ACS APPLIED MATERIALS & INTERFACES

Letter

Cite This: ACS Appl. Mater. Interfaces 2019, 11, 2758−2762

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Diversity of TiO_2: Controlling the Molecular and Electronic Structure of Atomic-Layer-Deposited Black TiO_2

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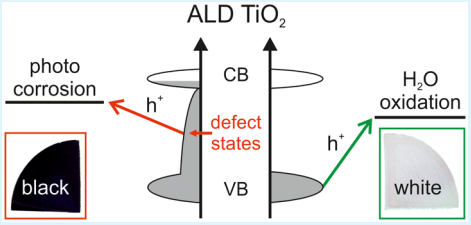
Supporting Information

ABSTRACT: Visually black, electrically leaky, amorphous titania (am-TiO_2) thin films were grown by atomic layer deposition (ALD) for photocatalytic applications. Broad spectral absorbance in the visible range and exceptional conductivity are attributed to trapped Ti^{3+} in the film. Oxidation of Ti^{3+} upon heat treatment leads to a drop in conductivity, a color change from black to white, and crystallization of am-TiO_2. ALD-grown black TiO_2, without any heat treatment, is subject to dissolution in alkaline photoelectrochemical conditions. The best photocatalytic activity for solar water splitting is obtained for completely crystalline white TiO_2.



KEYWORDS: *atomic layer deposition, titanium dioxide, oxide defects, crystallization, protecting overlayers, photocatalysis, water splitting*

Black titania (TiO_2) is a promising material for providing increased photocatalytic efficiency due to its pronounced solar absorption compared to conventional white or transparent, nonconductive TiO_2 with large bandgap (3.0−3.2 eV) which is capable of absorbing light only in the UV range.[1] Black TiO_2 is often synthesized from white TiO_2 via treatment in a reductive H_2 atmosphere that introduces disorder via oxide defects or H dopants into the TiO_2 structure.[1−4] On the other hand, transparent amorphous TiO_2 (am-TiO_2) thin film grown by atomic layer deposition (ALD) has shown exceptional charge transfer properties and is therefore utilized as a protection layer for unstable semiconductor materials in photoelectrochemical (PEC) applications.[5] However, the stability of ALD grown am-TiO_2 under PEC conditions has remained controversial, since most studies have involved an additional catalyst overlayer on am-TiO_2.[6] Recent work by Yu et al.[7] revealed a metastable intermediate within an ALD grown am-TiO_2 thin film on Si photoanode that induced corrosion, despite the additional Ni overlayer. We have shown that bare ALD grown am-TiO_2 is subject to rapid photocorrosion under PEC conditions.[8] Even crystalline TiO_2 that is believed to be extremely stable, has been shown to suffer from photohole induced corrosion under PEC conditions.[9] There is an urgent need for better understanding of the TiO_2 corrosion mechanism to be able to develop TiO_2-based materials for photocatalytic energy conversion devices. Here we report a direct synthesis of black TiO_2 by ALD and address the question of inherent stability of ALD-grown electrically leaky titania.

ALD of TiO_2 was carried out at 200 °C in a commercial ALD reactor using tetrakis(dimethylamido)titanium(IV) (TDMAT) and water as precursors and Ar as carrier/purge/venting gas.[8] N-type Si(100) wafer was used as a substrate with the exceptions of optical and electrical measurements for which a transparent quartz (SiO_2) glass was used as a substrate. The TiO_2 film thickness of 30 nm was optimized in terms of PEC efficiency for water oxidation, and thus chosen for detailed analysis.

Figure 1 shows the UV−vis absorption results of ALD TiO_2 after deposition and after annealing in oxidizing (air) and reducing (UHV) conditions. The oxidized sample depicts characteristic absorption behavior of rutile TiO_2 with absorption edge at 387 nm (3.2 eV) and no absorption in the visible range. In contrast, the absorption edge for the as-deposited TiO_2 was observed at 344 nm (3.6 eV), which is strongly blue-shifted from the absorption edge of rutile TiO_2 and the absorption edge is followed by a broad absorption that gives rise to the black color of the TiO_2 film.

