<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Study of Multilevel High-Resistance States in HfOx-Based Resistive Switching Random Access Memory by Impedance Spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Date</strong></td>
<td>2015-07-07</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10220/39539">http://hdl.handle.net/10220/39539</a></td>
</tr>
<tr>
<td><strong>Rights</strong></td>
<td>© 2015 IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, in any current or future media, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works, for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other works. The published version is available at: [<a href="http://dx.doi.org/10.1109/TED.2015.2445339">http://dx.doi.org/10.1109/TED.2015.2445339</a>].</td>
</tr>
</tbody>
</table>
Study of Multilevel High Resistance States in HfO$_x$-Based Resistive Switching Random Access Memory by Impedance Spectroscopy


Abstract—Multilevel high resistance states are achieved in TiN/HfO$_x$/Pt resistive switching random access memory device by controlling the reset stop voltage. Impedance spectroscopy is used to study the multilevel high resistance states. It is shown that the high resistance state can be described with an equivalent circuit consisting of the major components $R_s$, $R_p$, and $C$ corresponding to the series resistance of the TiON interfacial layer, the equivalent parallel resistance and capacitance of the leakage gap between the TiON layer and the residual conductive filament, respectively. These components show a strong dependence on the stop voltage, which can be explained in the framework of oxygen vacancy model and conductive filament concept. On the other hand, $R_s$ is observed to decrease with DC bias, which can be attributed to the barrier lowering effect of the Coulombic trap well in the Poole-Frenkel emission model.

Index Terms—Impedance spectroscopy, multilevel high resistance states, resistive switching random access memory (RRAM).

I. INTRODUCTION

Resistive switching random access memory (RRAM) based on metal oxides like Al$_2$O$_3$, ZnO, NiO, TiO$_2$, and Cu$_2$O is promising in the application of next-generation non-volatile memory due to its simple structure, low power consumption, high read/write speed, and good reliability [1]-[7]. Recently, multilevel resistance states in RRAM devices have been demonstrated to increase the storage density of the RRAM device [8], [9]. Until now, most of the research works were focused on the performance improvement and reliability of the multibit storage, there are relatively few studies on the mechanism for the multilevel resistance states of RRAM device. In this work, impedance spectroscopy is employed to investigate multilevel high resistance states in TiN/HfO$_x$/Pt RRAM structure. Impedance spectroscopy is a powerful tool to examine the conduction properties of dielectric thin films, making it suitable for resistive switching property study [10], [11]. For the TiN/HfO$_x$/Pt RRAM structure used in this work, the multilevel high resistance states may be attributed to the different rupture degrees of the conductive filament, which is hard to be detected by the microscopic techniques such as transmission electron microscopy and scanning probe microscopy. However, through the analysis of the impedance measurement, we have been able to obtain information about the redox reaction relating to the change of TiON interfacial layer and rupture of the conductive filament for different high resistance states.

II. EXPERIMENT

The TiN/HfO$_x$/Pt RRAM structure was fabricated with the following sequence. Firstly, a 500 nm SiO$_2$ film was deposited on an 8-inch p-type Si wafer by plasma-enhanced chemical vapor deposition to prevent the leakage during the switching operation of the RRAM device. Then, 50 nm Pt/20 nm Ti layer was deposited by electron-beam evaporation to form the bottom electrode on the SiO$_2$ film. Subsequently, a 10 nm HfO$_x$ layer was deposited by atomic layer deposition on the bottom electrode. Finally, a 100 nm TiN layer was deposited onto the HfO$_x$ layer using DC sputtering and patterned to form the top electrode with the area of about 4 $\mu$m$^2$. A Keithley 4200 semiconductor characterization system was used to characterize the switching properties of the device. Impedance measurement of different high resistance states was carried out with an Agilent E4980A Precision LCR Meter in the frequency range of 20 Hz to 2 MHz with a 30 mV AC signal.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the typical bipolar resistive switching behavior...
of the TiN/HfO/Pt RRAM structure under different reset stop voltages ($V_{\text{stop}}$) ranging from -1.3 V to -2.0 V. Multilevel high resistance states can be achieved by varying $V_{\text{stop}}$. The inset of Fig. 1 shows the values of the high resistance states created with different $V_{\text{stop}}$ (read at 0.1 V) and the corresponding $V_{\text{set}}$.

To examine the behavior of different high resistance states, we conducted the complex impedance measurement after each process, and the oxygen ions will move back to the HfO layer to eliminate the oxygen vacancies, which will widen the gap between the top electrode and the residual conductive filament, and thus the resistance value will increase due to the gap widening [14]. In this case, the $V_{\text{set}}$ during the following set process also increases with the magnitude of $V_{\text{stop}}$, as demonstrated in the inset of Fig. 1. It is because that a larger $V_{\text{set}}$ is needed to rebuild the conductive filament for a wider leakage gap.

