We have synthesized Ge nanocrystals on co-sputtered Ge + SiO$_2$ films using Rapid Thermal annealing (RTA). The RTA temperature ($T_p$) was varied from 500 °C to 1200 °C and the RTA duration was 300s. The investigation of nanocrystals was made from the Transmission Electron Microscope (TEM), High Resolution Electron Microscope (HREM) images, and Raman Spectra. The sizes of the nanocrystals were quantified in the range of 20 to 80 Å for the increase of RTA temperatures from 750 to 1000°C.

5.1. Sample Details

The samples were co-sputtered in Argon ambient temperature using an ANELVA Sputtering System (SPH-210). The target was a SiO$_2$ of 4" diameter with 4 pieces of Ge (99.999% pure, 10mm x 10mm x 0.3mm) attached. The Argon pressure and rf power were fixed at $3 \times 10^{-3}$ mbar and 100 W respectively. The thickness of our samples was kept constant at 1500 Å.

RTA was carried out in Argon ambient using an A.S.T. Rapid Thermal Processor (Model: SHS 10). In our present work, the samples were annealed with $T_p$ varied from 500 to 1200 °C for 300s, and the RTA ramp-up and ramp-down rates were fixed at 50 °C/s.

For the study of phonon confinement theory, with the present sputtering conditions, the RTA temperature was maintained at 800°C and the average size of Ge nanocrystals was controlled by varying the volume ratio of Ge to SiO$_2$. To vary the volume ratio of Ge to SiO$_2$, the number of Ge targets on the SiO$_2$ target at the moment of sputtering was varied from 2 to 10. We have not exactly determined the concentration of Ge in the samples. Therefore, in this thesis, we
use the number of Ge targets during the sputtering to specify the sample instead of the concentration of Ge in the film.

5.2. Sample Characterization

The TEM experiments were carried out using a Philips CM300 FEG system with an operating voltage of 300 kV. The High-Resolution Electron Microscopic (HREM) images were obtained by operating a JEM-200 CX electron microscope at 200 kV. Throughout this work, the average sizes and number of crystallites were determined directly from TEM images.

Room temperature conventional back scattering Raman and Photoluminescence measurements were carried out at the same spot of the samples using 488 nm line of Ar⁺ ion laser as an excitation source. The spectra was recorded using a SPEX Raman Spectrometer equipped with a double monochromator and multichannel detection system.

5.3. Results and Discussion

5.3.1. Growth of Ge nanocrystals

Figure 5.1 shows a TEM image and a HREM image for an as-deposited film obtained by placing 4 Ge targets on the SiO₂ during the sputtering. The TEM pattern in 5.1 (a) is a halo, which is very similar to that of amorphous Ge (a-Ge). The High Resolution image in (b) shows no clear lattice fringes of crystallites. These results indicate that in as-deposited films, Ge nanocrystals do not exist and Ge atoms are supposed to be incorporated into SiO₂ matrices in form of monomer, dimmer trimmer or large clusters.
The purpose of this work is to observe the growth of nanocrystals over a wide area of the samples. For this purpose, dark field images with a lower magnification may be useful rather than high-resolution images. Figure 5.2 shows Electron Diffraction patterns and dark field images of an as-deposited sample (a) and samples annealed at $T_a = 600^\circ$C (b), $700^\circ$C (c) and $800^\circ$C (d). The samples were obtained by placing 4 targets on the SiO$_2$ target. The dark field image in Figure 5.2(a) shows no distinct structure. This is consistent with the HREM image in Figure 5.1(b). After RTA at $600^\circ$C, a few bright spots appear in the dark field image in Figure 5.2(b). After rapid thermal annealing at $700^\circ$C (Figure 5.2(c)), the number of spots increases and fairly sharp rings appear on the electron diffraction pattern, although the diffuse halo is still superposed on the sharp rings. If the RTA temperature is increased up to $800^\circ$C, the number of the spots (Figure 5.2(d))
increases abruptly. Furthermore, the diffuse halo almost completely disappears and only the sharp rings remain on the electron diffraction pattern.

