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Formation of Ge nanocrystals and SiGe in PECVD grown SiN_x:Ge thin films

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Abstract

Formation of Ge nanocrystals in SiN_x matrices has been studied using plasma enhanced chemical vapor deposition in both as deposited samples as well as in post-vacuum annealed samples. Low temperature and short duration anneals in vacuum resulted in Ge nanocrystals whereas prolonged anneals at higher temperatures resulted in Ge nanocrystals accompanied with SiGe formation at the SiN_x/Si interface. Raman Scattering Spectroscopy was extensively used to track the formation of various phonon modes during the diffusion of Ge through SiN_x and into the Si substrate.

Keywords: Raman Scattering Spectroscopy; Ge nanocrystals

1. Introduction

Interest in silicon (Si) and germanium (Ge) semiconductor nanocrystals has recently received considerable attention for both fundamental and technological reasons [1,2]. Due to the possibility of integration with advanced Si-based microelectronics, the case of silicon (Si) and germanium (Ge) nanocrystals has added importance. Bulk Si and Ge are indirect gap materials, which makes them poor light emitters restricting their use in the optoelectronic devices. However, there are studies that suggest that the reduction of size down to the nanometer scale would make nanoscale Si and Ge efficient light emitters. Work on Si nanocrystals in various matrices has already led to much higher efficiencies and to tunable light emission in the visible part of the spectrum [3].

Ge nanocrystals in SiO_x matrices have been fabricated and studied with various techniques. In all of these approaches Ge nanocrystals of varying dimensions were obtained. Both TEM work and Raman scattering have proved valuable in tracking the nanocrystal formation. Ge nanocrystals in SiO_x matrices have also shown promise in flash memory applications. However, efficient PL from Ge nanocrystals in SiO_x is still difficult to obtain, possibly due to traps [4]. This and the possibility of host matrix dependent optical and electronic properties, makes fabrication of Ge nanocrystals in different dielectric matrices attractive. SiN_x is a material with a higher elastic modulus than SiO_x and has a higher dielectric constant. Fabrication of Ge nanocrystals in SiN_x matrices is interesting due to several points raised above. However, very little has been done in this area. Qu et al. [5] have reported fabricating Ge

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quantum crystallites in a-SiN_x matrices using PECVD. They have used FTIR spectroscopy to observe the presence of Ge–N, Si–Si, Si–N and Si–Ge bonds. Their scant Raman data indicate the presence of Ge–Ge modes. In a separate report [6] the same team reported detailed X-ray data and little else. In this work, we prepared Ge nanocrystals in SiN_x matrix using PECVD and studied both the as-grown as well as furnace annealed samples using Raman scattering and photoluminescence measurements.

2. Experimental procedure

The germanosilicate films were grown in a PECVD reactor (PlasmaLab 8510C) on Si substrates using 185 sccm SiH_4 (2% in N_2), 45 sccm NH_3 and varying flow rates of GeH_4 (2% in He) as precursor gases, at a substrate temperature of 350 °C, a process pressure of 1000 mTorr under an applied RF power of 10 W. The samples were then annealed both under nitrogen and in vacuum environment in a quartz oven at temperatures ranging from 700 to 1000 °C for 15–60 min. The thicknesses of the films were varied between 0.125 and 0.5 μm. Various samples with 90 sccm of GeH_4 flow rate were studied. Raman scattering experiments were carried out using a 1-m double monochromator with GaAs photomultiplier and photon counting electronics. Various lines of an Ar^+ laser, in particular 488 nm, were used to excite the spectra. Care was taken to minimize the heating of the sample during the experiment by using a cylindrical lens to focus the light onto the sample.

3. Results and discussion

Typical Raman spectra of the SiN_x:Ge samples grown with 90 sccm of GeH_4 flow and annealed in nitrogen environment is shown in Fig. 1. As-grown spectra of the samples are typical of silicate and germanosilicate glasses. The spectrum is broad and continuous and has a characteristic feature, on the low wavenumber side centered at ~80 cm^{-1}. We suspect that this is the so-called Boson peak seen in most glasses [7]. Also a broad peak at ~270 cm^{-1} is seen. This peak is indicative of Ge–Ge modes. The fact that it is quite broad suggests that the size of the crystallites is very small, has a large size distribution and is referred to as a quasi-amorphous peak [8]. Annealing at 800 °C for 10 min in vacuum, the Ge–Ge mode at 300 cm^{-1} sharpens and increases in

