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# Simulation of ion-irradiation stimulated Ge nanocluster formation in gate oxides containing GeO<sub>2</sub>

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## Abstract

Process simulations were performed for a novel fabrication technique of Ge nanoclusters (NCs) located in the thin gate oxide of a MOS field effect transistor, which will be applied in non-volatile random access memories (nvRAMs). The simulations start from a thin GeO<sub>2</sub> layer buried in the gate oxide, which might be produced by heteroepitaxy of a thin Ge layer in (001)Si followed by a special oxidation of Si and Ge avoiding Ge segregation. The present process simulations predict that the recently reported transformation of such a GeO<sub>2</sub> layer into Ge NCs by thermal annealing can be accelerated by ion irradiation. It is even more important that under ion irradiation the chemical reduction of GeO<sub>2</sub> should be achieved at lower process temperature. The limiting mechanism of the transformation of GeO<sub>2</sub> into Ge NCs during thermal annealing is shown to be thermally activated detachment of Si monomers from the Si/SiO<sub>2</sub> interface into SiO<sub>2</sub>. Thus, ion beam mixing of Si into SiO<sub>2</sub> stimulates the Ge NC formation. The process simulations were performed by a specifically adapted and extended multicomponent kinetic Monte Carlo code. © 2002 Published by Elsevier Science B.V.

*Keywords:* Process simulation; Nanocluster; Ion beam mixing; Gate oxide

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## 1. Introduction

A great effort is currently devoted to the fabrication of NC-based non-volatile random access memories (NC-nvRAMs), which can retain information without power source (Fig. 1). Tailoring of size and size distribution of NCs embedded in the gate oxide, required for proper operation, is a challenge for materials research. The two processes being favored at present are the self-organization of NC  $\delta$ -layers after ion implantation [1] and the

deposition of Si aerosols [2]. However, due to the broad size distribution of NCs fabricated by these methods their size dependent characteristics can be obscured. For this reason we suggest an alternative process taking advantage of the growth of a few atom layer thick Ge “wetting” layer during Ge heteroepitaxy on Si(001) [3,4] in combination with a special Si oxidation and chemical reduction of GeO<sub>2</sub> [5,6] during thermal treatment. The idea is to use this oxidized Ge “wetting” layer as the basis for nucleation of Ge NCs embedded in the gate oxide. It has been found recently [5,6] that during thermal annealing Ge oxide will be reduced by elemental Si, detached from Si/SiO<sub>2</sub> interface and provide chemical reaction  $\text{Si} + \text{GeO}_2 \rightarrow \text{Ge} +$

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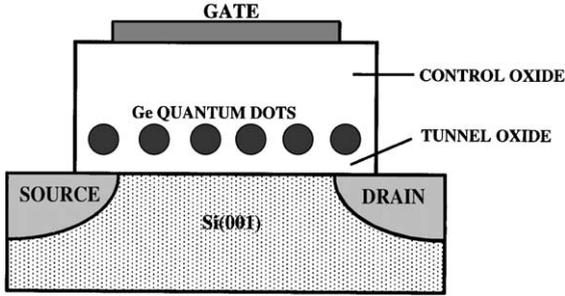


Fig. 1. The schematic structure of NC-based non-volatile memory MOS field-effect transistor.

SiO<sub>2</sub>. As Ge diffusion coefficient is lower than that of Si, the dissolved Ge produced by reduction of GeO<sub>2</sub> may precipitate not far from the initial location of GeO<sub>2</sub>, providing the precise control of the size and location of Ge NCs. The detachment of elemental Si from Si/SiO<sub>2</sub> interface is a thermally activated process and can be strongly suppressed at temperatures lower than 1200 K. Therefore it is expected that during thermal treatment the transformation of GeO<sub>2</sub> into Ge NCs will be promoted by ion irradiation. In this contribution the influence of ion irradiation on the transformation of GeO<sub>2</sub> into Ge NCs within the SiO<sub>2</sub> matrix is studied by atomistic Monte Carlo (MC) simulation. It is shown how, in comparison with pure thermal treatment, ion-irradiation induced detachment of Si monomers from interface accelerates the Ge precipitation.

## 2. Model

### 2.1. Thermodynamic evolution

The atomistic processes are governed by a sequence of randomly repeated elementary events (like bond breaking, diffusional jumps of atoms, chemical reaction, etc.). Their simulation should take into account both energetic and statistical aspects. The first is usually described by ab initio methods or molecular dynamics, while the second is related to continuum models. The bridge between these two approaches, still providing information on the atomic scale, is suitably conducted by kinetic MC calculations. This advantage is

achieved due to simplified treatment of particle interactions. The evolution of these particles is determined by their mutual interactions containing all the information of the surrounding matrix. The effective interaction is usually limited by the nearest neighbor (NN) sites. The potentials, associated with shift from regular atomic positions (like strain fields), are difficult for consistent implementation.

