

Study of Stress Evolution of Germanium Nanocrystals embedded in Silicon Oxide Matrix

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Abstract—Germanium (Ge) nanocrystals had been synthesized by annealing co-sputtered SiO₂-Ge in N₂ and/or forming gas (90% N₂ + 10% H₂) at temperatures ranging from 700 to 1000°C from 15 to 60 min. It was concluded that the annealing ambient, temperature and time have a significant influence on the formation and evolution of the nanocrystals. We also showed that a careful selective etching of the annealed samples in hydrofluoric solution enabled the embedded Ge nanocrystals to be liberated from the Si oxide matrix. From the Raman results of the as-grown and the liberated nanocrystals, we established that the nanocrystals generally experienced compressive stress in the oxide matrix and the evolution of these stress states was intimately link to the distribution, density, size and quality of the Ge nanocrystals.

Index terms—Germanium nanocrystals, hydrogen reduction, stress

I. INTRODUCTION

The observation of visible photoluminescence from nanometer scale germanium (Ge) crystals embedded in silicon (Si) oxide matrix has spurred intense research interest in this subject area mainly due to the potential electronics and optoelectronics applications [1,2]. However, an area that is relatively unexplored in the research of Ge nanocrystals in Si oxide matrix is regarding the stress experienced by the nanocrystals in such system. Wellner *et al.* [3] had concluded that the Raman peak position of results of Ge nanocrystals in Si oxide was strongly affected by compressive stress. The Ge nanocrystals were obtained from annealing Si oxide layers implanted with Ge. The group of Sharp has recently reported results [4,5] on the mechanism of stress relaxation in Ge nanocrystals embedded in Si oxide. Again, the samples were oxide layers implanted with Ge. We have observed changes in the Raman peak position in our cosputtered samples when annealed under different conditions [6] and attributed this to either the variation in the Ge nanocrystal size or stress. In this paper, we report a comprehensive study on the development of stress experienced by Ge nanocrystals in Si

oxide matrix using a combination of Raman and transmission electron microscopy techniques. We have followed the procedure outlined by Sharp *et al.* [4] to secure free standing Ge nanocrystals from those originally embedded in Si oxide matrix. This enables us to examine the effect of the compressive stress exerted on the nanocrystals on the Raman spectra independent of the size effect. Following which, we obtain data on the hydrostatic pressure exerted on the nanocrystals by the Si oxide matrix and discuss the origin of such stress.

II. EXPERIMENT

Samples were cosputtered in argon at ambient temperature. The target was a 4 in. SiO₂ disk with two pieces of Ge (99.999% pure, 5 mm × 10 mm × 0.3 mm) attached. The argon pressure and rf power were fixed at 3×10⁻³ mbar and 100 W, respectively. The Ge, GeO₂ and GeO_x concentrations were estimated to be ~ 7, 46 and 47%, respectively by x-ray photoelectron spectroscopy technique. The thickness of our samples was approximately 280 nm. The annealing was carried using a conventional furnace at temperatures ranging from 600 to 1000°C for duration of 15 to 60 mins. Annealing was carried out in either a N₂ or forming gas (10%H₂+90%N₂) ambient. The TEM experiments were carried out using a field emission gauge system with an operating voltage of 300 kV.

III. RESULTS & DISCUSSIONS

The Raman spectra of our samples annealed in N₂ between 700 to 1000°C for 15 mins were featureless indicating no formation of Ge nanocrystals. This is reasonable as in the present set of samples the absolute Ge content is low even after all the Ge oxides had been reduced. Thus the Ge atoms are unable to overcome the barriers to nucleation. We have, in fact, prepared samples with a higher absolute Ge content and found that it was possible to form Ge nanocrystals without hydrogen [6,7].