Figure 5.2 shows Electron diffraction patterns and dark electron micrographs taken before and after thermal annealing; (a) as-deposited, (b) annealed at 600°C and (c) annealed at 700°C (d) annealed at 800°C

Figure 5.3 shows Raman Spectra of Ge embedded in SiO₂ film matrix as a function of Rapid Thermal annealing temperature. As-deposited films show a broad Raman feature centered at 277 cm⁻¹ which corresponds to the amorphous Ge¹. The samples RTA at 600°C also show a broad Raman centered ~ 285 cm⁻¹. Films RTA at 700°C indicate a sharp peak at 300.5 cm⁻¹ due to crystalline Ge which indicate the initiation of crystallization process. A broad shoulder however, can be seen over the low frequency side. Films RTA at 750°C show a very large asymmetrical broadening which can be because of the both sharp peak and broad shoulder together. Such broad Raman band may be due to the presence of amorphous Ge with Ge nanocrystals. However, it is to be noted that in early reports such broad feature have been discussed in terms of Ge clusters of size less than 2 nm. Ovsyuk et al.² prepared Ge nanocrystals in GeO₂ films. In their annealing study a broad shoulder over the low frequency side was observed. Similar observation was reported by Fuji et al.³ and claimed as the Ge clusters are...
Fig. 5.3. Raman spectra of Ge embedded in SiO\textsubscript{2} matrix as a function of RTA temperature. (RTA for 300 Sec)

responsible for such Raman feature. Our photoluminescence studies in these samples (700 and 750°C) also indicate that the Ge is in different form from that of amorphous. The as-deposited films are amorphous and did not show any luminescence, whereas, the films annealed at 600°C and higher are luminous. Further Rapid Thermal Annealing at higher temperatures (800-1000°C) result in a
sharp Raman peak with asymmetrical broadening over the low frequency side of the spectra as seen in figure 5.3. The Raman line shape clearly indicates the formation of nanocrystals. The RTA dependence of the Raman spectrum depends on the Ge concentration in films. We found that as the Ge concentration decreases, RTA at a higher temperature is necessary to obtain samples showing the sharp peak on the Raman spectrum. For example, the sample obtained by placing 7Ge targets on the SiO₂ target during sputtering shows the sharp Raman peak for T₀ = 500 °C. In contrast to this, the sample obtained by placing 3 Ge targets does not show the sharp peak until T₀ is raised to 800 °C. All the samples prepared showed the sharp peak for T₀ = 800 °C. However, under our experimental condition (annealing time of 300s) T₀ = 800 °C is a necessary and sufficient condition to prepare samples containing no clusters.

In the preceding subsection, we concluded that RTA at 800 °C for 300s is necessary to prepare good nanocrystalline samples. To examine the crystallinity, size and shape of the nanocrystals in detail, we performed HREM study of the films RTA at 800 °C for 300s. Figure 5.4 shows the results of electron diffraction (a), and HREM (b) and (c) studies for a sample obtained by placing 2 Ge targets on the SiO₂ target. The electron diffraction pattern shows sharp rings corresponding to those of bulk Ge with the diamond structure. Therefore, the dark patches seen in Fig. 5.4(b) are the Ge nanocrystals grown in the SiO₂ matrix. Figure 5.4(c) clearly shows the lattice fringes inside Ge nanocrystals. From the distance between the fringes (0.33 nm) and the angle between the crossed fringes (70.5°), we can identify them fringes with the {111} planes of the diamond structure. Each nanocrystal is a single crystal and the crystallinity is rather good. Almost all nanocrystals do not have any dislocations.
Fig. 5.4  Electron diffraction pattern, (a), and high resolution Electron micrographs, (b) and (c), for Ge microcrystals embedded in SiO<sub>2</sub> film. (c) is an enlarged image of the area indicated in (b) at 800°C (RTA for 300 Sec)
Fig. 5.5. Representative size distribution of Ge microcrystals embedded in SiO₂ thin films. The size was measured directly from high resolution electron micrographs.

Figure 5.5 shows the size distribution of nanocrystals obtained from the HREM image shown in Fig. 5.4. The average size is 6.1 nm with the standard deviation of 1.7 nm. From Figures 5.4 and 5.5, we can conclude that the good crystalline samples which contain nanocrystals with good crystallinity and narrow size distributions, can be prepared by the rf co-sputtering and RTA at 800 °C.

5.3.2. Size dependence of Raman Scattering

In this section, we discuss the size dependence of the Raman Spectrum. All the data shown here are for the samples RTA at 800 °C for 300s for which Ge is in nanocrystalline structure. Figure 5.6 shows the spectra observed for the nanocrystals together with that of bulk Ge crystal. On the right-hand side of the
corresponding sample is given. The full width at half maximum (FWHM) of each peak is also given in the figure.

