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A ZnTaO_x Based Resistive Switching Random Access Memory

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The improved resistive switching performance of TaO_x by introducing ZnO was reported in this paper. By co-sputtering, the ZnTaO_x device shows better endurance, lower operating voltage and more uniform resistance distribution. The improvement is mainly due to the more abundant intrinsic defects such as oxygen vacancies which facilitates the formation of conductive filaments in the oxide compound.

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Among various non-volatile memory devices, the resistance switching random access memory (RRAM) has outstood for its high-density storage capability, low operation voltage/current and fast switching speed. Besides those intensively studied oxide materials for the RRAM fabrication, such as TiO₂,¹ NiO,² ZnO,³ HfO_x,⁴ and ZrO₂,⁵ recently Ta₂O₅ or TaO_x based RRAM device has been frequently investigated due to its excellent endurance performance and switching speed. Based on the filament dynamic mechanism, both unipolar and bipolar resistive switching (RS) behavior were reported with desirable endurance and retention properties.^{6,7} Similar as other oxide-based devices, the formation and rupture of conductive filament (CF) which is related to the chemical composition of oxygen determine the RS behavior in TaO_x RRAM. One of the effective ways to obtain better RS performance in TaO_x RRAM is how well the oxygen ion or oxygen vacancy concentration is controlled. Therefore, quite some work has been carried out to understand the behavior of oxygen vacancies in resistance switching. For example, F. Kurnia et al. investigated the evolution of oxygen vacancies based CF and achieve the forming-free RS in Pt/TaO_x/Pt structure.⁸ By applying different voltage on the 1-transistor-1-memristor (1T1M) device, F. Miao et al. successively tuned the conduction channel in TaO_x which related to the oxygen concentration, and obtain varied switching behavior.⁹ Moreover, Ta was used instead of Pt as top electrode on TaO_x by J. S. Chen's group to form an oxygen vacancy reservoir of supplying or storing the oxygen vacancies at the Ta/TaO_x interface, and further realize the multilevel switching property.¹⁰ Here we demonstrate another way to engineer the oxygen vacancies in TaO_x and result in better RS performance. By mixing various oxides with TaO_x, the concentration of oxygen vacancies could be adjusted, and among them, ZnO shows the best improvement of operation parameters.

The simplest metal-insulator-metal (MIM) structure was applied to fabricate the RRAM testing cell. The commercial ITO glass was employed as the substrate and bottom electrode. All the oxide films were deposited by RF magnetron sputtering system. Indium balls pressed on top of the sample were used as the top electrodes. The sputtering power for all oxides (Ta₂O₅, ZnO, Ga₂O₃ and NiO) were the same (100 W) and the sputtering chamber was kept in the Ar atmosphere (flow rate 30 sccm) with the pressure of 5×10^{-3} Torr at room temperature. Besides the pure TaO_x device, the TaO_x was co-sputtered with other 3 targets respectively to form ZnTaO_x, GaTaO_x and NiTaO_x films for comparison. The thickness of all four films was 100 nm. The components of oxide films were examined by EDX measurement with SEM scanning the surface of samples. The I-V characteristics were measured by a semiconductor parameter analyzer in diode mode (two-terminal contacts). The ITO bottom electrode was always grounded while biases with different polarity and intensity were applied on In top electrode during test.

It is well known that non-stoichiometric TaO_x ($x < 2.5$),⁶ ZnO_x ($x < 1$)¹¹ and GaO_x ($x < 1.5$)¹² are all n-type semiconductor due to the existence of oxygen vacancies acting as donors for generating electrons, while non-stoichiometric NiO_x ($x > 1$)¹³ is a p-type semiconductor because of the excess oxygen ions acting as acceptor for generating holes. The dynamics of these intrinsic defects directly relate to the conduction mechanism of oxide film. All oxide films were characterized by EDX measurement as shown in Fig. 1 in order to examine the chemical composition. The observed strongest O, Ta, Zn, Ga and Ni signals correspond to the energy of 0.525, 1.964, 1.012, 1.051, 0.851 keV, respectively. The composition statistics shows the atomic ratio of Ta : Zn/Ga/Ni is approximately 4:1. Thus, the TaO_x was confirmed mixed with other 3 types of oxides by co-sputtering to form new compounds but not doped by Zn, Ga or Ni.