The above arguments could be verified with the impedance measurement. The complex impedance measurement is conducted after the reset process by applying a 30 mV small AC signal in the frequency range of 20 Hz to 2 MHz without DC bias. The scatter plot in Fig. 2 shows the complex impedance spectra of the high resistance state after reset operation with the $V_{\text{stop}}$ of -1.3 V. The approximately semicircle shape of the Nyquist plots (-$Z''$ VS $Z'$) indicates that the high resistance state can be modelled as a parallel connection of a resistor and a capacitor in series with some resistors, as shown in the inset of Fig. 2. The RRAM devices with other sizes ($5 \times 5$ $\mu$m$^2$ and $8 \times 8$ $\mu$m$^2$) are also tested, and similar semicircle shapes of the Nyquist plots are observed (not shown here). This indicates that device size in the range has no influence on the equivalent circuit. The impedance of the equivalent circuit can be described with

$$Z = R_s + R_f + R_t + \frac{R}{1 + \omega^2 R^2 C^2} - \frac{j \omega R^2 C}{1 + \omega^2 R^2 C^2}$$

(1)

where $Z$ is the complex impedance, $\omega$ is the angular frequency, $R_s$, $R_f$, and $R_t$ are the equivalent series resistance for the TiON interfacial layer, residual conductive filament and measurement connections, respectively, and $R$ and $C$ are the equivalent parallel resistance and capacitance of the leakage gap, respectively. As discussed above, the redox reaction between the TiN electrode and the oxygen ions during the set process results in a TiON interfacial layer, which is more resistive than the pure TiN electrode. Though the series resistance should be the sum of the resistance of the TiON interfacial layer, residual filaments and measurement connections, the last two items can be neglected because of their much lower values [15]. Therefore, (1) can be rewritten as

$$Z = Z' + j Z'' = R_s + \frac{R}{1 + \omega^2 R^2 C^2} + j(-\frac{\omega R^2 C}{1 + \omega^2 R^2 C^2})$$

(2)

where $Z'$ and $Z''$ are the real part and imaginary part of the complex impedance, respectively. The fitting with (2) to the measurement data is shown in Fig. 2. An excellent agreement between the fitting and measurement is achieved, which indicates that the equivalent circuit shown in the inset of Fig. 2 can well describe the electrical characteristic of the RRAM structure. The fitting yields the values of 5336 $\Omega$, 8741 $\Omega$ and 9.81 pF for $R_s$, $R$ and $C$, respectively. With the obtained $R_s$ value, one may estimate the resistivity $\rho$ of the TiON interfacial layer with $\rho = (A/\text{TiON})R_s$, where $\text{TiON}$ is the thickness of the interfacial layer, and the device area $A = 4$ $\mu$m$^2$. Under the assumption that $\text{TiON}$ is 5 nm [16], [17], the resistivity is estimated to be $\approx 400$ $\Omega$ cm, which is within the reported resistivity range of TiON films [18].
reset process at different \( V_{\text{stop}} \), and the result is shown in Fig. 3(a). The Nyquist plots of all \( V_{\text{stop}} \) can be well fitted with (2), which indicates that all the high resistance states can be modelled with the equivalent circuit shown in the inset of Fig. 2. The values of the components in the equivalent circuit are shown in Fig. 3(b). The \( R_s \) value has an obvious decreasing trend when the \( V_{\text{stop}} \) changes from \(-1.3 \) V to \(-2.0 \) V. Since TiON is more resistive than pure TiN, the decrease of the \( R_s \) means more TiON is reduced to TiN for a larger \( V_{\text{stop}} \). The parallel \( RC \) element represents the leakage gap between the top electrode and the residual conductive filament, and the modulation of the gap width is responsible for the changes in the \( R \) and \( C \) values. As shown in Fig. 3(b), the \( R \) value increases with the increase of \( V_{\text{stop}} \), which means the width of the leakage gap gradually increases. It is reasonable to argue that the recombination of the oxygen vacancies with the oxygen ions supplied from the TiON layer or even the surrounding HfO \(_x\) layer is enhanced as the \( V_{\text{stop}} \) changes from \(-1.3 \) V to \(-2.0 \) V. It is worth noting that \( R \) and \( R \) have an opposite evolution tendency, while the change of the \( \text{DC} \) resistance, shown in the inset of Fig. 1, is consistent with the evolution of \( R \) because the \( R \) value is much larger than the \( R_s \) value. The capacitance of the \( RC \) element should be inversely proportional to the width of the leakage gap between the top electrode and the residual filament, being similar to the situation of a parallel plate capacitor; thus the decrease in the \( C \) value with \( V_{\text{stop}} \) suggests that a larger \( V_{\text{stop}} \) results in a wider leakage gap. Therefore, both dependence of \( R \) and \( C \) on \( V_{\text{stop}} \) suggest that the leakage gap width increases with \( V_{\text{stop}} \), which explains the increase of the \( \text{DC} \) resistance with \( V_{\text{stop}} \) as shown in the inset of Fig. 1.

