



Article

# Non-Volatile Memory Based on ZnO Thin-Film Transistor with Self-Assembled Au Nanocrystals

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**Abstract:** Non-volatile memory based on thin-film transistor is crucial for system-on-panel and flexible electronic systems. Achieving high-performance and reliable thin-film transistor (TFT) memory still remains challenging. Here, for the first time, we present a ZnO TFT memory utilizing self-assembled Au nanocrystals with a low thermal budget, exhibiting excellent memory performance, including a program/erase window of 9.8 V, 29% charge loss extrapolated to 10 years, and remarkable endurance characteristics. Moreover, the memory exhibits favorable on-state characteristics with mobility, subthreshold swing, and current on–off ratio of  $17.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , 0.71 V/dec, and  $10^7$ , respectively. Our study shows that the fabricated TFT memory has great potential for practical applications.

**Keywords:** TFT memory; NVMs; nanocrystals; SoP; ALD

## 1. Introduction

Recently, thin-film transistors (TFTs) based on transparent oxide semiconductors have been widely explored for pixel driving in display panels, showcasing significant promise for integration into system-on-panel (SoP) [1–4] owing to the inherent advantageous properties in oxide semiconductors, including high mobility, low process temperature, and transparency to visible light [5,6]. Among them, ZnO thin-film transistors have attracted extensive research interests due to their simple composition, non-toxicity, low cost, insensitivity to visible light, and the possibility of large-scale preparation [7,8]. ZnO is a wide and direct band gap semiconductor with a large excitation energy of ~60 meV, often crystallizes in the hexagonal wurtzite structure, and displays an intrinsic n-type conductivity [9]. A high degree of crystallinity is usually obtained in ZnO films, even deposited using relatively low temperatures [10]. Active-matrix liquid–crystal display (AMLCD) and active-matrix organic light-emitting diode (AMOLED) driving arrays based on ZnO TFTs have been successfully fabricated [11,12]. In a System-on-Panel, while TFTs can perform basic information processing to achieve comprehensive functionalities, devices capable of information storage are indispensable. Due to the similarity in structure to TFTs and ease of integration, TFT-based non-volatile memory offers great advantages for SoP [13–19].

The nanocrystals (NCs) charge-trap memory presents notable advantages over traditional floating-gate memory owing to discrete charge storage sites, particularly in terms of programming efficiency, endurance, and retention characteristics [20]. Various types of non-volatile nanocrystal memories have been explored, including semiconductor nanocrystals and metal nanocrystals. Metal nanocrystal memories, in particular, can offer significant benefits such as a wide range of available work functions, minimal energy perturbation due to carrier confinement, and enhanced coupling to the channel [21,22], which make them superior in charge storage ability. The dimension and shape of the metal NCs have a significant impact on the memory effect. The desired shape of NCs is typically spherical or quasi-spherical, which allows for uniform charge distribution and facilitates the trapping



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and retention of charge within the NCs. The spherical shape also minimizes defects and irregularities that could interfere with charge storage and retention, ensuring optimal memory performance [23]. When the size of metal NC is less than 4 nm, the Coulomb blockade effect will become pronounced, which raises the electrostatic potential of NCs, prevents the entry of additional electrons and influences program, erase, and retention characteristics [24]. Large-size NCs are favorable for large tunneling current and fast programming speed. The spacing of NCs should be larger than 4 nm so that lateral tunneling between NCs is negligible, and dense NCs are preferred to minimize the statistical variations. Thus, high density and large size are favorable when taking the trade-off with the NC number density into account [25]. Generally, the reported metal NC sizes ranged from 4 nm to 20 nm, and the density was in the order of  $10^{11}$ – $10^{12}$   $\text{cm}^{-2}$  [13,20–22,26–28].

To meet the needs of complex transparent and flexible electronic systems, non-volatile memories based on ZnO TFTs using metal nanocrystals as charge storage layers are beginning to attract attentions [26–28]. However, realizing high-performance ZnO TFT memory is still challenging. Park et al. presented a ZnO-based TFT memory using Al NCs with an average diameter of 7 nm and a density of about  $1.6 \times 10^{12}$   $\text{cm}^{-2}$ . A significant program-erase (P/E) window was achieved at low operating voltage [27]. Nevertheless, it suffered from poor retention and endurance characteristics due to the inferior quality of the tunneling oxide, worsened by damage incurred during the sputtering process of the ZnO channel. Al metal particles formed by sputtering are prone to oxidation in subsequent processes, leading to alterations in its characteristics. In addition, the low work function of Al significantly contributed to the observed decrease in retention time. Kang et al. investigated a ZnO TFT memory based on a top-gate structure [28]. Sputter-condensed Pd nanoclusters with an average size of 5 nm and density of  $1.0 \times 10^{12}$   $\text{cm}^{-2}$  were utilized as the charge storage medium, and 5.8 V P/E window was obtained under +18 V/200 ms and –18 V, 200 ms P/E operations, indicated that more than 13 electrons were trapped in each Pd nanocluster. However, the deposition process of the tunneling oxide layer inevitably caused physical damage to the active channel, resulting in inadequate on-state characteristics, including channel current and subthreshold swing.

For TFT memory to be practically applied in flexible and transparent electronic systems, both good non-volatility and sufficient on-state characteristics are required. Therefore, a charge storage medium with excellent charge storage ability and immunity to charge leakage is needed, along with optimal fabrication methods and process flows, to achieve good overall performance. Among various metal NCs, Au NCs exert a great memory effect owing to their stable chemical properties [29]. With a high density of states around the Fermi level, Au NCs possess an excellent capacity to store electrons [21]. Moreover, the high work function of Au NCs enables the formation of a deep quantum well between the tunneling and blocking oxide layers, ensuring minimal charge loss of the memory device during retention. Atomic layer deposition (ALD) is a chemical deposition technique based on layer-by-layer, self-limiting and saturated surface reactions, which can be used to grow dense, pinhole-free, and conformal thin films [30]. More importantly, ALD minimizes material damages during fabrication compared to methods like sputtering, which reduces the traps in the films. ZnO thin-film transistors fabricated by ALD presented superior transistor performance [8,31]. Furthermore, by employing high-reactivity precursors in ALD, high-quality oxide films can be grown at very low temperature [32]. Together with the capability of large-scale deposition, ALD is considered an optimal method for the fabrication of transparent flexible electronic devices [33].

