The Impact of Different Si Surface Terminations in the (100) p-Si | n⁺-Si | Cu Junction with Respect to the Photo Electrochemical Performance

Céline Steinert, Sven Tengeler, Bernhard Kaiser, and Wolfram Jaegermann

Institute for Materials Science, Technical University of Darmstadt, 64287 Darmstadt, Germany

The (100) p-Si | n⁺-Si | Cu interface is investigated with respect to the electronic band structure and the electrochemical performance. Thin layers of metallic copper were deposited stepwise by E-beam deposition and analyzed in-line by XPS after each deposition step. For this purpose, different silicon surface terminations were prepared: hydrogen termination, thermal oxide (7 Å) and native oxide (3 Å). After contact formation the initial flatband situation of the n⁺-Si layer changes to an upward band bending depending on the Si surface termination: 0.45 eV for the H termination, 0.35 eV for the native oxide and 0.27 eV for the thermal oxide. The electrochemical performance measured by cyclic voltammetry for each junction correlates to the respective energy band alignment. While the H terminated surface with the highest upward band bending leads to the worst electrochemical performance, the surface passivated with thermal oxide and the lowest upward band bending results in the best electrochemical performance. For the two passivated surfaces, the thickness of the passivating oxide layer may also be an issue. The Si surface with a thicker thermal oxide (7 Å) shows better band alignment and electrochemical performance compared to the Si surface with a thinner native oxide (3 Å).

Due to worldwide growing industrialization, the energy demand has been drastically increased within the last decades. In order to preserve our environment and limit global warming, the development of efficient renewable energy sources is urgently needed. However, wind and solar power as most promising alternative sources suffer from their inherent volatility with strongly variable energy fluxes with time, which are not in phase with the societal consumption needs. Storable and transportable fuels from renewable energies are essential. Here, natural photosynthesis, which is the most important and prototype method of harvesting solar energy, acts as natural role model. Photoelectrochemical cells may develop to a key technology, especially when they will be able to convert CO₂ directly into fuels, using sunlight. The first essential part of such a device is the photoabsorber, which has to drive the photoelectrochemical reaction.

In the model system presented here, a (100) p-Si | n⁺-Si junction serves as photoabsorber material which will be compared to bare p-Si. Another important part of the photoelectrochemical device is an appropriate catalyst which allows high current densities at low potentials when being in contact to an electrolyte. As Cu is known to be able to reduce CO₂ to CO, CH₄, C₂H₄ and alcohols in aqueous potentials when being in contact to an electrolyte. As Cu is known to be able to reduce CO₂ to CO, CH₄, C₂H₄ and alcohols in aqueous electrolytes, Cu is used as prototype catalyst for the present study as well. For CO₂ reduction the use of Si based multijunction solar cells directly inserted into the electrolyte is planned. However, because of limited multijunction sample availability the PV/electrolyser coupling was investigated first using single crystalline Si as model substrate.

Especially in the last years there have been a lot of publications in the field of CO₂ reduction. While Urbain et al. used Cu foam connected by wires to a Si solar cell for the electrocatalytic CO₂ reduction reaction (CRR), a CuAg cathode was used by Gurudayal et al. Furthermore, solar energy conversion was realized by Sugano et al. with a wired photovoltaic photoelectrochemical system with Au nanoparticles as the CRR active cathode. Also, Au thin films have been proven to work as catalyst to form CO as CRR product. Besides Cu and Au, further catalyst materials have been utilized for the CRR e.g. IrOₓ, Ru, Mo and W. However, the deposition of a catalytic active thin film directly onto the semiconductor surface has not been investigated in a systematic way so far. In a first step Cu as most promising CRR catalyst is used for this purpose. KHCO₃ is employed as appropriate electrolyte in all performed experiments as described in previous work. One major condition for an effective system is the successful coupling of the PV component to the electrolysis component without any losses in photo current (recombination) and photo voltage (energy alignment) across the interface.

