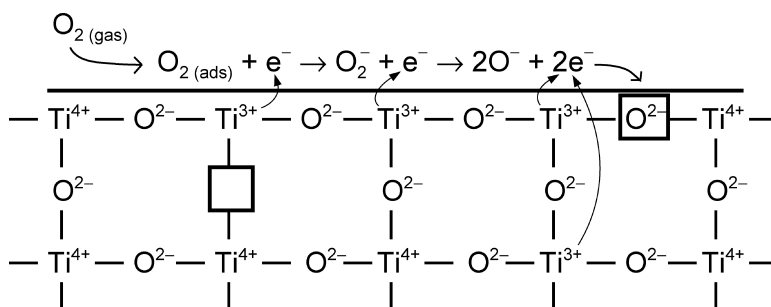


Reactivity of Titanium Dioxide with Oxygen at Room Temperature and the Related Charge Transfer

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Reactivity of Titanium Dioxide with Oxygen at Room Temperature and the Related Charge Transfer

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Abstract: The measurements of electron work function were applied for *in situ* monitoring of the charge transfer during oxidation and reduction for well-defined titanium dioxide, TiO₂, at room temperature. The TiO₂ specimen was initially standardized at 1173 K in the gas phase of controlled oxygen activity, at $p(\text{O}_2) = 10$ Pa, and then cooled down in the same gas phase. The work function changes were monitored during oxidation at room temperature at $p(\text{O}_2) = 75$ kPa and subsequent reduction at $p(\text{O}_2) = 10$ Pa. It is shown that oxidation of TiO₂ at room temperature results in fast oxygen chemisorption, involving initially the formation of singly ionized molecular oxygen species, followed by the formation of singly ionized atomic oxygen species, and subsequent slow oxygen incorporation. Although all these processes lead to work function increase, the components of the work function changes related to the individual processes may be distinguished based on different kinetics. The obtained work function data indicate that oxidation results in rapid surface coverage with singly ionized molecular oxygen species, which are subsequently dissociated leading to the formation of singly ionized atomic species. The related chemisorption equilibria are established within 2 and 5 h, respectively. Oxygen incorporation leads to slow work function changes, which achieve a maximum within 100 h. The determined work function data were assessed by using a theoretical model that describes the electrical effects related to different mechanisms of TiO₂ oxidation. The work function data indicate that oxygen incorporation leads to structural changes of the outermost surface layer resulting, in consequence, in a change of the external work function component. Reimposition of the initial gas phase, $p(\text{O}_2) = 10$ Pa, leads to partial desorption of weakly adsorbed molecular species formed during oxidation.

1. Introduction

Metal oxides exhibit a strong reactivity with oxygen, which is an intrinsic part of the atmosphere. Oxidation of oxides may be considered in terms of oxygen chemisorption and its incorporation into the oxide lattice resulting, in consequence, in a change of properties.^{1,2} Awareness is growing that the effect of oxygen on properties of oxides, especially on their catalytic and photocatalytic properties, may be substantial.³ So far, little is known on this effect.

Oxidation of metal oxides at lower temperatures is mainly limited to physical adsorption.^{2,3} At moderate temperatures, at which the lattice transport is quenched but electronic transitions may be activated, the physically adsorbed species (molecules and/or atoms) become ionized, leading to the formation of several chemisorbed species, such as O⁻ and O₂⁻.² Catalytic and photocatalytic properties of oxides are closely related to the concentration of these species.³ Therefore, knowledge of the mechanism of oxygen chemisorption is essential for understanding of catalytic properties.

Oxidation of oxides at elevated temperatures results in oxygen incorporation into the lattice leading to a change in oxide

nonstoichiometry and the related defect disorder resulting, in consequence, in a change of the chemical potential of electrons.¹ The latter process leads to a change in the ability of the oxide crystal to donate or accept electrons during chemical reactions.

Awareness is growing that properties of oxides are determined by their nonstoichiometry, and the related oxygen activity, rather than by their crystalline structure. In other words, the crystals of the same structure may exhibit a wide range of properties, which are closely related to its nonstoichiometry and the related defect disorder. Therefore, there is a need to understand the effect of nonstoichiometry and defect disorder on properties.

The materials-related data for oxides are well-defined only for specimens obtained by following well-known processing conditions at elevated temperatures, including the temperature, oxygen activity and the rate of cooling. TiO₂ is not an exception. This is the reason why defect-related properties have been studied at elevated temperatures corresponding to the gas/solid equilibrium.¹

Thermodynamically reversible defects are formed/removed during the reaction between oxide lattice and oxygen in the gas phase. The reaction rate depends on temperature. The gas/solid equilibrium for the oxide-oxygen system may be established at elevated temperatures. Then the changes of oxygen activity result in a rapid imposition of new concentration of defects at the gas/solid interface and subsequent propagation of these defects into the bulk. The rate of the latter process, which is diffusion-controlled, increases with temperature. The TiO₂-O₂

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(3) Bielanski, A.; Haber, J. *Catal. Rev. Sci. Eng.* **1979**, *19*, 1-41.

system at room temperature is considered as quenched. Then the defect disorder of the bulk phase and the related properties are independent of oxygen activity in the gas phase. However, the changes of oxygen activity at room temperature may still lead to changes in chemisorption equilibria and the composition of a near-to-surface layer.² The question is: what is the extend of reactivity between the TiO₂ lattice and oxygen at room temperature? The aim of the present work is to address this question.

The reactivity of TiO₂ is strongly influenced by its defect disorder. Therefore, the reactivity-related data are well-defined only for specimens of well-defined defect disorder.

The present work aims to study the reactivity between TiO₂ and oxygen by using the TiO₂ specimen of well-defined oxygen nonstoichiometry and the related defect disorder. The reactivity, and the related charge transfer, will be studied by using the measurements of work function (WF). The specific aim is to assess the mechanism and the kinetics of the interactions between the TiO₂ surface and oxygen, in terms of the related electronic mechanisms. The logical objective of the study is to assess the effect of oxygen on properties of TiO₂ as a photocatalysts.

The experimental part of the present work will be preceded by short outline of several issues that are important for the final message of the study, including:

- (1) Postulation of the Problem. This section will consider the present state of understanding on the effect of oxygen on surface vs bulk properties and the reactivity of TiO₂.
- (2) Literature Overview. This section considers the data on the reactivity between oxygen and the TiO₂ lattice, which have been reported in the literature.
- (3) WF of Oxide Semiconductors. This section provides definitions of terms and the related equations.
- (4) Surface Reactivity Model. This section considers the effect of oxygen on WF of metal oxides.

