Oxygen adsorption at noble metal/TiO₂ junctions

F. Hossein-Babaei¹,a, Navid Alaei-Sheini¹,b, Mehdi M. Lajvardi¹,c
¹Electronic Materials Laboratory, Electrical Engineering Department, K. N. Toosi University of Technology, Tehran 16317-14191, Iran
²fhbabaei@kntu.ac.ir, bnavid_alaei@ee.kntu.ac.ir, cm.lajvardi@gmail.com

Abstract. Electric conduction in titanium dioxide is known to be oxygen sensitive and the conductivity of a TiO₂ ceramic body is determined mainly by the concentration of its naturally occurring oxygen vacancy. Recently, fabrications and electronic features of a number of noble metal/TiO₂-based electronic devices, such as solar cells, UV detectors, gas sensors and memristive devices have been demonstrated. Here, we investigate the effect of oxygen adsorption at the noble metal/TiO₂ junction in such devices, and show the potentials of these junctions in chemical sensor fabrication. The polycrystalline, poly-phase TiO₂ layers are grown by the selective and controlled oxidation of titanium thin films vacuum deposited on silica substrates. Noble metal thin films are deposited on the oxide layers by physical vapor deposition. Current-voltage (I-V) diagrams of the fabricated devices are studied for Ag/, Au/, and Pt/TiO₂ samples. The raw samples show no junction energy barrier. After a thermal annealing in air at 250°C, I-V diagrams change drastically. The annealed samples demonstrate highly non-linear I-V indicating the formation of high Schottky energy barriers at the noble metal/TiO₂ junctions. The phenomenon is described based on the effect of the oxygen atoms adsorbed at the junction.

1. Introduction
We have recently reported that the electron energy barrier formed at the junction between a noble metal and titanium dioxide depends on the oxygen content of the interface [1], which strongly affects the main electronic features of such contacts. Noble metal/TiO₂ contacts are utilized as active components in TiO₂-based electronic devices or for connecting such devices to the outside circuitry. Many TiO₂-based electronic devices, such as those used or considered as solar cells [2, 3], varistors [4], ultraviolet detectors [5, 6], memristors [7, 8], and gas sensors [9, 10] are exposed to corrosive environments and/or operate at elevated temperatures and their connections to the external circuitry require utilizing noble metals. In some of these devices, the contact between the noble metal and TiO₂ plays an active role in the operation of the device, as well [11, 12].

Here, we report fabrication and characterization of Schottky diodes with platinum-, gold-, and silver-TiO₂ structures on silica substrates and show that the reverse currents in these devices are sensitive to environmental parameters. The reverse current of these diodes can be drastically reduced by thermal annealing in air or pure oxygen; in the case of silver-TiO₂ diodes, the reverse current at -0.5 V reduces down to 4 × 10⁻¹¹ Amm⁻². It is shown that these metal/metal oxide junctions are suitable platforms for the fabrication of a number of low power consuming sensors.

2. Experimental
The metal/TiO₂ contacts examined are of the structure schematically shown in Figure 1. The oxide layers are produced on silica substrates by the direct oxidation of 400 nm-thick titanium thin films...
previously deposited by thermal evaporation in vacuum. The oxide layers are 700 nm thick. The oxidation process is controlled and stopped when a 30 nm-thick layer of metallic titanium still remains unoxidized. This degree of accuracy in oxidation process stoppage is achieved by monitoring the electrical conductance and, hence, thickness, of the remaining titanium layer. As shown in Figure 1, the titanium conductance is continuously read via two aluminum test points deposited on the titanium. It is shown that a thin layer of aluminum can protect titanium from oxidation [13]. The grown oxide layer is 700 nm thick and contains both rutile and anatase phases as described in reference [1].

Noble metal layer (anode) is deposited by thermal evaporation of the 5N purity metal in vacuum; selective area (1.5 mm x 5 mm) deposition is achieved by photoresist liftoff. A fine gold wire is cemented to the anode using silver paste; the position of the connection is on the extended tail of the noble metal layer outside the TiO$_2$ layer area. Wire connection to the titanium thin film (cathode) underneath the TiO$_2$ layer is made in a similar way on both of the aluminum pads (Figure 1), which are connected together outside the device to form the cathode connection wire. After preliminary electrical examinations, the fabricated diode is annealed in different atmospheric conditions at 250 °C for 120 min while it is DC-biased at -0.5 V. Samples are reexamined after completion of the annealing process.

