Solid-State Electrochemistry in Molecule/TiO₂ Molecular Heterojunctions as the Basis of the TiO₂ “Memristor”

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The commercial importance of microelectronic memory components has driven a broad research effort into configurations that provide greater speed, lower volatility, higher density, or longer cycle life than current devices based on magnetic or charge storage.1,2 The advent of molecular electronics has introduced memory devices based on changes in molecular conformation or redox state, including rotaxanes,3–5 phenylethynyl compounds,6,7 and nitroaromatic compounds.8,9 In our previous investigation,31 we noted the sensitivity of junction structure to the ambient atmosphere, but did not explore it in detail. We subsequently determined that atmosphere, notably humidity and oxygen content, plays an important role in the mechanism of bias-induced conductance changes in TiO₂. The current work was undertaken to understand chemical factors affecting conductance switching of molecule/TiO₂ heterojunctions and their bearing on the conductance switching mechanism. Nitroazobenzene, fluorine, and aminodecane were compared as molecular layers, and the oxides included TiO₂, SiO₂, and Al₂O₃. Oxygen vacancies and hydration in the TiO₂ were manipulated during and after junction fabrication, in order to elucidate the conductance switching mechanism responsible for the behavior of molecule/TiO₂ devices. The results are interpreted in terms of their relevance to the broad range of TiO₂ memory devices, including the Pt/TiO₂/Pt memristor.

Experimental

Molecular junctions of the “cross-junction” configuration were fabricated on a thermally grown silicon dioxide surface as described in detail previously.32–34 Briefly, a 0.5 mm wide strip of oxide and Au was deposited perpendicular to a 0.5 mm strip of pyrolyzed photoresist film (PPF) previously modified with molecular layers to form a junction.0.0025 cm² in area. PPF is similar to glassy carbon in structure, with <0.5 nm surface roughness and a resistivity of 0.006 Ω cm.35,36 Ten nanometers of TiO₂ was deposited in an electron-beam evaporator (Kurt J. Lesker PVD75) at a rate of 0.02 nm/s. Rutile was used as the target, and the pressures of O₂ and H₂O were controlled in a range of 10−5 and 10−7 Torr, respectively, during deposition as measured by a re-

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The text continues discussing the behavior of various memory devices that contain TiO₂, both the electronic response and underlying mechanism are strong functions of device fabrication and testing parameters. The hysteretic current density-voltage (j-V) behavior reported for various TiO₂-containing memory devices was recently associated with a postulated circuit element dubbed a “memristor,” for the case of Pt/TiO₂/TiO₂/Pt devices with an intentional layer of oxygen deficient TiO₂.23,29 The existence and behavior of a memristor may have wide-ranging importance to circuit theory and design, including those involving embedded memory devices. Although the report by Yang et al.29 proposed a mechanism based on transport of oxygen vacancies in TiO₂, there may also be redox processes and ion motion involved, and a detailed mechanism is unclear. Prior to the “memristor” reports, we continued our investigation of the mechanism of bias-induced conductance changes in TiO₂ by directly depositing TiO₂ from rutile onto a molecular layer by electron beam evaporation.23,29 Carbon/fluorene/TiO₂/Au junctions exhibited robust, reversible conductance switching, with the junction conductance increasing by several orders of magnitude after the Au electrode was biased negative. Replacing the TiO₂ with a nonredox active oxide (Al₂O₃) completely eliminated conductance switching. We proposed a mechanism based on the fluorene layer acting as a tunneling barrier, such that a negative shift occurs in the Fermi level of TiO₂ when Au was biased negative, resulting in reduction of TiO₂ to the more conductive TiIII oxide.30 This TiO₂ reduction process amounts to dynamic doping of TiO₂ by electron injection from the imposed electric field.