Here, the annealed system is considered as the chemically inert solid matrix SiO<sub>2</sub> containing the two phases GeO<sub>2</sub> and Ge. Two types of diffusing species are included—Si and Ge. For the description of non-ballistic effects, the NN Ising model is used. The positions of the impurity atoms are restricted to a face-centered cubic (fcc) lattice. The fcc lattice holds some elements of diamond-like symmetry and exhibits isotropic properties. That makes it suitable for description of bulk and surface diffusion in Si as well as precipitation in amorphous matrices like SiO<sub>2</sub>. The lattice constant of the considered nanophase determines the length scale of the model.

The bond energy  $E_{\alpha\beta}$  between two NN impurity atoms (denoted as  $\alpha$  and  $\beta$ ) defines the precipitation process. The bond strengths between Si and Ge impurities are taken from standard textbooks and follow the ratios  $E_{\text{SiSi}}:E_{\text{SiGe}}:E_{\text{GeGe}} = 1.25:1.12:1$ . After the reaction  $\text{Si} + \text{GeO}_2 \rightarrow \text{Ge} + \text{SiO}_2$  the Ge is allowed to leave from the GeO<sub>2</sub> phase into SiO<sub>2</sub> without further constraints (see Fig. 2). It is assumed that the bond energy of an impurity atom surrounded by different NN impurity atoms depends additively upon the number of bonds:

$$E_B(n_{\text{SiSi}}, n_{\text{GeGe}}, n_{\text{SiGe}}) = n_{\text{SiSi}}E_{\text{SiSi}} + n_{\text{GeGe}}E_{\text{GeGe}} + n_{\text{SiGe}}E_{\text{SiGe}}. \quad (1)$$

Each Si or Ge atom is allowed to jump from an initial site  $i$  to an empty site  $f$ . In the framework of the Metropolis algorithm [7] the transition probability  $P_{if}$  for one atom to jump is given by

$$P_{if} = \begin{cases} \tau_0^{-1} \exp(-E_A/kT), & \Delta E < 0, \\ \tau_0^{-1} \exp[-(E_A + \Delta E)/kT], & \Delta E \geq 0, \end{cases} \quad (2)$$

$$\Delta E = \sum_{\text{SiSi, GeGe, SiGe}} (n_f - n_i)E_B,$$

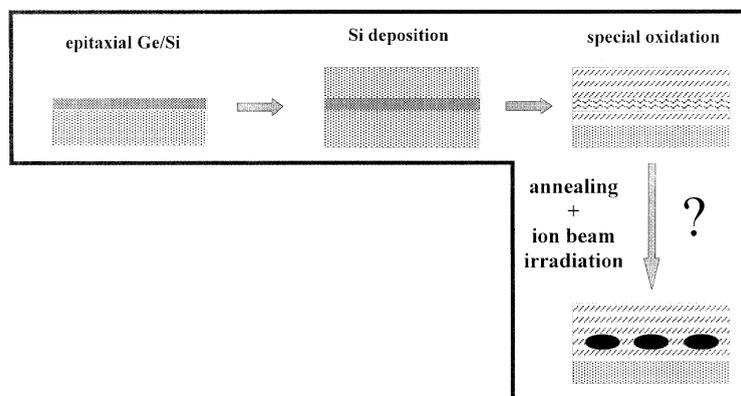


Fig. 2. The scheme of the studied process for fabrication of Ge NCs imbedded within the gate oxide. A thin Ge layer and a Si layer are deposited by MBE and then oxidized. Here it is studied how the formation of Ge NCs during annealing can be accelerated by ion irradiation.

where  $\tau_0^{-1}$  denotes the frequency of jump attempts, and  $n_{if}$  represents the number of NN bonds at the two sites (indices, pointing the bond type, are omitted).  $E_A$  is the diffusion barrier. Here  $E_A$  is assumed to be independent of the number and configuration of NNs of the jumping atom, but it is different for different kinds of impurities. During one MC step each impurity atom is stochastically checked for a jump attempt to a randomly chosen NN position. The MC step is associated with the time scale by the diffusion coefficient via Einstein's relation. In order to accelerate the calculations, the fastest process is normalized to unity, i.e.  $P_{if}$  is multiplied by  $\tau = \tau_0 \exp(E_A/kT)$ . Thus,  $\tau$  is the time interval corresponding to a single MC step. It should be pointed out that this time is temperature dependent.

The number of jump attempts per MC step was put larger for Si than that for Ge, providing the difference in their diffusion coefficients.

