

Electronic supplementary information for: Electronic structure and morphology of dark oxide on zinc generated by electrochemical treatment

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1 Time evolution of oxide thickness and ellipsometric spectra during electrochemical treatment at different potentials

In addition to the data presented in the main article, oxide growth was analysed at 2.2 V, 3.2 V and 5.2 V. While the 1.2 V shown in the main article and the 2.2 V shown here are still in the passive regime of the current–voltage curve, at 3.2 V and 5.2 V one is in the transpassive regime, where oxygen evolution occurs on the surface. Here the thickness was analysed in a procedure different from the procedure described in the main article, because the procedure described in the main article holds only for layer thicknesses below 10 nm. Here, using literature data for the dielectric function of Zn [1], ZnO [2], and water [3], ellipsometric spectra for with different thicknesses of the layer of ZnO were simulated. Subsequently, the Δ at 700 nm was plot against the layer thickness, and the resulting curve was fit to a second order polynomial. This polynomial was then used to determine the layer thickness increase from the decrease in Δ with time at the respective potential. For the different oxidation potentials, results are shown in Fig. 7, Fig. 11, Fig. 15.

To emphasise spectral changes, spectra of Ψ are shown, and combined with two other plots. In the first type of plot (Fig. 2, Fig. 5, Fig. 9, and Fig. 13), the change $\delta\Psi = \Psi - \Psi_i$ with reference to the initial measurement Ψ_i at open circuit potential (OCP) is shown. The

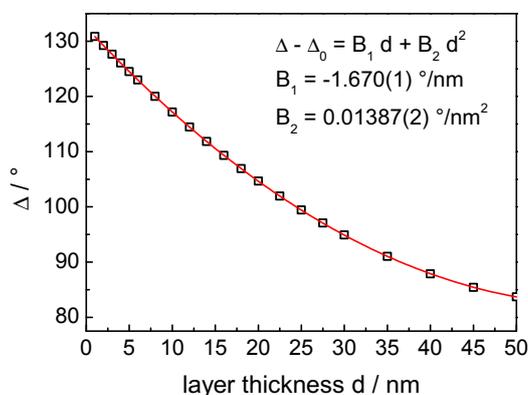


Fig. 1: Ellipsometric parameter Δ at 700 nm as function of layer thickness with polynomial used in further analysis.

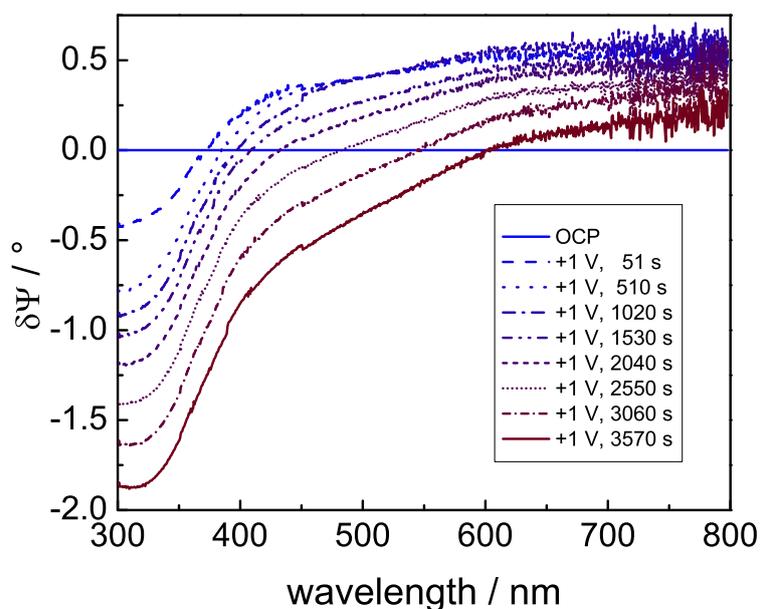


Fig. 2: Time evolution of difference $\delta\Psi$ in ellipsometric parameter Ψ recorded during oxidation at +1.2 V with respect to the initial measurement at OCP. Figure is based on the oxidation part of the data shown in Fig. 3 of the main manuscript.

rationale for this plot comes from the perturbation parameter formulation, where the presence of a layer can be accounted for by an additive term in the ellipsometric ratio [4]. The second plot presents the ratio Ψ/Ψ_i of Ψ with respect to Ψ at OCP. This plot can be rationalised as a reflectance difference spectrum. Following the argument in section 3.2 of the main article, $\frac{\Psi}{\Psi_i} \approx \frac{|r_p|}{|r_{p,i}|}$. This type of plot is shown in Fig. 3, Fig. 6, Fig. 10 and Fig. 14.

