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# The Impact of Different Si Surface Terminations in the (001) n-Si/NiOx Heterojunction on the Oxygen Evolution Reaction (OER) by XPS and Electrochemical Methods

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The interaction between (001) n-Si and NiO<sub>x</sub> was investigated with regard to the oxygen evolution reaction (OER), applicable either for water splitting or CO<sub>2</sub> reduction. Thin layers of nickel oxide were deposited step by step by reactive sputter deposition and analyzed in-situ after each step using X-ray photoelectron spectroscopy (XPS). This was performed for silicon with different surface preparations: H-termination, thermally grown oxide (2 Å) and a monolayer of native oxide (4 Å). Upon contact formation the initial flatband like situation in the Si substrates changed to a 0.35 to 0.4 eV upward band bending for all three heterojunctions, with an alignment of the valence bands favorable to hole extraction. With near identical heterojunction performance and identical NiO<sub>x</sub> catalyst layers ( $\eta(10 \text{ mA/cm}^2) = 0.44 \pm 0.01 \text{ V}$  vs. RHE on Ni) an equally identical performance for the OER would be expected. While the native oxide covered sample shows the expected performance in cyclic voltammetry measurements the others fall short of expectations. Using chopped light measurements, this under-performance could be attributed to a higher density of defect states at the silicon surface. Apparently a 4Å SiO<sub>2</sub> layer is sufficient protection to prevent the formation of defect states during NiO<sub>x</sub> deposition, thinner protective layers or none at all result in increased defect states, while thicker layers perform poorly due to their high resistance.

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Direct photoelectrochemical devices are an exciting approach to the storage of renewable energies. Depending on the preferred energy cycle they can be used either for water splitting or CO<sub>2</sub> reduction, in the end it is only a question of the employed catalysts and necessary overpotentials. A direct photoelectrochemical device has two main functional parts, which do not necessarily have to be physically separate. First, there is the photoabsorber, basically a solar cell, who has to supply the necessary photovolage  $U_{ph}$  and photocurrent  $J_{ph}$  to power the desired redox reaction. Second, the catalytic surface, which is in direct contact with the electrolyte and should be catalytically active, thus allowing high current densities at low overpotentials  $\eta$ . In an ideal case the total device performance should be a result of those two contributions only.

Initial research on water splitting was focused on a single semiconducting material performing well in both functions. This was first demonstrated on a TiO<sub>2</sub> electrode by Fujishima and Honda in 1972.<sup>1</sup> In such a device the photoabsorber functionality is defined by the interface junction between semiconductor and electrolyte. Investigated materials were mostly wide bandgap materials, as they could, in theory, provide the necessary  $U_{ph}$ .

However, the double function of the semiconductor electrolyte interface makes an evaluation of such devices difficult, as it is hard to determine whether a lack of performance is a result from poor current voltage (IE) behavior of the junction or the poor catalytic performance of the material. Furthermore, the necessary large bandgaps only allow for the use of a small portion of the solar spectrum, thus reducing the overall efficiency. Therefore, research in more recent times is increasingly focusing on buried junctions, where one or more pn or pin junctions are responsible for the IE performance. As most non-oxide semiconducting materials will degenerate fast under operative conditions in contact with the electrolyte, at least one additional layer is needed, either as part of a heterojunction or as an additional protective layer. If needed, such a design can be expanded further by a catalyst layer optimized for the desired redox reaction. While silicon is a well understood material and readily available in high quality, its bandgap of 1.12 eV is too small to yield a sufficient  $U_{ph}$  to power either water splitting or CO<sub>2</sub> reduction. However, it is a very convenient model system to investigate the interaction of the different functional layers needed in more advanced devices. The obtained results can then be applied to further optimize devices based on multijunction solar cells.<sup>2-6</sup>

Especially in the last few years, there have been a lot of great accomplishments in this direction. McDowell and Hu<sup>7,8</sup> investigated the performance of n-Si | TiO<sub>2</sub> heterojunctions and TiO<sub>2</sub> covered np<sup>+</sup> homojunctions with an additional Ni catalyst, achieving good long term stability. Sun and He<sup>9,10</sup> used NiO<sub>x</sub> layers instead of TiO<sub>2</sub>, thus foregoing the need of an additional catalyst layer, and Mei<sup>11</sup> employed an Ir | IrO<sub>x</sub> structure instead. While Seger et al.<sup>12,13</sup> found that a thin metal layer on the silicon prior to metal oxide deposition resulted in improved performance by reducing the oxidation of the silicon substrate.

However, the focus in those works is more on the total device performance as a function of preparation parameters, like annealing times and layer thickness. There is less information on the energetic situation at the interfaces, in terms of band bending and possible barriers for the charge carriers. Therefore, it is the goal of this work to further improve upon the understanding of functional protective and catalytic layers by

- 1. investigating  $SiO_2$  layers of various thickness as a means of protecting the n-type silicon substrate during the  $NiO_x$  deposition and
- 2. relating the physical properties of the produced n-Si |  $SiO_2$  | NiO<sub>x</sub> heterojunction with the observed electrochemical oxygen evolution reaction (OER) performance.

