

Supporting Information

Photoelectrochemical Properties of GaN Photoanodes with Cobalt Phosphate Catalyst for Solar Water Splitting in Neutral Electrolyte

Jumpei Kamimura,^{*,†} Peter Bogdanoff,[‡] Fatwa F. Abdi,[‡] Jonas Lähnemann,[†]

Roel van de Krol,[‡] Henning Riechert,[†] and Lutz Geelhaar[†]

[†]*Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany*

[‡]*Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institute for Solar Fuels,*

Hahn-Meitner-Platz 1, 14109 Berlin, Germany

E-mail: kamimura@pdi-berlin.de

Detailed analysis by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy

We studied in an analytical scanning electron microscope the GaN template on which the largest amount (corresponding to a passed charge of 162 mC/cm^2) of cobalt phosphate (Co-Pi) had been deposited. We focused on this sample, as still the amount of Co-Pi is at the detection limit of the employed techniques. Figures S1(a) and (b) present top-view micrographs acquired with the conventional and in-lens detectors of the SEM, respectively. In general, while conventional detectors predominantly image morphological features, in-lens detectors have a higher sensitivity for material contrasts. Particularly, surface coatings can strongly modify the escape of low energy secondary electrons that contribute to the in-lens detector signal, whereby even monolayer graphene can be imaged.¹⁻³ Indeed, the conventional SEM image [Figure S1(a)] reveals only the surface morphology, i.e. the terraces of the original GaN template separated by macrostep edges. In contrast, the in-lens detector image [Figure S1(b)] exhibits dark regions on the terraces and bright areas at the macrostep edges, which already indicate a variation in the coverage of the Co-Pi film. EDX spectra from the two types of regions are presented in Figure S1(c). The spectrum from

a terrace demonstrates the presence of cobalt and phosphorus in the sample, consistent with previous reports on Co-Pi catalysts.^{4,5} On the other hand, the EDX spectrum from a step edge does not contain any feature characteristic for Co-Pi. Therefore, we conclude that the bright regions near the step edges in Figure S1(b) correspond to a lower film thickness of the deposited Co-Pi.

