Interdependence of electroformation and hydrogen incorporation in titanium dioxide

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Nanoporous titanium dioxide films are exposed to molecular hydrogen gas during electroformation. In addition to the usual reversible increase of the conductance of the films as hydrogen is offered, an irreversible decrease of the conductance is observed. The behavior is interpreted in terms of a phenomenological model where current carrying, oxygen-deficient filaments form inside the TiO$_2$ matrix in which hydrogen incorporation decreases the carrier density.

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Titanium dioxide is one of the most intensely studied metal oxides in present research. Besides its tremendous relevance in fundamental science related to transition metal oxides,[1,2] it has also shown a wide spectrum of phenomena as diverse as photocatalysis,[3] photovoltaic activity,[4] doping-induced ferromagnetism,[5] or electrochromism.[6] Two of the most important potential applications of TiO$_2$ are electroformation,[7,8] i.e., a dependence of the sample conductance on the charge that has flown through it, and sensing of various gases.[2] The experimental conditions for studying electroformation-based effects like memristive switching[9,10] or operation of artificial synapses[11], and for the detection of gases[12,13] are very similar. Typically, in both experiments, a DC voltage is applied to two electrodes with TiO$_2$ in a suitable structural composition in between, and the current is measured as a function of some controlled parameters like the voltage amplitude or the concentration of the gas to be sensed. So far, electroformation and gas sensing have been studied separately, while the question whether there is an interdependence between gas sensing and electroformation in this material appears self-evident. This is not only of fundamental interest, but also relates to established as well as possible future applications. For example, electroformation may be one reason for drift effects in gas sensors, or the coupling strength an artificial synapse provides may be controllable by atmospheric additives. A suitable demonstration system for studying such an interdependence should show electroformation in response to applied voltages and sense an offered gas on a similar time scale. Also, in order to study the dynamics of the responses, the system should react with sufficiently large time constants.

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Here, it is demonstrated that these requirements are
well met by nanoporous titanium dioxide films $^{15,17}$ of $5 \mu m$ thickness, exposed hydrogen of low volume fraction ($c \lesssim 250$ ppm), the demonstration system at our focus. After describing the sample preparation and the experimental setup, we present the measurements and interpretation within a conventional picture based on the formation of conductive filaments which are embedded in a more insulating TiO$_2$ matrix and contain nonstoichiometric, reduced titanium oxide TiO$_{2-\delta}$ with $0 < \delta < 1$.

A commercially available Ti foil (purity 99.6%) of $125 \mu m$ thickness is anodically oxidized at room temperature in a solution of 75% H$_2$SO$_4$ in DI water. A voltage source provides the oxidation voltage which was increased in steps with a current limitation of 200 mA. The growth was stopped at a voltage of 150 V. The temperature of the electrolyte is kept below 30°C. This produces a nanoporous oxide layer of about $5 \mu m$ thickness, composed of a mixture of mostly rutile with a small admixture of anatase. $^{17}$ The oxide surface is coated with Pt paste yielding a contact area of $3 \times 3 \times 5 mm^2$. The sample morphology before and after Pt coating is shown in the inset of Fig. 1 (a).

The sample is mounted into a chip carrier and inserted in a measurement chamber with controlled temperature and atmosphere. Prior to each measurement sequence, the sample is heated to $180^\circ$C in synthetic dry air for six hours. In order to start the experiments from a well-defined state, we initialize the sample before each measurement sequence as follows. The grounded sample is exposed to dry air for one hour at $T = 180^\circ$C. Detailed microscopic studies on single crystalline TiO$_2$(110) surfaces indicate a complicated interplay between surface defects and adsorbed O$_2$. $^{18}$ In our system, exposure to O$_2$ heals the point defects partially and leaves the sample in a weakly reduced state. Afterwards, a voltage of $V = -30 V$ is applied to the Pt electrode with respect to the grounded Ti substrate for 12 hours, again in dry air. During this time, electroformation is expected to drive oxygen ions (O$^{2-}$) towards the Ti substrate, where they may leave the film. $^{19}$ The resulting oxygen vacancies, which act as donors, $^{20}$ drift towards the Pt cathode. Following the widely used model of electroformation in comparable systems, $^{8,10}$ it is assumed that filaments form inside a titanium dioxide matrix which predominantly carry the current. They are composed of two phases in series with different values of $\delta$, a phase 1 of high conductivity $\sigma_1$ (larger $\delta$) and a phase 2 with a lower conductivity $\sigma_2$, $^{21}$ see the inset in Fig. 1 (a). After initialization, the phase boundary, located at $x_b$, thus resides close to the Pt electrode, and the sample has a low conductance. All subsequent experiments are carried out at room temperature, in the dark and in a nitrogen atmosphere (99.999%) to which molecular hydrogen is added via a gas flow controller.