In our previous investigation,31 we noted the sensitivity of junction structure to the ambient atmosphere, but did not explore it in detail. We subsequently determined that atmosphere, notably humidity and oxygen content, plays an important role in the mechanism of bias-induced conductance changes in TiO₂. The current work was undertaken to understand chemical factors affecting conductance switching of molecule/TiO₂ heterojunctions and their bearing on the conductance switching mechanism. Nitroazobenzene, fluorine, and aminodecane were compared as molecular layers, and the oxides included TiO₂, SiO₂, and Al₂O₃. Oxygen vacancies and hydration in the TiO₂ were manipulated during and after junction fabrication, in order to elucidate the conductance switching mechanism responsible for the behavior of molecule/TiO₂ devices. The results are interpreted in terms of their relevance to the broad range of TiO₂ memory devices, including the Pt/TiO₂/Pt memristor.

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C10N layer thickness was measured as 2.1 nm/H2O849eral PPF/Fl/TiO2 experiments were performed in a cryogenic probe station/Sand removed. Al2O3 and SiO2 were deposited under the same conditions as precursors and aminodecane by oxidation of 1-amino-n-decane. 38 TiO2 was deposited through the same shadow mask as TiO2 at a rate of 1.7 and 1.9 nm by AFM "scratching" as reported previously. 37 The residual gas analyzer (Stanford Research Systems RGA/200). Au was deposited through the same shadow mask as TiO2 at a rate of 0.02 nm/s, and O2 and H2O pressures were controlled to be (3–5) × 10−6 and (1–2) × 10−6 Torr, respectively, during Au deposition. Al2O3 and SiO2 were deposited under the same conditions as TiO2. In all cases reported below, 10 nm oxide and 15 nm Au layers were used as determined with a quartz crystal microbalance during deposition and verified by atomic force microscopy (AFM). Several PPF/Fl/TiO2/Pt junctions were prepared with 15 nm of Pt instead of Au, and they behaved similarly to Au junctions, including their response to H2 and UV light. Fluorene (Fl) and nitroazobenzene (NAB) were deposited on PPF from their diazonium ion precursors and aminodecane by oxidation of 1-amino-n-decane. Molecular layer thicknesses for Fl and NAB were determined to be 1.7 and 1.9 nm by AFM “scratching” as reported previously. The C10N layer thickness was measured as 2.1 ± 0.3 nm using the same AFM method. Electronic properties of junctions were characterized in a three wire configuration described previously, in which ohmic voltage losses in the PPF lead were corrected. Controlled atmosphere experiments were performed in a cryogenic probe station (Janis Research ST 500), which was turbo pumped to a base pressure of ~5 × 10−6 Torr. During controlled atmosphere experiments, the sample chamber was refilled with desired gas back to ~1 atm after initial evacuation. All voltages are stated as PPF relative to Au, and positive current indicates electron flow from the Au through the junction to PPF. Junction sealing was conducted by attaching a piece of glass cover onto junctions with epoxy (LePage 5-Minute Epoxy). Controlled humidity was produced in a desiccator containing water/glycol mixtures and measured by a humidity and temperature recorder (Barnstead RHTEMP101). Ambient humidity varied between ~25 and 50% during the several month period when junctions were tested in lab air.