The present study demonstrates that the electrochemical performance of an integrated photoelectrochemical device can be predicted and optimized by investigating the electronic structure at the interface between its two main parts: the Si junction as the photoabsorber and the Cu as the catalytically active layer. For this reason this interface was investigated by in-line X-ray photoelectron spectroscopy (XPS) analysis after the stepwise deposition of Cu on the Si surfaces with different surface terminations. At first, bare p-doped Si wafers were used as reference before analyzing the (100) p⁺-Si junctions. Furthermore, cyclic voltammetry was used to determine the electrochemical performance of each system. With this approach a basic understanding on how the different band alignments due to different surface terminations impact the CRR is achieved. Similar characterization experiments were also reported for the oxygen evolution reaction recently.

**Experimental**

**Sample preparation.**—The experiments were performed on 1 cm × 1 cm pieces of 100 nm diameter (100) boron doped p-type silicon wafers (p = 10¹⁶ cm⁻³) with and without a 50 nm thick arsenic doped n⁺-type silicon layer on top (n = 10¹⁰ cm⁻³). All samples were first cleaned in an ultrasonic bath for 10 min in acetone, isopropanol and MilliQ water. For the Si surface termination with native oxide no further preparation steps were necessary. For the hydrogen terminated Si surface the sample was first etched in piranha solution (H₂SO₄:H₂O₂ = 2:1) at 80°C for 10 min and afterwards in 5% HF also for 10 min. After another etching step in freshly prepared piranha for again 10 min at 80°C, the sample was finally etched for 10 min in 40% NH₄F at room temperature. In between each step the sample was thoroughly rinsed with MilliQ water. Afterwards, the sample was introduced into ultra high vacuum (UHV) at the Darmstadt Integrated System for Fundamental research (DAISY Fun). In order to obtain thermally grown oxide a sample with a H terminated surface was introduced to a deposition chamber of the DAISY Fun where it was held in a mixed oxygen argon atmosphere (50 sccm O₂, 50 sccm Ar, 0.1 mbar) for 45 min at 800°C.
Interface experiments.—Before depositing the first layer of Cu on the differently prepared Si samples, the bare substrates were analyzed by XPS in order to check if the surface is free of any contaminations. Afterwards the samples were transferred into a deposition chamber where a thin layer of Cu was deposited by electron beam deposition at pressures of $10^{-7}$ mbar or better. Subsequently, the samples were analyzed again by XPS followed by another Cu deposition and so on, until the Cu 2p emissions became dominant and the Si substrate was barely visible any more. The XPS measurements were all performed at a pressure of $5 \times 10^{-10}$ mbar or better using a Specs Phoibos 150 setup (Focus 500 with XR50M). For all measurements a monochromatic Al K$_\alpha$ line of 1486.64 eV was used as X-ray excitation. Survey measurements were obtained with a pass energy of 20 eV while all detail spectra were measured with a pass energy of 10 eV. The spectrometer was calibrated against the Cu 2p, Ag 3d and Au 4f core levels as well as the valence band edges. As evaluation software Igor Pro was used.

To calculate the band bending before and after contact formation the Si 2p$_{3/2}$ emission line needs to be analyzed. For the initial band alignment the position of the corresponding Si 2p$_{3/2}$ emission line is determined. Accordingly, the distance between the valence band to the Fermi level can be determined by subtracting the known value of the Si bandgap ($E_g = 1.12$ eV) which results in the band bending $E_B$.

$$E_B = 1.12 \text{ eV} - (98.74 \text{ eV} - E_{B_\text{Si}}(\text{Si } 2p_{3/2})) - (E_{C_B} - E_F).$$

Analogous to this approach the band alignment after contact formation can be determined when evaluating the measured XP spectra after the last Cu deposition step.

