Electrochemical reduction of undoped and cobalt-doped BiFeO_3 induced by water exposure: Quantitative determination of reduction potentials and defect energy levels using photoelectron spectroscopy

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The interaction of BiFeO_3 and Co-doped BiFeO_3 thin film surfaces with water vapor is examined using photoelectron spectroscopy. Water exposure results in an upward shift of the Fermi energy, which is limited by the reduction of Bi and Fe in undoped BiFeO_3 and by the reduction of Co in oxidized Co-doped BiFeO_3 . The results highlight the importance of surface potential changes induced by the interaction of solid surfaces with water and the ability of photoelectron spectroscopy to quantitatively determine electrochemical reduction potentials and defect energy levels.

Keywords:

BiFeO_3 , electrochemistry, reduction, water, photoelectron spectroscopy

The interaction of water with solid surfaces is fundamental to photocatalytic water splitting and purification, heterogeneous catalysis, corrosion and gas sensing.¹⁻⁵ In order to understand the underlying interaction mechanisms, the adsorption of water on solid surfaces has been extensively studied using surface science techniques, such as electron spectroscopies or scanning tunneling microscopy and spectroscopy.⁶⁻¹¹ Due to the ultrahigh vacuum environment in many experimental studies, the majority of studies utilizes adsorption of water at cryogenic temperatures with low water dosages. The emphasis of these studies often lies on the chemical interaction of water with the surfaces, which includes the discrimination between a molecular or a dissociative adsorption of water, the identification of preferred adsorption sites and the role of surface and sub-surface defects.

In addition to the chemical interactions at the interface, also electronic surface potentials are important, particularly for semiconducting electrodes. As an example, the changes of surface potential upon gas adsorption is the physical origin of the gas sensing properties of materials such as ZnO and SnO₂.⁵ However, the surface Fermi energy is not free to change at the surface. If the Fermi energy at the surface is pushed upwards towards the electrode's reduction potential, ϕ^{red} , or downwards towards its oxidation potential, ϕ^{ox} , the electrode becomes thermodynamically unstable against reduction or oxidation.^{11,12}

An approach to calculate the reduction and oxidation potentials from basic thermodynamic quantities has been introduced by Chen and Wang and exemplified for a variety of semiconducting electrodes.¹³ For certain cases, the energy levels associated with ϕ^{red} and ϕ^{ox} can be obtained directly from photoelectron spectroscopy. For example, a reduction of Fe³⁺ to Fe²⁺ for a Fermi energy 1.75 eV above the valence band maximum ($E_{\text{F}} - E_{\text{VB}} = 1.75 \text{ eV}$) has been identified in hematite Fe₂O₃.¹⁴ According to the band edge energies of Fe₂O₃ obtained from interface analysis using XPS,¹⁴ this level is placed $\sim 0.29 \text{ eV}$ below the water reduction potential, which disables a direct water splitting using Fe₂O₃.

Therefore, it is important how the surface potential is modified by water adsorption. A couple of examples have been reported where the adsorption of water is accompanied by a

substantial upward shift of the Fermi energy.^{15–18} For example, the Fermi energy in TiO₂, ZnO and SnO₂ can be raised to even above the conduction band minimum, $E_F - E_{CB} > 0$, by exposure to water vapor at room temperature. It may therefore be possible that the adsorption of water itself causes a reduction of the surface if the Fermi energy is raised up to the reduction potential of the material.

In this contribution, the exposure of BiFeO₃ surfaces to water vapor at room temperature is studied using in-situ photoelectron spectroscopy. BiFeO₃ is a widely studied material due to its coupling between ferroelectric and ferromagnetic properties.¹⁹ Related to its ferroelectric properties are observations of electrically conducting ferroelectric domain walls^{20,21} and a peculiar photoactivity.^{22–26} BiFeO₃ has in fact also been investigated as electrode for solar water splitting.^{27–29}

Photoelectron core level and valence band spectra recorded of undoped (BFO) and 10% Co-doped BiFeO₃ (BFCO) are shown in Fig. 1. Black, blue and red spectra represent the sample state after thermal cleaning, oxygen plasma treatment and water exposure, respectively. The valence band, Bi 4f, Fe 2p and O 1s spectra of the clean undoped BiFeO₃ are representative for a set of samples prepared by different techniques. In particular, the Fermi energy is found at $E_F - E_{VB} = 1.2 \pm 0.1$ eV and the peak shape and satellite structure of the Fe 2p emission are characteristic for Fe³⁺.¹⁴

After oxygen plasma treatment, the shapes of the valence band and of the Bi 4f and Fe 2p core levels do not change. A small shoulder towards higher binding energy appearing in the O 1s spectrum can be explained by the presence of adsorbed oxygen species. After oxygen plasma treatment, the binding energies of all spectra are reduced by the same amount. The shifts correspond to a lowering of the Fermi energy to $E_F - E_{VB} = 0.51 \pm 0.1$ eV.