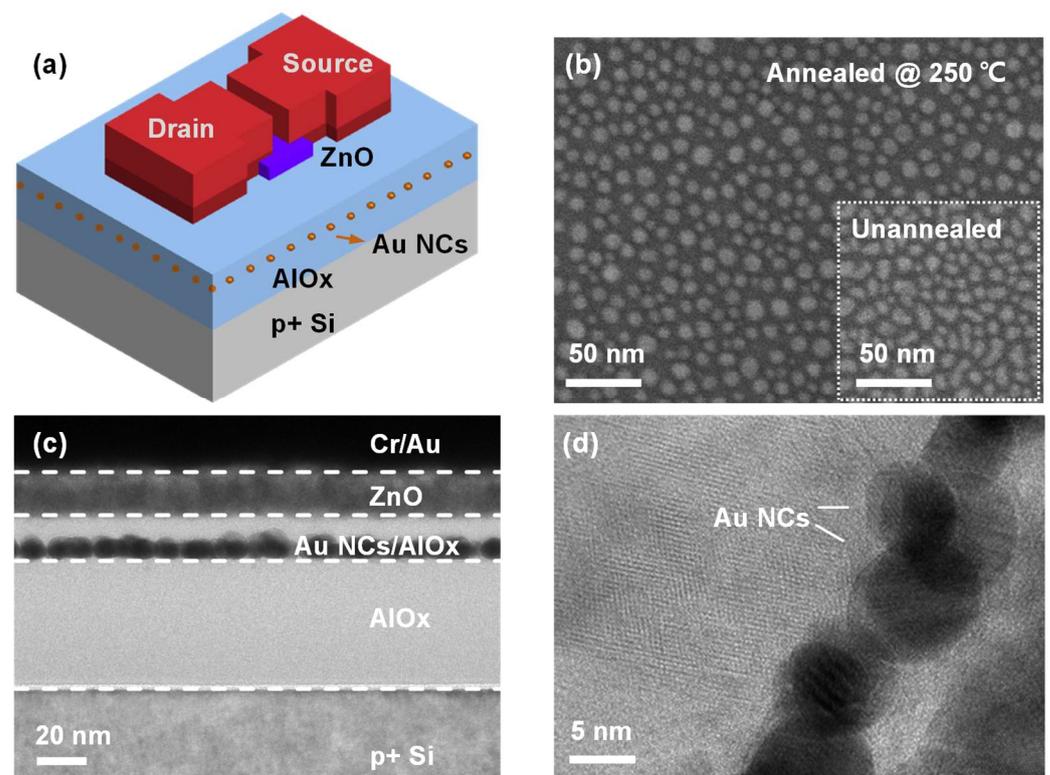
Here, we present a non-volatile memory based on a ZnO thin-film transistor prepared at low temperature, for the first time, with self-assembled Au nanocrystals as the charge storage layer. Both the ZnO channel and the  $\text{AlO}_x$  oxide layer in the memory were prepared by ALD to ensure good thin-film quality. The results show that well-isolated Au nanocrystals were formed self-assembly by annealing at a low temperature of 250 °C, with an average size of 8 nm. The TFT memory shows excellent charge storage capability, including a P/E window of 9.8 V at a programming voltage of 15 V, a P/E window of 7 V extrapolated

to 10 years, and a P/E window of 9.7 V after  $10^4$  P/E cycles. In addition, the TFT memory presents favorable on-state characteristics with field-effect mobility of  $17.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $I_{\text{ON}}/I_{\text{OFF}}$  exceeding  $10^7$ . The superior non-volatility and on-state performance make it promising for applications in transparent and flexible electronic systems.

## 2. Materials and Methods

### 2.1. Device Fabrication

The schematic structure of the proposed ZnO TFT memory is shown in Figure 1a. The device adopted a staggered TFT structure, with heavily doped p-type silicon ( $0.001 \text{ } \Omega \cdot \text{cm}$ – $0.005 \text{ } \Omega \cdot \text{cm}$ ) serving as the bottom gate. For the fabrication, firstly, 50 nm  $\text{AlO}_x$  was deposited on RCA-cleaned p+ silicon substrate by ALD (TFS200, Beneq, Espoo, Finland) at  $200 \text{ }^\circ\text{C}$ , with Trimethylaluminum (TMA) and  $\text{H}_2\text{O}$  as precursors, which served as the blocking oxide layer. A cycle of  $\text{AlO}_x$  deposition consisted of 0.7 s pulse of TMA, 10 s of purging using  $\text{N}_2$ , 1 s pulse of  $\text{H}_2\text{O}$ , and 15 s purging using  $\text{N}_2$ . The growth rate of  $\text{AlO}_x$  was 0.12 nm per cycle, as determined by thickness measurement by an ellipsometer. Subsequently, for the fabrication of Au NCs, a 1.5 nm Au layer was deposited by thermal evaporation (JSD-400) at room temperature under a vacuum of  $2 \times 10^{-4} \text{ Pa}$  and followed by rapid thermal annealing in an  $\text{N}_2$  atmosphere at  $250 \text{ }^\circ\text{C}$  for 1 min. Next, the 10 nm  $\text{AlO}_x$  tunneling oxide layer was deposited by ALD at  $250 \text{ }^\circ\text{C}$ , using the same precursors and deposition parameters. Next, 16 nm ZnO was deposited on the tunneling oxide by ALD at  $100 \text{ }^\circ\text{C}$  in the same chamber without vacuum breaking, with Diethylzinc (DEZn) and  $\text{H}_2\text{O}$  as precursors. The pulse times of DEZn and  $\text{H}_2\text{O}$  were both 0.3 s, and the following  $\text{N}_2$  purging times were 20 s and 25 s, respectively. The measured growth rate of ZnO was 0.13 nm per cycle. The growth parameters of  $\text{AlO}_x$  and ZnO are summarized in Supplementary Table S1. More details about the process can be found in our previous paper [31].



**Figure 1.** (a) Schematic of the proposed TFT memory; (b) SEM image of Au NCs on  $\text{AlO}_x$  blocking oxide after annealing, insert is the SEM image of the unannealed sample; (c) cross-sectional TEM image of the fabricated TFT memory; (d) high-resolution TEM image of Au NCs in the TFT memory.