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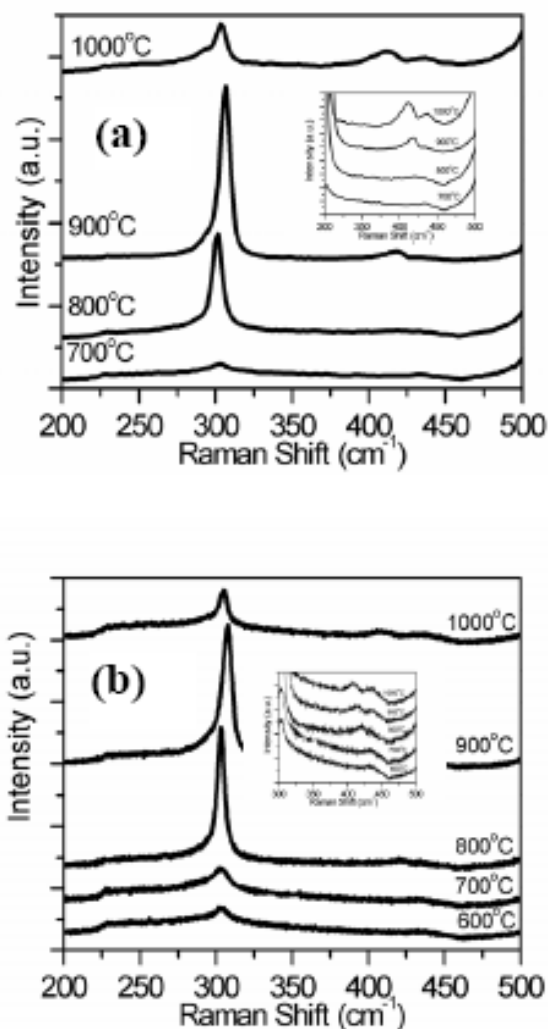


Fig. 1. Raman spectra of samples annealed between 700°C to 1000°C in forming gas for (a) 15min and (b) 60 min. The inset shows the growth of the low frequency Si peak between 300 to 500 cm^{-1} , with increase in annealing temperature due to the localized Si-Si optic mode in near vicinity of Ge atoms.

On the other hand, it has been suggested that [8,9] H_2 can assist in the formation of Ge nanocrystals in Si oxide matrix as H_2 can (i) act as reductant for germanium oxides and provide elemental Ge for nanocrystal formation and (ii) increase the diffusivity value of Ge atoms in silicon oxide matrix via the formation of hydroxyl groups in the oxide. The hydroxyl groups will act as network modifier and open up the oxide structure thus enhancing the diffusivity of Ge [10]. In addition, the increase in the diffusivity of Ge can also be due to the formation of volatile fast diffusing GeH_x species when annealed with H_2 . Therefore, we performed the annealing of our samples in forming gas.

Figures 1 (a) and (b) show the Raman spectra of samples annealed between 700 to 1000°C in forming gas for 15 and 60 mins, respectively. Figure 1(a) shows that a small peak at 305 cm^{-1} is observed for sample annealed at

700°C, indicating the growth of Ge nanocrystal in the oxide matrix. The peak intensity increases and the peak position moves to higher wavenumber as the annealing temperature increases from 800 to 900°C. The peak intensity reduces drastically coupled with a shift to a lower wavenumber for the peak position when the sample was annealed at 1000°C. Figure 1(b) shows that when annealing time increases to 60 minutes, the variation of the peak intensity and position with respect to annealing temperature follow exactly those shown in Fig. 1(a) except that nanocrystal growth can be observed at a lower temperature of 600°C with the increase in annealing time.

Figures 2(a) and (b) show the cross section TEM images of samples annealed at 900 and 1000°C in forming gas for 15 mins, respectively. It can be seen from Fig. 2(a) that Ge nanocrystals can be found in a region near the middle of the oxide layer for sample annealed at 900°C. The number of nanocrystals reduced drastically for samples annealed at 1000°C. Apparently, at 1000°C the rate of diffusion of Ge away from the silicon oxide matrix is faster and it dominates over the nucleation rate of Ge. At 900°C, the nucleation rate is faster than the rate of diffusion of Ge.

We have previously showed that with high temperature annealing in N_2 , Ge atoms near the sample surface will outdiffuse into the ambient due to the low solubility of Ge in Si oxide. Ge atoms will also diffuse into the Si substrate for those located near the Si substrate as Si and Ge are totally miscible. With H_2 in the annealing ambient, we expect the diffusivity of Ge atoms to increase to enhance nucleation.