## 2.2. Ballistic effects

The Si monomer generation is governed either by their thermally assisted detachment from Si/SiO<sub>2</sub> interface or by ion-irradiation forced displacement. For each impact in Si matrix by a decelerating ion or an associated recoil, impurity atoms may be knocked out according to a distribution function and become particles mobile by diffusion. A promising approach to describe irradiation effect

on this process is the concept of collisional mixing (CM), i.e. the displacements of atoms [8]. The incorporation of CM into kinetic MC simulations requires some simplifying assumptions [9]:

- a displacement probability related to the nuclear energy deposition and a system-specific displacement length  $\lambda$  are assumed (which have been calculated with the TRIM program);
- the displacement distribution is isotropic and exponentially decaying, i.e.  $f(R) \propto \exp(-R/\lambda)$ ;
- all continuously computed displacements are projected onto the nearest lattice sites;
- impurity atoms are stochastically chosen for displacement attempts.

In the simulation process each Si or Ge atom has a probability  $P_{DP} = w_0 \exp(-R/\lambda)$  to be displaced by a distance  $R$  during one MC step. The parameters  $w_0$  and  $\lambda$  respond for the CM process.

## 2.3. Chemical reduction of GeO<sub>2</sub> by Si monomers

The generation of elemental Ge in SiO<sub>2</sub> is mainly provided by the chemical replacement reaction



where a potential reductant Si is produced by the detachment from Si/SiO<sub>2</sub> interface and the diffusion into SiO<sub>2</sub>.

According to our model, if an Si atom attempts to jump to or is displaced onto a site occupied by  $\text{GeO}_2$ , chemical reaction (3) takes place, which adds  $\text{SiO}_2$  to the inert matrix and releases mobile, elemental Ge.

The estimation of change in the Gibbs energy [6] shows that the spontaneous chemical reaction (3) is provided in temperature range 600–1100 K.

#### 2.4. The cell and boundary conditions

For our kinetic 3D MC simulation we use as the initial structure a cell of  $64 \times 64 \times 128$  lattice sites with a 12 monolayer thick Si layer at the bottom, followed by 18 monolayers  $\text{SiO}_2$  and three monolayers  $\text{GeO}_2$ . Finally, this sequence of layers is covered by a thick  $\text{SiO}_2$  layer, the so-

called control oxide of Fig. 1. Periodical boundary conditions were used in the interface plane. At the top we used reflecting boundary condition, at the bottom—fixed ones. Thus the simulation for an infinite layer, rather than for a cell, was performed.

### 3. Results and discussion

Examples of thermally (a) and ion-irradiation (b) assisted transformation of a  $\text{GeO}_2$  layer into a Ge NC layer are presented in Fig. 3. Si atoms are plotted in grey, Ge monomers in light grey, strongly bonded Ge in black. The  $\text{GeO}_2$  layer is presented as semitransparent. The process of NC formation proceeds via Si monomer detachment, its diffusion, chemical reaction with  $\text{GeO}_2$ , then Ge