2. Postulation of the Problem

Titanium dioxide, TiO₂, is a nonstoichiometric compound.¹ Undoped TiO₂ has been commonly considered as an n-type semiconductor.^{1,4,5} Its nonstoichiometry has been represented by the formula TiO_{2-x}, which is consistent with oxygen deficit (the nonstoichiometry, x , is closely related to the concentration of both ionic and electronic defects). The latter term may be related to the chemical potential of electrons, $\mu(e')$:

$$\mu(e') = \mu^0(e') + RT \ln n \quad (1)$$

where n is the concentration of electrons and the terms R and T have their traditional meaning. The term $\mu(e')$ is the key quantity, which determines the ability of TiO₂ to either donate or to accept electrons. Therefore, knowledge of specific processing conditions, and the related oxygen nonstoichiometry, is essential for correct assessment of the reactivity of TiO₂.

Recent studies of the authors have shown that TiO₂ may exhibit both n- and p-type properties.⁶⁻⁸ The latter properties are determined by titanium vacancies.⁸ Then TiO₂ exhibits an apparent oxygen excess (its formula may then be expressed as TiO_{2+x}). Therefore, the general formula, which represents both n- and p-type TiO₂ is TiO_{2 ± x}.

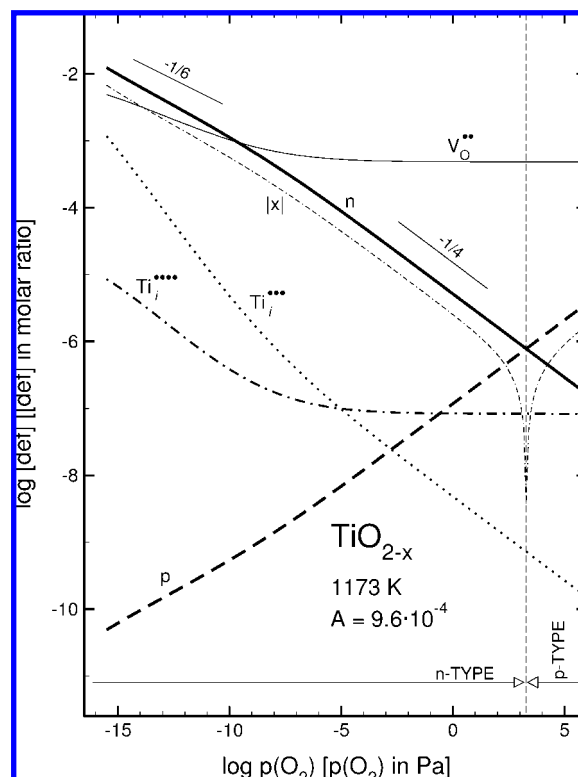


Figure 1. Defect diagram showing the effect of oxygen activity on the concentration of both ionic and electronic defects for TiO₂ at 1173 K (in this case, A is related to the equilibrium concentration of titanium vacancies).⁸

The reactivity in the metal oxide–oxygen system, such as the TiO₂–O₂ system, depends on temperature and the amount and energy of photons, if the system is exposed to light. At lower temperatures, when the transport in the TiO₂ lattice is quenched, the reactivity is limited to the adsorbed layer. Then changes of oxygen activity in the gas phase lead to the formation of different adsorbed oxygen species. As temperature increases, the interactions in the TiO₂–O₂ system initially involve the outermost surface layer, then a near-to-surface layer, and finally the bulk phase. In the latter case, the changes of oxygen activity in the gas phase lead to a fast propagation of the new oxygen activity within the lattice.

The recent studies of the authors led to the determination of the effect of oxygen activity on the concentration of both ionic and electronic defects, which is represented in the form of a diagram shown in Figure 1. As seen, such diagram allows to predict the effect of processing conditions, specifically the isothermal effect of oxygen activity, on the concentration of electronic charge carriers. Similar diagrams may be derived at any temperature corresponding to gas/solid equilibrium and for controlled concentrations of aliovalent ions represented by the quantity A .⁶

The performance of TiO₂-based photoanode in photoelectrochemical cells for water splitting is closely related to its

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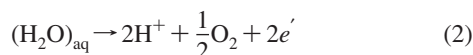
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reactivity with water, leading to its decomposition according to the following reaction.^{9–11}



As seen, the byproduct of this reaction is oxygen. This is the reason why oxygen is an important agent in water splitting. Therefore, knowledge of the mechanism and the kinetics of the reactivity between oxygen and TiO_2 is essential for correct understanding of the performance of TiO_2 as photoelectrode for water splitting and photocatalyst for water purification.

So far, however, little is known on the reactivity of oxygen with the TiO_2 surface at room temperature and its effect on electrical properties. The present work aims at addressing this issue. Specifically, the objective of the present study is to assess the effect of oxygen on surface properties of well-defined TiO_2 in terms of WF measurements. The experimental part of this study will be preceded by the definition of basic terms, such as WF of oxide semiconductors, and basic relationships, such as the effect of oxygen on work function.

The reactivity of TiO_2 with oxygen, and the related WF changes, depend on light conditions as well. The effect of light on WF changes during oxidation and reduction at room temperature will be discussed later (Section 4).

3. Brief Overview of the Literature

The effect of oxygen on surface properties of TiO_2 has been studied by using surface sensitive tools, mainly X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), thermoprogammed desorption (TPD), and WF.^{12–27}

Henrich et al.¹² claimed that exposure of both nearly perfect surface and highly defected surface to oxygen leads to oxygen chemisorption in the form of doubly ionized oxygen ions, O^{2-} . This claim, however, contradicts the report of Bielanski and

Haber,³ who claim that the O^{2-} species are not stable in the adsorbed layer and can only be stabilized by the crystal field. Henrich¹³ claimed that the Ti^{3+} sites are associated with a strong, dissociative adsorption of water, whereas molecular water is present on the perfect TiO_2 surfaces.

Lo et al.¹⁴ reported a complex approach in studies of O_2 chemisorption on oxygen-rich and oxygen-deficient TiO_2 (100) single crystal. They claim that presence of Ti^{3+} sites is of particular importance as these sites are associated with strong, dissociative adsorption of water while molecular water is present on the near-stoichiometric surfaces (the Ti^{3+} rich monolayer is formed on the top of TiO_2 surface that is stable under illumination). Adsorption of water and oxygen on TiO_2 (100) at room temperature at the exposure of 10^5 L results in WF changes by $\Delta\Phi = -0.8$ eV and $\Delta\Phi = 0.2$ eV, respectively, where 1 L is the exposure at 10^{-6} Torr during 1 s ($1 \text{ L} = 1.33 \cdot 10^{-4} \text{ Pa} \cdot \text{s}$). Lo et al. have shown that the TiO_2 disordered surface, induced by Ar sputtering, exhibits larger WF changes ($\Delta\Phi = 0.3$ eV). Henrich^{12,13} reported that water adsorption on defected and perfect TiO_2 at 10^8 L results in WF decrease by $\Delta\Phi = 0.50$ and 0.44 eV, respectively.

