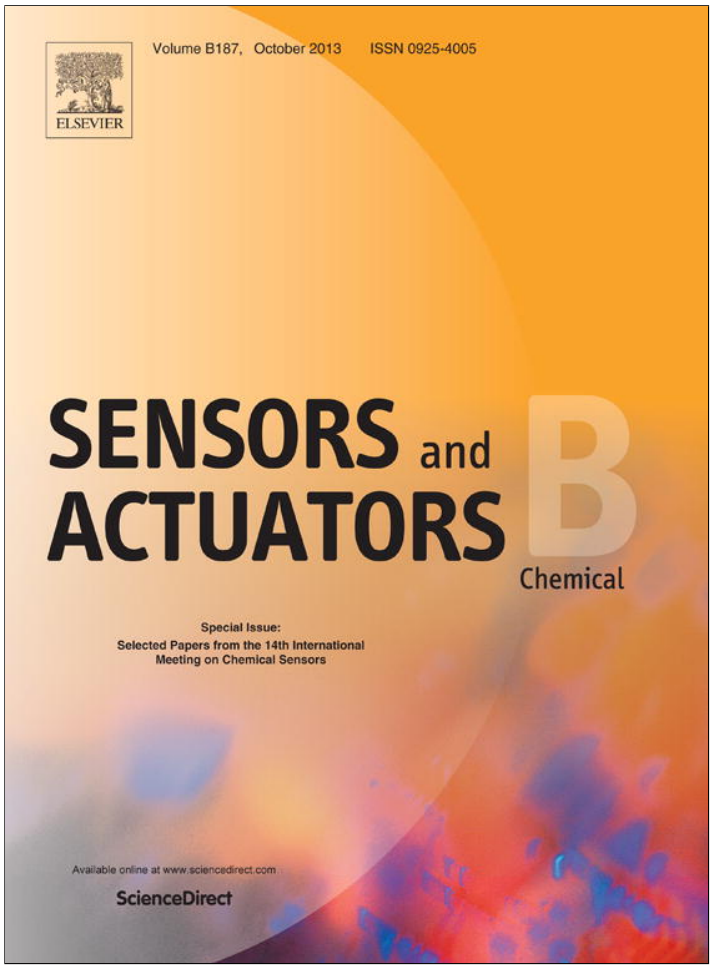

Sensors and Actuators B 187 (2013) 262–266

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Diode type Ag–TiO_2 hydrogen sensors

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ARTICLE INFO

Article history:
Available online 19 November 2012

Keywords:
Noble metal–metal oxide gas sensors
Hydrogen sensor
Oxygen sensor
Ag–TiO_2 Schottky junction
titanium oxide
Diode type sensors

ABSTRACT

The use of diode type noble metal–metal oxide gas sensors is spreading due to their unique gas sensing properties such as ultra high responses, reproducibility and long life time. In this paper, hydrogen and oxygen detection using Ag–TiO_2–Ti diodes is reported. The *I–V* characteristics of these diodes are highly sensitive to the partial pressure of hydrogen contamination in the surrounding atmosphere. Reducing atmosphere alters the population of pre-adsorbed oxygen species on silver surface, thereupon, the energy barrier height established at the Ag–TiO_2 junction reduces and the junction behaves as an ohmic contact in a highly reducing atmosphere. This reversible transition from Schottky to ohmic behaviour was modelled qualitatively and quantitatively based on the hydrogen–silver interaction. The model was experimentally confirmed. It was also shown that the fabricated Ag–TiO_2–Ti devices are good oxygen sensors at low O_2 contamination in argon atmosphere.

1. Introduction

Despite their many high quality factors, ceramic hydrogen sensors suffer from their limited dynamic range of sensitivity and slow response; whereas Schottky type noble metal–metal oxide hydrogen sensors show wide dynamic range of sensitivity to hydrogen along with very high and fast hydrogen response which makes them good hydrogen sensors [1,2]. Hydrogen sensors are vastly used in safety applications, transportation and medical diagnostics.

When a diode type gas sensor encounters a gas contaminated atmosphere, the change of potential barrier established at its junction causes *I–V* characteristics to change exponentially. In Schottky type gas sensors the gas-sensor interactions usually take place at the metal surface. The utilized metal in these structures are usually noble metals due to their elevated operating temperature and corrosive environment of sensors. Noble metals form diode type sensors with the ceramic oxide of interests. On the other hand chemoresistivity is originated from the barrier established at grain boundaries of the ceramic used. The gas interaction with the adsorbed oxygen in grain boundaries causes resistance changes. In a recent work [2], it was shown that the Schottky type sensitivity is orders of magnitude larger than chemoresistive responses.

