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Influence of HfO_x composition on hafnium oxide-based memristor electrical characteristics

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Abstract

The influence of a variable oxygen concentration in HfO_x ($x < 2$) layers on the forming process and resistive switching of $TaN/HfO_x/Ni$ ReRAM cells is investigated. We demonstrate that resistive switching is possible only for those cells for which the Hf/O ratio in a HfO_x layer corresponds to a narrow range for which $x \approx 1.8$. The decrease of oxygen concentration in the oxide layer is shown to lead to, on the one hand, the decrease in the I_{ON}/I_{OFF} ratio and, on the other hand, to the elimination of the forming process. The analysis of XPS spectra of HfO_x films for a wide range of compositions revealed that the range of x, for which resistive switching is possible, corresponds to a maximum concentration of the Hf_4O_7 phase. The influence of HfO_x phase composition on resistive switching is discussed.

1. Introduction

ReRAM CELL, quite often referred to as memristor [1–3], represents a non-volatile memory device with a metal-insulator-metal structure in which the information is retained by means of changing the resistance of the insulator layer. A typical ReRAM cell is capable of maintaining two non-volatile states—the high resistivity state (HRS) and low resistivity state (LRS). HfO_x-based resistive memory devices have already demonstrated a high number of resistive switching cycles ($\sim 10^{10}$) [4] and quite large I_{ON}/I_{OFF} ratio ($\sim 10^3$) [4, 5]. In spite of the active study on such type of memory having been conducted since 2008 [1], a number of challenges are yet to be overcome. For example, it is desirable to eliminate the forming process which inevitably takes place prior to the first resistive switching act and may occur at voltages which are much higher than the ones required for the resistive switching [2, 6]. Also, it is still under debate what structural changes occur in the oxide layer when the device is switched from HRS to LRS or vice versa. In addition, the charge transport mechanisms in these devices are yet to be fully understood.

Since a typical insulator layer in ReRAM represents a non-stoichiometric transition metal oxide film, the ratio between the concentrations of oxygen atoms and metal atoms in the film (referred to as parameter x hereafter) seems to play a major role in resistive switching. For example, in [7] on TaO_x-based ReRAM cells tantalum oxide layer resistivity was found to increase exponentially as oxygen concentration in this layer increased. In other works [3, 8, 9] this concentration was varied by different means in order to produce TaO_x layers with varying [O]/[Ta] ratio. The value was found to influence the ability of ReRAM cell to exhibit resistive switching and the ratio of resistances in LRS and HRS. Therefore, the determination of the value of x seems to be quite interesting. However, in works regarding the impact of oxide stoichiometry on ReRAM cell properties the values of x are either not stated or contradict the ones stated in other works and therefore this issue requires further investigation. Moreover, there seems to be no similar comprehensive study of HfO_x-based resistive memories. We present an investigation of the hafnium oxide oxygen concentration influence on various electrical parameters of ReRAM (e.g., forming voltage and I_{ON}/I_{OFF} ratio) and show that the most optimized performance of HfO_x-based resistive memories can be reached at $x \approx 1.8$.

