Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

About Degradation and Regeneration Mechanisms of NiO Protective Layers Deposited by ALD on Photoanodes

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Supporting Information

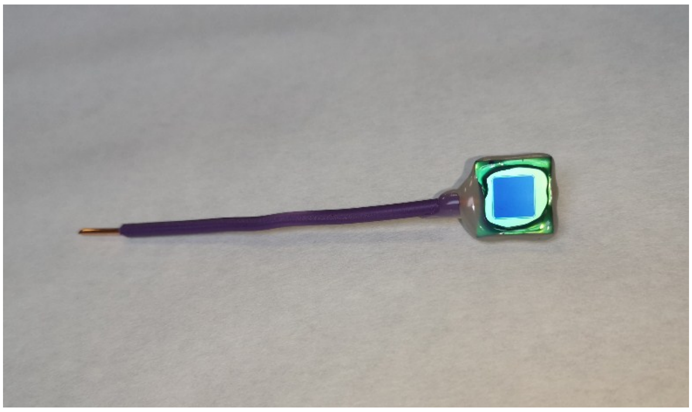

Fig. S. 1: p^+n-Si photoanode, where a 0.5 cm^2 active area (darker region) was lithographically defined by SiO_2 passivation on a silicon n-type wafer (0.1-0.5 ohm.cm resistivity), ALD-protected and further Ag paint soldered to a Cu wire and isolated with thermoplastic.

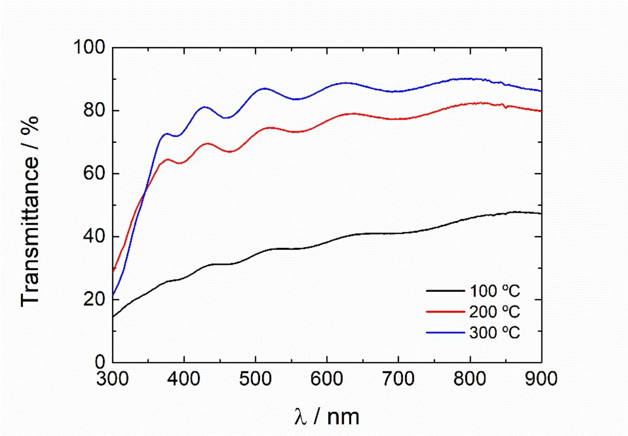

Fig S. 2: transmittance measurements of NiO layers grown at 100 (black), 200 (red) and 300 ºC (blue) on top of glass substrates.

V vs RHE	***R1 / Ohm***	***R2 / Ohm***	***C2 / F***	***R3 / Ohm***	***CPE3-T / $F\cdot S^{A3-1}$***	***A3***
1.1	*2.293*	*426.9*	*1.40E-06*	*3.01E+18*	*1.01E-04*	*0.83*
1.2	*2.229*	*428.9*	*1.39E-06*	*5.10E+11*	*1.38E-04*	*0.83*
1.3	*2.093*	*419.1*	*1.38E-06*	*7244*	*4.89E-04*	*0.76*
1.4	*2.407*	*430.1*	*1.37E-06*	*6.46E+11*	*4.43E-04*	*0.87*
1.5	*2.054*	*430.5*	*1.36E-06*	*6104*	*3.11E-04*	*0.88*
1.6	*2.13*	*371.1*	*1.35E-06*	*447.9*	*2.74E-04*	*0.83*
1.7	*2.223*	*246.1*	*1.32E-06*	*179.2*	*2.39E-04*	*0.82*
1.8	*2.366*	*144.7*	*1.25E-06*	*97.5*	*1.93E-04*	*0.85*
1.9	*1.822*	*82.2*	*1.19E-06*	*56.59*	*2.05E-04*	*0.85*

Table S. 1: EIS fitted values of Fig. 6a using the modelled circuit presented in Fig. 6a (inset).

