Electrodeposited zinc oxide nanorods coated with atomic-layer deposited iron oxide

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Overview

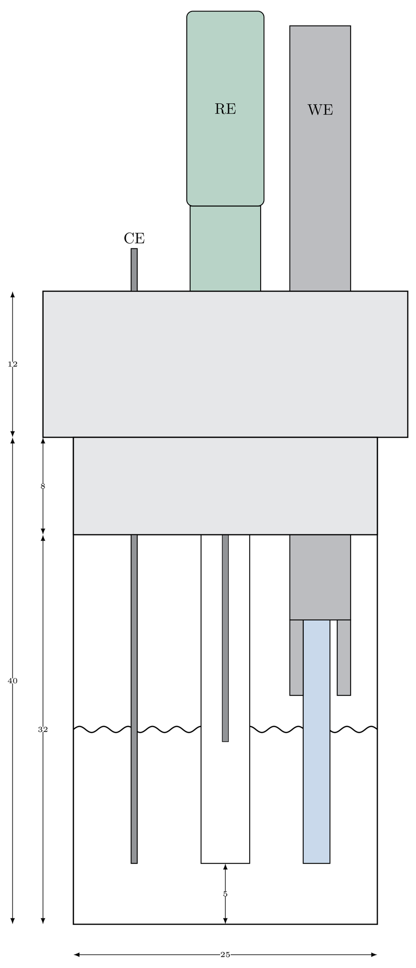
- Zinc oxide nanorods were electrodeposited on transparent conductive oxide (on sodalime glass).
- On top of the ZnO, iron oxide (hematite) was deposited using ALD to evenly coat the ZnO layer.
- The material was characterised using UV/Vis spectroscopy, X-ray fluorescence, and scanning electron microscopy.
- The samples are intended for use as photoelectrochemical hydrogen evolution anodes (yet to be tested).

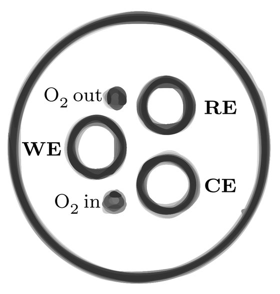
Configuration of the electrodeposition cell

The working electrode is kept at a potential negative to the reduction potential of O_2, which causes oxygen gas near the electrode to be reduced to hydroxide ions. The hydroxide ions react with the zinc ions and forms zinc hydroxide, zinc oxyhydroxide or zinc oxide (depending on temperature).

$$\tfrac{1}{2}\,O_2 + H_2O + 2\,e^- \leftrightarrow 2\,OH^- \qquad (E^\circ = 0.40\,V)$$

$$Zn^{2+} + 2\,OH^- \rightarrow ZnO + H_2O$$





The oxygen is supplied by oxygen-bubbling into the headspace compartment (electrolyte solution is saturated prior to cell on). The schematic to the right shows the electrodeposition cell seen from the side (drawn to scale). The schematic to the left shows the configuration of the cell as seen from above.

Atomic-layer deposition of iron oxide

This technique was chosen because it can evenly deposit material on a substrate of arbitrate shape and form. Substrate needs only be thermostable (essentially). The ALD technique is a tad slow, and expensive. No other technique (available to us) would be able to deposit an even layer of material on our uneven ZnO sample, especially not without interacting or degrading the ZnO layer.

