Water Interaction with Sputter-Deposited Nickel Oxide on n-Si Photoanode: Cryo Photoelectron Spectroscopy on Adsorbed Water in the Frozen Electrolyte Approach

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The interaction of water with a magnetron-sputtered nickel oxide thin film on an n-type silicon photoanode is investigated in perspective to oxygen evolution. The substrate was exposed in-situ stepwise to gas phase water up to 10 L at liquid N2 temperature and analyzed via X-ray and UV photoelectron spectroscopy in the so-called frozen electrolyte approach. Photoemission of the pristine NiO layer shows the presence of stoichiometric NiO and Ni2O3 as well as of non-stoichiometric phases. In the monolayer range, molecular and dissociative adsorption is detected assigned to the NiO respective Ni2O3 phase. Initially, the emission of the molecular adsorbed water species interacting with NiO is found at 0.8 eV lower binding energies as compared to water related emission for higher coverages with binding energies commonly assigned to H2O-H2O interaction. In addition to the chemical analysis, the electronic structure of the n-Si/SiOx/NiOx/H2O photoanode is measured and discussed.

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Most semiconducting materials, especially silicon, are unstable and degrade or passivate rapidly under photoanodic conditions in aqueous electrolytes.1 Nickel oxide thin films are promising catalysts for the hydrogen and the oxygen evolution reaction (OER)2 and provide chemically stable coatings for silicon, while being transparent, antireflective and electronically conductive in addition.3–5 Elementary charge transfer processes located at a solid/liquid interface, are still scarcely approached by scientific studies on an atomistic scale.6 Especially the energetics of the photocatalytic dissociation of water on semiconducting materials is still unclear. In general, the determination of the chemical and electronic interaction at the interface between metal oxides and liquid electrolytes on an atomistic scale via surface science methods suffers from the so-called pressure gap.7,8 One way to bridge the gap, model experiments at low temperatures can be utilized to monitor the surface chemistry by means of photoelectron spectroscopy under ultra-high vacuum. Regarding double layer formation, the frozen-electrolyte approach has already shown its potential in the past.9

The principle mechanism of the oxygen evolution (OER) at nickel hydroxide based electrodes was investigated early on a more chemical basis10 with various phase transitions involved.11 It has been found that Ni(OH)2 and NiOOH species at the surface are a prerequisite for any photocatalytic activity. However, the exact mechanism is still under debate12 with the role of nickel oxide only little discussed. A first step for a better understanding is to study the reactivity of a pristine nickel oxide surface upon water adsorption. For NiO(100) it has been demonstrated that a perfect surface exhibits no reactive interaction with H2O unless oxygen vacancies induce the dissociation of water13 or adsorbed O2− ions at defect sites on a pre-oxidized surface enhance the reactivity. In contrast to NiO(100), theoretical studies predict dissociative water adsorption for NiO(111).14 Further to oxygen vacancies sub-coordinated Ni surface atoms are active in dissociative water adsorption.15 It also has been found that Ni increases the OER activity of iron oxide and vice versa.16 Thereby, the photocatalytic performance of hematite can be dramatically enhanced by the formation of a hematite-NiOα−Ni(OH)2 composite heterostructure.17 However, no literature was found for Ni2O3 as an effective catalyst for water splitting. Obviously, there are many open questions dealing with the interaction of water with nickel oxide on an atomic scale revealing the exact reaction paths and the accompanying energy schemes. In this publication

we present in-situ X-ray (XPS) and UV-photoelectron spectroscopy (UPS) analysis of stepwise adsorbed water on a magnetron-sputtered thin NiO film grown on thermally oxidized n-doped silicon. During the interface experiment under dark condition, the sample was kept at LN temperature in order to suppress instantaneous desorption of water in this cryogenic photoelectron spectroscopy (CryoPES) approach.