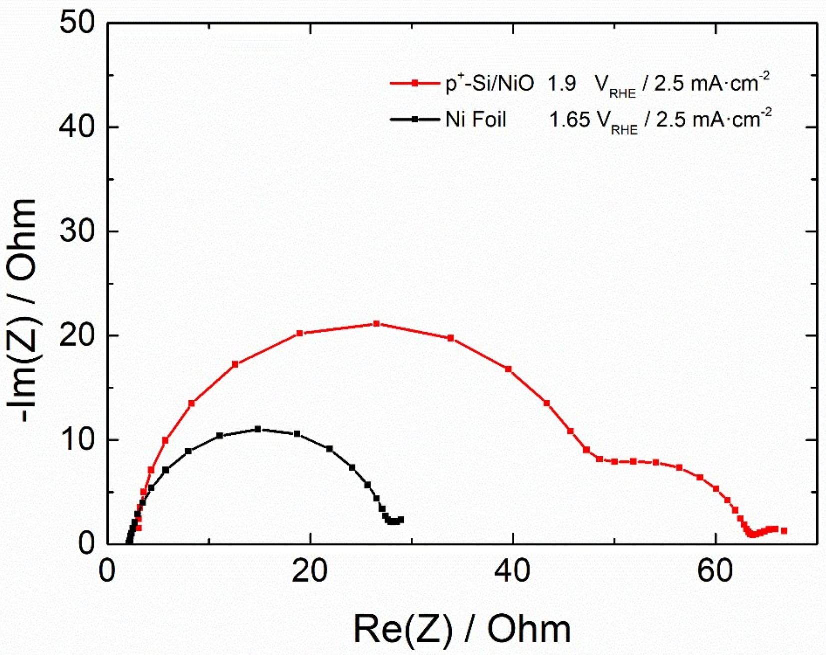

Fig. S. 3: EIS measurements of a Ni Foil and a protected p^+*-Si with 100 ºC NiO by ALD at similar current values and thus, at different potential using the modelled circuit presented in Fig. 6a (inset). Results are presented in Table S. 2.*

t / h	R1 / Ohm	R2 / Ohm	C2 / F	R3 / Ohm	CPE3-T / F·S^{A3-1}	A3
Ni Foil	*2.15*	*0*	*0*	*26.04*	*8.92E-04*	*0.89*
100 ºC NiO p^+-Si	*2.99*	*41.96*	*1.16E-06*	*18.9*	*3.80E-04*	*0.78*

Table S. 2: EIS fitted values of Fig. S. 3 using the modelled circuit presented in Fig. 6a (inset).

t / h	R1 / Ohm	R2 / Ohm	C2 / F	R3 / Ohm	CPE3-T / F·S^{A3-1}	A3
0	*2.9*	*41.9*	*1.16E-06*	*18.9*	*3.80E-04*	*0.78*
1	*3.6*	*52.8*	*1.16E-06*	*36.3*	*2.63E-04*	*0.78*
3	*3.5*	*54.3*	*1.14E-06*	*35.8*	*2.48E-04*	*0.79*
6	*3.6*	*55.2*	*1.14E-06*	*35.7*	*2.51E-04*	*0.79*
9	*3.8*	*57.1*	*1.13E-06*	*35.3*	*2.36E-04*	*0.80*
12	*3.6*	*55.7*	*1.16E-06*	*34.3*	*2.46E-04*	*0.80*
15	*4.0*	*59.7*	*1.12E-06*	*37.1*	*2.41E-04*	*0.79*
18	*3.5*	*57.7*	*1.18E-06*	*35.8*	*2.56E-04*	*0.78*
21	*3.7*	*56.8*	*1.14E-06*	*33.8*	*2.40E-04*	*0.79*
24	*3.8*	*56.1*	*1.13E-06*	*32.8*	*2.45E-04*	*0.79*

Table S. 3: EIS fitted values of Fig. 6c using the modelled circuit presented in Fig. 6a (inset).

