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Effect of Nitrogen Doping on Variability of TaO_x -RRAM for Low-Power 3-Bit MLC Applications

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The switching uniformity and reliability of the TaO_x based resistive random access memory (RRAM) device were investigated with varying nitrogen doping concentration. The nitrogen doped samples shows excellent electrical and reliability characteristics such as small switching variability for 3-bit multilevel per cell (MLC), low power operation and good retention properties. Compared with control sample, improved device characteristics of nitrogen doped device can be explained by nitrogen induced filament confinement.

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Resistive random access memory (RRAM) is considered as the most promising candidate for next generation non-volatile memory by solving scaling limit and power consumption problem of conventional charge-storage-memory devices.[1,2] Among all the filamentary RRAM devices, TaO_x based RRAM shows excellent performances, like good switching speed (below 10 ns) and high cycling endurance ($\sim10^{12}$) with low power consumption ($\sim$ 0.1 pJ per operation) .[3-6]

Considering ultra-high density memory application, we need to develop multi-bit per cell storage capability (either by changing compliance or changing reset voltage).[7] However, the conventional filamentary RRAM suffers from non-uniform distribution and poor reliability (Endurance, Retention etc.) because of the stochastic nature of the formation or rupture of the conducting filamentary path. T. Ninomiya et al. described that, low current operation with sufficient retention can be achieved by forming a conducting filament with a small size and high concentration of V_O.[8] The variability at low current operation can be improved by controlling the number of oxygen vacancy (V_O) defects in the switching layer. The controlled amount of V_O can form defined path for conduction for the subsequent voltage pulse after forming process and reduce the variability thereby. It is known that doping the oxide with appropriate species can significantly control the number of active V_O and can modify the activation energy for oxygen vacancy migration which facilitates to improve the retention at high temperature as well.[3] Nitrogen species (almost same size with oxygen, so can easily fit to the oxygen vacancy) can be the good choice which can be doped by reactive sputtering process. W. Kim et al. introduced nitrogen in the AlO_x layer and investigated the current conduction mechanism of the RRAM device with feasibility of the 2-bit MLC characteristics.[9] H. Xie et al. showed improved uniformity of the HfOx based RRAM by plasma treated nitrogen doping.[10]

In this letter, we have focused on switching variability of TaO_x RRAM to meet the requirement of 3-bit MLC operation with varying nitrogen concentration. We found that, sample with optimum nitrogen concentration exhibits excellent 3-bit MLC operation. Furthermore this device also showed good retention characteristics.

Experimental

Ta (TE)/N-TaO_x/Pt devices are fabricated by using 250 nm via-hole structures with Pt bottom electrode sample. About 9 nm TaO_x is deposited by reactive sputtering in the presence of nitrogen gas as a mixture of ($Ar+N_2$) gases. With varying nitrogen flow rate (0$\sim$15%), the nitrogen concentration of various samples was controlled. Finally, both Ta top electrode ($\sim$50 nm) and Pt capping layer was deposited by sputtering. All the devices were measured by semiconductor device analyzer (Agilent B1500A). During measurement, positive or negative voltage was applied at the top electrode while the bottom electrode was always grounded.

Results and Discussion

Figure 1 shows the comparisons between the two bipolar switching devices based on TaO_x and N-TaO_x oxide layers respectively. It is to be noted that, all the devices, measured in this study were forming less. Both devices were measured under low compliance current ($\sim$40 μA), where N-TaO_x based device showed improved uniformity compared with the control undoped device (Figure 1a and Figure 1b). The uniformity of reset current and reset voltage are also significantly improved by nitrogen doping (Figure 1c). There is a significant current overshoot in case of without doped device during reset operation, while the N-TaO_x device reduces the overshoot current. As the effective radius of the filament is decreased due to the filament confinement by nitrogen doping (will be discussed later), relatively less amount of current (i.e. electron) will flow through the filament of N-TaO_x device comparing with the without doped device. At the same time, to pass the same sufficient current through the thinner filament N-TaO_x device needs little bit higher voltage which causes high reset voltage. N-TaO_x based device also showed very good data retention property even at low current operation ($\sim$20 μA) (showed in Figure 1d at 0.2 V read voltage). It sustains up to 2.5×10^4 s at 125°C which is good enough as the resistive switching memory device. This significant retention improvement is due to the suppression of oxygen vacancy (V_O) diffusion by the presence of N- species.[11] It is also reported that, smaller and denser filament shows improve retention properties.[12]

