Boron Doped Diamond Foil (BDDF) as an Efficient Back Contact for TiO₂ Photoelectrodes

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Abstract: In the present work, we investigate the efficiency of TiO₂ photoelectrode layers on boron doped diamond foil (BDDF) in comparison with a classic conducting glass (FTO) back contact. Crystalline thin TiO₂ layers were prepared on the substrates by two different methods: (i) deposition of metallic Ti thin films followed by thermal oxidation to form TiO₂ (TO-TiO₂), (ii) reactive sputter deposition of TiO₂ thin films and crystallization of these layers (SP-TiO₂). Optimized layers show that TO-TiO₂ films on BDDF deliver a significantly higher incident photon to current efficiency (IPCE) compared to directly sputtered SP-TiO₂ layers and these layers on BDDF also outperform conducting glass (FTO) as a back contact. We ascribe this beneficial effect of the BDDF back contact to the formation of an intermediate conductive phase of Ti-carbides at the TO-TiO₂/BDDF interface.

Introduction

In 1972, Fujishima and Honda exploited the photocatalytic properties of TiO_2 to decompose H_2O to H_2 and O_2 in a photoelectrochemical setting.^[1] In the wake of this finding, TiO_2 over time became the most investigated material for photocatalytic^[2–4] and photoelectrochemical water splitting.^[5–7] This is not only because of the suitable energetics of TiO_2 to generate H_2 under illumination but even more because of the high resistivity of TiO_2 to (photo)corrosion.^[8–10]

TiO_2 is an n-type semiconductor with a band gap of $\sim 3 - 3.2\text{eV}$ and it exhibits a rather low quantum efficiency in its pristine and unbiased state due to rapid recombination of photo-generated electrons and holes. In order to construct photoelectrodes that provide an enhanced separation of photo-generated charge carriers due to an applied electric field, often conductive glass such as FTO or ITO are employed as a back contact to TiO_2 layers.^[7,11–15] On this back contact, titanium dioxide thin films can be fabricated by a range of different methods such as powder blading,^[16] spray pyrolysis, reactive-sputter deposition of TiO_2 ^[15,17] or deposition of Ti metal followed by thermal oxidation.^[18]

In the present work, we investigate the use of an alternative conductive back contact to TiO_2 layers that is BDDF (boron doped diamond foil). Generally, BDD is used as electrodes when a wide working potential window is required to generate highly reactive species while still maintaining a high resistance against corrosion.^[5,19,20] At the same time, the energetics of BDD electrodes seems very suitable as a back contact to TiO_2 . Additionally, for Ti layers deposited on BDD by sufficiently energetic processes, the formation of TiC interphases has been reported. These compounds can act as an ohmic contact^[21,22] between the Ti layer and BDD. In fact, even sputter-deposition of titanium on diamond is reported to form a Ti-C compound directly during deposition.^[22–24]

In this work, to explore BDDF as a back-contact for TiO_2 photoelectrodes, we used two approaches: i) deposition of metallic Ti and subsequent annealing of it to form TiO_2 , and ii) direct reactive sputter deposition of TiO_2 on BDDF. We characterize the photoelectrochemical behavior of the oxide layers on BDDF and compare the results with TiO_2 layers prepared on “classic” fluorine-doped tin oxide (FTO) substrates. We observe a significantly lower charge transfer resistance and highly improved photoelectrochemical performance for the thermally oxidized Ti on BDDF. We ascribe this to TiC formation at the Ti/BDDF interface that then acts as a highly beneficial charge transfer mediating back contact.