The gas sensitivity of Schottky type structures originates from both the chemical sensitivity of the metal oxide and the Schottky type sensitivity of the metal–semiconductor junctions. Indeed, the origin of the extremely high atmospheric sensitivity observed in Schottky type structures has been unclear in the background literature for many years and different mechanisms were introduced [3–13]. Considering orders of magnitude higher Schottky type sensitivity than chemoresistive responses [2] it is clear that properties of Schottky type noble metal–metal oxide gas sensors are mainly determined by gas sensing properties of the utilized Schottky junction.

In this paper, we investigated some novel gas sensing features of Ag–TiO_2–Ti Schottky type diodes and described them by a model. The suggested model can be applied to other noble metal–metal oxide Schottky type hydrogen sensors considering different hydrogen–metal interactions. It is demonstrated that these devices are highly sensitive to low partial pressure of oxygen in argon atmosphere while they show no hydrogen sensitivity after long stay in pure argon chamber. It is shown that hydrogen sensing occurs only at the presence of pre-adsorbed oxygen species on silver surface. Hydrogen reduces the adsorbed oxygen species on the silver surface causing extremely high variations in the obtained *I–V* diagram of the device.

On the basis of previous work [2], hydrogen saturation response of Ag–TiO_2–Ti Schottky type diodes was calculated and measured directly. The results were compared with the sensor response to pure argon. Both data were in complete agreement and proved that barrier reduction in hydrogen or argon is due to lack of oxygen in the ambient of sensor and hence, the barrier established at the junction stems only from the adsorbed oxygen species on silver surface.

2. Experiment

Ag–TiO_2–Ti structures were fabricated by 30 min thermal oxidation of titanium chips at 700 °C in air. The thickness of titanium

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http://dx.doi.org/10.1016/j.snb.2012.11.017