The sample initialized this way shows both typical hydrogen sensing behavior $^{14,16,21}$ and electroformation, as illustrated in Fig. 1. The current response to a closed loop variation of the applied voltage from $-10 V$ to $10 V$ and back is hysteretic, see Fig. 1 (a), indicating electroformation. $^{22,23}$ When positive voltages are applied,
the current increase is consistent with a drift of the donor-like defects oxygen vacancies towards the Ti electrode, and with them the phase boundary in the filament. As the voltage sweep direction is reversed at $V = 10$ V, phase 1 continues to grow and the current keeps increasing. The absence of a significant hysteresis for negative voltages can be explained by a negatively biased Pt/TiO$_{2-\delta}$ Schottky barrier, which decreases the electric field at the phase boundary. In the following, we concentrate on studies under positive, time-independent bias voltages, where the Schottky barrier is open and electroformation manifests itself as a current that increases with time $t$, see Fig. 4(b). For $V < 2$ V, we find that the current is approximately constant over our measurement periods (up to 3 hours). This corresponds to an electric field of $\approx 4 \times 10^5$ V/m, below which electroformation is negligible over the time scales of relevance here. For $V = 10$ V, the current increases by approximately two orders of magnitude as time proceeds. Saturation is reached after 20 to 90 minutes, depending on the measurement, and afterwards, the current is slightly decreasing. While the shape of this current function is reproducible, its amplitude varies up to a factor of 100. In addition, some of these traces reveal current jumps and varying noise levels (not shown). This phenomenology indicates that some, but not excessively many, filaments with varying properties are formed in a configuration that differs among nominally identical measurement sequences. Within the model system composed of just one filament as sketched above, the current saturation corresponds to the state where phase 1 extends across the whole filament ($x_b = d$).

The sample also responds sensitively to atmospheric hydrogen, with a detection threshold of molecular hydrogen volume fractions $c({\text{H}_2})$ in the atmosphere well below 15 ppm, see the inset of Fig. 1(b). Here, the bias voltage was 1 V. This response is well known in comparable samples [15, 16, 24]. Even though the details of the sensing mechanism are not yet fully understood, 24, 25 it is widely accepted that the molecular hydrogen splits catalytically at the Pt film, and the H atoms diffuse into the TiO$_{2-\delta}$ [14, 20] where they occupy either interstitial or substitutional places. 27, 28 Interstitial hydrogen forms O-H groups with the oxygen of the host crystal and acts as donor. 29, 31 with a corresponding increase of the conductivity. The time constant of the approximately exponential current change is $\approx 2$ min for $c({\text{H}_2}) = 15$ ppm and decreases rapidly as $c({\text{H}_2})$ is increased, and the sensing is essentially reversible. The sensing response is superimposed to a slowly increasing current background, which we attribute to incomplete recovery after hydrogen is turned off, possibly in combination with irreversible processes.

In Fig. 2(a), the current in response to $V = 10$ V is shown as a function of time in the interval where the electroformation increases the conductance. The sample is exposed to a sequence of hydrogen pulses of 3 min. duration with a period of 18 min., and $c({\text{H}_2})$ is varied between 15 ppm and 250 ppm. In response to the first hydrogen pulse, offered at $t \approx 1$ min., the current first decreases and then begins to increase. This decrease can become larger than one order of magnitude. For $c({\text{H}_2}) < 100$ ppm, it dominates the overall behavior and the conventional sensing response is not observed. Only for $c({\text{H}_2}) \geq 100$ ppm, a current peak starts to develop shortly after the drop. The negative response gets faster as $c({\text{H}_2})$ is increased, while its amplitude shows no correlation with the hydrogen volume fraction and also fluctuates among measurement traces under nominally identical conditions (not shown). The effect is still visible in response to the second hydrogen pulse, but only for $c({\text{H}_2}) \leq 60$ ppm. Afterwards, the sample responds to hydrogen pulses by the well-known increase of the current. [15, 16, 24] Furthermore, for $c({\text{H}_2}) \leq 30$ ppm, hydrogen sensing and electroformation appear approximately as a superposition, while for larger hydrogen volume fractions, no further increase of the current due to electroformation can be observed after the first or second hydrogen pulse. This indicates that compared to the time dependence in inert atmosphere, the exposure to hydrogen accelerates the electroformation.

