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Charge retention in quantized energy levels of nanocrystals

Aykutlu Dâna[a,*], İmran Akça[a], Orçun Ergun[a], Atilla Aydınlı[a], Raşit Turan[b], Terje G. Finstad[c]

[a]Department of Physics, Bilkent University, 06800 Ankara, Turkey
[b]Department of Physics, Middle East Technical University, 06800 Ankara, Turkey
[c]Department of Physics, University of Oslo, P.O. Box 1048, Blindern, 0316 Oslo, Norway

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Abstract

Understanding charging mechanisms and charge retention dynamics of nanocrystal (NC) memory devices is important in optimization of device design. Capacitance spectroscopy on PECVD grown germanium NCs embedded in a silicon oxide matrix was performed. Dynamic measurements of discharge dynamics are carried out. Charge decay is modelled by assuming storage of carriers in the ground states of NCs and that the decay is dominated by direct tunnelling. Discharge rates are calculated using the theoretical model for different NC sizes and densities and are compared with experimental data. Experimental results agree well with the proposed model and suggest that charge is indeed stored in the quantized energy levels of the NCs.
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1. Introduction

The observation of formation of nanocrystals (NCs) by annealing of silicon dioxide films having excess Si or Ge has attracted attention due to optical and electronic properties of such nanostructures [1–4]. In particular, Ge NCs embedded in amorphous silicon oxide (a-SiO) films have been subject of study, because of low temperature of formation, compatibility with standard integrated circuit fabrication processes and for their potential applications in optoelectronic and memory devices. The NCs are candidates as storage media for electron storage cells in flash memory devices [5,6]. Since many parameters of NCs such as density, size and composition can be adjusted by proper choice of fabrication parameters, they offer flexibility in design of NC flash memory cells. However, a better understanding of charge storage mechanism is important in optimization of device performance. Recent studies have proposed a model describing the storage of carriers in NC-MOS devices assuming storage in deep-traps [7–9] associated with NCs and trap energy level engineering was investigated to improve device performance.

In this paper, we investigate an alternative mechanism for carrier storage by assuming carrier storage in NC energy levels instead of deep traps. Based on this assumption, we present a theoretical model that includes the effect of NC dimensions and density to calculate the discharge dynamics. Germanium NC-MOS capacitors have been fabricated and characterized using capacitance measurements. Results are compared with theory, showing agreement on size and density-related discharge properties.

2. Theoretical modelling

A typical NC memory element cross section is shown in Fig. 1. Based on the assumption that only NCs are responsible for charge storage, the flat-band voltage shift ΔV_{FB} is approximately given by [10]

$$\Delta V_{FB} = \frac{q_{nc}}{\varepsilon_{ox}}\left(t_{cox} + \frac{\varepsilon_{ox} t_{nc}}{2\varepsilon_{Ge}}\right), \quad (1)$$

*Corresponding author. Tel.: +90 312 2903201; fax: +90 312 2664579.
E-mail address: aykutlu@fen.bilkent.edu.tr (A. Dâna).

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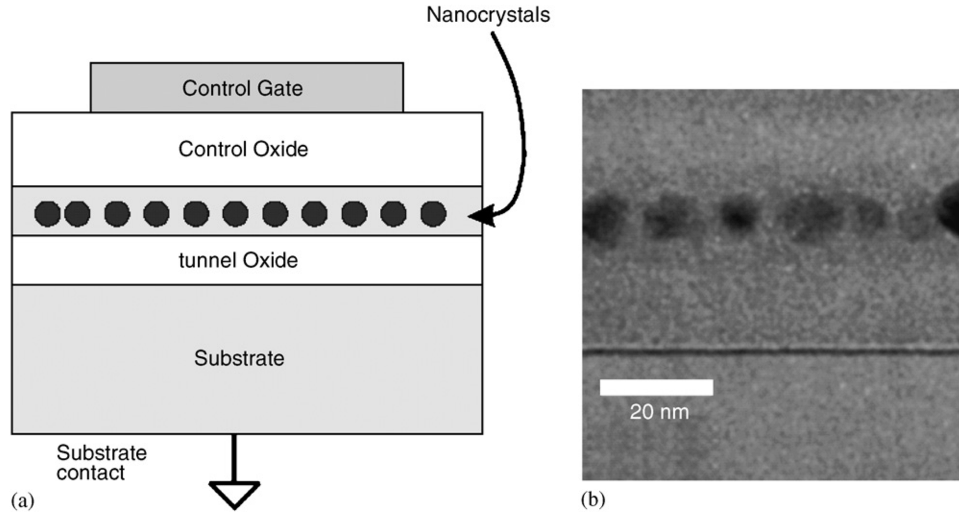