Determination of film thickness.—The film thickness was determined by the numerical solution of

$$I_{Cu} = \frac{N_{Cu}}{N_{Si}} \frac{1 - \exp\left(-\frac{d_{Cu}}{\lambda_{Cu2p} \cos \theta}ight)}{\exp\left(-\frac{d_{Cu}}{\lambda_{Cu2p} \cos \theta}ight)} \exp\left(-\frac{d_{Cu}}{\lambda_{Cu2p} \cos \theta}ight)$$

for the thin Cu layer on the bulk Si substrate.22,23 Here, $I_{Cu}$ and $I_{Si}$ are the integrated core level line intensities which are corrected with a Shirley background.24 $\lambda_{Cu}$ and $\lambda_{Si}$ are the inelastic mean free paths (IMFP) for the kinetic energy of the electrons in the thin surface layer. Cu and N$_{Cu}$ as well as N$_{Si}$ are the materials atomic densities. The electron emission angle is defined as $\theta$. In order to determine the layer thickness of the oxide, the initial Si 2p peak intensity needs to be taken into account. In order to remove the background of the spectrum a Shirley background correction has been applied. Additionally to the Si 2p peak the SiO$_2$ peak can be seen at 103.5 eV (literature: 103.2 eV).25 For calculating the layer thickness $d$ of the SiO$_2$ the relation of the integrated core level lines $I_{Cu2p}$ and $I_{Si2p}$ needs to be taken into account. Furthermore, the materials atomic densities N$_{Si}$ and N$_{SiO2}$, the inelastic mean free path $\lambda$ of SiO$_2$ and the electron emission angle $\theta$ are defining the layer thickness as shown in the following equation

$$d_{SiO2} = \lambda_{SiO2} \cos \theta \ln \left(1 + \frac{I_{SiO2}N_{Si}}{I_{Si2p}N_{SiO2}} \right).$$

The photo electrochemical performance of the p-Si | thermal oxide | Cu reference sample is shown in Figure 2. The displayed chopped light CV shows the difference between the CV measurements under illumination and in the dark. First, it can be pointed out that the sample does not show a classic chopped light behavior as the dark current density reaches values below 1 mA/cm$^2$ for potentials smaller than −0.9 V vs. RHE. This behavior differs from expectations for an ideal Schottky barrier.19,33 The reason for this behavior is the occurrence of Fermi level pinning at midgap position which is already evident from the p-Si | SiO$_2$ surface before contacted to Cu (Fig. 1). The remaining midgap defects in the Si | SiO$_2$ phase boundary lead to effective tunneling across the junction without sharing the desired diode behavior across the interface. The p-Si | thermal oxide | Cu junction represents a basic model system, which is not expected to supply enough current to drive the CRR.

pn$^+$-Si | Cu interfaces.—In order to analyze the initial electronic band structure of the three different Si surface terminations prior to Cu deposition and to verify whether the surfaces are free of contaminations, survey spectra were measured by XPS, as displayed in the supplementary information figure S 1. This step is important in order to understand the basic model system before coming to the more complex system of pn$^+$-Si junctions in contact with Cu as catalyst. The determined band alignments of p-Si | thermal oxide before and after contact formation with Cu are shown in Figure 1. Here, Figure 1A shows the initial situation before contact formation. For the thermal oxide there is a large downward band bending of 0.4 eV which is also found after extensive preparation steps as etching to form H terminated surfaces or subsequent oxidation to form a thermal oxide. A preferable flatband situation is not achieved in our experiments, which is due to midgap defects at the p-Si surface and Fermi level pinning as a consequence. In Figure 1B it can be seen that for the p-Si | thermal oxide sample the band bending is slightly reduced from 0.4 eV to 0.3 eV when brought into contact with Cu. Presumably the band alignment after contact formation is not determined by the Cu contact but by the initial Fermi level pinning. In such cases, which are expected to be the dominating case for most experiments using Si as substrate, the contact properties to a metal as e.g. a Cu thin film deposited onto a p-Si | thermal oxide sample will be dominated by Fermi level pinning.26,27