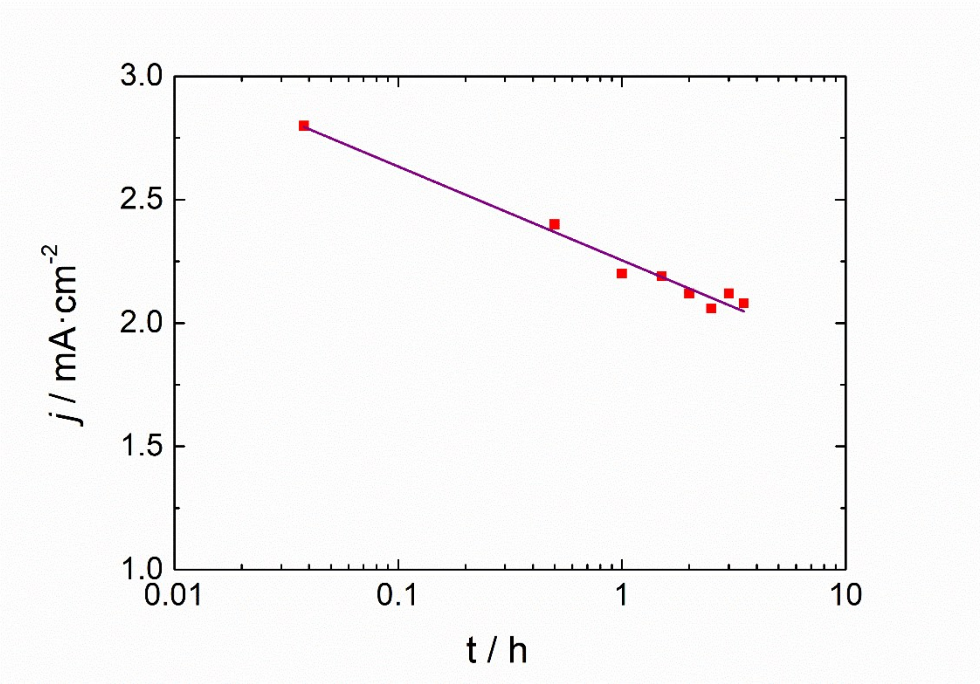

Fig. S. 4: Stability measurement of the same sample represented in Fig. 6b in a logarithmic time scale and the correspondent fitting of the measured values, polarized at 1.9 V vs RHE in 1 M KOH.

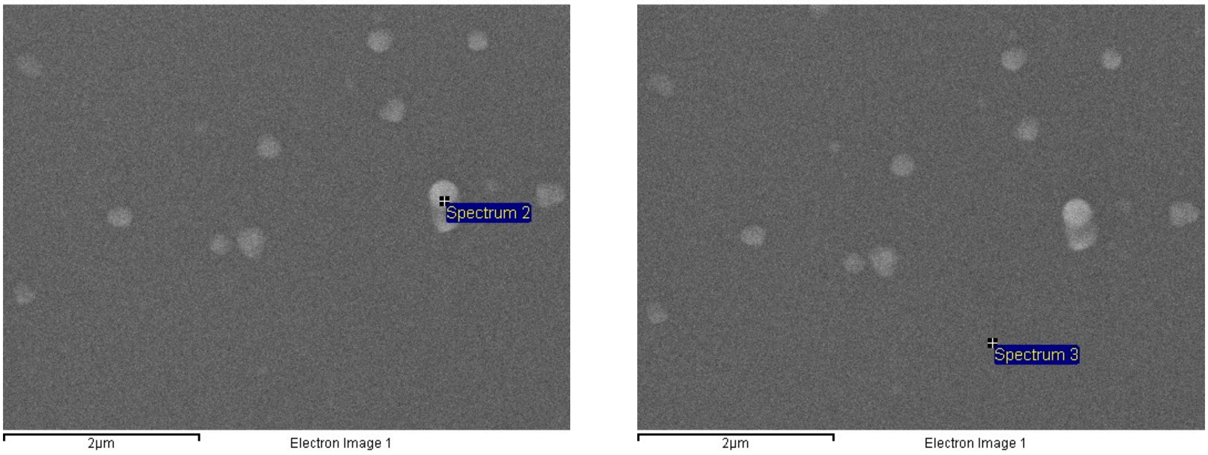

Fig. S. 5: selected spots where the EDX measurements presented in Table S.1 were performed.