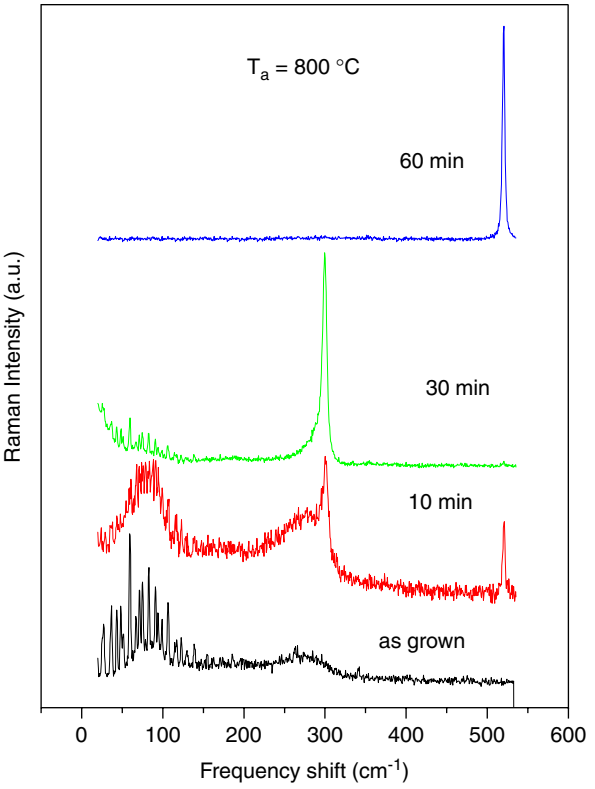

Fig. 1. Raman spectra of SiN_x:Ge films grown with 90 sccm of GeH_4 and annealed in N_2 at 800 °C. Growth of Ge phonon mode at 300 cm^{-1} as annealing time increases is finally quenched due to oxidation of Ge.

intensity, suggesting the onset of Ge nanocrystal formation. Increasing the duration of annealing further to 30 min leads to a narrower Ge–Ge mode observed at ~300 cm^{-1} even more. This suggests that the size distribution has narrowed down and average nanocrystal diameter has increased. Interestingly, longer annealing times over 60 min result in total quenching of the Ge–Ge mode. The peak at 520 cm^{-1} is due to the Si substrate and changes in its intensity are only related to changes in the transparency of the film. The reason for quenching the Ge Raman signal at prolonged anneals can be oxidation of the Ge nanocrystals due to minute amounts of oxygen in the annealing atmosphere. In order to investigate the reason for quenching of the Ge peak, the samples were annealed under vacuum in the 10^{-5}–10^{-6} Torr range. It was seen (see Fig. 2) that the general trend of the data is the same as those samples annealed in nitrogen environment except that for samples annealed in vacuum the Ge–Ge peak at 300 cm^{-1} persists even after annealing for 60 min. The annealing temperature to obtain

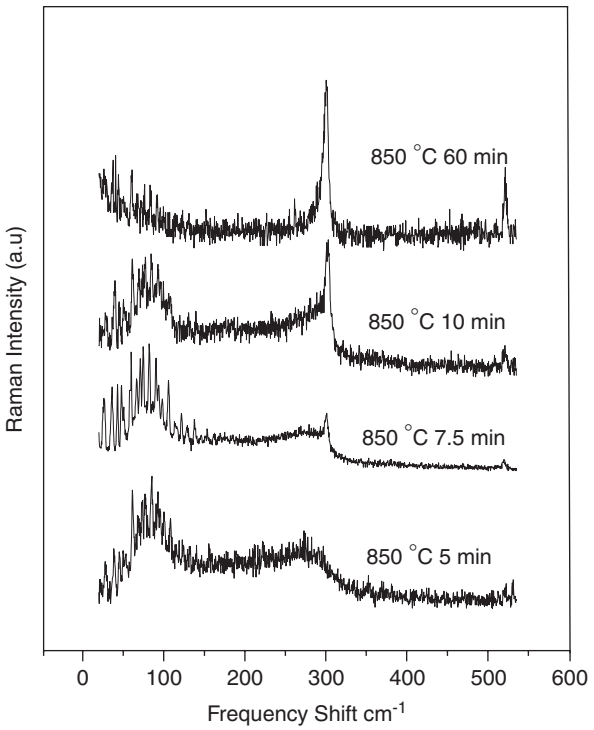

Fig. 2. Raman spectra of SiN_x:Ge films annealed in vacuum at 850 °C for various durations. Growth of Ge phonon mode at 300 cm^{-1} as a function of annealing time observed, without any quenching.