Results

We previously reported hysteresis and conductance switching in a Fl/TiO2 heterojunction, with a high conductance state following a +3 V set pulse and a low conductance state after a −3 V erase pulse. 31 In the course of changing laboratories and installing an E-beam evaporation system, we noted that junction behavior was a strong function of the atmosphere during TiO2 evaporation and after removal from the vacuum chamber. In particular, variations in water and O2 levels during and after deposition had major consequences for junction conductance and switching. Accordingly, these variables were controlled and monitored with a residual gas analyzer during TiO2 and Au deposition, and conditions were determined that produced reproducible junction behavior. To assess junction reproducibility, 10 PPF/Fl/TiO2/Au junctions were prepared with controlled O2 (2–4 × 10−5 Torr) and H2O (0.5–1 × 10−5 Torr) pressures during TiO2 deposition, and characterized electronically in air within 1 h after fabrication. For initial current j-V curves obtained at a scan rate of 1000 V/s, the voltage (mean ± standard deviation) at which the current density reached +0.05 A/cm2 was 1.65 ± 0.11 V, while it reached ~0.05 A/cm2 at ~1.25 ± 0.05 V for negative bias. Figure 1A shows j-V curves for a PPF/Fl/TiO2/Au junction made with controlled H2O and O2 levels at two voltage scan rates. A 1 V/s slow scan shows pronounced hysteresis, very similar to that reported previously, while the hysteresis is absent for the 1000 V/s scan. As described in previous papers, 31 we have found a pulse and scan paradigm more useful than a single j-V curve for investigating memory effects, in which fast 1000 V/s scans are acquired before and after set and erase voltage pulses. The 1000 V/s scans are fast enough to minimally perturb the junctions, and provide a snapshot of the j-V behavior following various voltage pulses. Figure 1B shows a “memory cycle” of fast scans acquired before (initial), after a +3 V, 100 ms set pulse, and again after a −3 V, 100 ms erase pulse. As reported previously, the set pulse shape shows a smooth increase in current with time after application of the +3 V bias, as expected from Fig. 1A. Figures 1C and D show the effect of decreasing the pulse durations to 10 and 1 ms, respectively. Figure 1C shows qualitatively similar behavior to that reported previously for 100 ms pulses, with a +3 V set pulse generating a large increase in conductance and a −3 V erase pulse causing a conductance decrease. As apparent in Fig. 1D, the set conductance is smaller for the shorter, 1 ms pulses, and the erase is incomplete for a 1 ms, −3 V pulse. We found that the erase process is more complete when the erase pulse is significantly longer than the set pulse, with a 1 ms, +3 V set and 50 ms, −3 V erase pulse producing a good contrast between the set and erased j-V curves.

The set dynamics are shown as a function of pulse voltage and...
pulse length in Fig. 2. We noted that even a 1000 V/s positive scan could partially set the junction; thus, only negative scans were used to elucidate the relationship between set state conductance and pulse conditions, and the junction was erased and allowed to rest for >2 h between set pulses. Figure 2a shows $j$-$V$ curves of the initial state, and after a series of +3V set pulses lasting from 10 μs (the lower limit of the instrument), to 100 ms. The set state conductance increases monotonically with pulse length in the range studied, and pulses longer than 100 ms often caused irreversible junction damage. Figure 2b shows $j$-$V$ curves following 50 μs set pulses of increasing voltage, from 0.5 to 4.5 V. The junction shows negligible change after a 50 μs set pulse lower than 2 V, but the set state conductance increases with set pulse voltage above 2 V until it reaches a maximum at +3.5 V. To minimize junction damage caused by high currents, many of the results reported henceforth were obtained with 1 ms, +3 V set, and 50 ms, −3 V erase pulses. A read/set/erase memory cycle using these conditions is shown in Fig. 3A.

We next observed the effect of postdeposition atmosphere on device behavior by exposing completed junctions to various conditions after removal from the electron beam chamber. Figure 3A was obtained in ambient air, then the same junction was exposed to vacuum (≈5 x 10$^{-6}$ Torr) for 12 h, and the memory cycle of Fig. 3B was obtained using otherwise identical conditions. Vacuum exposure nearly completely eliminated the conductance increase caused by a +3 V set pulse. Furthermore, the large increase in conductance observed during a 100 ms, +2.2 V pulse shown in Fig. 3C was completely eliminated in a vacuum. We previously attributed this increase in conductance during a set pulse to reduction of TiO$_2$ observed before exposure to vacuum.