We proceed by studying how the sample reacts to $\text{H}_2$ after the current has reached its maximum undisturbed by hydrogen exposure, i.e. when $x_3 = d$ in our model system, see Fig. 2(b). Again, an initial decrease of the current in response to the first $\text{H}_2$ pulse is observed, which is pronounced for $c({\text{H}_2}) = 15$ ppm and 30 ppm, but barely visible at larger volume fractions. Occasionally, this decrease is quite dramatic, as illustrated in Fig. 2(d), where the current decreases by a factor of 16. For subsequent hydrogen pulses, this decrease vanishes rapidly as observed for smaller waiting periods, and two responses of opposite sign are observed. In addition to the current increase, a simultaneous process takes place that decreases the current continuously in the presence of hydrogen. This manifests itself in current plateaus between the hydrogen pulses that form steps towards smaller currents as time proceeds. While the positive response is essentially reversible, this additional decrease of the conductance is irreversible but can be reset by our initialization procedure. This interplay is well illustrated by the evolution of the current during a long hydrogen pulse, see Fig. 2(e). Here, $c({\text{H}_2}) = 0$ ppm was applied for 15 minutes. After the initial increase of the current, an approximately linear decrease is observed which stops when $\text{H}_2$ is turned off. Furthermore, for very low hydrogen volume fraction, the current plateaus in between two hydrogen pulses develop a small positive slope as a function of time.

Clearly, electroformation and hydrogen sensing films are interdependent in this system. We interpret this behavior in terms of a phenomenological model and support it by numerical simulations of the electroformation process under hydrogen exposure. First of all, a decrease
of the conductance of TiO$_2$ or weakly reduced TiO$_{2−δ}$ in response to hydrogen exposure is not to be expected, considering that interstitial hydrogen acts as donor. [28, 31] We therefore assign the observed decrease of the current to the reduced phase 1 in our model system, see Fig. 1(a). One possible mechanism is the substitutional occupation of oxygen vacancies by hydrogen, which has been suggested to localize one of the two delocalized electrons from the oxygen vacancy, thereby decreasing the electron density in the conduction band. Furthermore, since the binding energy of a hydrogen-oxygen vacancy complex has been calculated to be 0.49 eV larger than that of one of the oxygen vacancy, this complex is expected to be quite stable, in agreement with the observed irreversibility.

![FIG. 3](Color online). (a) Simulations of the evolution of the current and the phase boundary in a filament if only an exponential increase of the conductivity (time constant of $τ_A = 200$ s) by hydrogen exposure is assumed. $τ_A$ is also the recovery time after H$_2$ is turned off. The initial conductivities are chosen as $σ_1(t = 0) = 6 \times 10^{-12}$ Sm and $σ_2(c_3, t = 0) = 2 \times 10^{-12}$ Sm, and the final values are $σ_1(c_3, t = ∞) = 7.5 \times 10^{-12}$ Sm and $σ_2(t = ∞) = 3.5 \times 10^{-12}$ Sm, corresponding to a hydrogen volume fraction $c_3$. (b) Simulation as in (a), but with the additional mechanism B included that decreases the conductivity of phase 1 exponentially with a time constant of $τ_B = 10$ s to values $σ_1(c_3, t = ∞) = 4.67 \times 10^{-12}$ Sm, $σ_1(c_3, t = ∞) = 4.2 \times 10^{-12}$ Sm and $σ_1(c_3, t = ∞) = 4.1 \times 10^{-12}$ Sm, while the values for phase 2 are $σ_2(c_3, t = ∞) = 2.6 \times 10^{-12}$ Sm and $σ_2(c_3, t = ∞) = 2.2 \times 10^{-12}$ Sm.

Within the simple model for electroformation based on drifting oxygen vacancies, the velocity $v$ of the phase boundary located at $x_b(t)$ is determined by the electric field in phase 1. It appears plausible that as hydrogen is offered, the conductivity ratio $σ_2/σ_1$ increases, since the interstitial hydrogen incorporation (mechanism A) will take place on both phases, leading to identical conductivity contributions. Consequently, the current increases and the electric field in phase 1 will increase at the expense of that one in phase 2. This accelerates the motion of the phase boundary. Mechanism A can easily be taken into account in the numerical model for electroformation developed by Strukov et al. [3]. In the simulation we assume a single filament with a length of 5 μm and an oxygen vacancy drift mobility of $10^{-15}$ m$^2$/Vs. In each phase, an intrinsic conductivity is assumed to exist in parallel to a hydrogen-induced one. In Fig. 3(a), the result of such a calculation is shown for an exponential increase of the conductivity by a factor of 1.25 for phase 1 and a factor of 1.75 for phase 2, respectively, both with a time constant of 200 s. As expected, both the current and the velocity $v$ of the phase boundary increase during the hydrogen pulse and decrease again after the hydrogen is turned off.

