E-04          | 0.91              | 8.96E-06         | 0.87             |
| 0         | 6.42           | 112.40         | 1.26E-09       | 0.98           | 21.99            | 46.68          | 8.97E+03          | 9.81E-04          | 0.91              | 9.65E-06         | 0.86             |
| 0.1       | 7.34           | 111.60         | 1.45E-09       | 0.97           | 22.33            | 41.65          | 9.98E+03          | 9.70E-04          | 0.91              | 1.08E-05         | 0.86             |
| 0.2       | 6.24           | 112.70         | 1.48E-09       | 0.97           | 22.15            | 39.28          | 1.31E+04          | 9.55E-04          | 0.91              | 1.15E-05         | 0.85             |
| 0.3       | 6.06           | 112.80         | 1.48E-09       | 0.97           | 22.00            | 39.87          | 1.37E+04          | 9.47E-04          | 0.91              | 1.12E-05         | 0.85             |
| 0.4       | 7.28           | 111.60         | 1.53E-09       | 0.97           | 21.91            | 39.47          | 1.45E+04          | 9.58E-04          | 0.92              | 1.10E-05         | 0.85             |
| 0.5       | 9.13           | 109.70         | 1.54E-09       | 0.97           | 21.95            | 39.23          | 1.54E+04          | 9.88E-04          | 0.92              | 1.10E-05         | 0.85             |
| 0.6       | 13.48          | 105.20         | 1.42E-09       | 0.98           | 21.99            | 39.35          | 1.30E+04          | 1.04E-03          | 0.91              | 1.09E-05         | 0.85             |
| 0.7       | 15.56          | 103.20         | 8.26E-09       | 0.82           | 22.82            | 34.07          | 7.25E+03          | 1.13E-03          | 0.90              | 1.84E-05         | 0.79             |
| 0.8       | 8.74           | 109.10         | 6.63E-10       | 0.94           | 23.72            | 31.11          | 1.88E+03          | 1.24E-03          | 0.89              | 2.14E-05         | 0.77             |
| 0.9       | 0.40           | 118.70         | 4.46E-09       | 0.80           | 21.87            | 21.51          | 1.28E+03          | 1.28E-03          | 0.86              | 1.21E-05         | 0.85             |
| 1         | 1.97           | 116.00         | 1.18E-09       | 0.89           | 21.57            | 14.07          | 1.25E+03          | 1.31E-03          | 0.82              | 1.00E-05         | 0.85             |
| 1.1       | 0.00           | 117.50         | 2.98E-10       | 0.99           | 22.08            | 14.21          | 1.16E+03          | 1.44E-03          | 0.81              | 1.06E-05         | 0.85             |

<sup>a</sup>This data set fit with impedance model shown in Figure7a; Units- R<sub>s</sub>, R<sub>0</sub>, R<sub>con</sub>, R<sub>d</sub>, R<sub>film</sub> (Ω)

C<sub>0</sub>, C<sub>film</sub>, C<sub>FTO</sub> (F)

