Crystallinity Study of Germanium Nanodots Synthesized via reduction of Si_{0.54}Ge_{0.46} Oxides

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Nanocrystalline germanium (nc-Ge) was synthesized via wet oxidation of rf sputtered Si0.54Ge0.46 films. The films were wet oxidized at 600 °C for 60 min to form Si, Ge, Or, followed by rapid thermal annealing in a N_2 ambient for 300 s at 1000 °C. The heterogeneous growth of nc-Ge in this work is governed by the supersaturation and the diffusivity of Ge atoms during annealing. The degree of crystallization of the nc-Ge is determined by the annealing temperature, duration and cooling rate. Raman spectroscopy indicate that the optimum annealing temperature is 700 °C as this yields nc-Ge with good crystallinity, as seen from the small FWHM of the Ge-Ge Raman peak. When the annealing temperature is set higher or lower than 700 °C, degradation in the film crystallinity is observed from the Raman spectra. A longer annealing duration or a slower cooling rate will also result in films with better crystallinity. The improvement in film crystallinity with longer annealing duration is verified from the TEM electron diffraction patterns

Key words: Silicon Germanium, Nanocrystal, Oxidation, Growth

1. INTRODUCTION

Due to the indirect band gap property of bulk silicon (Si), intense research on nanometer-sized Si crystal structures as light emitting material has been motivated. The discovery of red photoluminescence (PL) from porous Si by Canham has ignited the quest for Si based optoelectronics.¹ However, given the smaller Bohr's radius of Si (~5 nm) as compared to Ge (~24 nm), the latter has notably been receiving attention as another promising candidate. Numerous nc-Ge synthesis methodologies have been proposed. These include co-sputtering², ion implantation³ and reduction of silicon germanium oxides4.

We have previously shown that metal-oxide-semiconductor (MOS) capacitor with nc-Ge embedded within the oxide exhibits charge storage capability.⁵ While it is of great interest to understand the charge storage mechanism, the solution to fabricating good nc-Ge has to be achieved first. Hence, the main objective of this work is to obtain spherical nc-Ge embedded in silica matrix with superior crystallinity and uniform size distribution.

2. EXPERIMENTAL PROCEDURE

The substrates used for the deposition of Si_{0.54}Ge_{0.46} films were p-type silicon wafers with (100) orientation and resistivity of 4-8 Ω -cm. A 5 nm rapid thermal oxide (RTO) layer was grown on the Si substrate via oxidation at 1000 °C for 35 s. A layer of amorphous Si_{0.54}Ge_{0.46} film of ~10 nm was then radio frequency (rf) sputtered in Ar on the RTO at room temperature. The sputtering pressure and rf power were set at 3.3 mTorr and 100 W, respectively. The sputtering target consisted of intrinsic (111) Ge pieces attached to a 4 inch undoped Si wafer. The Ge pieces were evenly distributed across the wafer surface to ensure uniform distribution of Ge in the sputtered Si_{0.54}Ge_{0.46} film. The Ge content was measured using the Rutherford backscattering technique.

Polycrystalline $Si_{0.54}Ge_{0.46}$ films were prepared by annealing the amorphous films in pure N2 ambient at 800 °C for 6 h.⁶ Wet oxidation of the polycrystalline Si0.54Ge0.46 films was carried out in a conventional three zone furnace at 600 °C for 60 min. After the oxidation was completed, a 50 nm layer of capping silicon oxide deposited via sputtering. Nc-Ge was then was synthesized by rapid thermal annealing the structure in pure N₂ using various annealing profiles.

PL measurements, at 1 nm resolution, were carried out at room temperature using a HeCd (325 nm) laser source. Raman spectroscopy was used to monitor the crystallinity of synthesized nc-Ge. The Raman experiments were performed using a Renishaw Raman spectrometer with the 514 nm line of an Ar ion laser as the excitation source. Transmission electron microscopy (TEM) analyses were carried out using a Philips CM300 field emission system at an operating voltage of 300 kV.