After the deposition of all functional layers, the ZnO layer was patterned using photoresist (S1818, SHIPLEY, Tustin, CA, USA) and UV lithography (H93-37, Nanguang, China) and then wet etched ( $\text{H}_3\text{PO}_4$ , 10%) into  $150\ \mu\text{m} \times 300\ \mu\text{m}$  cubes, which served as the isolated active channel layer for the TFT memory. Then, source and drain electrode patterns were created by photoresist (N4340, Allresist, Strausberg, Germany) and UV lithography. Next, 10 nm Cr and 50 nm Au were prepared using electron beam evaporation on the patterns at room temperature, under a vacuum of  $2 \times 10^{-4}$  Pa, and the S/D electrodes were formed by a lift-off process. The channel length and width of the device were 50  $\mu\text{m}$  and 200  $\mu\text{m}$ , respectively, which were defined by the spacing and width of source and drain electrodes. The process flows are illustrated in Supplementary Figure S1. In addition, the control device without Au NCs was also fabricated simultaneously. No post-annealing was involved during the fabrication process of the devices.

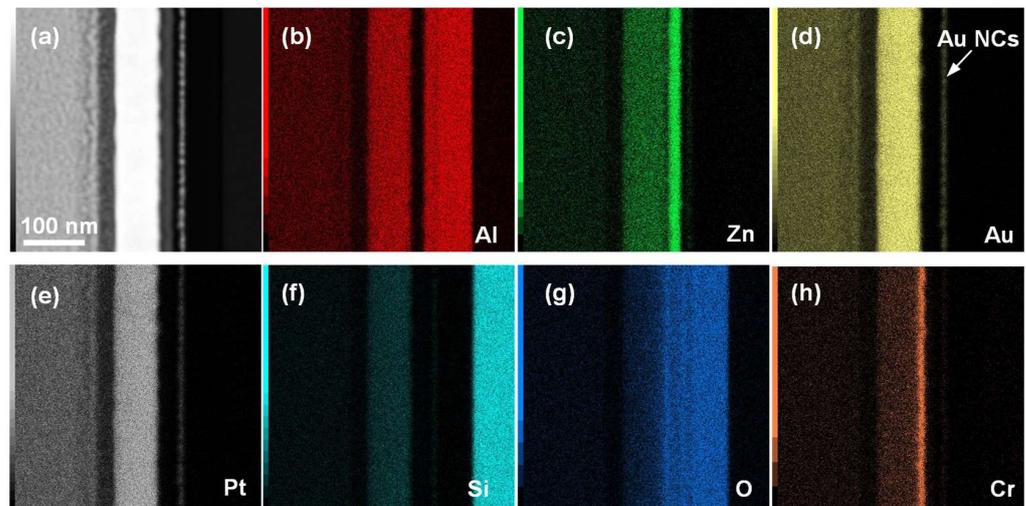
## 2.2. Device Characterization

The device structure was characterized by a field emission transmission electron microscope (JEM-F200, JEOL, Tokyo, Japan) with an acceleration voltage of 200 kV, the morphological characterization of metal nanocrystals was performed by scanning electron microscopy (Sirion, FEI, Hillsboro, OR, USA). The thickness of the  $\text{AlO}_x$  film and ZnO film were measured by an ellipsometer (Alpha-SE, J.A. Woollam, Lincoln, NE, USA), and the electrical characteristics of the memory device were measured with a semiconductor characterization system (Keithley 4200scs, Cleveland, OH, USA).

## 3. Results and Discussion

Figure 1b shows the SEM image of deposited 1.5 nm Au on the  $\text{AlO}_x$  blocking oxide layer after annealing for 1 min at 250 °C in a nitrogen atmosphere, together with the SEM image of the unannealed sample. It is evident that the deposited metal transformed from irregularly shaped islands to metal nanocrystals (NCs) with a round shape and uniform distribution after annealing. The average diameter of the fabricated Au NCs was 8 nm, with an areal density of  $4.2 \times 10^{11}\ \text{cm}^{-2}$ . The formation of Au NCs can be interpreted as a self-assembly process, where the thermal energy given by annealing increases the surface mobility of the Au atoms, making them self-assemble into spherical nanocrystals with a lower total energy state [21]. Our results indicate that the process can occur even at a low temperature of 250 °C, which significantly reduces the thermal budget during device preparation and facilitates the integration of the memory devices on flexible substrates that cannot tolerate high temperatures. Au-O has a Gibbs free energy of  $-221.8 \pm 20.9\ \text{kJ/mol}$ , which is higher than that of Al-O with  $-511 \pm 3\ \text{kJ/mol}$  [22]. This facilitates the stabilization of Au NCs on  $\text{AlO}_x$ , and the large difference in bond energy promotes the self-assembly of Au at relatively low temperature. The cross-sectional TEM image of the fabricated memory device was shown in Figure 1c, and the HR-TEM image of Au NCs in the device was shown in Figure 1d. A clear layered structure was observed, with Au NCs sandwiched between the amorphous  $\text{AlO}_x$  tunneling oxide layer and blocking oxide layer, which served as the material for charge storage. The HRTEM image of ZnO was shown in Supplementary Figure S2. It can be seen that the deposited ZnO had a polycrystalline morphology consisting of many columnar grains with different orientations. It was also observed that the ZnO channel was conformal and exhibited a distinct interface with the  $\text{AlO}_x$  tunneling layer, which facilitated the steep switching of the TFT memory under the gate control. Furthermore, Figure 1d reveals that the prepared Au NCs have a regular circular cross-section, which, in combination with the top-view SEM image in Figure 1b, suggests that the fabricated Au NCs were uniformly distributed, well-isolated, three-dimensional spheres. The annular dark field image of the fabricated TFT memory was illustrated in Figure 2a, and the EDS mapping profile of Al, Zn, Au, Cr, Si, and O elements are shown in Figure 2b–h. It can be seen that the TFT memory has a clear layered structure, and Au NCs were uniformly arranged in a consistent plane, isolated to an active

channel by the  $\text{AlO}_x$  tunneling layer. The EDS spectrum for element analysis was given in Supplementary Figure S3.



