Metadata of the chapter that will be visualized in SpringerLink

Book Title	Numerical Methods and Applications	
Series Title		
Chapter Title	Multi-scale Computational Framework for Evaluating of the Performance of Molecular Based Flash Cells	
Copyright Year	2015	
Copyright HolderName	Springer International Publishing Switzerland	
Corresponding Author	Family Name	**Georgiev**
	Particle	
	Given Name	**Vihar P.**
	Prefix	
	Suffix	
	Division	Device Modelling Group
	Organization	University of Glasgow
	Address	Glasgow, UK
	Email	vihar.georgiev@glasgow.ac.uk
Author	Family Name	**Asenov**
	Particle	
	Given Name	**Asen**
	Prefix	
	Suffix	
	Division	Device Modelling Group
	Organization	University of Glasgow
	Address	Glasgow, UK
	Division	
	Organization	GoldStandartSimulation Ltd.
	Address	Glasgow, UK
	Email	

Abstract	In this work we present a multi-scale computational framework for evaluation of statistical variability in a molecular based non-volatile memory cell. As a test case we analyse a BULK flash cell with polyoxometalates (POM) inorganic molecules used as storage centres. We focuse our discussions on the methodology and development of our innovative and unique computational framework. The capability of the discussed multi-scale approach is demonstrated by establishing a link between the threshold voltage variability and current-voltage characteristics with various oxidation states of the POMs. The presented simulation framework and methodology can be applied not only to the POM based flash cell but they are also transferrable to the flash cells based on alternative molecules used as a storage media.

Keywords (separated by '-')	Multi-scale modelling - Molecular electronics - Multi-bit non-volatile memory - Polyoxometalates

Multi-scale Computational Framework for Evaluating of the Performance of Molecular Based Flash Cells

Vihar P. Georgiev[1(✉)] and Asen Asenov[1,2]

[1] Device Modelling Group, University of Glasgow, Glasgow, UK
vihar.georgiev@glasgow.ac.uk
[2] GoldStandartSimulation Ltd., Glasgow, UK

Abstract. In this work we present a multi-scale computational framework for evaluation of statistical variability in a molecular based non-volatile memory cell. As a test case we analyse a BULK flash cell with polyoxometalates (POM) inorganic molecules used as storage centres. We focuse our discussions on the methodology and development of our innovative and unique computational framework. The capability of the discussed multi-scale approach is demonstrated by establishing a link between the threshold voltage variability and current-voltage characteristics with various oxidation states of the POMs. The presented simulation framework and methodology can be applied not only to the POM based flash cell but they are also transferrable to the flash cells based on alternative molecules used as a storage media.

Keywords: Multi-scale modelling · Molecular electronics · Multi-bit non-volatile memory · Polyoxometalates

1 Introduction

In the last few decades the flash cell technology has experienced significant changes, mainly in terms of the physical dimension of devices. This has been achieved primarily by reducing the tunnel oxide thickness in order to improve the programming/erasing performance. However, further scaling of the current NAND flash memory cells faces significant challenges. One of them is the existence of strong coupling between the floating gates in neighbouring cells that can result in cross talk and errors in a write and read operation (Kim 2010; Park 2009). Another challenge is the occurrence of a charge loss in the floating gate that happens due to a trap-assisted tunnelling in the tunnelling oxide, which jeopardises a write/erase cycling process (Amoroso 2013).

In order to overcome these technological issues charge trapping memories have been extensively researched. They are based on storing charge inside a silicon nitride or a high-k dielectric aiming to suppress the floating gate to gate disturbance. The charge trapping memories also provide immunity to localized defects in the tunnelling oxide and corresponding charge leakage (Lu 2012; Ma 2011).

I. Dimov et al. (Eds.): NMA 2014, LNCS 8962, pp. 1–8, 2015.
DOI: 10.1007/978-3-319-15585-2_22

However, the random number and position of the traps creates significant additional variability in the threshold voltage of the programmed flash cells (Amoroso 2010).