Results and Discussion

In a set of preliminary experiments, we explored the feasibility to create defined thermal TiO_2 layers on BDD. For this, we first deposited Ti layers for three different time intervals of 10, 30 and 60s on BDDF (Ti/BDDF) as described in the experimental section and subsequently oxidized the Ti layers in air at 450°C for 3h to form TiO_2 . The SEM images in Figure 1 and S1 show the as-deposited metallic Ti layers on BDDF and the respective layers after thermal oxidation (TO- TiO_2). From the SEM images, the thermal oxide layers form a continuous film, free from defects, and they show good adhesion to the BDDF substrate. The table in Figure 1c gives the layer thicknesses before (as-deposited) and after the heat treatment. It can be seen that the conversion of metallic Ti to oxide occurs with an average thickness expansion factor of 1.84.

c)

Sample	10s deposition	30s deposition	60s deposition
As-deposited (Ti on BDDF)	38 nm	67 nm	92 nm
Annealed (TO- TiO_2 on BDDF)	67 nm	124 nm	177 nm

Figure 1. SEM top and inset cross-section view of TiO_2 layers on conductive BDDF and FTO substrates: (a1) As-deposited Ti on BDDF for 30s (Ti/BDDF) before annealing and (a2) heat treated Ti/BDDF to form a thermal oxide layer on BDDF (TO- TiO_2 /BDDF). Reactive sputter-deposited 120nm TiO_2 on FTO: (b1) before annealing and (b2) after annealing (SP- TiO_2 /FTO). (c) The table illustrates the as-deposited thickness of metallic Ti layers prepared by 10, 30 and 60s deposition and the thickness of thermal oxide layers formed on concerning Ti/BDDF layer after annealing at 450°C for 3h.

Figure 2 and S2 depicts the photocurrent spectra for the different oxides; this includes thermal oxide layers prepared by annealing of Ti layers on BDDF and FTO as well as layers produced by reactive sputtering on BDDF and FTO. The highest photoresponse (IPCE) of all layers is observed for TO-TiO₂/BDDF with an average oxide layer thickness of ~124nm from 30s deposited Ti layer. In order to compare the thermal oxide layers with sputter-deposited layers, we deposited by reactive sputtering a ~120nm thick TiO₂ film on the BDDF substrate (SP-TiO₂/BDD), i.e., with the same thickness that showed the highest IPCE for thermal oxides. To evaluate the contribution of the back-contact, we also fabricated thermal and sputtered oxide layers on FTO substrates (SEM cross-section images of these layers are shown in Figure 1b). From the photoresponse in Figure 2a, it is clear that all layers produced on FTO exhibit an inferior photoresponse than any of the thermal oxide layers on BDDF. The higher photoelectrochemical performance of the thermally oxidized Ti layers than sputter deposited TiO₂ layers on BDDF can be explained by the formation of more conductive Ti_xC_y phases at the oxide and BDDF interface as we will show below.

Figure 2. (a) IPCE data plotted versus wavelength for thermal oxide layers prepared by 10, 30 and 60s deposition of Ti on BDDF and subsequent annealing; thermal oxide layer on FTO (TO-TiO₂/FTO); annealed sputter-deposited TiO₂ on FTO (SP-TiO₂/FTO) and BDDF (SP-TiO₂/BDDF). (b) Photocurrent density recorded under illumination (at a wavelength of 325nm) plotted versus the applied potential for TO-TiO₂/BDDF, TO-TiO₂/FTO, SP-TiO₂/BDDF and SP-TiO₂/FTO layers measured in 0.1M Na₂SO₄ vs Ag/AgCl.

The photocurrents were also recorded as a function of applied potential from -800 to 500mV at a fixed wavelength of 325nm (Figure 2b). For all investigated samples, an onset of photocurrent is observed at a voltage of approximately -200mV vs Ag/AgCl. Apparently, over the entire investigated voltage range, the highest photoresponse was observed for TO-TiO₂/BDD, followed by TO-TiO₂/FTO layer. Also over the entire voltage range, for the reactive-sputtered TiO₂ layers on FTO and BDDF, the photoresponse is substantially lower than for thermally oxidized Ti layers on FTO or BDDF.