The shape of the curves in both the $\delta\Psi$ and the Ψ/Ψ_i plots look very similar, as expected for a system with sufficiently small deviations from the initial state. Due to the analogy to reflectance difference spectra, we focus on the discussion of the Ψ/Ψ_i representation. A value < 1 indicates a lower reflection amplitude in the sample compared to the initial reference state, e.g. due to an absorption in the surface layer. For all oxidation potentials, the main electronic absorption of ZnO becomes clearly visible below 370 nm. An upward shift in the curves is expected for increasing layer thickness in the case of the presence of a non-absorbing layer, in analogy to the parallel shift in curves of Δ , which is observed in the presence of thin layers on top of the substrate. Strong dispersion in the refractive index of the overlayer causes a slope in the curves. In the curves at 1.2 V (Fig. 3), 2.2 V (Fig. 6) and 3.2 V (Fig. 10) oxidation potential, a significant change in slope is observed from a relatively flat region at high wavelengths to a higher slope at wavelengths below ≈ 650 nm. This change is attributed to the onset of the absorption originating from the intragap states. It coincides with the bend in the curves of Ψ in the raw data. Further details are discussed in the main article.

The spectra at 5.2 V (Fig. 14), and in part also the spectra at 3.2 V (Fig. 10) for longer oxidation times, i.e. with layer thickness above ≈ 10 nm differ from those at other potentials. The main electronic absorption of ZnO is visible as a maximum, as for thicker layers, not only the substrate dominates the overall reflection properties. Rather, the role of the layers increases. The absorption attributed as intragap states starting at ≈ 650 is also visible as a maximum here. In the raw data with oxide layer, however, no feature is visible at this wavelength. The observation of a maximum in the difference spectra is therefore attributed to the presence of the absorption in the initial measurement at OCP, where it is clearly visible in the spectrum. This discussion indicates that ideally, one should measure the oxide-free substrate to obtain reference spectra.

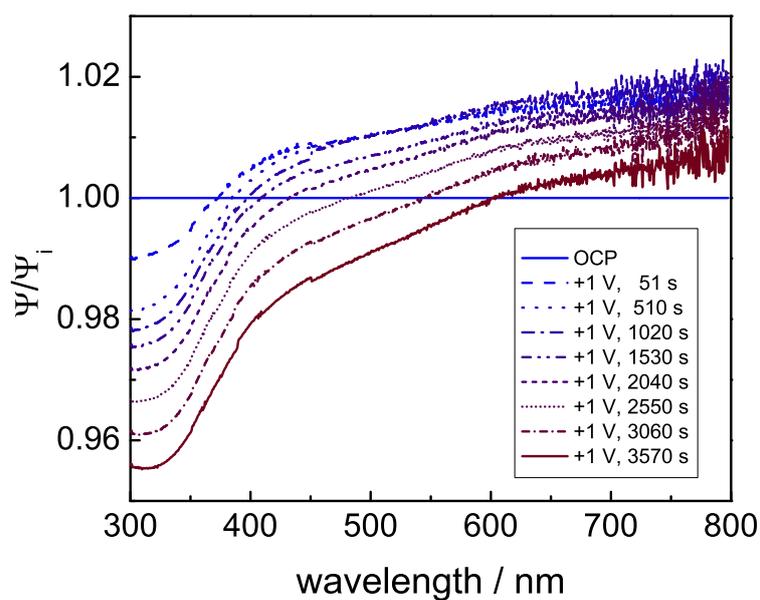


Fig. 3: Time evolution of ratio of ellipsometric parameter Ψ with respect to the initial measurement at open circuit potential recorded during oxidation at +1.2 V. Figure is based on the oxidation part of the data shown in Fig. 3 of the main manuscript.