Nickel oxide was selected as catalyst system because Ni is earth abundant,  $NiO_x$  is a known hole conductor<sup>14</sup> and a promising catalyst for the OER.<sup>15–17</sup>

## Experimental

All experiments were performed on pieces of a 4 inch (001) phosphorus doped n-type silicon wafer with a resistivity of  $0.2\Omega$  cm obtained from MicroChemicals. Prior to any other treatments the samples were cleaned in an ultrasonic bath for 10 min in acetone, isopropanol and then MilliQ water respectively. This was followed by three different treatments to produce the desired surface terminations:

• **n-Si | H-term.:** silicon with hydrogen termination. The sample was etched in piranha solution (H<sub>2</sub>SO<sub>4</sub>: H<sub>2</sub>O<sub>2</sub>=2:1) at 80°C for 10 min, rinsed with MilliQ water, followed by a 6 min oxide removal step in 5% HF, rinsed again, etched in piranha solution at 80°C for 10 min, rinsed, and then subjected to a final 6 min oxide removal step in NH<sub>4</sub>F.<sup>18</sup> Subsequently, the sample was thoroughly rinsed, dried under N<sub>2</sub>, mounted on a sample holder and introduced into ultra high vacuum (UHV) at the Darmstadt Integrated System for Fundamental research (DAISY Fun)<sup>19</sup> within 5 minutes of the last preparation step.

• n-Si | therm. Ox.  $(2 \pm 1 \text{ Å})$ : silicon with approx. 1 monolayer of thermally grown oxide. The same preparation path as for the H-terminated Si was used. After an initial X-ray photoelectron spectroscopy measurement in order to confirm that the etching procedure yielded the desired results, the sample was transferred (in-situ) to a deposition chamber (base pressure  $1 \times 10^{-7}$  mbar), where it was held at 800°C for 23 min in a mixed argon oxygen atmosphere (50 sccm each, 0.1 mbar) for the oxide growth.

• n-Si | nat. Ox.  $(4 \pm 1 \text{ Å})$ : silicon with native oxide. Only the initial cleaning treatment, but without the MilliQ water, was performed.

Chemicals used were 96%  $H_2SO_4$  (VLSIn grade - BASF), 31%  $H_2O_2$  (VLSIn grade - BASF), 5% HF (VLSI Selectipur - BASF), and 40%  $NH_4F$  (semiconductor grade VLSI Puranal - ALDRICH).

The goal of this work was to investigate the impact of different  $SiO_2$  passivation layers on the OER performance of n-type silicon nickel oxide heterojunction. This was achieved by investigation of the created heterojunction properties via XPS interface experiments.<sup>20</sup> First, the prepared n-Si surfaces were characterized via photoelectron spectroscopy (XPS). They were then transferred (in-situ) to a deposition chamber, where a thin NiO<sub>x</sub> layer was deposited via magnetron sputtering at room temperature and with a power setting of 15 W. The deposition was performed in a 0.03 mbar argon/oxygen atmosphere (19.6 sccm Ar and 0.4 sccm O<sub>2</sub>) employing a 99.99% pure Ni target obtained from Kurt J. Lesker.

Subsequently, another XPS measurement was performed followed by another depositions step and so on, until the substrate signal was barely visible. All XPS (Specs Phoibos 150, Focus 500 with XR50M) measurements were performed at pressures of  $5 \times 10^{-10}$  mbar or below. As X-ray excitation, a monochromatized Al<sub>Ka</sub> line at 1486.74 eV was used with the detector calibrated against the Cu 2p, Ag 3d, and Au 4f core levels as well as the respective valence band edges with deviations below 0.05 eV. If not mentioned otherwise all spectra were measured with a pass energy of 5 eV. Evaluation of the XPS spectra was performed with CasaXPS,<sup>21</sup> employing Shirley backgrounds and GL(30) Voight function components. The valence band and the secondary electron edge were evaluated with step functions in CasaXPS, which allow the determination of the surface work function  $\Phi$  and the position of the valence band maximum  $E_{VBM}$ . For the measurement of the secondary electron edge a -3V bias was used.

The thickness of the respective  $SiO_2$  and  $NiO_x$  layers  $d_A$  was determined via numerical solution of

$$\frac{I_A}{I_B} = \frac{N_A}{N_B} \frac{1 - \exp\left(\frac{-d_A}{\lambda_A(E_{kin,A})\cos\theta}\right)}{\exp\left(\frac{-d_A}{\lambda_A(E_{kin,B})\cos\theta}\right)}$$
[1]

for a thin layer A on the bulk material B.<sup>20,22</sup> In above eq.  $I_A$  and  $I_B$  are the corrected integrated core level line intensities of the respective elements or species,  $\lambda_A (E_{kin, A})$  and  $\lambda_A (E_{kin, B})$  are the inelastic mean free paths (IMFP) for the respective electrons kinetic energy in

the thin surface layer A, while  $N_A$  and  $N_B$  are the materials atomic densities.  $\theta$  is the electron emission angle.