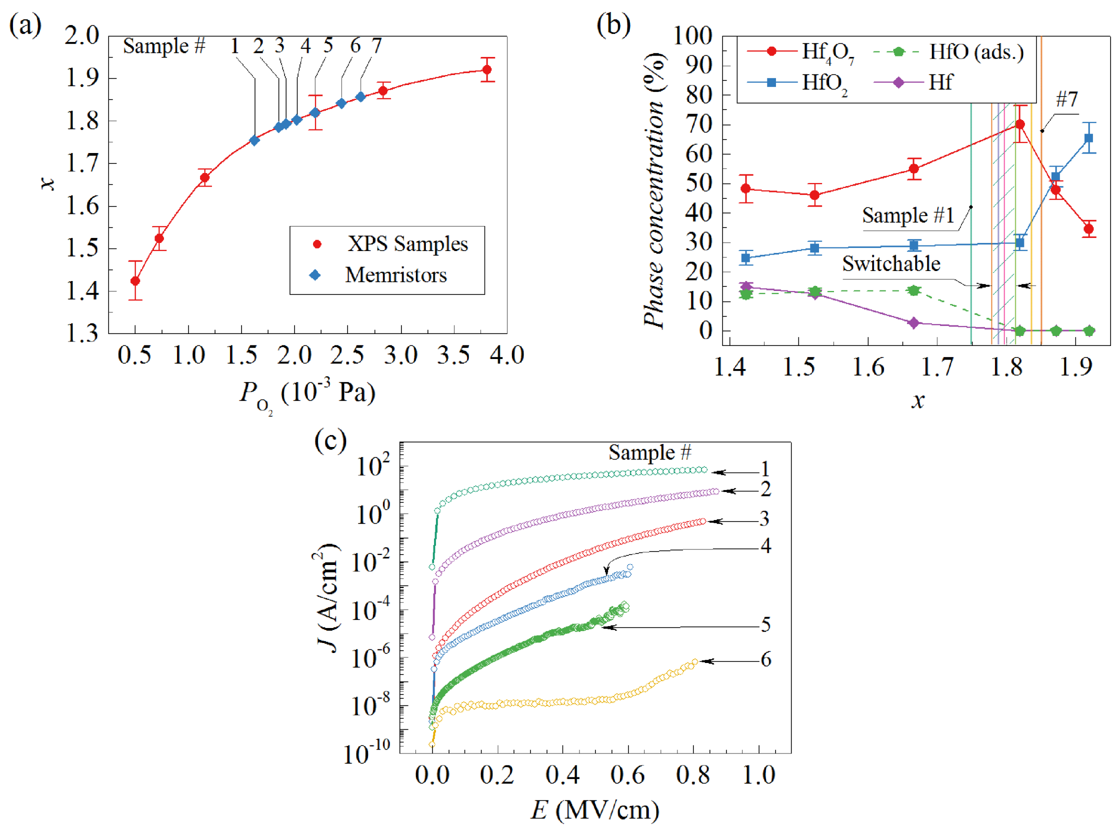

Figure 1. (a) Correlation between the parameter x of HfO_x films and O_2 partial pressure obtained in our previous work [10] (red circles). Blue rhombs represent this correlation values corresponding to the samples studied in this work. (b) Dependence of various phases concentration in HfO_x on parameter x [10]. The HfO (ads.) phase is present only at the film surface. The data points were obtained by the XPS analysis of various HfO_x films in our previous work [10]. The vertical lines represent the values of parameter x for each sample studied in this work. The dashed area marks the approximate range of x, for which the resistive switching in HfO_x-based memristors is achievable. (c) Current density versus electric field for various TaN/HfO_x/Ni memristors measured before the forming step.

Table 1. List of TaN/HfO_x/Ni samples studied in this work.

Sample	P_{O2} (10^{-3} Pa)	x	Resistive switching
1	1.62	1.75 ± 0.05	No
2	1.85	1.78 ± 0.05	Yes
3	1.92	1.79 ± 0.05	Yes
4	2.02	1.80 ± 0.05	Yes
5	2.19	1.81 ± 0.05	Yes
6	2.44	1.84 ± 0.05	No
7	2.62	1.85 ± 0.05	No

2. Experiments

A number of samples with TaN/HfO_x/Ni ReRAM cells were prepared for the study. First, a 50 nm thick TaN bottom electrode was deposited by ion beam sputtering deposition (IBSD) on the Si/SiO_2 substrate. Then a 28 nm thick HfO_x active layer was deposited by the same method with different partial oxygen pressures (P_{O2}) in the depositing chamber for various samples to prepare oxide layers with a varying Hf/O ratio (x), as presented in table 1. Finally, a 50 nm thick Ni layer was deposited by electron beam evaporation through metallic masks with square-shaped windows of width a (100, 156, 312, 625 and 1250 μm) to obtain cells with different areas. The I–V curves were measured using semiconductor device parameter analyzer Agilent B1500A.

3. Results and discussion

Our earlier investigations of HfO_x films with varying oxygen concentrations deposited by IBSD on silicon substrates by XPS allowed for obtaining the correlation between the oxygen partial pressure P_{O2} and x [10], as presented in figure 1(a). This correlation was used to obtain the value of x for each sample studied in this work.

