Supplementary Information

A More Random and Secure Image Encryption Method: A Novel True Random Number Generator Based on W / Ta_2O_5 / Ag Memristor

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Figure S1a-c shows the resistance mechanism of the W/Ta_2O_5/Ag structure memristor when the applied voltage amplitude is 1V and 2V. When a positive voltage is applied to the Ag electrode of the device, Ag oxidizes to become Ag+, and Ag+ moves to the W electrode under the action of applied electric field, and combines with electrons near the bottom electrode to undergo a reduction reaction to become Ag. Then Ag continues to accumulate near the W electrode to form conductive wires, and a conductive channel is formed inside the device. Switch from high resistance state to low resistance state. When negative voltage is applied to the Ag top electrode of the device, the internal conductive wire breaks, the internal conductive channel breaks, and the device switches from the low resistance state to the high resistance state. However, when the applied bias amplitude increases to 3V, the type of conductive wire of the device changes from a simple conductive wire composed of Ag to a conductive wire composed of Ag and oxygen vacancy, as shown in **Figure S1d-f**. When a positive voltage is applied to the Ag top electrode of the device, the Ag at the top oxidizes into Ag+, and the Ag+ moves to the W bottom electrode under the action of applied electric field, and then combines with electrons near the bottom electrode to undergo a reduction reaction into Ag. At the same time, a small amount of oxygen vacancy (VO) in the dielectric layer also moves near the bottom electrode under the action of electric field to form a local oxygen-rich region, and some studies have shown that Ag is more likely to drift in oxygen-rich environment, resulting in lower Forming voltage or even no obvious Forming process of the memristor. Ag and oxygen vacancy continuously accumulate near the W electrode to form a hybrid conductive wire, and a conductive channel is formed inside the device, which switches from a high resistance state to a low resistance state. When a negative voltage is applied to the Ag electrode of the device, the oxygen vacancy is induced to recombine with nearby oxygen ions and some Ag atoms are repelling back to the top electrode, the conductive wire is broken, the internal conductive channel is disconnected, and the device switches from a low resistance state to a high resistance state.

In the process of RESET, conductive filaments composed of pure Ag atoms often decrease the resistance value of the high resistance state due to incomplete breakage of conductive filaments and the presence of residual Ag atoms dispersed in oxides. However, the mixing mechanism of conductive filaments formed by oxygen vacancy and Ag atom together is better than that of pure Ag atom conductive filaments due to the participation of oxygen vacancy. The number of Ag atoms involved in the formation of conductive filaments will be reduced, thus reducing the possibility of residual conductive filaments and dispersed Ag atoms in the oxide layer during RESET, and improving the stability of the I-V characteristic curve during the cyclic scanning of the memristor.

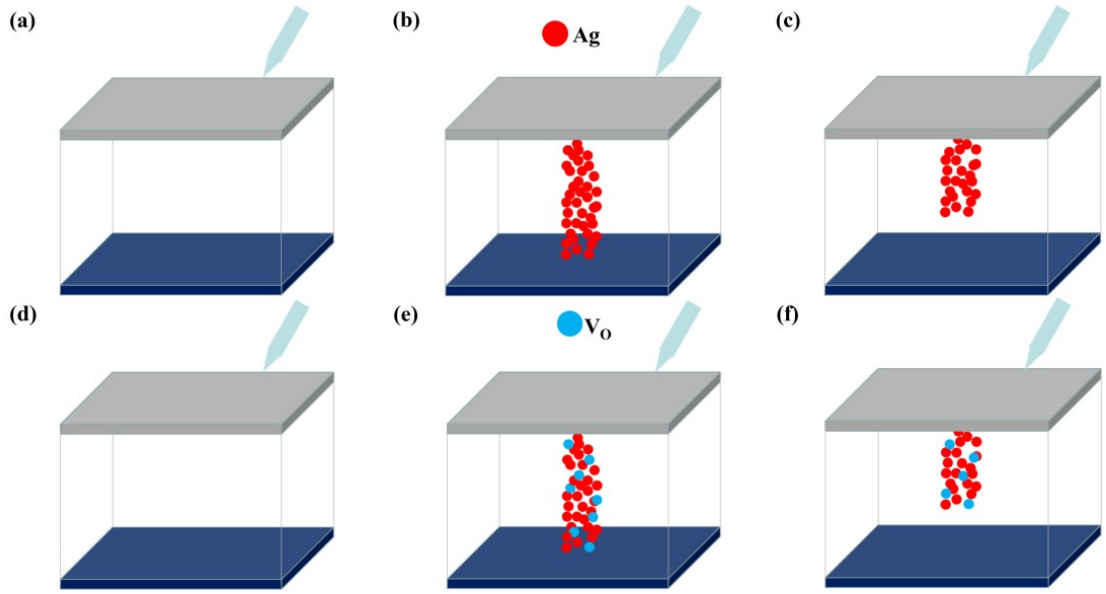

Figure S1 Schematic diagram of resistance mechanism (a) ~ (c) voltage is 1V, 2V (a) initial state (b) plus positive bias (c) plus negative bias (d) ~ (f) voltage is 3V (d) initial state (e) plus positive bias (f) plus negative bias

(1) The equation governing oxygen vacancy drift-diffusion.

