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Memory Properties of Ge quantum dots and rings MOS structure prepared by Pulsed Laser Deposition

Xiyong Ma
Institute of Photoelectrical Materials, Shaoxing University, Shaoxing 312000, Zhejiang Province, P. R. China.

E-mail: maxy@zscas.edu.cn

Abstract. New memory structures using threshold shifting from charge stored in quantum dots (QDs) and quantum rings (QRs) of Germanium (Ge) are described. The QDs and QRs of Ge were prepared on a p-Si (100) matrix by means of pulsed laser deposition (PLD) using the droplet technique combined with rapid annealing. The perfect planar nanorings with well-defined sharp inner and outer edges were formed via an elastic self-transformation of droplet process, which is probably driven by the lateral strain of the Ge/Si layers under annealing treatment. A significant shift of threshold-voltage of 1.2 V and 2.5 V were observed in Ge QDs and QRs memory devices, respectively, when an operating voltage of 8 V was implemented on the device. It is attributed to the effect of Coulomb blockade and better interface properties of the Ge nanostructures.

1. Introduction
These years, nanocrystals based memory devices have attracted much research interest because of their high speed and small scale for the next generation as compared with the conventional floating gate (FG) structures [1-3]. In particular, Ge nanocrystals including quantum dots memory devices possess high speed for the high-mobility channel material and a charge-retention time [4,5]. Additionally, owing to the low carrier effective mass, the quasi-ballistic transport in Ge nanocrystal, the MOSFETs of Ge may lead to a better device performance than that of Si MOSFETs. In this paper, two kinds of memory nanostructures, Ge quantum dots and rings, are proposed, in which the core layer is composed either by Ge quantum dots (QDs) or by planar Ge quantum rings (QRs) that were grown by the pulsed laser deposition (PLD) technique based on the elastic strain of Ge droplets. Typically, the synthesis of Ge quantum dots and rings nanostructures relies on the self-assembly and self-organization processes of molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) using the large strain property of Ge/Si heterolayers [6-8]. In the present experiments, the QDs were obtained by droplet technology of PLD, while the planar QRs were obtained by the self-transformation process of Ge quantum dots into nanorings under annealing at 600°C in the presence of Ar gas. The as-grown Ge QDs and QRs were observed through field-emission scanning-electron microscopy (FESEM). The memory devices have a significant threshold-voltage shift at a low operating voltage of 8 V due to charge trapping in the Ge microstructures.
2. Experimental details

Ge QDs and QRs thin films were deposited on p-Si (100) substrates by pulsed laser deposition at room temperature. An irradiation with a wavelength of 248 nm, an energy density of 1.2 J/cm$^2$ and a pulse duration of 25 ns from a pulsed KrF excimer laser (Lambda Physik LPX 305) was used to ablate the Ge single crystal (100) target (99.99%) placed on a rotating holder inside a vacuum chamber. The laser beam was focused with three pieces of lens, introduced into the deposition chamber through a ultraviolet window, and finally ripped into the target at an angle of 45°. Two cleaned Si substrates were placed on a holder facing the target in the vacuum chamber, one was served as a reference sample. A tuned oxide layer about 5 nm thick was formed by thermal oxidation of the substrates at 800°C for 30 min in the presence of oxygen gas after the experimental chamber being pumped down to $10^{-6}$ Torr. Two Ge QDs films were deposited for 30 min in Ar gas that was used as both a working and buffer gas at 100 Pa background pressure. The as-grown Ge reference uncapped sample was removed for characterization by FESEM. Then a 10 nm thick silicon oxide was further grown on the QDs layer of the other sample as a control oxide layer by means of ablating a Si single-crystal (100) target in the presence of an oxygen atmosphere at 800°C. Two Ge QRs samples are prepared almost the same procedure as the QDs samples except the as grown QRs samples are an in-situ annealing at 600°C for 5 min, then the reference QRs sample was took out for EFSEM observation, and the other QRs sample for continually thermally grown a SiO$_2$ caper layer. After the Al electrodes and back contact were patterned and sintered on both the QDs and QRs nanostructure, current-voltage ($I$-$V$) and capacitance-voltage ($C$-$V$) measurements were performed using a semiconductor parameter analyzer model HP4156 at room temperature to investigate the leakage behavior of the Ge nanosacle memory devices.

3. Results and discussion

Figure 1 shows the FESEM images of Ge quantum dots prepared by PLD droplet technique. As can be seen, some quantum dots are evenly scattered on the Si substrate, the average size of them is about 900 nm, and the height is about 80 nm. The QDs take almost an identical hemisphere shape except two of them are partly overlapped. An enlarged image is shown in Fig.1b, it shows a spherical dot. The top surface takes a shape of a structure as a spire that tapers to a point at the top. From this, we can deduce the process of Ge nanoring formation: first, under the powerful pulsed laser the solid Ge was melted and transformed into microdrolets in the atmosphere of cool Ar. Then Ge QDs were formed when the droplets fall on the Si substrate, and finally transformed into nanorings in situ of 600°C annealing in the presence of Ar.

![Figure 1](image1.png)

**Figure 1.** (a) SEM image of Ge quantum dots with diameters of 0.90 μm. (b) The high magnification shows the perfect dot with spherical symmetry.