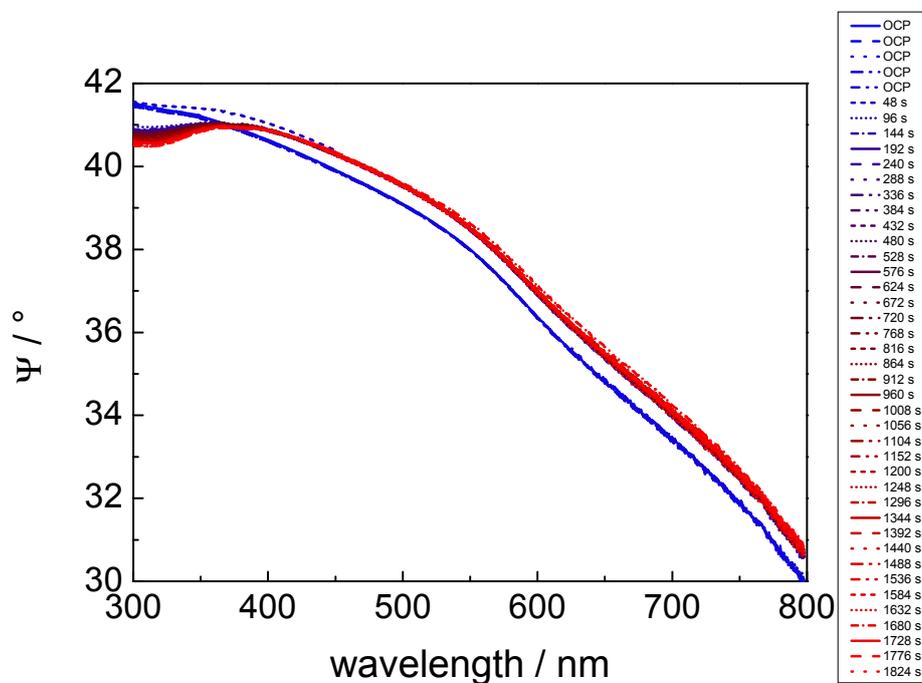


Fig. 4: Time evolution of ellipsometric parameter Ψ with treatment at 2.2 V for the time as indicated in the graph. Initial spectra are recorded at open circuit potential.

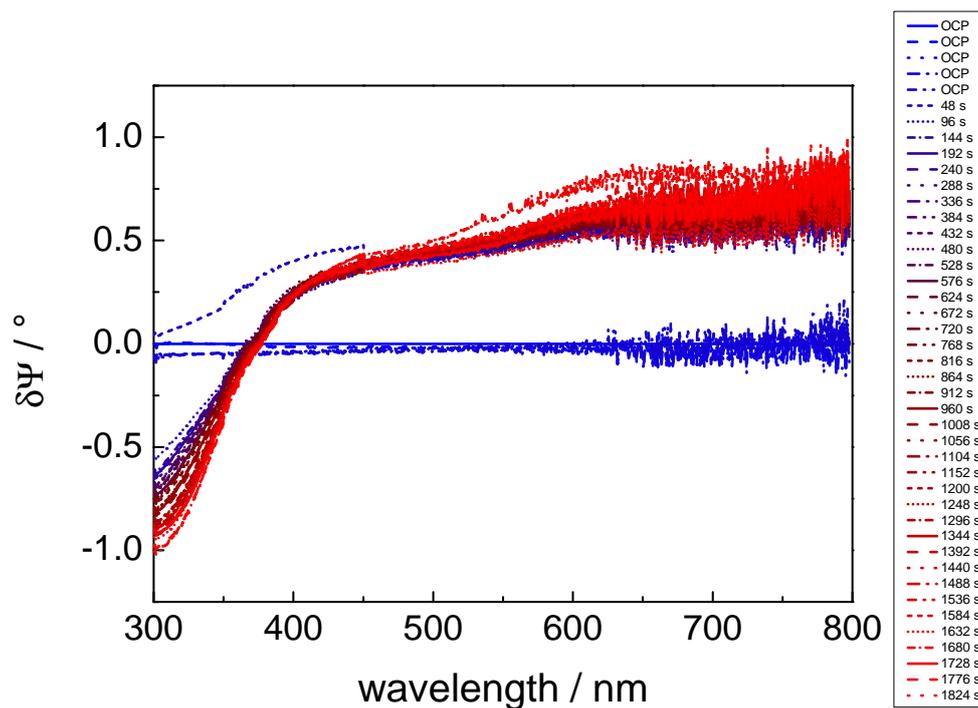


Fig. 5: Time evolution of difference $\delta\Psi$ in ellipsometric parameter Ψ recorded during oxidation at +2.2 V with respect to the initial measurement at OCP.