Results and Discussion

The photo electrochemical performance of the p-Si | thermal oxide | Cu interface was investigated as reference system. The aim of using this very basic model sample was to obtain a systematic understanding of the electronic and catalytic properties of Si | Cu interfaces. However, we expect that advanced model systems containing buried junctions such as pn$^+$-Si | Cu and pin-Si | Cu will be desired as integrated photo electrochemical device and therefore we have put our emphasis on such systems.
the supplemental information S 2. For the hydrogen terminated surface, the two dominant emissions are Si 2s and Si 2p with binding energies of 151.05 eV and 99.98 eV, respectively, which are in agreement to literature.25,34–36 There is also a very small amount of oxygen present in the sample with the H terminated surface as can be deduced from the O 1s line and the O KLL Auger line at 531 eV and 979.15 eV, respectively.37,38 The corresponding XP detail spectrum of the Cu LMM Auger line for all samples can be seen in the supplemental information S 6. The specific photoelectron lines of Si also dominate the spectra of the two samples with additional oxide layers. While the intensities of the Si 2s and Si 2p lines are comparable, the O 1s and O KLL lines are more intense for the sample with the thicker (7 Å) thermal oxide as compared the thinner (3 Å) native oxide layer. It can be concluded from figure S 2 that the H terminated sample and the sample with the thermal oxide are free of any severe contamination. The native oxide sample shows a photoelectron line at 285 eV which is specific for C 1s. As this sample did not undergo a piranha etching procedure the carbon contamination from storage in ambient air was not removed.

After this initial analysis, on all three Si surfaces with different termination, Cu was deposited stepwise, followed again by XPS analysis after each step. In Figure 3, the evolution of the XP spectra during the interface experiment is shown for the Si sample with the native oxide layer. The H terminated and thermal oxide samples are shown in Figures 4 and 5, respectively. In the corresponding survey spectra which are supplementary shown in figure S 3 only the substrate and Cu overlayer photoelectron lines appear. As there are no additional photoelectron lines visible, especially from carbon, these samples are free of any contamination. Moreover, it can be seen that the intensities of the initial oxygen and silicon lines decrease with each deposition step, and the characteristic lines for copper Cu 2s, Cu 2p and Cu LMM emerge. It can also be concluded from the Si 2p_{3/2}, O 1s and Cu 2p emission lines that no chemical reaction occurs at the H terminated interface but at the interfaces with native and thermal SiO2. When the detail spectra Si 2p, O1s and Cu 2p of the differently prepared pn+-Si surfaces (see Figure 3, Figures 4 and Figure 5) are compared to each other, they basically show the same behavior and spectral features. As main difference the contribution of the SiO2 related emission feature at around 103.5 eV is evident, its thickness will be evaluated below. Furthermore, there is a difference in the development of the O1s emission line for the H terminated surface and the surfaces with SiO2 interlayers. While there is no oxygen reaction for the pn+-Si:H | Cu interface, it can be observed for the interfaces with additional SiO2 layers. Otherwise, there are some minor differences in the binding energy values due to a slightly different band energy diagram which will be also discussed in more detail below. The maximum of the Si 2p line shifts to lower binding energies due to contact formation to copper. Furthermore, it can be noticed that the initial Si 2p emission shows a minimum at 100.2 eV. This high resolution feature indicates the initial electronic flatband situation. As soon as the Si substrate is covered with Cu this minimum vanishes and additionally the entire Si 2p peak broadens. At a binding energy of 103.5 eV the SiO2 emission is found, which also decreases with increasing Cu layer thickness. The intensity ratio of SiO2 and Si will be discussed later. While the Si 2p peak vanishes, the Cu 2p peak increases with ongoing deposition steps.