An additional sample, n-Si | therm. Ox.  $(8 \pm 1 \text{ Å})$  | NiO<sub>x</sub>  $(39 \pm 4 \text{ Å})$ , was prepared under similar conditions and subsequently used for an in-situ H<sub>2</sub>O adsorption experiment.<sup>23</sup>

Once the interface experiments were completed the samples were stored under UHV conditions, and subsequently extracted in order to perform the electrochemical (EC) measurements. For this, an ohmic back contact was created using a scratched GaIn contact, the used eutectic was obtained from Alfa Aesar and is 99.99% pure metal,  $^{10,24,25}$  before placing the sample on an etched copper foil and inserting it in a dedicated electrochemical cell (Zahner PECC-2). N<sub>2</sub> bubbled 0.1 M KOH was used as electrolyte. An Ag/AgCl reference electrode previously calibrated against a reducible hydrogen electrode (RHE) was employed in a standard three electrode setup to control the potential. The measurements were performed without ambient light using a Zennium and PP221 potentiostat setup (Zahner-elektrik). All EC experiments followed the same procedure, see supplemental information. A 625 nm LED with a power setting of 200 W/m<sup>2</sup> was used as light source for the respective measurements.

An approx. 50Å NiO<sub>x</sub> film was deposited on Ni foil for the investigation of the catalytic performance of the magnetron sputtered films. All deposition parameters, except the deposition time, were identical to the interface experiments. The measurement was performed in 0.1 M KOH and corrected for serial resistance of 96 $\Omega$  determined from electrochemical impedance spectroscopy (EIS) at open circuit potential (OCP) of 0.84 Vvs.RHE.

Unfortunately, the n-Si | H-term. | NiO<sub>x</sub> interface experiment sample broke during insertion into the EC cell due to the copper sheet being slightly bend. Therefore, the respective EC measurements were performed on a substitute sample prepared with the same deposition parameters and an identical total deposition time, but without intermediate deposition breaks. The resulting NiO<sub>x</sub> layer of the substitute sample is  $(28 \pm 4)$  Å, see figures S1 and S2 in the supplemental information.

#### **Results and Discussion - XPS Interfaces**

Prior to the XP detail spectra a survey measurement was performed in order to check for contaminations. As expected for ex-situ samples, low amounts of carbon and oxygen from adsorbed water and hydrocarbons were found on the samples after introduction into UHV, see Figure 1 for the survey of n-Si | H-term prior and post NiO<sub>x</sub> deposition. For all experiments the Ni 2p, O 1s, C 1s and Si 2p core level regions were recorded along with the secondary electron and the valence band edge. No elements beside those four mentioned above were found on any of the samples.

The three relevant detail spectra regions (Ni 2p, O 1s and Si 2p) for the  $(9 \pm 1)$  Å NiO<sub>x</sub> deposition step on n-Si | nat. Ox.  $(4 \pm 1$  Å) are displayed in Figure 2.

For the Si  $_{2p}^{2p}$  region a total of five components is employed. One doublet pair for the bulk silicon  $(Si_{2p}^{bulk})$ , one doublet pair for the Si<sup>4+</sup> of silicon oxide  $(Si_{2p}^{SiO2})$ , and a single component for the sub-oxide.

For the O 1s region there are three components. One for the silicon oxide  $(O_{1s}^{SiO2})$  and two for the nickel oxide. The two nickel oxide components can be associated with NiO and Ni<sub>2</sub>O<sub>3</sub> from their binding energy positions of 529.3 to 529.4 eV (literature: 529.4 to 529.9 eV) for NiO and 530.7 to 531.1 eV (literature: 530.9 to 531.7 eV) for Ni<sub>2</sub>O<sub>3</sub>.<sup>27-32</sup> The mixed nickel oxide layer as a whole will be referred to as NiO<sub>x</sub>, and the  $O_{1s}^{NiO}$  and  $O_{1s}^{Ni2O3}$  components were used to determine the NiO<sub>x</sub> stoichiometry.

The Ni 2p region is more difficult to interpret, as the line shape is complex. Uhlenbrockt et al.<sup>26</sup> investigated a pure NiO single crystal cleaved under UHV conditions and found that a perfect NiO surface exhibits the characteristic peak at 853.4 to 854.4 eV but also an additional shoulder at 855.6 eV which overlaps with the characteristic peak for Ni<sub>2</sub>O<sub>3</sub> and Ni(OH)<sub>2</sub> at 855.1 to 856.6 eV,<sup>27–32</sup> see gray areas in Figure 2. Therefore the Ni 2p spectra was fitted according to<sup>33</sup> with



Figure 1. Survey spectrum (XPS), obtained with a 20 eV pass energy, of the hydrogen terminated sample before NiO<sub>x</sub> deposition and after the last deposition step with a total nickel oxide layer thickness of  $(32 \pm 5\text{\AA})$ . Apparently only traces of oxygen and carbon, but no other contaminants could be detected. During the interface experiment only nickel and oxygen were deposited on the sample.

a total of seven components, but as those cannot be clearly associated with specific oxidation states at this point, only the resulting envelope is shown. They do provide a good fit thought, and allow for an accurate determination of the total Ni 2p peak area, used for layer thickness determination. It should be mentioned that while the high binding energy NiO<sub>x</sub> component will be mostly Ni<sub>2</sub>O<sub>3</sub>, an evaluation of the stoichiometric data for the final deposition steps results in a O:Ni ratio of up to 1.8 instead of the expected 1.5. Thus, other oxygen rich nickel oxide species might be present, which also explains the high full width half maximum (FWHM) values around 2.8 eV obtained for  $O_{1s}^{Ni2O3}$  in contrast to 1.1 eV for  $O_{1s}^{NiO}$ . The respective detail spectra for the whole n-Si | nat. Ox. interface experiment are presented in Figure 3. In the Si 2p region the whole peak is shifted to lower binding energies, which is the result of an upward band bending in the silicon near the interface (as the core level moves closer to the Fermi energy). The observed band bending is called diffusion potential ( $V_D$ ). Besides the shift in binding energy and the expected decrease in Si 2p intensity, a slight increase of the Si4<sup>+</sup> related signal is visible indicating that NiO<sub>x</sub> also forms a mixed SiO<sub>2</sub>/NiO<sub>x</sub> layer below the NiO<sub>x</sub>.