The increased absorption below the band gap energy is characteristic to free charge carrier absorption or absorption due to intraband gap states. The broad absorption of the as-deposited sample following approximately a logarithmic trend from 350 to 800 nm suggests trapped charge carriers within the band gap, which are assigned later to Ti^{3+}.[10] This is supported by the blue-shift in absorption edge compared to rutile TiO_2 which we interpret as the Moss−Burstein effect[11] due to the excess population of the conduction band. Interestingly, annealing under reductive conditions induced a clear decrease in the absorption at 528 nm that corresponds to the absorption of trapped holes in TiO_2.[12] Recently, we showed that the same

Received: November 23, 2018
Accepted: January 4, 2019
Published: January 4, 2019

DOI: 10.1021/acsami.8b20608
ACS Appl. Mater. Interfaces 2019, 11, 2758−2762

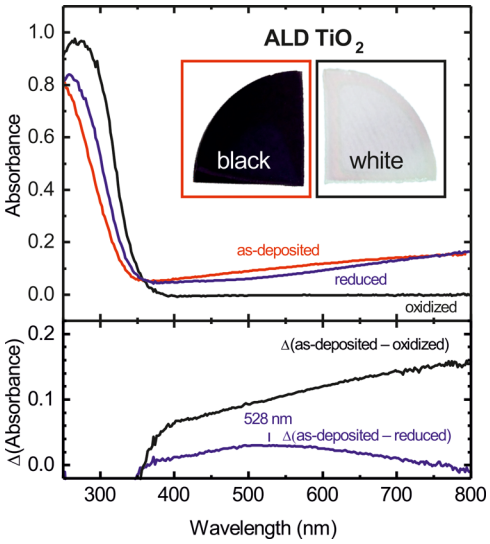


Figure 1. Absorbance of a 30 nm thick black TiO_2 film measured after ALD growth (as-deposited), after annealing in air at 500 °C (oxidized) and after annealing in ultrahigh vacuum (UHV) at 600 °C (reduced). The inset shows pictures of 200 nm thick TiO_2 films after deposition (black) and after annealing in air at 500 °C (white). The difference spectra in the bottom presents the change in absorbance induced by the heat treatments.

reductive heat treatment improved the stability of black am-TiO_2 under PEC conditions, which was attributed to the formation of O^- species via electron transfer from O to Ti.[8] The clear change in optical absorption suggests that the electron transfer is accompanied by the recombination of trapped holes.

Oxidation induced changes on the charge carrier distribution were studied in terms of electrical conductivity and optical absorption as shown in Figure 2. The oxidation treatment was carried out under ambient air by placing the sample into a preheated tube furnace for 45 min. In addition to the aforementioned broad absorbance in the Vis range and enlarged bandgap (Figure 2b, Figure S1) black TiO_2 exhibits exceptionally high conductivity of 150 S/m (Figure 2a). A slight change in the properties was observed upon oxidation at 200 °C followed by more dramatic change for increasing temperatures.

The slight change in the TiO_2 film properties after oxidation at 200 °C is reasonable since the ALD growth was performed at the same temperature. The drastic changes in the electrical and optical properties correlate perfectly with each other and can be explained by the oxidation of the trapped charge carriers that are responsible for the enhanced conductivity and absorption in the Vis range.

Figure 3 shows scanning electron microscope (SEM) images and grazing-incidence X-ray diffraction (GIXRD) patterns for the oxidized samples. The as-deposited black TiO_2 was found to be amorphous followed by gradual crystallization upon oxidation. In addition to rutile, the crystallized films were found to contain some brookite TiO_2, and quite surprisingly, after oxidation at 350 °C a strong anatase peak appeared. X-ray photoelectron spectroscopy (XPS) reveals that nitrogen (1.8 at. %) is segregated onto the surface at 350 °C that coincides with the formation of the anatase phase (Figure 3c inset). This implies that the small ALD residue concentration of nitrogen plays an important role in the phase stabilization of TiO_2 under these oxidative annealing conditions, although complete crystallization into the most stable rutile TiO_2 via less stable anatase TiO_2 is often observed in the annealing treatments of TiO_2.[13] Furthermore, the nitrogen concentration within the black am-TiO_2 structure is most likely contributing to the broad absorption in a range of 500–900 nm shown in Figure 1 by providing nitrogen induced in-gap states.

SEM images (Figure 3a) reveal that crystallization initiates at 250 °C, which is not yet clear from the GIXRD (Figure 3b). Most importantly, crystallization was found to follow the oxidation of the trapped charge carriers.