Gopel et al.¹⁵ reported that oxygen vacancy forms a complex with two Ti^{3+} ions. They claimed that the oxygen vacancies are the active sites for dissociative adsorption of oxygen and hydrogen at room temperature on the TiO_2 (110) surface. They determined that oxygen chemisorption at $p(\text{O}_2) = 6.7 \cdot 10^{-4}$ Pa and 303 K on TiO_2 , which is outgassed at 600 K and $p(\text{O}_2) = 4 \cdot 10^{-3}$ Pa for 2 h, results in WF changes by 0.25 eV.

Yanagisawa and Ota¹⁶ studied thermal desorption and photostimulated desorption of preadsorbed $^{18}\text{O}_2$. They reported that desorption of O_2 occurs at 530 K whereas photodesorption (UV illumination) already at 300 K. Hugen-Schmidt et al.¹⁷ observed that water adsorption on nearly perfect surface of TiO_2 (110) leads to WF decrease by 1.1 eV whereas only ~ 0.1 eV is related to downward band bending. They also reported the active sites for molecularly adsorbed H_2O are Ti^{4+} sites.

Lu et al.^{18,19} observed two distinct molecular oxygen chemisorption states on the TiO_2 (110) surface, including the α -state, which is formed at 105 K and can be irreversibly converted into the β -state at 250 K, whereas heating above 250 K results in O_2 dissociation.

Henderson et al.^{20–22} observed that annealing of TiO_2 (110) in vacuum above 800 K results in the formation of oxygen vacancies, which are associated with reduced surface cations. They reported that singly ionized molecular oxygen species, O_2^- , are formed on the TiO_2 (110) surface in the temperature range 100 K–300 K at the presence of oxygen vacancies.

Rothschild et al.²³ monitored oxidation of TiO_2 thin films at 473 and 600 K by using the measurements of the electrical conductivity. They observed two-stage oxidation kinetics, involving first stage of a logarithmic kinetics, which is considered in terms of oxygen chemisorption, and the second stage of parabolic kinetics, which is related to oxygen incorporation. Using computer simulation Lara-Castellas et al.^{24,25} have determined that the most stable chemisorption oxygen species on the TiO_2 (110) surface are singly ionized molecular species, O_2^- .

Menetrey et al.^{26,27} observed that dissociative adsorption of water is favored by the presence of oxygen vacancies, which are filled with the oxygen of the water molecule. Consequently, water adsorption leads to the formation of two surface OH groups, one attached to the incorporated oxygen ion and the remaining on a nearby bridging oxygen site.

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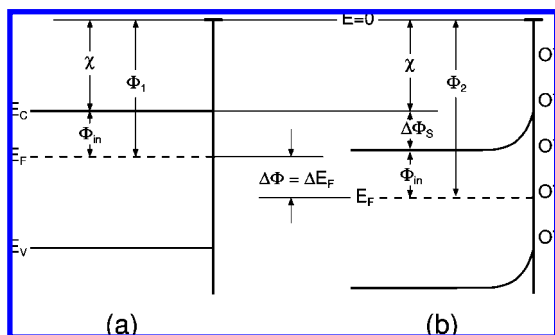


Figure 2. Effect of surface charge, caused by oxygen chemisorption, on work function (WF) for n-type semiconductor: (a) flat band model, (b) the band model representing the effect of oxygen chemisorption on band bending and the related work function component $\Delta\Phi_s$.

The above overview leads to the following general conclusions:

- (1) The reactivity of TiO_2 with both oxygen and water depends on the defect disorder of the surface layer. However, the reported data are incompatible and cannot be compared because the procedures applied to impose defect disorder, for example by ion bombardment, are not reproducible. Therefore, there is a need to assess the effect of defect disorder on reactivity for well-defined specimens.
- (2) There have been conflicting reports on the reactivity between TiO_2 and oxygen. The reactivity at room temperature has been considered in terms of the formation of either $\text{O}_2^{-24,25}$ or O^{2-12} species. The stability of the latter as a chemisorbed species requires verification.
- (3) So far, little is known on the dynamics of the TiO_2 oxidation, the oxidation mechanism and the related charge transfer.

4. Work Function of Oxide Semiconductors

Work function (WF) is the electrical property of the outermost surface layer and is defined as the energy required to remove electron from its Fermi energy position at the surface to the energy level outside the surface. Therefore, WF is reflective of the reactivity of the surface layer and WF measurements may be used for studies of the charge transfer accompanied by chemical reactions at the gas/solid interface, such as chemisorption of gases.^{2,28} Consequently, WF is reflective of the reactivity of the surface layer. Specifically, the WF measurements may be applied for *in situ* determination of the charge transfer at the oxide/oxygen interface, involving oxygen chemisorption and its incorporation into the oxide lattice.^{2,28}

The WF of oxide semiconductors involves the following components:²⁸

$$\Phi = \Phi_{\text{in}} + \Phi_s + \chi \quad (3)$$

where Φ_{in} is the internal WF, Φ_s is the WF component related to band bending, and χ is the external WF. These components are shown in Figure 2a representing a flat band model of an n-type semiconductor.

The internal WF component Φ_{in} is the energy difference between the Fermi energy and the bottom of the conduction band.²⁸ The component Φ_s is related to the surface charge produced either by chemisorption or segregation. This component is shown in Figure 2b representing an n-type semiconductor

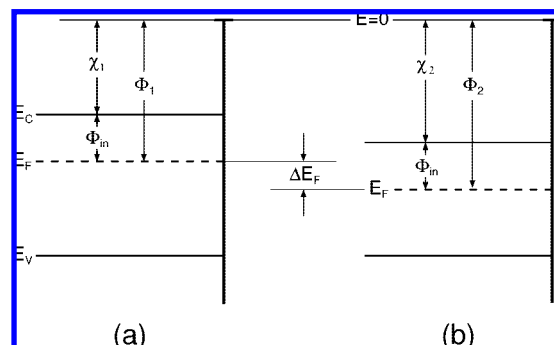


Figure 3. Effect of the external work function component χ on the WF changes for n-type semiconductor: (a) and (b) represent the semiconductors with the same Fermi energy level related to the WF component Φ_{in} and different external WF components χ_1 and χ_2 , respectively.

involving a negative surface charge produced by acceptor-type chemisorbed oxygen species. Therefore, when surface properties are determined by the component Φ_s , the related WF changes may be considered in terms of the concentration and the valency of species at the surface, such as chemisorbed species.