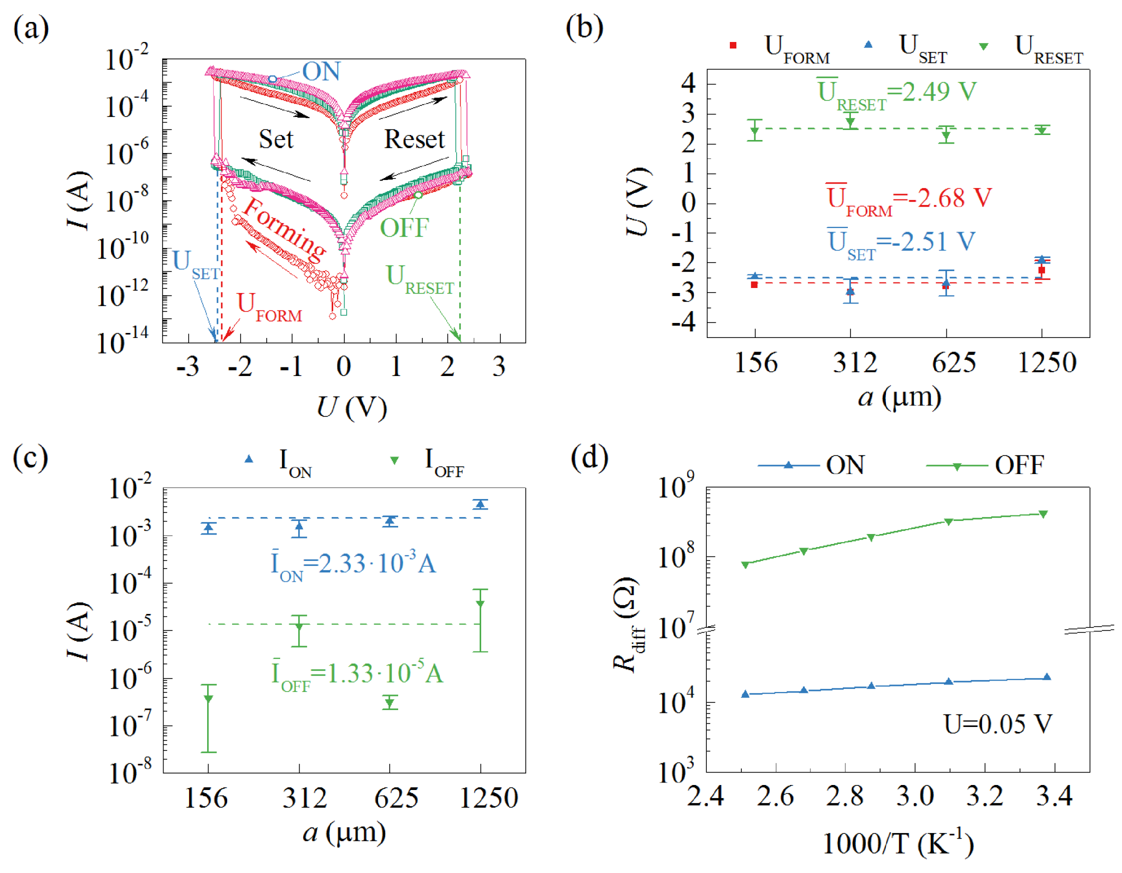

Figure 2. (a) Typical *I–V* curves of the 156 × 156 μm^2 TaN/HfO_x/Ni memristor demonstrating several switching cycles. (b) Forming voltage, set voltage and reset voltage dependences on the memristor area (area = a^2). (c) I_{ON} and I_{OFF} dependence on the memristor area (at 2.0 V bias). (d) The differential resistance (R_{diff}) dependence on temperature for LRS (ON) and HRS (OFF) of the TaN/HfO_x/Ni memristor at 0.05 V bias.

Additionally, that investigation of HfO_x films demonstrated that there were three phases in them—metallic phase (Hf), hafnium sub-oxide Hf_4O_7 and stoichiometric oxide HfO_2 and the ratio of these phases correlated with parameter x (figure 1(b)).

A comparison of *J–E* curves of ReRAM cells with varying oxygen concentration in HfO_x layer measured prior to the forming process demonstrated that their electrical properties were quite different from each other despite that the values of x for various HfO_x layers were close to each other (table 1). It can be seen in figure 1(c), that HfO_x conductivity rapidly increases by almost 10 orders of magnitude as the oxygen concentration in the hafnium oxide film decreases from the sample with the highest x (sample #7) to the sample with the lowest x (sample #1).