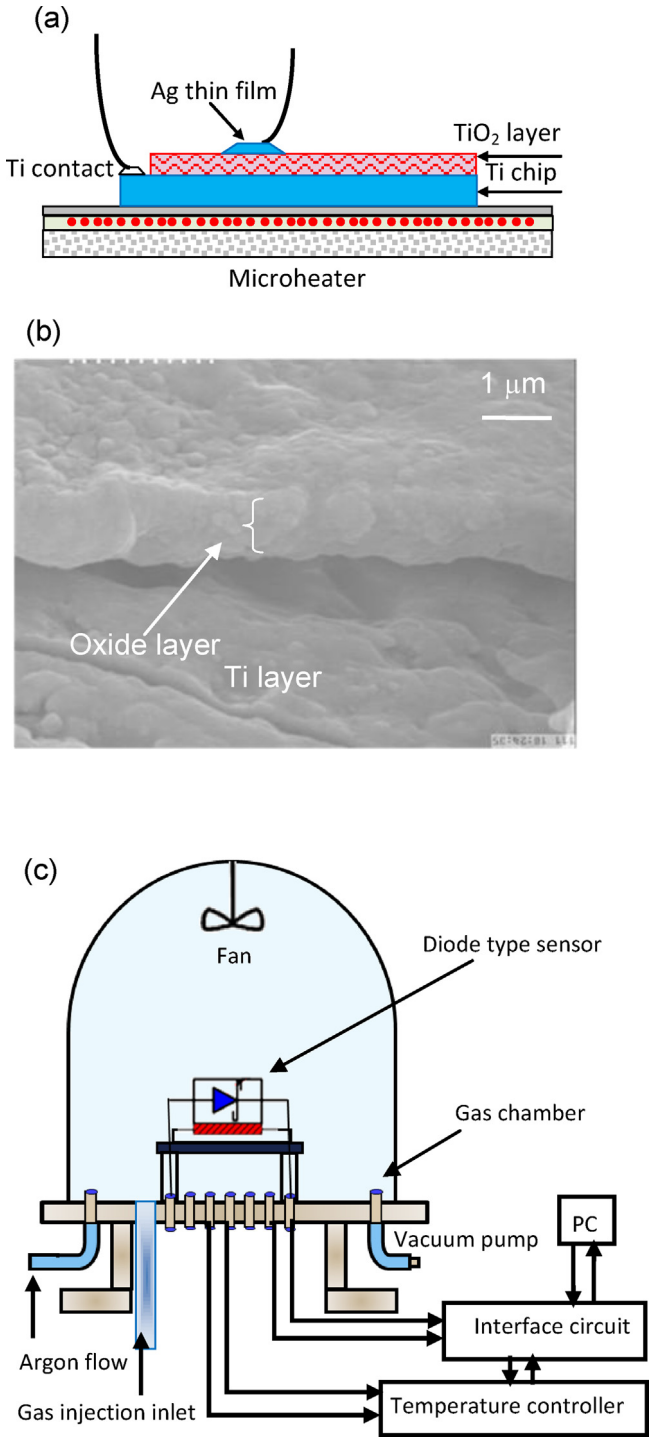

Fig. 1. The schematic diagram of (a) the resulted Ag–TiO_2–Ti device and (b) cross-section SEM micrograph of the TiO_2 layer grown on Ti substrates by thermal oxidation at 700 °C in air. In (b), the oxide layer is delaminated from the titanium surface. The schematic diagram of the experimental setup is shown in (c).

dioxide layers were ~1 μm. The schematic diagram of the resulted Ag–TiO_2–Ti device and cross-section micrograph of the TiO_2 layer grown on Ti substrates are depicted in Fig. 1a and b, respectively. The residual titanium on the back side titanium oxide (shown in Fig. 1b) was used as an ohmic contact. The Schottky contact was formed by 1 mm^2 silver deposition on top surface of oxide layer. The method of silver deposition was thick film deposition followed by partial sintering of silver particles at 400 °C. The deposited silver layer is thick enough (>300 nm) to secure its continuity after sintering. During the sintering process, silver grain growth occurs and a porous texture of silver aggregate is generated on oxide layer. The resulted contact specification is almost independent from deposition method and is defined by sintering temperature. Using this technique, fabrication of Ag–TiO_2–Ti structures with low contact to contact distances is facilitated without utilizing cumbersome submicron lithography techniques. This method decreases the oxide series resistance which is required to minimize the chemoresistive response of the oxide in comparison with the Schottky type sensitivity of the sensor [2].

The current passing through reversed biased Ag–TiO_2–Ti samples were measured by a keithly 238 source measure unit, however, at forward bias conditions the migration of Ag^+ ions occurred during *I–V* measurements and caused instabilities. This unwanted effect was solved by utilizing experimental procedure described in Ref. [14]. In this procedure, the diode was used in series with a resistor and a voltage pulse was applied to the circuit as an input. A certain point of temporal voltage diagram of the Schottky diode and the diode current measured at that point was assumed as a valid point on the forward *I–V* curve of the Schottky diode fabricated. Here, our emphasis is on reverse current measurement so more details of forward current measurement are not presented here and will be find in Ref. [14]. Although the device current in both forward and reverse regime is gas sensitive, the reverse current was chosen for gas sensitivity measurements as it demonstrates higher responses. All measurements were carried out at 300 °C. The elevated operating temperature was provided by the micro-heater positioned underneath the substrate (see Fig. 1a).

Gas sensing properties of sensors were studied in two different background atmospheres: clean air and argon ambient. Hydrogen sensitivity was recorded by hydrogen injection in clean air contained chamber but oxygen sensing was studied in argon atmosphere by injection of oxygen into the argon filled chamber. First of all the sensor was positioned in a sealed chamber. Then the vacuum pump started to suction the chamber air. Simultaneously, the argon flow was injected into the chamber (see Fig. 1c). After ~3 h the chamber was filled with pure argon and oxygen existed neither in the chamber nor in the sensor surface.

Prior to each gas sensing measurement, a predetermined amount concentration of gas (oxygen/hydrogen) was injected into the chamber and was homogenized by a small electric fan then, the sensor was inserted into the chamber. The concentration variation was negligible during gas response measurement, which took less than few 10 s, and the chamber was assumed uniform. The schematic diagram of the experimental setup is presented in Fig. 1c.