Within the large Cu 2p splitting the observed signal remains quite flat, which indicates the deposition of mostly metallic Cu.40–42 Very weak satellites denote the negligible formation of Cu2O and of CuO.43–45 The Cu was deposited until a layer thickness of 81 Å was reached.

The aim of all performed XPS measurements was the investigation of the interfaces and thus of the energy band alignments of the differently treated pn+-Si surfaces. The investigated band diagrams for pn+-Si with and without oxide layer before and after being in contact with Cu are displayed in Figure 6. Here, fraction Figure 6 A shows the initial energetic situation of the pn+-Si | SiO2 before the Cu deposition. The bandgap of 1.12 eV for Si29 is sketched as well as the distance of the Fermi level to the valence band, which is 0.2 eV. This value was determined by the solution of

\[
E_F - E_{VB} = kT \ln \left( \frac{N_{vB}}{p} \right)
\]
where \( N_{VB} \) is the effective density of states (DOS) in the valence band and \( p \) is the doping concentration \( (p = 10^{-16} \text{ cm}^{-3}) \). In the \( n^+ \)-Si layer the doping concentration \( n \) is much higher \( (n = 10^{19} \text{ cm}^{-3}) \), which results in a very small distance of the Fermi level to the conduction band of 0.03 eV. With a slight upward band bending of 0.06 eV a flatband like situation for the \( n^- \)-Si top layer and a space charge layer between the \( pn^- \)-Si layers can be assumed as initial electronic structure. For this starting situation a Si 2p\(_{3/2}\) core level binding energy of 99.77 eV has been measured for the natural oxide terminated \( pn^- \)-Si surface. With the known value of \( E_B(VB) - E_B(Si \ 2p\_3/2) \) of 98.74 eV this corresponds to a value of \( E_F - E_{VB} \) of 1.03 eV in agreement to the presented energy diagram. Figure 6B shows the electronic band structure of \( pn^- \)-Si | native SiO\(_2\) | Cu. A band bending upwards of 0.35 eV induced in the \( n^+ \) surface layer can be noticed. In case of the thermal oxide this surface band bending is smaller having a value of 0.27 eV, as can be seen in Figure 6C. The reason for the more ideal band alignment in case of the thermal oxide might be the better surface passivation due to the higher layer thickness of 7 Å compared to only 3 Å for the native oxide. Furthermore, different properties of the oxide layers may play an additional role. For the hydrogen terminated system the initial electronic structure before the Cu deposition is illustrated in Figure 6D. With an initial band bending of only 0.01 eV at the surface a flatband situation in the \( n^- \) layer is given. When being in contact with Cu an upward band bending of 0.45 eV develops as illustrated in Figure 6E. These band bending changes in the topmost Si \( n^- \) layer can directly be deduced from the different shift of the Si 2p\(_{3/2}\) binding energy values with Cu deposition \( (E_B(pn^-\text{-Si} | \text{native SiO}_2 | \text{Cu}) = 99.48 \text{ eV}, E_B(pn^-\text{-Si} | \text{thermal SiO}_2 | \text{Cu}) = 99.56 \text{ eV} \) and \( E_B(pn^-\text{-Si:H} | \text{Cu}) = 99.38 \text{ eV} \). As the photo electrons, which come from the conduction band of the \( pn^- \)-Si junction, need to overcome the energetic barrier between \( n^- \)-Si and Cu, it is advantageous to have only a small upward band bending at this point. Thus, it can be concluded that the model system \( pn^- \)-Si | thermal SiO\(_2\) | Cu with a barrier of only 0.27 eV provides the best electronic transport properties followed by the model system \( pn^- \)-Si | native SiO\(_2\) | Cu with 0.35 eV and \( pn^- \)-Si:H | Cu with 0.45 eV barriers respectively. These differences in the band energy diagrams as deduced from the XPS interface experiments were compared to additional CV measurements.