The influence of oxidation on the molecular and valence band structure of black TiO_2 was studied with XPS and ultraviolet photoelectron spectroscopy (UPS), respectively. Figure 4 shows photoelectron spectra by comparing the as-deposited and 500 °C oxidized samples. It is evident from the XP survey spectra that the surfaces of ALD grown TiO_2 films are clean with a small concentration of carbon, which is mainly due to impurities from the air exposure, and <0.3 at. % of nitrogen (Figure 4a). The Ti 2p XPS transitions appear as peaks in the binding energy range of 450–480 eV (Figure 4c). The main Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks at binding energies of 458.8 and 464.5 eV, respectively, are accompanied by well-known charge transfer shakeup satellite peaks 13 eV above the main peaks.[14] These binding energies and satellite peaks are consistent with the Ti^{4+} state of the TiO_2. In addition, a clear shoulder at the binding energy of 457.5 eV can be seen in the XP spectrum measured from the as-deposited sample. This peak can be assigned to the Ti^{3+}, which can explain the increased absorption in the Vis range[15] and increased conductivity.

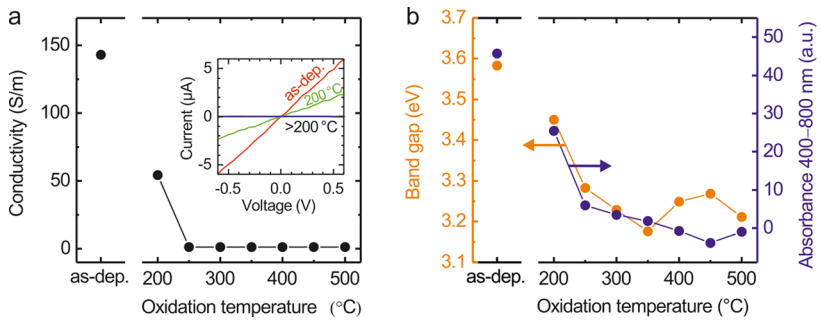


Figure 2. (a) Conductivity and (b) optical band gap and integrated absorbance from 400 to 800 nm for the ALD grown black TiO_2 films after they have been annealed at different oxidation temperatures. Inset in a shows the dramatic change of the *I*–*V* characteristics for the as-deposited TiO_2 film and the TiO_2 films after oxidation treatment at 200 °C and higher temperatures.

