



# Effects of control oxide material on the charging times of metal nanoparticles inside non-volatile memories: A 3-dimensional WKB calculation



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## ABSTRACT

We have investigated the influence of different control oxide materials on the charging times of metal nanoparticles (mNP) inside a [Si/SiO<sub>2</sub>/(mNP)/Control-Oxide/gate] non-volatile memory (NVM) in which the control oxide can have a higher dielectric constant  $\epsilon$  than that of SiO<sub>2</sub> like HfO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> as is the case in practice frequently. Our calculations are performed for both N-type and P-type substrates. We have used a previously published 3-dimensional Wentzel–Kramers–Brillouin (WKB) method of ours, which does not contain such adjustable parameters as effective area or capture cross-section which other 1-dimensional theories use. To obtain the total time for the charging of the NVM to saturation we calculate the times that successive electrons take to be incorporated into an mNP under a given applied voltage and a given duration of the charging pulse, each time updating the tunneling potential due to the incorporation of the extra electron into the mNP. We obtain an exponential dependence of these charging times on the dielectric constant of the control oxide for which we offer a simple explanation. The change with substrate type is on the other hand less pronounced. Our results are confirmed by experiment. In particular, when our method is applied to NVMs with SiO<sub>2</sub> and HfO<sub>2</sub> as the control oxide we obtain good agreement with experiment without using such adjustable parameter as effective area of emission. We finally show that if the fraction of the substrate area that is covered with mNP is used to estimate this parameter the error involved will be quite significant, i.e. a factor of 5 approximately.

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## 1. Introduction

In a previous paper [1] we proposed a method for calculating the charging times of metal nanoparticles (mNPs) embedded in a dielectric matrix together with the total number of electrons that these nanoparticle can accommodate according to the limitations of the coulomb blockade theory [2]. Our method differs from previous methods in that there are no adjustable parameters which are usually in the form of an effective area. This was accomplished by using a 3-dimensional tunneling theory which could calculate quantum mechanically the electron paths from the doped Si substrate to the metal surface. As a result we could calculate the exact current surface density  $J$  impinging on the metal nanoparticle and hence the total current  $I$ . In [1] we applied our method to the Si/SiO<sub>2</sub>/mNPs/SiO<sub>2</sub> system on an N-type Si substrate. However most Si based NVMs use P-type substrates [3,4] and furthermore other NVM units have been proposed – see Fig. 1 – which use as control oxide HfO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> [4,5]. These high dielectric constant oxides can induce substantial changes to the behavior of the NVM cells: a) because of their higher capacitance (compared to SiO<sub>2</sub>) they

can accommodate a higher number of electrons per mNP and most importantly b) they allow a higher percentage of the applied voltage  $V_C$  to be dropped along the tunneling oxide. Hence the charging time is heavily reduced. Furthermore the above factors depend exponentially on the tunneling oxide thickness. The study of these phenomena is the subject of this paper. Furthermore an extensive and critical comparison with available experimental data is made.

As in our previous publication there are no adjustable parameters in our calculations. The only numerical inputs to our calculation are a) the band-edge offsets between the oxides and Si and b) the Schottky barrier between the mNP and the oxides. These are well known (and at any rate they are not varied during our calculations).

## 2. Method

Our method has been presented in a previous publication [1], so we only give a brief description here emphasizing physical ideas and the basic differences from previous treatments. The first step is to calculate the potential energy inside the semiconductor and dielectrics self-consistently. This is done by solving the Poisson equation:

$$\nabla^2 V = \frac{-\rho}{\epsilon_r \epsilon} \quad (1)$$

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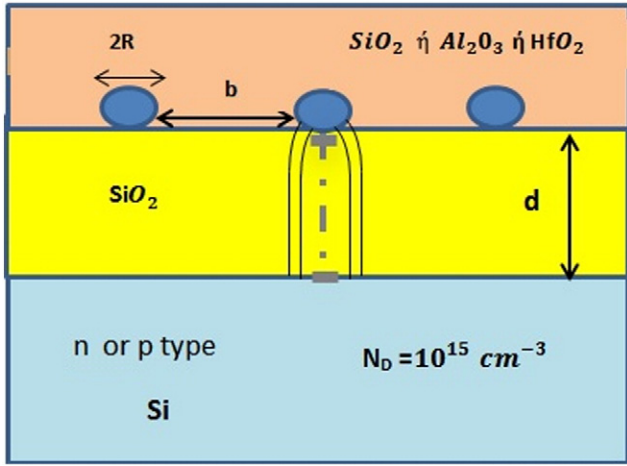


Fig. 1. Schematic of the unit cell under study showing lengths, types of materials and charging process.

together with the usual semiconductor expression for the electron density:

$$\begin{aligned} n &= N_C F_{1/2} \left( \frac{E_F - E_C}{kT} \right) \\ p &= N_V F_{1/2} \left( \frac{E_V - E_F}{kT} \right) \\ \rho &= e(p - n + N_D^+ - N_A^-). \end{aligned} \quad (2)$$

In the above equations the symbols have their conventional meaning and  $E_F$  is the quasifermi level of the electrons  $E_{Fn}$  for N-type substrates or the quasifermi level  $E_{Fp}$  of the holes for P-type substrates.