The electrical examination of the fabricated noble metal/TiO$_2$/Ti structures is carried out by plotting their current vs. voltage (I-V) characteristics. The I-V diagrams of each sample are plotted at different conditions, before and after annealing process. The experimental setup is shown in Figure 2. A source measure unit (Keithley-238) is utilized for the point-by-point measurements. Device currents, as low as 10$^{-10}$ A, are measured in a Faraday cage. All of the diodes examined are light sensitive [14-16]; all I-V measurements are carried out in a dark box. All reported observations are reproducible and the described device features have been re-checked on five samples.

![Figure 1. The schematic diagram of a noble metal/TiO$_2$ diode.](image)

3. Results and Discussion
Each noble metal/TiO$_2$/Ti diode consists of a noble metal/TiO$_2$ junction and a TiO$_2$/Ti contact connected in series. The TiO$_2$/Ti contact is ohmic [10, 12] and, hence, the nonlinear I-V graphs obtained for the fabricated noble metal/TiO$_2$/Ti structure is expected to stem from the nonlinearity of the noble metal/TiO$_2$ junction.

According to Figure. 3a, all samples have almost symmetric I-V characteristics and indicate almost zero junction barriers prior to thermal annealing. The symmetric nonlinearity observed in their respective I-V characteristics around V=0 (the vertical axes in all diagrams presented in Figure. 3) stems from the combination of different conduction mechanism, such as Pool-Frenkel [17], through the trap-populated titanium oxide adjacent to the interface. After annealing at 250 °C in air, all samples turned into Schottky diodes of high energy barriers. The observation of instability between ohmic and diode-like behaviors for silver/SnO$_2$ contacts has also been reported [18]. The after annealing I-V characteristics of all samples are presented in Fig. 3b demonstrating drastic change of characteristics.
(compare Figure 3a with Figure 3b). The obtained Arrhenius diagrams are given in Fig. 4a-c resulting close activation energies for the leakage currents of all annealed diode samples regardless of the nature of the metal/TiO$_2$ junction involved. This is attributed to the electron leakage through the traps in the carrier depleted region of the titanium dioxide layer adjacent to the junction. Domination of carrier leakage mechanisms such as Pool-Frenkel makes the reverse current independent from the barrier height established at the junction.

![Figure 2. The experimental setup for electrical examinations.](image)

![Figure 3. The I-V characteristics obtained for all types of fabricated noble metal/TiO$_2$/Ti diodes before (a) and after (b) the thermal annealing process.](image)
Figure 4. Arrhenius diagrams plotted for the reverse currents of (a) Ag/TiO$_2$, (b) Au/TiO$_2$, and (c) Pt/TiO$_2$ contacts.

To describe the zero junction barriers observed in all samples prior to the annealing regardless of the nature of the anode, Ag, Pt or Au, we note that in the electrical evaluations of parallel mechanisms, the one with the lowest barrier has the most profound effect. The quantitative information regarding the work functions of the metallic anodes and the electron affinity of rutile and anatase are given in reference [1]. However, in most of the junction cases examined, the observed zero barriers cannot be described based on commonly used concept that the junction energy barrier height is equivalent to difference between the metal work function and semiconductor electron affinity. Only in the case of silver/TiO$_2$ junction, this concept predicts a close to zero barrier height at the junction. For this prediction, the work function of silver, W$_{Ag}$, is assumed to be 4.3 eV [19, 20] for the polycrystalline silver layers, and the electron affinity of TiO$_2$ is taken to be 4.8 eV for rutile and 5.1 for anatase [21]. The latter parameter is different for rutile and anatase phases [22]; the value introduced is that of rutile as it results in a lower barrier height. This is because, in complex junctions, charge carriers choose the lowest barrier/resistance path and, hence, I-V characteristics of the junction is expected to approximately indicate the minimum barrier level taken place at the junction. On the other hand, none of the contacts possible in the cases of Au and Pt, according to this concept, can explain the observed zero barrier. We attribute this to the abundance of vacuum-generated vacancies at the surface of the TiO$_2$ layer during the metal deposition process, as it has been shown that high oxygen vacancy concentration can collapse the interface barrier in M/TiO$_2$ junctions [7]. Thermal annealing in air, compensates the oxygen vacancies and increases the oxygen concentration at the interface, which allows energy barrier buildup. Similar annealing processes, carried out in vacuum or Ar atmospheres has no effect on the reverse currents because they fail to provide oxygen required for barrier build up,
and the I-V characteristics remain symmetrical. The I-V characteristics plotted for all samples after thermal annealing in air are profoundly asymmetric and rectifying, indicating high interface energy barriers formed. The barrier heights calculated based on the first quarter of the I-V diagrams are reported in reference [1] indicating barrier heights of about 0.9 eV for all samples. This is consistent with the reported independence of the junction barrier height formed on the TiO$_2$ from the nature of the metallic anode [23].