An alternative is development of nanocrystal memories where the charge is stored on semiconductor microcrystals embedded in the cell gate dielectric (Compagnoni 2005; Shaw 2005). Although such approach allows storage of multiple charges on a single micro-crystal, these memories also suffer from a significant statistical variability due to the size distribution of the micro-crystals and related different injection conditions (Dimitrakis 2013).

One possible option for an improvement is to replace the nanocrystals with molecules. In principal, a chemical synthesis in combination with a molecular self-assembly of the redox-active molecules can yield a regular distribution (spatially and energetically) of charge-storage centers (Pro 2009; Musumeci 2011). This allows us to scale the memory cell down to a few nanometres, as shown when using the organic redox-active molecules based on ferrocene and porphyrin (Zhu 2013; Paydavosi 2011). However, the organic molecules display low retention time due to the small associated redox potentials. Moreover, incorporation of the organic molecules in the flash memory manufacturing cycle is connected with numerous challenges. Therefore, from the technological point of view, it would be advantageous to find molecules, which are compatible with the standard silicon flash manufacturing. This would simultaneously help to overcome the deficiencies associated with the low retention time of their organic counterparts.

2 Concept and Flash Cell Design

One possible candidate to create the multi-bit molecular based flash cell is the polyoxometalate molecule known also as a POM. These inorganic metal-oxide clusters are formed by early transition metal ions and oxo ligands (Fay 2007). POMs have attractive properties for potential NVM application due to their

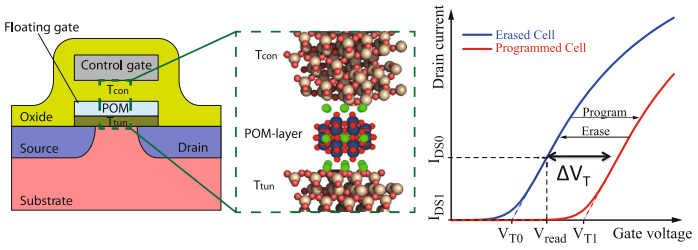


Fig. 1. Left: Schematic representation of a single-transistor BULK memory cell, indicating the aimed substitution of the poly-Si floating gate (FG) with an array of polyoxometalate molecules (POM layer). Right: Transfer characteristics (the source-drain current versus the control gate bias) of the device, illustrating the effect of programming the POM layer, leading to a shift of the voltage threshold (V_T) to higher values of the gate voltage

ability to undergo stable multiple and reversible oxidation/reduction processes. Also, incorporation of regular arrays of numerous POMs into SiO_2 has already been experimentally reported (Shaw 2011). As a result, we decided to concentrate our attention on possible integration of POMs with the floating gate (FG) of the current BULK flash cell architecture Fig. 1.

We consider the BULK flash cell with a gate area of $18 \times 18\,\mathrm{nm}^2$ as a template. The density of the POMs could vary significantly depending on the crystal structure, which determines the size of the molecule. In our calculations, that consider the gate area of $18 \times 18\,\mathrm{nm}^2$ and the crystal dimensions of the $[W_{18}O_{54}(SO_3)_2]^{4-}$POMs together with the $(CH_3H_7)_4N^+$ cations, we calculate that the optimal density of the molecules is $3 \times 10^{12}\,\mathrm{cm}^{-2}$. This density corresponds to nine molecules in the FG, which in our case are arranged in a 3×3 regular planar grid. The molecular layer starts 3 nm above the Si/SiO_2 interface and the entire gate stack is identical to our previously published work (Vilá-Nadal 2013; Georgiev 2014).

The selected POM has three stable and reversible reduction/oxidation states. It is therefore attractive for multi-bit charge storage. We should point out that in the process of chemical synthesis each molecule is surrounded on average by four positive charges (contra cations). Those cations are schematically presented as green points surrounding the molecule in Fig. 1 on the left hand side. The charge of the POM cluster on itself is 4- and each green chain has a single positive charge. On average 4 cations in total surround each POM, which means that the overall charge equals zero. However, with increasing of the oxidation state of the molecule from 4- to 5- the overall charge in the FG increases, which leads to a shift of the voltage threshold (V_T) to higher values of the gate voltage (V_G). The effect of the current-voltage characteristics and V_T is schematically presented in Fig. 1 on the right hand side.