Both adsorption and segregation may be considered in terms of the same concepts and laws. Hence, segregation refers to adsorption in the solid, where species are derived from the lattice, as opposed to adsorption, where species are derived from the gas phase. Although the importance of equilibrium segregation frequently is underestimated, the resultant segregation-induced concentration gradients are in fact a material property and thus have a strong impact on the performance of such materials. Segregation is a diffusional process and so may take place at elevated temperatures at which the lattice elements are sufficiently mobile. Therefore, it is important to recognize that the WF changes at elevated temperatures may also include a component related to segregation. However, the changes of WF at room temperature, when the lattice transport is quenched, are determined mainly by component Φ_s .

The external WF χ is determined by the surface structure.²⁸ Consequently, during chemisorption, leading to changes of Φ_s , the component χ remains constant. Also during oxidation, leading to oxygen incorporation without structural changes, the WF component χ remains constant. In certain cases, however, a change in the concentration of defects may lead to structural changes, which are induced by strong interactions between the defects.^{29,30} The effect of the component χ on WF is represented in Figure 3.

Oxidation and reduction of oxide semiconductors within a single phase regime, result in the WF changes that are determined by the components Φ_{in} and Φ_s , while external WF, χ , remains constant. Therefore:

$$\Delta\Phi = \Delta\Phi_{\text{in}} + \Delta\Phi_s \quad (4)$$

Equation 4 represents the case when oxidation of a metal oxide leads to both oxygen chemisorption and oxygen incorporation. The changes of the WF that are determined by the component $\Delta\Phi_{\text{in}}$ are represented by Figure 4.

It has been shown that oxidation at elevated temperatures is determined by the component $\Delta\Phi_{\text{in}}$ while the component $\Delta\Phi_s$ is negligibly small and, therefore, may be ignored.²⁸ Conversely,

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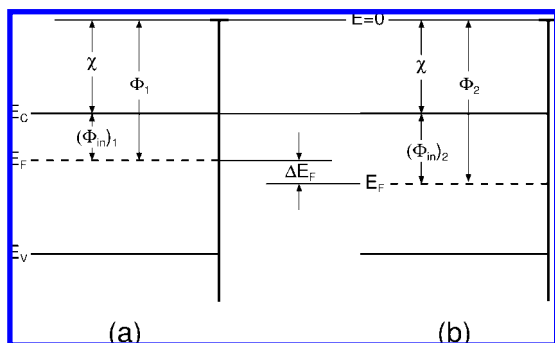


Figure 4. Effect of the internal work function component, Φ_{in} , on WF for n-type semiconductor: (a) and (b) represent semiconductors with high and low Fermi energy levels, respectively.

oxidation of oxides at room temperature results mainly in the WF changes due to the component $\Delta\Phi_s$ while the component $\Delta\Phi_{in}$ may be ignored. Then the WF changes may be considered in terms of the formation of oxygen chemisorbed species.

The effect of oxygen on WF of titanium dioxide has been reported by Figurovskaya et al.³¹ and Bourasseau et al.^{32–37} at room temperature, and by Odier et al.^{38–40} at elevated temperatures.

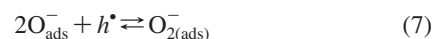
According to Figurovskaya et al.,³¹ oxidation at room temperature for a TiO_2 specimen initially reduced in vacuum, at $p(\text{O}_2) \approx 10^{-4}$ Pa, results in WF increase by 0.7 eV, and subsequent imposition of the vacuum leads to WF decrease by ~ 0.4 eV (Figure 5). Assuming that the WF increase is related to oxygen chemisorption, the observed partial WF decrease during reduction is related to a partial removal of weakly chemisorbed oxygen species, while the remaining electronic effect may be considered in terms of the surface coverage with strongly bonded oxygen species. As seen in Figure 5, at the same time oxidation leads to a decrease of electrical conductivity, which remains not affected by the imposition of reduced conditions. This effect indicates that the changes of the electrical conductivity are caused by the strongly chemisorbed oxygen species.

Extensive studies on the effect of oxygen on WF of TiO_2 , at the presence and absence of light, were reported by Bourasseau et al.^{32–37} This study, which included several experimental regimes (1–6), are summarized in Figure 6.

1. Oxygen at $p(\text{O}_2) = 267$ Pa was admitted at room temperature to the reaction chamber, involving a TiO_2 specimen that was initially outgassed in vacuum ($1.33 \cdot 10^{-4}$ Pa). The observed WF increase was considered in terms of the formation of singly ionized species according to the following subsequent reactions:



2. The specimen was exposed to UV light (in oxygen) leading to the formation of electron–hole pairs. The surface charge results in the transfer of electrons into the bulk phase, while the holes are transferred to the surface. In consequence, the increased activity of electron holes at the surface leads to a shift of the reaction (6) to the left resulting in the initial drop of WF:



3. At the moment corresponding to the minimum of WF (during light-on regime), the rate of the formation of the singly ionized molecular species becomes the predominant surface

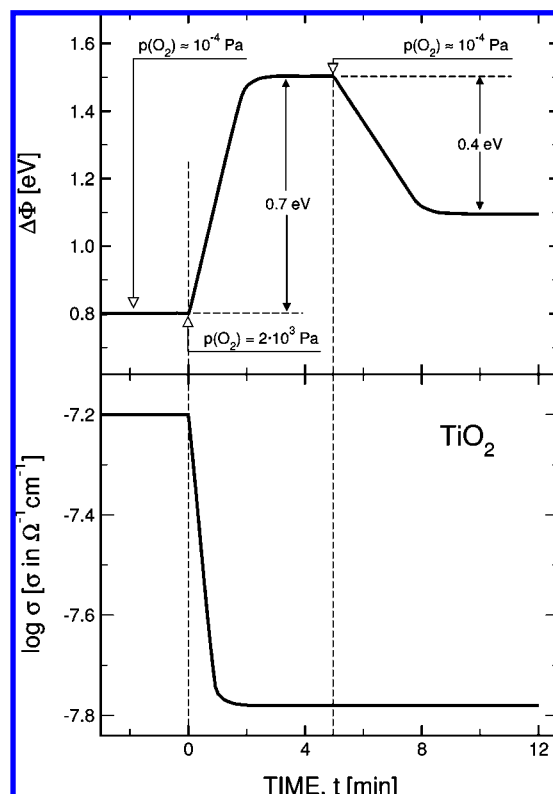


Figure 5. Effect of oxidation and reduction of undoped TiO_2 on WF and electrical conductivity at 298 K, according to Figurovskaya et al.³¹

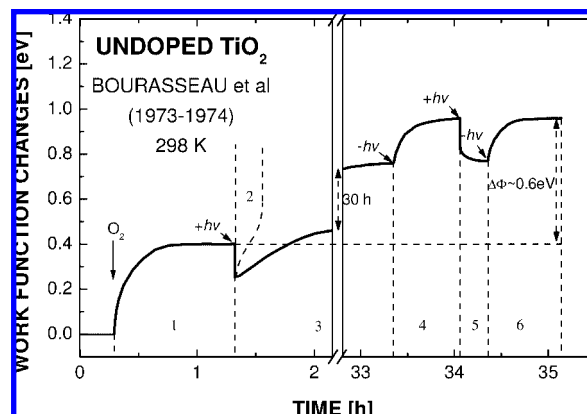


Figure 6. Work function for undoped TiO_2 in oxygen: $p(\text{O}_2) = 267$ Pa and in vacuum: $1.33 \cdot 10^{-4}$ Pa during the light-off and light-on regimes, according to Bourasseau et al.³⁶

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process leading to a slow WF increase over a prolonged period of time (30 h).