As expected, the O 1s region is initially dominated by the  $O_{1s}^{SiO2}$  component, before a thicker nickel oxide film signal results in increasing superimposition by the two NiO<sub>x</sub> components. From the shape of the Ni 2p core level spectrum we deduce that the initial (sub-monolayer) NiO<sub>x</sub> growth on n-Si | nat. Ox. is only Ni<sub>2</sub>O<sub>3</sub>. For thicker nickel oxide layers the amount of NiO increases until a final NiO:Ni<sub>2</sub>O<sub>3</sub> ratio of 0.85 is reached for the last deposition step. From the data of the other two interface experiments, to be found in the supplemental information, it can be concluded that the phase formation of the initially grown NiO<sub>x</sub> is determined by the nature of the silicon surface, see Table I. The oxygen free hydrogen terminated surface leads to the formation of NiO only, while increasing amounts of oxygen from the SiO<sub>2</sub> layer result in an equally increased growth of Ni<sub>2</sub>O<sub>3</sub>. With increasing NiO<sub>x</sub> layer thickness this difference disappears and the final NiO/Ni<sub>2</sub>O<sub>3</sub> ratios from 0.70 to 0.85 are close, see Table II.

The change in the NiO:Ni<sub>2</sub>O<sub>3</sub> ratio is in good agreement with the Ni 2p region, where the characteristic NiO peak (gray area in Figure 3) becomes more dominant for thicker nickel oxide films. Because of the change in the layer composition, and thus the overall peak shape, it is difficult to extract information on a possible band bending in the NiO<sub>x</sub> layer. However, previous works have shown that nickel oxide is commonly pinned by the high concentration of defects from missing nickel atoms, thus exhibiting no or little observable band bending.

Secondary electron edge and the valence band edge were evaluated as well, see Figure 4. For n-Si | nat. Ox. an initial workfunction  $\Phi$ of 4.36 eV was found for the oxide covered Si. With increasing NiO<sub>x</sub> layer thickness this value increases too, before converging to a value of 5.31 eV, the work function of NiO<sub>x</sub>, which is in good agreement with previous reports in the range from 5.0 to 5.6 eV.<sup>34–36</sup> Because nickel oxide has a bandgap of 3.1 eV or above<sup>37,38</sup> the valence band maximum at 0.73 eV is a clear sign of the NiO<sub>x</sub> layer being p-type, which is desirable for a material where holes have to pass through.

All of the above information for this and the other two interface experiments was used to construct band diagrams of the energetic situation of the heterojunctions. The six resulting band diagrams are



**Figure 2.** Detail spectra (XPS) of the Ni 2p 3/2, O 1s and Si 2p core level regions (black scatter) with the GL(30) components employed for the evaluation (areas), the resulting envelope (red line) and the employed Shirley background (black dash). O 1s and Si 2p clearly show the bulk silicon with an overlaying SiO<sub>2</sub> layer and a mixed NiO/Ni<sub>2</sub>O<sub>3</sub> on top. Such an assignment is more complicated for the Ni 2p3/2 region. However, comparison with pure NiO (in-situ cleaved NiO<sup>26</sup>) confirms a mixed NiO<sub>x</sub> phase. The intensity scaling is not identical (2x for O 1s and 4x for Si 2p).

Table I. Dependency of the initially grown nickel oxide species on the silicon surface. Apparently the availability of oxygen from a SiO<sub>2</sub> layer results in a preferred growth of the oxygen rich Ni<sub>2</sub>O<sub>3</sub> species.

sample	initial NiO <sub>x</sub> species		
n-Si   H-term.	NiO		
n-Si   therm. Ox. (2Å)	NiO and Ni <sub>2</sub> O <sub>3</sub>		
n-Si   nat. Ox. (4Å)	Ni <sub>2</sub> O <sub>3</sub>		

displayed in Figure 5. On top, the situations before contact are shown. Information of the Si substrates stems from the measurements of the  $NiO_x$  free substrates, while the  $NiO_x$  data was extracted from the samples after the last deposition step.

Apparently, all three preparation methods result in almost flatband like behavior. This is beneficial, because it indicates a low level of surface defects, which would act as dopants, thus inducing a band bending. These preparation procedures were reproducible, as can be seen for the values of  $n-Si \mid H$ -term and its substitute (top left, red) in Figure 5.

The three bottom band diagrams display the 'in contact' situation after the heterojunction was formed. All three Si samples exhibit upward band bending, which is expected because NiO<sub>x</sub> has a higher workfunction  $\Phi$ . Following the Anderson model<sup>39</sup> the induced band bending could be up to approx. 1 eV, the difference between work functions, but the observed values for V<sub>D</sub> only range from 0.35 to 0.40 eV. Within the margin of error, those values are virtually identical. The remaining potential drop from the Fermi-level alignment occurs in form of a dipole at surface states between the Si and NiO<sub>x</sub> layer, with oxide induced surface states effectively pinning the Fermi level. From the position of the pinned Fermi level it can be concluded that those surface states are located 0.5 to 0.6 eV or below the Si conduction band edge.