![Figure 3](image_url)

**Figure 3.** XP spectra of a \( pn^+ \)-Si sample with a native oxide layer on top after a step wise Cu deposition. Left: changing O1s emission. Middle: decreasing Si2p emission and shift to lower binding energy with ongoing Cu deposition. Right: Emerging Cu 2p emission with increasing film thickness.

![Figure 4](image_url)

**Figure 4.** XP spectra of a \( pn^- \)-Si sample with a hydrogen terminated layer on top after a step wise Cu deposition. Left: changing O1s emission. Middle: decreasing Si2p emission and shift to lower binding energy with ongoing Cu deposition. Right: Emerging Cu 2p emission with increasing film thickness.
Figure 5. XP spectra of a pn$^+$-Si sample with a thermal oxide layer on top after a step wise Cu deposition. Left: changing O1s emission. Middle: decreasing Si2p emission and shift to lower binding energy with ongoing Cu deposition. Right: Emerging Cu 2p emission with increasing film thickness.

measurements, to determine the influence of the energy level alignment on the electrochemical performance. It is assumed that the samples with lower energetic barriers at the n$^-$-Si | Cu interface deliver a better performance compared to the samples with higher barriers. The catalytic performance in CV for all three systems can be seen in Figure 7. First, it can be concluded that under illumination all samples reached a similar saturation current density of $-5.5$ to $-6$ mA/cm$^2$ under an illumination of 180 W/m$^2$. But, for obtaining a current density of $-2$ mA/cm$^2$ a potential of averaged $-0.7$ V (vs. RHE) was necessary for the pn$^+$-Si:H | Cu sample. For the pn$^+$-Si | native SiO$_2$ | Cu sample a potential of $-0.6$ V was sufficient while the pn$^+$-Si | thermal SiO$_2$ | Cu sample was able to reach a current density of $-2$ mA/cm$^2$ at an applied potential of only $-0.4$ V. These results are in excellent agreement with the expectations from the investigated electronic band structure of the samples since the electrochemical performance is improved for low band bendings after contact formation. Additionally, the layer thickness of the intermediate SiO$_2$ can be discussed. While the native oxide has only a thickness of 3 Å, the thermally grown oxide layer is 7 Å thick. As a thicker thermal oxide layer results in a better surface passivation compared to a thinner

Figure 6. Energy band diagrams before and after contact formation. A) pn$^+$-Si | SiO$_2$ before contact formation with flatband like situation, B) pn$^+$-Si | native SiO$_2$ | Cu with an upward band bending of 0.35 eV, C) pn$^+$-Si | thermal SiO$_2$ | Cu with an upward band bending of 0.27 eV, D) pn$^-$-Si:H before contact formation with flatband situation and E) pn$^+$-Si:H | Cu with an upward band bending of 0.45 eV. Due to the differences in the band alignments, different electrochemical performances are expected.
native oxide the electrochemical performance can be assumed to be improved.

In addition, all the samples show a strongly improved behavior compared to the p-Si | Cu sample Figure 2. There are well defined photo current voltage curves and low dark current curves as expected for a diode in the reverse saturation potential regime. Furthermore, the photo current onset is shifted from about −0.7 V to 0.0 V vs. RHE in the best case which is in good agreement to the photo voltage expected for the pn−/Si junction with the given doping concentration.

Conclusions

(100) pn−Si junctions with three different surface terminations (hydrogen, 3 Å native oxide and 7 Å thermal oxide) were covered with Cu as catalytically active layer for the CO2 reduction reaction. The interfaces of all model systems were investigated by XPS and the electrochemical performances were measured by cyclic voltammetry in comparison to the bare p-Si | Cu under an illumination of 180 W/m² with λ = 625 nm in 0.3 M KHCO3. Solid lines: EC behavior under illumination. Dashed lines: EC behavior in the dark. As predicted from the interface investigations the samples show different behaviors depending on the surface barrier height.