![Graph of Raman spectrum for Ge nanocrystals]

**Fig. 5.6.** Size dependence of Raman spectrum for Ge nanocrystals embedded in SiC thin films rapid thermally annealed at 800°C for 300 sec together with the spectrum of bulk Ge crystal

The sample with d = 15nm shows a relatively sharp peak at 300 cm\(^{-1}\). As mentioned earlier, this peak is assigned to the Ge nanocrystals embedded in the SiO\(_2\) matrix. The spectrum is very similar to that of the bulk Ge crystal, which shows a sharp peak at 298 cm\(^{-1}\) with the FWHM of 3.2 cm\(^{-1}\). As the size decreases, modifications of the spectral shape can be observed. First, the intensity of the peak decreases although the total volume of Ge in the samples is almost
the same. Secondly, the FWHM increases gradually and becomes $9.8 \text{ cm}^{-1}$ for the average size of 6.1 nm; the width is about three times larger than the bulk value. Thirdly, the peak slightly shifts to higher frequencies. Lastly, a broad tail appears at the low frequency side of the peak, and the peak becomes asymmetric.

![Plot of FWHM (a) and peak frequency (b) as a function of the particle size. Closed circles are experimental data and solid curves represent the calculated results.](image)

**Fig. 5.7.** Plot of FWHM (a) and peak frequency (b) as a function of the particle size. Closed circles are experimental data and solid curves represent the calculated results.
In figure 5.7, the FWHM and the peak frequency are plotted as a function of the particle size. Solid lines are results of theoretical calculations explained later. The FWHM strongly depends on the particle size, while the size dependence of the peak frequency is very small.

5.3.3. Comparison with Phonon Confinement Theory.

In a semiconductor nanocrystal, a phonon can no longer be described by a plane wave, but described by a wave packet localized inside the nanocrystal. As a result, not only q = 0 phonons but also phonons with a certain momentum near the center of the Brillouin zone can contribute to the first order Raman scattering. In other words, the wave vector selection rule during the Raman scattering process is partially broken down by the phonon confinement. Since the phonon dispersion curves are not flat, the Raman peak will shift, broaden and become asymmetric by the phonon confinement.

Based on the concept described above, Nemanich et al., Richter et al., and Campbell and Fauchet have derived formulae which describe the lineshapes of low dimensional materials. These formulae have often been applied to the Raman results of nanocrystalline Si films and the calculated Raman lineshapes have generally been in good agreement with the experimental ones. In order to explain the size dependent spectral changes observed in this work, we have calculated the Raman lineshape using the following expression given by Campbell and Fauchet:

$$I_\omega (\omega) = \int_0^{q_{\text{max}}} \frac{d^3 q}{[\omega - \omega (q)]^2 + (\Gamma_0/2)^2} \left| C(0,q) \right|^2$$

where $\omega(q)$ is the phonon dispersion relation, $\Gamma_0$ is the natural linewidth and $C(0,q)$ is a Fourier transform of a phonon confinement function.
Campbell and Fauchet\textsuperscript{6} proposed three different types of confinement functions, and compared the calculated spectra with the experimental ones. They concluded that the Gaussian confinement function

$$W(r) = \exp\left(-\alpha \frac{r^2}{L^2}\right)$$

is the most suitable one; where L is a nanocrystalline diameter, r is a distance from the center of the nanocrystals and \(\alpha\) is a coefficient explained below. Richter et al.\textsuperscript{5} also adopted the Gaussian confinement function and they selected 2 as the coefficient \(\alpha\). In this case, the phonon amplitude reduces to 1/e at the surfaces of nanocrystals. Campbell and Fauchet\textsuperscript{6} considered that the phonons might be confined in the subregion of the nanocrystals and selected \(8\pi^2\) as the coefficient \(\alpha\). In this case, the phonon amplitude becomes nearly 0 at the surfaces of nanocrystals.