Table II. Important parameters obtained from the performed experiments. The diffusion potential  $V_D$ , the hole barrier height  $\Phi_B$  and the NiO:Ni<sub>2</sub>O<sub>3</sub> ratio were obtained from the XPS interface experiments, while the OER onset, the potential for a current density of 4 mA/cm<sup>2</sup> and the maximum photocurrent density 'max  $J^{ss}$ ' are results of the electrochemical measurements in 0.1 M KOH.

$V_D$ [V]	$\Phi_B$ [ eV]	final ratio [NiO/Ni <sub>2</sub> O <sub>3</sub> ]	OER onset [V vs. RHE]	$J = 4 \text{ mA/cm}^2 \text{ (CV)}$ [V vs. RHE]	max. J <sup>ss</sup> [mA/cm <sup>2</sup> ]
0.40	0.06	0.85	1.44	$1.63\pm0.02$	5.82
0.36	0.12	0.73	1.34	$1.56 \pm 0.03$	6.04
0.35	0.14	0.85	1.22	$1.43 \pm 0.02$	6.05
-	-	0.73	1.57	$1.61\pm0.09$	-
	V <sub>D</sub> [V] 0.40 0.36 0.35	$\begin{array}{c c} V_D & \Phi_B \\ \hline [V] & [eV] \\ \hline 0.40 & 0.06 \\ 0.36 & 0.12 \\ 0.35 & 0.14 \\ \hline \end{array}$	$V_D$ $\Phi_B$ final ratio [NiO/Ni <sub>2</sub> O <sub>3</sub> ]           0.40         0.06         0.85           0.36         0.12         0.73           0.35         0.14         0.85           -         -         0.73	$V_D$ $\Phi_B$ final ratioOER onset $[V]$ $[eV]$ $[NiO/Ni_2O_3]$ $[V vs. RHE]$ 0.400.060.851.440.360.120.731.340.350.140.851.220.731.57	$V_D$ $\Phi_B$ final ratioOER onset $J = 4 \text{ mA/cm}^2$ (CV) $[V]$ $[eV]$ $[NiO/Ni_2O_3]$ $[V vs. RHE]$ $[V vs. RHE]$ 0.400.060.851.441.63 $\pm$ 0.020.360.120.731.341.56 $\pm$ 0.030.350.140.851.221.43 $\pm$ 0.020.731.571.61 $\pm$ 0.09



**Figure 3.** Detail spectra (XPS) of the Ni 2p3/2, O 1s and Si 2p core level regions over the course of the n-Si | nat. Ox. | NiO<sub>x</sub> in-situ interface experiment. The  $Si^{bulk}_{2p3/2}$  component position was used to monitor the band bending over the course of the experiment. The Ni 2p region shows that the nickel oxide is initially mostly Ni<sub>2</sub>O<sub>3</sub>, but the amount of NiO increases with NiO<sub>x</sub> layer thickness. This is supported by the Ni 2p spectra, which do not show the characteristic NiO peak (gray area) between 853.4 to 854.4 eV<sup>27–32</sup> for a NiO<sub>x</sub> layer thickness below 2.5Å. The full width half maximum (FWHM) is indicated by  $\Leftrightarrow$ .



Figure 4. Secondary electron edge (left) and the valence band edge (right) of the n-Si | nat. Ox. sample after the final deposition step.Both measurements were performed with XPS (pass energies of 0.3 and 20 eV respectively). The measurements from before the first and after the last deposition were used to construct the band diagrams in Figure 5.

As a result of the Fermi level pining the valence band edges of the Si and NiO<sub>x</sub> are aligned quite favorable, with holes only having to overcome a small barrier  $\Phi_B^h$  of 0.06 to 0.14 eV to cross Si | NiO<sub>x</sub> interface. However, in order to do so, the holes have to tunnel through the SiO<sub>2</sub> layer.



Figure 6. Detail spectra (XPS) of the Si 2p core level show Si<sup>4+</sup> for all 4 samples after the final deposition step. Obviously, the magnetron sputtering process oxidized the previously oxide free n-Si | H-term. sample.

While the obtained informations do not allow to determine the exact spatial position of the surface states, it is assumed that they are connected to the Si | SiO<sub>2</sub> interface. This should also the case for n-Si | H-term, which did not show any SiO<sub>2</sub> signal to begin with, but its surface is clearly oxidized over the course of the sputter deposition process, see Figure 6 for the Si 2p region of all three samples after the final NiO<sub>x</sub> deposition step. Compared to the SiO<sub>2</sub> initially



Figure 5. Band diagrams of the three samples before contact (top) and after formation of the heterojunction (bottom). Initially all samples exhibit flatband like behavior,  $NiO_x$  deposition induces an upward band bending of 0.35 to 0.40 eV in the Si substrate, which gives an indication of the possible photovoltage this junction could provide. Because the junctions are nearly identical and are all covered with the same catalyst material, their electrochemical behavior would be expected to be nigh identical.

found on the later two samples, the  $Si_{2p}^{SiO2}$  components post deposition display an increased full width half maximum (FWHM), indicating further sputter damage caused by the incoming nickel and oxygen ions.