Fig. 2a shows the I-V characteristics of all 4 devices in V-log (I) scale. The TaO_x, ZnTaO_x and GaTaO_x all exhibit similar bipolar RS behavior except NiTaO_x which only presents the nonlinear conduction with a small hysteresis lag. The set process in positive voltage region and reset process in negative voltage region are clearly illustrated in the figure. The as-prepared stacks are initially at high resistance state (HRS) and no forming process is required to initialize the devices. During one complete switching cycle, when the bias firstly sweeps to a positive threshold value (SET voltage), an abrupt increase of current occurs corresponding to the SET operation and the device is switched to low resistance state (LRS). A compliance current (CC) of 1 mA is imposed during the sweep to prevent device from permanent breakdown. Similarly, sweeping the voltage to another negative threshold value (RESET voltage) will bring the device to HRS, referring to RESET operation. Both the HRS and LRS will maintain without any sustaining bias, and could be read out by applying a small reading voltage

Figure 1. EDX spectrum of TaO_x, ZnTaO_x, GaTaO_x and NiTaO_x.

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Figure 2. (a) Bipolar RS under DC sweep mode of TaO_x, ZnTaO_x, and GaTaO_x devices; no RS in NiTaO_x (b) multiple switching cycles of ZnTaO_x device; the insets is device structure schematic.

(~ 0.1 V), manifesting the non-volatility of the RRAM device. Among the three RRAM devices, the TaO_x shows the largest average HRS resistance and SET voltage, while the ZnTaO_x gives the lowest ones, although their range of fluctuation does overlap with each other to some extent. Therefore we select the typical RS curves of each device in Fig. 2a for a better comparison. The multiple-cycle data of ZnTaO_x device was shown in Fig. 2b with the structure schematic in the inset. More than 200 stable bipolar switching cycles could be achieved and the SET voltage and RESET voltage fluctuate in $0.4 \sim 1.8$ V and $-0.1 \sim -1.4$ V, respectively. The original TaO_x device performs fair switching endurance under DC sweep mode (50–100 cycles) but the largest distribution of SET ($0.5 \sim 4.8$ V) and RESET ($-0.3 \sim -1.9$ V) voltages. Introducing GaO_x into TaO_x brings some improvement on the distribution of SET voltage ($0.5 \sim 2.8$ V) but the endurance degrades (~ 20 cycles). However, on the contrary, the ZnTaO_x leads to improvement in both switching stability and endurance, which will be shown in detail subsequently.

Fig. 3a shows the endurance characteristic of In/ZnTaO_x/ITO device under DC sweep mode at room temperature. In 200 repeating cycles, the resistance of both HRS and LRS distributes within a small range of voltage, which is suitable for practical use. The retention property is given in Fig. 3b to rate the non-volatility. By continuously sampling at different time, the resistances of both HRS and LRS remained almost unchanged in 10^5 s, based on which a desirable retention performance could be expected in RRAM application.

To further analyze the improvement of TaO_x based RRAM by introducing ZnO, more detail comparison of parameters among the TaO_x, ZnTaO_x and GaTaO_x devices were exhibited in Fig. 4. According to the cumulative probability statistics, ZnTaO_x with best endurance has much smaller distributing range of SET voltage ($0.4 \sim 1.8$ V), RESET

Figure 3. (a) Endurance performance in 200 repeating cycles; (b) Retention characteristic at room temperature of ZnTaO_x device.

voltage ($-0.1 \sim -1.4$ V), HRS resistance ($10 \sim 30$ k Ω) and LRS resistance ($200 \sim 500$ Ω) than TaO_x. GaTaO_x shows slightly better LRS resistance distribution than ZnTaO_x, however, the poor endurance undoubtedly rules it out of the competition. The performance of these three devices is compared in Table I. We can see that the resistance window of ZnTaO_x is slightly narrowed, which will be discussed later. However, it is an acceptable trade-off we would like to make because the resistance window of ZnTaO_x is still wide enough to guarantee an errorless reading while it stands out in all other parameters.¹⁴ Of these parameters, the differences in SET voltage and HRS resistance are quite large, while the differences in RESET voltage and LRS resistance are relatively smaller.