Figure 2a and 2b show the X-ray Photoelectron Spectroscopy (XPS) spectras (device of 3.2% nitrogen flow) to analyze the presence as well as the states of the nitrogen species and the presence of different sub-oxides, sub-oxinitrides phases respectively. The overlap between N 1s and Ta $4p_{3/2}$ region is resolved by peak fitting which is shown in Figure 2a. In general, oxidation moves the component to higher binding energy (BE) value due to having higher bonding energy of Ta-O bond than the Ta-N bond.[13] In our N-TaO_x sample, the BE of N 1s peak is 398.1 eV which is higher than the BE value of pure TaN (396.3 eV).[14] This indicates the presence of Ta-O bonds along with Ta-N bonds and the revealed N 1s peak is not for the pure TaN compounds but for the oxy-nitride compounds. In addition, Figure 2b shows the Ta 4f core level spectra analysis at the same depth of N-TaO_x sample as discussed before for N 1s region. After deconvolution, comparatively higher intense Ta $4f_{7/2}$ peak was found at 23.8 eV than the Ta $4f_{7/2}$ peak at 26.6 eV. This lower intense Ta $4f_{7/2}$ peak (26.6 eV) indicates the presence of small amount of Ta_2O_{5-x}.[14] On the other hand, the high intense peak corresponding to Ta $4f_{7/2}$ (23.8 eV) is shifted to lower binding energy compared to that of Ta_2O_5 (26.6 eV) and the value of BE is higher than that of the TaN (23 eV).[15] This phenomena is appeared due to the substitution of O atoms with N species

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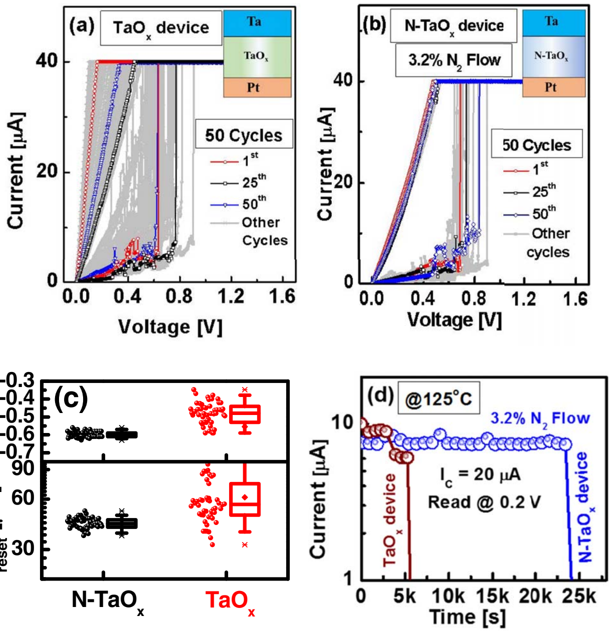

Figure 1. (a) & (b) DC switching characteristics of TaO$_x$ and N-TaO$_x$ based RRAM at low compliance current (~40μA). (c) Comparison of reset voltage and reset current of TaO$_x$ and N-TaO$_x$ devices; N-TaO$_x$ device shows better performance (d) N-TaO$_x$ device showed improved data retention properties for low compliance current (~20 μA) than the un-doped TaO$_x$ device.

and suggests the presence of TaO$_x$N$_y$.[15] More importantly, This instance Ta 4f$_{7/2}$ (23.8 eV) peak, which may be due to TaO$_x$N$_y$, is near to the BE value of metal like TaN (23 eV) or metallic Ta (22.0 eV).[16]

Different literatures mentioned about the effect of nitrogen doping in different oxides. T. arikado et al. stated that, nitrogen eliminates oxygen vacancy related gap states by changing the charged states of V$_O$ and thus reduces the leakage path due to the excess V$_O$.[11]