Experimental

Sample preparation.—A 4-inch (001) phosphor doped n-type silicon wafer was cleaned in an ultrasonic bath for 10 min. in acetone, isopropanol and ultra-pure water each. In order to produce a hydrogen terminated surface, it was then etched in H2SO4:H2O2 = 2:1 at 80°C for 10 min., rinsed with ultra-pure water, followed by a 10 min. oxide removal step in 5% HF. Afterwards it was rinsed with ultra-pure water, etched again in in H2SO4:H2O2 = 2:1 at 80°C for 10 min., rinsed, and subjected to a second 6 min. oxide removal step in NH4F.18 Chemicals used (all VLSI standards) were 96% H2SO4, 31% H2O2, 5% HF, and 40% NH4F. The sample was then thoroughly rinsed and dried under nitrogen flow, before being introduced into the ultra-high vacuum (UHV) deposition and analysis system Darmstadt Integrated System for Fundamental Research (DAISY-Fun)19 within 5 min. Following the growth of an 8 Å thermal oxide layer, NiOx was deposited on the sample via reactive magnetron sputtering. The NiO deposition was performed in-situ in a deposition chamber with a base pressure of 8·10−8 mbar, under 19.6 sccm Ar (99.999% pure) and 0.4 sccm O2 (99.995% pure) flow at 0.03 mbar, using a 99.99% pure nickel target at 15 W. A total deposition time of 540 s resulted in a 39 Å NiOx layer as determined from the relative intensities of the Ni 2p and Si 2p XPS core level spectra.20

Interface experimental.—Ultra-pure water was filled into a Schlenk-type glass flask connected to a separated adsorption chamber with a base pressure of 1·10−8 mbar. Freeze-pump cycling was used to purify the water. The dosage was controlled by a leak valve and the exposure time was varied stepwise to match the desired dosage from 0.1 L (Langmuir) to 10 L using uncorrected pressure readings. The sample was transferred on a LN-cooled manipulator from the adsorption chamber to the analysis chamber both held at a base pressure of 5·10−10 mbar for consecutive photoelectron spectroscopy. The sample was not subject to light irradiation to avoid unwanted photocatalytic reactions during the experiment. The analysis chamber
Table I. Full width at half maximum (FWHM) and initial binding energies in eV for the Ni2p3/2 and O1s core level components derived from XPS measurements.

| Core level Component | FWHM [eV] | Binding energy [eV] |
|----------------------|-----------|---------------------|
| Ni2p3/2 Peak I       | 1.1       | 854.0               |
| Ni2p3/2 Peak II      | 3.2       | 855.7               |
| Ni2p3/2 sat I        | 3.7       | 860.8               |
| Ni2p3/2 sat II       | 4.7       | 864.0               |
| O1s NiO              | 1.0       | 529.8               |
| O1s NiOOH            | 1.0       | 530.6               |
| O1s Ni(OH)2          | 1.0       | 531.1               |
| O1s Ni2O3            | 1.65      | 531.2               |
| O1s NiOOH            | 1.0       | 532.2               |
| O1s H2O-NiO          | 1.3       | 532.7               |
| O1s SiOx             | 1.4       | 533.0               |
| O1s H2O-H2O          | 1.5       | 533.5               |

is equipped with a SPECS Phoibos 150 analyzer and a SPECS Focus 500 X-ray source using the monochromatized AlKα line at 1486.74 eV for XPS and the HeI (21.2 eV) and HeII (40.8 eV) lines for UPS. In order to determine the workfunction, a bias-voltage of −3 V was applied. The interface experiment started with the analysis of the pristine nickel oxide surface, followed by four deposition steps of frozen water leading to a thickness of 0.1 L, 0.4 L, 1.6 L, and 10 L. At the end, the sample was slowly heated up to room temperature (RT) and measured again.

Spectra analysis.—The XP spectra were background subtracted using the Shirley method,21 while for the UP spectra a Tougaard background was subtracted.22 All UP spectra were HeI- and HeII-satellite corrected, respectively. A sputtered Au foil served as reference sample in order to calibrate the spectrometer by making use of the Au4f7/2 transition at 84.0 eV. The XPS core level peaks were fitted using a pseudo-Voigt function with a fixed ratio of 0.2 between the Lorentzian and Gaussian distributions. As a result, binding energy, line width and intensity are obtained and compared on a qualitative basis. Beyond that, intensity changes within the same region (e.g. O1s or Ni2p) were treated on a quantitative basis since cross section and kinetic energy are unchanged. The full width at half maximum (FWHM) and the initial binding energies for the deconvolution of the Ni2p3/2 and O1s core level are given in Table I. The parameters for the Ni2p3/2 components were chosen based on literature.23 The FWHM of the NiO component in the O1s core level was calculated by peak fitting of the pristine spectrum. The FWHM and binding energy of the SiOx component was deduced from the n-Si/SiOx spectrum previous to nickel oxide deposition. The larger values for the FWHM of the Ni2O3, H2O-NiO and H2O-H2O component are caused by the structurally less defined nature of these phases and the exact numerical values were optimized by the fitting routine. Additional information is provided in the discussion.