The *I–V* measurements of the samples after the forming process revealed that the reproducible resistive switching was achievable only for the samples with x lying in quite a narrow range between 1.78 and 1.81 (see the switchable region in figure 1(b) and table 1). The samples that satisfied this requirement demonstrated the bipolar resistive switching. Shown in figure 2(a) is a typical *I–V* curve for the memristor with $a = 156\ \mu m$ obtained from one of such samples. Forming voltages (U_{FORM}) appeared to be close to the voltages of resistive switching in contrast to other contributions [2, 6]. The I_{ON}/I_{OFF} ratio for our samples reached 4 orders of magnitude.

The forming (U_{FORM}) voltage, set voltage (U_{SET}) and reset voltage (U_{RESET}), as well as I_{ON} and I_{OFF}, demonstrated no dependence on the ReRAM cell area (figures 2(b) and (c)). The absence of area correlation for LRS indicates the local nature of conductivity. Indeed, in accordance with a well-known model [2, 5, 11], after the forming process, a filament shunting the bottom and top electrodes of the memristor is formed in the HfO_x layer and this filament limits the current flow. Moreover, since the I_{ON} values for the structures with different areas are very close to each other, it is likely that the filament has the same size for all of these structures. The lack of I_{OFF} dependence on the structure area is likely due to only partial dissolving of the filament during the reset switching process. As a result, the HRS conductivity is limited by this partially dissolved filament and a small HfO_x volume.