## Supporting Information

**Table S7: Impedance fit for 300°C O<sub>2</sub> / 500°C Ar Annealed Film<sup>a</sup>**

| Potential | R <sub>s</sub> | R <sub>0</sub> | C <sub>0</sub> | β <sub>0</sub> | R <sub>con</sub> | R <sub>D</sub> | R <sub>film</sub> | C <sub>film</sub> | β <sub>film</sub> | C <sub>FTO</sub> | β <sub>FTO</sub> |
|-----------|----------------|----------------|----------------|----------------|------------------|----------------|-------------------|-------------------|-------------------|------------------|------------------|
| -0.9      | 1.47           | 117.30         | 3.14E-10       | 0.98           | 21.46            | 125.60         | 1.28E+04          | 7.33E-04          | 0.92              | 6.67E-06         | 0.92             |
| -0.8      | 1.51           | 124.00         | 1.54E-09       | 0.96           | 17.52            | 183.90         | 3.66E+04          | 5.96E-04          | 0.93              | 7.43E-06         | 0.89             |
| -0.7      | 1.61           | 124.00         | 1.56E-09       | 0.96           | 16.01            | 204.60         | 5.16E+04          | 5.64E-04          | 0.94              | 4.57E-06         | 0.93             |
| -0.6      | 0.75           | 124.80         | 1.67E-09       | 0.95           | 19.07            | 156.00         | 4.95E+04          | 5.61E-04          | 0.94              | 1.04E-05         | 0.85             |
| -0.5      | 3.00           | 123.10         | 2.35E-09       | 0.93           | 17.96            | 150.60         | 5.36E+04          | 5.84E-04          | 0.94              | 7.68E-06         | 0.89             |
| -0.4      | 4.65           | 121.20         | 2.14E-09       | 0.94           | 18.94            | 135.30         | 5.73E+04          | 6.21E-04          | 0.94              | 1.01E-05         | 0.86             |
| -0.3      | 5.28           | 120.70         | 2.66E-09       | 0.92           | 18.96            | 123.30         | 4.34E+04          | 6.87E-04          | 0.93              | 1.15E-05         | 0.85             |
| -0.2      | 2.15           | 123.50         | 2.04E-09       | 0.94           | 18.82            | 114.10         | 2.92E+04          | 7.71E-04          | 0.92              | 1.22E-05         | 0.84             |
| -0.1      | 1.83           | 124.00         | 2.50E-09       | 0.92           | 17.54            | 106.50         | 1.60E+04          | 8.51E-04          | 0.92              | 1.00E-05         | 0.85             |
| 0         | 1.24           | 124.40         | 2.09E-09       | 0.94           | 17.16            | 91.85          | 6.76E+03          | 8.93E-04          | 0.91              | 1.09E-05         | 0.84             |
| 0.1       | 5.96           | 120.00         | 2.77E-09       | 0.92           | 18.00            | 75.00          | 3.24E+03          | 9.00E-04          | 0.92              | 1.00E-05         | 0.85             |
| 0.2       | 1.77           | 123.00         | 1.09E-09       | 0.98           | 16.90            | 60.99          | 1.03E+04          | 9.55E-04          | 0.88              | 1.00E-05         | 0.83             |
| 0.3       | 0.10           | 124.60         | 1.12E-09       | 0.98           | 15.71            | 66.12          | 1.57E+04          | 9.31E-04          | 0.91              | 1.01E-05         | 0.83             |
| 0.4       | 0.56           | 123.60         | 8.64E-10       | 0.99           | 14.77            | 63.39          | 1.70E+04          | 9.50E-04          | 0.91              | 1.00E-05         | 0.82             |
| 0.5       | 2.79           | 122.00         | 1.08E-09       | 0.98           | 11.90            | 62.64          | 1.72E+04          | 9.80E-04          | 0.92              | 3.08E-06         | 0.92             |
| 0.6       | 1.94           | 123.00         | 1.15E-09       | 0.98           | 10.61            | 60.80          | 1.55E+04          | 1.03E-03          | 0.92              | 1.84E-06         | 0.97             |
| 0.7       | 2.50           | 122.50         | 1.27E-09       | 0.97           | 10.03            | 55.11          | 7.88E+03          | 1.14E-03          | 0.91              | 1.41E-06         | 0.99             |
| 0.8       | 2.45           | 122.40         | 1.31E-09       | 0.89           | 10.29            | 45.84          | 1.02E+03          | 1.26E-03          | 0.89              | 1.74E-06         | 0.97             |
| 0.9       | 3.54           | 120.60         | 5.20E-10       | 0.95           | 12.18            | 25.99          | 8.72E+02          | 1.31E-03          | 0.84              | 4.47E-06         | 0.88             |
| 1         | 3.44           | 121.10         | 9.74E-10       | 0.91           | 12.30            | 7.66           | 9.84E+02          | 1.44E-03          | 0.76              | 3.58E-06         | 0.91             |
| 1.1       | 1.17           | 123.30         | 8.27E-10       | 0.92           | 12.24            | 14.20          | 8.86E+02          | 1.51E-03          | 0.77              | 3.97E-06         | 0.89             |

<sup>a</sup>This data set fit with impedance model shown in Figure7a; Units- R<sub>s</sub>, R<sub>0</sub>, R<sub>con</sub>, R<sub>d</sub>, R<sub>film</sub> (Ω)

C<sub>0</sub>, C<sub>film</sub>, C<sub>FTO</sub> (F)