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Enhanced formation of Ge nanocrystals in Ge : SiO_2 layers by swift heavy ions

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Abstract
In this paper we report the ability of swift heavy Xe ions with an energy of 480 MeV and a fluence of 10^{12} cm^{-2} to enhance the formation of Ge nanocrystals within SiO_2 layers with variable Ge contents. These Ge-SiO_2 films were fabricated by the co-sputtering of Ge and quartz sources which followed various annealing procedures. In particular, we found that the irradiation of the Ge : SiO_2 films with subsequent annealing at 500 °C leads to the formation of a high concentration of nanocrystals (NCs) with a size of 2–5 nm, whereas without irradiation only amorphous inclusions were observed. This effect, as evidenced by Raman spectra, is enhanced by pre-irradiation at 550 °C and post-irradiation annealing at 600 °C, which also leads to the observation of room temperature visible photoluminescence.

(Some figures may appear in colour only in the online journal)

1. Introduction

The physical properties of Ge and Si nanocrystals embedded in an SiO_2 matrix have been a subject of extensive studies in the last decade. While most of the effort has focused on the Si : SiO_2 system one would expect some significant advantages for the Ge : SiO_2 system. In particular, due to their deeper quantum wells, Ge nanocrystals (Ge-NCs) are of interest as possible charge storage sites in future non-volatile memories [1, 2] as well as various nanophotonic applications [3]. Also, the corresponding quantum confinement effects are stronger for Ge-NC due to the lower effective mass of the charge carriers and the higher dielectric permittivity. This is manifested by the significantly larger Bohr radius in Ge (22 nm, [4]) in comparison with that of Si (5 nm, [5]). As a result, Ge-NC arrays can be more attractive than Si-NC arrays for studies and applications of low-dimensional systems. At the same time, there are factors hindering the Ge-NC composite properties which are not typical of Si nanocrystals such as the high level of mechanical stresses in the Ge : SiO_2 system [6]. Considering the large interface-to-volume ratio in NC/matrix systems the stress and strain fields play an important role in determining the physical and thermodynamic properties of the NCs. In fact, the strain in Ge NCs is known to modify the electrical properties of the NCs significantly [7]. Such strains, which increase with the increase in the nanocrystals size and/or structural imperfections associated with stress relaxation, suppress the photoluminescence (PL) yield of Ge nanocrystals [8]. This makes the formation of small-sized Ge nanocrystals in an SiO_2 matrix, especially in relatively thick (hundreds of nanometres) Ge : SiO_2 layers, very difficult.

In this paper, we report the ability of swift Xe ion irradiation to modify or to create new small Ge nanocrystals in a Ge : SiO_2 system. This follows the success of our previous studies in affecting silicon nanocrystals that are embedded in an SiO_2 matrix. Those studies resulted in a few surprising effects such as the ordered distribution of NCs, the same orientation of the Si-NCs, the increase in the PL intensity and the possibility of observing low-dimensional properties of the ordered NC arrays in thick SiO_2 layers [9–11]. As we show below most

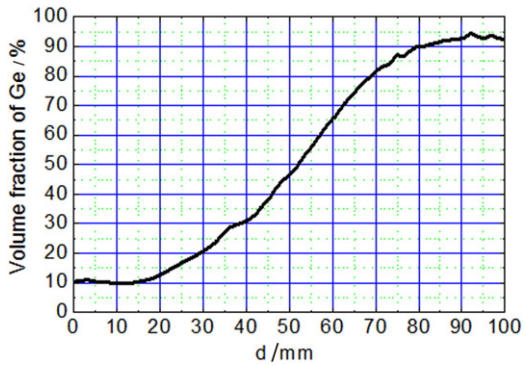

Figure 1. Fractional Ge phase content (given in vol%) as a function of the distance, d, from the low Ge content end of the film in the as-deposited (not annealed) Ge : SiO_2 layer (Ge-7).

of these effects can be reproduced in the more promising Ge : SiO_2 systems, in spite of the difficulties associated with controlling their properties.

