Thin Solid Films 517 (2008) 313–316

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Pulsed ion-beam assisted deposition of Ge nanocrystals on SiO_2 for non-volatile memory device

N.P. Stepina *, A.V. Dvurechenskii, V.A. Armbrister, V.V. Kirienko, P.L. Novikov, V.G. Kesler, A.K. Gutakovskii, Z.V. Smagina, E.V. Spesivtzev

Institute of Semiconductor Physics, Lavrenteva 13, 630090 Novosibirsk, Russia

ARTICLE INFO

Available online 27 August 2008

Keywords:
Nanocrystals
Memory
Ge/SiO2
Ion-assisted deposition

ABSTRACT

A floating gate memory structure, utilizing Ge nanocrystals (NCs) deposited on tunnel SiO_2, have been fabricated using pulsed low energy ion-beam induced molecular-beam deposition (MBD) in ultra-high vacuum. The ion-beam action is shown to stimulate the nucleation of Ge NCs when being applied after thin Ge layer deposition. Growth conditions for independent change of NCs size and array density were established allowing to optimize the structure parameters required for memory device. Activation energy E=0.25 eV was determined from the temperature dependence of NCs array density. Monte Carlo simulation has shown that the process, determining NCs array density, is the surface diffusion. Embedding of the crystalline Ge dots into silicon oxide was carried out by selective oxidation of Si(100)/SiO_2 /Ge(NCs)/poly-Si structure. MOS-capacitor obtained after oxidation showed a hysteresis in its C–V curves attributed to charge retention in the Ge dots.

1. Introduction

The self-assembling of silicon or germanium nanocrystals (NCs) embedded in SiO_2 layers has been widely studied, and memory effects in metal-oxide semiconductor (MOS) devices were reported [1,2]. Nanocrystals, embedded as charge-storage nodes in an oxide layer between the control and tunnel dielectric, reduce the problem of charge loss encountered in conventional flash memories. Superior Fowler/Nordheim tunneling characteristics of NCs memory have been demonstrated, which provide a scaling path to floating gate technology by reducing the tunneling oxide thickness. Ge-based single-electron memory device (SEMD) surpasses Si-based SEMD in terms of the writing/erasing time and the operating voltage [3]. The critical issue in fabrication of NC memory structures is the formation of nanometer-scale NCs with good uniformity and high spatial density. Lu et al. [4] showed that dot size of Ge nanocrystals affects charge loss rate and memory characteristics. Moreover, to suppress the tunneling distance fluctuation one should form in-plane distribution of NCs that is the problem for most of growth methods. We have developed a method for synthesizing of Ge NCs homogenous array located strictly in a plane on tunnel SiO_2 using pulsed low energy ion-beam induced molecular-beam deposition (MBD) in ultra-high vacuum [5]. Variation of growth parameters during Ge deposition allows to analyze the process of NCs nucleation and following overgrowth and to control Ge NCs size and array density.

2. Experimental setup

A 3.5 nm thick SiO_2 film was grown by thermal oxidation on (111) p-type silicon substrates at 850 °C (tunnel insulator). Molecular-beam deposition (MBD) was carried out in an ultra-high vacuum chamber of molecular-beam epitaxy setup equipped with effusion cell for Ge. The substrate temperature of Ge deposition was varied from 200 to 400 °C. Effective Ge layer thicknesses were in the range from 3 to 20 monolayers (ML). The rate of Ge growth was varied between 0.08 and 0.19 ML/s. We compared ion stimulation regime of Ge deposition and conventional MBD. In the first case ion-beam pulses with duration of 0.5–1 s and ion energy of 200 eV were applied at effective Ge layer thickness of 3 ML, 4 ML and 5 ML. For memory device Si(100)/SiO_2 (3.5 nm)/Ge(NCs)/poly-Si(25 nm) structure was oxidized in dry oxygen at 900 °C. Oxidation time was taken to oxidize polycrystalline Si (poly-Si) layer keeping Ge in a crystalline phase. Structural parameters were controlled with high-resolution transmittance electron microscopy (HRTEM), Electron Spectroscopy for Chemical Analysis (ESCA), and spectroellipsometry (SE).