In order to reproduce the observed time dependence of the current shown in Fig. 2(b) qualitatively, the hydrogen-induced process that decreases the conductivity (mechanism B) of phase 1 has to be taken into account as well. Here, we assume that in response to mechanism B, $σ_1$ decreases exponentially with a time constant of 10 s to a final value that depends on the hydrogen volume fraction, while it does not affect $σ_2$. Different hydrogen concentrations are modeled by different final conductivities for both phases. The simulation results are reproduced in Fig. 3(b). As hydrogen is offered, an initial decrease of the current is obtained which correlates with an acceleration of the phase boundary motion. A subsequent increase of the current indicates that mechanism B has finished and mechanism A begins to dominate the response. Here, $v$ remains larger than before because of the concentration of the electric field in phase 1. After hydrogen is turned off, the current increases more slowly due to the growth of phase 1 or, depending on the hydrogen volume fraction, decreases, in qualitative agreement with the experimental studies, see Fig. 2(b), and the time dependence of $v$ reflects the decreasing conductivity ratio $σ_2/σ_1$.

Since it has been recently established that electroformation leads to a transformation of TiO$_2$ into the Ti$_4$O$_7$ Magnéli phase inside filaments [11] which can be thought of as a local recrystallization of reduced TiO$_{2−δ}$, the interpretation in terms of oxygen vacancies may be too simplistic. However, the observed behavior can also be understood within the picture of a reduction of TiO$_2$ to different Magnéli phases Ti$_n$O$_{2n−1}$ with integer $n$. Let us assume that phase 1 is composed of the Ti$_4$O$_7$ Magnéli phase. Since it is well established that $σ(Ti_4O_7) ≈ 10^3 σ(TiO_2)$, it will have a larger conductivity than phase 2. Offering hydrogen may reduce Ti$_4$O$_7$ further, i.e., to Ti$_3$O$_5$ or Ti$_2$O$_3$. These phases are known to have smaller conductivities than Ti$_4$O$_7$, which would be a natural explanation for mechanism B and, by the way, also for the slight decrease of the current with time after $x_b$ has reached the cathode in the absence of hydrogen, see Fig. 1(b). Whether hydrogen can also act as a donor in Magnéli phases has not been studied so far to the best of our knowledge, but such a mechanism is in fact not required to explain our data.

We continue with the interpretation of the evolution of the current after it has reached its maximum, shown in Fig. 2(c-e), where $x_b = d$. In the absence of hydrogen, an approximately stable situation for the time scales considered here is established, where the current flows pre-
dominantly via the filaments. As hydrogen is offered, the current increases due to mechanism A in the surrounding TiO$_2$-$\delta$ matrix and possibly also inside phase 1. At the same time, a fast and a slow mechanism that decrease the current are observed, and both of them are irreversible. Since the fast mechanism has the same character as mechanism B described above, we attribute it to the occupation of oxygen vacancies as well. The slow mechanism may be related to a further, hydrogen-induced reduction of phase 1. If this process took place in TiO$_2$-$\delta$, an increase in current would result. However, a further reduction of TiO$_2$ will decrease the conductivity. The observed decrease of the current is thus consistent with a picture in which phase 1 contains both defective TiO$_2$-$\delta$ and various Magnéli phases. Furthermore, the small increase in between the hydrogen pulses at low c(H$_2$) could be due to migration of oxygen from the matrix into the filaments.

To summarize, it has been demonstrated that electroformation and hydrogen incorporation can coexist in titanium dioxide films. The two effects are interdependent. Atmospheric hydrogen accelerates the electroformation via a redistribution of the electric fields among the doped and the undoped phase. The experimental data are consistent with a picture where hydrogen doping increases the conductivity via hydroxylation. In addition, a rapidly decreasing, irreversible current component in response to hydrogen is observed. It is tentatively attributed to hydrogen occupying oxygen vacancies. A second, slower and also irreversible current-decreasing mechanism in response to hydrogen exposure is visible. It is consistent with the presence of Magnéli phases in the filaments with conductivities that decrease as they get further reduced. These results are not only of relevance for the study of drift effects in sensors made from materials that show electroformation, they also represent a concept for chemical control of electroformation and suggest that for a more quantitative understanding, the effects of hydrogen on Magnéli phases need to be studied on an atomistic level.