2. Experimental details

The samples used in this study were fabricated by co-sputtering from Ge and quartz sources (separated by a distance of 10 cm) onto elongated Si wafer substrates that are 12 cm long and yielded SiO_2 films with a variable Ge content. The thickness of the deposited films with variable Ge content and thus the Ge phase content in them (the volume % of the Ge phase) were determined by ellipsometry measurements at different positions along the deposited films, as described in detail previously [12]. The corresponding dependence of the fractional volume contents of the Ge phase on the distance d, from the Ge poor end, is presented in figure 1. All the samples used in this study had the same thickness of ∼500 nm. After annealing, the layer thickness decreased to ∼450 nm according to both ellipsometry and capacitance–voltage measurements (see below). The variation in the Ge content as given in figure 1 will be used below to characterize the layer properties. After the film deposition some of the samples (see table 1) were annealed at temperatures 550, 600 and 700 °C for 30 min, in order to form the germanium nanocrystallites within the SiO_2 matrix. These samples were used as references for the irradiated samples. Two of the samples, one as deposited and the other after annealing at 550 °C (see table 1), were irradiated at 300 K, with 470 MeV Xe ions to a fluence of 10^{12} cm^{-2} from a U-400 FLNR JINR cyclotron. The ion beam homogeneity of the irradiated surface (that was achieved using beam scanning in the horizontal and vertical directions) was better than 5%. The above irradiation regime was chosen following our previous work on Si nanocrystals [9–11]. As was found there, the exposure of Si : SiO_2 to a 10^{12} cm^{-2} fluence of high-energy heavy ions leads to significant structural transformations. The irradiated samples and one of the reference samples were then subjected to annealing at 500 °C for 20 min in an Ar ambient.

Our ellipsometry measurements were performed by the use of a scanning ellipsometer MICROSCAN with an He–Ne laser source (632.8 nm) and high spatial resolution (5 μm). The angle of incidence that yielded the highest resolution was

Table 1. Details of pre- and post-depositions of the samples used in this study.

Sample	Initial annealing	Irradiation details	Additional annealing
Ge-1	550 °C, 30 min	—	500 °C 20 min
Ge-2	550 °C, 30 min	—	600 °C 20 min
Ge-3	600 °C, 30 min	—	—
Ge-4	700 °C, 30 min	—	—
Ge-5	550 °C, 30 min	Xe, 470 MeV, 10^{12} cm^{-2}	600 °C 20 min
Ge-6	—	Xe, 470 MeV, 10^{12} cm^{-2}	500 °C 20 min
Ge-7	—	—	—

65°. The fractional Ge content in the films was extracted from the absorption and reflection coefficients and the application of the effective medium analysis for a three-dimensional isotropic layer according to the Bruggeman approximation [12]. High-frequency (1 MHz) capacitance–voltage characteristics were used for the determination of the layer thickness from the layer capacitance measured near the film end of low Ge content. For the identification of the structure of the Ge : SiO_2 films we have employed Raman spectroscopy. The Raman spectra were recorded in the back-scattering geometry. The 514.5 nm Ar^+ laser line was used as the excitation source and a Triple spectrometer (T64000 Horiba Jobin Yvon) with a micro-Raman setup was used for light detection. We have also used a system of INTEGRA-Spectra spectrometer (NT-MDT) with excitation of a 532 nm solid-state laser line for the same purpose. In both cases the spectral resolution was about 1.5 cm^{-1}. All Raman spectra were measured at room temperature. To avoid heating of the films, the laser beam was slightly defocused to a spot diameter of about 6–8 μm when the laser power reaching the sample was within the 3–4 mW range. For our high-resolution transmission electron microscopy (HRTEM) and selected area diffraction (SAD) measurements on the cross sections of Ge-SiO_2 layers we used a high-resolution transmission electron microscope (JEOL JEM 2100 LaB_6), which was operated at 200 kV.