3. Results and discussion

The *I–V* diagrams of the fabricated Ag–TiO_2 diodes were studied in clean air and in pure hydrogen. The device demonstrated rectifying behaviour in air while the observed Shottky barrier at Ag–TiO_2 junction vanishes in pure hydrogen and the device behaves linearly (Fig. 2a and b). The established barrier at the junction (1.7 eV at ~300 °C in clean air) was described by considering the effect of oxygen adsorption on the Ag surface and hence, metal work function increases [14–16]. The hydrogen sensing mechanism of Ag–TiO_2 is described by considering the hydrogen interaction with the adsorbed oxygen spices which are pre-adsorbed on silver surface. Oxygen reduction from silver surface decreases the silver work function which lowers the height of junction barrier (SBH) established at the junction. The reduction of SBH exponentially increases the current passing through device. At a highly reducing atmosphere considerable portion of adsorbed oxygen are removed and the Schottky barrier does not exist anymore. In this case, the current is orders of magnitude larger than that measured in clean air and

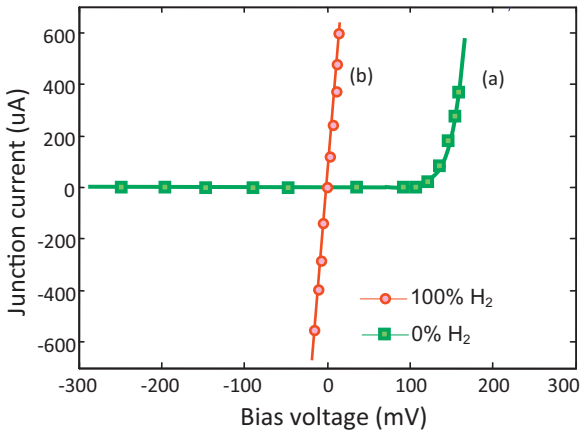

Fig. 2. The *I–V* diagrams obtained for a sample Ag–TiO_2–Ti structure in (a) clean air and (b) in pure hydrogen.

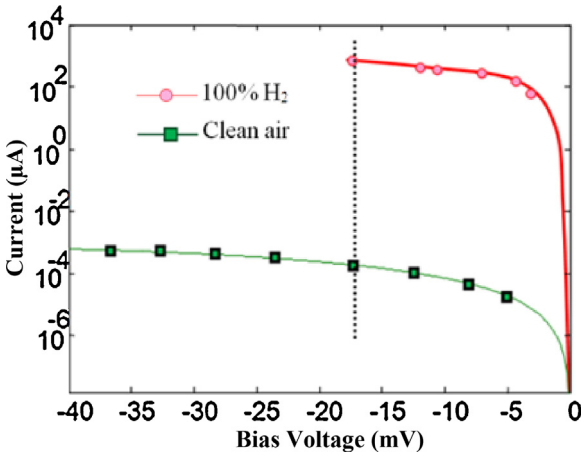

Fig. 3. The logarithmic scale presentation of reverse *I–V* characteristics shown in Fig. 2, demonstrating hydrogen response level as high as 10^5.

also the behaviour of junction is ohmic due to the junction barrier deficiency. In this quantitative model the effect of gas adsorption on TiO_2 and its electron affinity variation is disregarded as it is stated in the literature that the electron affinity of TiO_2 is hardly affected by atmospheric fluctuations [17]. Hence, we consider noble metal work function variations responsible to the gas sensing properties obsereved in fabricated Ag–TiO_2 diodes.

Considering two completely different behaviours of the sensor in hydrogen atmosphere and in clean air, the maximum attainable response of the sensor can be calculated by the model described below. The details are explained in Ref. [2].

At a constant biasing voltage and an appropriate operating temperature (T), the response of a sample sensor to the presence of a contaminant is defined as:

$$\mathrm{SR} = \frac{I_g}{I_a}, \tag{1}$$

in which I_a and I_g are the reverse currents measured in clean and contaminated air, respectively. The reverse current passing through a Schottky diode with low oxide series resistance is controlled solely by the Schottky barrier height (SBH):

$$I_a \approx AA^*T^2e^{(-\varphi/KT)} \tag{2}$$

where A^* is the Richardson constant of the oxide utilized. A and φ are the area and the SBH established at the junction. In a highly reducing atmosphere which SBH decreases to zero I_g is related to the oxide resistance (R_s), and hence the maximum response of the sensor can be calculated from the following equation:

$$\mathrm{SR}_{\max} = \frac{I_g}{I_a} = \frac{(V/R_s)}{AA^*T^2e^{(-\varphi/KT)}} = \frac{V}{AA^*T^2R_s}e^{(\varphi/KT)} \tag{3}$$

Using Eq. (3) and the experimental data obtained from several Ag–TiO_2 diodes, the possibility of obtaining response levels as high as $\sim 10^5$ is clearly indicated. The estimated saturation response by this model is compatible with the data given in Fig. 2 which is replotted in logarithmic scale (see Fig. 3). As shown in Fig. 3, the reverse current can increase by five orders of magnitude in response to 100% hydrogen.

