## A Calculation with No Fitting Parameters of the Charging Time of Metal Nanoparticles Inside Non-Volatile Memories: Effects of Voltage Pulse Duration.

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Metal nanoparticles (mNP) inside a dielectric matrix are found in non-volatile memory cells, (see figure 1). Charging the mNPs constitutes an act of programming and the time of charging is the programming time. There have been works [1] that calculate this time but because of the use of 1-dimensional (1-D) WKB expressions for the tunneling current they introduce parameters such as effective area or capture cross section, the values of which are found by comparison to experiment. In this work we use a 3-D WKB approximation [2] to calculate the tunneling current which together with a 3-dimensional solution of the Poisson equation allows us to calculate the charging times of the mNP without the use of fitting parameters. It is also worth pointing out that the existence of metal –as opposed to semiconducting NP- necessitates a 3-D treatment because of the additional reason that electric field lines terminate normally on metal nanospheres, thus bending highly inside the tunneling oxide. The agreement we obtain with the measured experimental times -without any fitting parameters- is more than satisfactory.

The key point of the 3-D tunneling method we use [2] is that the transmission coefficient is not a property of an emitting surface but of an electron path through a tunneling region from, say, point  $\mathbf{r}_1$  to point  $\mathbf{r}_2$ . The electron path from  $\mathbf{r}_1$  to  $\mathbf{r}_2$  need not necessarily be a straight line. Then an electron tunneling from  $\mathbf{r}_1$  to  $\mathbf{r}_2$  with normal (to the barrier) energy  $E_n$  has a transmission coefficient  $T(E_n)$ :

$$T = \exp\left(-\frac{2}{\hbar}\int_{r_1}^{r_2}\sqrt{2m[V(r) - E_n]}dr\right)$$

where the path from  $\mathbf{r}_1$  to  $\mathbf{r}_2$  needs to be evaluated by quantum mechanics. Then the current density at the end point  $\mathbf{r}_2$  is:

$$J(r_2) = \frac{emkT}{2\pi^2\hbar^3} \int_{E_c}^{\infty} T_{r_2}(E_n) \log\left(1 + \exp\left(\frac{E_F - E_n}{kT}\right)\right) dE_n$$

where V(r) is the potential energy in the tunneling region (solution of the Poisson equation plus image correction term),  $E_F$  is the Fermi level at the semiconductor and the rest of the symbols have their conventional meaning. The total current impinging on the metal NP surface can be evaluated by a surface integral of J over the mNP surface without asking the question how much of the emitted current falls onto the mNP. The total time to charge the mNP with N electrons is the sum of the times  $\Delta t_n=I_n/e$  where  $\Delta t_n$  is the time to put the nth electron in the mNP when n-1 electrons are already in. At each stage of this procedure (from n to n+1) the 3-D Poisson equation is solved again together with the above equations and a new potential and set of transmission coefficients are calculated. The procedure stops when the maximum number of electrons allowed by the Coulomb blockade condition is reached. Our method has been applied to NVMs of the form Si/SiO<sub>2</sub>/mNP/control oxide/gate where the control oxide is SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> or HfO<sub>2</sub>.

The method is exemplified in figure 2 where we show our calculated paths together with the corresponding transmission coefficient for an NVM with  $SiO_2$  as control oxide and d=3.5nm. It can be seen that as one moves away from the normal below the centre of the sphere the transmission coefficient

decays rapidly and so will the current density do. Then the surface integral for the current converges. In figure 3 we show our calculated times to put n electrons in the mNP at constant gate voltage  $V_G = 6V$  for different types of control oxide. Again d=3.5nm. We observe that the change of control oxide may make a difference of 4 orders of magnitude in the charging time. This is due to the fact that as the dielectric constant of the control oxide increases a higher percentage of  $V_G$  drops along the tunneling oxide, thus facilitating tunneling. The effect of the gate voltage itself is shown in figure 4 where we show the time to charge the mNP with 1 electron as a function of  $V_G$ . For the HfO<sub>2</sub> (highest dielectric constant) the gate voltage can make a difference of 2 orders. From our results we obtain for the HfO<sub>2</sub> NVM that for an applied  $V_G = 6V$  for 2seconds, the number of electrons is 7. The experimental value in [3] is 7.5 seconds.



Fig. 1: Schematic of the unit cell under study showing lengths and types of materials.



Fig. 3: Time to charge the mNP with n electrons in NVM unit cells with different types of control oxides. All calculations are at constant gate voltage  $V_G$  of 6V and constant d=3.5nm



Fig. 2. Electron paths from the substrate to one of the spheres during the charging period together with the corresponding T's



Fig. 4: Time to charge each mNP with one electron as a function of gate voltage for different type of control oxide NVM. The  $SiO_2$  tunneling oxide thickness is again constant at d=3.5nm.

## References

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