3. Experimental results

Following the information on the size and concentration of the Ge NCs in our samples we turn in figure 2 to the Raman spectra as observed near the high Ge content end of the film, before and after the 550 °C annealing. The spectra revealed a broad peak centred at 270 cm^{-1}. This peak, known to be related to amorphous germanium, was observed in all our samples, whether as deposited or annealed. The formation of amorphous Ge clusters is also evidenced by our corresponding HRTEM image and the SAD ring pattern shown in figure 3(a). These reveal that the Ge-1 layer contains only amorphous Ge clusters with an average diameter of about 5 nm. The simulation of the SAD ring patterns in the inset confirms that mainly amorphous Ge inclusions are observed in this sample. In contrast, within the rings of figure 3(b), which correspond to the Xe irradiated sample Ge-6, there are bright spots that indicate the presence of NCs with different orientations. As

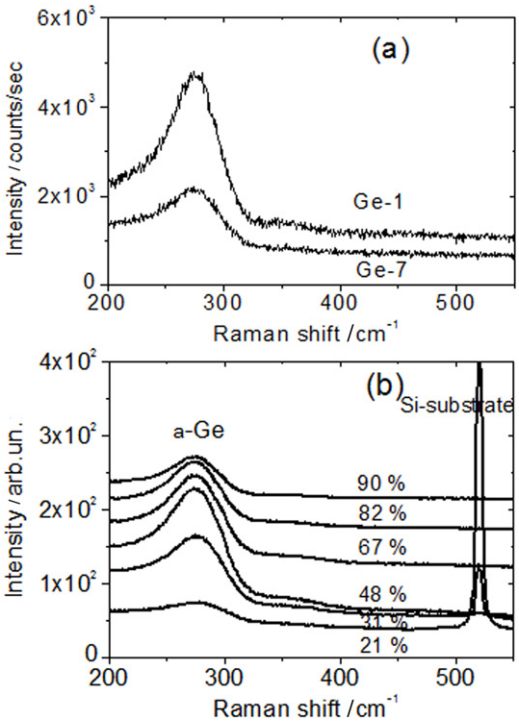

Figure 2. (*a*) Observed Raman spectra at $d = 60$ mm (65% of Ge) for both, as-deposed sample Ge-7 and sample Ge-1, after the initial annealing. (*b*) Raman spectra of Ge-1 after additional annealing (500 °C for 20 min). The Ge contents at the measured positions along the film are indicated near the corresponding Raman traces. The Raman spectra are shifted along the vertical axis for convenience.

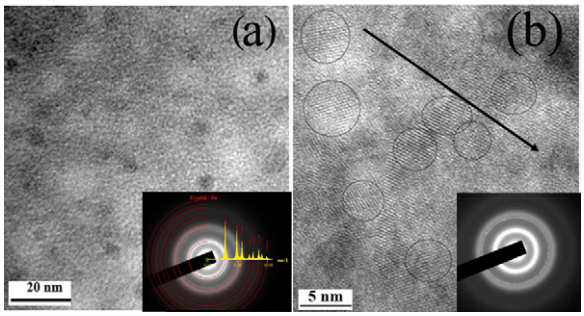

Figure 3. High-resolution TEM micrographs of the Ge : SiO_2 films with a Ge content of 83 vol% as obtained on the non-irradiated sample Ge-1 (*a*) and on the irradiated sample Ge-6 (*b*). The insets present the selected area diffraction (SAD) patterns of the corresponding layers. The SAD pattern in (*a*) also shows simulated ring patterns for amorphous Ge while the SAD pattern given in (*b*) clearly demonstrates the presence of Ge-NCs in the irradiated film.

seen in the HRTEM image of figure 3(*b*) the size of the Ge NCs is of the order of 3–5 nm which is in good agreement with our estimates from the Raman spectra to be described below.

The Raman spectra measured on our reference samples Ge-3 and Ge-4, which were annealed at 600–700 °C, showed that in addition to the 270 cm^{-1} peak, a new peak associated with crystalline germanium is observed. The NC peak has a maximum at 289–293 cm^{-1} for different positions in sample Ge-3 and 293–297 cm^{-1} for different positions (i.e. different Ge contents) along sample Ge-4. The important point here