Results and Discussion

Surface chemistry.—In contrast to the complex and controversially discussed nature of the Ni2p core level emission,24–27 the nickel oxide substrate, hydroxylated species and molecular water can be discriminated clearly in the O1s core level. Additionally, the O1s peak provides information of the full NiO thin film, as it has a thickness of less than 5 nm and the SiO2 peak of the underlying silicon is still detectable for the pristine substrate as shown in Figure 1a. The main feature at 529.4 eV is assigned to the O2− lattice oxygen.23,28 For the pristine layer the broader structure at higher binding energies is assigned to Ni2O3, but upon water exposure also hydroxylated nickel oxide species appear in this binding energy region.23,28 For the pristine layer the broader structure at higher binding energies is assigned to Ni2O3, but upon water exposure also hydroxylated nickel oxide species appear in this binding energy region.23,28 Initially, a strongly attenuated silicon oxide peak and minor carbon oxide contaminations are present around 533.0 eV.

With increasing water adsorption, the broader structure at higher binding energies changes and can only be satisfyingly reproduced,

![Figure 1](image_url)
when taking three different hydroxide species into account. Considering partial charge in the initial state the components at 530.6 eV, 531.2 eV, and 532.2 eV can be assigned to NiOOH, Ni(OH)2, and NiO2 species, respectively. The species to which the respective oxygen emission is assigned is indicated by an underline in the molecule formula. Nickel oxide hydroxide species are known to be present as surface layer on nickel oxide in contact with water or aqueous electrolytes. The different hydroxides can be reliably distinguished according to recent combined XPS and IR studies.

With increasing water exposure, a new feature arises at around 533.0 eV that can be fitted satisfyingly with two components at 532.7 eV and 533.5 eV, respectively. The latter one is typical for interacting H2O molecules in a multilayer film. However, up to a water exposure of 1.6 L, the species at 532.7 eV is dominant and only for 10 L, the species at 533.5 eV becomes predominant. As in the UP spectra below the fingerprint of molecular water is observed at low water exposure, we assign the first species at 532.7 eV to a H2O-NiO species, physisorbed onto stoichiometric nickel oxide.

Remarkably, the signal of stoichiometric NiO is only affected by the general attenuation due to the water adsorption, while the initial Ni2O3 emission changes its line shape due to additional components of hydroxylated species. After annealing to room temperature, these hydroxylated species partly remain on the surface. From a more accurate peak fitting of the O1s core level, we deduce that mainly Ni3O4 and presumably defect sites including phase boundaries are reactive upon water adsorption while on NiO water is physisorbed. This corresponds to experiments on NiO(100) single crystals which show no dissociative water adsorption. In general, the reactivity of nickel oxide toward water depends on crystal orientation, pretreatment, and Ni sub-coordination at the surface. As the NiO phase is not exclusively (100) terminated it will add to a small extent also to dissociative water adsorption.

The evolution of the Ni2p core level for the stepwise water adsorption and desorption is shown in Figure 1b. The nature of the Ni2p structure is complex, dominated by correlation effects of the valence band, including multiplet structures and final state effects. Using a four component fit, the Ni2p emission can be well approximated. For the pristine sample the emissions of Ni2+, Ni3+, and Ni5+ in Ni2O3, NiO2, and Ni3O4 as well as non-stoichiometric phases have overlapping shoulders that contribute to the simple Voigt peaks I at 854.0 eV and II at 855.7 eV. Additionally, the broader feature at 855.7 eV is known to include contributions from hydroxylated species, namely Ni(OH)2 (Ni2+, Ni3+, Ni5+) and NiOOH (Ni2+, Ni3+, Ni5+) that are all summarized under the term h-NiOx. Unfortunately, further stoichiometric phases cannot be deconvoluted here due to their complex signature. Despite of the ambiguity of the Ni2p core level emissions, the relative changes of peak II compared to peak I supply information about the formation of surface hydroxides.