Fig. 1. (a) Schematic cross-section of a NC-MOS capacitor, and (b) example TEM micrograph of a calibration sample showing germanium nanocrystal band with 7.4 nm average diameter NCs.

where q_{nc} is the total stored charge in the NCs, t_{cox} is the control oxide thickness, t_{nc} is thickness of the layer containing the NCs, ε's are the effective dielectric constants of respective materials. An important parameter of the NC-MOS device is the maximum flat-band voltage shift ΔV_{max}. This is the flat-band voltage shift when all available NCs of density N_{nc} carry an electron i.e. $q_{nc} = qN_{nc}$. It is seen that ΔV_{max} depends on device geometry through Eq. (1) and also on NC density. Due to large Coulomb charging energy, average number of electrons per NC can be assumed to be smaller than one.

In order to evaluate retention properties of NC-MOS memory elements, discharging currents must be calculated. Since there are many device parameters that collectively determine the charge–discharge currents, a simple closed-form formula cannot be obtained that covers all cases. Therefore, retention and erase currents are addressed separately.

During retention, the device is in depletion and $V_{gate} = 0$. If NC bound states are responsible for storage of carriers, discharge occurs by tunnelling from the NC ground state to the substrate, either by direct or trap-assisted tunnelling. For the calculation of the discharge current, the barrier height of tunnelling carriers must be calculated. The barrier height is a function of the NC ground state energy given by $V_B(E) = V_{B0} - E_{nc}$, where V_{B0} is the bulk barrier height and E_{nc} is the energy of electron stored in the NC. The energy levels of uncapped germanium NCs have recently been measured directly as a function of size, using scanning tunnelling spectroscopy [11]. The conduction band minimum of Ge NCs as a function of size is given by

$$E_{CBM}(d_{nc}) = E_{CBM}(\infty) + \frac{11.86}{d_{nc}^2 + 1.51d_{nc} + 3.394}, \qquad (2)$$

where the energies are in eV, d_{nc} is the NC diameter in nm and $E_{CBM}(\infty)$ is the conduction band minimum for bulk germanium. If we assume a Gaussian size distribution for the NCs, the density of states, $D_{nc}(E)$, can then be calculated through Eq. (2) for electrons as plotted in Fig. 2.

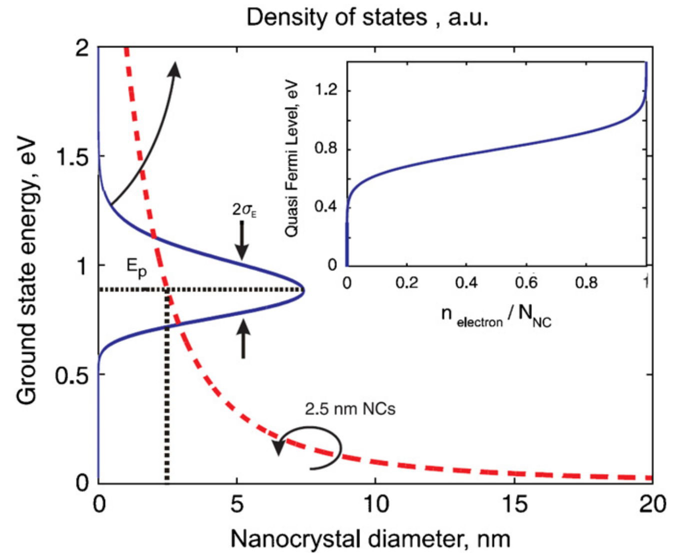

Fig. 2. Schematic description of density of states (solid curve) for the ground states of NCs with average diameter of 2.5 nm. Dotted curve shows electron ground state of NCs as a function of size as described by Eq. (2). Inset shows the quasi-Fermi level as a function of number of electrons per NC.

Assuming thermal equilibrium within the NC layer, the quasi-Fermi level can be calculated implicitly (inset of Fig. 2) for a given total stored charge. Escape of carriers near or above the quasi-Fermi level dominates the discharge current. As a result of reduced barrier height at the quasi-Fermi level for a large number of carriers per NC, discharge current increases with the number of stored carriers (or the flat-band voltage shift). This reduction in barrier height, along with the increase in the tunnel oxide field, results in the super-exponential charge decay

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