While the band diagrams do not allow the precise determination of the heterojunctions current potential (IE) performance (like fill factor or maximum power point),  $V_d$  gives a good estimate of the achievable photovoltage  $U_{ph}$ , because it is the upper limit. However, it is still possible that  $U_{ph}$  exceeds  $V_D$  as the measured band bending is a superimposition of the band bending within the first nanometers of the silicon substrate. Because of the exponential dependency of the band bending on the distance from the initial surface, the real band bending can be higher. The total depletion layer width  $W_D$  in silicon for a doping concentration  $n_D$  of  $3 \times 16 \text{ cm}^{-3} \text{ is}^{40}$ 

$$W_D = \sqrt{\frac{2\varepsilon_0 \varepsilon_s V_D}{q n_D}} \approx 130 \,\mathrm{nm}$$
 , [2]

thus the obtained value for  $V_D$  is assumed to be accurate, as the dimension of the interface region is small compared to the dimension of the depletion layer.

### **Results and Discussion - Electrochemistry**

In an ideal case, the total performance of an integrated water splitting device is a simple combination of the buried junctions IE behavior with the catalytic performance of the topmost layer in contact with the electrolyte. As discussed in the previous section, all three samples should exhibit similar IE behavior due to similar band alignments in the dark. The covering  $NiO_x$  layers are also almost identical, thus their total EC performance should be close nearly identical as well.

The catalytic performance of the magnetron sputtered NiO<sub>x</sub> films was characterized via cyclic voltammetry (CV) measurements, see Figure 7. In order to obtain a current density of  $4 \text{ mA/cm}^2$  an overpotential  $\eta$  of 0.38 V was needed, 0.44 V for  $10 \text{ mA/cm}^2$ . This is in good agreement and even slightly better than previously reported values between 0.47 and 0.55 V for unconditioned NiO<sub>x</sub>.<sup>15,17</sup>

The OER onset potential for the catalyst on metal is approx. 1.57 Vvs.RHE. Because of the expected photovoltage of 0.35 to 0.4 V or below, the OER onset for the three differently prepared photoanodes should be shifted by a similar amount toward a more cathodic potential, resulting in an OER onset at approx. 1.17 to 1.22 Vvs.RHE



**Figure 7.** Current density in respect to the OER (1.23 Vvs.RHE) overpotential  $\eta$  from cyclic voltammetry measurements. Approximately 50Å NiO<sub>x</sub> were deposited on a nickel sheet (same parameters as for the interface experiments). The EC measurement was performed in 0.1 M KOH and corrected for the serial resistance  $R_S$  obtained via EIS.



**Figure 8.** Comparison of the current cyclic voltammetry behavior of the 3 different silicon/nickel oxide interfaces under  $200 \text{ W/m}^2$  illumination with  $\lambda = 625 \text{ nm}$  in 0.1 M KOH. While the heterojunction properties from the interface experiments (see Figure 5) would indicate a similar EC behavior for all samples, this is obviously not the case.

for all three samples. Figure 8 displays the CV curves for all three samples without correction for ohmic loss ( $R_s$  approx. 100 $\Omega$ ). All curves show the general behavior expected for this kind of device, no anodic current at low anodic potentials, steep current increase as the OER starts, and saturation of the current density as a result of the limited light intensity. However, their OER onset clearly occurs at different potentials, contradicting the initial expectation.

While the n-Si | nat. Ox. (4 Å) | NiO<sub>x</sub> with an OER onset of 1.21 Vvs.RHE is in excellent agreement with the expectations, the other two samples display onsets at 1.30, respective 1.46 Vvs.RHE instead, indicating a 0.1 to 0.25 V reduced  $U_{ph}$ , a loss of up to 57%. Apart from this, the samples behave identical. They display a similar slope, which indicates similar IE performance and resistance, which is in good agreement with the obtained serial resistance  $R_s$  values of approx. 100 $\Omega$  obtained from electrochemical impedance spectroscopy (EIS) measurements. The same is true for the saturation photocurrent.

In order to explain the unexpected difference of  $U_{ph}$  and thus the EC behavior one has to take the time dependent behavior into account. Figure 9 displays a chopped light measurement of n-Si | nat. Ox. | NiO<sub>x</sub>. The sample was illuminated for 2s, followed by 2s in the dark while the potential was ramped up at the same 10 mV/s as for the CV measurements. For lower potentials there is a high anodic current flow  $J^{on}$  a the beginning of the illumination cycle, but this current quickly decreases over the course of the 2s illumination interval until it converges to a steady state value  $J^{ss}$ , see inset in Fig. 9. Once the light is switched of, there is a fast dissipating cathodic current flow. This behavior is typical as a positive electrical charge is accumulated at the electrode surface during illumination, back in the dark the current flow is reversed when the charge dissipates, thus giving rise to the cathodic current.<sup>41-43</sup>

It is apparent that  $J^{on}$  has its onset at a significantly more cathodic potential than  $J^{ss}$ . Both values differ for potentials below approx. 1.3 Vvs.RHE, and are equal at higher potentials. Similar measurements were performed for the other two samples. The resulting values for  $J^{on}$  and  $J^{ss}$  are displayed in Figure 10. Obviously, all three samples display an almost identical behavior of  $J^{on}$  in the potential range from approx. 0.4 to 1.2 Vvs.RHE. For higher potentials,  $J^{on}$ aligns with  $J^{ss}$  for all three samples, but with a different speed, faster for n-Si | nat. Ox. (4Å), slower for n-Si | therm. Ox. (2Å) and slowest for n-Si | H-term.