Exposing the oxidized sample to water vapor results in pronounced shifts of the spectra to higher binding energies. Most strikingly, an additional doublet appears at lower binding energy in the Bi 4f spectrum. Its binding energy of 157.11 eV indicates the formation of metallic Bi. A partial reduction of the sample is also observed in the Fe 2p emission, which

Figure 1: X-ray photoelectron spectra of undoped (BFO) and Co-doped BiFeO₃ (BFCO) samples.

exhibits a shoulder at lower binding energy. This is characteristic for Fe^{2+} .¹⁴ The additional emission above the valence band maximum is also related to the appearance of the reduced Bi and Fe species. The shoulder in the O 1s spectrum can be explained by adsorbed hydroxide species. In addition to the chemical changes induced by water exposure, all spectra shift to higher binding energies, indicating an upward shift of the Fermi energy to $E_F - E_{\text{VB}} = 1.65 \pm 0.1 \text{ eV}$. The chemical reduction and an identical Fermi level position are also observed for a BiFeO_3 thin film grown by pulsed-laser-deposition, which has been exposed to water vapor after the thermal cleaning without intermediate oxygen plasma treatment. Reduced Bi and Fe are also observed after water exposure to sintered BiFeO_3 bulk ceramics.

Compared to the clean undoped BiFeO_3 , the spectra of the Co-doped BiFeO_3 in Fig. 1 exhibit different Fe 2p and valence band spectra. The Fe 2p spectrum is slightly broadened compared to the undoped sample. It is believed that this change is not related to a change of oxidation state of the Fe but rather to changes in environment caused by Co-doping. For a doping of 10%, it is likely that most Fe atoms have at least one Co atom as second nearest neighbor. This will change the crystal field splitting and thereby affect the shape of the spectrum. The different shapes of the valence band spectra are also related to the contribution of the Co states, which depends on the oxidation state of the Co, as discussed below.

The binding energies of the main emission in the Co 2p spectra appear at 779.8 eV ($\text{Co } 2p_{3/2}$) and 795.16 eV ($\text{Co } 2p_{1/2}$), respectively. The binding energy separation between the main line and the related satellites amounts to 6.51 eV for the cleaned sample. This is a clear signature for Co being in the oxidation state +II.^{30,31} It is assumed that the Co^{2+} -ions are compensated by oxygen vacancies.

The satellite structure of the Co 2p emission changes upon further sample treatments. After oxygen plasma treatment, the energy separation between the Co 2p main line and the satellite increased to 9.5 eV, which is clear evidence for a change of the oxidation state of the Co ions to Co^{3+} .^{30,31} Apparently, the oxygen vacancies have been removed by the

plasma treatment. The shape of the valence band is also affected by the oxygen plasma. In particular, the onset of the valence band emission becomes steeper and the binding energy difference between the valence band maximum and the core levels decreases. This can be explained by the removal of Co^{2+} -related electronic states from the top of the valence band. The presence of additional states at the valence band maximum of Co-doped BiFeO_3 is consistent with the reduction of the band gap by Co-doping.²⁶

Due to the contribution of the Co-states to the valence band and the different shape of the Fe 2p emission, the determination of the Fermi energy in the band gap cannot be directly extracted from the valence band maximum position as for undoped BiFeO_3 . However, as the valence band of the oxygen plasma treated sample is comparable to that of the clean undoped sample and apparently not affected by Co states, it turns out that the Bi 4f and O 1s peaks can be used for following the Fermi energy of the differently treated Co-doped sample. Using this procedure, the Fermi energy of the cleaned and the oxygen plasma treated sample can be obtained as $E_F - E_{\text{VB}} = 1.1$ and 0.45 eV, respectively.