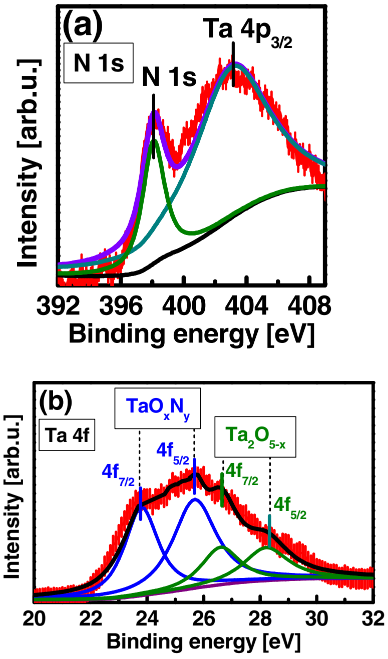

Figure 2. (a) XPS spectra (3.2% nitrogen flow device) confirms the nitrogen doping by the overlapped N 1s and Ta 4p$_{3/2}$ peak in N 1s region. (b) Ta 4f core level spectra confirm the presence of TaO$_x$N$_y$ with small amount of Ta$_2$O$_{5-x}$.

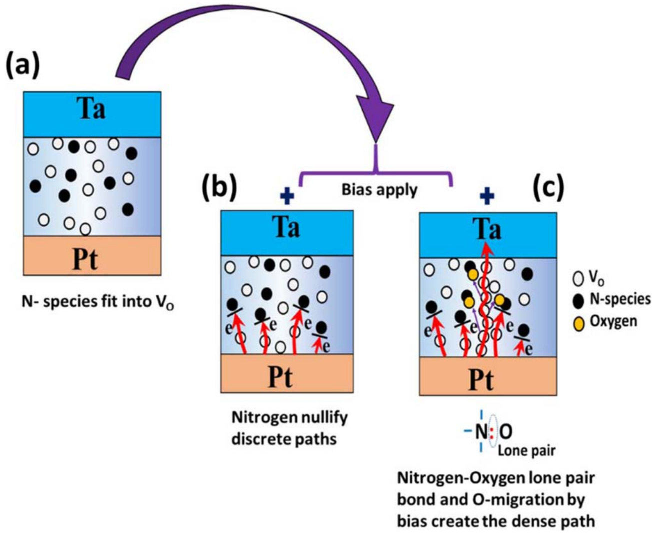

Figure 3. The schematic representation to describe the denser controlled filament formation by nitrogen incorporation.

The same effect is also found in case of nitrogen doped TaO$_x$ in several literatures.[14,17] From the XPS analysis and the above literature review, it can be said that, nitrogen doping reduces the variability by eliminating the extra leakage path of the filament in the N-TaO$_x$ layer. Y. E. Syu et al. showed another important effect of nitrogen in the oxide layer.[18] They proposed that, nitrogen doping can confine the oxygen migration of the switch layer. They stated that, nitrogen can catch the oxygen atom to localize the oxygen ion near the conducting path of filament. Furthermore, due to the higher bonding energy of N-O bond than the O-O bond, the reliability of N-dopped RRAM is improved. Figure 3 show the schematic representation to describe the denser controlled filament formation by nitrogen incorporation. Nitrogen doping in the TaO$_x$ switching layer can be attributed as the technique which can reduce the variability by negating excess conducting path (Figure 3a and 3b) and confines the filament in a localized region by catching the oxygen ion during bias application (Figure 3c). This confined filament can contribute to show linear LRS current even at low power switching which is confirmed later by the experimental data.

The effects of nitrogen doping on two device parameters, i) non-linearity (non-linearity $= (I\ @\ V_{LRS})/(I\ @\ \frac{1}{2}\ V_{LRS})$) and ii) variability (stand. dev. / mean, σ/μ) are investigated more specifically afterwards.[19] Nitrogen doping in different devices are controlled by changing nitrogen percentage from 0 to ~15% in (Ar + N$_2$) mixture during oxide deposition. The I-V measurements by changing compliance current of different devices are shown from Figure 4a to 4c. From these electrical measurements, it is found that, both the low nitrogen doping (~1.6%) (Figure 4a) and comparatively higher nitrogen doping (~7.7%) (Figure 4c) showed 2 bit storage capability, while ~4.8% nitrogen doping (Figure 4b) showed excellent 3-bit MLC characteristics.

