Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/matchar

Evolution of microstructural defects with strain effects in germanium nanocrystals synthesized at different annealing temperatures

Minghuan Zhang[a,b], Rongsheng Cai[a,b], Yujuan Zhang[a,b], Chao Wang[a,b], Yiqian Wang[a,c,*], Guy G. Ross[d], David Barba[d]

[a]The Cultivation Base for State Key Laboratory, Qingdao University, No. 308, Ningxia Road, Qingdao 266071, PR China
[b]College of Chemistry and Chemical Engineering, Qingdao University, No. 308, Ningxia Road, Qingdao 266071, PR China
[c]College of Physics Science, Qingdao University, No. 308, Ningxia Road, Qingdao 266071, PR China
[d]INRS-EMT, 1650 Boulevard Lionel-Boulet, Varennes, Quebec J3X 1S2, Canada

ARTICLE DATA

Article history:
Received 18 November 2013
Received in revised form
14 March 2014
Accepted 15 March 2014
Available online 22 March 2014

Keywords:
Ge nanocrystals
Evolution of defects
HRTEM
Stress

ABSTRACT

Ge nanocrystals (Ge-ncs) were produced by implantation of $^{74}Ge^+$ into a SiO_2 film on (100) Si, followed by high-temperature annealing from 700 °C to 1100 °C. Transmission electron microscopy (TEM) studies show that the average size of Ge-ncs increases with the annealing temperature. High-resolution TEM (HRTEM) investigations reveal the presence of planar and linear defects in the formed Ge-ncs, whose relative concentrations are determined at each annealing temperature. The relative concentration of planar defects is almost independent of the annealing temperature up to 1000 °C. However, from 1000 °C to 1100 °C, its concentration decreases dramatically. For the linear defects, their concentration varies considerably with the annealing temperatures. In addition, by measuring the interplanar spacing of Ge-ncs from the HRTEM images, a strong correlation is found between the dislocation percentage and the stress field intensity. Our results provide fundamental insights regarding both the presence of microstructural defects and the origin of the residual stress field within Ge-ncs, which can shed light on the fabrication of Ge-ncs with quantified crystallinity and appropriate size for the advanced Ge-nc devices.

1. Introduction

In the past two decades, much effort has been devoted to the study of germanium nanocrystals (Ge-ncs) due to their wide range of applications in new integrated optoelectronic devices and highly-efficient solar cells [1,2]. Compared with silicon nanocrystals, Ge-ncs exhibit strong visible photoluminescence and electroluminescence, which are suitable for fabrication of light-emitting devices [3–6]. The hole and electron mobilities of bulk Ge are 4.2 and 2.6 times higher than those of Si [7], so that the nanostructured germanium is very promising for the development of high-speed devices. Also, the weak energy bandgap of Ge (0.66 eV) can improve the quantum confinement effects inside Ge-ncs for promoting multiple exciton generation in third generation solar cells [8].

In recent years, ion implantation has been extensively employed to produce Ge-ncs with well-controlled depth and size distribution by adjusting the implantation and annealing

---

* *Corresponding author at:* The Cultivation Base for State Key Laboratory, Qingdao University, No. 308, Ningxia Road, Qingdao 266071, PR China. Tel./fax: +86 532 83780318.
E-mail address: yqwang@qdu.edu.cn (Y. Wang).

http://dx.doi.org/10.1016/j.matchar.2014.03.010
1044-5803/© 2014 Elsevier Inc. All rights reserved.

conditions [2,9,10]. Until now, a lot of studies have focused on the morphology, size effect and spatial distribution of Ge-ncs [9,11–14]. However, during the formation of Ge-ncs, specific defects can be produced within the nanocrystallites and thus affect their physical properties [15]. The Ge-ncs are also subject to complex stress effects, whose intensity may be related to both the nature and the concentration of their internal defects. The stress in Ge-ncs is generally associated with two different mechanisms: the first one originates from a local lattice mismatch between Ge crystal planes of different orientations, and the second one is related to volume expansion during the annealing process. To our knowledge, the evolution of microstructural defects, as well as their connection with the stress relaxation process as a function of the annealing temperatures has never been explored nor demonstrated.

In this paper, Ge-ncs embedded in the amorphous SiO_2 matrix were fabricated using ion implantation, followed by thermal annealing. The evolution of both Ge-nc dimensions and microstructural defects inside Ge-ncs has been investigated as a function of annealing temperatures using high-resolution transmission electron microscope (HRTEM) imaging. Two kinds of defects, namely planar (twins and stacking faults) and linear (dislocations) defects, are identified and quantified, showing two distinct evolutions. The variations of both dislocation concentration and the interplanar spacing of Ge-ncs give evidence of strong correlations between the formation of dislocations and the stress field, whose formation mechanisms and origins are discussed.