As next step we will check if further improvements in the procedure of Cu deposition onto the n+ Si layer by modified surface engineering processes or soft Cu deposition procedures will be possible. In addition other CO2 reduction catalysts will be tested. Finally, Cu and alternative catalytic active layers will be deposited onto p-i-n-Si multiasborsor structures.

Acknowledgments

Financial support through the a-leaf project (732840-A-LEAF) by the European Union and by the DFG in the framework of the Darmstadt Graduate School of Excellence for Energy Science and Engineering (GSC 1070) is gratefully acknowledged.

ORCID

Céline Steinert https://orcid.org/0000-0002-4246-8635
Sven Tengeler https://orcid.org/0000-0003-3405-4229

References

1. M. Mishra and D. M. Chua, Applied Catalysis A, 498, 126 (2015).
2. Y. Hori, Modern Aspects of Electrochemistry No. 42, Springer, (2008).
3. D. Ren, J. Fong, and B. S. Yeo, Nature Communications, 9, 925 (2018).
4. Z. Weng, Y. Wu, M. Wang, J. Jiang, K. Yang, S. Huang, X. Wang, Q. Ma, G. W. Brudvig, V. S. Batista, Y. Liang, Z. Feng, and H. Wang, Nature communications, 4, 415 (2013).
5. M. Gattrell, N. Gupta, and A. Co, Journal of the Electroanalytical Chemistry, 594, 1 (2006).
6. K. P. Kuhl, E. R. Cave, D. N. Abram, and T. F. Jaramillo, Energy & Environmental Science, 5, 7050 (2012).
7. F. Urban, P. Tian, N. M. Carretto, T. Andreu, L. G. Gerling, C. Voz, J. Arbiol, and J. R. Morante, Energy & Environmental Science, 10, 2256 (2017).
8. G. J. Bullough, D. F. Sranko, C. M. Towle, Y. Lum, M. Hettick, M. C. Scott, A. Javey, and J. Ager, Energy & Environmental Sciences, 10, 2222 (2017).
9. Y. Sugano, A. Ono, R. Kitagawa, J. Tamura, M. Yamaaki, Y. Kudo, E. Tsutsumi, and S. Mikoshiba, RSC Advances, 5, 54246 (2015).
10. J. T. Song, H. Ryoo, M. Cho, J. Kim, J. G. Kim, S. Chung, and J. Oh, Advanced Energy Materials, 7, 1601037 (2017).
11. T. Kern, S. Satio, and T. Moriya, Energy & Environmental Science, 8, 1998 (2015).
12. R. Kuriki, K. Sekizawa, O. Ishitani, and K. Maeda, Angewandte Chemie International Edition, 54, 2406 (2015).
13. J. Albo, M. Alvarez-Guerra, P. Castano, and A. Irabien, Green Chemistry (2013).
14. D. W. DeWulf, T. Jin, and A. J. Bard, Journal of the Electrochemical Society, 136(6), 1686 (1989).
15. Y. Hori, A. Murata, and R. Takahashi, Journal of the Chemical Society, Faraday Transactions 1, 85(8), 2309 (1989).
16. M. Ma, K. Djnashvili, and W. A. Smith, Angewandte Chemie International Edition, 128, 6792. (2016).
17. M. Azuma, K. Hashimoto, M. Hiramoto, M. Watanabe, and T. Sakata, Journal of the Electrochemical Society, 136(7), 1792 (2010).
18. H. H. Jesus-Cardona, C. del Moral, and C. R. Cabrera, Journal of the Electroanalytical Chemistry, 513(1), 45 (2001).
19. S. Tengeler, M. Fingerle, W. Calvet, C. Steinert, B. Kaiser, T. Mayer, and W. Jaegermann, Journal of the Electrochemical Society, 165(4), 38322 (2018).