4. Imposition of the light-off regime results in the increase of the surface population of O^- species, leading to a decrease of the surface concentration of electron holes and, consequently, leading to WF increase.

5. Reimposition of light-on regime results in restoration of WF to its value prior to the regime (4).

6. Reimposition of the light-off regime results in the same WF change as in the regime (4).

The studies of Odier et al.^{38–40} have determined the effect of oxygen partial pressure and temperature on the WF of TiO_2 at high temperatures. Odier and Loup³⁸ observed that the WF vs oxygen partial pressure dependence at 1670 K exhibits a change of slope at $p(O_2) = \sim 5 \cdot 10^{-3}$ Pa due to aggregation of defects at lower oxygen pressure and the random distribution above this level.

5. Surface Reactivity Model

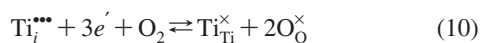
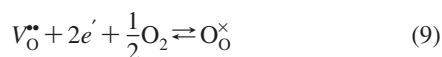
The reactivity between TiO_2 and oxygen may be considered in terms of both oxygen chemisorption or/and its incorporation into the oxide lattice. Oxidation of TiO_2 at lower temperatures, at which the lattice ionic diffusion is quenched, may be considered in terms of physical adsorption. The formation of physically adsorbed oxygen species, which is not accompanied by charge transfer, leads to surface coverage with oxygen species derived from the gas phase:



where $O_{2(gas)}$ and $O_{2(ads)}$ denote molecular oxygen species in the gas phase and in the adsorbed layer, respectively. Because these species are electrically neutral, their formation does not lead to WF changes.

At moderate temperatures the physically adsorbed oxygen species may ionize and subsequently dissociate leading to the formation of singly ionized molecular and atomic oxygen species, which are formed according to equilibria (5) and (6). They are considered weakly and strongly chemisorbed species, respectively.² Consequently, the singly ionized atomic oxygen species are much more difficult to remove from the surface than the singly ionized molecular species. The doubly ionized atomic species, O^{2-} , are stabilized by the crystal field when incorporated into the oxide lattice.³ The formation of all oxygen species leads to WF increase.

Oxygen incorporation, leading to a change in the concentration of thermodynamically reversible point defects, may be represented, using the Kröger-Vink notation,⁴¹ by the following equilibria:⁶



As seen, all these equilibria are interrelated. Oxidation results in a decrease of the concentration of both oxygen vacancies and titanium interstitials and, consequently, a decrease of the concentration of electrons. Therefore, both reactions 9 and 10 result in a reduction of the chemical potential of electrons and,

consequently, an increase of WF. As seen from equilibrium 11, oxidation also leads to the formation of titanium vacancies resulting, in consequence, in a decrease of the concentration of electrons as well. While all the above reactions leads to reduction of the chemical potential of electrons during oxidation, the transition rates of the equilibria 9 and 10 are substantially faster than that for the formation of titanium vacancies.⁴²

6. Effect of Oxygen on Work Function

The effect of $p(O_2)$ on WF of TiO_2 during oxidation may be considered in terms of either the changes in the concentration of chemisorbed oxygen species, and related surface charge, or the concentration of point defects. In the first case, oxidation leads to surface band bending, while the Fermi energy, E_F , in the bulk remains unchanged. In the second case, oxidation results in lowering of the Fermi energy due to reduced concentration of donors (oxygen vacancies and titanium interstitials) and increased concentration of acceptors (titanium vacancies). Quantitative assessment of the WF changes during oxidation requires knowledge of the WF components related to these two effects.

Oxygen incorporation into the lattice of TiO_2 may also be represented by the following general equilibrium:



where O^{2-} represents oxygen ions in the crystal. In equilibrium we have:

$$\Delta G = 2\mu^0(O^{2-}) - \mu^0(O_2) - kT \ln p(O_2) - 4\mu(e') = 0 \quad (13)$$

where $\mu(e') = E_F$. Therefore:

$$\Delta\Phi = -\Delta E_F = \frac{kT}{4} \Delta \ln p(O_2) \quad (14)$$

where k is the Boltzman constant and T is the absolute temperature. Equation 14 may be used for derivation the effect of $p(O_2)$ on WF changes of TiO_2 in terms of oxygen incorporation leading, according to equilibria 9–11, to a decrease in the concentration of electrons. The considerations on the effect of these equilibria on WF are limited to the outermost surface layer since WF is mainly sensitive to this layer.

Oxidation of TiO_2 may also be considered in terms of the following general equilibrium:



where z is the number of electrons involved in the reaction and α is the number of species formed from a single oxygen molecule. In equilibrium the following condition applies:

$$\Delta G = \alpha\mu^0(O_{3-\alpha}^{z/\alpha-}) - \mu^0(O_2) - z\mu(e') - kT \ln p(O_2) + \alpha kT \ln \frac{\Theta_{\alpha,z}}{1 - \sum \Theta_i} = 0 \quad (16)$$

where: ΔG is the free enthalpy change for the reaction 16, $\mu^0(O_{3-\alpha}^{z/\alpha-})$ is the standard chemical potential of chemisorbed oxygen species, $\mu^0(O_2)$ is the standard chemical potential of oxygen, and $\sum \Theta_i$ denotes the total coverage by all oxygen species. Equation 16 may be used for the determination of surface

(41) Kroger, F. A. *The Chemistry of Imperfect Crystals*; North Holland: Amsterdam, 1974; Vol. 3, p 275

(42) Nowotny, M. K.; Bak, T.; Nowotny, J. J. *Phys. Chem. B* **2006**, *110*, 16283.