3 Methodology

In this section we will briefly introduce the multi-scale simulation framework which we developed to evaluate the performance of the molecular storage flash memory cells. More details about the simulation methodology can be found in our previous publications (Vilá-Nadal 2013; Georgiev 2014). The multi-scale simulation framework links results obtained from the atomistic molecular simulations (first principle) with the continuum (mesoscopic) transistor simulations. The first principle calculations are based on the density functional theory (DFT) as implemented in the commercial simulator ADF 2008. The mesoscopic transistor simulations are performed with the commercial three-dimensional (3D) numerical device simulator GARAND (GARAND 2014). The simplified simulation flow diagram is presented in Fig. 2. The key component of this flow is the custom-built Simulation Domain Bridge that links the two distinct simulation domains atomistic and continuum.

In our simulation flow the DFT calculations provide the atomic coordinates and charges of a polyoxometalate molecule in a given redox state. It is vital

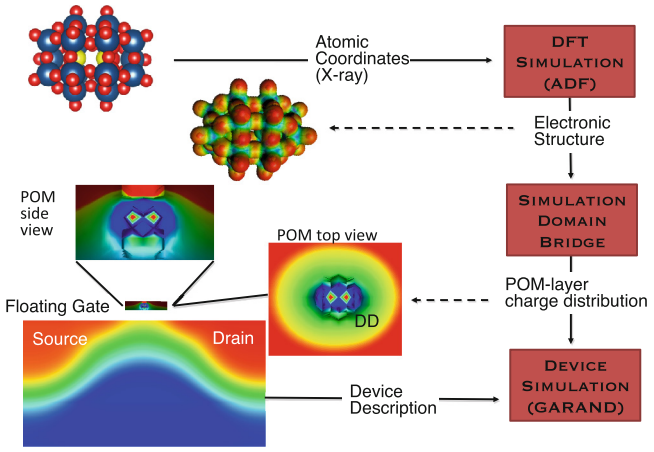
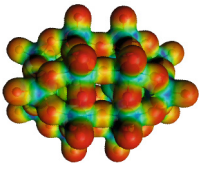


Fig. 2. Simplified block diagram of the simulation methodology, linking the atomistic molecular simulations (first principle) with the continuum (mesoscopic) transistor simulations



$[W_{18}O_{54}(SO_3)_2]^{4-}$

		X	Y	Z	MDC-q
1	O	-2.996	1.7533	0	-0.93357
2	O	-0.7393	1.2805	5.1309	-0.952574
3	O	-3.0671	0	6.3752	-0.617707
4	O	-4.6588	2.7977	2.0278	-0.602512
5	O	-2.9898	1.2983	3.7644	-0.910451
6	O	-4.0243	0	1.749	-0.899429
7	O	-1.6958	2.9372	2.0267	-0.944329
8	O	-1.5413	0	1.8242	-0.608756
9	S	0	0	1.2973	1.028495
10	W	-3.2746	1.805	1.9078	2.418012
11	W	-2.1678	0	4.9208	2.470102
12	O	-2.996	-1.7533	0	-0.93357

Fig. 3. Some atomic coordinates and charges of a polyoxometalate molecule in a given redox state obtained from the first principle simulations (DFT)

to consider the presence of cations in the process of fabrication or calculation of the flash cells. For this reason we take into account these positive charges in our work. In the first principle calculations the cations are presented with a continuum solvation model while in the device simulations they are described as 18 point charges around each POM. Some of these atomic charges of the molecule are represented in a table in Fig. 3.