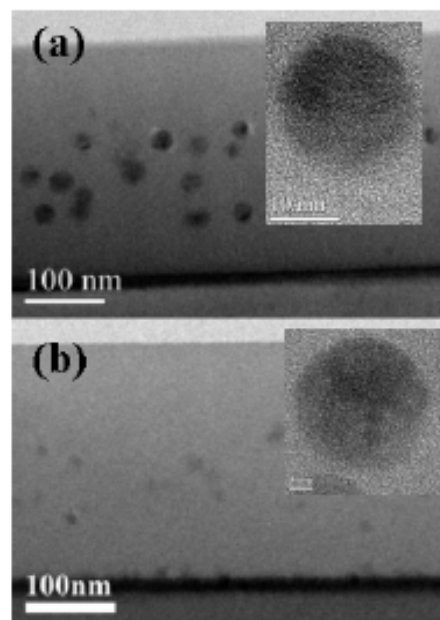


Fig. 2. TEM micrographs of samples annealed at (a) 900°C and (b) 1000°C in forming gas (10% H_2 , 90% N_2) for 15min. The insets are the high magnification TEM micrographs of the Ge nanocrystals from the corresponding samples.

When the sample was annealed at 900°C, the increase in the Ge atom diffusivity, as a result of the introduction of H₂, will increase the opportunity for nucleation even though the Ge content of our sample is comparatively low; as a result, nanocrystals can be observed in Fig. 2(a). The insets in Figs. 2(a) and (b) show the high magnification images of nanocrystals found in the oxides. The nanocrystals synthesized by annealing at 900°C are spherical and show good crystallinity with clear lattice fringes. The nanocrystals annealed at 1000°C, while spherical, is polycrystalline in nature and exhibits twinned structure thus indicating defective growth.

There are two factors here that can affect the growth of nanocrystals, the ambient (H₂) and temperature. When annealed below melting point of Ge (937°C) in H₂ ambient, it helps in the reduction of Ge oxides, and also the diffusivity of Ge atoms increases such that the nucleation rate is enhanced leading to a higher density of nanocrystals. However, with this increase in diffusivity, there will be some degree of outdiffusion when annealed at 900°C, as clearly shown in the two denude regions (near the oxide silicon interface and near the sample surface) of Fig. 2(a). When annealing is performed at 1000°C, the diffusivity of Ge atoms will increase drastically as it will be in the molten state and assisted by H₂. This leads to fewer and smaller nanocrystals in the oxide matrix. This significant increase in diffusivity enables the majority of the Ge atoms to outdiffuse into the ambient or into the Si substrate. This severely depletes the absolute Ge concentration in the Si oxide matrix and increases the barriers to nucleation significantly. As a result, very few nanocrystals can be observed in Fig. 2(b).

In both cases, there is a significant Ge pile-up near the Si-Si oxide interface. More nanocrystals can be found adjacent to the Ge layer inside the oxide for the sample annealed at 1000°C, probably due to the large increase in the Ge atom diffusivity. The huge increase in Ge diffusion towards the Si substrate, when annealing is performed at 900 and 1000°C, will result in Si-Ge bonds being formed at the Si surface. This accounts for the very clear Raman peaks at ~ 410-440 cm⁻¹ shown in the insets of Fig. 1. The intensity of these peaks becomes more prominent as the annealing temperature increase. These peaks are due to the localized Si-Si phonon mode (from the substrate) in the near vicinity of Ge atoms (due to diffusion when annealed at elevated temperatures) [11].

As mentioned earlier, we followed the method suggested by Sharp *et al.* [4] to obtain free standing Ge nanocrystals. With careful control of etching of the Si oxide layer using diluted hydrofluoric acid, free standing Ge nanocrystals were obtained. Typical Raman spectra of a pre- and post etched annealed samples are shown in the inset in Fig. 3. From the shift in the Raman peaks between the pre- and post-etched samples, it suggests that the nanocrystals experienced compressive stress.

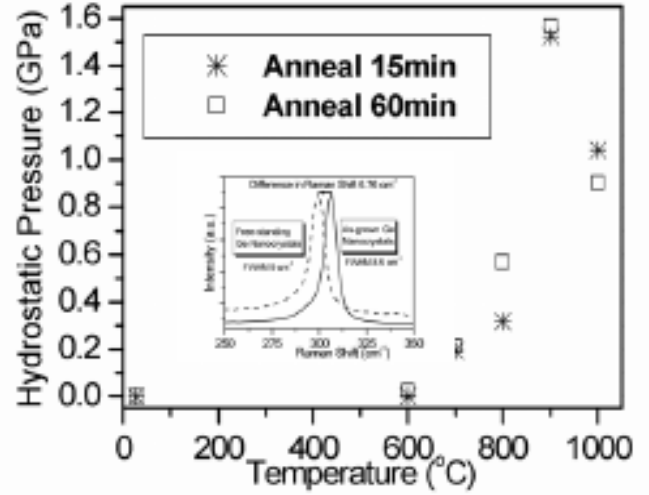


Fig. 3. Hydrostatic pressure (P) experienced by Ge nanocrystals embedded in Si oxide matrix as a function of annealing temperature. The inset shows a set of typical Raman spectra of samples annealed for 15min at 900°C before and after selective oxide matrix removal.