Table 1. Theoretical Work Function Changes of TiO₂ during Oxidation at 298 K Leading to the Formation of Different Oxygen Species, Including the p(O₂) Change Applied in the Present Work and That Reported by Figurovskaya et al.³¹

oxygen species	number of electrons, z	work function change [eV]	
		Present Work 10 Pa < p(O ₂) < 75 kPa	Figurovskaya et al. ³¹ 1.3·10 ⁻⁴ < p(O ₂) < 2 kPa
O ₂ ⁻	1	0.2291*	0.4178*
O ⁻	2	0.1146*	0.2089*
O ²⁻	4	0.0573	0.1045

* This value corresponds to the total surface coverage

coverage with oxygen chemisorbed species from the WF data. The most stable oxygen chemisorbed species include singly ionized molecular species, O₂⁻, and singly ionized atomic species, O⁻.^{2,3} Therefore:

$$\Sigma\Theta_i = \Theta_1 + \Theta_2 \quad (17)$$

where Θ_1 and Θ_2 denote the fraction of the surface coverage for the species O₂⁻ and O⁻, respectively. Combination of eqs 16 and 17 results in the following expression:

$$E_F = \frac{1}{z} [\alpha\mu^0(\text{O}_{3-\alpha}^{\alpha-}) - \mu^0(\text{O}_2)] - \frac{kT}{z} [\ln p(\text{O}_2) - \alpha \ln \frac{\Theta_{\alpha,z}}{1 - \Theta_1 - \Theta_2}] \quad (18)$$

The effect of oxygen activity on WF of oxide semiconductors may be expressed by the following equation:²⁸

$$\frac{1}{m_\Phi} = \frac{1}{kT} \frac{\partial \Delta\Phi}{\partial \ln p(\text{O}_2)} \quad (19)$$

where m_Φ is the exponent of the p(O₂) dependence of WF. Therefore, assuming that $\Delta\Phi = -\Delta E_F$, we obtain:

$$\frac{1}{m_\Phi} = \frac{1}{z} \left| 1 - \frac{\alpha}{x_{\alpha,z}} \frac{\partial x_{\alpha,z}}{\partial \ln p(\text{O}_2)} \right| \quad (20)$$

where the component $x_{\alpha,z}$, related to the activity of the specific chemisorbed species, is given by:

$$x_{\alpha,z} = \frac{\Theta_{\alpha,z}}{1 - \Theta_1 - \Theta_2} \quad (21)$$

The WF changes during isothermal oxidation of TiO₂ at room temperature according to eq 19, are shown in Table 1 in respect to the specific oxygen species. The data in Table 1 are related to the oxygen activity range applied in the present work: 10 Pa < p(O₂) < 75 kPa, and also to the oxygen activity range applied in the work of Figurovskaya et al.³¹ 1.3·10⁻⁴ Pa < p(O₂) < 2 kPa. As seen, the magnitude of the WF changes is closely related to the number of electrons involved in the formation of these species.

Comparing the WF data resulting from the theoretical model represented by eq 20 and the data in Figure 5, the following points could be made:

(1) Oxidation leads to WF increase by 0.7 eV within 2 min and then it reaches a stable value. The kinetics of the WF changes suggests that oxidation takes place within a single kinetic regime. On the other hand the total WF changes are consistent with the electrical effects predicted with the formation of both types of chemisorbed species (molecular and atomic) as well as oxygen incorporation. The latter process is expected to take place substantially slower than oxygen chemisorption. Therefore, there

is a need to determine the effect of oxidation on the WF data during a prolonged period of time in order to assess whether different kinetic regimes may be distinguished.

(2) The WF changes observed by Figurovskaya et al.³¹ suggest that chemisorption leads to a two-monolayer coverage, the first layer formed of singly ionized atomic species and the second layer consisting of singly ionized molecular species.

(3) The observed changes in electrical conductivity during oxidation are consistent with n-type properties of TiO₂. Again, the electrical conductivity data do not allow to distinguish between different kinetic regimes.

(4) The WF decrease by 0.4 eV during reduction is consistent with the theoretical effect related to desorption of singly ionized molecular species. The difference between the total WF changes during oxidation (0.7 eV) and the WF decrease during reduction (0.7 eV - 0.4 eV = 0.3 eV) suggests that oxidation leading to the formation of singly ionized atomic species and oxygen incorporation is irreversible. However, the latter process requires a verification.

(5) The absence of any changes in electrical conductivity during reduction indicates that removal of singly ionized molecular species does not have any effect on electrical conduction.

(6) The above conclusions require a verification due to the fact that the experimental conditions reported by Figurovskaya et al.³¹ does not include information about the oxygen activity values applied during reduction and oxidation. Therefore, the related theoretical WF data were determined based on a rough estimate of oxygen activities, which might correspond to their experimental conditions described only in general terms, such as "vacuum" and "oxygen admission", which are not defined in terms of the related oxygen activity. Therefore, the oxygen activity data shown in Table 1 and in Figure 5 (1.3·10⁻⁴ Pa during reduction and 2·10³ Pa during oxidation) should be considered as a rough estimate.

The above considerations leads to the following question: *What are the oxidation and reduction mechanisms of TiO₂ at room temperature and the related charge transfer?* The aim of the present work is to address this question through monitoring of the WF changes for well-defined TiO₂ specimen during oxidation and subsequent reduction over a prolonged period of time in well-defined experimental conditions.

7. Experimental Section

7.1. Specimen. The polycrystalline specimens of undoped TiO₂ were prepared from high purity (99.999%) Ti-isopropoxide: Ti[(CH₂)₂CH₂OH]₄. All vessels and containers used for the processing were made of platinum and polypropylene to prevent silicon contamination. Deionized water, in the amount required by the reaction, was slowly added into the Ti-isopropoxide/ethanol mixture leading to precipitation of TiO₂. The powder was cold pressed (200 MPa) into 15 mm diameter pellets and then sintered at 1423 K for 12 h. The scanning electron microscopy micrograph is shown in Figure 7. The total concentration of acceptor-type cation impurities was 33.9 ppm and the concentration of anions (Cl) was 20 ppm.

7.2. High Temperature Kelvin Probe. The WF measurement was based on the principle originally proposed by Kelvin,⁴³ which allows the conversion of a contact potential difference (CPD) between two solids, forming a dynamic capacitor, into an AC signal by bringing the capacitor into vibrations. This method was subsequently improved by Zisman,⁴⁴ Mignolet,⁴⁵ and Besocke and

(43) Lord, Kelvin *Philos. Mag.* **1898**, *46*, 82–120.

(44) Zisman, W. A. *Rev. Sci. Instrum.* **1932**, *3*, 376.

(45) Mignolet, J. C. P. *Farad. Disc. Chem. Soc.* **1950**, *8*, 326.

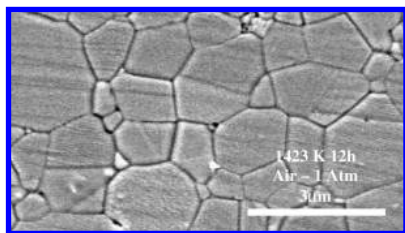


Figure 7. Scanning electron microscope micrograph of the polycrystalline TiO₂ studied in the present work.