In order to simulate and explore the realistic molecular based memory cells one option is to perform the transistor level simulations based on the continuum approach. In our case we relay on the 3D numerical device simulator GARAND. The data from the DFT calculations is transferred through the in-house built Simulation Domain Bridge as schematically depicted in Fig. 2. The bridge reads

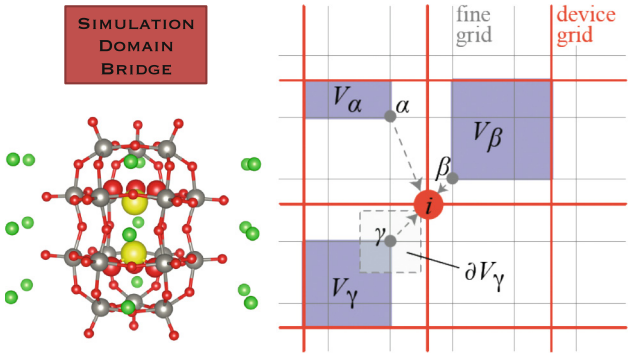


Fig. 4. 2D picture of the cloud-in-cell assignment of charge used from the domain bridge that reads the atomic charges from the DFT simulation and assigns the partial charges to the discretisation grid of GARAND

the atomic charges from the DFT simulation and assigns the partial charges to the discretisation grid of GARAND applying the cloud-in-cell technique. Figure 4 presents a 2D sketch of the cloud-in-cell assignment of charge. The spatial distribution of fractional charges (e.g., alpha, beta and gamma) obtained from the DFT calculations is mapped on the coarser discretisation grid used in the 3D device simulator. A part of each fractional charge is assigned to the node according to an inverse of the volume associated with the opposite node. The obtained electron density of the POM based on the BULK flash cell is presented in Fig. 5. In this way we are able to calculate the current-voltage characteristics (I_D-V_G) and threshold voltage (V_T) of the molecular based flash memory cells for various number, spatial and redox configurations of the POMs in the oxide.

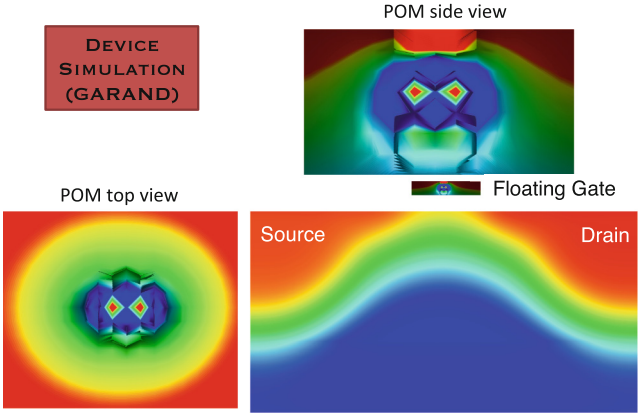


Fig. 5. Visual representation of electron density in the floating gate and in the body of the BULK cell obtained from the 3D numerical device simulator GARAND

Importantly, GARAND allows the introduction of various device architectures, such as BULK, FDSOI, FinFET and Nanowire. It also handles seamlessly intrinsic sources of statistical variability, such as random dopant fluctuation (RDF) and POMs' fluctuation (POMF). This allows us to obtain realistic and reliable evaluation for the POM flash technology. The 3D numerical simulations of the flash cell, performed with GARAND, deploy the drift-diffusion transport formalism and include density-gradient quantum corrections essential for the accurate modeling of the decananometer devices and for the resolution of the discrete localised charges.

4 Flash Cell Performance

In this section we present results of the analysis of the number of the charges in the FG for the BULK POM based flash cell. All transistors have 9 molecules in the FG and they are arranged in a 3×3 grid in the FG as illustrated in Fig. 6. Also, all devices have continuous doping and they are characterised by the absence of any sources of statistical variability. The main focus is on the programming window ΔV_T and the current-voltage (I_D-V_G) characteristics.

