A model for the electric conduction in metal/poly-TiO_2/metal structure

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Abstract. Intensely studied memristive devices have M'/MO/M'' structures, wherein MO is a nanometer-sized metal oxide crystallite sandwiched between the M' and M'' metal electrodes. The most widely used oxide for this purpose is TiO_2 and the electrodes are of noble metals such as platinum, silver, and gold. The memristive features of the device is believed to originate from the motion of the ionized oxygen vacancies within the oxide crystal. The operation of the device is further complicated by the motion of the mobile cations originating from the metal electrodes. The complexity of the device performance increases further when the noble metal electrodes form Schottky barriers at their junctions with TiO_2, as the conduction takes place through these energy barriers. In a recent publication, the authors have shown that, owing to the ohmicity of the Ti/TiO_2 junctions, electronic observations on the devices with Ti/TiO_2/Ti structure can be easier to model. The presented model clarified that in a Ti/poly-TiO_2/Ti structure, the ionic motion and the electronic conduction take place on the TiO_2 grain surfaces and grain boundaries rather than the grain interiors. Here, we show that the suggested model has important implications for chemical sensor design and fabrication.

Keywords: TiO_2, Polycrystalline, Oxygen vacancy, Chemical sensor.
1. Introduction

Profound resistance switching, observed in nanostructured metal oxide semiconductors, originates from the alteration of the conduction mechanism or route caused by the motion and reformattting of the distribution patterns of the present mobile ionic species [1]. The resistive memory devices (memristors) [2] operating based on such resistance switching are candidate memory devices for the future nanoelectronic circuits [3]. The memristor structures studied are generally of M'/MO/M'' type, where MO is a nanometer sized metal oxide crystallite sandwiched between the M' and M'' metal electrodes [4]. The most widely studied oxide for memristor fabrication is TiO$_2$ which is, in most cases, connected to noble metal electrodes such as platinum [5], silver [6], or gold [7], which add to the complexity of the device performance by forming Schottky energy barriers at the junctions with TiO$_2$ [8-10]. The motion, patterning and relaxation of the mobile ionic species at varying electric field levels form or eliminate different electron conduction routes and result in complex I-V characteristics generally difficult to predict. While the migration of the ionized oxygen vacancy (IOV) has been established as the most effective cause of resistance variations in these devices [11-16], it has been shown that the motions of all cations, including those originating from the electrodes, can determine the main conduction mechanism and promote hysteretic behaviors [3, 17, 18]. It appears that better understanding of the device performance would be afforded using samples with Ti/TiO$_2$/Ti structure in which the varieties of the candidate mobile species is limited. Moreover, unlike many other transition metals, no energy barrier is formed at the junction between titanium and TiO$_2$ [19-21] and the electronic structure of the device is simpler to model.

Here, we study the I-V characteristics of the Ti/poly-TiO$_2$/Ti structures made of 400 nm-thick oxide layers with asymmetric cross-sectional oxygen vacancy distributions and describe the obtained results based on the two different conduction mechanisms prevailing respectively in the low and high biasing fields. It is shown that the I-V diagram recorded for such a sample strongly depends on the biasing voltage sweeping frequency and the relative humidity level in the surrounding atmosphere.

2. Experimental

TiO$_2$ layers are grown on 10 mm $\times$ 10 mm Ti chips cut from 1 mm thick titanium foil by thermal oxidation at 650 °C for 60 minutes in air. Samples are air quenched from the soaking temperature. The temperature vs. time profiles used for the oxidation and quenching are given in figure 1a. Owing to the heat capacity of the Ti substrate and the refractory underneath, the samples cool asymmetrically. The thickness of the oxide layers is in the 350 to 400 nm range and the speed of cooling is higher at the top of the layer. According to the obtained XRD patterns, given in figure 1b, the grown oxide layers are of rutile phase. The oxide layers grown at lower temperatures, e.g. 500 °C, in similar conditions, are rutile and anatase mixtures [8, 22]. The Ti/TiO$_2$/Ti devices are made by selected area titanium deposition by thermal evaporation of the metal on the grown oxide layer. Each chip accommodates 16 samples as shown in figure 2a. The schematic diagram of the sample structure is given in figure 2b wherein the micrographs of the oxide layer are given as insets indicating a polycrystalline structure with average grain size of 50 nm.