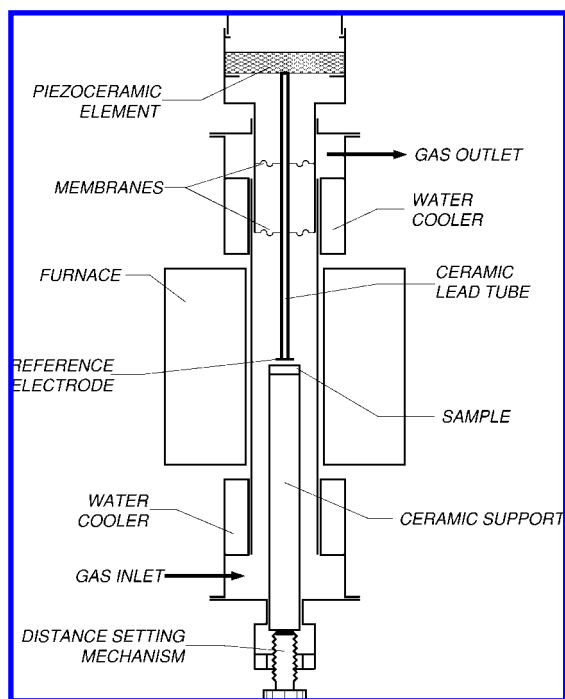


Figure 8. Schematic representation of the Kelvin probe applied in the present work.^{2,28}

Berger.⁴⁶ The solution proposed by Delchar and Tompkins⁴⁷ even allows the determination of the CPD by using a static capacitor.

The High Temperature Kelvin Probe (HTKP) was applied in present study. The HTKP allows *in situ* monitoring of the WF changes at elevated temperatures in a controlled gas phase composition.^{2,28}

The HTKP is shown schematically in Figure 8. The main part of the probe is the vibrating capacitor composed of a lower electrode (formed of the studied specimen) and an upper reference platinum electrode (Figure 9). The distance between the electrodes and the amplitude of vibrations was about 0.1 and 0.07 mm, respectively. The vibrating system, involving a piezo-ceramic element at one end and the Pt reference electrode at the other end, was suspended on two stainless steel membranes. The lower part of the probe was equipped with a micrometer for controlling the distance between the electrodes. Both lower and upper parts of the probe were equipped with water coolers to prevent these parts from overheating above 320 K when the dynamic capacitor is heated to high temperatures. The HTKP allows to determine the WF changes with an accuracy of 0.5 meV.

The WF changes may be determined by the measurements of the contact potential difference, CPD, which is equal to the difference between the WF values of the studied specimen and of the reference electrode, Φ_R :

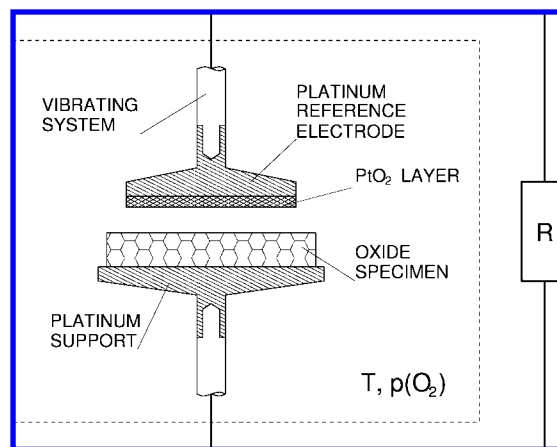


Figure 9. Entrance circuit for the WF measurements, including the dynamic capacitor.

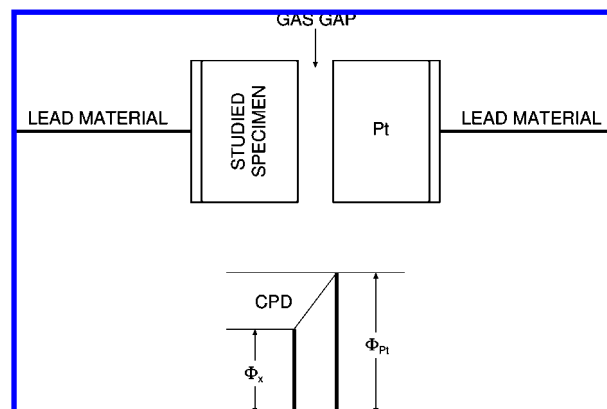


Figure 10. Formation of the contact potential difference, CPD, between the studied specimen and a Pt reference electrode, according to Wagner.⁴⁸

$$\text{CPD} = \frac{1}{e}(\Phi - \Phi_R) \quad (22)$$

The formation of the CPD is shown in Figure 10.⁴⁸ Platinum was applied in the present work as the reference electrode. It was shown that oxidation of Pt leads to the formation of a PtO₂ layer on the surface of Pt.²⁸ Therefore, the WF changes of platinum should be considered in terms of the electrical properties of the PtO₂ surface layer, which are expressed by eq 14.

The WF changes of the Pt reference electrode at room temperature may be ignored compared to the WF changes of metal oxides.^{28,31}

According to eq 22, the WF changes of the studied specimen, $\Delta\Phi_x$, may be determined from the CPD data only when the WF changes of the reference electrode are known:

$$\Delta\Phi_x = e(\Delta\text{CPD}) + \Delta\Phi_R \quad (23)$$

In certain conditions, when the WF changes of the reference electrode can be ignored, the WF changes of the studied specimen are equal to the changes of the CPD.²⁸

7.3. Procedure. Desired oxygen activity in the reaction chamber of the Kelvin probe was achieved using either oxygen or argon flowing through the chamber with the velocity rate of 50 mL/min (the oxygen activities imposed by these gases were 75 kPa and 10 Pa, respectively). The reaction gas entered the bottom of the probe's high temperature chamber and was removed at the upper part of the probe. Oxygen activity in the gas mixture was determined using zirconia oxygen gauge at the exit from the probe. The experiments

(46) Besocke, K.; Berger, S. *Rev. Sci. Instrum.* **1976**, *47*, 840.

(47) Delchar, T.; Tompkins, F. C. *Surf. Sci.* **1967**, *8*, 165.

(48) Wagner, C. Personal correspondence to J. Nowotny, 2 June 1977

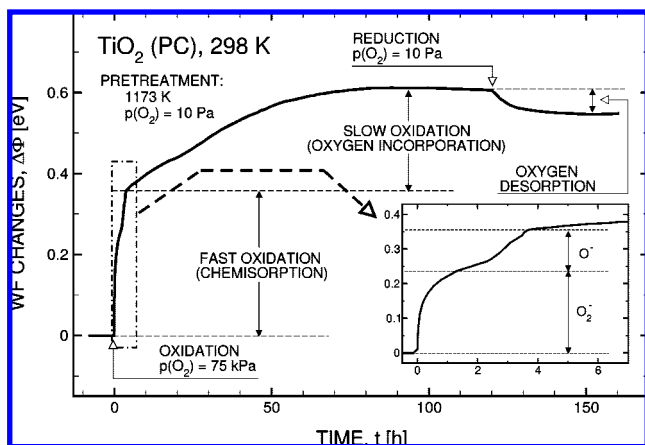


Figure 11. Work function changes of TiO_2 specimen during oxidation and reduction at room temperature.

when $p(\text{O}_2)$ was increased (argon was replaced with oxygen) were termed oxidation experiments. The reduction experiments were when $p(\text{O}_2)$ was reduced.