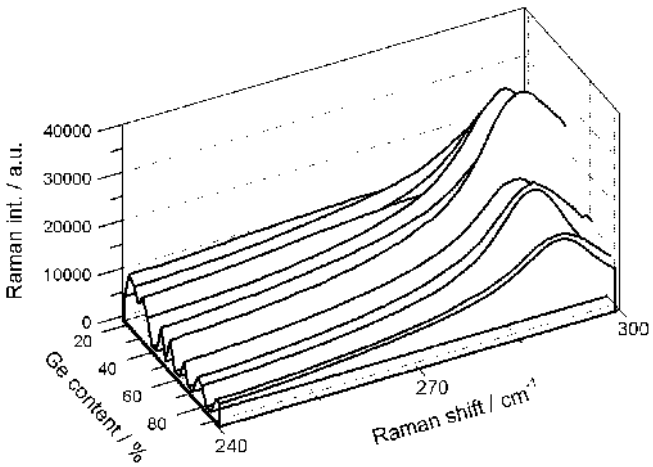

Figure 4. Raman spectra of the irradiated and annealed film, Ge-6, as a function of the Ge content along this film.

is that the Ge NC peak is red-shifted in comparison with that of the bulk crystalline Ge (300.5 cm^{-1}). The estimation of the NCs' diameters was then done using the relation between the crystallite size and the corresponding peak position in the Raman spectra (see, for example, [13–16]). Using the confinement model, for spherical and fully relaxed NCs, the diameter of the nanocrystallites is estimated to be about 2–5 nm for the 600 °C annealed sample (G-3) and 5–7 nm for the 700 °C annealed sample (G-4).

Turning to the results as obtained on the irradiated samples we show in figure 4 the Raman spectra of the as-deposed Ge-6 film that was irradiated with high-energy Xe ions and annealed at 500 °C after the irradiation. The spectra given in this figure for the entire length of the film indicate the formation of small-sized nanocrystallites, which are not detected in the non-irradiated films that were subjected to the same annealing procedure (see figure 2). In figure 5 we derive the size and the integrated intensities of the NC peaks from the measured spectra of sample Ge-6, as a function of the Ge content. The size of the NCs is estimated, as above, from the redshift of the NC peak in the Raman spectra [13–16] while the integrated intensities are proportional to the concentration of the NCs. We then note of course that the nearly constant value of the NC concentration for Ge contents higher than 40% in figure 5(*b*) is a reflection of the constant optical density of the Raman signal, which results from the increase in the Ge content that leads to a decrease in the effective thickness tested by the Raman signal on the one hand, and an increase in the concentration of the Raman excited NCs on the other hand.

4. Discussion

In this study we have shown that a combination of ion bombardment and annealing can assist the formation of small Ge nanocrystallites in the dielectric SiO_2 matrix. This is different from the cases of Ge-only films where the as-deposited films were subjected to ion irradiation. For example, in one such case Ge crystallization in the ion tracks was registered in amorphous Ge thin films after ion irradiation with energy losses higher than 5 keV nm^{-1} [17], while in other

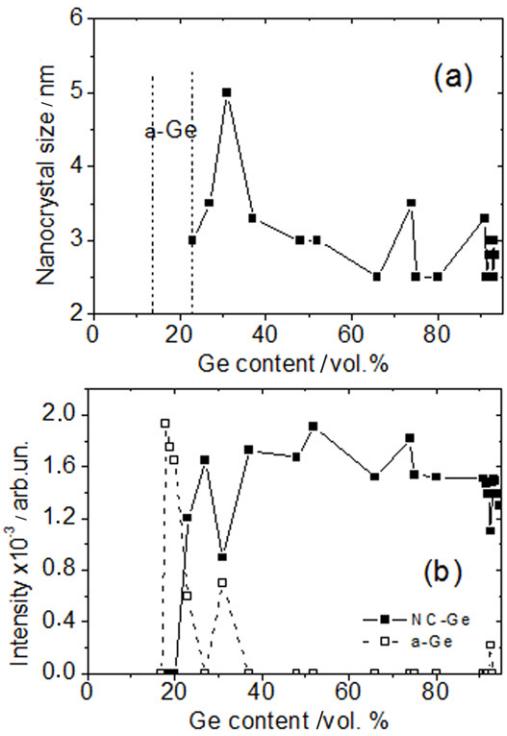

Figure 5. Size of the NCs (*a*) and the integrated intensity of the NC peak (*b*) as obtained from the Raman spectra dependence on the distance along sample Ge-6. The NC size was estimated from the position of the maxima of the NC peak in the Raman spectra while the integrated intensity of the spectra reflects the concentration of the NCs. Also shown is the relative intensity of the α-Ge phase in the film.

cases the formation of Ge nanoparticles in thin (5 nm) Ge layers [18, 19] was observed. In the latter case, shaping of the spherical Ge nanoparticles into discs and rods, due to the high-energy ion irradiation, was observed. In the above cases, the energy transfer from the ion to the solid takes place via excitation and ionization, which bring about the formation of high-temperature cylindrical zones along the ion path. Since, according to the SRIM code calculation, the specific ionizing energy losses of 480 MeV Xe ions are 17 keV nm^{-1} in SiO_2 and 24 keV nm^{-1} in Ge, such an energy deposition may induce amorphous–crystalline phase transitions in our Ge : SiO_2 samples.