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1. U. Diebold, Surf. Sci. Rep. 48, 53 (2003).
2. X. Chen and S. S. Mao, Chem. Rev. 107, 2891 (2007).
3. J. Joo, S. Kwon, T. Yu, M. Cho, J. Lee, J. Yoon, and T. Hyeon, J. Phys. Chem. B 109, 15279 (2005).
4. M. Grätzel, Nature 414, 338 (2001).
5. R. Ramaneti, J. C. Loder, and R. Jansen, Appl. Phys. Lett. 91, 012502 (2007).
6. F. Pichot, S. Ferrere, R. J. Pitts, and B. A. Gregg, J. Electrochem. Soc. 146, 4324 (1999).
7. D. B. Strukov, G. S. Snider, D. R. Stewart, and R. S. Williams, Nature 453, 80 (2008).
8. K. Szot, M. Rogala, W. Speier, Z. Klusek, A. Besbehm, and R. Waser, Nanotechnology 22, 254001 (2011).
9. J. J. Yang, M. D. Pickett, X. Li, D. A. A. Ohlberg, D. R. Stewart, and R. S. Williams, Nature Nanotech. 3, 429 (2008).
10. D.-H. Kwon, K. M. Kim, J. H. Jang, M. M. Jeon, M. H. Lee, G. H. Kim, X.-S. Li, G.-S. Park, B. Lee, S. Han, et al., Nature Nanotech. 5, 148 (2010).
11. M. D. Pickett, G. Medeiros-Ribeiro, and R. S. Williams, Nature Mat. 12, 114 (2013).
12. S. A. Akbar and L. B. Younkan, J. Electrochem. Soc. 144, 1750 (1997).
13. D. H. Kim, Y.-S. Shim, H. G. Moon, H. J. Chang, D. Su, S. Y. Kim, J.-S. Kim, B. K. Ju, S.-J. Yoon, and H. W. Jang, J. Phys. Chem. C 117, 17824 (2013).
14. N. Yamamoto, S. Tonomura, T. Matsuoka, and H. Tsubomura, Surf. Sci. 92, 400 (1980).
15. O. K. Varghese, D. Gong, M. Paulose, K. G. Ong, and C. A. Grimes, Sensors and Actuators B 93, 338 (2003).
16. M. Paulose, O. K. Varghese, G. K. Mor, C. A. Grimes, and K. G. Ong, Nanotechnology 17, 398 (2006).
17. M. El-Achhab, A. Erbe, G. Koschev, R. Hamouich, and K. Schierbaum, Appl. Phys. A 116, 039 (2014).
18. S. Wendt, R. Schaub, J. Matthiesen, E. Vestergaard, E. Wahlström, M. Rasmussen, P. Thostrup, L. Molina, E. Laegsgaard, I. Stensgaard, et al., Surf. Sci. 598, 226 (2005).
19. J. J. Yang, F. Miao, M. D. Pickett, D. A. A. Ohlberg, D. R. Stewart, C. N. Lau, and R. S. Williams, Nanotechnology 20, 215201 (2009).
20. P. Knauth and H. L. Tuller, J. Appl. Phys. 85, 897 (1999).
21. L. A. Harris, J. Electrochem. Soc. 127, 2657 (1980).
22. S. Lee, J. S. Lee, J.-B. Park, Y. K. Kyoung, M.-J. Lee, and T. W. Noh, APL Mat. 2, 066103 (2014).
23. R. Münstermann, T. Menke, R. Dittmann, and R. Waser, Adv. Mater. 22, 4819 (2010).
24. M. Cerchez, H. Langer, M. E. Achhab, T. Heinzel, D. Ostermann, H. Lüder, and D. Ostermann, Appl. Phys. Lett. 103, 033522 (2013).
25. U. Aschauer and A. Selloni, Phys. Chem. Chem. Phys. 14, 16595 (2012).
26. U. Roland, T. Braunschweig, and F. Roessner, J. Mol. Catal. A: Chem. 127, 61 (1997).
27. F. Filippone, G. Mattioli, P. Alippi, and A. A. Bonapasta, Phys. Rev. B 80, 245203 (2009).
28. T. Bjørheim, S. Stølen, and T. Norby, Phys. Chem. Chem. Phys. 12, 6817 (2010).
29. D. A. Panayotov and J. T. Y. Jr., Chem. Phys. Lett. 436, 204 (2007).
30. P. W. Peacock and J. Robertson, Appl. Phys. Lett. 83, 2025 (2003).
31. F. Herklotz, E. V. Lavrov, and J. Weber, Phys. Rev. B 83, 235202 (2011).
32. R. F. Bartholomew and D. R. Frankl, Phys. Rev. 187, 828 (1969).