The Ge QRs samples are prepared as the same condition as the Ge QDs in addition to following annealing at 600°C for 5 mins, the obtained Ge nanoring images are presented in Fig.2a. The pattern of
Ge QRs is multiform, there are separated single nanorings, poly nanorings that some nanorings are linked together, and nanocoil rings that a few rings jointed. The Ge nanorings with nearly homogeneous radius of curvature, ring shell and thickness. Clearly, the rings are characteristic of a two-dimensional structure, the thickness is much smaller than the diameter, and the width of the ring shell does not change. They have a typical a shell width of 155-158 nm, and a thickness of 25 nm measured by means of a DEKTAK profilometer, and the density is determined to be $2.3 \times 10^7 \text{ cm}^{-2}$. The image recorded at high magnification (Fig. 2b) shows the perfect circular shape of a complete ring, with uniform shell and flat surface. The separated single nanoring is formed via a self-deformation process of a droplet during the growth under thermal annealing treatment, accordingly, no dislocations are introduced into the QRs.

![Image](https://example.com/image.png)

**Figure 2.** SEM image of Fig.2 (a) shows the Ge QDs nanorings with the diameters of 1.2-1.4 μm, and the ring shell of 155-158 nm. (b) The high magnification shows the perfect ring with uniform shell and flat surface. (c) The schematic of illustrates the nucleation and growth of a nanoring.

J. Sormunen et al [9] self-Assembled InAs/InP quantum dots into quantum rings by annealing at 560°C. They found that the effect of temperature makes the InAs/InP dot-to-ring transformation. The formation mechanism of QRs is related to As/P exchange and the elastic strain relaxation of the QD/QR system. This diffusion, together with As/P exchange, may be the driving force for the mass redistribution from QD to QR, thus result in a modification of the QD morphology, even holes. Cui, J et.al [10] thought that the formation of SiGe/Si QRs is related to the QD strain distribution. By means of the surface segregation and diffusion, Ge atoms are released from the QD. They mix and alloy with Si on the QD side surface where the lateral lattice constant matches SiGe with varying composition. These reports verify the significance of strain-controlled surface diffusion effects. Based on these results, we developed the formation model of our Ge rings, showing in Fig. 2 c. In the first step, a droplet of Ge produced by the laser moves on the substrate with a powerfully kinetic energy. In the second step, a small dip initially appears upon the droplet when it touches on the substrate because the upside of the droplet will continually go forward under the inertia force. Additionally, a small part of the residual impact force under Ar gas buffering.
transfers into a lateral force, which drives the material of the droplet extending that has been demonstrated by the document of [11-12]. As a result, a cone-shaped structure is formed on the substrate. In the third step, that is, in the thermal annealing process, with the jointed forces of the large strain of Ge/Si layers and the lateral thermal diffusion force, a nanoring of Ge with a plane structure is developed on the substrate. Similarly, the poly-rings are formed by the same transformation process of Ge droplets by partly overlapped falling on the substrate. Finally, Ge planar nanorings are prepared by the droplets technique of PLD without fracture in the depositions.

The capacitance-voltage (C-V) characteristic of the Ge QDs and QRs uncapped samples measured under the bias -0.5 to 0.3 V is shown in Fig. 3. There is a platform in the QDs C-V curve in the bias region of -0.2 to 0.1 V, but two platforms appear in the QRs curve, which indicates that only a boundary of space charge region is located in the dots and two boundaries in the rings because of having an inner and an outer faces. The Coulomb blocking effects occur due to large holes confined in the QDs and QRs blocking the further extension of space charge region. As the reverse bias voltage increases above 0.15 V, the space charge region extends over the dot layer so the holes in the dot are completely pumped out.

![Figure 3. Capacitance-voltage traces of self-organized dots and rings. There is only a plateau in QDs curve while two flats in nanorings.](image)

Figure 4 shows the hysteresis curves of the C-V measurements for the capped Ge QDs and QRs memory devices in a bi-directional voltage sweep. Figure 4(a) gives a schematic diagram of the device structure used in this work, in which the core layer is composed either of QDs or QRs. The Ge nanostructure sandwiched between the oxide layers is utilized as a charge-storage element for a memory device. The voltage is swept between 5 and (-8) V or (-8) and 5 V counterclockwise, and the erasing voltage is fixed at (-8) V. It is found that it causes a threshold-voltage shift of 1.2 V in the QDs devices, a significant shift up to 2.5 V occurs in QRs sample at the low operating voltage of 8 V, which is large enough to be defined as 1 or 0 for circuit design. The large threshold-voltage shift may arise from the oxide traps, the Coulomb blockade effect, and most important, from the Ge/Si composite tunneling potential. The blockade effect of the discrete distribution of Ge nanorings leads to lower capacitance coupling of the nanoring memory device than that of a conventional FG memory device.
Figure 4. The hysteresis curves of the C-V measurements for the capered Ge QDs and QRs memory devices in a bi-directional voltage sweep. It causes a threshold-voltage shift of 1.2 V in the QDs devices, a significant shift up to 2.5 V occurring in QRs sample at the low operating voltage of 8 V.

4. Conclusions

Ge QDs and QRs based memory devices were fabricated by pulsed laser deposition. The Ge nanorings were formed by the transformation of Ge droplets into nanorings caused by the large strain and stress of Ge/Si layers. A significant shift of threshold-voltage of 1.2 V and 2.5 V was observed in QDs and QRs memory devices, respectively, when an operating voltage of 8 V was implemented on the device, which attributed to the effect of Coulomb blockade and better interface properties of the Ge nanostructure.

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Reference