Figure 5 summarizes the investigation of nitrogen doping and suggests the compact guideline to achieve the reliable low power 3-bit storage capability of the TaO$_x$ based RRAM device by doping with nitrogen. The devices showed high variability (σ/μ) as well as high non-linearity (data showed for ~30 μA compliance current in Figure 5) in the range of 0–3% nitrogen flow (marked by region ‘A’). Within this range, the nitrogen doping showed a little improvement than the without nitrogen doped device, but still not enough for the 3 bit switch ability. In this case, still there are enough V$_O$ to create discrete paths and it shows some non-linearity and variability in the different LRS state (for example Figure 4a). By increasing the nitrogen amount furthermore (3~6%, region ‘B’), it showed very improved properties with linear distinguishable LRS levels which

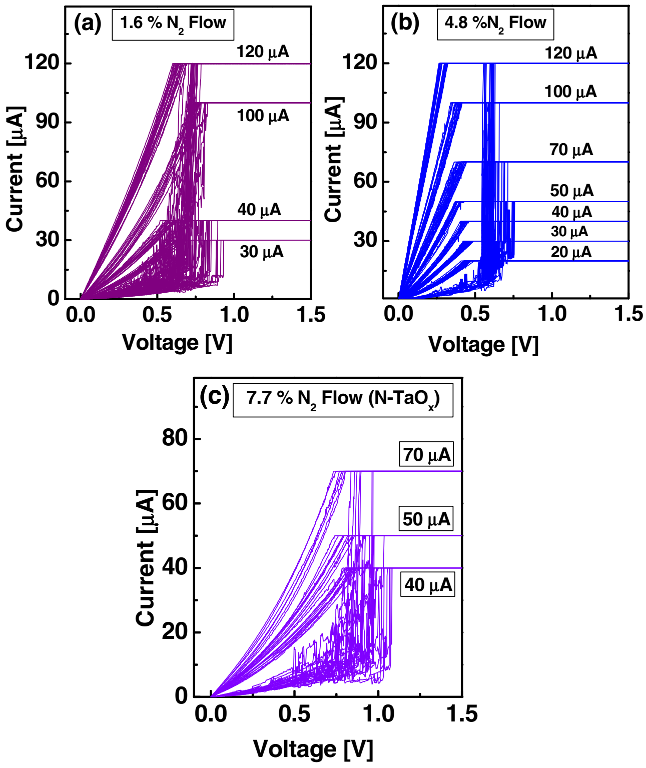

Figure 4. Investigation of the effect of nitrogen in the device to clearly identify the suitable range to get the 3-bit MLC feasibility. (a), (b) & (c) shows the electrical characteristics of increasing the concentration of nitrogen doping.

indicates metallic conduction path due to very confined filament and reducing discrete paths (for example Figure 4b). In this range, 3 bit MLC was found with very good stability within low power operation scheme (~10 µA ~ 120 µA compliance current). Further increase of nitrogen amount (~6–9%, region 'C') showed deviation from the previous results. The excess amount of nitrogen will fit in more oxygen vacancies and make the device difficult to form conducting path like before. In other way, it can be said, the nitrogen now starts to disturb the conducting filament and the filament confinement is lost. Non-linear LRS with increased noise at low compliance current indicate the increase of the variability again in this range (for example Figure 4c). So it needs to ensure the balance of the amount of oxygen vacancy and nitrogen for the successful improved switching with MLC characteristics. Above ~9% nitrogen flow shows insulating characteristics. It is due to incorporation of nitrogen in almost every V_O, which in turn eliminate any conducting path. It is also found that, both non-linearity and variability are higher in case of lower compliance current than the higher compliance current. It is due to the effect of defects is more sensitive in case of lower compliance current (small radius of filament), which is discussed with random telegraph-signal noise analysis in elsewhere.[20]

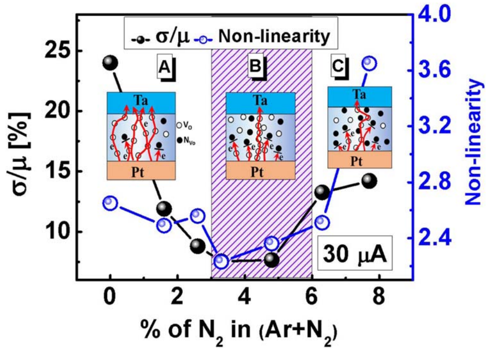

Figure 5. Analysis of the effect of nitrogen doping on the device of different nitrogen amount with the function of non-linearity and variability in 30 µA compliance current to set up the guideline for 3-bit MLC storage feasibility of N-TaO_x based RRAM device.

