Electronic supplementary information (ESI)

Evolution of carbon impurities in solution-grown and sputtered Al:ZnO thin films exposed to UV light and damp heat degradation

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Experimental

Seed Layer for CBD ZnO layers

Soda lime glass (SLG, MENZEL) substrates were cleaned ultrasonically in soap water, acetic acid, isopropanol and deionized water. 50mM ZnO (Sigma-Aldrich, >99.99%) was completely dissolved in a 5M ammonium hydroxide (Alfa Aesar, 28%). The resulting solution was spin coated on SLG substrates at a rate of 3000 rpm for 30 s, followed by drying at 100 °C for 5min, leading to a homogeneous seed layer coverage with grains up to 50 nm.

CBD of n-i-d ZnO

50mM ZnO, 3mM ammonium citrate (Alfa Aesar >97%) and 50mM NH_4NO_3 (Alfa Aesar >95%) were mixed in a 0.97 M ammonium hydroxide solution and stirred for at least 24 h, resulting in a saturated ZnO solution with pH~11.4-11.5. The CBD stock solution (250mL) was transferred through a 1 µm glass fiber filter to remove residual ZnO particles and then preheated for 15 min in a circulated heating bath at a set temperature of 90 °C. Then the samples were immersed in the preheated deposition solution for a total deposition time of 1 hour in an open glass beaker. The temperature of the deposition solution increased during the deposition time from 73 °C to 84 °C, as measured by a thermocouple.

CBD of AZO

50mM ZnO, 0.5 mM ammonium citrate and 50mM NH_4NO_3 were mixed in a 0.97 M ammonium hydroxide solution and stirred for 24 hours to prepare a saturated CBD stock solution. To form the doping solution, 100mM $Al(NO_3)_3 x9H_2O$ (Sigma-Aldrich >98%) and 50mM ammonium citrate were separately dissolved in deionized water (doping solution). The CBD stock solution (250mL) was transferred through a 1 µm glass fiber filter and then preheated in a circulated heating bath (set temperature 90°C) for 15 min under constant addition of the $Al(NO_3)_3$ doping solution by a syringe pump at a speed of 0.12 mL/min. After 15 min the seeded samples were immersed. The total deposition time was 1h under constant Al doping solution addition (0.12mL/min), resulting in a total aluminum concentration of ~3.5 mM and citrate concentration of ~2.25 mM at the end of the deposition process.