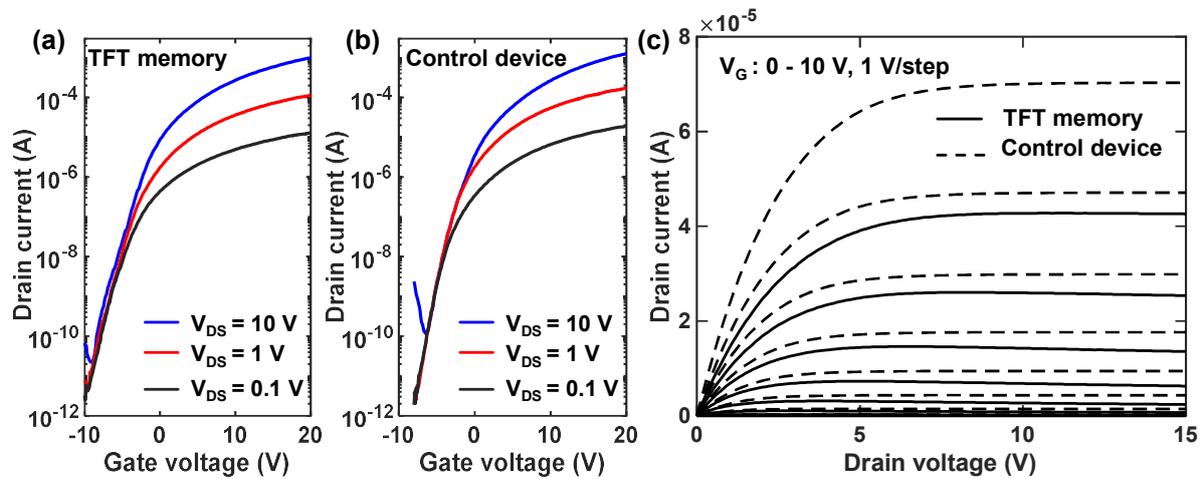
**Figure 2.** (a) Annular dark field image of the fabricated TFT memory; (b–h) EDS mapping profiles in the drain region, showing the distribution of Al, Zn, Au, Pt, Cr, Si, and O elements.

Figure 3a,b illustrates the transfer curves of TFT memory devices and control TFT devices at the initial state under different  $V_{DS}$ . It can be seen that both devices exhibited good switching characteristics under the control of gate voltage, with the current on–off ratios both exceeding  $10^7$ . The extracted threshold voltage ( $V_{th}$ ) and subthreshold swing were  $-6.0$  V,  $0.71$  V/dec for the TFT memory, and  $-4.8$  V,  $0.62$  V/dec for the control device at  $V_{DS} = 1.0$  V. Here, the threshold voltage is defined using the constant current method, which is the gate voltage when the drain-source current is equal to  $W/L \times 10^{-9}$  A. The threshold of the memory device is slightly lower than that of the control device due to the fact that Au has a higher work function than the Fermi level of ZnO, which introduces an additional accumulation of electrons at the  $\text{AlO}_x$ -ZnO interface. The field-effect mobility was obtained in the linear region by the following Equation (1) [34]:

$$\mu_{FE} = \frac{L}{WC_i V_{DS}} \cdot \frac{dI_D}{dV_{GS}} \quad (1)$$

where the measured capacitance density of gate-stack  $C_i$  was  $1.31 \times 10^{-7}$  F/cm<sup>2</sup> for the TFT memory and  $1.47 \times 10^{-7}$  F/cm<sup>2</sup> for the control device. The extracted mobility was  $17.6$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for the TFT memory and  $25.2$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for the control device. Some degradation was observed in both the subthreshold swing and field-effect mobility of the TFT memory compared to the control device. One reason for this is that the presence of Au NCs increases the roughness of the  $\text{AlO}_x$ -ZnO interface, leading to an increase in interface states at the  $\text{AlO}_x$ -ZnO interface and a reduction in electron mobility within the ZnO channel. The above results show that the fabricated TFT memory exhibits superior open-state performance compared to those reported in the literature. Table 1 compares the on-state and memory performance of various oxide semiconductor TFT-based memories. The continuous deposition of  $\text{AlO}_x$  and ZnO by ALD without vacuum breaking ensures a sharp and smooth interface, with a large grain size for reducing the carrier scattering by grain border traps, ensuring fast transport of electrons in the accumulated channel. A suitable carrier density of  $2.1 \times 10^{17}$  cm<sup>-3</sup> under the deposition temperature of  $100$  °C brings the memory good switching behavior with a high current on–off ratio. The benefits from using a non-destructive and low-temperature ALD technique show that improvements are significant for practical applications, as higher cell current enlarges the sensing margin

of the readout circuit, facilitating fast access of the cell state and allowing for increasing the number of memory cells in a NAND string.



**Figure 3.** (a,b) Transfer curves of fabricated TFT memory and control device; (c) output curves of fabricated TFT memory and control device.

**Table 1.** Comparison of TFT non-volatile memories based on an oxide semiconductor channel.

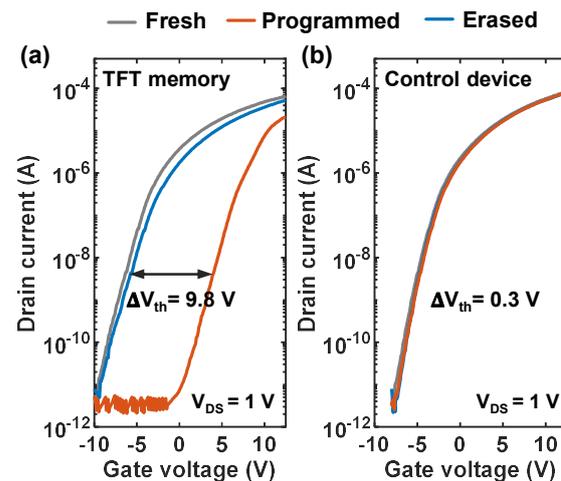
Ref.	Gate Stacks	Channel	P/E Condition	$\Delta V_{th}$	Charge Retention @10 yrs.	Mobility ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ )	$I_{ON}/I_{OFF}$	SS(V/dec)	Max. Process Temp.
This work	$\text{AlO}_x/\text{Au-NCs}/\text{AlO}_x$	ZnO (ALD)	P: +15 V, 100 ms E: −15 V, 1 s	9.8 V	71 %	17.6	$\sim 10^7$	0.71	250 °C
[13]	$\text{Al}_2\text{O}_3/\text{Ni-NCs}/\text{Al}_2\text{O}_3$	a-IGZO (Sputtering)	P: +18 V, 5 ms E: −20 V, UV light, 100 s	13.8 V	52%	7.1	$\sim 10^7$	0.70	300 °C
[17]	HfLaO/M-OH	a-IGZO (Sputtering)	P: 10 V, 1 s E: −10 V, 1 s	1.5 V	78.9 %	3.9	$2.7 \times 10^5$	0.23	400 °C
[28]	$\text{HfO}_2/\text{Pd-NCs}/\text{HfO}_2$	ZnO (Sputtering)	P: +18 V, 200 ms E: −18 V, 200 ms	5.8 V	83%	N/A	$\sim 10^3$	1.9	RT