To further study the RS behavior in these devices, the conduction property in the SET process was unveiled by plotting the I-V curve in log-log scale (Fig. 5). Two different types of conduction mechanism were found co-existing in all three RRAM devices, which could be classified to low voltage switching (LVS) (SET voltage usually < 2 V) and high voltage switching (HVS) (SET voltage usually > 2 V). In this figure, the HVS curve is collected from TaO_x sample and the LVS one is from ZnTaO_x sample. Both this two types of conduction display Ohmic behavior (slope ~ 1.0) in LRS, while the difference rises in the HRS part. Initially, under low external electrical field, both LVS and HVS show near Ohmic feature, although the HVS one shows larger deviation from the Ohmic standard (slope ~ 1.32). As the bias further increases approaching the switching threshold value, the slope of LVS becomes ~ 2 , which can be best explained by space charge limited conduction (SCLC). According to the SCLC mechanism, there are three steps of conduction: Ohmic behavior ($I \propto V$), Child's law ($I \propto V^2$) and drastic increase of current,¹⁵ which accurately fits our LVS case. However, the I-V nonlinearity in HVS under high electric field is much different (slope = 5.27). To further investigate this region,

Figure 4. (a) Cumulative probability statistic of (a) SET voltage (b) RESET voltage (c) HRS resistance and (d) LRS resistance in TaO_x, ZnTaO_x and GaTaO_x devices.

Schottky emission and Poole-Frenkel emission (PF emission) modes are applied, respectively. For Schottky emission, the relationship between current and voltage could be expressed as follows:¹⁶

$$I \propto T^2 \exp \left[\frac{e\sqrt{(eV)/(4\pi\epsilon_i\epsilon_0 d)}}{kT} \right]$$

And PF emission can be described as:¹⁶

$$I/V \propto \exp \left[\frac{e\sqrt{(eV)/(\pi\epsilon_i\epsilon_0 d)}}{kT} \right]$$

Where I is the current, V is the voltage, e is the electron charge, ϵ_0 is the permittivity of free space, ϵ_i is the dielectric constant, d is the thickness of film, k is the Boltzmann's constant and T is the temperature. After fitting the curve of this region to both two modes, PF emission better coincides with our case as shown in the inset of Fig. 5, in which the I - V curve is plotted in $\ln(I/V)$ - $V^{1/2}$ and $\ln(I)$ - $V^{1/2}$ scale, respectively.

As widely accepted, the Ohmic behavior in LRS directly relates to the formed filamentary paths consisting of oxygen vacancies in the

oxide film.¹⁷ Before the formation of filaments, the SCLC mechanism in HRS of LVS probably works on the defect-related shallow traps (oxygen vacancies) in the oxide films. At lower applied bias, the thermally generated carrier density is higher than the injected carrier density and the conduction follows Ohm's law. With the increasing bias, the injected carriers gradually fill all the traps and become dominated, inducing a higher current gain depicted in Child's law.¹⁸ As for the PF emission (corresponds to HRS of HVS in our case here), it is well attributed to thermal excitation of electrons from defect-related traps (oxygen vacancies) into conduction band by electric field enhancement.¹⁹ And usually, the electric field should be high enough (higher than SCLC mode) to activate the trapped electrons so as to dominate in conduction. Meanwhile, there is no effective interface barrier between the electrodes and oxides here, so the PF emission rather than Schottky emission model dominates in our case. It is worth mentioning that, between the Ohmic and PF emission region of HVS case, there exists a fluctuating "transition" region, including the current-controlled negative differential resistance (CC-NDR) phenomenon, in which the current decreases as the voltage increases. In some cases, the NDR behavior could be observed as precursor to

Table I. The overall comparison of SET voltage (V_{SET}), RESET voltage (V_{RESET}), resistance of HRS (R_{HRS}), resistance of LRS (R_{LRS}) (median value and standard deviation given), resistance window and endurance.