The electron affinity for rutile has been reported to be in the 3.9-4.8 eV range [21, 24, 25] while that of anatase is 5.1 eV [21]. Hence, any metallic anode is expected to form a smaller interface barrier with anatase than with rutile. Regarding the anode work function, however, the smallest is expected to form the lower barrier. Work functions of Pt, Au and Ag at various forms are given in reference [1] indicating that the smallest values are related to their polycrystalline form. $W_{Pt}$ for polycrystalline platinum is reported to be 5.6 eV [26] and it has been reported to grow as much as 1.0 eV upon oxygen adsorption to its surface. Hence, oxygen adsorption on Pt at its junction with anatase can increase the junction barrier from 0.5 to 1.5 eV.

For Au/TiO$_2$ contact, however, these numerical values lead to a barrier height approximately around 0.4 eV. This is in contrast with the observed 0.9 eV junction barrier. It appears that higher levels of oxygen coverage occurs on the gold surface at the junction than that reported for the (110) surface of a gold crystal layer [27]. The results indicate that, indeed, gold surface at the junction with TiO$_2$ can accommodate oxygen atoms stably up to high coverage levels. This would result in a larger work function for the gold electrode and further increase of the junction barrier.

$W_{Ag}$ reported for polycrystalline silver [19] is smaller than the electron affinity of anatase [21]. Hence, zero energy barrier is predicted for the Ag/TiO$_2$ junction from this stance. However, $W_{Ag}$ has been reported to grow up to 7.0 eV when silver surface is covered with an oxygen monolayer. Silver differs from gold in that, at room temperature, oxygen is stable up to 25% coverage [28, 29], which according to theoretical predictions [28], translates to a $W_{Ag}$ of 6.2 eV. This considerable change in $W_{Ag}$ results in a 1.0 eV barrier.

4. Conclusions

Major electronic features of noble metal/TiO$_2$ junctions were studied. While all vacuum-deposited noble metal anodes formed ohmic contacts with TiO$_2$, an hour of thermal annealing at 250 °C in air converted them all to Schottky junctions of ~0.9 eV energy barrier heights. The barrier height formed after annealing in air is almost independent from the nature of the noble metal anode. Thermal annealing in inert or reducing atmospheres failed to assist barrier formation. The dependence of the barrier height on the oxygen partial pressure of the annealing atmosphere indicates possibility of sensing oxidizing or reducing atmospheres with different noble metal/TiO$_2$ diodes.

References

[1] Hossein-Babaei F, Lajvardi M M and Alaei-Sheini N 2015 The energy barrier at noble metal/TiO$_2$ junctions *Appl. Phys. Lett.* **106** 083503

[2] McFarland E W and Jing T 2003 A photovoltaic device structure based on internal electron emission *Nature* **421** 616-8

[3] Kim H S et al. 2013 High efficiency solid-state sensitized solar cell-based on submicrometer rutile TiO$_2$ nanorod and CH$_3$NH$_3$PbI$_3$ perovskite sensitizer *Nano Lett.* **13** 2412-7