Figure 3a gives the X-ray diffraction patterns of as-deposited BDDF, annealed Ti (converted to TiO_2) on BDDF ($\text{TO-TiO}_2/\text{BDDF}$) and annealed sputter-deposited TiO_2 on BDDF ($\text{SP-TiO}_2/\text{BDDF}$). The peaks at 43.92° and 75.3° correspond to the (111) and (220) crystal planes of cubic diamond (JCPDS 006-0675). TiO_2 formed by thermal oxidation of Ti on BDDF ($\text{TO-TiO}_2/\text{BDDF}$) clearly shows a rutile signature at 27.44° , while $\text{SP-TiO}_2/\text{BDDF}$ consists of a mixture of anatase and rutile with peaks located at 25.28° corresponding to the (101) crystal plane of anatase (JCPDS 021-1276) and at the 27.44° rutile peak. In the case of TO-TiO_2 and SP-TiO_2 on FTO, after annealing, both layers are entirely converted to rutile phase as apparent from the XRD in Figure S5 in Supporting Information. This shows that not the different amounts of anatase and rutile phases are key to major differences observed in the photoresponse but that the two major effects are due to the substrate and the formation method of the oxide. Please note that also in the FTO case a deposition of metal followed by thermal oxidation leads to much higher photoresponse. In fact, there are reports that thermal oxidation of Ti metal deposit on FTO leads to a favorable solid-state reaction of metal and FTO, which has been reported to improve the electrical contact and adhesion of the oxide layers.^[18] However, clearly for the thermal layer formed on BDD an even higher IPCE magnitude can be reached than for the corresponding layer on FTO.

Figure 3. (a) XRD patterns of ref-BDDF, TO-TiO_2 and SP-TiO_2 layers on BDDF after annealing at 450°C for 3h (inset shows the XRD pattern between 22 and 29°). (b) XPS survey spectra of ref-BDDF, TO-TiO_2 and SP-TiO_2 layers on BDDF. (c) High-resolution XPS spectra of C1s region for TO-TiO_2 and SP-TiO_2 layers measured at the interface between TiO_2 and BDDF.

A comparison of XPS spectra of reference (ref) BDDF, TO-TiO₂/BDDF and SP-TiO₂/BDDF is shown in Figure 3b, a high resolution C1s XPS spectrum of ref-BDDF layer is shown in Figure S6 in Supporting Information. For the plain BDDF, a strong C1s peak is identified at 284.78eV that corresponds to C-C bonds. The tail at higher binding energies can be assigned to the carbonyl and carboxylic species e.g., C-O/C-N and O-C=O bonds respectively, in line with the literature.^[25] The amount of boron is in the range of ppm and is hence below the detection limit of XPS. The XPS survey spectra of the different oxide peaks for TO and SP samples do not change very much. However, the sputter depth profiles (Figure S7 in Supporting Information) indicate a clear difference in the elemental distributions at the oxide/BDDF interface. The difference is particularly apparent in the high-resolution C1s peak taken at the interface (Figure 3c). Both spectra show a main peak at 284.7eV assigned to the C-C (diamond) bond and a significant tail to low (Ti-C) binding energy of 282.5eV,^[26] particularly pronounced for the TO-TiO₂/BDDF sample. In other words, in the case of thermal oxidation, TiC is formed at the interface. This compound has been reported in the literature as electron transfer mediator on diamond layers.^[21]

Figure 4. Bode impedance and phase angle plot for ref-BDDF, SP-TiO₂/BDDF and TO-TiO₂/BDDF layers (impedance measured in 0.1M Na₂SO₄ at OCP under dark conditions).

Therefore, we measured impedance spectra for TO-TiO₂/BDDF and SP-TiO₂/BDDF in Na₂SO₄ electrolyte (Figure 4a and Table S1 in Supporting Information) to evaluate the charge transfer behaviour of thermal oxide and sputter deposited layers. EIS and its fitting indicate that thermally oxidized TO-TiO₂/BDDF has a significantly lower charge transfer resistance (1.99MΩ/cm²) compared with the sputtered oxide layer on BDDF (11.84MΩ/cm²) substrate. These findings strongly support the crucial role of the TiC layer at the TO-TiO₂ and BDDF interface for an efficient back contact.

Overall, we investigate in the present work the photoresponse of titania layers produced on BDDF and compare them to oxide layers formed on FTO. For both substrates, we find that depositing a metallic Ti layer onto the conductive substrates and subsequent thermal conversion of this metal layer to an oxide (in both cases rutile is formed) leads to much higher photocurrents than direct deposition of TiO₂ layers by reactive sputtering onto the conductive substrates. This can be ascribed to interfacial diffusion and solid-state reactions of the metal with the substrate. In the case of TO-TiO₂/BDDF, we are able to identify an interfacial TiC layer that acts as a beneficial mediator for charge transport at the oxide-BDDF substrate interface. Most remarkable is that this mediated back contact on BDDF leads to a higher incident photon-to-electron conversion yield than on FTO.