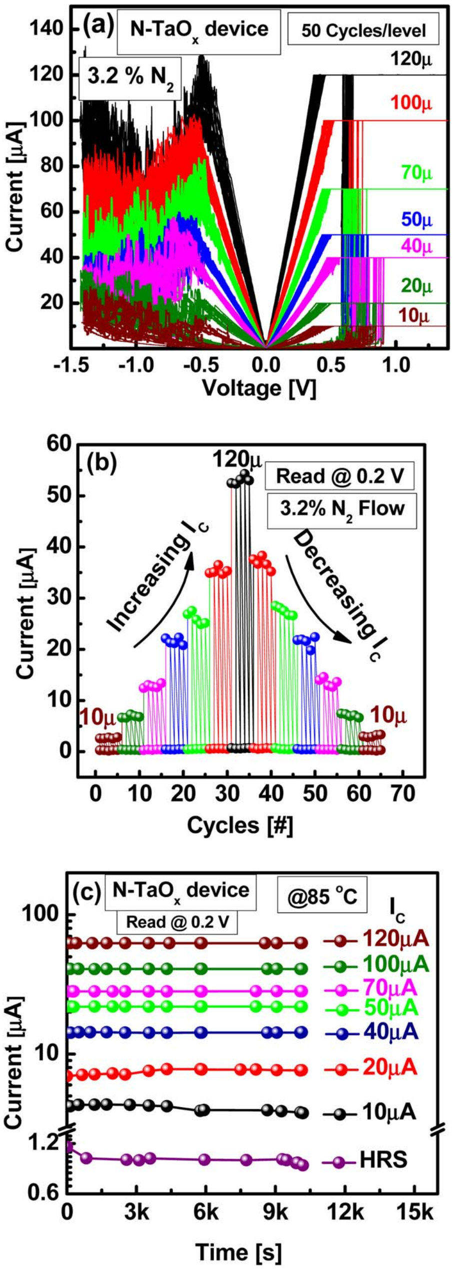

Figure 6. (a) Stable and improved 3-bit MLC switching characteristics of N-TaO_x device for 3.2% nitrogen flow, showing 50 cycles for each level ranging from 10 µA to 120 µA compliance current. (b) Demonstration of switch-ability among 8 levels (7 LRS and 1 HRS) by continuous pulse for 3 bit MLC operation from lowest to highest compliance current and vice-versa. Obtained levels are successfully switched among each other. (c) High temperature retention of MLC levels confirming good nonvolatile behavior.

To ensure the reliability of the above mentioned range (region 'B') for 3 bit storage capability, some more devices are checked within the range. Figure 6a shows the stable and improved 3-bit MLC switching characteristics of N-TaO_x device for 3.2% nitrogen flow, which shows 50 cycles for each level ranging from 10 µA to 120 µA compliance current. Figure 6b confirms the good switch-ability among LRS levels by applying continuous pulse form the lowest compliance current (10 μA) to the highest compliance current (120 μA) and vice versa. That means, this device can maintain controlled filament radius in different compliance current. Figure 6c shows the good retention characteristics without degradation for every distinguishable resistance state, which confirm the non-volatility of the device.

Conclusions

By engineering the process of controlling the conducting filament with incorporating nitrogen in the V_O of TaO_x based RRAM device, improved uniformity at low operation current is achieved which also showed good data retention property. Optimum nitrogen concentration is investigated with the function of non-linearity and variability which further showed very good feasibility for excellent low power 3-bit MLC characteristics. It is reported that, N-species combined with some V_O and reduce the discrete path of conduction and made confined filament. This filament confinement is confirmed by the linear LRS current (metallic conduction path) and the improved variability of the device by nitrogen doping.

Acknowledgments

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