Figure 4 shows the transfer curves of the TFT memory and control device at the initial state, programmed state, and erased state. The programming was performed by applying a voltage pulse of 15 V and 100 ms to the gate, while −15 V and 1 s were used for erasing, both with source and drain grounded. It can be seen that the  $V_{th}$  of the TFT memory shifted from −6.0 V to 4.0 V after programming and returned to −5.8 V after erasing. The P/E window of 9.8 V between the programmed state and erased state, compared to the 0.1 V P/E window of the control device, indicated the excellent memory performance of our TFT memory, which is attributed to the storage of electrons by Au NCs. Notably, no significant degradation in on-state performance was observed for both devices after programming and erasing, while the  $V_{th}$  of both devices was slightly higher than that in the fresh state after a series of erasing operations. One possible reason is that some electrons were trapped by some deep-level traps in the tunneling oxide during programming and cannot return to the channel after erasing. To evaluate the capability of Au NCs to trap electrons, the number of electrons trapped by NCs was calculated by Equation (2):

$$n = \frac{C_{BO}\Delta V_{th}}{q\sigma_{NCs}} \quad (2)$$

where  $C_{BO}$  is the capacitance density of the  $\text{AlO}_x$  blocking oxide,  $\Delta V_{th}$  is the P/E window, and  $\sigma_{NCs}$  is the density of Au NCs. According to the calculation, about 20 electrons were trapped by an Au NC after programming of 15 V, 0.1 s, which is higher than those

reported in the literature [20,28,29]. Due to the high density of states around the Fermi level and stable chemical properties so that its surface properties will not be affected by annealing and subsequent processes, along with the appropriate average size of 8 nm and regular spherical morphology, our results show that the self-assembled Au NCs can provide large charge-trapping density, which ensures excellent non-volatility of the TFT memory. Furthermore, the power consumption during programming and erasing were calculated as 2.18 nJ and 2.13 nJ, respectively. Details of the calculation can be found in the Supplementary Information. If the power consumption needs to be further reduced, feasible approaches include reducing the P/E window by adjusting the P/E time, reducing P/E voltage, and shrinking the device size.



**Figure 4.** (a,b) Transfer curve of TFT memory and control device at fresh state, after 15 V, 100 ms programming and after −15 V, 1 s erasing.

Figure 5a illustrates the  $V_{th}$  of the memory cell under two conditions: fresh cell after a fixed programming time of 100 ms and programmed cell after erasure for 1 s. Various gate voltage amplitudes were applied for programming and erasing with the source and drain grounded. It can be observed that a significant shift in threshold voltage occurred for the fresh cell when the applied gate voltage exceeded 9 V, while for the erased state,  $V_{th}$  decreased with increasing erase voltage amplitude, and the shift became saturated at −18 V. Figure 5b shows the threshold voltage of the fresh cell and programmed cell of the TFT memory under 15V/−15V programming/erasing voltage amplitudes with different pulse widths. It is observed that the  $V_{th}$  shift of the fresh cell significantly increased with longer programming times beyond 0.1 ms, reaching 10 V at 100 ms. For the programmed cell, a significant  $V_{th}$  shift was observed after an erasing time exceeding 1 ms and reaching 9.8 V after erasing for 1 s. The above results show that the TFT memory has good programming and erasing performance. A large part of the reason for this, in addition to the high charge-trapping density of Au mentioned above, is attributed to the use of  $AlO_x$ , a high-k dielectric with a measured k-value of 8.2, which significantly enhances the coupling between the control gate and the channel, resulting in obviously  $V_{th}$  shifts under gate voltage pulse.

The programming and erasing mechanisms of the TFT memory can be elucidated through the band diagram of the device structure. Figure 6a–c illustrates the band diagram of the TFT memory structure at flat band, programming, and erasing. The band gap of ZnO is determined to be 3.25 eV by optical transmittance spectrum; details can be found in Supplementary Figure S4. As shown in Figure 6b, the Fowler–Nordheim (FN) tunneling was used for the programming of the device since a positive program voltage was applied to the gate while keeping the source and drain grounded. The FN tunneling current is notably influenced by the field strength of the tunneling oxide, which correlates with the applied write voltage [35]. As the programming voltage exceeded 9 V, the bending of the energy band allowed electrons to tunnel across the triangular barrier into Au NCs through

FN tunneling, resulting in a significant change in  $V_{th}$ . When erasing was performed, the negative gate voltage raised the energy level of Au NCs through capacitive coupling, and the charge stored in the NCs also increased the energy level of the NCs. Despite Au having a high work function of about 5.4 eV, the electrons stored in the Au nanocrystals can return to the channel through FN tunneling under a large gate voltage. This is evidenced by the observed strong electric field dependence of the threshold voltage shifts during erasing.

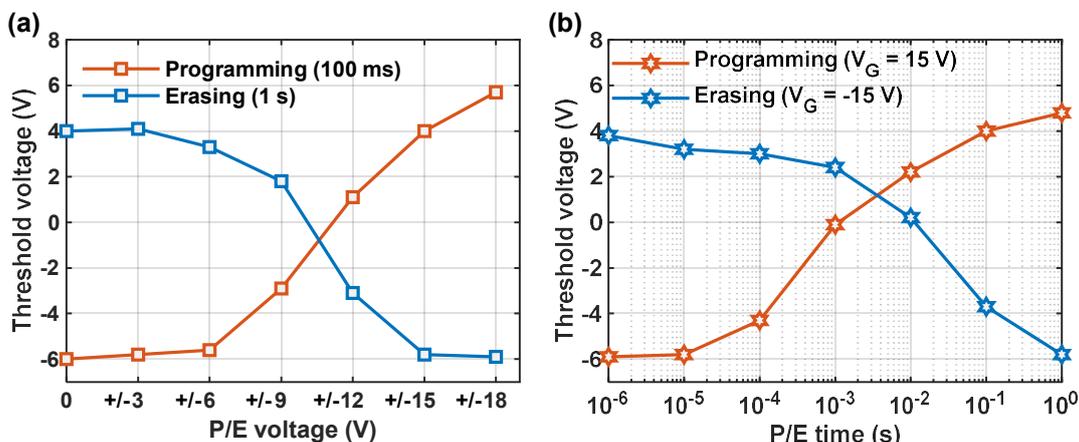


Figure 5. P/E characteristics of TFT memory. (a)  $V_{th}$  versus P/E voltage; (b)  $V_{th}$  versus P/E time.