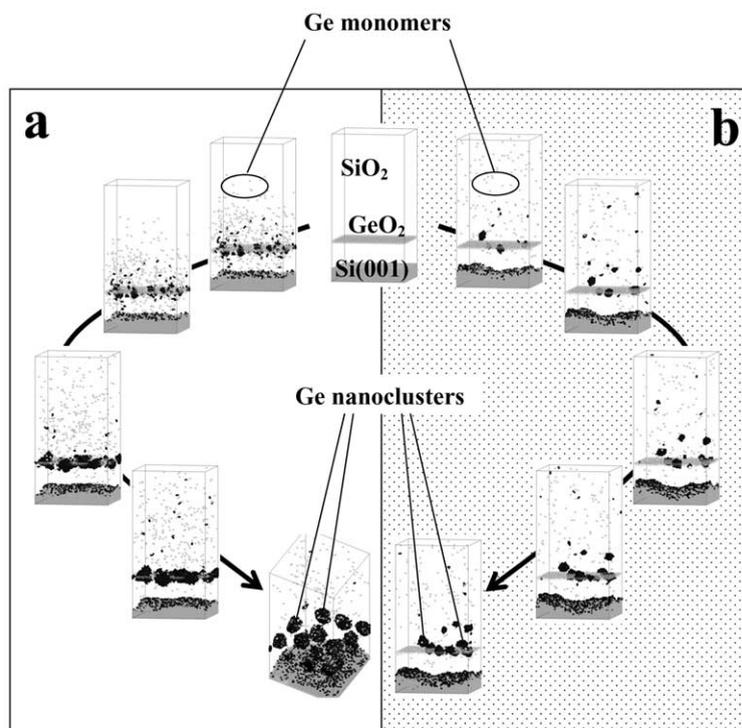


Fig. 3. The sequence of images obtained by an atomistic Monte Carlo simulation. (a) Thermally assisted formation of Ge NCs within gate oxide ( $E_{\text{SiSi}}/kT = 1.7$ ,  $D_{\text{Si}}/D_{\text{Ge}} = 1000$ ,  $w_0 = 0$ ). The full number of MC steps is  $1.5 \times 10^7$ . (b) Ion irradiation assisted formation of Ge NCs within gate oxide ( $E_{\text{SiSi}}/kT = 3.0$ ,  $D_{\text{Si}}/D_{\text{Ge}} = 1000$ ,  $w_0 = 0.01$ ,  $\lambda = 3$ ). The full number of MC steps is  $7.5 \times 10^7$ . Note that duration of MC time step is temperature dependent due to elimination of the migration barrier  $E_A$ .

monomer diffusion and Ge cluster nucleation and growth. In the case without ion irradiation, Si detachment requires rather high temperatures. It may be roughly estimated that  $E_{\text{SiSi}}/kT = 1.7$  corresponds to a temperature of about 2000 K. At lower temperatures the Ge NC formation will be limited by Si monomer detachment from the Si/SiO<sub>2</sub> interface. However, Maeda [6] found the effect of the Si/SiO<sub>2</sub> interface fed chemical reduction of GeO<sub>2</sub> at a temperature as low as 800 °C. In this experiment, the mixed Si and Ge oxide layer on Si(001) was prepared by high-frequency magnetron sputtering followed by thermal annealing. One reason for the high rate of Si detachment at such a low temperature as found in this experiment without ion irradiation could be a small amount of hydrogen dissolved in SiO<sub>2</sub>, which weakens the bond strength of Si and results in a kind of internal hydrogen etching at the Si/SiO<sub>2</sub> interface. It is known, e.g., that after ion implantation SiO<sub>2</sub> soaks in moisture, and that hydrogen resulting from this moisture increases solubility of Ge in SiO<sub>2</sub> [10].

In Fig. 3(b) the sequence of images presenting the simulated formation of NCs within SiO<sub>2</sub> under ion irradiation at low temperature is shown. The Ge NCs are distributed near the GeO<sub>2</sub> layer. It demonstrates the possibility of NC low-temperature synthesis due to detachment of Si monomers, which is now much less limited than by thermodynamics. The process takes a larger number of MC steps than that in the case of high temperature, where no irradiation was used (Fig. 3(a)). However, without ion irradiation, no NC is produced at those lower temperatures.

In both Fig. 3(a) and (b) the effect of Si/SiO<sub>2</sub> interface roughening is pronounced. This is due to the action of Ge, which tends to be located at protuberances rather than at cavities of the interface, thus making it non-stable.

In Fig. 4 the predicted conditions of low-temperature NC formation are presented as a “phase diagram” in coordinate system ( $w_0, D_{\text{Si}}/D_{\text{Ge}}$ ). It is seen that at low flux density ( $w_0 < 0.01$ ) the formation of NCs is strongly suppressed. The reason for this is an extremely low probability of Si atom detachment at Si/SiO<sub>2</sub> interface under  $E_{\text{SiSi}}/kT > 2$ .

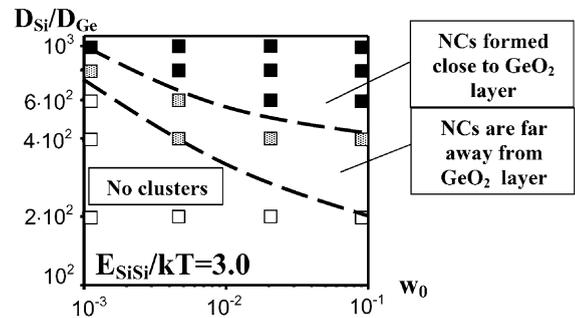


Fig. 4. The predicted low-temperature conditions of NCs formation as dependent on the collisional mixing factor ( $w_0$ ) and diffusion coefficient ratio  $D_{\text{Si}}/D_{\text{Ge}}$ .

#### 4. Conclusion

Process simulations based on a multi-component kinetic 3D lattice MC code predict that the formation of Ge NCs in SiO<sub>2</sub> by chemical reduction of GeO<sub>2</sub> can be accelerated or can be performed at much lower temperatures due to ion beam mixing of the Si/SiO<sub>2</sub> interface. It is shown that both thermally and ion-irradiation assisted Si detachment increase the roughness of Si/SiO<sub>2</sub> interface. The simulations were performed by a specifically adapted and extended kinetic MC code.

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