3. RESULTS AND DISCUSSION

3.1 Photoluminescence Study

Figure 1 shows the PL spectra of the as-oxidized Si_{0.54}Ge_{0.46} film and films that have been subsequently annealed in pure N₂ for 300 s at various temperatures. Two distinct peaks are observed at ~3.1 eV and ~2.5 eV. The intensity of both the peaks is weak for the as-oxidized samples and increases by a factor of almost five after the films were annealed for 300 s at 800 °C. The peak intensity subsequently reduces for samples annealed at 900 °C and 1000 °C for the same duration.



Fig. 1. PL spectra of as-oxidized $Si_{0.54}Ge_{0.46}$ film and films that have been subsequently annealed in N_2 at various temperatures for 300 s.

Zacharias and Fauchet, having observed similar peaks, suggested that the origin of the 3.1 eV peak is due to oxygen related defects during reconstruction of Ge-O bonds of crystallized hexagonal GeO₂.⁷ This explains the weak blue (3.1 eV) peak observed on the as-oxidized sample as the low oxidation temperature is not sufficient to crystallize the available GeO₂. The orange-green (~2.5 eV) peak may originate from the silica host matrix itself. The Si_xGe_yO_z film formed at a low oxidizing temperature of 600 °C and the sputtered capping oxide are prone to defects created by the nonstoichiometric SiO_x. The broadening of this peak at lower energy is due to the fact that the band gap of the oxygen deficient SiO_x depends strongly on the composition and varies from 1.8 eV to 4 eV.⁸

The decreased intensity of the peaks after annealing at 1000 °C is probably caused by the concurrent reduction of GeO₂ by the nonstoichiometric SiO_x as no known reducing agent such as H₂ was introduced during annealing. As the annealing was carried out at 1 atm in the absence of a reducing agent, direct decomposition of GeO₂ by thermal energy is thermodynamically not feasible. The peak intensity reduction is more pronounced at higher annealing temperature due to the higher reduction rate of GeO₂ by SiO_x. Thus, synthesizing Ge nanodots by annealing at 1000 °C significantly reduces the oxygen related defects in GeO₂ and SiO_x.

3.2 Raman Spectra

Samples were subjected to annealing under different profiles as shown in Fig. 2. All samples were initially annealed for 300 s at 1000 °C as such a temperature has been shown, in section 3.1, to substantially reduce the oxygen related defects. The annealing temperatures that followed after the 1000 °C step were varied at 900 °C, 800 °C, 700 °C and 510 °C for 60 s. The cooling rate for the annealing profiles was set at 30 °C/s. The Raman spectra for the different annealing temperatures are shown in Fig. 3a. The single peak at a Raman shift of



Fig. 2. Rapid thermal annealing profile of the samples.



Fig. 3. Raman spectra of nc-Ge for (a) different annealing temperatures T_s at a fixed duration t of 60 s after the 1000 °C step; (b) $T_s = 700$ °C for various durations t; and (c) different cooling rates.

~300 cm⁻¹ is due to optical phonon scattering of the nc-Ge embedded in the SiO₂ matrix. It is also worth mentioning that the other prominent peak at 400 cm⁻¹, which accounts for optical phonons due to Si-Ge atomic pairs, was not observed for all samples indicating a complete oxidation of the original Si_{0.54}Ge_{0.46} film. The intensity of the peak increases by a factor of 3 as the subsequent annealing temperature T_s was reduced from 900 °C to 700 °C. However, the sample that was annealed at 510 °C shows a reduction in intensity by a factor of 7.5. There is also a variation in the full width at half maximum (FWHM) of the peaks for the different Ts. The FWHM decreases from 9.4 cm⁻¹ to 7.6 cm⁻¹ when T_s was reduced from 900 °C to 700 °C but increases to 12.2 cm⁻¹ when T_s was further reduced to 510 °C. No apparent peak shift is observed for all samples. These observations imply that Ge nanodots grown at 700 °C yield better crystal quality, hereafter known as nc-Ge, as compared to higher or lower annealing temperatures.