The satellite region of the Ni2p core level consists of two broad features at 860.8 eV (sat I) and 864 eV (sat II), which are affected in intensity by the transformation of nickel oxide to hydroxylated species as well as by the transformation of Ni(OH)2 to NiOOH. Due to the water-free preparation under UHV conditions emissions from hydroxylated nickel species can be excluded in the Ni2p spectrum of the pristine nickel oxide thin film. Upon stepwise water adsorption, the relative peak area of peak II compared to peak I rises from 77 to 79% as denoted in Figure 1b. After desorption, this value decreases marginally to 78%. In compliance to the observations of the pristine nickel oxide thin film (asis), the OH valence band features can be assigned, respectively. In addition, the binding energy distance between the two different molecular water species, H2O-NiO and H2O-H2O is highlighted.

The binding energy distance between the two peaks is about 3.3 eV. On NiO(100), a similar separation in the binding energy of 3.3 eV has been reported for OH-. Presumably, the exact energy distance is depending on the reaction mechanism, oxidation state and adsorption site. The features are most intense after 0.1 L water adsorption and are still observable after desorption indicating water dissociation due to the nickel oxide surface and in part chemisorption of OH-. By taking the XPS results into account, the OH valence band features can be assigned to the formation of Ni(OH)2 and NiOOH in the surface region. Moreover, the unique fingerprint of molecularly adsorbed water is clearly visible in the difference spectra after 0.1 L. But the distinct features at 6.1 eV (1b orbital), 12.1 eV (1b2 orbital), and 8.4 eV (3a1 orbital) are usually expected at about 1 eV higher binding energies in case of hydrogen bond and dipole-dipole interacting water molecules in a multilayer. We relate the water emissions at lower binding energy to water molecules physisorbed to nonreactive NiO surfaces. After 10 L water adsorption the water emission shifts to higher binding energies typical for multilayer water. Due to the supreme surface sensitivity
After desorption, the ratio only slightly decreases again to 3.7. This likely corresponds to the formation of NiOOH and Ni(OH)$_2$.

Indeed, XPS analysis indicates that upon water adsorption, predominantly the Ni$_2$O$_3$ phase and presumably defective sites and phase boundaries are reactive. If water dissociates, hydroxylated species form (h-NiO$_x$). In contrast, water mostly physisorbs on NiO (H$_2$O-NiO) which leads to the observation of the molecular water surface species with emissions at around 1 eV lower binding energies as compared to the multilayer regime when the typical H$_2$O-H$_2$O interaction is dominant. After desorption, the two molecular water species are fully removed from the surface. Only some chemisorbed hydroxylated h-NiO$_x$ species remain. As already mentioned, besides the stoichiometric phase, multiple surface characteristics are known to influence water dissociation: Crystal orientation, defect sites, bond saturation and pretreatment with oxygen plasma amongst others. Especially the fact, that Ni$_3$O$_2$ shows a much higher reactivity compared to NiO should be further pursued with regard to an application as OER catalyst.

**Energy level alignment**—Figure 5a schematically shows the band diagram of the layered n-Si/SiO$_x$/NiO$_x$ system before and after water adsorption. The thickness of the intermediate SiO$_x$ layer is about 2–3 nm. The band bending upward of the n-Si toward the oxide layer was calculated to be 0.4 eV considering the bulk position of the valence

gives further rise to the assumption that mainly the Ni atoms act as docking sites for hydroxylated nickel species h-NiO$_x$. In total, the results from XPS core level and UPS valence band analysis draw a consistent and plausible picture of the surface chemistry upon water adsorption which allows us to create a schematic interface model.
band maximum according to doping concentration and the measured position. The sputtered nickel oxide thin film has a thickness of less than 5 nm. The valence band maximum is measured about 0.6 eV below the Fermi-level and the work function was calculated from the secondary electron onset (not shown in the spectra) to be $\Phi_{\text{NiO}} = 4.8$ eV. Both values correspond well to identically prepared thin films\textsuperscript{45} as well as to solution processed NiO$_x$ films.\textsuperscript{46} For the bandgap of the NiO$_x$ thin film a value of 3.7 eV has been assumed based on literature.\textsuperscript{46} Upon water adsorption, gradual energy level shifts were detected in the range of 100 meV. However, while the Si2p core level shifts 0.1 eV to lower binding energies, the nickel oxide core level shifts 0.1 eV to higher binding energies. This means that the water induced band bending at the NiO$_x$/H$_2$O interface is about 0.2 eV. The energy level positions and band bending of the n-Si/SiO$_x$/NiO$_x$ photoanode in contact with water is indicated as dashed lines in Figure 5a. After water desorption the band bending is nearly fully reversed.