In order to obtain a theoretical Raman lineshape, we must integrate equation (1) over the entire Brillouin zone. However, the integration is difficult because of the anisotropy of the phonon dispersion relations. As long as the particle size remains large enough, significant contribution to the integral comes from a relatively small region at the center of the Brillouin zone and the anisotropy in that region is not so large. Therefore, we can assume that the Brillouin zone is spherical and the phonon dispersion curves are isotropic. In actual calculations, we used Campbell’s confinement function together with the dispersion relation. The phonon dispersion curve was taken from the Neutron Scattering data of Nilsson et al.\textsuperscript{10} With this choice of the dispersion curve, the calculated Raman lineshape depends most drastically on the size. Therefore, the results of our calculation give an upper bound of the size dependent shift and broadening of the Raman peak.

Figure 5.8 shows a comparison between a measured and calculated spectrum. Solid line is the measured spectrum and dashed line is the calculated spectrum. The experimental spectrum is that for sample with the average size of
7.7 nm. As will be shown in Fig. 5.7 (b) the peak frequencies of the calculated spectra are much lower than those of experimental ones. Therefore, in order to compare the spectral shape, the calculated spectrum is shifted to align it with the measured one. In figure 5.8, we can see that the agreement of the lineshape is fairly good around the peak.

![Graph](image-url)

**Fig. 5.8** Comparison of measured and calculated Raman spectra for d=7.7nm

The solid lines in Fig. 5.7 show the FWHM and the peak frequency of the calculated spectra as a function of the particle size. The FWHM increases as the size decreases, while the peak frequency decreases. In figure 5.7 (a), a fairly good agreement of the FWHM between the experimental and calculated Raman peaks can be seen, although the experimental values are always slightly lower than the calculated results. In contrast to this, the agreement is very poor for the peak frequency. The calculations predict low-frequency shifts (red shift) as the size decreases, while the experimental results show small high-frequency shifts (blue shift).
We should note that the model used for the calculation is essentially qualitative and quantitative discussion is not so meaningful. In fact, as described above, the result of the calculation is very sensitive to the choice of the confinement function. For example, in the present calculation, the peak frequency of nanocrystal with 6nm in diameter is about 5 cm⁻¹ lower than the bulk peak frequency (300 cm⁻¹), but the frequency obtained using Richter’s confinement function is only about 1 cm⁻¹ lower than the bulk value. Therefore, the quantitative difference of the peak frequency between experimental and calculation is not important. The most important experimental result is that our samples do not show any low frequency shifts (red shift) predicted by the calculations.

The possible reason for the discrepancy in the experimental and calculated size dependence of the peak frequency is the compressive stress present in the nanocrystals. The origin for the compressive strain is due to the difference in the distance between the nearest neighbour of Ge and SiO₂.

In order to estimate the nanocrystal sizes, the Raman line broadening (Γ) of the experimental and theoretical values are compared. The calculated values of Γ as a function of nanocrystal size is shown in Figure 5.9. From Figure 5.10 it is seen that we get approximately the same Raman line broadening for the samples annealed at RTA temperatures from 600 to 1000°℃. From the comparison of calculated and measured Γ values the nanocrystals sizes were quantified in the ranges of 20 to 80 Å for the increase of annealing temperature from 750 to 1000°℃. Figure 5.11 shows the nanocrystal size as a function of annealing temperatures.
Fig. 5.9. Calculated Raman line broadening as a function of nanocrystal size.
Fig. 5.10. Raman spectra of Ge nanocrystals with different size.
Fig. 5.11. Nano crystal size dependence on RTA Temperature
5.4. Conclusion

We have synthesized Ge nanocrystals on co-sputtered Ge + SiC films using Rapid Thermal annealing (RTA). The RTA temperature (Tp) was varied from 500 to 1200 °C and the RTA duration was 300 s. The structural properties of the Ge nanocrystals synthesized by the RTA were characterized by Transmission Electron Microscope (TEM), Raman Spectroscopy and High Resolution Electron Microscope (HREM). Our TEM pictures showed that the Ge nanocrystals were spherical and evenly distributed in films at 800°C. From the Raman spectra obtained, it was shown that the crystallization process was initiated for the samples rapid thermal annealed at 700°C and pure nanocrystals were obtained for RTA temperatures of 800°C and higher. Phonon confinement theory was studied and the estimated nanocrystal size are found to vary between 20 and 80 Å for the increase of RTA temperatures from 750 to 1000°C. From HREM study, it was shown that the good crystalline samples which contain nanocrystals with good crystallinity and narrow size distributions, can be prepared by the rf co-sputtering and RTA at 800°C for 300s. Hence it is shown that RTA is highly suitable for synthesizing semiconductor nanocrystals.
References