In the resistance switching mechanism of oxide memristors, the drift motion and diffusion motion of oxygen vacancies play a major role. Considering the high baseline concentration of oxygen vacancies, the generation and recombination of oxygen vacancies have much less impact on the resistance switching behavior compared to drift and diffusion motion. Therefore, in finite element simulations, only the drift and diffusion of oxygen vacancies are considered.

The migration flux of oxygen vacancies can be described by the following equation:

$$\frac{\partial n_D}{\partial t} = \nabla \cdot \left(D\nabla n_D - v n_D + D S n_D \nabla T \right)$$

The left side of the equation is the rate of change of oxygen vacancy concentration per unit volume with time,n_D is the oxygen vacancy concentration in units of m^{-3}. D is the diffusion coefficient of oxygen vacancies in units of m^2/s. v is the drift velocity of oxygen vacancies in units of m/s. S is the Soret diffusion coefficient in units of K^{-1}.

For diffusion motion, the oxygen vacancy diffusion coefficient D and temperature T satisfy the equation:

$$D = D_0 \exp\left(-\frac{E_a}{kT}\right)$$

$$D_0 = 0.5a^2 f$$

In which D_0 is the diffusion coefficient pre-factor, E_a is the activation energy for oxygen vacancy migration in eV. k is the Boltzmann constant; f is the escape frequency in Hz.

For drift motion, the drift velocity v and temperature T satisfy the equation:

$$v = 2af exp\left(-\frac{E_a}{kT}\right)\sinh\left(\frac{qaE}{kT}\right)$$

a is the distance of ion transition in m.

(2)The equation of current continuity

The equation of current continuity can be expressed as follows:

$$\nabla \cdot \sigma \nabla \Psi = 0$$

σ is the electrical conductivity in S/m. Ψ is the electric potential.

The local conductivity of oxide films satisfies the following relationship with respect to the oxygen vacancy concentration:

$$\sigma = \sigma_0 exp\left(-\frac{E_{AC}}{kT}\right)$$

σ_0 is the pre-exponential factor of conductivity, and E_{AC} is the activation energy of conductiom, both parameters are related to the oxygen vacancy concentration n_D.

(3)The Joule heating equation

The mechanisms of oxygen vacancy migration and diffusion, as well as current continuity, are both affected by temperature. Therefore, studying the dynamic changes in temperature is crucial in research and simulations. When voltage is applied to the memristor, the intensified motion of charges leads to a significant increase in heat generated by collisions between charges. This heat cannot be fully dissipated, resulting in a localized temperature rise in the oxide thin film.

The dynamic changes of heat and temperature can be described by the following equation:

$$\rho C_p \frac{\partial T}{\partial t} - \nabla \cdot k_{th} \cdot \nabla T = J \cdot E$$

C_p is the specific heat capacity at constant pressure, measured in J/(kg·K). k_{th} is the thermal conductivity coefficient related to the oxygen vacancy concentration n_D measured in W/(m·K).

Figure S2 shows the I-V curve of the electrothermally coupled memristor model based on oxygen vacancy diffusion.