Addition to Figure 1: Inset of Figure 1d, UV-VIS transmission data of CBD AZO and sputtered AZO.
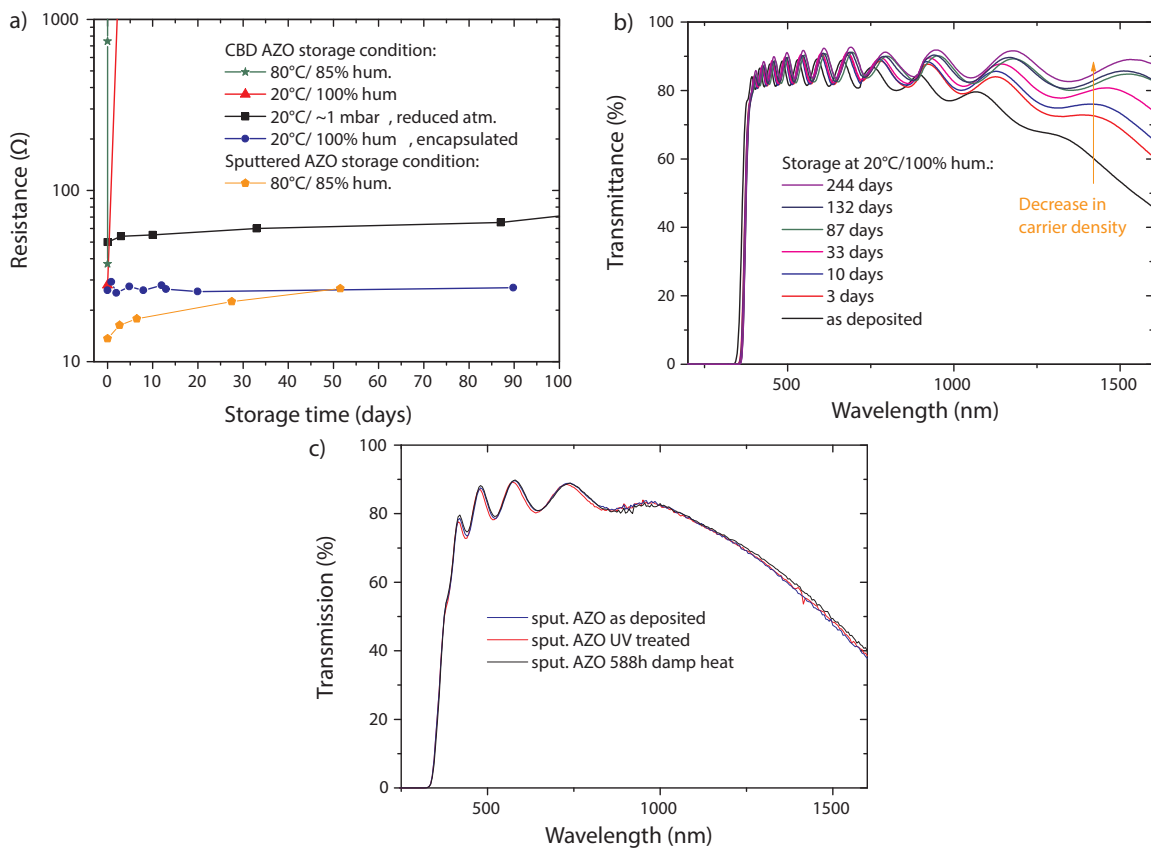

Fig. S1 a) Magnified inset of Figure 1d: Resistance degradation kinetics of CBD AZO/sputtered AZO samples stored under different conditions b) Transmission spectra of CBD AZO exposed to 100% rel. humidity at 20°C. The decreasing carrier density with humidity exposure time can be observed by the increasing NIR transmission. c) Transmission of sputtered AZO for as deposited, UV treated and damp heat exposed samples.

Assignment of FTIR peaks (this work) and comparison to literature data

Table S1: List of FTIR peaks observed in this work (Figure 2) and literature values for ZnO-citrate related IR vibration modes. Sodium citrate reference spectra can be found in Figure S1.

Wavenumber [cm^{-1}]	Species and vibr. mode	Wavenumber [cm^{-1}]	Species and vibr. Mode
570-592	ZnO-A$_1$LO, ZnO-E$_1$LO [1]	1394….1410 1390 1370	Free V$_s$(COO$^-$) [2] V$_s$(COO$^-$Na$^+$) [3] η_1(COO$^-$)Au [4]
690	Al-(O,OH,C), exact compound not identified	1430 1420…1490 1392…1474 1405	CH$_2$ bending (citrate) [5] Adsorbed V$_s$(COO$^-$) [2] ZnCO$_3$ modes [6] η_2(COO$^-$)Au [4]
760	SLG substrate/	1580 1568 1558	Free v$_{as}$ (COO$^-$) [2] v$_{as}$ (COO$^-$Na$^+$) [3] η_2(COO$^-$)Au bridging/chelating [4]
~860	Carboxyl species	1622 1611 1650	Adsorbed v$_{as}$ (COO$^-$) [2] η_1(COO$^-$)Au [4] H$_2$O [3]
905	SLG substrate (red shift as a function of film thickness, due to overlap with the carboxyl species at ~860 cm^{-1})	1725	v(COOH) [7]
1270	CH$_2$ wagging/twisting [2]	2000-2500	Measurement artefacts from diamond ATR crystal
1303	Out of plane deformation (O-H) [2]	2920/2850	C-H vibration modes
		~3000-3500	O-H vibrations modes