After water exposure, no clear satellite peak is observed in the Co 2p spectrum, indicating a mixed $\text{Co}^{2+}/\text{Co}^{3+}$ oxidation state as in Co_3O_4 .³⁰ In contrast to the undoped sample, no metallic Bi and no reduction of Fe is observed after water exposure of the oxidized Co-doped sample. However, water exposure also results in an increase of binding energy, which can be translated into a Fermi level position of $E_F - E_{\text{VB}} = 0.8$ eV after water exposure. The observed Fermi level positions of the differently treated undoped and Co-doped samples are summarized in Fig. 2.

The results described above provide unambiguous evidence that room temperature exposure of water to the surface of undoped BiFeO_3 leads to an upward shift of the Fermi energy and to a chemical reduction. For the oxidized Co-doped sample, the upward shift of the Fermi energy is limited at a lower Fermi energy and no reduction of Fe and Bi is observed. Instead, the dopant is reduced upon water exposure. The observations can be explained on the same basis if it is assumed that the exposure of water results in an adsorption behaviour,

Figure 2: Fermi energies of undoped and Co-doped BiFeO_3 after oxygen plasma treatment (blue lines) or water exposure (red lines). In undoped BiFeO_3 , the Fermi energy is raised to $E_F - E_{\text{VB}} = 1.65 \text{ eV}$ upon water exposure for both as prepared and oxidized samples. Further shifts are not possible due to the reduction of both Bi and Fe. In oxidized Co-doped BiFeO_3 , water exposure results in an upward shift of the Fermi energy to $E_F - E_{\text{VB}} = 0.8 \text{ eV}$, at which a reduction of the Co occurs. In reduced $\text{Bi}(\text{Co,Fe})\text{O}_3$, oxygen vacancies compensate for Co^{2+} and the Fermi energy can raise until the reduction of Bi and Fe is induced.

which is accompanied with a donation of electrons to the substrate resulting in an upward shift of the Fermi energy. In the case of undoped BiFeO_3 , the shift of the Fermi energy is large enough to reach the reduction potential of BiFeO_3 . For the oxidized Co-doped BiFeO_3 , the electrons donated to the substrate are consumed to reduce the Co atoms and change the oxidation state from Co^{3+} to Co^{2+} . The Co 2p spectra clearly indicate that the amount of electrons provided by the water molecules is not sufficient to reduce all Co ions. Therefore, the Co doping inhibits the Fermi energy to raise enough for reducing the Fe and the Bi.

The mechanism of electron donation to the substrate cannot be resolved by the presented experiments. However, an electron donor effect of adsorbed water is consistent with observations of high Fermi energies in ZnO and SnO_2 after water exposure.^{15,18,32} In this case, a chemical reduction of the substrate, that is the generation of oxygen vacancies, is not sufficient to induce such high Fermi energies in these materials, as the energy level of the oxygen vacancies is not high enough in the band gap.³³

The Fermi energy, at which the reduction of the BiFeO_3 occurs ($E_F - E_{\text{VB}} = 1.65 \text{ eV}$), can be assigned to the reduction potential of BiFeO_3 . The energy agrees well with the ϕ^{red} observed in Fe_2O_3 ($E_F - E_{\text{VB}} = 1.75 \text{ eV}$),¹⁴ when the difference in energy position between BiFeO_3 and Fe_2O_3 of 0.1 eV ³⁴ is taken into account. Therefore, the $\text{Fe}^{3+/2+}$ charge transition is apparently aligned in these two materials as depicted in Fig. 2. Such an alignment of transition metal impurity levels has also been observed in III-V semiconductors.³⁵ This agreement must be considered with caution, as the latter is different from the present situation because the transition metals are just dilute impurities in the III-V compounds. Nevertheless, an alignment of charge transition levels might be useful to estimate the reduction potentials of other compounds. In this respect, the determination of the $\text{Co}^{3+/2+}$ charge transition at 0.8 eV above the valence band maximum of BiFeO_3 could be used to estimate the reduction potential of other Co-containing compounds.

In order to quantify the reduction potentials with respect to the hydrogen evolution potential H^+/H_2 , the energies of the band edges need to be known. SrTiO_3 is a good