In order to further investigate the optimum annealing profile for synthesizing nc-Ge, similar samples were annealed at 1000 °C for 300 s, and the annealing temperature was subsequently reduced to 700 °C for different durations t. The purpose of this experiment is to investigate the effect of annealing time with respect to the crystallinity of Ge nanodots. The Raman spectra of the samples annealed for different duration at 700 °C is shown in Fig. 3b. The crystallinity of the Ge nanodots is determined by the intensity and the FWHM of the peak at ~300 cm⁻¹. The intensity of the peak increases by a factor of 4.5 when the annealing duration changes from 0 s to 60 s. A reduction in FWHM of the peak is observed from 15.8 cm⁻¹ to 7.9 cm⁻¹ as the duration of the annealing increases. These observations imply the improvement in crystallinity of the Ge nanodots as the annealing duration increases. There is a small shoulder at the higher energy side of the 300 cm⁻¹ peak, which indicates a poorer crystallinity of the Ge nanodots. The shoulder becomes less prominent as the annealing time increases, again indicating an improvement in crystallinity.

Figure 3c shows the Raman spectra of oxidized samples that have been annealed at 1000 °C for 300 s in pure N₂ and subjected subsequently to different cooling rates. No second step annealing was performed for these samples. An increase in the intensity by a factor of 6.9 is observed for the 300 cm⁻¹ peak as the cooling rate is reduced from 30 °C/s to 5 °C/s. A reduction in FWHM from 13.0 cm⁻¹ to 8.7 cm⁻¹ is also observed. These observations indicate that an improvement in the crystallinity of Ge nanodots can be obtained by reducing the cooling rate of the annealing profile.

3.3 TEM Observation

The plan view TEM images of samples annealed subsequently at $T_s = 700$ °C for 0 and 60 s are shown in Fig. 4a and 4b, respectively. Nanoclusters with random sizes and shapes are observed for samples that have been annealed at 700 °C for 0 s as depicted in Fig. 4a. The appearance of narrow grain boundaries separating the nanoclusters indicates the onset of Ge nanodot growth (see inset of Fig. 4a). Given the limited annealing time at 700 °C, formation of Ge nanodots is restricted by the diffusion of Ge atoms although the annealing tempera-



Fig. 4a. Plan view TEM micrographs of nc-Ge synthesized via rapid thermal annealing at 1000 °C for 300 s with no subsequent second step annealing. Inset shows a lower magnification image of the same sample.



Fig. 4b. Plan view TEM micrograph of nc-Ge synthesized via rapid thermal annealing at 1000 °C for 300 s with subsequent second step annealing at 700 °C for 60 s.



Fig. 5. (a) TEM electron diffraction pattern of Ge nanoclusters in Fig. 4a; (b) TEM electron diffraction pattern of nc-Ge in Fig. 4b.

ture favors nucleation. The contraction of the nanoclusters into nanodots as seen in Fig. 4b after annealing at 700 °C for 60 s indicates the diffusion of Ge atoms to nucleating sites, hence participating in the growth of nc-Ge. As compared to Fig. 4a, nc-Ge in Fig. 4b has a more uniform size distribution and the shape is spherical. The density of the nc-Ge is -5×10^{11} cm⁻² and the mean diameter distribution is 9.48 nm with a standard deviation of 1.61 nm. Although there is no evidence of coalescence of the nc-Ge at annealing time of 60 s, this is still possible if the annealing time is further increased.

As deduced from the Raman spectra in section 3.2, the crystallinity of nc-Ge is better than that of Ge nanoclusters. This is further verified from the electron diffraction patterns of the two cases. Figures 5a and 5b show the TEM electron diffraction patterns for Ge nanoclusters and nc-Ge, respectively. Distinct diffraction rings with bright flakes are seen for nc-Ge as compared to the nanoclusters. Two low intensity rings as marked in Fig. 5b are not seen in Fig. 5a. The large contrast in the intensity of the rings between the nc-Ge and nanoclusters provides confirmation that Ge nanodots grown at 700 °C for 60 s yield better crystallinity, apart from having a more uniform size and shape.

3.4 Growth Mechanism

The progress of an isothermal phase transformation is often represented by plotting the fraction of transformation as a function of time and temperature which is also known as the Transformation Time Temperature (TTT) diagram. The fraction of transformation in our work is indicated by the crystallinity of Ge nanodots as observed in the Raman spectra of various selected samples.