In our experiments, the projection range of the ions was 36.8 μm for Xe ions so that the ions penetrated the substrate far beyond the NC-SiO_2 layer. The electronic stopping losses of the ions in the oxide layers were then the dominating ones. The irradiation leads to the ionization of atoms in the material such that after $\sim 10^{-12}$ s the energy is transferred to anisotropic heating of the layers due to the thermalization process. Using the value of ionization losses, we could estimate the temperature inside the ion tracks [10, 11]. As follows from this estimation, the local transient temperature along the ion track in our experiments could be as high as 1500–2000 °C with the ion track heating time being about 10^{-11}–10^{-10} s. This means that almost all the inter-atomic bonds along the ion tracks could be broken, leaving the atoms free and making them capable of being displaced in the lattice from their regular lattice sites. This can bring about new bonds in the material and result in subsequent amorphization or crystallization of the previously existing Si nanoparticles as well as the formation of new NCs in the SiO_2 layer along the ion tracks.

We have also found that the NC generation after the additional annealing at a higher (600 °C) temperature (Ge-5) causes a strong decrease in the Ge NC size and an increase in the NC concentration in comparison with the case of the non-irradiated samples (G-2). In particular, the NC size was found to decrease in the irradiated samples approximately by a factor of 2 (5–8 nm in the irradiated sample in comparison with 8–15 nm in the reference layers). In fact, we have observed a similar effect (a decrease in the NC size and an increase in the concentration) when we studied Si nanocrystals embedded in a SiO_2 layer [9, 20], but in that case the effect of size decrease was not as pronounced ($\sim$15% for the same ion dose and an even higher electron energy losses) as here. This suggests that the ion-induced effects are stronger in the Ge-NC composites in comparison with those in the Si-NC composites. Further evidence for this fact is suggested by the comparison made in figure 6 between the Raman spectra of the non-irradiated and irradiated samples, Ge-2 and Ge-5, respectively. In those spectra, we see the coexistence of the amorphous and crystalline nanoparticle phases. In particular, we have seen that the Ge-NC peak height is significantly higher after the irradiation with swift heavy ions. By considering the spectral peak positions in the two cases one can conclude that 600 °C annealing leads to the formation of 5–8 nm nanocrystallites, in the Xe irradiated samples, while in the non-irradiated films the size of the nanocrystallites is 8–15 nm. This leads to our conclusion that swift heavy ion irradiation results in the formation of higher concentration of smaller size Ge nanocrystals. Our PL measurements on both Ge-2 and Ge-5 samples showed that indeed a visible luminescence is found only in the irradiated sample. In particular, we have observed a broad peak centred at 640 nm, with an intensity that is strongly dependent on the Ge content. This dependence is peaked at a fractional content of 30 vol% (inset of figure 6(*b*).

In samples such as ours the compressive stress in the Ge NCs, due the SiO_2 matrix, is known to result in the formation of defects and thus in the consequent suppression of inter-band PL [8]. In contrast, the formation of small NCs in the irradiated sample Ge-5 was accompanied by the appearance of PL at some Ge content values as is typical of systems of NCs that are embedded in a dielectric matrix [21]. We should also mention that the ordering of the lattice plane orientations in the NCs along the ion tracks in the oxide layers of the irradiated samples and the formation of NC chain arrays were the most striking findings that followed the irradiation of Si-NCs : SiO_2 systems [9–11]. The TEM images of our present irradiated layers with Ge-NCs demonstrate, however (figure 3(*b*)), that there is no orientation of lattice planes perpendicular to the ion tracks in these NCs. The maximal deviation is about 60°, and the majority of the NCs have an orientation that is close to the ion track but is not really an ordered distribution of the NCs. This fact, however, gives the hope that further optimization of the irradiation and annealing conditions will yield more significant results.