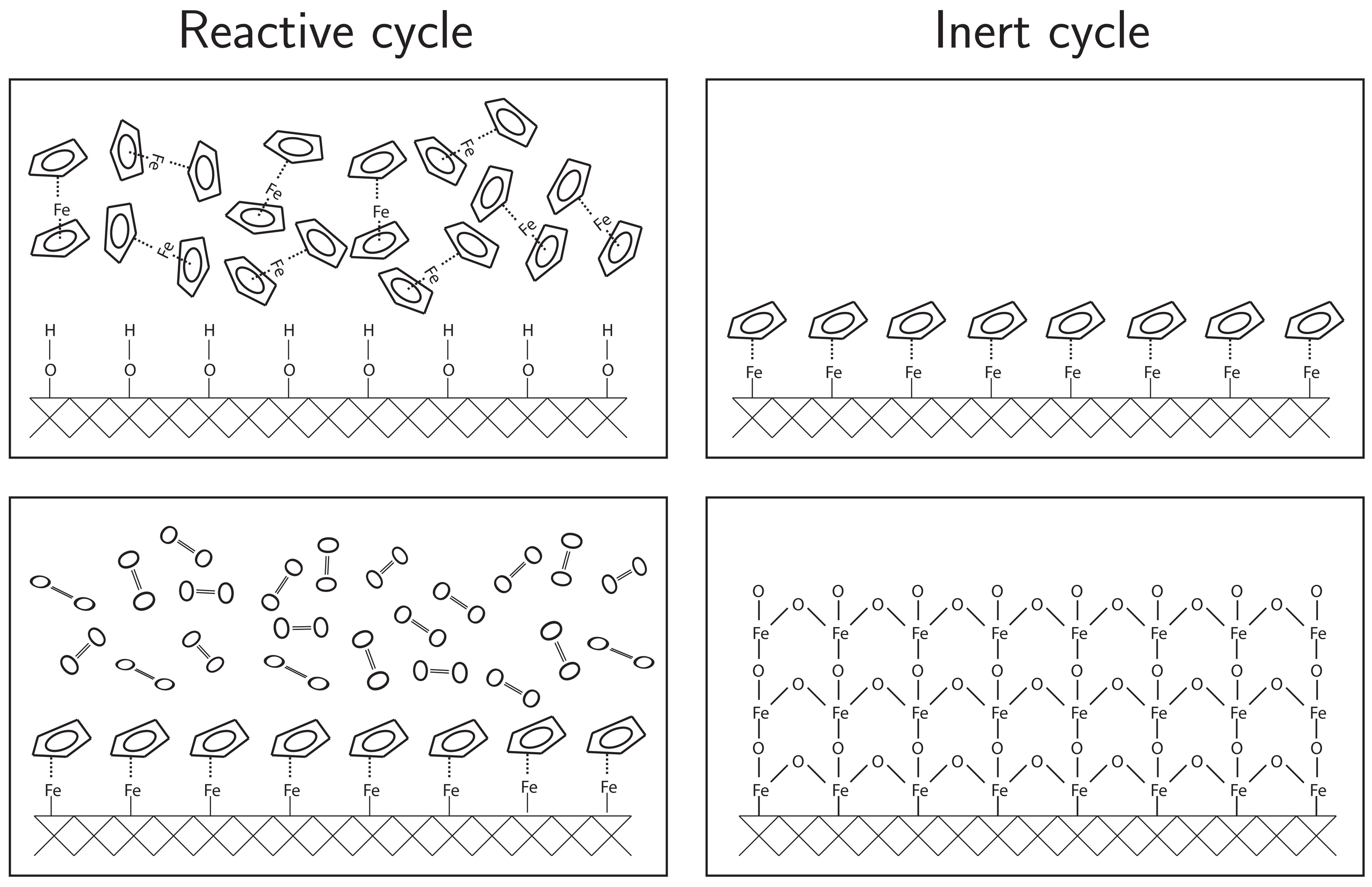
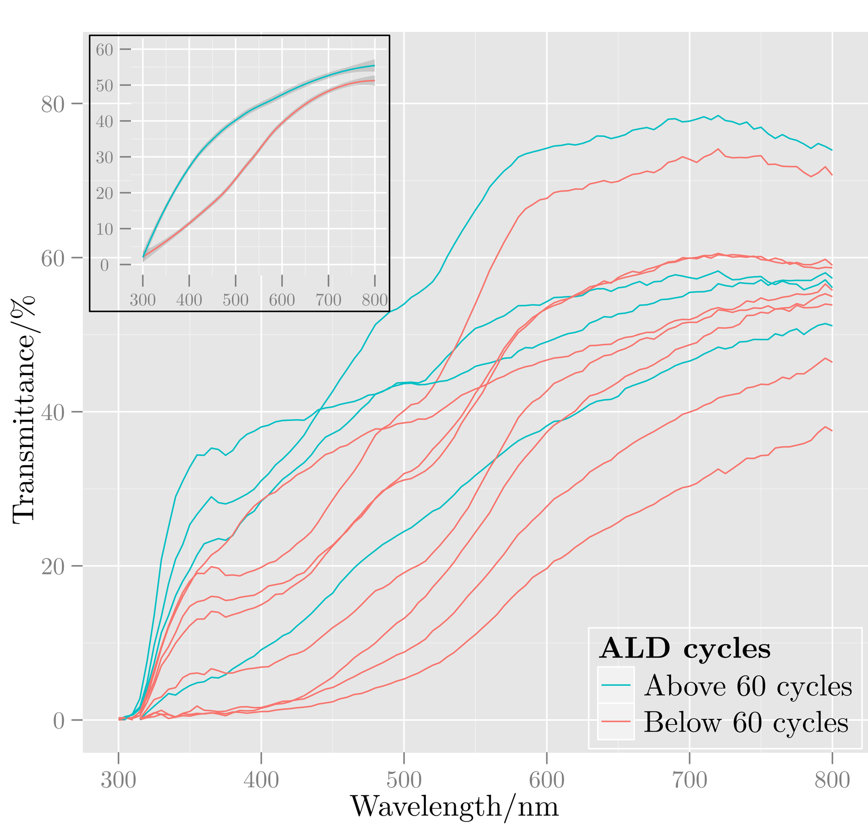