The stress could come from (i) the pressure exerted on the nanocrystal surface by the Si oxide matrix due to volumetric expansion of Ge (~6%) [3] when it solidifies from the liquid to the solid phase, and (ii) the fast growth rate experienced by the nanocrystals as a result of enhanced diffusivity (with the introduction of H₂ in the annealing ambient). By comparing the Raman spectra of our pre- and post-etched annealed samples, the hydrostatic pressure, P , in the nanocrystals can be estimated as [12]:

$$P = \frac{\omega_{embedded} - \omega_{etched}}{3\gamma\omega_0(S_{11} + 2S_{12})} \quad \text{Eqn. 1}$$

where $\omega_{embedded}$ and ω_{etched} are the Raman peak positions of the nanocrystals embedded in Si oxide and free standing Ge nanocrystals, respectively and ω_0 is the Raman peak position of and bulk Ge, $\gamma = 0.89 \text{ cm}^{-2}$ is the mode-Grüneisen parameter [12], S_{11} and S_{12} are components of the elastic compliance tensor with $S_{11} + 2S_{12} = 0.44 \times 10^{-12} \text{ dyn}^{-1} \text{ cm}^2$.

The values of P for our samples annealed under different conditions are plotted in Fig. 3. It can be seen that P increases gradually from 0 to 0.32 GPa as the annealing temperature increases from 600 to 800°C for an annealing duration of 15 mins. There is a sharp increase in the value of P to 1.52 GPa when the annealing temperature increases to 900°C follow by a drastic reduction to 1.04 GPa at an annealing temperature of 1000°C.

Our Raman results in Fig. 1 indicate that nanocrystals started to form at 700°C, and the number of nanocrystals reached a maximum at 900°C. This has been confirmed by the TEM results in Fig. 2. As the number of nanocrystals embedded in a fixed volume of Si oxide increases, it is reasonable to expect that greater compressive stress will be exerted on the nanocrystals. Our TEM image of the sample

annealed at 800°C for 15 mins show small (~5 nm in diameter) nanocrystals embedded in the bulk of the silicon oxide matrix. As the size of the nanocrystals was smaller compared to those annealed at 900 or 1000°C, the compressive stress is therefore smaller as it would be relatively easy for the oxide matrix to accommodate these nanocrystals. The reduction in the P value (see Fig. 3) for samples annealed at 1000°C from that annealed at 900°C is due to the large reduction in the number of nanocrystals in the sample annealed at 1000°C.

Note that when annealed at 1000°C, the viscosity of Si oxide would decrease and this will assist in the relief of stress for the nanocrystals. This will also contribute to the reduction in P for the sample annealed at 1000°C. It is also pertinent to note that our TEM images have shown that defective nanocrystals with multiple twinning and single crystalline nanocrystals were obtained from the sample annealed at 1000°C and 900°C, respectively. Again, the defective nature of the 1000°C annealed nanocrystals will provide another conduit for stress relief.

In Fig. 3 for samples annealed at 800°C, the diffusion length ($\propto t^{1/2}$) would be doubled when the annealing time was increased from 15 to 60 minutes. We have indicated earlier that as nucleation is dominating at this temperature, the nanocrystals would grow and increase in number as the annealing duration increases. This causes an increase in P in Fig. 3. At 900°C, the slight increase in the value of P means that nanocrystals will only grow slightly. At 1000°C, an increase in annealing duration will result in even more Ge diffusing away from the silicon oxide matrix and thus further reducing the number of nanocrystals. This explains the reduction in the P value when one compares the samples annealed at 1000°C for 15 and 60 mins.

IV CONCLUSION

It has been shown from our Raman and TEM results that the annealing ambient (e.g., H_2), temperature and duration play a significant role in the formation, growth and evolution of Ge nanocrystals in Si oxide matrix. It has also been established that the compressive stress experienced by the nanocrystals in the oxide matrix is intimately link to the density, size and crystal quality of the Ge nanocrystals.

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