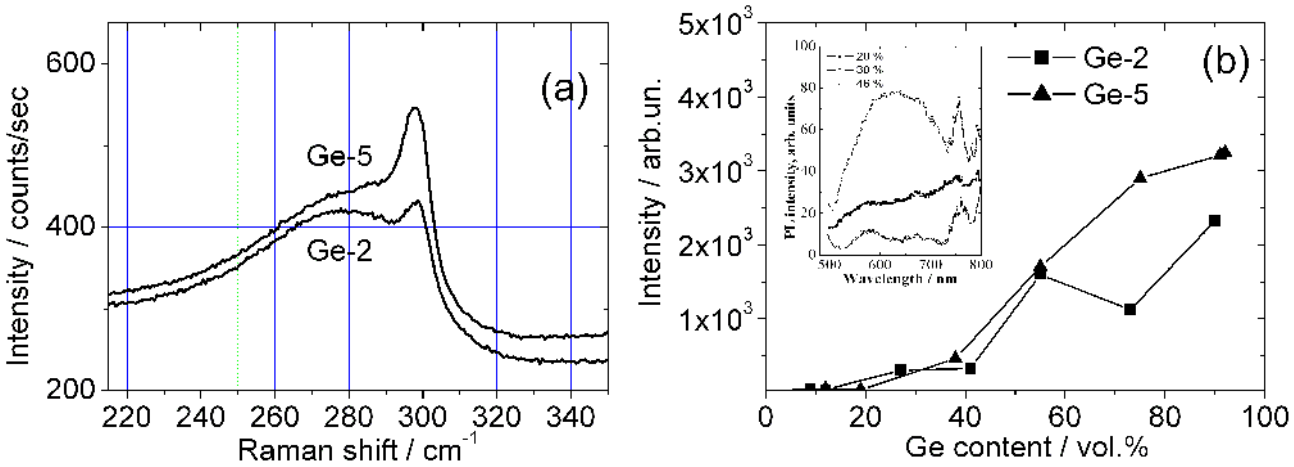

Figure 6. (*a*) Raman spectra as measured on the films with a Ge content of 75%. This is for the non-irradiated Ge-2 and the irradiated Ge-5 samples. (*b*) Ge content dependence of the integrated intensity of the NC peak in the Raman spectra. The inset shows the PL spectra for the irradiated sample Ge-5.

As shown above, the irradiation of $Ge:SiO_2$ with high-energy heavy ions results in the formation of NC systems that possess properties that are not typical of the reference non-irradiated samples. In particular, we found that the irradiation of the studied films enhances the formation of Ge nanocrystallites or modifies the existing NCs in the host matrix. The appearance of PL shows the potential of using our irradiation–annealing approach for controlling Ge NC formation which may then enable the fabrication of $Ge:SiO_2$ layers with other interesting and/or desirable properties.

5. Conclusions

In this study we have demonstrated the ability of swift Xe (480 MeV, 10^{12} cm^{-2}) ion irradiation to modify and/or create new Ge nanocrystals in $Ge:SiO_2$ films with variable Ge contents. In particular, a high concentration of NCs with a size of 2–5 nm was revealed in layers of irradiated and subsequently annealed (at 500 °C) films. Without irradiation, only amorphous Ge inclusions were observed in layers that were annealed under the same conditions. For non-irradiated and irradiated samples that were annealed at 600 °C we found a higher concentration of Ge NCs with NC size of 5–8 nm for the irradiated sample. This is in comparison with the non-irradiated sample where the NC size was found to be 8–15 nm. Hence, swift heavy ion irradiation appears to be promising for the formation of higher concentration of small-sized Ge nanocrystals. The understanding of the fundamental mechanisms that control the properties of nanocrystalline films, which are modified with high-energy ions, may give us the key to the alteration of the properties of nanoscale materials and lead to the solution of various problems that are encountered in the applications of such materials. In particular, high-energy ion irradiation can be used as a tool for 3D structuring of composite materials allowing the control of the NCs' size, and/or their atomic plane orientation.

Acknowledgments

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