FTIR spectra of reference compounds (powder)

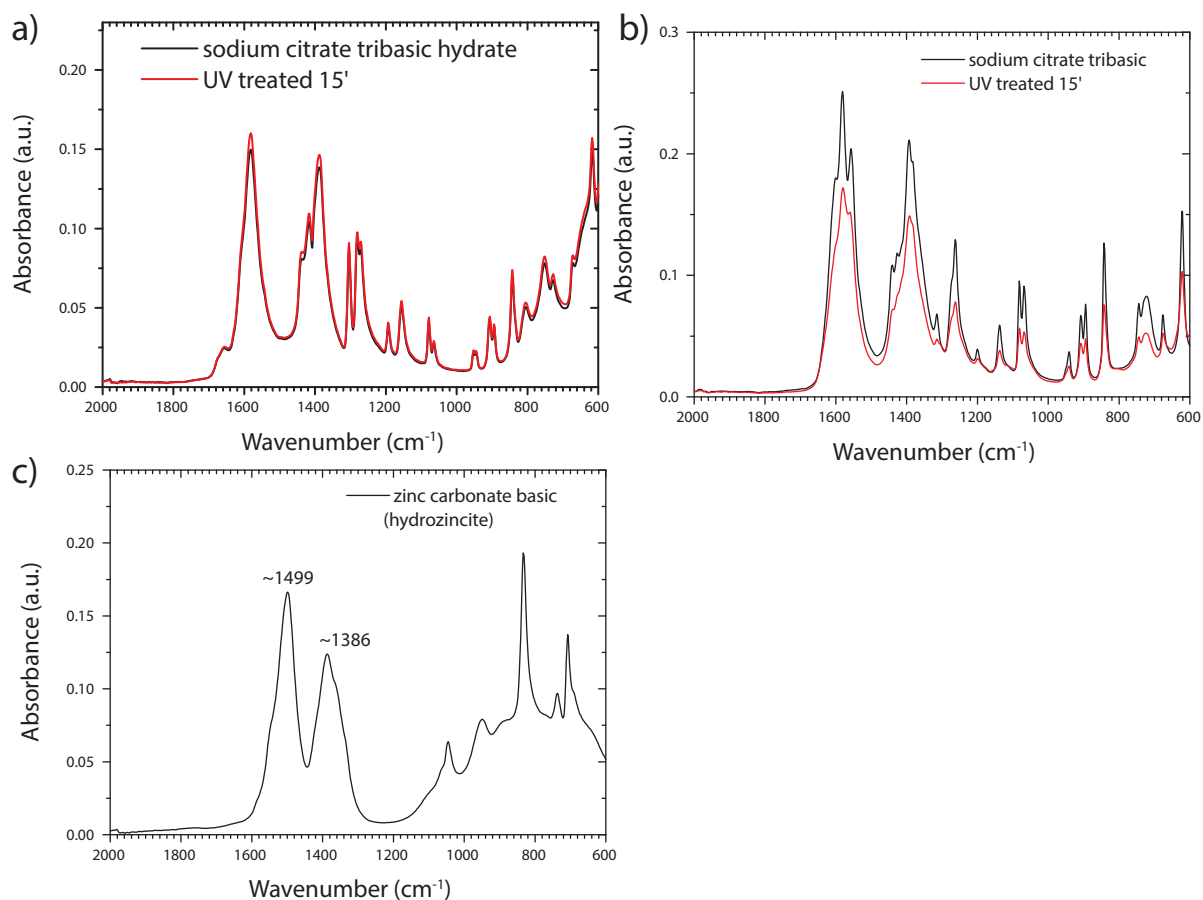**Fig. S2** reference compounds measured by ATR FTIR. Citrate reference compounds were exposed to a UV treatment at ~100°C to evaluate potential decomposition of the citrate compound: a) sodium citrate tribasic hydrate (no decomposition found upon UV exposure) b) sodium citrate tribasic hydrate dried at 160 °C (no decomposition upon UV exposure) and c) zinc carbonate basic (hydrozincite)

