Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Two-bit memory and quantized storage phenomenon in conventional MOS structures with double-stacked Pt-NCs in an HfAlO matrix

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## Supplementary Information

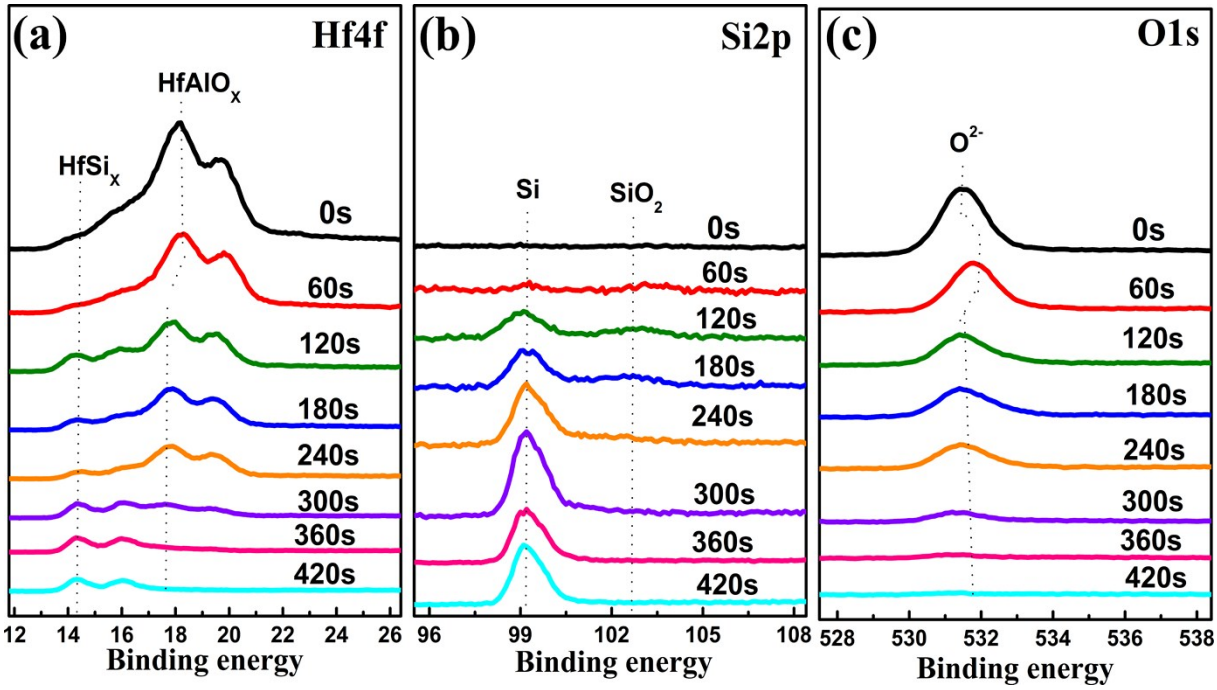


**Fig. S1** The XPS spectra of Hf4f(a), Si2p(b) and O1s(c) binding energy peaks for 5nm HfAlO deposited the p-Si substrate, which Ar+ gradually etch from 0 to 420s. The etched sample are fabricated at the optimized experiment condition.

As the XPS spectra presents, the Hf 4f 7/2 binding energy located at 18.14 eV as the Ar+ etch from 0 to 60s on the surface of fabricated samples indicated that the chemical component is the HfAlO matrix, as shown in Fig. S1 (a). After etch for 120s, observation for the double peaks of Hf 4f demonstrates that the Hf has two valence in this layer. In addition, the Hf 4f shift to lower binding energy direction (red-shift), hence, the $HfSiO_x$ generates during annealing process. The oxygen atom of outer ambient may penetrate into the HfAlO films to occupied the oxygen vacancy, the residual oxygen atom may through the HfAlO films, and then has a chemical reaction with the Si substrate. As the etching reaching to 300s, the peaks O 1s are not detected, as shown in Fig. S1 (c), but the double Hf 4f binding energy peaks is very obvious, therefore, We deduced that $HfSi_x$ are the main component near the p-Si substrate. By contrast, In the Fig. S1 (b), the energy peaks of $SiO_2$ is not obvious, therefore, the oxygen atoms at the interfacial just reacts with Hf atom. The Al 2p peaks located at 74.5eV have a little changes, which has not shown here. Therefore, the interfacial layer between HfAlO matrix and p-Si substrate are mainly composed by the $HfSiO_x$ and $HfSi_x$.[1, 2]

By contrast, the C-V curves for control device just has an negligible hysteresis, but the obvious flat band voltage shift (memory window) has been detected in the device with stacked Pt-NCs. We, therefore, deduced the multi-bit and quantized storage effects are mainly contributed by the Pt-NCs rather than the interfacial layers.