Figure 3. (Color online) Conductance switching of Fl/TiO$_2$ junctions in air and vacuum: 1 ms, 3 V set pulse, 50 ms, −3 V erase pulse, scan rate 1000 V/s. (A) air and (B) same junction after exposure to vacuum for ~12 h. (C) is the response to a +2.2 V, 100 ms pulse in air and in vacuum, and (D) is the same data on an expanded scale.
To verify the role of TiO$_2$ in conductance switching, we substituted SiO$_2$ and Al$_2$O$_3$ for the TiO$_2$ in Fl/TiO$_2$ junctions. As shown in Fig. 5B and C, substitution of TiO$_2$ with SiO$_2$ or Al$_2$O$_3$ of equal thickness completely eliminates switching behavior, and results in permanently insulating junctions. Figure 6 shows the overlays of initial $j$-$V$ curves of Fl junctions with different oxides in air and vacuum ($\sim 5 \times 10^{-6}$ Torr). All three types of junctions acted as capacitors at low voltage, with a constant current observed for a given scan rate expected for a parallel plate capacitor. The apparent dielectric constants of the junctions were calculated from the capacitive current, assuming a junction thickness of 12 nm. The apparent dielectric constants decreased when the junctions were exposed to vacuum for all three oxides and equaled 4.2 (Fl/SiO$_2$), 5.2 (Fl/Al$_2$O$_3$), and 10.5 (Fl/TiO$_2$) in vacuum. For a bias magnitude above $\sim 1.5$ V, the current across the Fl/TiO$_2$ junction increased dramatically, indicating electron injection into the TiO$_2$ conduction band, whereas Al$_2$O$_3$ and SiO$_2$ always block electron transfer in the voltage range studied.

Although we proposed previously$^{31}$ that H$_2$O may be involved in a bias induced redox reaction of TiO$_2$, the current results show that H$_2$O is a requirement for conductance switching in Fl/TiO$_2$ junctions. In order to elucidate further the importance of TiO$_2$ reduction to conductance switching, chemical and photo-induced TiO$_2$ reduction were investigated and compared to the effects of a voltage bias. The initial $j$-$V$ curve in Fig. 7A was obtained from a Fl/TiO$_2$ junction exposed to vacuum for $\sim 1$ h. Then, the sample chamber was filled with 5% H$_2$ gas for $\sim 12$ h, resulting in a $j$-$V$ curve with

![Figure 4](image-url)

**Figure 4.** (Color online) Conductance switching of Fl/TiO$_2$ junctions in air of varying humidity after vacuum exposure. Erase pulse was $-3$ V, 50 ms, and junctions were set by a 1000 V/s scan to $+2.7$ V. (A) Initial 1000 V/s scans acquired in 3, 24, and 60% humidity, (B) in 3% humidity, (C) in 24% humidity, and (D) in 60% humidity.

![Figure 5](image-url)

**Figure 5.** (Color online) Comparison of $j$-$V$ curves for PPF/Fl/oxide/Au junctions using the same conditions as Fig. 4: (A) PPF/Fl/TiO$_2$/Au, (B) PPF/Fl/SiO$_2$/Au, and (C) PPF/Fl/Al$_2$O$_3$/Au.
much higher conductance. Upon replacing the H₂/N₂ atmosphere with O₂, the junction conductance decayed back to the initial state in ~2 h. Exposure of the junction to UV light also changed junction conductance, as shown in Fig. 7B. The initial *j-V* curve was obtained in a vacuum then the junction was exposed to a UV “black light” (UVG-11 with 4 W mercury vapor tube, Thomas Scientific). UV light caused a large increase in junction conductance which persisted in vacuum until exposure to O₂ restored the conductance to that observed before UV exposure. Without oxygen, the UV-treated junction conductance decayed quite slowly, requiring more than 15 h in vacuum to relax to the initial state. The results of Fig. 7 establish that chemical reduction and oxidation with H₂ and O₂, and photoreduction with UV light produce conductance changes in the Fl/TiO₂, which are qualitatively similar to those induced by an applied bias, in both direction and reversibility. It should be noted that the bias-induced changes occurred with millisecond and submillisecond pulses, while conductance changes induced by H₂ and O₂ were much slower, requiring many minutes.