Nucleation of nc-Ge in a SiO₂ matrix occurs heterogeneously. The melting temperature of pure Ge is 937 °C. Therefore, annealing the samples at 1000 °C does not yield any nucleation of nc-Ge although Ge atoms have high diffusivity and impinge on each other. The driving force for nucleation, ΔG_v , is essentially zero as it is proportional to the undercooling, $\Delta T=937~^{\circ}C$ – T_s. However, even at temperatures slightly below 937 °C, the nucleation rate is still negligible as a critical undercooling ΔT_c needs to be reached. The nucleation rate is also exponentially dependent on the mobility of the Ge atoms, given by $exp(-\Delta G_m/kT)$, whereby ΔG_m is a constant. The exponential term decreases as the temperature decreases.9 One should expect a low rate of nucleation at large ΔT as the Ge atoms will have difficulty diffusing to nucleating sites. Hence, a maximum nucleation rate is obtained at intermediate undercoolings.

Similarly, low growth rates are governed thermodynamically at small undercoolings (with ΔT still larger than ΔT_e) which causes low supersaturation. At larger undercoolings, growth is kinetically driven, whereby Ge atoms will be restricted by slow diffusion.⁹ Thus, a maximum growth rate will again occur at some intermediate undercooling.

Results in sections 3.2 and 3.3 have affirmed that nc-Ge with best crystallinity are observed when the annealing temperature is 700 °C. Fig 4a shows the formation of Ge nanoclusters with random size and shape when samples are cooled rapidly at 30 °C/s from 1000 °C. The crystallinity of these clusters is poor as depicted in Fig. 3c. Due to the high cooling rate, diffusivity of Ge atoms to nucleation sites is hampered. Hence, the objective of the second annealing step at 700 °C is to enable favorable diffusivity of Ge atoms. As shown in Fig. 4b, nc-Ge is formed from the original nanoclusters shown in Fig. 4a.

This is consistent with the nucleation and growth theory which proposes that the effective transformation rate occurs at intermediate undercoolings. Synthesizing Ge nanodots at high temperature; i.e. 900 °C does not provide good quality crystals as the supersaturation is low due to the small undercooling when compared to the melting temperature of Ge at 937 °C. Similarly, the quality of Ge nanodots grown at low temperature; i.e. 510 °C is compromised as the growth is in the diffusion limited regime.

4. CONCLUSION

Oxygen related defects of Ge nanodots and the silica matrix is suppressed as the annealing temperature increases. However, a high temperature does not favor growth as the driving force for precipitation is low. A double step annealing profile was applied to synthesize Ge nanodots with good crystallinity, size distribution and shape. The improved crystallinity of the nanodots was determined from the decrease in the FWHM of the Raman spectral peak and this was verified from the electron diffraction patterns. The mean diameter of nc-Ge synthesized is 9.48 nm with a standard deviation of 1.61 nm.

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References

[1] L.T. Canham, Appl. Phys. Lett. 57, 1046 (1990).

[2] Y. Maeda, Phys. Rev. 51, 1658 (1995).

[3] T. Gebel, L. Rebohle, W. Skorupa, A.N. Nazarov, I.N. Osiyuk and V.S. Lysenko, Appl. Phys. Lett. 81, 2575 (2002).

[4] D.C. Paine, C. Caragianis, T.Y. Kim, Y. Shigesato and T. Ishahara, Appl. Phys. Lett. **62**, 2842 (1993).

[5] W.K. Choi, W.K. Chim, C.L. Heng, L.W. Teo, V. Ho, V. Ng, D.A. Antoniadis and E.A. Fitzgerald, Appl. Phys. Lett. 80, 2014 (2002).

[6] W.K. Choi, L.K. Teh, L.K. Bera, W.K. Chim, A.T.S.Wee and Y.X. Jie, J.Appl. Phys. 91, 444 (2002).

[7] M. Zacharias and P.M. Fauchet, Appl. Phys. Lett 71, 380 (1997).

[8] M. Zacharias, D. Dimova-Malinovska and M. Stutzmann, Philos. Mag. A 73, 799 (1996).

[9] D.A. Porter and K.E. Easterling, Phase Transformation in Metals and Alloys (Chapman & Hall, London, 1992), p. 185.

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