The chopped light response can help interpret the supposed differences in  $U_{ph}$ . For this one has to consider what happens with the defect states at the Si surface during illumination. The three band diagrams



**Figure 9.** Chopped light measurements (displayed here: 1st run on n-Si | nat. Ox. | NiO<sub>x</sub>, 2*s* pulse of 200 W/m<sup>2</sup>) can provide additional insights. If the onset current ( $J^{on}$ ) and the steady state current ( $J^{ss}$ ) differ significantly this indicates a significant impact of recombination at the NiO<sub>x</sub>/electrolyte interface. Obviously, this is here the case for potentials below approx. 1.4 Vvs.RHE.

at the top of Figure 11 display the situation at the electrode surface of n-Si | H-term under illumination and for different bias potentials:

- (A) will be close to the flatband potential at approx. 0.5 Vvs.RHE where  $J^{on} \approx J^{ss}$ , while
- (B) describes the situation from approx. 1.0 to 1.5 V vs. RHE, where  $J^{on}$  deviates for the three samples, and
- (C) is a schematic of the situation at high anodic potentials, were no transient behavior is observed, thus  $J^{on} \approx J^{ss}$  again.



**Figure 10.**  $J^{on}$  (dashed) and  $J^{ss}$  (solid) from the 1st chopped light measurement performed on each sample. Apparently all samples, show an almost identical current density response for their transient onset current  $J^{on}$ . This indicates that the buried heterojunctions do indeed provide a similar current voltage behavior, and the observed differences in the CV are mostly a result of recombination in the NiO<sub>x</sub> layer and its interfaces.

For small anodic potentials  $U_1$  (A) there is either flatband or a small upward band bending in the Si substrate as a result of the incoming light hv. Photons are effectively absorbed in the silicon and the resulting hole electron pairs (excitons) are separated by the electric field in the depletion layer Electrons will move further into the bulk toward the back contact while the holes travel toward the NiO<sub>x</sub> side. Once the holes reach the n-Si | SiO<sub>2</sub> interface some of them will tunnel through the SiO<sub>2</sub> layer and reach the NiO<sub>x</sub> layer, from where



**Figure 11.** Band diagrams of the situation at the n-Si / NiO<sub>x</sub> / electrolyte interfaces for different applied bias potentials (top). The high number of defect states in n-Si | H-term can trap photoexcited holes near the surface, the resulting electric field opposes  $U_{ph}$  thus giving rise to the observed transient behavior in Figures 9 and 10. Increasing bias potentials will eventually result in Fermi-level pinning at the very same defect states, thus preventing the bias potential portion needed to overcome the pinning from being used for the OER. This effect is diminished for samples with a lower defect state density, (bottom right). Apparently, a protective SiO<sub>2</sub> layer can reduce the amount of defect states created during NiO<sub>x</sub> deposition.

they will be able to tunnel into adsorbed electrolyte molecules, thus participating in the OER.

At this point, the defect states at the n-Si | SiO<sub>2</sub> interface, are located below the Fermi level  $E_F$ . Thus, they are fully occupied with electrons. The remaining photoexcited holes move to those energetically favorable defect states where they will be trapped. This gives rise to a positive charge at the Si surface and will induce an electric field opposing  $U_{ph}$  and eventually preventing further holes from reaching the surface. At the beginning of an illumination cycle the defect states are still empty, thus the freshly created holes move to the surface giving rise to the initially observed anodic current ( $J^{on}$ ), until an equilibrium is reached ( $J^{ss}$ ) as all defect states are occupied. The result is the observed transient behavior.

If the bias potential is increased to  $U_2$ , most of this potential is dropped across the depletion layer shifting the Si band edges downward in regard to the electrolyte. This is displayed in the schematic at the bottom right of Figure 11. Eventually this will lead to the Fermi level crossing the defect state energy, situation (B). From this point on, a further increase of the bias potential does not induce any further changes in the Si depletion layer. Instead more and more electrons are excited from the defect states are empty, but the bias potential necessary to empty the defect states is essentially lost. However, less electron filled defect states also mean less available defect states for the incoming holes under illumination, thus a diminishing of the transient behavior.

A further increase of the bias potential to  $U_3$  results in all defect states being empty, situation (C) in Figure 11. Bias potential will again drop in the depletion layer and is thus available to drive the OER. As there are no more defect states available for incoming holes to occupy, there will be no transient behavior and  $J^{on} = J^{ss}$ .

Now, if there were less defect states, for example as result of a protective  $SiO_2$  layer on top of the silicon substrate during  $NiO_x$  deposition, the basic mechanics discussed above would still remain unchanged, but their magnitude could vary. The initial situation for this case is displayed in bottom left of Figure 11. Less defect states would result in a smaller portion of the bias potential being necessary to overcome the Fermi level pinning Instead, the additional potential is be available to drive the OER.