In order to reduce the atmospheric effects on Fl/TiO₂ junctions, samples were sealed with a small section of a glass microscope slide (~1 × 1 mm) attached directly on top of the junction with epoxy. Figure 8A shows the effects of humidity on the conductance change following a “set” pulse for an unsealed junction and is consistent with the results shown in Fig. 4A and B. When a junction was sealed in ~24% air, then exposed to varying humidity, the effect of humidity changes on conductance was negligible (Fig. 8B). The glass/epoxy seal was less effective for blocking changes induced by H₂ and O₂, presumably due to their small size and low polarity permitting permeation through epoxy and glass. As shown already in Fig. 7A, an unsealed junction treated with H₂ was completely restored to its initial state by 2 h of O₂ exposure. The sealed junction also showed a conductance increase with H₂ exposure (Fig. 8C), but the return to low conductance in O₂ was much slower, requiring at least 44 h to reach its low conductance state. Sealing is also beneficial to the retention of the high-conductance state of a Fl/TiO₂ junction after a set pulse. The current at ~1.4 V decayed by 69% within 1 min after a 3 V set pulse, and returned to its initial value after 11 min. The current at ~1.4 V for a sealed junction decayed 40% within 1 min after the set pulse and was still twice as large as the value preceding the set pulse after 11 min. Similarly, the UV-

![Figure 6](http://www.jecs.org/content/jes/156/1/P29.P37/2009.P33)<br>Figure 6. (Color online) Overlays of initial *j-V* curves for Fl/TiO₂, Fl/SiO₂, and Fl/Al₂O₃ junctions in air and vacuum, using the conditions of Fig. 4: (A) in air, (B) after ~2 h in vacuum, (C) same as (B), but with magnified current density axis.
induced conductance increase is also sensitive to air and O₂, with a junction in air showing very little conductance increase upon UV exposure.

The memory cycle shown in Fig. 3A could be repeated for at least tens of cycles for a given junction. The repetitions were indistinguishable from the initial cycle provided the period between repetitions was long (i.e., >2 h). Longer endurance was evaluated by repetitive set/erase cycles consisting of 1 ms set pulses and 50 ms erase pulses, repeated every 10 min. As shown in Fig. 9, the magnitudes of the currents decreased gradually with repeated memory cycles, with the set current at −1.5 V decreasing by 20% after 66 cycles and 75% after 456 cycles. However, this decrease was reversed if the junction was left at open circuit in air for two days, indicating that the current decline did not result from irreversible chemical changes.

To consider the effects of molecular structure on conductance switching, PPF/molecule/TiO₂/Au junctions were prepared with NAB or C₁₀H₂₁NH(C₁₀N) layers in place of fluorene, with all three molecular layers having measured thicknesses (by AFM) between 1.7 and 2.1 nm. All conditions of deposition, atmosphere, and electronic testing were kept constant, with the exception of the PPF surface modification. Figure 10 compares memory cycles of Fi/TiO₂, NAB/TiO₂, and C₁₀N/TiO₂ junctions in air with 26% humidity and all other conditions identical. Unlike the major changes noted in Fig. 5A when the oxide composition is changed, different molecular layers had relatively minor effects on conductance switching. All three cases showed a reversible increase in conductance following a +3 V set pulse, and all three were erased by a −3 V pulse. Fi/TiO₂ and C₁₀N/TiO₂ often showed higher conduc-

Figure 8. (Color online) Behavior of sealed and unsealed PPF/Fl/TiO₂/Au junctions with changes in atmosphere, in the order indicated. A single device was used for each panel. (A) unsealed. 1. Initial (same curves for 14 and 26% humidity); 2. After a set pulse for a junction exposed to 26% humidity for 1 day; 3. After set pulse for same junction after exposure to 14% humidity for 1 day. (B) Same sequence as (A), but with a sealed junction. (C) Sealed junction, initial, after ~12 hrs in H₂/N₂ (1 atm), and after 2 hours in 1 atm O₂. (D) Initial, in air; 2. After ~12 h in 5% H₂/N₂ (1 atm); 3–5, after 1, 20, and 44 h in 1 atm O₂, respectively.