2. Experimental

$^{74}Ge^+$ ions were implanted into a SiO_2 film grown on (100) Si at a fluence of 8×10^{16} cm^{-2}, with an ion energy of 70 keV, using an IBS/IMC 200 commercial implanter. This apparatus consists of a plasma source, a magnet mass separator, an accelerator line and a target chamber. Fig. 1 presents a schematic diagram for the process of ion implantation. Firstly, ions are generated by the plasma source and provided with an initial velocity after the first acceleration. Then, $^{74}Ge^+$ ion isotopes are isolated in the magnet mass separator and are electrostatically accelerated to the desired energy in the accelerator line. Eventually, impinging ions are implanted into the silicon oxide sample in the target chamber. The samples were then separately annealed under ultrahigh purity N_2 atmosphere for 1 h at annealing temperatures of 700 °C, 800 °C, 850 °C, 900 °C, 1000 °C and 1100 °C, respectively. To avoid any accidental contamination by the annealing ambient, the gas flux was filtered using an additional nitrogen purifier.

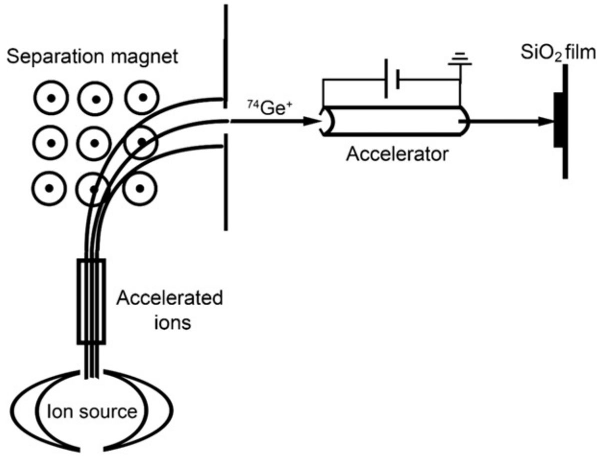

Fig. 1 – The schematic diagram for the process of ion implantation.

The cross-sectional specimens ([011] zone axis for Si substrate) for transmission electron microscopy (TEM) observations were prepared by conventional techniques of mechanical polishing and ion thinning. Selected-area electron diffraction (SAED), bright field (BF) and HRTEM were carried out using a JEOL JEM2100F TEM operating at 200 kV.

3. Results and Discussion

Typical BF TEM images are presented in Fig. 2(a)–(f) for samples annealed at 700 °C, 800 °C, 850 °C, 900 °C, 1000 °C and 1100 °C, respectively. In order to facilitate their comparison as a function of the annealing temperature, all these images were recorded at the same magnification. The BF TEM images were obtained with Si substrates oriented along the [011] zone axis. In Fig. 2, Ge-ncs are observed in the upper region of the SiO_2 film, up to a depth of 65 ± 5 nm in all studied samples. Such a value is consistent with the maximum ion path of 70 keV Ge^+ implanted into a fused silica target, calculated using the SRIM computer code [16]. The average sizes of Ge-ncs are determined from a precise analysis of TEM images and summarized in Table 1. These measurements are plotted in Fig. 3, showing that the size of the Ge-ncs observed in different samples increases with the annealing temperatures, from 5.95 nm at 700 °C to 28.15 nm at 1100 °C. Such an increase of the Ge-nc dimensions can be associated with the coalescence of small nanocrystals, according to a mechanism described in previous reports [10,17]. It is also consistent with the general trend observed by scanning electron microscopy (SEM), for Ge-ncs synthesized at different annealing temperatures in fused silica [2].

Extensive HRTEM analysis reveals two different kinds of microstructural defects inside Ge-ncs, namely, planar defects and linear defects. The relative concentrations of planar and linear defects are presented in Table 2 for each studied sample. Furthermore, the changing trends of different defects are clearly shown in Fig. 4. As shown in Fig. 4(a), the relative concentration of planar defects, especially twinning and stacking faults, is almost independent of the annealing temperature up to 1000 °C. However, from 1000 °C to 1100 °C, its concentration decreases dramatically. For the linear defects, i.e. dislocations, their concentration varies considerably with the annealing temperatures, as shown in Fig. 4(b). Fewer dislocations are observed in the Ge-ncs with an average size smaller than 6 nm annealed at 700 °C. According to some literature [18,19], as the grain size or feature size is reduced, there is a critical size below which the defect content can be virtually reduced to zero. For annealing temperatures increasing up to 900 °C the dislocation percentage increases up to ~26%. It then decreases to ~20% for the annealing at 1000 °C and drastically increases up to ~35% for the annealing at 1100 °C.