This effect is displayed in the bottom right of Figure 11, where a small amount of defect states (red: n-Si | nat. Ox. | NiO<sub>x</sub>) results in a higher usable potential, once the Fermi level pinning is overcome, as would be the case for a sample with a higher defect density (orange: n-Si | H-term | NiO<sub>x</sub>). In conclusion, the observed difference in the EC behavior between the three samples is a direct result of the defect state density at the Si surface. Apparently, the H-terminated Si surface will incur a high defect density during the nickel oxide deposition via magnetron sputtering, thus resulting in the observed later onset of  $J_{ss}$ .

In case of the  $(2 \pm 1)$ Å therm. Ox. SiO<sub>2</sub> layer, the thin protective SiO<sub>2</sub> reduced the defect state density, thus having more bias potential available for the OER. Finally, the  $(4 \pm 1)$ Å nat. Ox. SiO<sub>2</sub> layer, reduces the amount of defect states even further. There is almost no shift to higher anodic potentials as result of Fermi level pinning. However, even thicker SiO<sub>2</sub> layers do not result in further improvement. Instead, the resistance of a thicker SiO<sub>2</sub> layer leads to a worse OER performance with a significantly lower current slope.

Last, the photocurrent density has to be discussed. The saturation values for  $J^{ss}$  in Figure 10 are between 5.82 and 6.05 mA/cm<sup>2</sup>, see Table II. For a wavelength of 625 nm the energy per photon is

$$E_{\lambda} = \frac{hc}{\lambda} = \frac{1240 \,\text{eV}}{625 \,\text{nm}} = 3.18 \times 10^{-19} \text{J}$$
 . [3]

While the sample is illuminated with a power density of  $P_{\lambda} = 200 \text{ W/m}^2$ , this value is reduced to approx. 67% by reflection losses at the air/SiO<sub>2</sub>/KOH/NiO<sub>x</sub>/SiO<sub>2</sub>/Si interfaces.<sup>44–47</sup> Thus, the incoming photon flux is

$$I_0 = \frac{P_{\lambda}}{E_{\lambda}} = \frac{134 \,\mathrm{W/m^2}}{3.18 \times 10^{-19} \mathrm{J}} = 4.24 \times 10^{16} \mathrm{s^{-1} cm^{-2}}$$
[4]

which yields

$$J_0 = q \cdot I_0 = 6.8 \,\mathrm{mA/cm^2}$$
 [5]

as the maximum attainable photocurrent density. This is in agreement with the obtained results, confirming that most of the incoming light can be used for the OER if the necessary overpotential is applied.

### Conclusions

(001) n-Si samples with three different surfaces: a H-terminated (oxide free) surface, a thermally grown  $(2 \pm 1)$ Å (SiO<sub>2</sub> layer and a native  $(4 \pm 1)$ Å SiO<sub>2</sub> layer, were covered with NiO<sub>x</sub> as a catalyst layer for the oxygen evolution reaction. They were investigated with XPS interface experiments and electrochemical methods The interface experiments between the n-Si samples and in-situ magnetron sputtered NiO<sub>x</sub> clearly show that the Fermi level alignment between the two materials results in an upward band bending in the Si substrates. Regardless of the initial surface preparation, all three heterojunctions display nearly identical properties with diffusion potentials  $V_D$  from 0.35 to 0.40 eV and hole barriers  $\Phi_B^h$  from 0.06 to 0.14 eV, further band bending is prevented by Fermi level pinning from defect states.

The NiO<sub>x</sub> by itself has proven an very good catalyst for the OER, providing a current density of  $10 \text{ mA/cm}^2$  at a potential of  $(1.67 \pm 0.01)$  Vvs.RHE. Because all three n-Si samples are covered with the same catalyst, and exhibit identical heterojunction properties, a similar electrochemical behavior was expected, with a current response that is roughly 0.4 V more cathodic than for the NiO<sub>x</sub> on Ni. This behavior was only confirmed for n-Si | nat. Ox.  $(4 \pm 1\text{ Å})$ , with exactly the expected OER onset of 1.21 Vvs.RHE. The other two samples showed weaker shifts, approximately 0.3 V for n-Si | therm. Ox.  $(2 \pm 1\text{ Å})$  and only 0.1 V for n-Si | H-term.

With the help of chopped light measurements, this disparity was traced to different defect state densities at the silicon surface. As the resulting Fermi level pinning depletes part of the applied bias potential, thus it appears like the samples would provide different photovoltages  $U_{ph}$ . From the investigated samples it can be concluded that a thin SiO<sub>2</sub> layer, like the  $(4 \pm 1)$ Å native oxide layer yields the best results. Thinner layers do not sufficiently protect the Si substrate, while thicker layers have a too high ohmic resistance. Thus, a controlled and reproducible method of growing such a protective SiO<sub>2</sub> layer of exactly the right thickness is required in order to reduce sputter induced defect states.

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Erratum: The Impact of Different Si Surface Terminations in the (001) n-Si/NiOx Heterojunction on the Oxygen Evolution Reaction (OER) by XPS and Electrochemical Methods [*J. Electrochem. Soc.*, 165, H3122 (2018)]

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Figure 6 on page H3126 should appear as



**Figure 6.** Detail spectra (XPS) of the Si 2p core level show  $Si^{4+}$  for all 4 samples after the final deposition step. Obviously, the magnetron sputtering process oxidized the previously oxide free n-Si | H-term. sample.