Illustration: Mattis Fondell

- Precursor: ferrocene
- Chamber at 450 °C
- ALD cycles: 35, 50, 62, 75, 87, 100 (corresponds to layer thicknesses 2 nm to 20 nm)

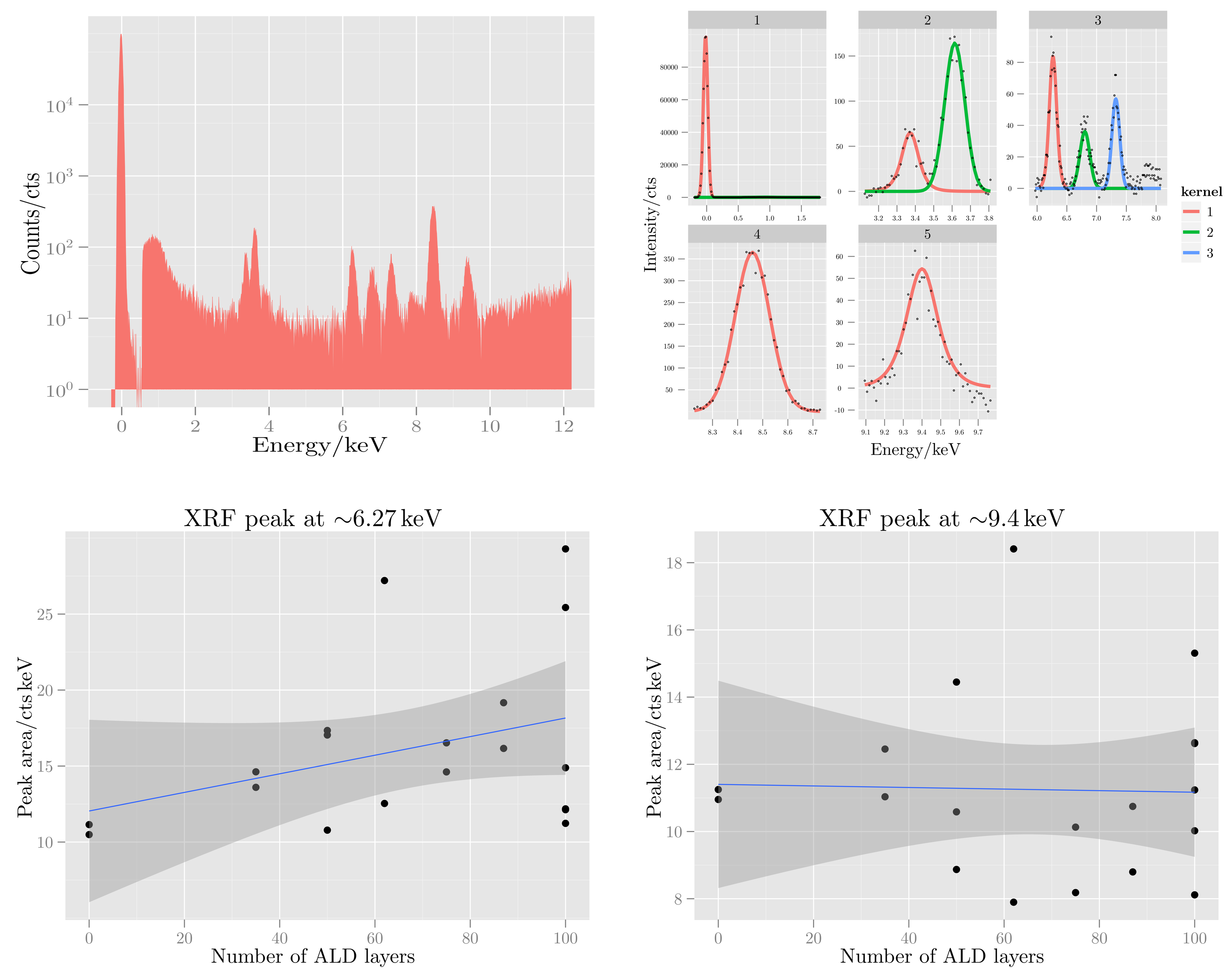
Optical transmittance weakly correlated to ALD cycles



Transmittance spectra were recorded on a Perkin-Elmer Lambda 900 with an integrating sphere. Hypothesis was that attenuation in transmittance would correlate with iron oxide thickness (ALD cycles).

The observed relationship is not so straightforward. Grouping the recorded spectra (inset) alleviates the problem slightly, but the result is quite sensitive to grouping range. This weak correlation may have been due to variations in substrates, or perhaps just too few samples to get good statistics.