Experimental Section

The microcrystalline diamond (001) layers with a boron content of 12550 ppm were fabricated on single crystalline silicon wafers with a diameter of ~15cm using hot filament chemical vapor deposition (HFCVD). Prior to the coating procedure, the surface was seeded with non-conductive nanodiamond crystals ($4.2 \pm 0.5\text{nm}$) that get incorporated into the growing diamond layer. The coating atmosphere was kept constant at 98% H₂ and 2% CH₄ at a pressure of 6mbar. Boron doping was established by a constant flow of 0.4mln of gaseous trimethyl borate throughout the deposition period. A mean area energy of 8.5W/cm² was supplied by tungsten filaments. The deposition was carried out at a mean substrate temperature of 830°C for 230h which resulted in a diamond layer thickness of 76μm. In order to obtain free-standing BDDF layers, the diamond layers were detached from the silicon template as described in the reference.^[27]

Ti thin films were deposited on the BDDF substrate by cathodic arc deposition using an industrial-scale TINA 700 plant by VTD. A base pressure of 5×10^{-5} was established before a constant argon flow rate was set at 50sscm. For Ti deposition, a high purity Ti target was and the target-to-substrate distance of 300mm was maintained during deposition. A deposition time of 30s lead to film thicknesses in the range of 57-77nm (no external heating). Onto 2 x 1.5cm² BDDF substrate, we sputtered metallic Ti layers using three different deposition times of 10, 30 and 60s. Alternatively, the 2 x 1.5cm BDDF samples were used to directly fabricate TiO₂ layers on BDDF by DC magnetron reactive sputtering. The deposition was conducted by utilizing a SP-P-US-6M-32 Createch (Germany) set-up as described in the given reference.^[28] For comparison, deposited layers of metallic Ti and TiO₂ were also prepared on FTO substrates (FTO slides, Solaronix, 7Ωcm). Subsequently, Ti films were oxidized in a tubular furnace at

450°C for 3h in air to produce thermal oxide layers from the metallic Ti – this also provided directly crystallized TiO₂ layers.

The morphology of the samples was investigated with a field-emission scanning electron microscope (FE-SEM S4800 Hitachi). The crystal structure was analysed by X-ray diffraction (XRD, X'pert PhilipsMPD with a Panalytical X'celerator detector, Germany) using graphite monochromized CuK α radiation (wavelength 1.54056Å). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a high-resolution X-ray photoelectron spectrometer (PHI 5600) with monochromatic AlK α radiation (1486.6eV, 300W) for excitation (peaks were shifted to the Ti2p position at 458eV).

For photoelectrochemical characterization, the incident photon to current conversion efficiency (IPCE) was measured in 0.1M Na₂SO₄ by utilizing an Oriel 6365 150 W Xe-lamp equipped with an Oriel Cornerstone 7400 1/8 m monochromator between -800mV to 500mV.^[29]

In order to examine the charge transfer characteristics, electrochemical impedance spectroscopy (EIS; IM6, Zahner, Germany) was performed at open circuit potential (OCP) under dark conditions in 0.1M Na₂SO₄. Measurements were carried out by applying an amplitude of ± 10 mV in the frequency range from 100kHz to 10mHz. The electrochemical and the photoelectrochemical characterizations were carried out in a three-electrode configuration, consisting of TiO₂ on conductive substrate (BDDF or FTO) as a photoanode, platinum counter and Ag/AgCl (3M KCl) as a reference electrode.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] A. Fujishima, K. Honda, *Nature* 1972, 283, 37.

[2] K. E. Karakitsou, X. E. Verykios, *J Phys Chem* 1993, 97, 1184.

[3] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* 2001, 293, 269.