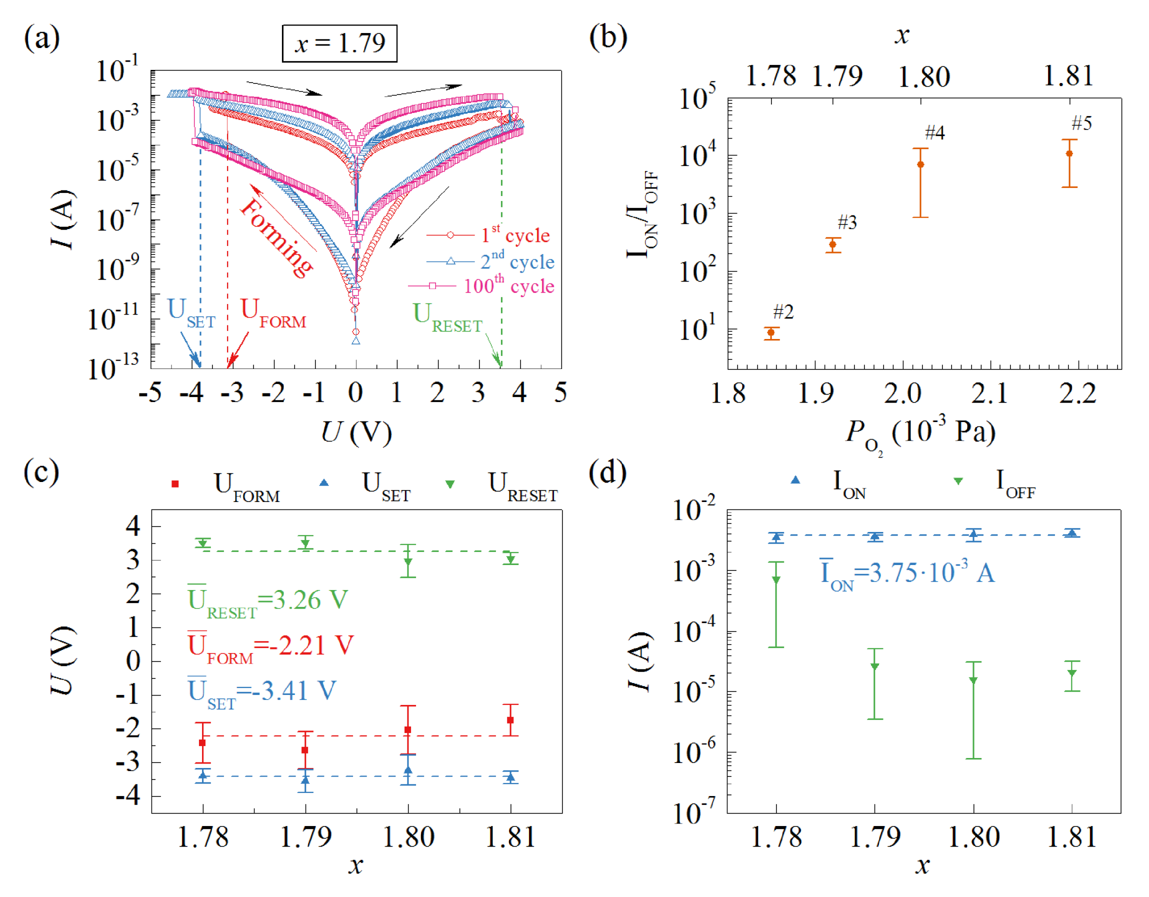

Figure 3. (a) I–V curves of the 100 × 100 μm^2 TaN/HfO_x/Ni memrirstor with $x = 1.79$. (b) I_{ON}/I_{OFF} dependence on O_2 partial pressure and parameter x of hafnium oxide at 2.0 V. (c) The forming voltage, set voltage and reset voltage dependences on parameter x of hafnium oxide. (d) I_{ON} and I_{OFF} dependence on the parameter x of hafnium oxide at the 2.0 V bias applied to the memristor.

Presented in figure 2(d) is the temperature dependence of the differential resistance of one of our samples both in HRS and LRS. As the temperature increased, the memristor resistance decreased both in HRS and LRS. Such a result for LRS is quite unexpected, as the filament is assumed to be metallic [2, 11, 12]. Quantum-chemical calculations of structural and thermodynamic properties of hafnium suboxides using DFT approximation predicted two intermediate semiconductor oxide phases to be existing, namely HfO and Hf_4O_7, with a varying bandgap (0.4–1.1 eV) [13]. It seems to be quite possible that various non-metallic phases are mixed to form the filament [14]. As mentioned above, the resistive switching is possible for the samples with a parameter x close to 1.8. Interesting enough, this value of x corresponds to the maximum concentration of the Hf_4O_7 phase in HfO_x films (see figure 1(b)).

A comparison of various electrical parameters of HfO_x memristors with different x within the switchable range is presented in figure 3. As can be seen, there is no correlation between U_{FORM}, U_{SET} and U_{RESET}, and x. Also, the level of I_{ON} remains the same for all memristors within the switchable range of x, which can be accounted for the same diameter and chemical composition of the conducting filament. However, I_{OFF} rapidly increases with a decrease of oxygen concentration in the HfO_x film, especially at voltages close to U_{SET} and U_{RESET}, leading to a decrease of the I_{ON}/I_{OFF} ratio (figure 3(b)). This can be accounted for the leakage current increase caused by an increase of oxygen vacancies concentration in a HfO_x film. It is also interesting to note that the forming part of I–V curves of samples with x within the switchable range starts to resemble the HRS part as x decreases until they are completely inseparable and, therefore, the forming step is completely eliminated, as one can see in figure 3(a).

It is worth noting that the forming voltages for the memristor samples demonstrated no dependence on the value of x and generally were lower than the subsequent set voltages. We assume that this is due to the method used for HfO_x layer depositing, namely IBSD, which produces oxide layers of not very high level of conformity and morphological perfection in comparison with the ALD method. Therefore, HfO_x layers produced by IBSD are likely to contain morphological defects which may assist in the process of filament formation. Nevertheless, the exact reason of such forming behavior is not quite clear and this issue requires further experimental investigation.

4. Conclusion

The correlation between the electrical properties of TaN/HfO_x/Ni structures and the oxygen concentration in the IBSD-deposited HfO_x layer proved to be quite strong. The resistive switching was found to be possible only for the devices with HfO_x layers with x ranging from 1.78 to 1.81, which corresponds to the maximum concentration of the Hf_4O_7 phase. Furthermore, the I_{ON}/I_{OFF} ratio proved to be decreasing at low oxygen concentrations. At the same time, U_{SET}, U_{RESET} and I_{ON} showed no correlation with both the structure area and parameter x, which points to the local nature of memristor conductivity in LRS (namely the filament model). These results also point to the conducting filament appearing to be of the same chemical composition and size for HfO_x memristors with a varying oxygen concentration. The decrease of memristor resistance both in HRS and LRS with the increase in temperature suggests that the conducting filament created in the HfO_x film bulk is likely to be of semiconductor nature rather than the metallic one.

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