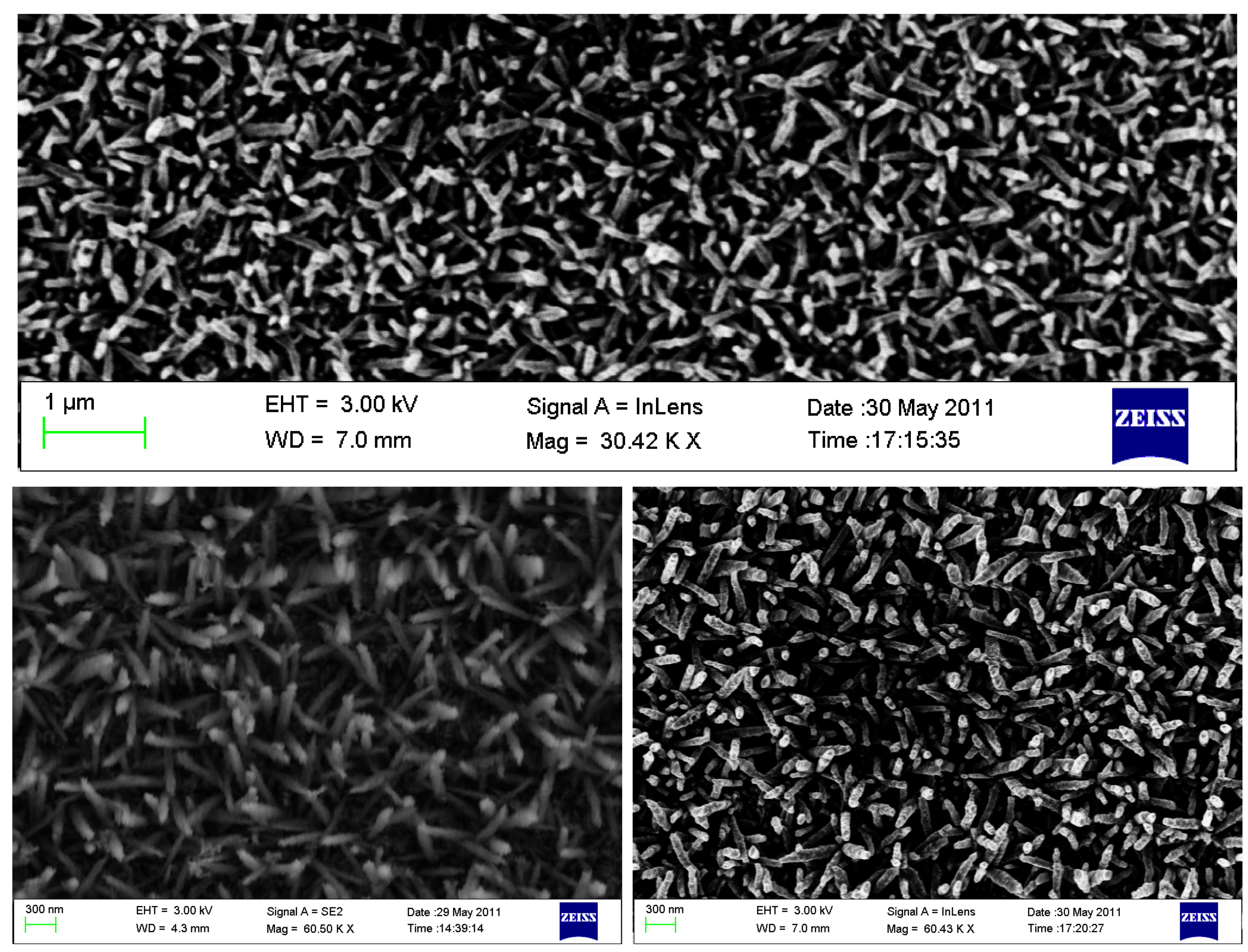
Probing layer thicknesses with XRF



X-ray fluorescence spectroscopy was used in an attempt to measure the relative amounts of Zn and Fe across all samples. As expected, the iron peak area is seen to increase with increasing number of ALD cycles.

Top left: a typical ALD spectrum. Top right: we used an adaptable peak deconvolution technique by Davies et al. to get peak areas, FWHM, etc. Bottom left: iron peak area increases with ALD cycle. Bottom right: zinc peak area is independent of ALD cycle.

Film morphology probed with SEM



Top: electrodeposited ZnO nanorod coverage was quite homogeneous. Bottom left: electrodeposited ZnO on FTO substrate. Bottom right: the same sample, after coating with a 100 cycles thick iron oxide layer.

Acknowledgement

Atomic-layer depositions were performed by fellow Ph.D. student Mattis Fondell.

Bibliography

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