In order to investigate the device performance we assume that each POM molecule has three easily accessible redox states. These are the parent (n = 4), 1x reduced (n = 5) and 2x reduced (n = 6) states. Each of these states corresponds to one bit of stored information. The parent flash cell has 0 total charge in the floating gate because the nine POMs charge is neutralised (even though they are negatively charged) by the positively charged cations which are represented by the point charges in our simulations Fig. 4. In the case of the 1x reduced NVM cell the total amount of charges in the FG is −9q (q a unit charge of electron). This corresponds to one extra electron per POM in comparison to the parent configuration. Correspondingly, the 2x reduced transistors have −18q charges in comparison to the parent structure and −9q charges in comparison to the 1x reduced NVM cell. By embedding the charge distributions obtained from

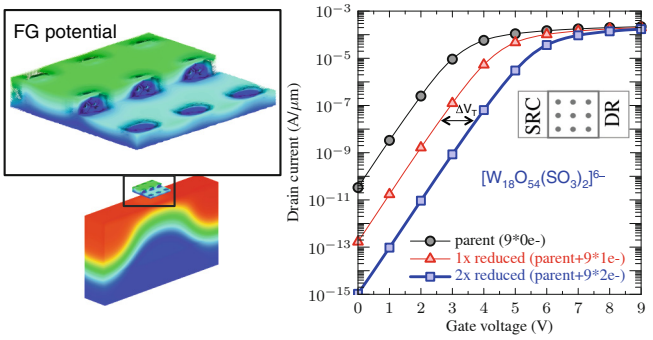


Fig. 6. 3D representation of electron density of the BULK transistor and 3D depiction of the floating gate potential where POMs are arranged in a symmetrical 3×3 grid

the DFT for each POM in the corresponding redox state, two different bits are encoded when considering two distinct V_T shifts of the flash cell.

Several important observations can be made from the data presented in Fig. 6. Firstly, with increasing of the oxidation state the voltage threshold shifts to higher gate voltages. This is due to the fact that the charge inside of the floating gate increases. As a result, the influence of the floating gate on the current flow is less pronounced and requires a higher gate voltage in order to turn the transistor ON. Secondly, the ON-current ($V_G = 0.9V$) is almost constant for all devices. On a contrary to the ON-current, the OFF-current ($V_G = 0.0V$) shows significant decrease with increasing of the redox state of the molecule. Lastly, the subthreshold slope for all devices is identical, which shows the same level of degradation.

5 Conclusions

In this paper we have presented comprehensive hierarchal and numerical simulations of evaluating the performance of the molecular based flash cells. Our results have shown the device performance in terms of the programming window and current-voltage characteristics. We have also demonstrated that our computational framework provides not only qualitative but also quantitative guidelines for design and optimisation of the molecular based flash cells. Overall, the results of our analysis highlight the important considerations relevant to the molecular based flash cell technology.

References

Kim, Y.S., et al.: New scale limitations of the floating gate cells in NAND flash memories. In: IEEE International Reliability Physics Symposium (RPS), pp. 599–603 (2010)

Park, M., et al.: Direct field effect of neighboring cell transistor on cell-to-cell interference of NAND Flash cell arrays. IEEE Electron Device Lett. **30**(2), 174–177 (2009)

Amoroso, S.M., et al.: Impact of statistical variability and 3D electrostatics on post-cycling anomalous charge loss in nanoscale flash memories. In: IEEE International Reliability Physics Symposium (RPS) pp. 3.B.4.1–3.B.4.6 (2013)

Lu, C.Y.: Future prospects of NAND flash memory technology the evolution from floating gate to charge trapping to 3D Stacking. J. Nanosci. Nanotechnol. **12**(10), 7604–7618 (2012)

Ma, C.H., et al.: Novel random telegraph signal method to study program/erase charge lateral spread and retention loss in a SONOS flash memory. IEEE Trans. Electron Devices (TED) **58**(3), 623–630 (2011)

Amoroso, S.M., Maconi, A., Mauri, A., Campagnoli, C.M.: 3D Monte Carlo simulation of the programming dynamics and their statistical variability in nanoscale charge-trap memories. IEDM Tech Digest, pp. 22.6.1–22.6.4 (2010)