Figure 9. (Color online) j-V curves (1000 V/s) from a glass/epoxy sealed Fl/TiO₂ junction obtained at various points in a series of memory cycles consisting of +3 V, 1 ms set and −3 V, 50 ms erase pulses, repeated at 10 min intervals. A. Initial, after set pulse, and after erase pulse for first cycle; (B) 66th cycle; (C) 456th cycle; (D) two days at rest after the 456th cycle.
tance after a set pulse than NAB/TiO₂, although the difference was not dramatic. The rectification reported previously for NAB/TiO₂ junctions was less pronounced for the 1.9 nm thick NAB layer compared to the 4.5 nm layer used previously. 32

Discussion

We previously used Raman spectroscopy to conclude that NAB can be reduced in a PPF/NAB/oxide/Au junction by a negative bias applied to the PPF contact. 33 The observation that molecule/TiO₂ junctions containing the redox inactive molecular layers fluorene and C₆H₅N also exhibit conductance switching confirms the conclusion that the switching can occur without known structural changes in the molecule accompanying redox activity. Furthermore, substituting a redox inactive oxide (SiO₂ or Al₂O₃) completely eliminates conductance switching, even though previous experiments showed that NAB still undergoes reduction if a bias is applied to a PPF/NAB/Al₂O₃/Au junction. 34 These results all confirm the conclusion that TiO₂ is the active agent for the observed switching behavior, rather than the molecular layer. Although NAB can be reduced in a NAB/Al₂O₃ junction, the overall conductance is controlled by the insulating oxide layer, which is presumably unchanged by the applied bias. As noted previously, partially reduced TiO₂ is expected to have a conductivity many orders of magnitude higher than TiIV oxide, due to the creation of conduction band electrons upon reduction. 35,31

The similarity between a Fl/TiO₂ junction set by a positive pulse and one chemically reduced by H₂ or photoreduced by UV light support the conclusion that the applied bias causes electrochemical reduction of the TiO₂ during the set procedure. As noted above, the bias-induced reduction is much faster than that caused by H₂ with at least part of the difference attributable to mass transport of H₂ into the junction interior. The most likely route for H₂ entry into the junction is through a partially porous Au layer visible in scanning electron microscopy images (not shown) of the completed junction. As noted regarding Fig. 7, the conductance increase induced by H₂ or UV light is completely reversed by exposure to O₂. The absence of conductance switching when water is excluded implies that the reduction reactions are dependent either on water itself or on an ion derived from water (i.e., H⁺ or OH⁻). We proposed Reaction 1 as a possible reduction mechanism previously, 31 but Reaction 2 is another possibility.

\[
2\text{TiO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{Ti}_2\text{O}_3 + 2\text{OH}^- \quad [1]
\]

\[
\text{TiO}_2 + \text{H}_2\text{O}^+ + e^- \rightarrow \text{TiO(OH)} + \text{H}_2\text{O} \quad [2]
\]

For the case of photoreduction by UV light, a useful precedent is provided by Szczepankiewicz et al. 39,40 who monitored the photoreduction of TiO₂ with infrared spectroscopy and proposed that the dominant reaction is between hydrated TiIV sites and photogenerated conduction band electrons, as shown in Reaction 3.

\[
e^- + \text{Ti}^{IV} \text{O}^-\text{H} \rightarrow \text{Ti}^{III}\text{O}^-\text{H}^- \quad [3]
\]

Reactions 1-3 share the common properties of producing TiIII with its mobile d-band electrons, requiring water, and involving a reaction between conduction band electrons and TiIV sites. Because the TiO₂ is polycrystalline and disordered, it is difficult to be more precise about specific lattice sites, including the role of possible oxygen vacancies or small amounts of mobile ions from water or impurities. The proposal 30 of bias induced drift of positively charged oxygen vacancies in the memristor is not fundamentally different from reduction of TiIV to TiIII with accompanying motion of O² ions. Because O²⁻ is energetically difficult to form, particularly at room temperature, it is more likely that ions derived from water are the mobile species, notably OH⁻. 32