Eq. (3) is also practical in all Schottky type gas sensors which demonstrate reversible transition from Schottky to ohmic behaviour (such as Pt–TiO_2–Ti and Au–TiO_2–Ti diodes) at different atmospheres. This behaviour alteration from Schottky type behaviour in the reference atmosphere (clean air) to linear behaviour in a highly gas contaminated atmosphere is due to reduction of the junction barrier to zero which is the most important requirement to use the model. It is also interesting to mention that this quantitative model is applicable to different noble metal–TiO_2–Ti structures without considering interactions take place on their active gas sensing surfaces. For example, although hydrogen responses of Au-TiO_2 and Ag–TiO_2 are similar [18], hydrogen–silver interaction [19,20] is completely different from that take place on gold surface at the presence of hydrogen [21].

Gas sensing mechanism of Ag–TiO_2–Ti structure is completely different from other noble metal–TiO_2–Ti structures as the barrier formation at the junction stems only from oxygen adsorption on the Ag surface and is not its intrinsic feature: While other noble metals form Schottky diode in contact with TiO_2, silver work function [16] is smaller than that of TiO_2 [22] and makes ohmic junction with TiO_2 [23] when the partial pressure of oxygen is zero. At the presence of oxygen in the working atmosphere of Ag–TiO_2 (such as is clean air), oxygen adsorption on the Ag surface occurs and leads to the silver work function increase which causes barrier formation at the junction.

In the case of Ag–TiO_2 structures, hydrogen species fail to get adsorbed on to silver surface [19,20] and hydrogen detection is due to reduction of the adsorbed oxygen from the Ag surface. This qualitative model predicts that long stay in pure argon, similar to ~10 s exposure to pure hydrogen, makes the junction behave linearly. In the argon atmosphere, the adsorbed oxygen atoms are gradually desorbed and cause the barrier reduction which inturn increases the reverse current passing through the device. The concept was proved by measuring the device current in argon atmosphere (Fig. 4).

According to Fig. 4 the sensor response to pure argon, calculated by Eq. (1), is $\sim 10^5$ which is as high as the saturation response of the sensor obtained in pure hydrogen. These experiments prove that positioning the sensor in pure argon and in pure hydrogen atmosphere are alike and both cause oxygen removal from the silver surface. The model also predicts that a sensor in argon chamber shows no response to injection of hydrogen to that chamber. The prediction was verified experimentally.

The slope of diagram shown in Fig. 4 indicates oxygen sensitivity of the device. The high slope part of the diagram at low concentration of oxygen (<300 ppm) indicates high device sensitivity to very low oxygen partial pressure in argon atmosphere. Typical transient responses of Ag–TiO_2 diode to different levels of oxygen contamination in argon are depicted in Fig. 5. In fact, the Ag–TiO_2–Ti structure is sensitive to the partial pressure of oxygen in its surrounding atmosphere but it is hydrogen sensitive only when oxygen species exist on the silver surface. Transient responses of a sample Ag–TiO_2 diode to low levels of hydrogen contamination in air are shown in Fig. 6. It should be noticed that the reference gas in oxygen and

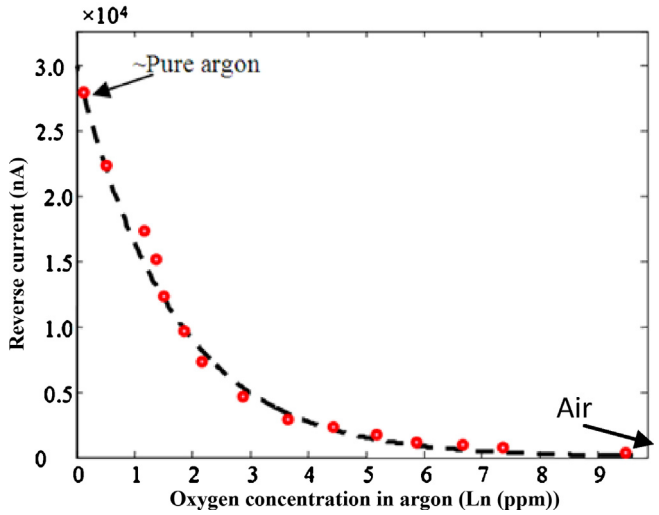

Fig. 4. The variations of the reverse current of the diode vs. oxygen concentration in argon.