Compagnoni, C.M., Ielmini, D., Spinelli, A.S., Lacaita, A.L.: Optimization of threshold voltage window under tunneling program/erase in nanocrystal memories. Trans. Electron Devices (TED) **52**(11), 2473–2479 (2005)

Shaw, J., Hou, T.H., Raza, H., Kan, E.C.: Statistical metrology of metal nanocrystal memories with 3-D finite-element analysis. Trans. Electron Devices (TED) **56**(8), 1729–1736 (2009)

Dimitrakis, P., et al.: Quantum dots for memory applications. Phys. Status Solidi A **210**(8), 1490–1504 (2013)

Pro, T., Buckley, J., Huang, K., Calborean, A., Gely, M., Delapierre, G.: Investigation of hybrid molecular/silicon memories with redox-active molecules acting as storage media. IEEE Trans. Nanatechnol. **8**(2), 204–213 (2009)

Musumeci, C., Rosnes, M., Giannazzo, F., Symes, M., Cronin, L., Pignataro, B.: Smart high-k nanodielectrics using solid supported polyoxometalate-rich nanostructures. Nano **5**(12), 9992–9999 (2011)

Zhu, H., et al.: Non-volatile memories with self-assemble ferrocene charge trapping layer. App. Phys. Lett. **103**, 053102 (2013)

Paydavosi, S., et al.: High-density charge storage on molecular thin films - candidate materials for high storage capacity memory cells. IEEE IEDM, vol. 11-543, pp. 24-4-1 (2011)

Fay, N., et al.: Structural, electrochemical, and spectroscopic charac-terization of a redox pair of sulfite-based polyoxotungstates: α-$[W_{18}O_{54}(SO_3)_2]^{4-}$ and $\alpha[W_{18}O_{54}(SO_3)_2]^{5-}$. Inorg. Chem. **46**, 3502 (2007)

Shaw, J., et al.: Integration of self-assembled redox molecules in flash memories. IEEE Trans. Electron Devices **58**(3), 826 (2011)

Vilá-Nadal, L., et al.: Towards polyoxometalate-cluster-based nano-electronics. Chem. Eur. J. **19**(49), 16502–16511 (2013)

Georgiev, V.P., et al.: Optimisation and evaluation of variability in the programming window of a flash cell with molecular metal-oxide storage. IEEE Trans. Electron Devices (2014, in press). doi:10.1109/TED.2014.2315520

GARAND. http://www.GoldStandardSimulations.com

MARKED PROOF

Please correct and return this set

Please use the proof correction marks shown below for all alterations and corrections. If you wish to return your proof by fax you should ensure that all amendments are written clearly in dark ink and are made well within the page margins.

Instruction to printer	*Textual mark*	*Marginal mark*
Leave unchanged	··· under matter to remain	
Insert in text the matter indicated in the margin		New matter followed by or
Delete	through single character, rule or underline or through all characters to be deleted	or
Substitute character or substitute part of one or more word(s)	through letter or through characters	new character or new characters
Change to italics	under matter to be changed	
Change to capitals	under matter to be changed	
Change to small capitals	under matter to be changed	
Change to bold type	under matter to be changed	
Change to bold italic	under matter to be changed	
Change to lower case	Encircle matter to be changed	
Change italic to upright type	(As above)	
Change bold to non-bold type	(As above)	
Insert 'superior' character	through character or where required	or under character e.g. or
Insert 'inferior' character	(As above)	over character e.g.
Insert full stop	(As above)	
Insert comma	(As above)	
Insert single quotation marks	(As above)	or and/or or
Insert double quotation marks	(As above)	or and/or or
Insert hyphen	(As above)	
Start new paragraph		
No new paragraph		
Transpose		
Close up	linking characters	
Insert or substitute space between characters or words	through character or where required	
Reduce space between characters or words	between characters or words affected	