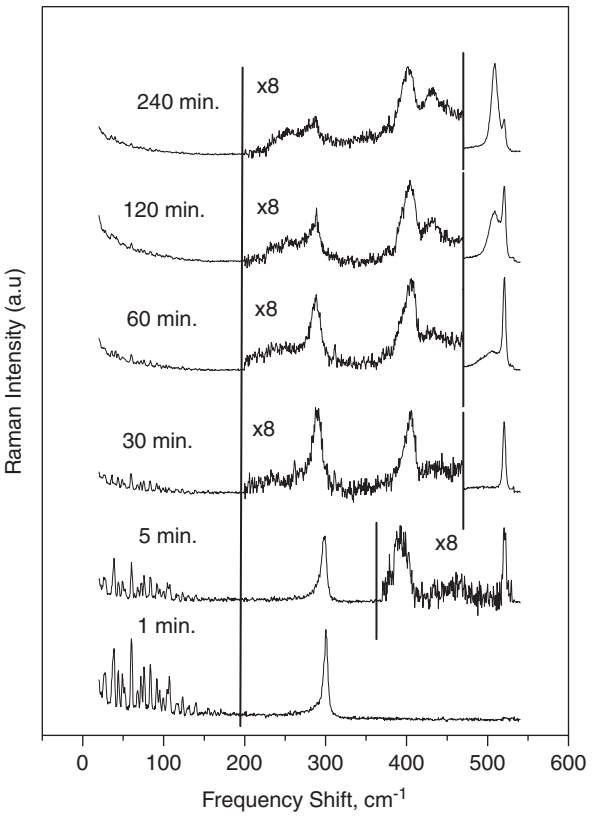

Fig. 3. Raman spectra of samples with prolonged vacuum anneal of SiN_x:Ge films at 1050 °C.

a similar Ge–Ge Raman signal appears to be slightly higher for vacuum conditions than in nitrogen atmosphere possibly due to increased thermal time constants. From these data it is clear that at moderate temperatures of 800–850 °C annealing in vacuum for 10–60 min results in Ge nanocrystals. The size distribution narrows down at longer anneal times, indicating the presence of larger nanocrystals of germanium. Absence of quenching of the Raman peak under vacuum conditions indicates that oxidation can indeed be responsible for the disappearance of nanocrystalline germanium. The phonon confinement model described elsewhere [9] is used to relate the Raman spectra to crystal size distribution. For samples grown with 90 sccm of GeH_4, the Ge nanocrystal sizes range from 6 to 18 nm for anneal times of 7.5–15 min. The full-width at half-maximum of the Ge–Ge mode peak decreases from 8 cm^{-1} down to 6 cm^{-1} when the nanocrystal size becomes 18 nm. The maximum shift of the Ge–Ge peak similarly is of the order of 0.8 cm^{-1} towards lower wavenumbers (Fig. 3).

Prolonged vacuum annealing of SiN_x:Ge films at 1050 °C was also performed. For anneal temperatures of 1050 °C even at 1 min, Ge nanocrystals reorder to display a very sharp Ge–Ge mode at ~300 cm^{-1} with very small size distribution. The opacity of the film does not allow observation of the Si substrate at 520 cm^{-1}. After 5 min of annealing, formation of SiGe formation is observed as indicated by the Si–Ge mode at 420 cm^{-1}. Si phonon line of the underlying substrate also becomes visible at 520 cm^{-1}. Further increases in the anneal time decrease the Ge–Ge mode at 300 cm^{-1} and increase the strength of the Si–Ge peak at 420 cm^{-1}. All this is indicative of diffusion of Ge through the nitride layer and the formation of the SiGe layer at the Si substrate–nitride interface. After annealing for 60 min, broadening and weakining of the Ge–Ge mode continues accompanied by enhancement of the Si–Ge mode. However, a shoulder on the low frequency side of the Si substrate peak at 520 cm^{-1} starts to appear. This is a Si–Si localized vibrational mode (LVM). Longer