The energy band diagram, charge transfer processes and catalytic activity of an n-Si/NiO$_x$ photoanode without an SiO$_x$ interlayer are discussed in Ref. 3. In the present case, the band bending upwards promotes the migration of photo-generated holes into the NiO$_x$ thin film during water splitting. But in contrast to the n-Si/NiO$_x$ interface discussed in Ref. 3, the SiO$_x$ interlayer reduces the valence band offset between n-Si and NiO$_x$ significantly, facilitating hole transport. On the other hand, the insufficient charge transport in SiO$_x$ might have a negative influence on the general performance. At the NiO$_x$/H$_2$O interface, a slight band bending upwards supports hole transport toward the electrolyte. For practical use, the NiO$_x$ surface is usually electrochemically activated and transforms into a h-NiO$_x$ layer.\textsuperscript{47–49} In the present model experiment, we observe the formation of an h-NiO$_x$ layer upon contact to water even without activation. Therefore, by engineering the NiO$_x$ surface, the catalytic performance could be further enhanced. Strategies to increase the fraction of Ni$_2$O$_3$ phases and possibly induce defect sites could be post-annealing or oxygen plasma treatment, amongst others. Although the work function is always a parameter of the whole sample, the evolution shown in Figure 5b demonstrates that the work function changes upon water adsorption are mainly governed by the dominant water species in the (sub-) monolayer and multilayer regime, respectively. Between 0.2 L and 1.6 L, where H$_2$O-NiO species are dominant, the work function is slightly increasing from 4.8 eV for pristine NiO$_x$ to 4.9 eV. Only for water coverages in the multilayer regime, where H$_2$O-H$_2$O interaction becomes dominant, the work function is decreasing by 0.3 eV to 4.6 eV. After desorption, the work function increases again to 4.8 eV. With photoemission only one integrated work function value for a polymorphous film can be measured. Using these integrated work function values, the ionization potential IP of the 1b$_1$ orbital is considerably higher for the H$_2$O-H$_2$O species (IP = 11.8 eV) than for the H$_2$O-NiO species (IP = 11.0 eV). This might be an important fact for water-splitting but local work function variations have to be considered in addition.

Conclusions

Magnetron-sputtered nickel oxide thin films on thermally oxidized n-type silicon were prepared. Stoichiometric NiO and Ni$_2$O$_3$ phases were found but non-stoichiometric portions and defects have to be considered in addition. Upon water adsorption, dissociative water was predominantly observed on Ni$_2$O$_3$ including respective defect sites and phase boundaries. Furthermore, the formation of Ni(OH)$_2$ and NiOOH was proven with UPS and XPS. Two different molecularly adsorbed water species could be distinguished: In the (sub-) monolayer regime, the interaction of H$_2$O with inert NiO over hydrogen bonds was dominant (H$_2$O-NiO) while in the multilayer regime a second species was detected which shows the typical binding energies of multilayer water. After water desorption induced by heating up to RT, only traces of chemisorbed Ni(OH)$_2$ and NiOOH species were left on the surface. In principal, the band diagram of the
n-Si/SiO2/NiO photoanode in contact to water exhibits a beneficial alignment for the hole transport to the electrode/electrolyte interface. Additionally, the difference in binding energy of the observed water species (H2O-NiO versus H2O-H2O) points to a high usability of nickel oxide and its derivatives with respect to photocatalysis. The experiments demonstrate that surface sensitive information on the reactivity of the solid/liquid interface can be obtained under highly controlled conditions in the UHV on an atomic scale by CryoPES.

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