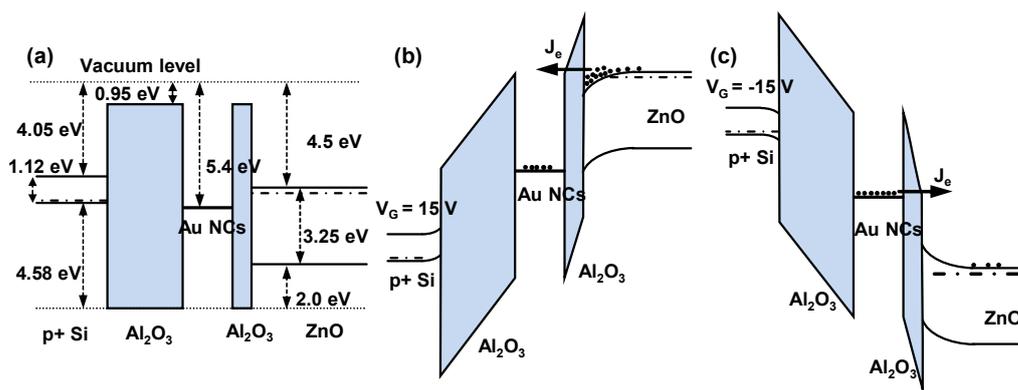
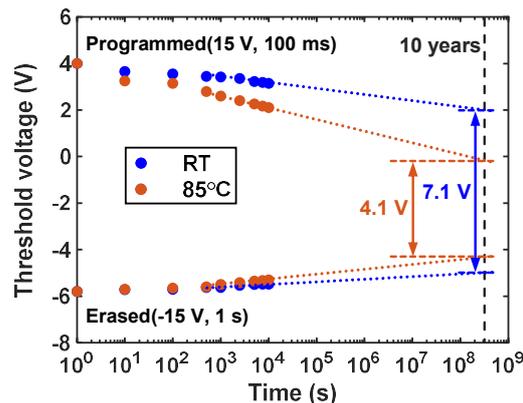


Figure 6. Band diagram of proposed ZnO TFT memory. (a) flatband; (b) programming; (c) erasing.

Furthermore, we observe that the programming efficiency of the TFT memory was higher than that of erasing, as programming always achieves the same  $V_{th}$  shift in less time. This is due to the asymmetric energy band structure of the device, as shown in Figure 6b,c, where the barrier between ZnO and AlO<sub>x</sub> is 3.55 eV, while the barrier between Au and AlO<sub>x</sub> is about 4.35 eV. Consequently, the FN tunneling current for programming is higher than that for erasing, resulting in a shorter programming time. Therefore, the programming and erasing time selected at a chosen P/E voltage of 15 V were 100 ms and 1 s, respectively, to ensure a stable P/E window during repetitive operations. In addition, our results indicate that although the hole barrier between ZnO and AlO<sub>x</sub> is only 2 eV, erasing cannot be realized by hole injection because the observed  $V_{th}$  of erased cells is always higher than that of the fresh cells under various erasing settings. This difficulty arises from the inherent properties of ZnO as a wide-band semiconductor, which naturally exhibits strong n-type conducting, making it challenging to generate sufficient holes through inversion [36].

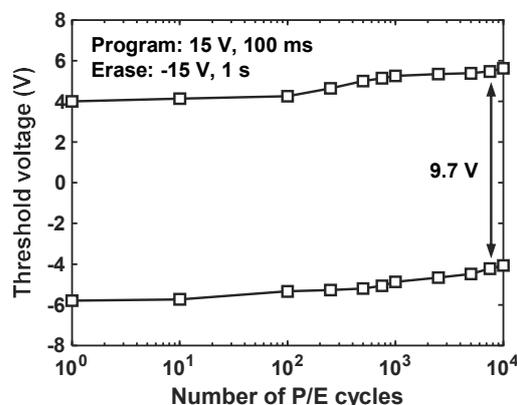
Figure 7 illustrates the retention characteristics of the TFT memory cell at room temperature and 85 °C. The  $V_{th}$  of the programmed cell and erased cell were monitored over time. At room temperature, it can be seen that the P/E window gradually decreased from 9.8 V to 8.6 V at 10<sup>4</sup> s and further to 7 V when extrapolated to 10 years, representing a 29% loss of stored charge. At an elevated temperature of 85 °C, the P/E window decreased at a

faster rate, with the extrapolated P/E window at 10 years reduced to 4 V, corresponding to a 59% loss of stored charge. The acceleration of charge loss with increasing temperature indicates a significant impact of temperature on the leakage current from the Au NCs to the channel under retention mode. Our prepared Au NCs TFT memory exhibits excellent retention properties for two main reasons. Firstly, the high work function of Au NCs enables the forming of a deep quantum well in  $\text{AlO}_x$ , reducing the probability of electron tunneling. Secondly, the dense, pinhole-free, and insulated nature of the ALD-prepared  $\text{AlO}_x$  significantly reduces the leakage current from Au NCs, which is proven by the AFM (Multimode 8, Bruker, Billerica, MA, USA) image and current density curve of deposited  $\text{AlO}_x$  tunneling oxide in Supplementary Figure S5.