- [4] A. Fujishima, X. Zhang, D. A. Tryk, *Surf Sci Rep* 2008, 63, 515.
- [5] C. Terashima, R. Hishinuma, N. Roy, Y. Sugiyama, S. S. Latthe, K. Nakata, T. Kondo, M. Yuasa, A. Fujishima, *ACS Appl Mater Interfaces* 2016, 8, 1583.
- [6] P. Roy, C. Das, K. Lee, R. Hahn, T. Ruff, M. Moll, P. Schmuki, *J Am Chem Soc* 2011, 133, 5629.
- [7] K. P. Sokol, W. E. Robinson, J. Warnan, N. Kornienko, M. M. Nowaczyk, A. Ruff, J. Z. Zhang, E. Reisner, *Nat Energy* 2018, 3, 944.
- [8] K. Lee, A. Mazare, P. Schmuki, *Chem Rev* 2014, 114, 9385.
- [9] X. Chen, S. S. Mao, *Chem.Rev.* 2007, 107, 2891.
- [10] U. Diebold, *Appl Surf Sci* 2003, 48, 53.
- [11] P. Qin, M. Paulose, M. I. Dar, T. Moehl, N. Arora, P. Gao, O. K. Varghese, M. Grätzel, M. K. Nazeeruddin, *Small* 2015, 11, 5533.
- [12] T. R. B. Foong, Y. Shen, X. Hu, A. Sellinger, *Adv Funct Mater* 2010, 20, 1390.
- [13] M. Grätzel, *J Photochem Photobiol A Chem* 2004, 164, 3.
- [14] J. Yuan, H. Li, S. Gao, Y. Lin, H. Li, *Chem Commun* 2010, 46, 3119.
- [15] D. Luo, K. Nakata, A. Fujishima, S. Liu, *J Photochem Photobiol C Photochem Rev* 2017, 31, 139.
- [16] B. O'Regan, M. Grätzel, *Nature* 1991, 353, 737.
- [17] C. Terashima, R. Hishinuma, N. Roy, Y. Sugiyama, S. S. Latthe, K. Nakata, T. Kondo, M. Yuasa, A. Fujishima, *ACS Appl Mater Interfaces* 2016, 8, 1583.
- [18] J. Krýsa, H. Krýsová, Z. Hubička, Š. Kment, J. Maixner, L. Kavan, *Photochem Photobiol Sci* 2019, 18, 891.
- [19] K. Nakata, T. Ozaki, C. Terashima, A. Fujishima, Y. Einaga, *Angew Chemie Int Ed* 2014, 53, 871.
- [20] J. H. T. Luong, K. B. Male, J. D. Glennon, *Analyst* 2009, 134, 1965.
- [21] S. Kono, T. Teraji, H. Kodama, K. Ichikawa, S. Ohnishi, A. Sawabe, *Diam Relat Mater* 2015, 60, 117.

- [22] T. Tachibana, B. E. Williams, J. T. Glass, *Phys Rev B* 1992, *45*, 11975.
- [23] V. Fisher, D. Gandini, S. Laufer, E. Blank, C. Comninellis, *Electrochim Acta* 1998, *44*, 521.
- [24] X. Chen, G. Chen, F. Gao, P. L. Yue, *Environ Sci Technol* 2003, *37*, 5021.
- [25] N. Simon, G. Charrier, A. M. Gonçalves, D. Aureau, P. Gautier, M. Ndjeri, A. Etcheberry, *Electrochem commun* 2014, *42*, 17.
- [26] W. P. Leroy, C. Detavernier, R. L. Van Meirhaeghe, A. J. Kellock, C. Lavoie, *J Appl Phys* 2006, *99*, 63704.
- [27] M. A. Lodes, F. S. Kachold, S. M. Rosiwal, *Philos Trans R Soc A Math Phys Eng Sci* 2015, *373*, 20140136.
- [28] S. Hejazi, M. Altomare, N. T. Nguyen, S. Mohajernia, M. Lickleder, P. Schmuki, *Appl Mater Today* 2019, *14*, 118.
- [29] S. Ozkan, N. T. Nguyen, A. Mazare, P. Schmuki, *ChemElectroChem* 2018, *5*, 3183.