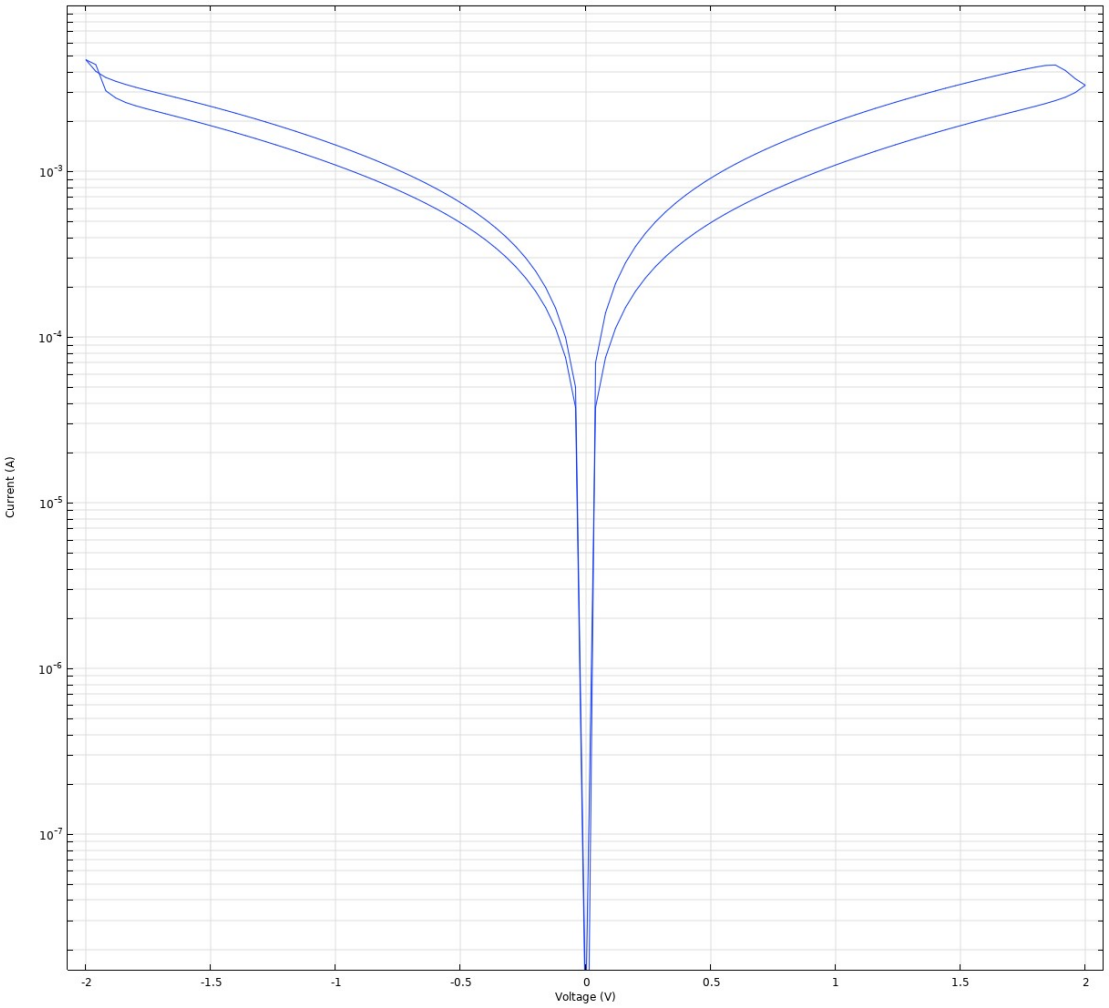

Figure S2 Simulation results of the I-V characteristic curves

Figure S3 shows the comparison of the I-V curves obtained by the electrical-thermal coupling simulation model with the experimental test data, and it is found that both exhibit a similar trend. This indicates that the established electro-thermal coupling model accurately reflects the actual resistive switching mechanism of the device.

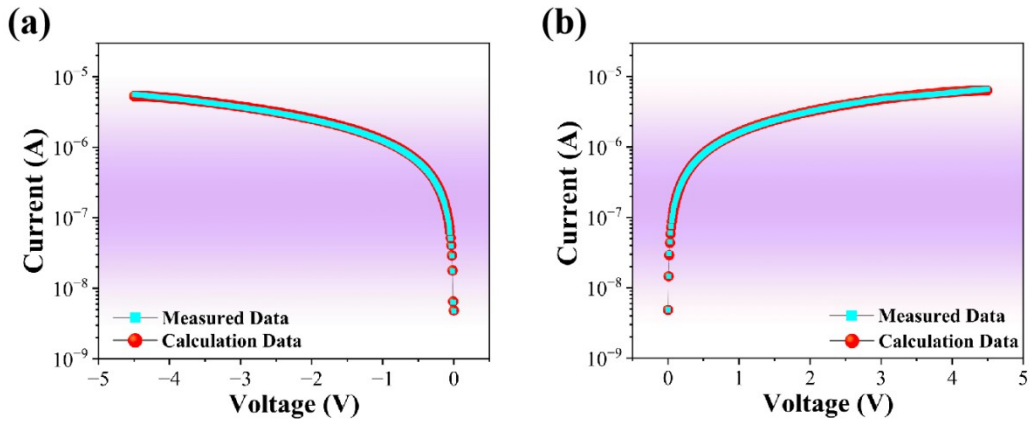

Figure S3 Comparison of device I-V characteristic curve test results and simulation results (a) SET process (b) RESET process