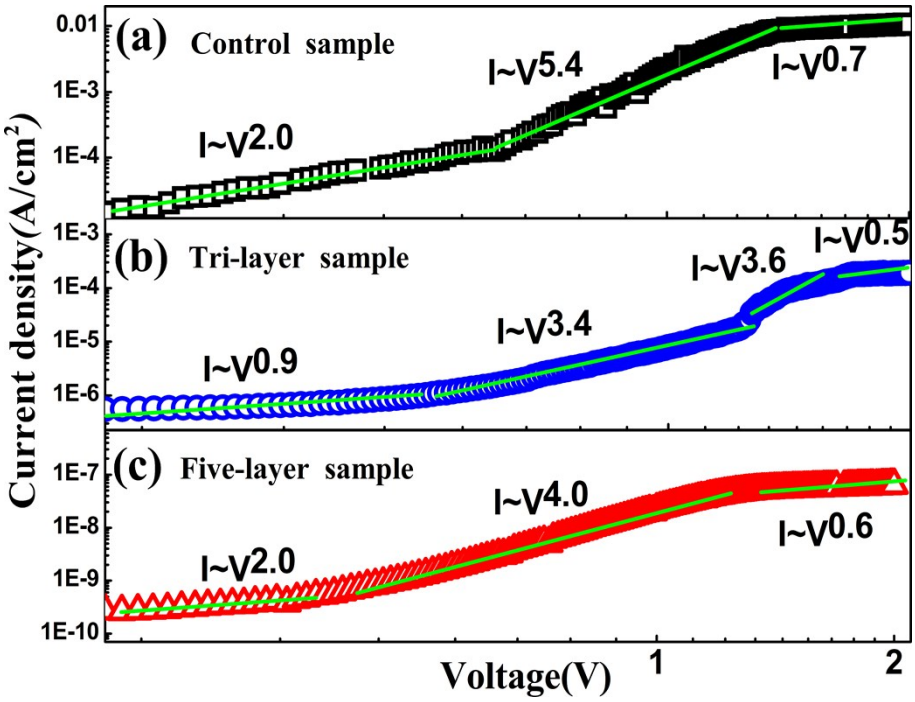


**Fig. S2** The double logarithm current-voltage curves based the J-V curves, the (a), (b) and (c) is the fitting plot results for the control , tri-layer, and five-layer samples, respectively.

Due to the difference work function and band energy for the Pt-NCs, HfAlO matrix and interfacial layer, the traps/ de-traps establishment and occupation may dominate and play an important role in the electron tunneling and storage process.

The double logarithm I-V curves are made based upon the I-V curves in Fig. S2 (a), (b), and (c). The fitting for control sample, tri-layer sample, and five-layer sample illustrated the trapping effects in our devices. The Pt nanoparticles embedded in the HfAlO films equal to added the number of deep trap. The trap induced current increasing or decreasing can be described as:[3,4]

$$J = (\frac{\theta}{\theta+1})\frac{9}{8}\varepsilon_r\varepsilon_0\mu\frac{V^2}{L^3}$$

where $\theta = (N_c / N_t)\exp^{-(E_c-E_t)/kT}$ is the ratio of free electron to trapped electron, $N_c$ is the effective density of states in the conductive band, $N_t$ is the number of emptied electron traps, $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the static dielectric constant, $\mu$ the electron mobility, V is the applied voltage and L is the film thickness. On the low electric field, the voltage sweep from 0—0.6

V, the fitting result of I~$V^2$ for control sample demonstrated the trapes such as oxygen vacancy are filled by the injected charges, namely, the $N_t << N_c$ illustrate that majority traps are occupied by electrons, the current-voltage sample described by $J = (9/8)\varepsilon_0\varepsilon_r\mu V^2 / L^3$. However, at a high electric field, the current steep current increasing, which can be described by $J \sim V^m$, m>3. Therefore, the fitting results of I~$V^{5.4}$ illustrate that most of injected charges are the free electrons, which contributed to the increasing current, as the Fig.S2 (a) shown. As the electric field continue increasing, the fitting results of I~$V^{0.7}$ for control sample illustrate that the screening and block effects from stored charges may dominate the current behavior. Similarly, the fitting results for tri-layer samples of the I-$V^{0.9}$ illustrate the current tunneling is the Ohmic conduction mechanism. On one hand, the traps is sharply increasing due to the Pt-NCs embedded in films; on the other hand, tremendous de-traps and new barrier can be established in the tri-layer samples. The fitting results of I-$V^{3.4}$ and I-$V^{3.6}$ at high electric field demonstrates the traps and deep traps are filled by electrons completely, as shown in Fig.S2 (b). The fitting results for five-layer samples, the traps and deep traps are occupied at the smaller electric field compared with the control or tri-layer samples, as the Fig.S2 (c). That why the tri-layer samples has a relative wide flat band voltage shift. Therefore, the Pt-NCs embedded in HfAlO films corresponds to establish traps and de-traps, which dominate the density of stored charges, and its tunneling behavior.

## Reference


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