XPS Zn$_{LMM}$ peak fitting procedure

Figure S3 presents an example of the fit procedure to determine the highest kinetic energy Auger LMM line which is required for the calculation of the Auger parameter. The fit is empirical and accounts for two separate peaks[8], setting a peak separation of 3.2 eV [9]. The L$_3$M$_{4,5}$M$_{4,5}$ fine structure (similar as being described in Weightman et al.[10] for metallic Zn) is not taken into account in this work as we are not aware of reference values for the L$_3$M$_{4,5}$M$_{4,5}$ fine structure of ZnO.
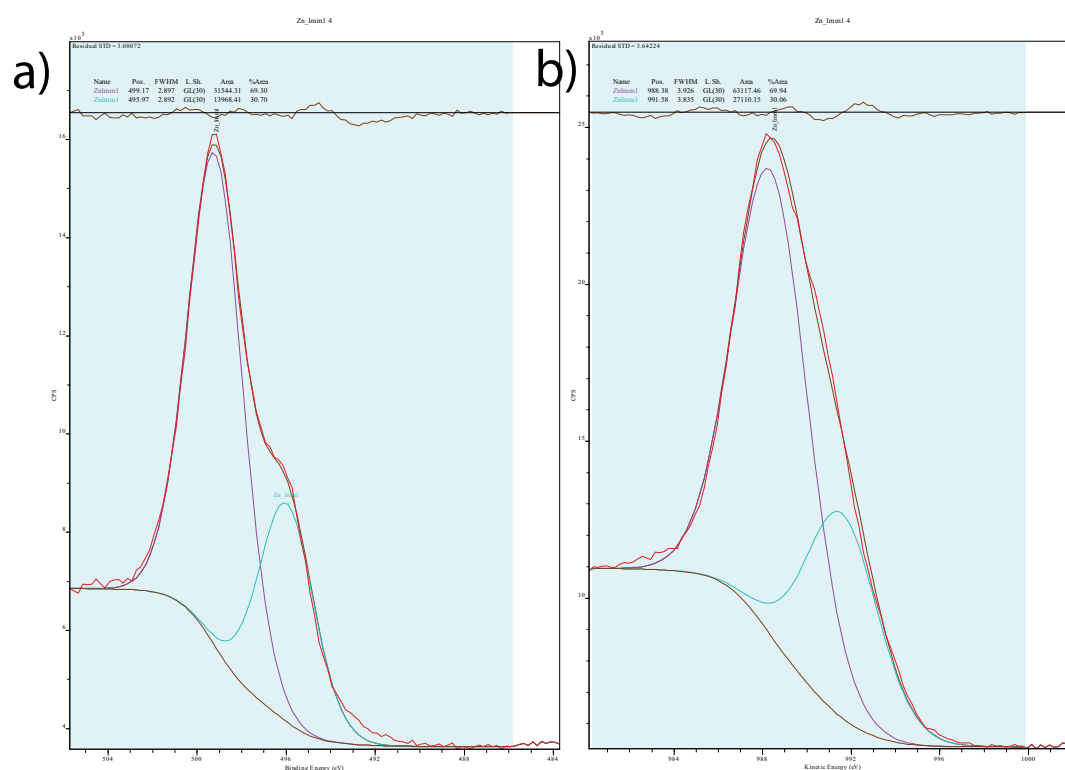

Fig. S3 Zn L$_3$M$_{4,5}$M$_{4,5}$ a) CBD AZO as deposited b) Sputtered AZO as deposited. For highly doped samples the modified Auger parameter is slightly overestimated with the given fit, due to an additional shoulder contribution from free electron screening effects on the lower binding energy side.[11]

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