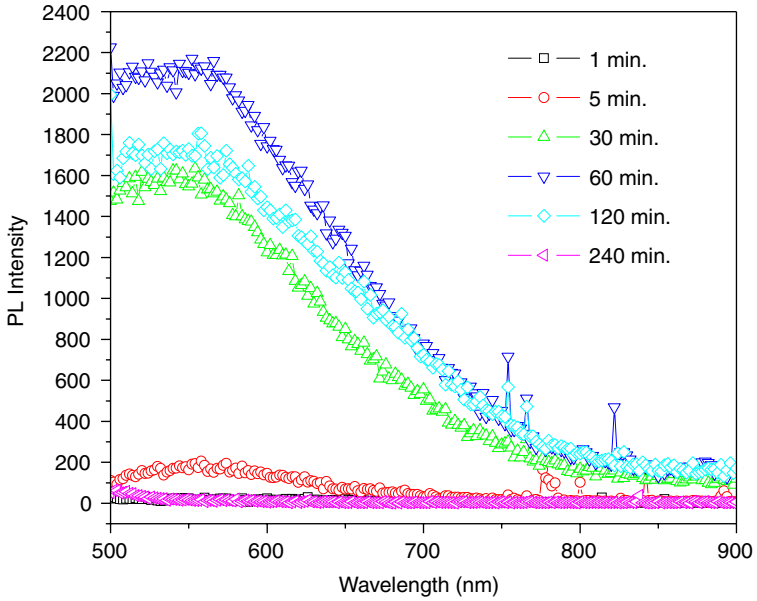

Fig. 4. Visible PL spectra of SiN_x:Ge films annealed at various durations at 1050 °C in vacuum under 488 nm excitation.

anneal times result in further detoriation of the Ge–Ge peak. This may be indicative of Si out-diffusion from the substrate consuming the Ge nanocrystals in the nitride layer. A high-energy shoulder of the SiGe peak develops into a peak of its own when the anneal time reaches 120 min.This is thought to be the Si–Si LVM with more than one Ge in the vicinity [10]. When the anneal time reaches 240 min the Si–Si LVM dominates the Si phonon mode at 520 cm^{-1}. The Ge–Ge at 300 cm^{-1} becomes even broader.

We have also performed photoluminescence experiments on the SiN_x:Ge system (Fig. 4). We find that as-grown samples do not display PL signal. Annealing samples at 1050 °C for durations up to 60 min increase the PL intensity observed. Further increases in the anneal times decreases the PL observed. Finally all the spectra in Fig. 4 have almost exactly the same spectral shape. This is contrary to quantum confined emission behavior. PL emission from quantum confined Ge nanocrystals should shift to longer wavelengths as the anneal times increase since this causes nanocrystal size to increase also. We suspect that the observed PL is due to a defect luminescence center in the blue-green part of the spectrum. At anneal times up to 60 min, diffusion of Ge through the SiN_x film results in defects in the film which give rise to the observed PL. Longer annealing times with perhaps both Ge and Si diffusing through the SiN_x layer give rise to doping of the defect centers or emergence of different defect centers, quenching the observed PL.

4. Conclusions

We have grown SiN_x:Ge thin films using PECVD. Raman scattering was used to monitor the formation of Ge nanocrystals for as-grown and nitrogen and vacuum annealed samples. Prolonged annealing results in the formation of SiGe alloy at the Si substrate–SiN_x interface. This also results in the deterioration of the Ge nanocrystals in the nitride layers. PL spectra obtained from the SiN_x:Ge suggests that luminescence originates from defect centers and is not consistent with the quantum confinement-based luminescence expected from Ge nanocrystals despite the fact that Raman scattering points to their presence.

Acknowledgments

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References

[1] Tiwari S, Rana F, Hanafi H, Hartstein A, Crabbe EF, Chan K. Appl Phys Lett 1996;68:1377.
[2] Kanoun M, Souifi A, Baron T, Mazen F. Appl Phys Lett 2004;84:5079.
[3] Pavesi L, Dal Negro L, Mazzoleni C, Franzò G, Priolo F. Nature 2000;408:440.
[4] Razzari L, Gnoli A, Righini M, Dâna A, Aydinli A. Appl Phys Lett 2006;88:181901.
[5] Qu XX, Chen KJ, Huang XF, Li ZF, Feng D. Appl Phys Lett 1994;64:1656.
[6] Qu XX, Chen KJ, Wang MX, Li ZF, Shi WH, Feng D. Solid State Commun 1994;90:549.
[7] Montagna M, Villiani G, Duval E. J Raman Spectroscopy 1996;27:707.
[8] Rath S, Hsieh ML, Etchegoin P, Stradling RA. Semicond Sci Technol 2003;18:566.
[9] Fujii M, Hayashi S, Yamamoto K. Appl Phys Lett 1990;57:2692.
[10] Alonso MI, Winer K. Phys Rev B 1989;39:10056.