DOI: 10.1021/acsami.8b20608
ACS Appl. Mater. Interfaces 2019, 11, 2758–2762

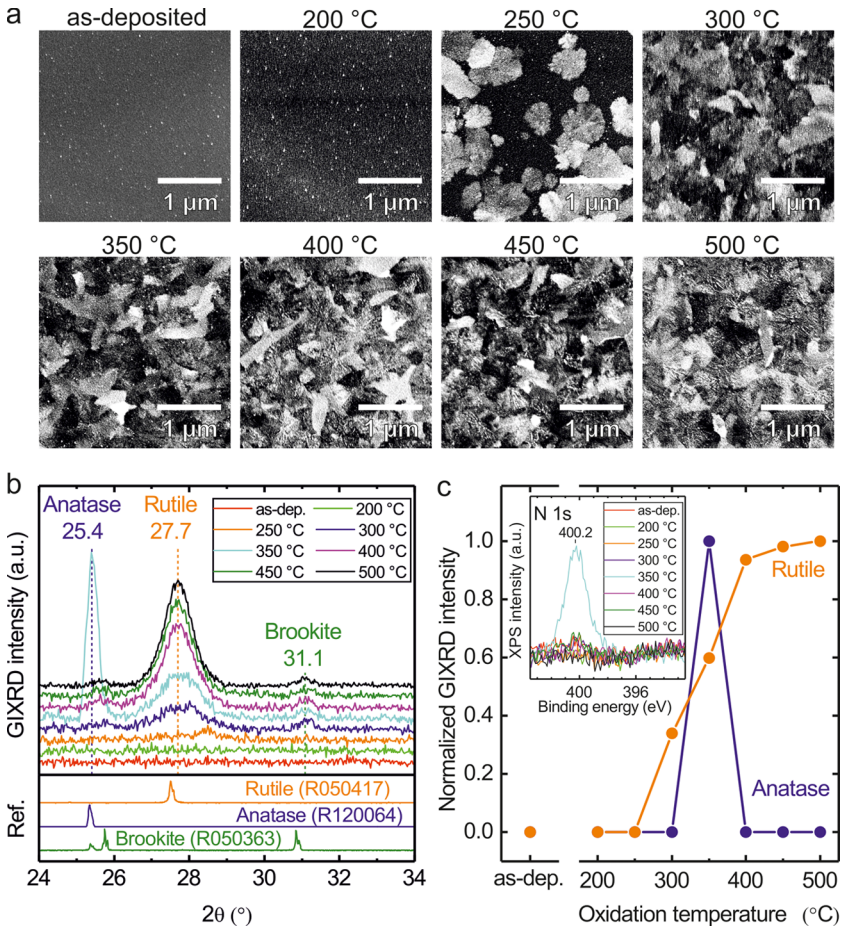


Figure 3. (a) SEM images, (b) GIXRD patterns, and (c) normalized GIXRD intensities of the anatase and rutile peaks for the ALD-grown black TiO_2 films at different oxidation temperatures. Inset in c shows XP spectra of N 1s.

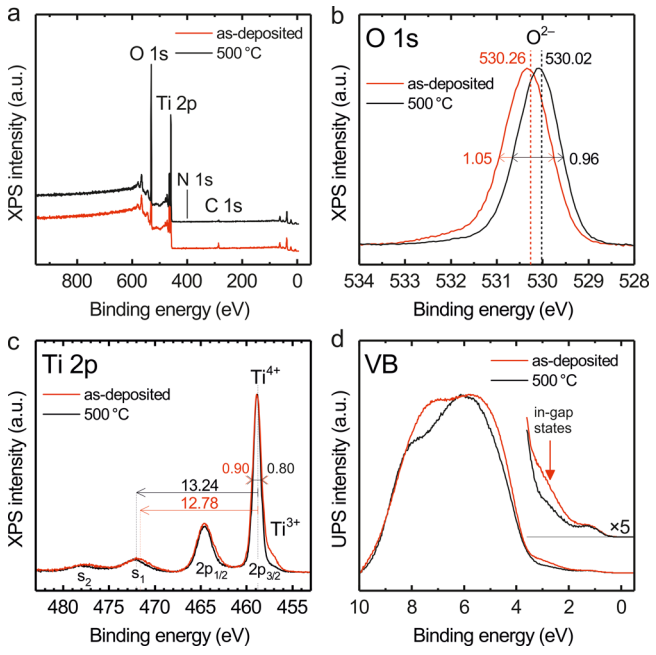


Figure 4. XP (a) survey spectra, (b) O 1s, (c) Ti 2p, and (d) UPS spectra of the valence band (VB) for the ALD-grown black TiO_2 film and 500 °C oxidized film.

The O 1s XPS peak is centered at 530 eV as expected for O^{2-} anions of the TiO_2 structure[16] and the peak is slightly shifted to a lower binding energy upon oxidation (Figure 4b). This 0.2 eV shift and the decrease in the full width at half-maximum (fwhm) of the O 1s and Ti 2p XPS peaks take place gradually with increasing oxidation temperature (Figure S2) and are a result of the ordering of the amorphous phase to the crystalline rutile phase of TiO_2. We note that no such gradual change in neither Ti^{3+} concentration or in O/Ti ratio with temperature was observed (Figure S2a). The majority of Ti^{3+} was oxidized already at 200 °C and the O/Ti ratio was close to 2 throughout the temperature range.

The shakeup satellite peak originates from the excitation of a valence electron to a previously unoccupied state by the outgoing Ti 2p photoelectron according to the sudden approximation of photoemission.[17] Thus, any change in the valence band structure, i.e. Ti−O bonding, may reflect to the charge transfer energy. Indeed, the UPS spectrum of the as-deposited sample (Figure 4d) reveals in-gap states at 2.5 eV that are efficiently removed upon oxidation treatments. Following the removal of in-gap states, the Ti $2p_{3/2}$ shakeup separation energy was observed to increase with oxidation temperature. The changes in the Ti−O bonding are also evident from the changes in the O 1s binding energy as pointed out above. Therefore, the in-gap states can be assigned to the lattice disorder[18] and the subtle deviations in electronic structure compared to crystalline rutile TiO_2 presented above characterize the unique electronic structure of amorphous

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ALD TiO_2. We note that the careful monitoring of the oxidation-treatment-induced changes in the electronic structure allowed the distinction between the doping,[19] $Ti^{2+/3+}$ defects,[8] oxygen vacancies,[20] and the lattice-disorder-induced in-gap states.