3. Experimental results

3.1. Growth of Ge nanocrystals on SiO_2

HRTEM image of samples prepared by conventional MBD and ion-assisted deposition, respectively, are shown in Fig. 1. Ion action causes an increase of NCs array density and a decrease in a NCs size. Moreover, a homogeneous NCs size distribution is achieved by the use

* Corresponding author.
E-mail address: nstepina@mail.ru (N.P. Stepina).

0040-6090/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2008.08.160

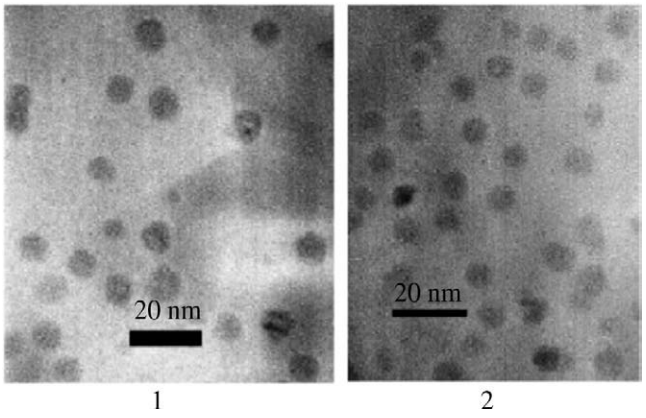

Fig. 1. HREM images of the samples prepared with conventional MBD (1) and with pulsed ion-beam action during MBD (2) at T=250 °C and Ge flux J_{Ge}= 0.1 ML/s.

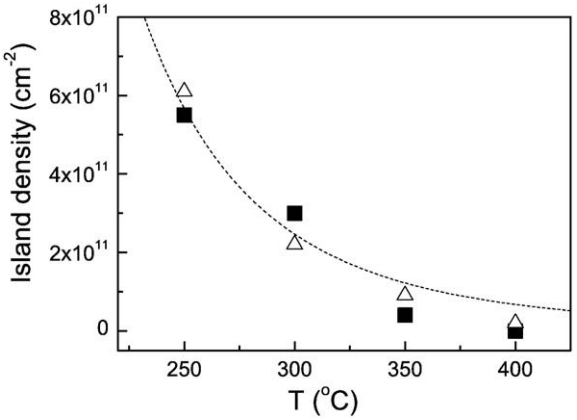

Fig. 3. Temperature dependence of NCs density. HTREM data—full squares, fitting with Arrhenius plot—dashed line, MC simulation—open triangles. (20 ML of Ge deposited, J_{Ge}=0.125 ML/s.)

of pulsed regime of ion irradiation. In our previous work [6] ion-beam action was interpreted in terms of cluster reduction caused by ion impacts, knocking atoms out of cluster. This leads both to the decrease in an average NC size and to the increase in the NCs density (due to precipitation enforced by atoms knocked out to the SiO_2 surface). Both effects were reproduced by Monte Carlo simulation [6].

The growth parameters were varied in order to find the conditions, which meet the requirements of memory device operation. The detailed ESCA spectra of Ge 2p doublet from samples with 20 Ge ML grown at difference temperatures are presented in Fig. 2. Ge $2p_{3/2}$ line components located at 1217.7 eV and at 1220.0 eV binding energies are related to pure and partially oxidized Ge, respectively. The relative intensity of Ge–Ge component, proportional to Ge layer thickness on SiO_2, is reduced with increase of deposition temperature. The estimated effective thicknesses of Ge film were 20 ML at deposition temperature 200 °C, 8.5 ML at 250 °C, 1 ML at 300 °C and 0.27 ML at 350 °C. At 400 °C practically no Ge was found on the SiO_2 surface. There is clear indication of Ge desorption during deposition at temperatures higher than 200 °C. HREM data have shown that while NCs array density decreases significantly with temperature (Fig. 3), NCs size remains practically unchangeable. We believe that desorption strongly affects the average size of NCs. Recently Hocevar et al. [7] have shown that the behavior of InAs NCs size as dependent on temperature is even inverted from increase to decrease due to desorption.