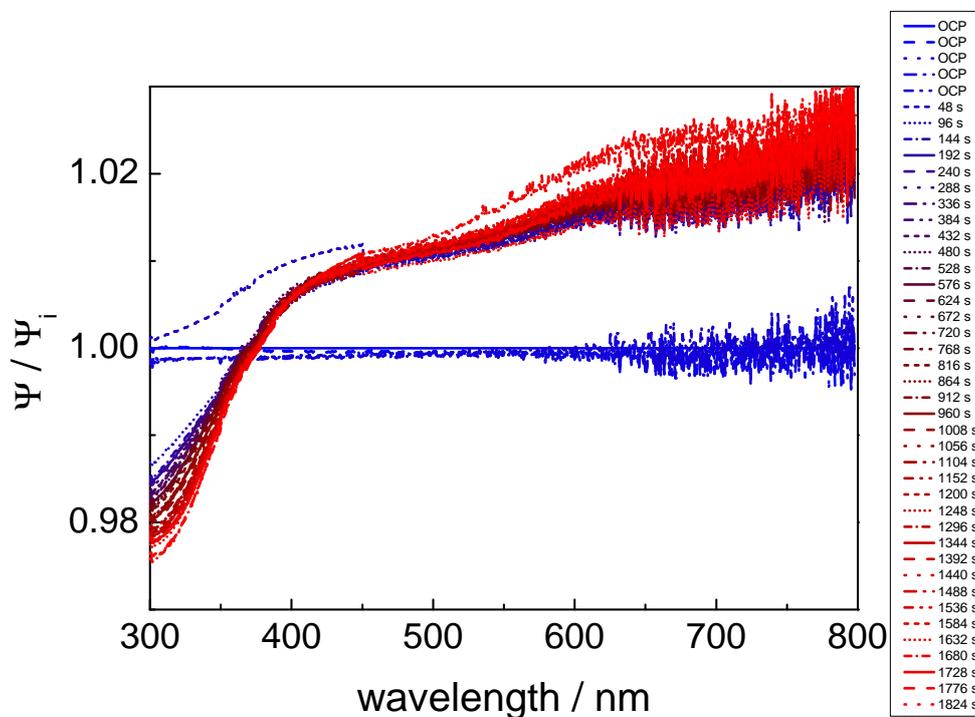


Fig. 6: Time evolution of ratio of ellipsometric parameter Ψ with respect to the initial measurement at open circuit potential recorded during oxidation at +1.2 V.

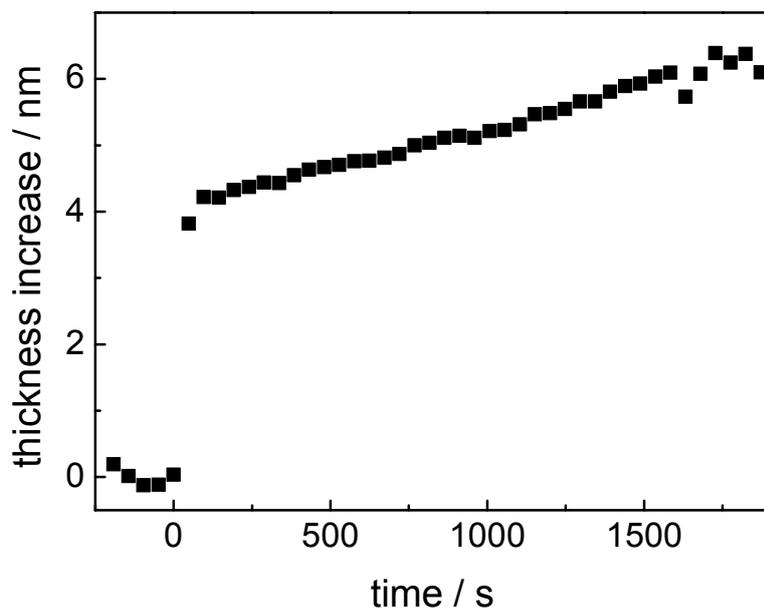


Fig. 7: Time evolution of of thickness difference to OCP state after treatment at 2.2 V for the time as indicated in the graph.