**Figure 7.** Retention characteristics of fabricated ZnO TFT memory under RT and 85 °C.

Figure 8 shows the endurance characteristics of TFT memory. It can be observed that the  $V_{th}$  of both erased and programmed cells increased with the increase of P/E cycles, with the rate of change being larger after 500 cycles. Despite this, the TFT memory maintained a P/E window of 9.7 V after  $10^4$  cycles. The shifts of  $V_{th}$  with the P/E cycle in both states were related to the degradation of tunneling oxide. Voltage stress in the P/E cycle induces trap generation in the tunneling oxide, which could capture electrons and lead to an increase in  $V_{th}$  of the memory over cycling. Moreover, unbalanced programming and erasing can also shift the  $V_{th}$  of erased cells and programmed cells in the same direction. To mitigate this, the voltage and time of programming and erasing should be more finely tuned. Overall, the high-quality  $\text{AlO}_x$  tunneling oxide enables the TFT memory to obtain robust endurance, making it favorable for practical applications.



**Figure 8.** Endurance characteristics of fabricated ZnO TFT NCs memory.

#### 4. Conclusions

In conclusion, we successfully fabricated a high-performance ZnO TFT non-volatile memory, with self-assembled Au NCs sandwiched between  $\text{AlO}_x$  and a maximum process

temperature of 250 °C. The high work function and proven exceptional charge-trapping capability of the Au NCs provide the excellent non-volatility to the memory. The use of high-k dielectric AlO<sub>x</sub> enhances the program and erase performance of the memory and ensures the long retention. Together with the low-temperature ALD ZnO channel, our TFT memory exhibits both excellent on-state performance and memory characteristics, including field-effect mobility, subthreshold swing, and current on–off ratio of 17.6 cm<sup>2</sup>V<sup>−1</sup>s<sup>−1</sup>, 0.71 V/dec, and 10<sup>7</sup>, respectively, and the P/E window of 9.8 V under 15 V, 100 ms programming and −15 V, 1 s erasing, which maintained to 7 V when extrapolated to 10 years. The memory demonstrated impressive endurance performance with a 9.7 V P/E window after 10<sup>4</sup> P/E cycles. Combined with the low-temperature and large-scale fabrication capability of the process technology, our ZnO TFT memory exhibits great potential for integration into SoP and flexible electronic systems as a crucial component of memory modules.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano14080678/s1>.

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## References

1. Wager, J.F. Transparent Electronics. *Science* **2003**, *300*, 1245. [[CrossRef](#)] [[PubMed](#)]
2. Nomura, K.; Ohta, H.; Takagi, A.; Kamiya, T.; Hirano, M.; Hosono, H. Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors. *Nature* **2004**, *432*, 488. [[CrossRef](#)] [[PubMed](#)]
3. Nathan, A.; Jeon, S. Oxide electronics: Translating materials science from lab-to-fab. *MRS Bull.* **2021**, *46*, 1028. [[CrossRef](#)]
4. Zhang, N.; Zhao, W.; Yao, C.; Zhang, J.; Huang, T.; Dong, S.; Luo, J.; Liu, Y.; Ye, Z. Transparent Multi-Level NAND Flash Memory and Circuits Based on ZnO Thin Film Transistor. *IEEE Electron. Device Lett.* **2023**, *44*, 610. [[CrossRef](#)]
5. Yu, X.; Marks, T.J.; Facchetti, A. Metal oxides for optoelectronic applications. *Nat. Mater.* **2016**, *15*, 383. [[CrossRef](#)] [[PubMed](#)]
6. Kim, H.J.; Park, K.; Kim, H.J. High-performance vacuum-processed metal oxide thin-film transistors: A review of recent developments. *J. Soc. Inf. Disp.* **2020**, *28*, 591. [[CrossRef](#)]
7. Hoffman, R.L.; Norris, B.J.; Wager, J.F. ZnO-based transparent thin-film transistors. *Appl. Phys. Lett.* **2003**, *82*, 733. [[CrossRef](#)]
8. Wang, W.; Li, K.; Lan, J.; Shen, M.; Wang, Z.; Feng, X.; Yu, H.; Chen, K.; Li, J.; Zhou, F.; et al. CMOS backend-of-line compatible memory array and logic circuitries enabled by high performance atomic layer deposited ZnO thin-film transistor. *Nat. Commun.* **2023**, *14*, 6079. [[CrossRef](#)]
9. Özgür, Ü.; Alivov, Y.I.; Liu, C.; Teke, A.; Reshchikov, M.A.; Doğan, S.; Avrutin, V.; Cho, S.-J.; Morkoç, H. A comprehensive review of ZnO materials and devices. *J. Appl. Phys.* **2005**, *98*, 041301. [[CrossRef](#)]
10. Tynell, T.; Karppinen, M. Atomic layer deposition of ZnO: A review. *Semicond. Sci. Technol.* **2014**, *29*, 043001. [[CrossRef](#)]
11. Hirao, T.; Furuta, M.; Furuta, H.; Matsuda, T.; Hiramatsu, T.; Hokari, H.; Yoshida, M.; Ishii, H.; Kakegawa, M. Novel top-gate zinc oxide thin-film transistors (ZnO TFTs) for AMLCDs. *J. Soc. Inf. Disp.* **2007**, *15*, 17. [[CrossRef](#)]
12. Park, S.-H.K.; Ryu, M.; Hwang, C.-S.; Yang, S.; Byun, C.; Lee, J.; Shin, J.; Yoon, S.M.; Chu, H.Y.; Cho, K.I.; et al. Transparent ZnO Thin Film Transistor for the Application of High Aperture Ratio Bottom Emission AM-OLED Display. *SID Symp. Dig. Tech. Pap.* **2008**, *39*, 629. [[CrossRef](#)]
13. Qian, S.-B.; Shao, Y.; Liu, W.-J.; Zhang, D.W.; Ding, S.J. Erasing-Modes Dependent Performance of a-IGZO TFT Memory with Atomic-Layer-Deposited Ni Nanocrystal Charge Storage Layer. *IEEE Trans. Electron. Devices* **2017**, *64*, 3023–3027. [[CrossRef](#)]
14. Mondal, S.; Venkataraman, V. All inorganic solution processed three terminal charge trapping memory device. *Appl. Phys. Lett.* **2019**, *114*, 173502. [[CrossRef](#)]
15. Lee, H.; Beom, K.; Kim, M.; Kang, C.J.; Yoon, T. Nonvolatile Memory and Artificial Synaptic Characteristics in Thin-Film Transistors with Atomic Layer Deposited HfO<sub>x</sub> Gate Insulator and ZnO Channel Layer. *Adv. Electron. Mater.* **2020**, *6*, 2000412. [[CrossRef](#)]
16. Bae, S.-H.; Ryoo, H.-J.; Seong, N.-J.; Choi, K.J.; Kim, G.H.; Yoon, S.M. Characterization of nanoscale vertical-channel charge-trap memory thin film transistors using oxide semiconducting active and trap layers. *J. Vac. Sci. Technol. B* **2021**, *39*, 043202. [[CrossRef](#)]