The Poisson equation is solved in a unit cell using periodic boundary conditions [1]. This ansatz neglects variations from one cell to another (in the spacing and radius of the mNPs) but it is the best that can be done under the circumstances. The band diagram is obtained directly from the Poisson solution by simply adding the appropriate discontinuities at each interface, i.e. either the band edge offsets or the corresponding Schottky barriers. Once the Poisson potential is known the quantum mechanical (i.e. most probable) path of each electron on its way from Si to the mNP through the dielectric barrier (see Fig. 1) can be calculated using a 3-dimensional WKB method developed by Peierls and Kapur [6] and later by Das and Mahanty [7]. Then the transmission coefficient along a path (say C) is given by the path integral relations

$$\begin{aligned} T &= \left[ \frac{|\nabla V|_{r=r_2}}{|\nabla V|_{r=r_1}} \right]^{1/2} \exp(-T_{12}) \\ T_{12} &= \frac{2}{\hbar} \int_{r_1}^{r_2} \sqrt{2m[V(r) - E]} dr. \end{aligned} \quad (3)$$

The path, say C, (not a straight line), starts at point  $r_1$  in Si and ends at  $r_2$  on the metal surface. Given  $T(C)$  the current density  $J$  along this path can be calculated using the Landauer formula [8]. The usefulness of the above procedure is that the current density  $J(r)$  impinging on the metal surface can be evaluated. Then the total current can be computed by a simple arithmetic surface integral without the need of parameters such as “effective area”, “capture cross section” and so on. Then the extra time to put the  $n$ th electron in the mNP is  $\Delta t_n = e/J_n$ . Note that we write  $\Delta t_n$  because the time to put the  $n$ th electron in the mNP – when  $(n-1)$  electrons are already in – is different at each  $n$ th stage and so is  $J_n$ . At every stage of charging we recalculate the potential self-consistently. Electrons here tunnel one by one. The process of charging is stopped when the electric field reverses direction. Then tunneling in the opposite direction would result. This is the general

condition of the Coulomb blockade theory from which the usual simplified formula for the allowed number of electrons  $N_{\max}$  in an mNP:

$$C_{CO} V_G > e(N_{\max} - 1/2) \quad (4)$$

(where  $C_{CO}$  = control oxide capacitance) is derived. However this simplified formula Eq. (4), assumes metal electrodes while in our case we have an N-doped or P-doped Si substrates (with a potential drop inside it), so Eq. (4) cannot be used and the more general electric field reversal (or energy lowering) condition is used.

### 3. Results

Our calculated band-diagrams along a vertical direction passing through the center of a sphere for  $d = 3.5$  nm and  $V_G = 5$  V when 3 electrons reside in the mNP are shown in Fig. 2a and b for a  $\text{SiO}_2/\text{mNP}/\text{SiO}_2$  unit with N- and P-type substrates respectively and in Fig. 2c and d for a  $\text{SiO}_2/\text{mNP}/\text{HfO}_2$  unit likewise. Note that because our calculated potential varies in 3 dimensions the band diagram will differ from vertical line to vertical line from the substrate to the gate. For the relative dielectric constants of  $\text{SiO}_2$  and  $\text{HfO}_2$  we have taken the values 3.9 and 25 respectively. The Schottky barriers of the oxides to the mNP have been taken to be equal to their “perfect crystal” values of half the band gap, i.e. 4.45 eV for the  $\text{SiO}_2/\text{mNP}$  interface and 2.65 eV for the  $\text{HfO}_2/\text{mNP}$  interface respectively.

It is important at this stage to analyze the differences observed in Fig. 2a–d as these will form the basis for the explanation for the rest of results on charging times to follow. The main difference lies in the higher electric field in the tunneling region and consequently the lowering of the tunneling barrier when  $\text{HfO}_2$  is substituted for  $\text{SiO}_2$  as the control oxide of the NVM. This is due entirely to the high  $\epsilon$  of  $\text{HfO}_2$  which allows a higher portion of the applied voltage to be dropped along the tunneling oxide of the NVM. (Note that the barrier is given by the area under the potential curve according to the WKB Eq. (3) above.) By contrast the type of the substrate has a lower effect on the barrier shape although it should be noticeable that an N-type substrate facilitates tunneling to the mNPs compared to a P-type substrate and this difference is more pronounced in the  $\text{HfO}_2$  containing NVM. Note also that in our calculation of the transmission coefficient (Eq. (3)) we have included the necessary image corrections to the potential  $V(x,y,z)$ . Given now the latter we can calculate the electron paths using the 3D-WKB approximation and then the corresponding transmission coefficient  $T$  for each path and finally the current. Such typical paths may be found in our previous publication [1].

Fig. 3 gives the time  $t_N (= \sum \Delta t_n)$  it takes to charge each mNP successively with  $N$  electrons at constant applied voltage  $V_G = 8$  V when the control oxide of the NVM unit is  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{HfO}_2$ . For the relative dielectric constant of  $\text{Al}_2\text{O}_3$  we have taken the value 9.0. The nanoparticle radius  $R$  and spacing  $b$  between nanoparticles have been chosen to be the same as in the experimental investigation of Lee et al. [10] for a  $\text{Si}/\text{SiO}_2/\text{mNP}/\text{SiO}_2$  NVM. The calculations in this figure for the other types of control oxide NVMS are intentionally performed with the same  $R$  and  $b$  of experimental devices with  $\text{HfO}_2$  as control oxide follow below. Since geometrical values are the same, the variations in this figure come exclusively from the fact that as the  $\epsilon$  of the control oxide increases a higher proportion of  $V_G$  drops along the tunneling region in accordance with the results of Fig. 2. It can be seen that the charging times vary by 4 orders of magnitude. In particular they may vary from 1 msec to several seconds. Furthermore each mNP of the  $\text{HfO}_2$  cell can accommodate several electrons, not just 1 or 2. This is a result of its high dielectric constant and the Coulomb blockade condition (as noted above, approximately  $C_{CO} V_G > e(N_{\max} - 1/2)$ ) but this maximum is rarely attained in experiments. We note again that in our calculations the maximum is obtained by the more general condition of electric field reversal which simplifies to the above condition when the tunneling

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