The titanium chip acts as the backside electrode and is connected to the measurement circuitry using conductive paste and silver wire. The top Ti electrode is connected to the measurement system via a pressure-connected titanium probe which can move from one device to another using a manually controlled x-y-z micromanipulator. This connection method prevents contamination of the oxide layer with foreign metallic species. All samples are briefly annealed at 50 °C in air, which proved to improve the evenness in the electrical features among similar samples. All samples are primarily tested by the application of an AC voltage of 1 V peak-to-peak to the sample connected in series with a 100 Ω resistor; samples allowing current levels above 1 mA/mm$^2$ are rejected. The experimental setup is depicted in figure 3.
Figure 1. (a) The temperature vs. time diagrams of the oxidation and quenching processes, and (b) the XRD patterns of the grown oxide layers. The inset in (a) schematically presents the uneven distribution of the oxygen vacancies.

Figure 2. (a) The photograph of the Ti/poly-TiO$_2$/Ti samples fabricated on a thermally oxidized titanium chip. (b) The schematic diagram of the device structure. The insets in (b) are the plan and cross-sectional view micrographs of the TiO$_2$ layer.
3. Results and Discussion

The I-V diagram of the sample at five different voltage sweeping frequencies of 0.01, 0.1, 1.0, 10, and 100 Hz are shown in figure 4. The applied field is considered positive when the connection probe is positively biased with respect to the Ti substrate. These diagrams are plotted after the reduction of the current contribution of the parallel capacitor of the sample devices, which is considerable particularly at 100 Hz. In figure 4, the configuration of the I-V diagram respective to 100 Hz is in agreement with the previous reports on the Ti/TiO₂ contacts [8, 10, 19-22]. This diagram presents characteristics consistent with the symmetric structure of the device, the zero junction energy barrier, ohmic connection between the titanium electrodes and TiO₂, and normal electronic conduction through an n-type space-charge-limited medium. The resistance of the oxide layer calculated based on the slope of the profile at around zero biasing is 0.3 MΩ. Considering the geometry of the device, the calculated conductivity for the rutile layer is $8.3 \times 10^{-9}$ S/cm. The I-V diagrams recorded by utilizing low voltage sweeping frequencies are strikingly different. At 0.01 Hz, for instance, the device presents a rectifying diode-like I-V profile and a “soft breakdown” at around biasing voltage of $+1.5$ V. This is encountered with a profound reduction in the sample resistance and hysteretic behavior of the device.

![Figure 3](image-url) The experimental setup used for the I-V measurements on the Ti/poly-TiO₂/Ti samples.

![Figure 4](image-url) The I-V diagrams of a Ti/poly-TiO₂/Ti diode recorded using different voltage sweeping frequencies.
We have proposed a model which describes the observed resistance change, the asymmetric profile, hysteretic behavior, the strong dependence of the I-V profiles of the device on the voltage sweeping frequency, and the I-V characteristics change upon thermal annealing in air [1]. The model assumes ionized oxygen vacancy (IOV) motion on the surface of the grains, rather than the grain interior. The IOVs motion is in the direction of forming conductive filaments within the grain boundary regions; the process is schematically presented in figure 5. This assumption is justified as we prove that the field applied through the whole I-V profile is an order of magnitude lower than the level required for the IOV mobilization within the rutile crystal.

The implications of the proposed model are interesting as the surface conduction would allow influence of the external species on the conduction process. For instance, it was predicted that the water monomers adsorbed to the surface of the rutile grains should affect the IOV motion therein and, hence, alter the conductance through the polycrystalline layer. Our quantitative considerations, based on the results of direct STM observations of the oxygen vacancy migration on rutile {110} facets [23-26], showed that the presence of the H₂O molecules and hydroxyl group decrease the activation energy of the IOV migration. Our experimental results, presented in figure 6, verify the predictions of the model. According to these results, considering a constant forward biasing level, say +1.5 V, the device current increases with the relative humidity level in the surrounding atmosphere.

Figure 5. (a-d) The schematic presentation of the IOV filament formation within the grain boundaries after applying step voltage.
Figure 6. The I-V diagram of the Ti/poly-TiO$_2$/Ti device plotted at two different relative humidity levels.

4. Conclusions
Due to the uneven distribution of the oxygen vacancy, the I-V characteristics of the diode with Ti/poly-TiO$_2$/Ti structure is strongly asymmetric. In the forward biased device, the current is conducted via conductive filaments formed by the motion of the IOVs on the surfaces of the grains. Interactions between the grain surface and the surrounding atmosphere is easy and, hence, the described conduction mechanism can easily be influence by environmental parameters.

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