[4] Bueno P R et al. 1996 Effect of Cr$_2$O$_3$ in the varistor behaviour of TiO$_2$ *J. Materials Sci. Lett.* **15** 2048-50

[5] Hossein-Babaei F, Lajvardi M M and Boroumand F A 2012 Large area Ag–TiO$_2$ UV radiation sensor fabricated on a thermally oxidized titanium chip *Sens and Actuators A: Physical* **173** 116-21

[6] Kong X et al. 2009 Metal-semiconductor-metal TiO$_2$ ultraviolet detectors with Ni electrodes *Appl. Phys. Lett.* **94** 123502

[7] Yang J J et al. 2008 Memristive switching mechanism for metal/oxide/metal nanodevices
Kolka Z, Biolek D, Biolkova V 2015 Improved Model of TiO\textsubscript{2} Memristor Radioengineering 24

Kim I D et al. 2006 Ultrasensitive chemiresistors based on electrospun TiO\textsubscript{2} nanofibers Nano Lett. 6 2009-13.

Hossein-Babaei F and Rahbarpour S 2011 Titanium and silver contacts on thermally oxidized titanium chip: electrical and gas sensing properties Solid-State Electronics 56 185-90.

Yang J J et al. 2011 Metal/TiO\textsubscript{2} interfaces for memristive switches Appl. Phys. A: Materials Science & Processing 102 785-9

Hossein-Babaei F and Rahbarpour S 2011 Separate assessment of chemoresistivity and Schottky-type gas sensitivity in M–metal oxide–M’ structures Sens and Actuators B: Chemical 160 174-80

Raybould D, Chipko P, Fischer W E 2006 US Patent 7,135,238

Xue H et al. 2007 TiO\textsubscript{2} based metal-semiconductor-metal ultraviolet photodetectors Appl. Phys. Lett. 90 201118

Xing J et al. 2011 Highly sensitive fast-response UV photodetectors based on epitaxial TiO\textsubscript{2} films J. of Physics D: Applied Physics 44 375104

Huang H et al. 2011 Low dark current MSM UV photodetectors with Pt schottky contacts Electron Device Lett. 32 530-2

Ohring M 2001 Materials science of thin films. Academic press

Hossein-Babaei F, Moghadam S and Masoumi S 2015 Forming ohmic Ag/SnO\textsubscript{2} contacts Materials Lett. 141 141-4

Dweydari A W and Mee C H B 1975 Work function measurements on (100) and (110) surfaces of silver physica status solidi 27 223-230

Michaelson H B 1977 The work function of the elements and its periodicity J. of Appl. Phys. 48 4729-33

Scanlon D O et al. 2013 Band alignment of rutile and anatase TiO\textsubscript{2} Nature materials 12 798-801

Tang H et al 1994 Electrical and optical properties of TiO\textsubscript{2} anatase thin films J. of Appl. Phys. 75 2042-7

Zhong N, Shima H, Akinaga H 2010 Rectifying characteristic of Pt/TiO\textsubscript{x}/metal/Pt controlled by electronegativity Appl. Phys. Lett. 96 2107

Könenkamp R and Rieck I 2000 Electrical properties of schottky diodes on nano-porous TiO\textsubscript{2} films Materials Science and Engineering: B 69 519-21

Schierbaum K D et al. 1991 Schottky-barrier and conductivity gas sensors based upon Pd/SnO\textsubscript{2} and Pt/TiO\textsubscript{2} Sens and Actuators B: Chemical 4,1 87-94

Jakobi K, 3.1.2.4 Work Function Data, Ed. by G. Chiarotti, Springer Materials, The Landolt–Börn Stein Database http://www.springermaterials.com DOI:10.1007/10086058_16

Xu Y, Mavrikakis M 2003 Adsorption and dissociation of O\textsubscript{2} on gold surfaces: effect of steps and strain J. of Phys. Chemistry B 107 9298-307.

Li W X, Stampfl C and Scheffler M 2002 Oxygen adsorption on Ag (111): A density-functional theory investigation Physical Review B 65 075407

Allen M W, Alkaisi M M and Durbin S M 2006 Metal Schottky diodes on Zn-polar and O-polar bulk ZnO Appl. Phys. Lett. 89 3520