	TaO _x	GaTaO _x	ZnTaO _x
V_{SET} (V) (Med, StdDev)	0.5 ~ 4.8 (2.2, 1.165)	0.5 ~ 2.8 (1.2, 0.593)	0.4 ~ 1.8 (0.8, 0.294)
V_{RESET} (V) (Med, StdDev)	-0.3 ~ -1.9 (-0.9, 0.487)	-0.2 ~ -1.6 (-0.4, 0.337)	-0.1 ~ -1.4 (-0.6, 0.336)
R_{HRS} (Ohm) (Med, StdDev)	60 k ~ 1.3M (307 k, 211 k)	17 k ~ 170 k (50 k, 36 k)	10 k ~ 30 k (16 k, 3.7 k)
R_{LRS} (Ohm) (Med, StdDev)	200 ~ 1.2 k (491, 194.8)	200 ~ 350 (264, 42.1)	200 ~ 500 (309, 60.9)
Resistance Window	16 ~ 2600	48 ~ 850	20 ~ 150
Endurance (n)	50 ~ 100	~ 20	>200

Figure 5. The I-V curve of SET process drawn in log-log scale (the HVS curve refers to TaO_x sample and the LVS one corresponds to ZnTaO_x sample); the inset shows the fitting curve of Schottky emission with $\ln(I)-V^{1/2}$ and PF emission fitting with $\ln(I/V)-V^{1/2}$ scale.

reversible switching (both unipolar and bipolar switching) and is responsible for Joule heating that assists generating large concentration of oxygen vacancies to form metallic suboxide conductive channel (described as CFs) in oxide film.²⁰ The NDR only exists right before the soft breakdown (SET) and is not reversible.

For our devices, the HRS conduction in ZnTaO_x sample's switching cycles mainly belongs to SCLC mode, while the SCLC and PF emission modes both occur in TaO_x and GaTaO_x ones (PF emission is more probably found in TaO_x than GaTaO_x). Based on the conduction analysis above, the different switching behaviors could be interpreted as varied concentration of intrinsic defects by mixing different oxides with TaO_x. The lower density of defects in pure TaO_x leads to a larger initial or HRS resistance and hence a larger resistance window. The dominant conduction mechanism in TaO_x is PF emission related with HVS. The higher SET voltage, as well as more Joule heat is required not only to excite electrons from defects for HRS conduction, but also generate enough oxygen vacancies to form reliable CFs for LRS conduction. The as-prepared ZnTaO_x cell has the lowest HRS resistance (trade-off with resistance windows), suggesting that the defects become more abundant in ZnTaO_x (including grain boundaries, dislocation and more oxygen vacancies). Meanwhile it also becomes easier for CF to form under relatively lower electric field, which ultimately leads to the low and uniformly distributed SET threshold. The most probable HRS conduction is also transformed from HVS PF emission mode to LVS SCLC mode. These conclusions does coincide with the parameters comparison in Fig. 4 analysis that the varied concentration of intrinsic defects determines the larger difference in resistance of HRS and the difficulty of setting; while attributing to the similar property of existing CFs in three devices, the resistance of LRS and RESET voltage show not that significant differences. Meantime, as the filaments are more robust and stable in ZnTaO_x, the HRS and LRS resistances also distribute more uniformly. Similar to ZnTaO_x, introducing n-type GaO_x to TaO_x also helps to increase the defect density in GaTaO_x. The forming-free phenomenon in all three devices

is related to the pre-existence of defects in the films caused by the ion bombardment in sputtering.^{21,22} As for p-type NiO_x, there should be a reduction of oxygen vacancies after combining it with n-type TaO_x, leading to unswitchable oxide compound.

To summarize, TaO_x, ZnTaO_x, GaTaO_x and NiTaO_x films were deposited by magnetron sputtering system to fabricate RRAM cells. Among them, the ZnTaO_x sample exhibited evident improvement of RS performance, including better endurance, smaller operating voltage and more stable resistance distribution. The improved behavior is mainly attributed to the introduction of more intrinsic defects such as oxygen vacancies by mixing TaO_x with ZnO_x facilitating a filament switching. The SCLC mechanism dominates the HRS conduction in LVS of ZnTaO_x; while for HVS in TaO_x and GaTaO_x, the HRS conduction could be understood by PF emission mechanism accompanied with CC-NDR phenomenon.

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