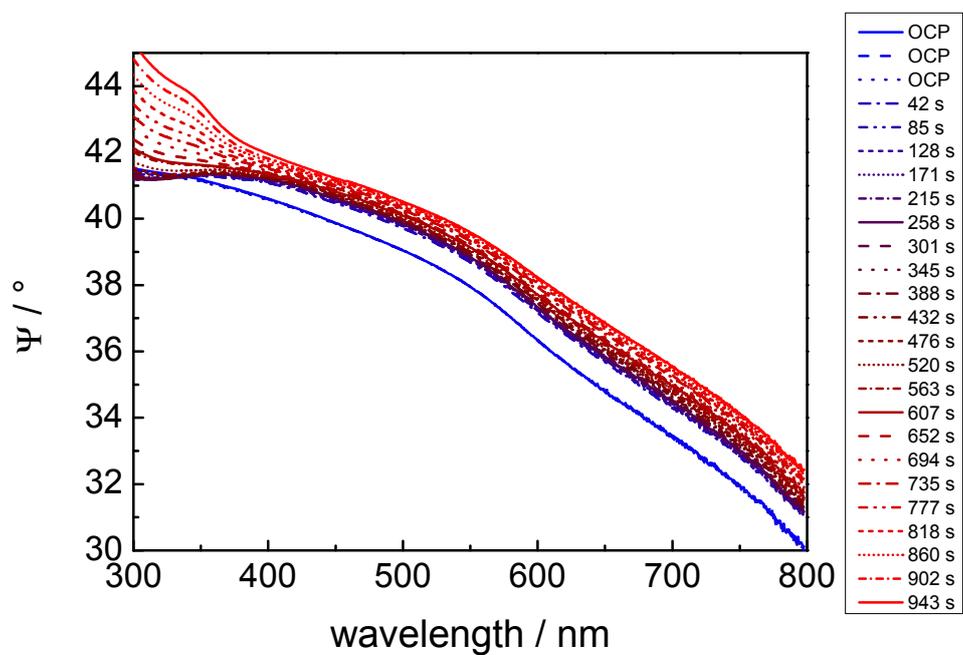


Fig. 8: Time evolution of ellipsometric parameter Ψ with treatment at 3.2 V for the time as indicated in the graph. Initial spectra are recorded at open circuit potential.

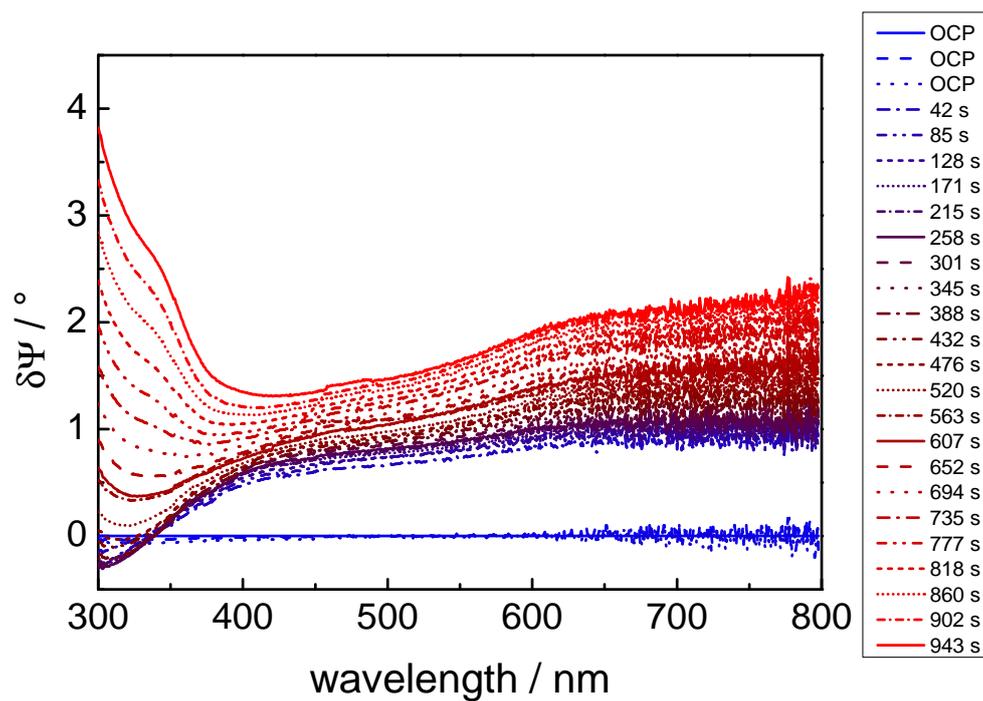


Fig. 9: Time evolution of difference $\delta\Psi$ in ellipsometric parameter Ψ recorded during oxidation at +3.2 V with respect to the initial measurement at OCP.