20. W. Kern, S. Satio, and T. Moriya, Journal of the Electrochemical Society, 137(6), 1587 (1990).
21. W. Jaegermann, B. Kaiser, J. Ziegler, and L. Klett, Photoelectrochemical Solar Fuel Production, Springer, 1 ed. (2016).
22. S. Gimenez, J. Bisquet, S. Tengeler, B. Kaiser, D. Chaussewde, and W. Jaegermann, Applied Surface Science, 400, 6 (2016).
23. P. M Peas and S. J. Spencer, Surface and Interface Analysis, 33, 640 (2002).
24. D. A. Shirley, Physical Review, 5, 4709 (1972).
25. P. J. Grumithan, P. J. Grumithan, R. P. Vasquez, B. F. Lewis, and J. Masrijar, Journal of Vacuum Science and Technology, 16, 1443 (1979).
26. L. He, W. Zhou, D. Cai, S. S. Mao, K. Sun, and S. Shen, Catalysis. Science & Technology, 7, 2632 (2017).
27. V. Lehmann and H. Foll, Journal of the Electrochemical Society, 135(11), 2831 (1988).
28. M. Malizia, B. Seger, I. Chorkendorff, and P. C. K. Voterberg, Journal of Materials Chemistry A, 2, 6847 (2014).
29. F. J. Himpel, G. Hollinger, and R. A. Pollak, Physical Review B, 28, 7014 (1983).
30. C. C. Hobbs, L. R. C. Fosseca, A. Knizhnik, V. Dhandapani, S. B. Samavedam, W. J. Taylor, J. M. Grant, L. R. G. Dip, D. H. Triyoso, R. I. Hegde, D. C. Gilmer, R. Garcia, D. Roan, M. L. Loyveyo, R. S. Rae, E. A. Hekt, H. Tseng, S. G. H. Anderson, and B. E. White, IEEE Transactions on Electronic Devices, Vol. 51, 6 (2004).
31. O. F. Sankey, R. E. Allen, and J. D. Dow, Solid State Communications, 49(1), 1 (1984).
32. R. T. Tung, Physical Review Letters, 84, 6078 (2000).
33. Prof. E. H. Rhoderick, M. A., M. Sc., Ph. D., C. Eng., and F. lnst. P., F. inst. E. E., 85, 6078 (2000).
34. J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, s. l.: Physical Electronics, Inc., 1995.
35. Z. H. Lu, P. McCaffrey, B. Brau, G. D. Wnek, R. M. Wallace, L. C. Feldman, and S. P. Tay, Applied Physics Letters, 71, 2764 (1997).
36. D. F. Mitchell, K. B. Clark, J. A. Bardwell, W. N. Lennard, G. R. Massoumi, and I. V. Mitchell, *Surface and Interface Analysis*, 21, 44 (1994).
37. S. K. Chawla, N. Sankarraman, and J. H. Payer, *Journal of Electron Spectroscopy and Related Phenomena*, 61, 1 (1992).
38. Y. A. Teterin, K. E. Ivanov, A. Y. Teterin, A. M. Lebedev, I. O. Utkin, and L. Vukchevich, *Journal of Electron Spectroscopy and Related Phenomena*, 101–103, 401 (1999).
39. M. C. Biesinger, L. W. M. Lau, A. R. Gerson, and R. S. C. Smart, *Applied Surface Science*, 257, 887 (2010).
40. R. Padiyath, J. Seth, S. V. Babu, and L. J. Matienzo, *Journal of Applied Physics*, 73, 2326 (1993).
41. M. Dai, J. Kwon, M. D. Halls, R. G. Gordon, and Y. J. Chabal, *Langmuir*, 26(6), 3911 (2010).
42. J. P. Espinós, J. Morales, A. Barranco, A. Caballero, J. P. Holgado, and A. R. González-Elipe, *The Journal of Physical Chemistry, B*, 106, 6921 (2002).
43. G. Panzner, B. Egert, and H. P. Schmidt, *Surface Science*, 151, 400 (1989).