The influence of oxidation on the performance of initially black TiO_2 as a photocatalyst for H_2O oxidation was studied as shown in Figure 5 and Figure S3. In accordance with our

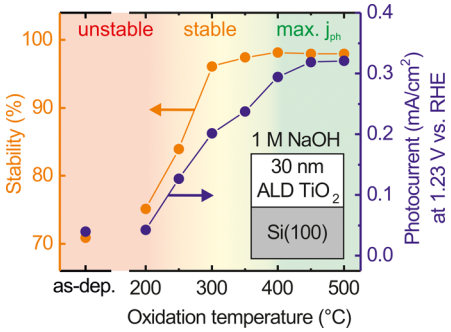

Figure 5. Photoelectrochemical stability and photocurrent (in 1 M NaOH) of the ALD grown, initially black, TiO_2 film after oxidation in temperature range from 200 to 500 °C.

previous work,[8] the as-deposited black TiO_2 exhibits PEC instability and negligible photocurrent at 1.23 V vs RHE in 1 M NaOH. Only slight change in the PEC stability was observed upon oxidation at 200 °C followed by more dramatic change for increasing temperatures. Therefore, the oxidation of trapped charge carriers at 200 °C does not alone provide an explanation for the PEC stability nor for the increase in photocurrent with oxidation temperature. A reasonable stability is obtained after oxidation at 300 °C and above, whereas photocurrent continues to increase reaching saturation value for samples oxidized at >400 °C. The photocurrent was found to improve with the degree of TiO_2 crystallization and reach saturation for crystallized rutile TiO_2.

The improvement in PEC stability was found to correlate with crystallization, which supports earlier results that the stability of crystalline TiO_2 outperforms the amorphous phase.[21] Albeit the complete crystallization of TiO_2 thin film required oxidation at >400 °C, the SEM images (Figure 3a) show that the surface is mostly crystallized already at 300 °C. Thus, the crystallized surface alone is sufficient requirement to endow improved PEC stability to the TiO_2 thin film. Although am-TiO_2 has been shown to both experimentally and theoretically exhibit several orders of magnitude higher dissolution rates in 1 M NaOH than crystalline polymorphs,[22] we emphasize that the stability of black am-TiO_2 can also be improved by controlling the defect distribution.[8]

The unique properties of disordered ALD-TiO_2 include controlling the Ti^{3+} self-doping via growth temperature and thermal modification of defect and crystal structure. Recently we showed that annealing in UHV results in increase in Ti^{3+} states in the film and promotes PEC stability via the formation of O^-.[8] The facile modification treatments manifest the diversity of ALD-TiO_2 in applications ranging from conductive interlayers, to electrically leaky protection layers and photocatalyst materials.

In the present study, we have shown that black TiO_2 with enhanced absorbance in the wavelength range of 400−800 nm can be deposited as a conformal amorphous thin film using ALD. We have demonstrated that the physicochemical properties of TiO_2 can be controlled by postannealing treatments either in reductive or oxidative conditions. The black as-deposited TiO_2 shows exceptionally high electrical conductivity of 150 S/m, but suffers from poor PEC stability and dissolves in alkaline conditions. Annealing treatment in extremely reductive conditions (UHV) at 500 °C transforms the black as-deposited TiO_2 into a photoelectrochemically stable phase of black TiO_2 retaining its amorphous structure.[8] On the other hand, oxidation in air at 500 °C crystallizes TiO_2 into rutile phase with the maximum efficiency as photocatalyst for photoelectrochemical H_2O oxidation. The unprecedented diversity of ALD-TiO_2 can be rationalized by the propensity of the molecular structure toward local changes in the bonding configuration that affects the charge carrier densities via modified electronic structure. This unfolds the tremendous optoelectronic properties of TiO_2.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b20608.

UV−vis absorption, XPS, PEC data as a function of oxidation temperature, and experimental details (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Academy of Finland (decision numbers 141481, 286713 and 309920). H.A. and B.D.B. were supported by the Jenny and Antti Wihuri Foundation. M.H. was supported by the TUT's Graduate School and Emil Aaltonen Foundation.

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