Spectrum 2			Spectrum 3		
Element	Weight%	Atomic%	Element	Weight%	Atomic%
C K	15.84	28.17	C K	30.38	48.55
O K	**15.34**	**20.49**	**O K**	**8.57**	**10.28**
F K	7.06	7.94	F K	1.73	1.75
Al K	0.29	0.23	Al K	0.00	0.00
Si K	52.31	39.79	Si K	56.13	38.36
S K	0.14	0.10	S K	0.08	0.05
Ni K	**9.01**	**3.28**	**Ni K**	**3.12**	**1.02**
Totals	100.00		Totals	100.00	

Table S. 4: EDX quantifications of spots selected in Fig. S. 5, presenting significant extra Ni and O where bumps are visible by SEM.

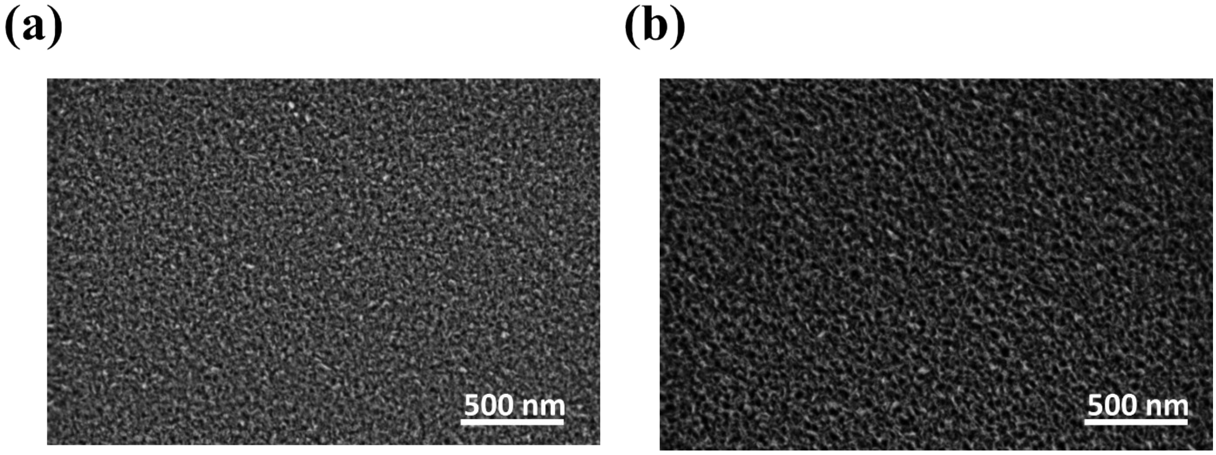

Fig. S. 6: SEM images of NiO layers grown on top of Si at deposition temperatures of 200 ºC (left) and 300 ºC (right) after 100 cycles between 1.1 and 2 V vs RHE in 1 M KOH electrolyte in dark conditions. No morphology changes can be seen.