17. Zhang, C.; Li, D.; Lai, P.T.; Huang, X.D. An InGaZnO Charge-Trapping Nonvolatile Memory with the Same Structure of a Thin-Film Transistor. *IEEE Electron. Device Lett.* **2022**, *43*, 32. [[CrossRef](#)]
18. Sun, C.; Li, C.; Samanta, S.; Han, K.; Zheng, Z.; Zhang, J.; Kong, Q.; Xu, H.; Zhou, Z.; Chen, Y.; et al. Computational Associative Memory with Amorphous Metal-Oxide Channel 3D NAND-Compatible Floating-Gate Transistors. *Adv. Electron. Mater.* **2022**, *8*, 2200643. [[CrossRef](#)]
19. Zhang, N.; Zhao, W.; Zhang, X.; Liu, Y.; Dong, S.; Luo, J.; Ye, Z. Transparent Floating Gate Memory Based on ZnO Thin Film Transistor with Controllable Memory Window. *IEEE J. Electron. Devices* **2022**, *10*, 275. [[CrossRef](#)]
20. Tiwari, S.; Rana, F.; Hanafi, H.; Hartstein, A.; Crabbé, E.F.; Chan, K. A silicon nanocrystals based memory. *Appl. Phys. Lett.* **1996**, *68*, 1377. [[CrossRef](#)]
21. Liu, Z.; Lee, C.; Narayanan, V.; Pei, G.; Kan, E. Metal nanocrystal memories. I. Device design and fabrication. *IEEE Trans. Electron. Devices* **2002**, *49*, 1606. [[CrossRef](#)]
22. Chang, T.-C.; Jian, F.-Y.; Chen, S.-C.; Tsai, Y.-T. Developments in nanocrystal memory. *Mater. Today* **2011**, *14*, 608. [[CrossRef](#)]
23. Rao, R.A.; Steimle, R.F.; Sadd, M.; Swift, C.; Hradsky, B.; Straub, S.; Merchant, T.; Stoker, M.; Anderson, S.; Rossow, M.; et al. Silicon nanocrystal based memory devices for NVM and DRAM applications. *Solid-State Electron.* **2004**, *48*, 1463. [[CrossRef](#)]
24. She, M.; King, T.-J. Impact of crystal size and tunnel dielectric on semiconductor nanocrystal memory performance. *IEEE Trans. Electron. Devices* **2003**, *50*, 1934–1940.
25. Hou, T.-H.; Lee, C.; Narayanan, V.; Ganguly, U.; Kan, E.C. Design Optimization of Metal Nanocrystal Memory—Part I: Nanocrystal Array Engineering. *IEEE Trans. Electron. Devices* **2006**, *53*, 3095. [[CrossRef](#)]
26. Gupta, D.; Anand, M.; Ryu, S.-W.; Choi, Y.-K.; Yoo, S. Nonvolatile memory based on sol-gel ZnO thin-film transistors with Ag nanoparticles embedded in the ZnO/gate insulator interface. *Appl. Phys. Lett.* **2008**, *93*, 224106. [[CrossRef](#)]
27. Park, B.; Cho, K.; Kim, S.; Kim, S. Transparent nano-floating gate memory on glass. *Nanotechnology* **2010**, *21*, 335201. [[CrossRef](#)] [[PubMed](#)]
28. Kang, I.-S.; Kim, Y.-S.; Seo, H.-S.; Son, S.W.; Yoon, E.A.; Joo, S.-K.; Ahn, C.W. High-performance and room-temperature-processed nanofloating gate memory devices based on top-gate transparent thin-film transistors. *Appl. Phys. Lett.* **2011**, *98*, 212102. [[CrossRef](#)]
29. Rezk, A.; Abbas, Y.; Saadat, I.; Nayfeh, A.; Rezeq, M. Charging and discharging characteristics of a single gold nanoparticle embedded in Al<sub>2</sub>O<sub>3</sub> thin films. *Appl. Phys. Lett.* **2020**, *116*, 223501. [[CrossRef](#)]
30. Cho, M.H.; Choi, C.H.; Jeong, J.K. Recent progress and perspectives on atomic-layer-deposited semiconducting oxides for transistor applications. *J. Soc. Inf. Disp.* **2022**, *30*, 175. [[CrossRef](#)]
31. Chen, X.; Zhang, G.; Wan, J.; Guo, T.; Li, L.; Yang, Y.; Wu, H.; Liu, C. Transparent and Flexible Thin-Film Transistors with High Performance Prepared at Ultralow Temperatures by Atomic Layer Deposition. *Adv. Electron. Mater.* **2019**, *5*, 1800583. [[CrossRef](#)]
32. Groner, M.D.; Fabreguette, F.H.; Elam, J.W.; George, S. Low-Temperature Al<sub>2</sub>O<sub>3</sub> Atomic Layer Deposition. *Chem. Mater.* **2004**, *16*, 639. [[CrossRef](#)]
33. Ding, S.-J.; Wu, X. Superior Atomic Layer Deposition Technology for Amorphous Oxide Semiconductor Thin-Film Transistor Memory Devices. *Chem. Mater.* **2020**, *32*, 1343. [[CrossRef](#)]
34. *IEEE Standard 1620-2008*; IEEE Standard for Test Methods for the Characterization of Organic Transistors and Materials. IEEE Standard: Piscataway, NJ, USA, 2008.
35. Sze, S.M.; Li, Y.; Ng, K.K. *Physics of Semiconductor Devices*, 4th ed.; John Wiley & Sons: Hoboken, NJ, USA, 2021.
36. Shoute, G.; Afshar, A.; Muneshwar, T.; Cadien, K.; Barlage, D. Sustained hole inversion layer in a wide-bandgap metal-oxide semiconductor with enhanced tunnel current. *Nat. Commun.* **2016**, *7*, 10632. [[CrossRef](#)] [[PubMed](#)]

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