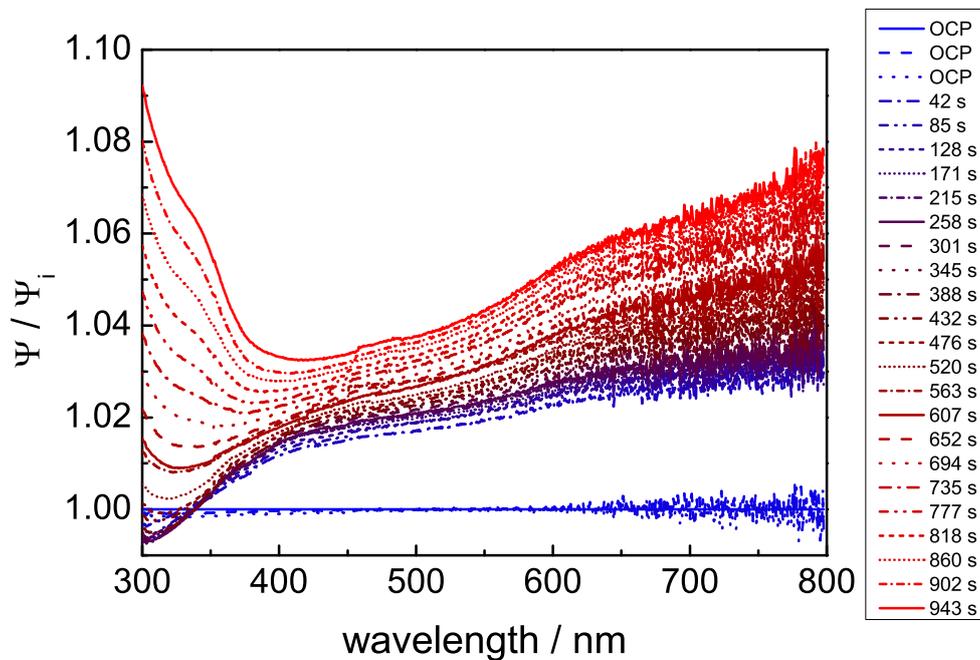


Fig. 10: Time evolution of ratio of ellipsometric parameter Ψ with respect to the initial measurement at open circuit potential recorded during oxidation at +3.2 V.

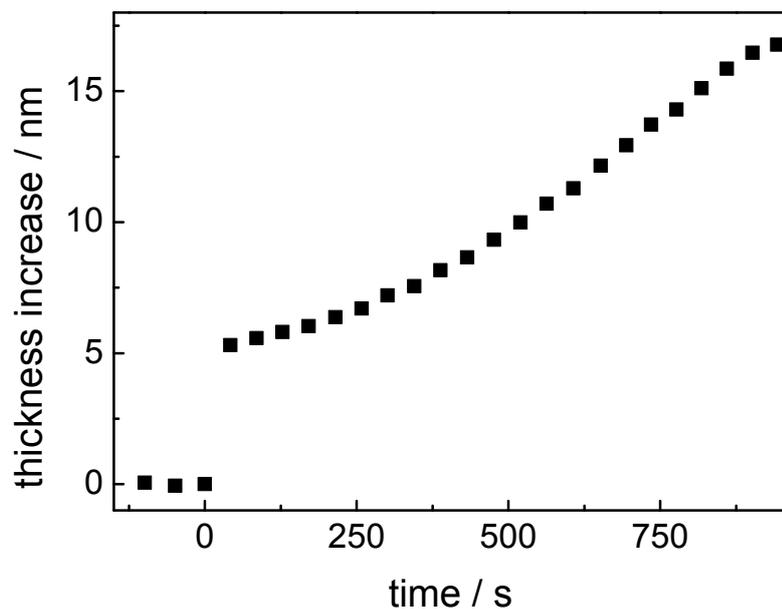


Fig. 11: Time evolution of of thickness difference to OCP state after treatment at 3.2 V for the time as indicated in the graph.