Szczepankiewicz et al. 39,40 also proposed a kinetic model for photoreduction of hydrated TiIV to TiIII, which stated that the rate of generation of TiIII is proportional to the concentration of hydrated TiIV times the concentration of conduction band electrons \([e^-]_c\). For the bias induced reduction studied here, \([e^-]_c\) is the space charge of electrons injected from Au into the TiO₂. This space charge will be larger for higher positive bias, and the hydrated TiIV concentration is higher in higher humidity. This model is consistent with the current observation of more rapid and larger conductance increases at more positive bias and higher humidity, up to a limit. Henderson 41 reported that the first several layers of water absorbed onto TiO₂ reacted with the surface much more strongly than water-water interactions in a multilayer, and the initial water layer contributes to TiO₂ hydration. After the initial water layers are adsorbed, more water did not increase TiO₂ hydration and depleted conduction band electrons. 33 The continued increase in capacitance and low voltage conductance with humidity shown in Fig. 4D implies that another charge transport mechanism may be operative at high water content, such as ionic conduction of protons or other small ions in a “damp” junction. The fact that high water content is deleterious to conductance switching implies that ion motion is not in itself sufficient to explain the observed conductance changes. However, it is still possible that ion motion accompanying hydration, such as H⁺ transport between water molecules, may play a role in controlling local electric fields and in compensating space charge generated by electron injection and TiIV reduction.

If TiO₂ hydration was kept constant by controlling humidity at a moderate level of ~26%, the set state conductance became a function of set pulse voltage and length, as shown in Fig. 2. At voltages of >2 V, electrons inject into the TiO₂ conduction band and the set state conductance starts to increase as a result of electron trapping and formation of TiIII. When the bias is >3.5 V, the set state conductance reaches a maximum. The asymptotic approach of the conductance to a maximum value with time after set pulse initiation is expected for a kinetic model involving reduction of a finite number of hydrated TiIV sites by injected electrons, and represents a combination of the kinetics of electron injection into the conduction band and the reduction reaction of Eq. 1 and 2.
Conclusions

The current results add several significant points to the previously proposed conductance switching mechanism mediated by TiO$_2$ redox chemistry. First, bias-induced reduction of Ti$^{IV}$ to Ti$^{III}$ oxide is necessary and sufficient to explain the observed conductance changes, with no requirement for identifiable redox activity in the molecular layer. Second, water is essential to the reduction process, presumably via partial hydration of Ti$^{IV}$ oxide, although high water levels are deleterious to conductance switching. Although there is no direct evidence that water permits ion motion, it is still possible that mobile ions are involved in conductance switching. Although motion of oxygen vacancies (with +2 charge) or oxygen anions (−2) is possible, the high energy required to form these species may make ion transport by H$^+$ or OH$^−$ more likely. Third, chemical reduction and oxidation with H$_2$ and O$_2$ as well as photochemical reduction by UV light produce similar changes in junction conductance to those caused by a voltage pulse, but on a slower time scale. Fourth, the observations are consistent with a mechanism involving electron injection into the TiO$_2$ when the bias on Au is less than −2 V, followed by a reaction of the injected electrons with hydrated Ti$^{IV}$ sites to produce Ti$^{III}$ oxide. The higher conductivity of Ti$^{III}$ compared to Ti$^{IV}$ oxide produces the observed conductance increase, and this change persists until the Ti$^{III}$ is reoxidized. Finally, the “dynamic doping” of Ti$^{III}$ responsible for the observed conductance changes in Fl/TiO$_2$ heterojunctions amounts to a solid-state electrochemical process, with Ti$^{IV}$ reduction occurring at or near the negatively biased electrode. Although the detailed mechanism of the hysteresis recently associated with the memristor containing only Pt, TiO$_2$, and oxygen-deficient TiO$_x$ may differ strongly on composition and fabrication, bias-induced reduction of Ti$^{IV}$ to Ti$^{III}$ mediated by water is at least one likely mechanism.

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