8. Results and Discussion

8.1. Standardization. The properties of metal oxides at room temperature, including WF, depends essentially on its pretreatment conditions, including annealing conditions at elevated temperatures and the conditions of cooling. Therefore, the WF data of the TiO_2 specimen at room temperature are well-defined only when the specimen has been initially annealed at elevated temperature in the gas phase of controlled oxygen activity and subsequently cooled with controlled rate in the same gas phase. Therefore, the aim of the initial standardization of the studied TiO_2 specimen at 1173 K in the gas phase of controlled oxygen activity, $p(\text{O}_2) = 10$ Pa, was to impose a well-defined oxygen activity in the specimen and the related defect disorder, which is shown in Figure 1.⁸ While cooling results in a change of the concentration of defects, especially of electronic defects that are trapped on ionic defects, the application of well-defined standardization conditions and reproducible cooling conditions allows to obtain reproducible properties of the TiO_2 specimen after cooling. Most importantly, well-defined standardization and cooling procedure allows to achieve the TiO_2 specimen with well-defined chemical potential of electrons and reactivity. As shown above, the reactivity with oxygen at room temperature, and the related charge transfer, may be monitored by the WF changes during oxidation and reduction. The related WF changes are shown in Figure 11.⁴⁹

8.2. Oxidation and Reduction. As seen in Figure 11, the rate of the WF changes during oxidation allows to distinguish the following two kinetic regimes:

- (1) Fast WF increase, taking place within 4 h, which is related to oxygen chemisorption.
- (2) Slow WF increase, leading to a saturation and the total WF change at the level of ~ 0.61 eV. The latter effect is related to oxygen incorporation.

The observed decrease of the WF after oxidation at $p(\text{O}_2) = 75$ kPa, induced by a decrease of oxygen activity to $p(\text{O}_2) = 10$ Pa, will be considered in terms of desorption of the weakly chemisorbed oxygen species.

As seen in Figure 11, the observed fast WF changes may be considered within two kinetic regimes; the first lasting 1–2 h and the second one, related to slower WF changes, lasting 2 h. As seen in Table 1, the initial rapid WF increase by 0.23 eV, is

consistent with the formation of singly ionized molecular species, which are considered as a weak type of oxygen chemisorption. The subsequent slower WF increase by ~ 0.12 eV is consistent with the formation of singly ionized atomic species.

As seen in Figure 11, the relatively fast WF changes within the initial 4–5 h, are followed by very slow WF increase. On one hand, the observed kinetics of the WF changes is consistent with the oxygen incorporation kinetics expected at room temperature. However, the related electrical effect (~ 0.26 eV) is substantially larger than the theoretical electrical effect, determined by eq 14, which is related to oxygen incorporation ($\Delta\Phi = 0.0573$ eV). The discrepancy between the theory, derived for the ideal model assuming that oxidation does not lead to changes of the external WF, indicates that this assumption is not valid in the case under the present consideration. In other words, the observed effect is consistent with the assumption that oxidation leads to substantial structural changes within the outermost surface layer, which are induced by strong interactions between defects.

As seen, the imposition of reduced gas phase composition, $p(\text{O}_2) = 10$ Pa, results in a WF decrease by 0.03 eV, which is caused by desorption of predominantly weakly bonded form of oxygen species. The value of the WF changes, which is only a fraction ($\sim 14\%$) of that observed during oxidation, is reflective of the reversible type of oxygen chemisorption, while the remaining part is related to oxygen species chemisorbed irreversibly.

8.3. Impact on Catalytic Properties. Oxygen plays an important role in TiO_2 photocatalysis. One of the basic cathodic reactions involves the formation of singly ionized molecular species, O_2^- .^{4,50} These species are formed according to equilibrium 5. According to Bourasseau et al.,^{32–37} the singly ionized molecular species are also formed by light-induced oxidation of the singly ionized atomic species, represented by the shift of equilibrium 6 to the left. The data obtained in the present work allow to make the following conclusions about the effect of oxygen on properties of TiO_2 :

- (1) Oxidation leads to rapid formation of the singly ionized molecular species. These species are weakly bonded to the surface.
- (2) In dark conditions the singly ionized molecular species are subsequently transformed into the singly ionized atomic species, which are irreversibly bonded to the TiO_2 surface. Under light, these species have the tendency to be converted into the singly ionized molecular species.
- (3) Prolonged oxidation of TiO_2 in dark conditions results in slow oxygen incorporation into the TiO_2 lattice leading to a change of its defect disorder, the related chemical potential of electrons and reactivity.
- (4) One may expect that light will lead to the shift of equilibria 5 and 6 to the left, resulting in consequence in oxygen desorption. Prolonged exposure to light may even lead to oxygen removal from lattice sites, however, this process is extremely slow and as such may be ignored.

9. Conclusions

It was shown that WF is a surface sensitive electrical property, which may be used for *in situ* monitoring of the reactions taking

(49) Bak, T.; Nowotny, J.; Nowotny, M. K.; Sheppard, L. R. *Int. J. Ionics* **2006**, *12*, 247–251.

(50) Nakato, Y.; Akanuma, H.; Magari, Y.; Yae, S.; Shimizu, J. I.; Mori, H. *J. Phys. Chem. B* **1997**, *101*, 4934.

place at the surface of oxide semiconductors, such as TiO_2 . The related WF changes during oxidation and reduction may be assessed in terms of the reactivity mechanisms and the related charge transfer.

The WF data determined in the present work indicate that oxidation of undoped titanium dioxide at room temperature leads to rapid oxygen chemisorption, resulting in the formation of singly ionized molecular and atomic oxygen species, and subsequent slow oxygen incorporation. Full surface coverage with the chemisorbed molecular and atomic oxygen species can be achieved within 2 and 5 h, respectively. It is argued that subsequent oxygen incorporation leads to structural changes within the outermost surface layer resulting, in consequence,

in a change of the external work function component. These structural changes are most likely due to the changes in the interactions between point defects, leading to the formation of larger defect aggregates. Reimposition of the initial gas phase composition before oxidation, $p(\text{O}_2) = 10 \text{ Pa}$, leads to a partial removal of weakly adsorbed singly ionized molecular species.

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