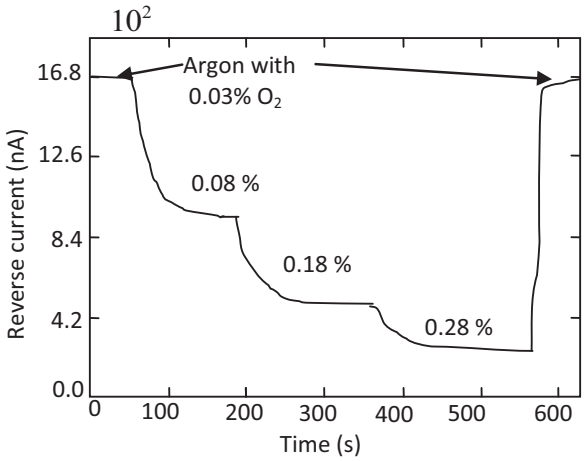

Fig. 5. Typical transient responses of Ag–TiO_2 diode to low levels of oxygen contamination in argon.

hydrogen sensing are argon and clean air respectively which are the beginning and ending points of diagram shown in Fig. 4.

As shown in Fig. 6 the hydrogen responses of the sensor at low hydrogen concentrations were less than 1% of its saturation response related to 100% hydrogen (~10^5). For example 4% hydrogen in air caused 40 times increase in the reverse current of the diode which is much lower than ~10^5 maximum sensor response. This means that the barrier reduction was not too much and the sensor acts as a diode with a lower SBH. At low hydrogen concentrations, the reverse current passing through the device was still controlled solely by the Schottky barrier height, and hence, the gas response of the sensor (SR_{low}) can be written as below:

$$SR_{low} = \frac{I_g}{I_a} = \frac{AA^*T^2e^{(-\varphi_g/KT)}}{AA^*T^2e^{(-\varphi_a/KT)}} = e^{((\varphi_a-\varphi_g)/KT)} = e^{(\Delta\varphi/KT)} \quad (4)$$

in which φ_g and φ_a are SBHs at low concentration level of gas and in clean air. Eq. (4) shows that sensor response to 4% hydrogen is equivalent to 0.18 eV barrier reductions.

Ag–TiO_2–Ti structures can be easily fabricated in submicron dimensions and as gas sensors they have many good quality factors which make them suitable to be utilized in specific applications such as gas analyzers when integrated with a microchannel [24]. They also can be used in automotive industries due to their rigid structures and long life time.

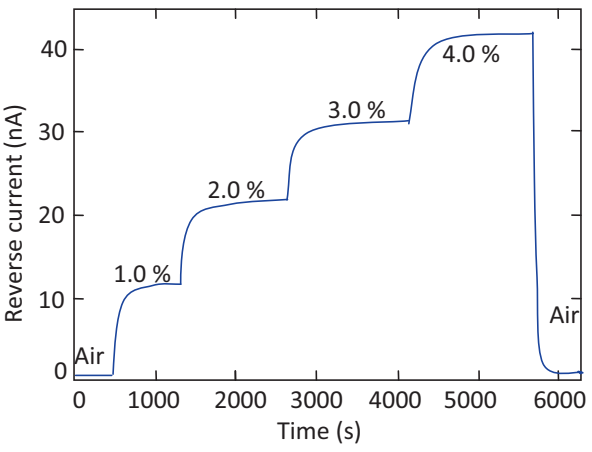

Fig. 6. Transient responses of a sample Ag–TiO_2 diode to different levels of hydrogen contamination in air.

4. Conclusion

The *I–V* characteristics of Ag–TiO_2–Ti structures were studied in pure hydrogen and in clean air. The results showed reversible transition from Schottky to ohmic behaviour at different atmospheres. It was also shown that the reverse current of the device shows hydrogen responses as high as 5 orders of magnitude. The measured saturation response of the sensors was both quantitatively and qualitatively modelled. It became clear that the rectifying properties of Ag–TiO_2 diodes are related to the oxygen adsorption on silver surface and oxygen removal from the sensor surface is the gas sensing mechanism in these sensors. Accordingly, long stay in pure argon is similar to exposure to pure hydrogen because adsorbed oxygen species are gradually desorbed from silver surface in argon ambient. The outcome verified by direct current measurements in both hydrogen and argon atmospheres. It was also shown that fabricated devices are not only good hydrogen sensors but also can be used as leak oxygen sensors in Argon atmosphere.

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