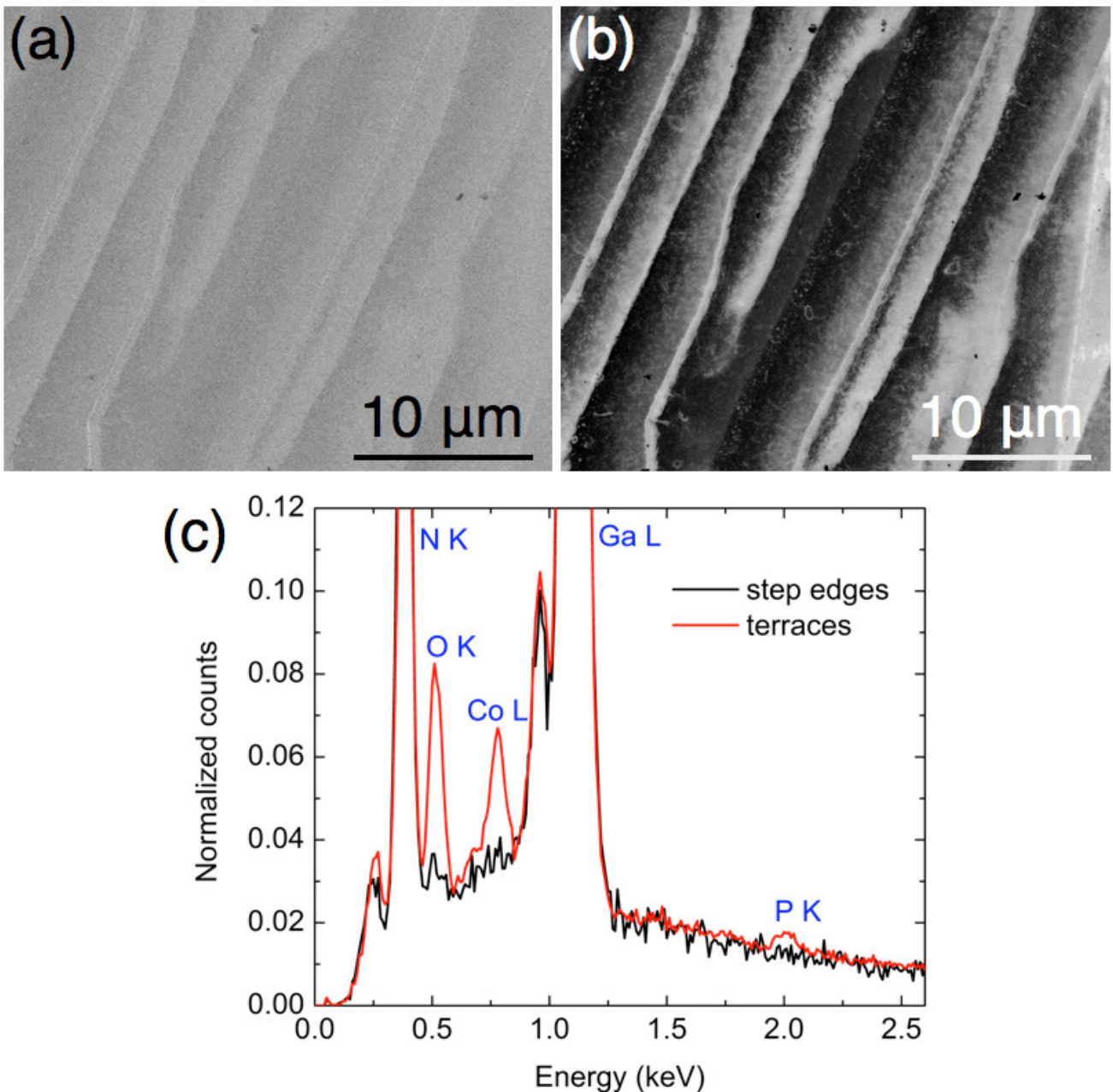


Figure S1. Top-view SEM images of the same area of Co-Pi deposited on a GaN template (passed charge 162 mC/cm²) obtained with (a) the conventional detector and (b) the in-lens detector. (c) EDX spectra taken on a terrace [dark area in (b)] and at a step edge [bright area in (b)] with the microscope operated at an acceleration voltage of 4.5 kV.

Current-voltage curves for GaN layers in different electrolytes

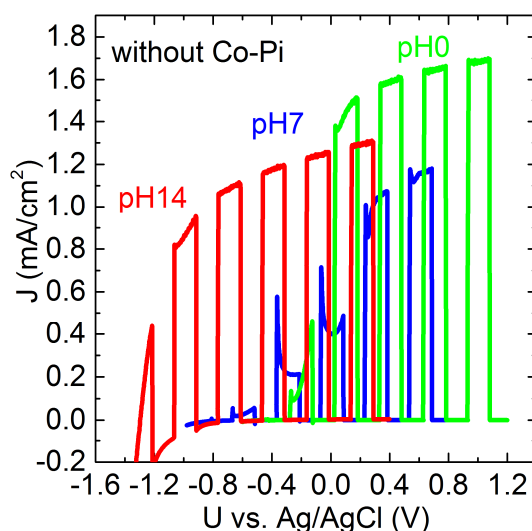


Figure S2. Current-voltage curves for GaN layers in three different electrolytes, H₂SO₄ (pH0), KPi (pH7), and NaOH (pH14) under chopped Xe lamp illumination.

References

1. Kochat, V.; Pal, A. N.; Sneha, E. S.; Sampathkumar, A.; Gairola, A.; Shivashankar, S. A.; Raghavan, S.; Ghosh, A. High Contrast Imaging and Thickness Determination of Graphene with in-Column Secondary Electron Microscopy. *J. Appl. Phys.* **2011**, *110*, 014315.
2. Wofford, J. M.; Oliveira, M. H.; Schumann, T.; Jenichen, B.; Ramsteiner, M.; Jahn, U.; Fölsch, S.; Lopes, J. M. J.; Riechert, H. Molecular Beam Epitaxy of Graphene on Ultra-Smooth Nickel: Growth Mode and Substrate Interactions. *New J. Phys.* **2014**, *16*, 093055.
3. Lähnemann, J.; Flissikowski, T.; Wölz, M.; Geelhaar, L.; Grahn, H. T.; Brandt, O.; Jahn, U. Quenching of the Luminescence Intensity of GaN Nanowires under Electron Beam Exposure: Impact of C Adsorption on the Exciton Lifetime. *Nanotechnology* **2016**, *27*, 455706.
4. Kanan, M. W.; Nocera, D. G. In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co²⁺. *Science* **2008**, *321*, 1072–1075.
5. Khnayzer, R. S.; Mara, M. W.; Huang, J.; Shelby, M. L.; Chen, L. X.; Castellano, F. N. Structure and Activity of Photochemically Deposited “CoPi” Oxygen Evolving Catalyst on Titania. *ACS Catal.* **2012**, *2*, 2150–2160.