reference, as the derivation of its band edges with respect to H^+/H_2 should not be affected by polaron formation. This is evident from the possibility to dope SrTiO_3 by Nb to electron concentrations above 10^{20} cm^{-3} . Photoemission studies of interface formation have found the valence band maximum of BiFeO_3 to be 0.1 eV above that of Fe_2O_3 ³⁴ and that of Fe_2O_3 to be 1.1 eV above that of SrTiO_3 .^{14,34} With this alignment, the reduction potential of BiFeO_3 is derived to be 0.3 eV below H^+/H_2 . This is in very good agreement with the work of Chen and Wang, who calculated ϕ^{red} of BiFeO_3 to be 0.26 V below H^+/H_2 . However, this agreement might be fortuitous. For example, the ϕ^{red} calculated by Chen and Wang for Fe_2O_3 is -0.01 V , which is $\sim 0.3 \text{ eV}$ higher than the photoemission value.¹⁴ A discrepancy in ϕ^{red} can also arise as photoemission is probing surface properties, while the calculation is based on bulk thermodynamic properties. Nevertheless, the $\text{Fe}^{3+/2+}$ charge transition level observed for Fe_2O_3 using XPS is yet in very good agreement with that calculated by density functional theory,³⁶ indicating that the difference between bulk and surface energy levels is not necessarily big.

In summary, we have presented a study of room temperature water exposure of undoped and Co-doped BiFeO_3 using in-situ photoelectron spectroscopy. Water exposure clearly induces an upwards shift of the Fermi energy. In undoped BiFeO_3 , the shift is large enough that the Fermi energy reaches the reduction potential of BiFeO_3 , which results in the formation of reduced Fe and Bi species. Co-doped samples exhibits a Co oxidation state depending on sample treatment. Co is present as Co^{2+} in samples heated in a low oxygen pressure. Oxygen plasma treatment removes oxygen vacancies, thereby lowering the Fermi energy and changing the oxidation of Co to +III. Water exposure on such oxidized samples also results in an upward shift of the Fermi energy. In this case, the shift is limited by the partial reduction of Co, which occurs for a Fermi energy 0.8 eV above the valence band maximum. Co doping therefore inhibits the reduction of BiFeO_3 itself. The reduction potential of BiFeO_3 is derived at 1.65 eV above the valence band maximum. According to band alignment studies in comparison to SrTiO_3 , this corresponds to an energy of 0.3 eV below the water reduction

potential. BiFeO_3 is therefore not suitable for direct water splitting.

The results described in this manuscript emphasize that the consequences of water adsorption for the electronic surface properties are crucial for understanding solid/water interactions. Evidently, water can act as an electron donor on oxide surfaces and thereby induce an electrochemical reduction. This reduction might be suppressed by suitable doping, such as by Co in BiFeO_3 , if the oxidation state of the dopant can be controlled. The described results also demonstrate that the reduction potentials and stability limits can be quantified using photoelectron spectroscopy with in-situ sample preparation.

Experimental

Thin films of BiFeO_3 and of Co-doped BiFeO_3 with 20 nm thickness were synthesized chemical solution deposition (CSD)²⁶ onto $5 \times 5 \text{ mm}^2$ $\text{SrTiO}_3(100)$ single crystal substrates coated with 10 nm of $\text{La}_{4.7}\text{Sr}_{0.3}\text{O}_3$. X-ray diffraction confirmed oriented growth of the BF(C)O along the pseudocubic (002) direction. The root-mean-square roughness of the films has been determined using atomic force microscopy as 3 and 2 nm for the undoped and the Co-doped sample, respectively.

XPS analysis was performed within the DArmstadt Integrated SYstem for MATerials Research (DAISY-MAT), which combines a multi-technique surface analysis system and several vacuum chambers for thin film deposition and sample treatments with a vacuum sample transfer system.³⁷ The sample surfaces were first cleaned by heating them in $1 \cdot 10^{-2}$ mbar of O_2 at 400 °C for 2 hours. No residual carbon contaminations were detected after this treatment while the Bi/Fe ratio of the samples remains unaffected. Further oxidation of the samples was performed using a tectra GenII plasma source (tectra, Frankfurt on the Main) operated in atom mode at an oxygen flux (or pressure) of 3 sccm (or $3.3 \cdot 10^{-4}$ mbar) for 15 min. Water exposure was performed at room temperature in an atomic-layer-deposition chamber attached to the system.³⁸ During exposure, water was dosed through an ALD-3-

valve while continuously evacuating the chamber. The valve was opened 30 times for 0.5 s. In between the pulses, the valves was closed for 60 s. After water exposure, the chamber was evacuated until a pressure of $< 5 \cdot 10^{-7}$ mbar, before the sample was transferred to the analysis chamber. Photoelectron spectra were recorded using a Physical Electronics PHI 5700 spectrometer (Chanhassan, MN) with monochromatic Al K α radiation. Binding energies are referenced to the Fermi energy, which was calibrated using a sputter-cleaned Ag foil.

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