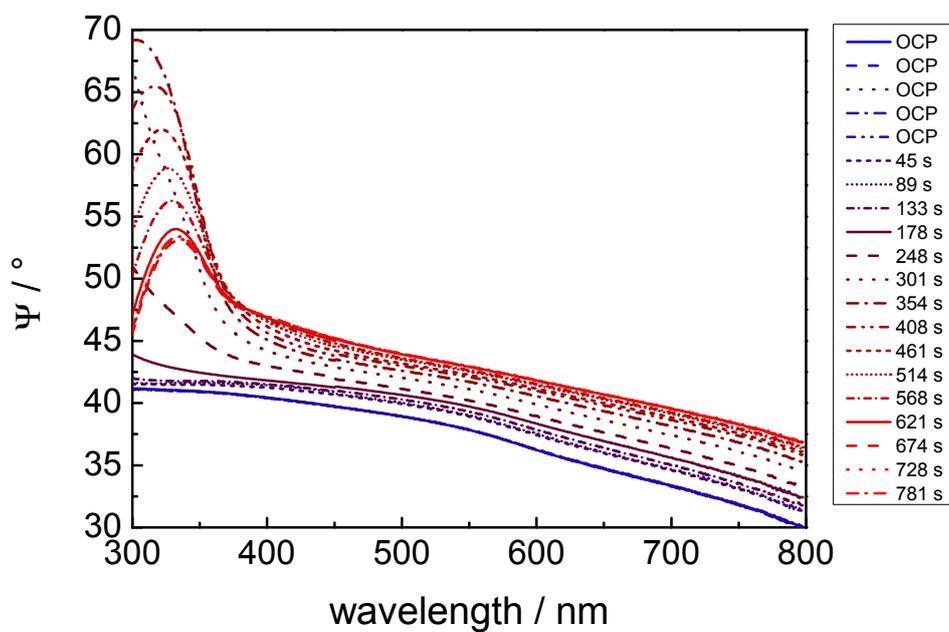


Fig. 12: Time evolution of ellipsometric parameter Ψ with treatment at 5.2 V for the time as indicated in the graph. Initial spectra are recorded at open circuit potential.

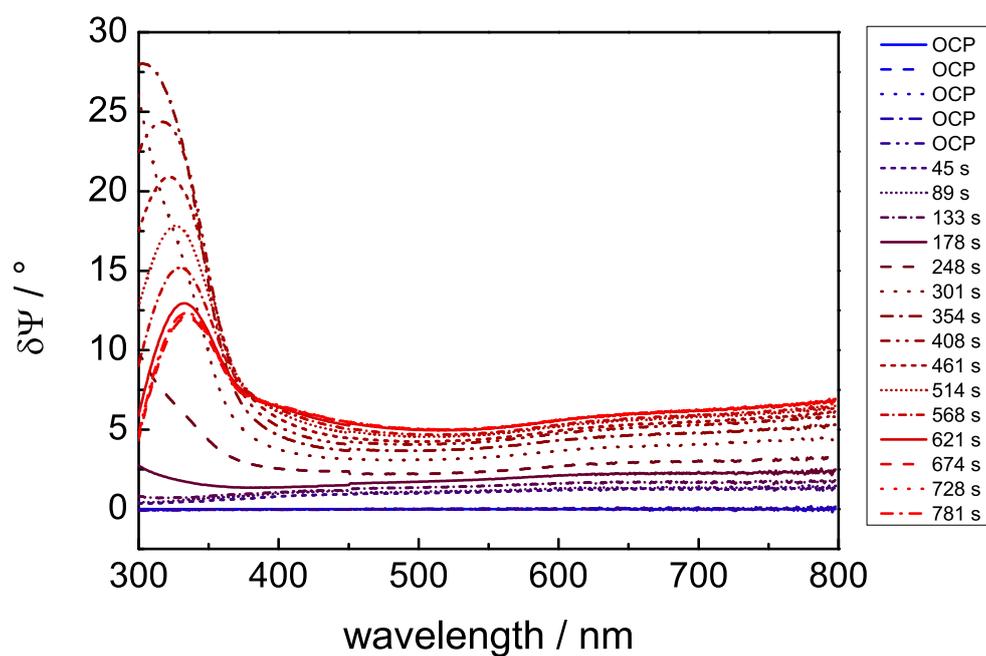


Fig. 13: Time evolution of difference $\delta\Psi$ in ellipsometric parameter Ψ recorded during oxidation at +5.2 V with respect to the initial measurement at OCP.