Figure S4a presents the endurance characteristics of the device tested under ambient conditions. The testing procedure involved applying a SET voltage of 2 V to switch the device to the low-resistance state (LRS), followed by applying a read voltage of 0.1 V to measure the LRS current. Subsequently, a RESET voltage of -2 V was applied to switch the device to the high-resistance state (HRS), and the HRS current was then measured by applying the read voltage again. The test results indicate that the HRS current ranged from 2×10^{-6} A to 3.9×10^{-5} A over 300 cycles, showing that the HRS window remained relatively stable. However, a slight upward drift in HRS current was observed with increasing cycles, which can be attributed to the incomplete rupture of Ag-based conductive filaments and the presence of residual Ag atoms in the oxide during the RESET process, leading to a gradual decrease in the HRS resistance. The LRS current ranged from 1.1×10^{-4} A to 2.6×10^{-4} A, with the on/off ratio maintaining a magnitude of approximately 10^1. **Figure S4b** shows the retention time of the measured LRS resistance, where the device was first switched to the LRS by applying a SET voltage of 3V, and the resistance was measured every 0.4s using a 0.1V read voltage. It can be observed that the retention time at room temperature exceeds 1000 seconds. The endurance and the device retention time data demonstrate that the device has good durability and retention characteristics, and also proved that TRNG based on W / Ta_2O_5 / Ag structure memristor also has good durability.

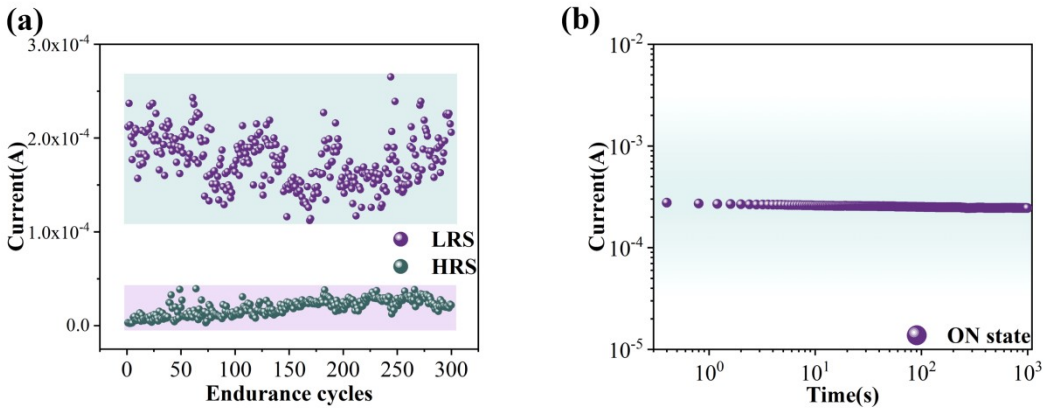

Figure S4 (a) Durability test (b) Device holding time

Figures S5a-b display the test results obtained from XPS characterization of the Ta_2O_5 film, focusing on the Ta4f and O1s peaks. The Ta_2O_5 layer mainly contained $Ta4f_{5/2}$ (28.4 eV) and $Ta_54f_{7/2}$ (26.4 eV), indicating that the Ta_2O_5 film deposited by magnetron sputtering basically conformed to the stoichiometric ratio, with tantalum being fully oxidized and minimal defects present (**Figure S5a**). In addition, oxygen exists in two forms: lattice oxygen (O_L, 530.8 eV) and vacancy oxygen (O_V, 532.3 eV), as illustrated in **Figure S5b**.

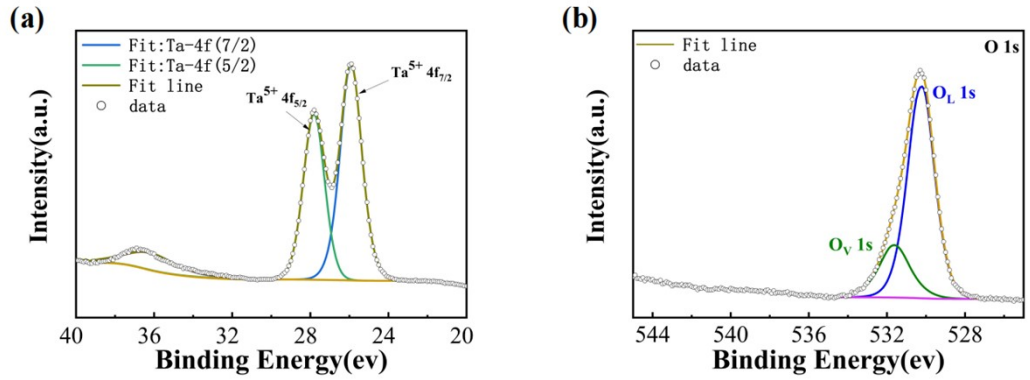

Figure S5 (a) Ta4f and (b) O1s XPS spectra of the Ta_2O_5 film