\( C \) can be described with \( C = \varepsilon_0 \varepsilon_r \alpha \frac{A}{t} \), where \( \varepsilon_0 \) is the permittivity in vacuum, and \( \varepsilon_r \) and \( t \) are the dielectric constant and thickness of the leakage gap, respectively; and \( R \) can be assumed to be \( R = \frac{R_0 \varepsilon_\text{exp}(\alpha t)}{\varepsilon_0} \), where \( R_0 \) and \( \alpha \) are two constants as it has been suggested by Monte Carlo simulation that \( R \) has an exponential dependence on \( t \) [19], [20]. Under the above assumptions, one may find the simple relationship between \( R \) and \( C \) as follows

\[
\ln R = \ln R_0 + \frac{\varepsilon_r \varepsilon_0 A}{C} (3)
\]

The linear relationship between \( \ln(R) \) and \( 1/C \) predicted by (3) roughly agrees with the experimental result, as shown in Fig. 4.

To examine the influence of \( \text{DC} \) bias on the complex impedance measurement, a positive voltage ranging from \( 0 \) V to \( 0.25 \) V was superimposed to the \( \text{AC} \) signal during the impedance measurement, and the complex impedance spectra of the high resistance state under different positive \( \text{DC} \) biases are shown in Fig. 5(a). The semicircle shape of all the Nyquist plots indicates that the \( \text{DC} \) bias has little influence on the equivalent circuit of the high resistance state. The values of \( R_s \), \( R \) and \( C \) obtained from the fitting as a function of the \( \text{DC} \) bias are shown in Fig. 5(b). Only the \( R \) has an obvious decreasing trend with the increase of \( \text{DC} \) bias. The little change of both \( R_s \) and \( \text{DC} \) indicates that the redox reaction at the TiN/HfO \(_x\) interface is not significant under the influence of a small positive \( \text{DC} \) bias and the leakage gap should change little or remain unchanged. Therefore the change of the \( R \) value cannot originate from the leakage gap modulation effect. Previous studies on the current transport in HfO \(_x\)-based RRAM device show that Poole-Frenkel emission model can well describe the conduction of the high resistance state; and the oxygen vacancies inside the HfO \(_x\) layer could act as the Coulombic traps in the Poole-Frenkel emission model [21], [22]. When a bias is applied to the switching layer, one side of the barrier height of the Coulombic traps will be reduced, the probability for the electrons escaping from the trap well by thermal...
emission increases, thus the $R$ value will decrease with increasing $DC$ bias [23]. The decrease of $R$ with $DC$ bias is indeed observed in Fig. 5(b). This is also consistent with the experimental result shown in Fig. 5(c) that the $DC$ resistance of the high resistance state decreases with the read voltage ($V_{\text{read}}$).

IV. CONCLUSION

In conclusion, impedance spectroscopy is a useful technique to study multilevel high resistance states in HfO$_2$-based RRAM device. The analysis of complex impedance suggests that the redox reaction at the TiN/HfO$_2$ interface and the modulation of the leakage gap should be responsible for the changes in the parameters of the equivalent circuit of the RRAM device. The leakage gap widening effect is shown to be the main reason for the higher resistance value associated with a larger $|V_{\text{app}}|$. Both $R$, and $C$ show little change with $DC$ bias; however, $R$ decreases with the $DC$ bias, which can be attributed to the barrier lowering effect of the Coulomb trap well in the Poole-Frenkel emission model.

REFERENCES


P. Liu received the B.S. degree from the Nanyang Technological University (NTU) of Electrical and Electronic Engineering, Singapore. He is currently pursuing the Ph.D. degree at NTU.

Y. Liu received the Ph.D. degree from Nanyang Technological University, Singapore, in 2005. He joined the University of Electronic Science and Technology of China, Chengdu, China, where he has been a Full Professor since 2008.

P. S. Lee received the Ph.D. degree from National University of Singapore (NUS), Singapore, in 2001. She is currently an Associate Professor with the School of Materials Science and Engineering, Nanyang Technological University, Singapore.

X. P. Wang received the B.Eng. and M.Eng. degrees from Tsinghua University, Beijing, China, and Ph.D. degree from National University of Singapore, Singapore, in 1999, 2002, and 2007, respectively. He is currently a Scientist with the Institute of Microelectronics, Agency for Science, Technology and Research, Singapore.

H. Y. Li received the Ph.D. degree in semiconductor physics and devices from the Changchun Institute of Physics, Chinese Academy of Science, Changchun, China, in 1999. She is currently a Scientist with the Institute of Microelectronics, Agency for Science, Technology and Research, Singapore.

G. Q. Lo received the M.S. and Ph.D. degrees in electrical and computer engineering from the University of Texas at Austin, Austin, in 1989 and 1992, respectively. Since 2004, he has been with the Institute of Microelectronics (IME), Agency for Science, Technology and Research, Singapore. He is currently the Laboratory Director for IME’s Semiconductor Process Technology and the Program Director of Nanoelectronics and Photonics program.