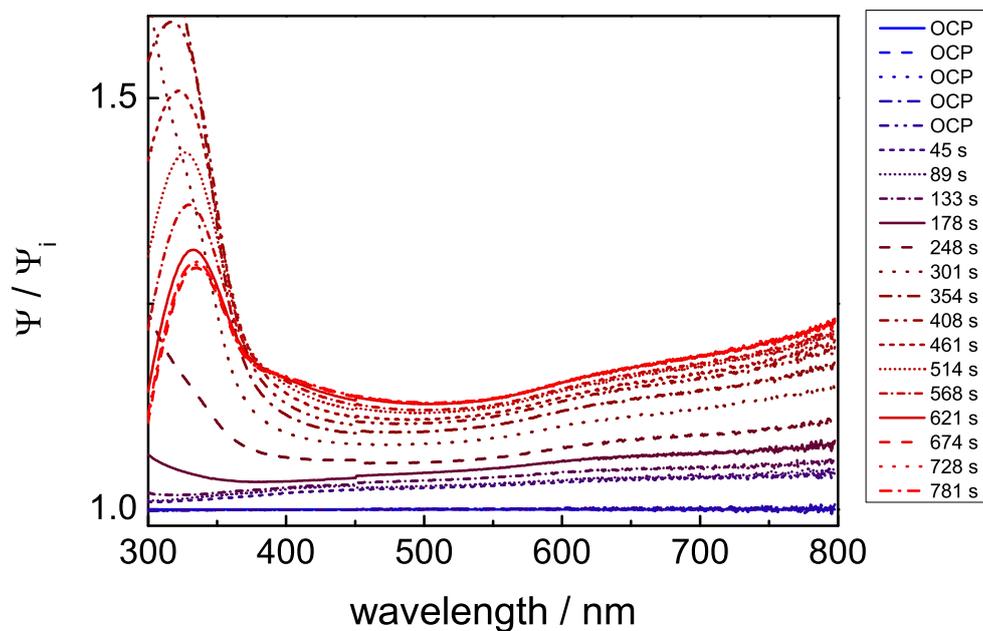


Fig. 14: Time evolution of ratio of ellipsometric parameter Ψ with respect to the initial measurement at open circuit potential recorded during oxidation at +5.2 V.

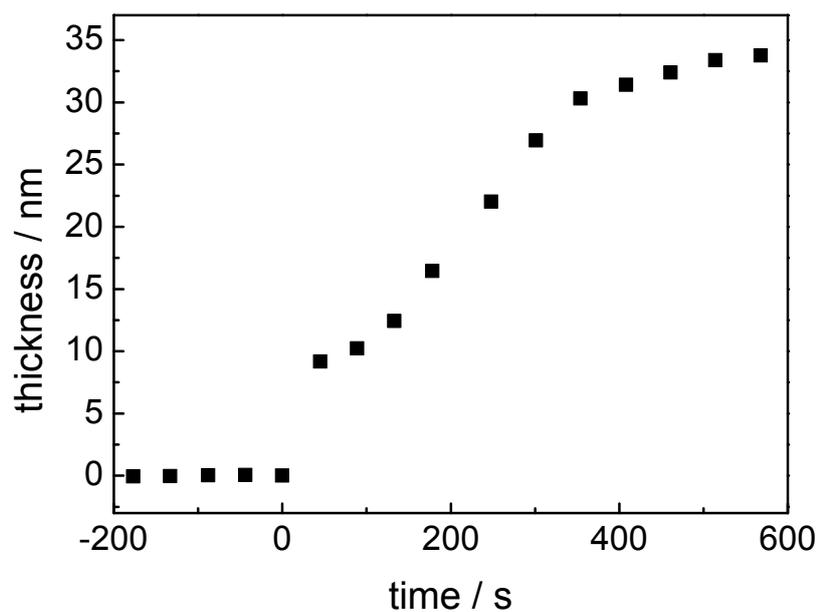


Fig. 15: Time evolution of of thickness difference to OCP state after treatment at 5.2 V for the time as indicated in the graph.

References

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