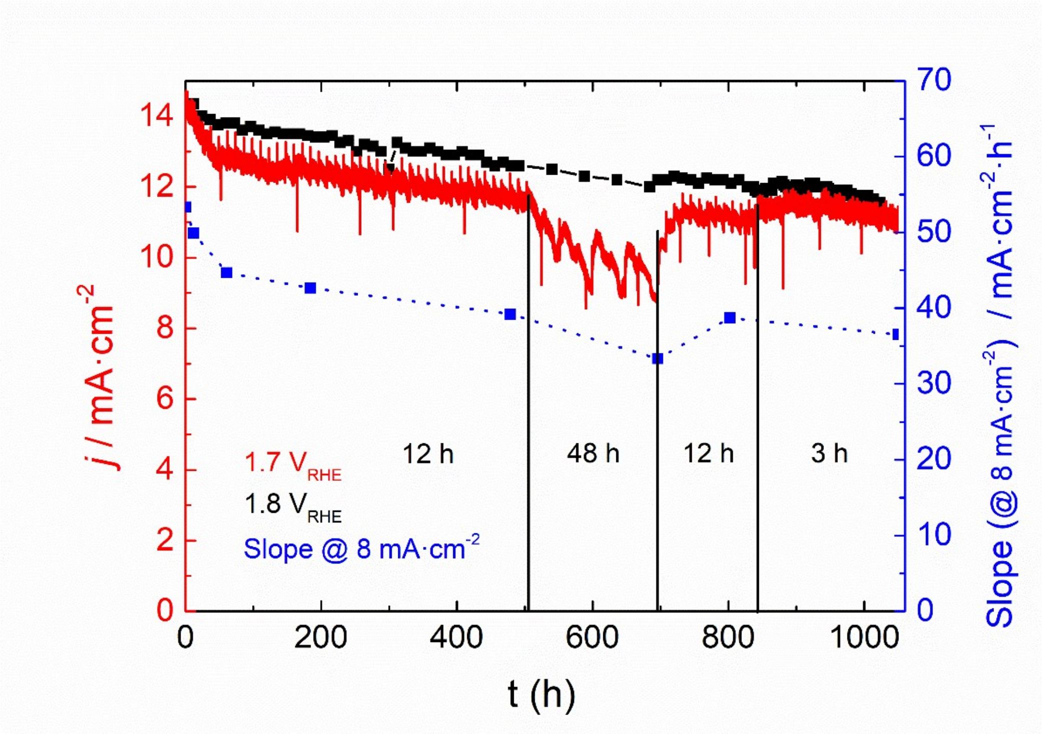

Fig. S. 7: p$^+$n-Si photoanode protected with NiO deposited at 100 ºC and measured under 1 sun illumination in 1 M KOH. red) 1000 h stability measurement at 1.7 V vs RHE cycled 6 times every 12, 48 or 3h. black) measured current density at more anodic potential (1.8 V vs RHE), where the current density is limited by the number of minority carriers photogenerated in the p-n junction.

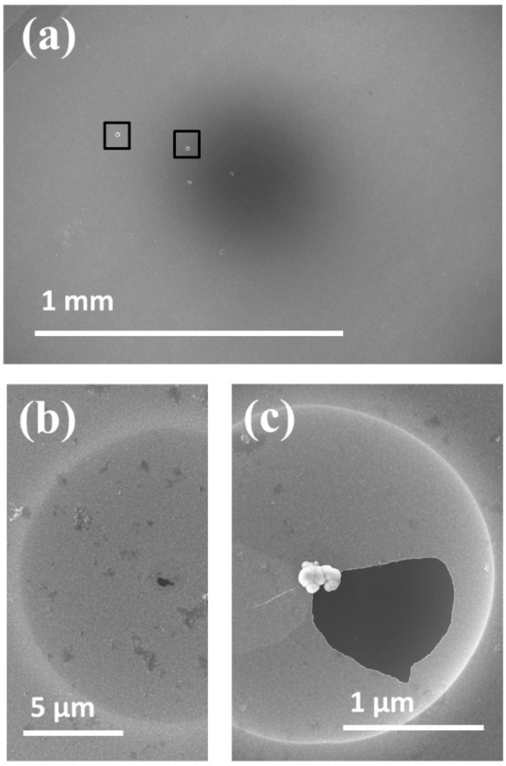

Fig. S. 8: a) SEM top view image of the n^+p*-Si photoanode NiO protected at 100 ºC presenting very few etched regions. Zoom in two of the etching regions, where b) a few tens of nanometers hole can be seen and c) a particle is present, both probable fabrication defects of the NiO layer allowing KOH to etch the silicon beneath*