To determine the activation energy, limiting the NCs density, Arrhenius curve (dashed line in the Fig. 3) was plotted, and E_A=0.25 eV was found to provide the best fitting of the experimental temperature dependence.

Another growth parameter, providing an independent control of NCs array density, is Ge flux. Fig. 4 demonstrates the Ge flux dependence of NCs density (HRTEM data) and of amount of Ge deposited (ESCA data). One can see a very strong and unexpected dependence: the more the flux is the less Ge remains on SiO_2. Thus, using temperature and Ge flux variation, NCs array density required for memory device can be achieved. To find a way of manipulating NCs size, 5 samples with 3, 5, 8, 10 and 20 ML of Ge were prepared at 200 °C and 0.083 ML/s Ge flux. It turned out, that the amount of deposited material affects only the NCs size. The density of NCs array estimated from HRTEM images (Fig. 5) for all the samples proves to be practically the same and equal to $\sim 1.5\times10^{12}$ cm^{-2}, so that the additional Ge deposition from 3 to 20 ML leads only to overgrowth of nuclei from 3 to 5.5 nm without change in NCs areal density.

We proposed that the activation energy E_A=0.25 eV characterizes the process of surface diffusion, which limits the NCs nucleation. To

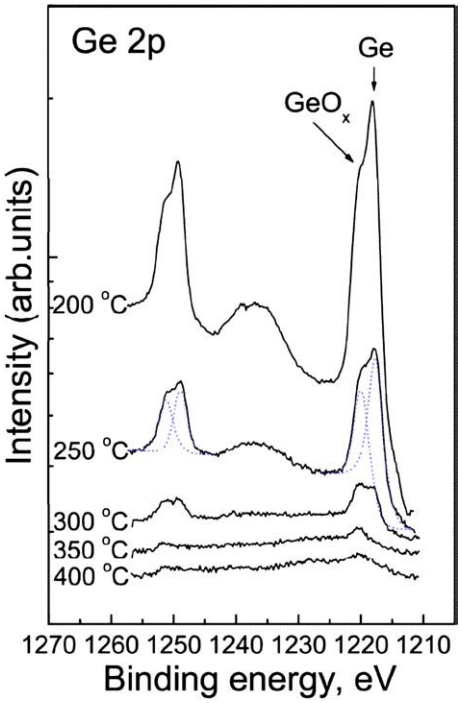

Fig. 2. ESCA spectra for 2p Ge deposited at different temperature using ion-assisted MBD.

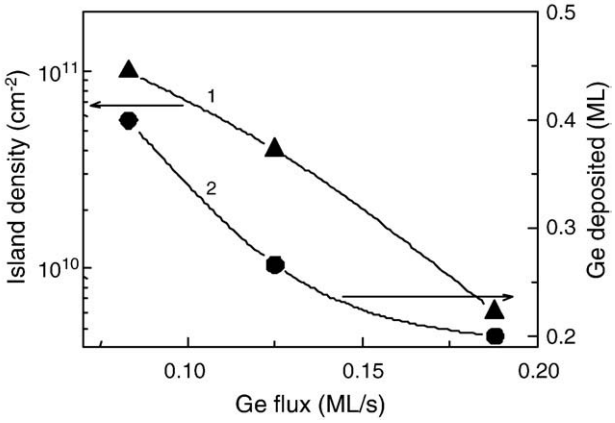

Fig. 4. NCs array density (HRTEM data—1) and amount of Ge (ESCA data—2) as dependent on germanium flux, T=300 °C.