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EFFECT OF SIZE OF Ge NANOCRYSTALS EMBEDDED IN SiO_2 ON RAMAN SPECTRA

W.K. Choi, Y.W. Ho and V. Ng

Microelectronics Laboratory, Department of Electrical and Computing Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117576

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Abstract. In this paper, we investigate the effect of Ge nanocrystal size on the Raman results. The Ge nanocrystal size distributions of samples rapid thermally annealed at 800 and 1000 °C for 300 s were obtained from the TEM pictures. We constructed the theoretical Raman spectrum based on the phonon confinement model taking into account of the size distribution of the nanocrystals. By taking into account of the Ge nanocrystal size distribution, we found a good fit between the experimental and theoretical Raman results at the lower wavenumber portion from the Raman peak for samples annealed at 800 and 1000 °C. Our model, however, is not able to account for the portion in the Raman spectra above the Raman peak. We suggest that stress in the annealed films maybe responsible for this discrepancy.

1. INTRODUCTION

There has been keen interest in synthesizing Ge nanocrystals in silicon oxide (SiO_2) by furnace annealing the co-sputtering Ge+SiO_2 films. This method of synthesis of Ge nanocrystals may not be compatible with the development trend of integrated circuits as it involves annealing at elevated temperatures for a prolonged period of time (> 30 minutes) [1,2]. 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 600 to 1000 °C and the RTA duration (t_p) from 0 to 300 s [3,4]. We have presented the microstructural [5] and photoluminescence [5,6] results of the Ge nanocrystals synthesized by the RTA method.

We have shown that the Raman spectrum of the as-sputtered sample showed [3,4] a broad band at 303.4 cm^{-1}. For samples RTA at 700 and 800 °C for 300 s, a sharp Raman peak at 300 cm^{-1} with asymmetrical broadening over the low frequency portion of the spectrum was observed. For sample annealed at 1000 °C, the Raman spectrum is very similar to the as-sputtered film. We have attributed the pronounced broadening of the Raman peak of the 1000 °C annealed sample to the broadening caused by the size distribution. Our preliminary TEM results showed [5] that the Ge nanocrystals were spherical and evenly distributed in films RTA at 800 °C. For film RTA at 1000 °C, Ge nanocrystals with diameters (δ) of 20-28 nm were observed near the Si-SiO_2 interface.

Bearing in mind the TEM results mentioned earlier, it is highly probable that size distribution is the main cause for the collapse of the Raman signal of the sample annealed at 1000 °C. In this paper, we examine the effect of size distribution on the Raman spectra of our samples. The theoretical Raman response was constructed based on the phonon confinement model proposed by Fauchet and Campbell [7]. We have, however, followed the suggestions of Gonzalez-Hernandez *et al.* [8] and Bottani *et al.* [9] and modified the phonon confinement model such that it took into account of the distribution of Ge nanocrystals in the SiO_2 matrix. The information on the size distribution was obtained from the TEM pictures.

Corresponding author: W.K. Choi, e-mail: elechoi@nus.edu.sg

2. EXPERIMENT

The samples were co-sputtered in argon at ambient temperature using an Anelva sputtering system (SPH-210H). The target was a 4" SiO_2 disc with 6 pieces of Ge (99.999% pure, 10mm × 10mm × 0.3mm) attached. The argon pressure and rf power were fixed at $3 \cdot 10^{-3}$ mbar and 100 W respectively. The thickness of our samples was kept constant at 3000Å.

RTA was carried out in argon ambient using an A.S.T. rapid thermal processor (model: SHS 10). Details of the RTA process can be found in our previous papers [3,4]. In this work, the samples were annealed with T_p varied from 600 to 1000 °C for 300 s, and the RTA ramp-up and ramp-down rates were fixed at 30 °C/s.

The TEM experiments were carried out using a Philips CM300 FEG system with an operating voltage of 300 kV. The Raman measurements were carried out at room temperature with the 514.5 nm line of an Ar ion laser as an excitation source.

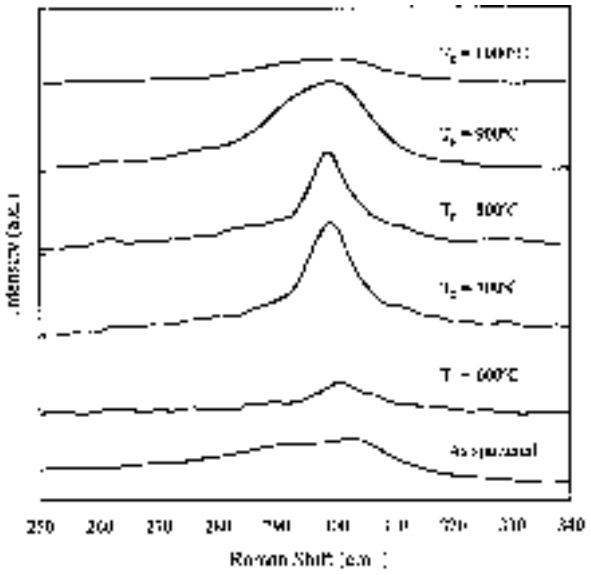

Fig. 1. The Raman spectra of co-sputtered Ge+SiO_2 samples rapid thermally annealed at different temperatures.

3. RESULTS AND DISCUSSION

Fig. 1 shows the Raman spectra of the as-sputtered sample and the samples annealed at 600 °C–1000 °C for 300 s. Note that the spectra were obtained from different samples (co-sputtered at the same run) rapid thermal annealed at the temperatures stated. It can be seen that the as-sputtered film shows a broad hump, indicating amorphous Ge [10]. Annealing the sample at 600 °C give rise to a small peak at 300 cm^{-1}. At 700 °C, the peak at 300 cm^{-1} becomes more prominent. This shows that the Ge nanocrystals are becoming better formed as the annealing temperature increases. At 800 °C, a sharp Raman peak was observed. However, when annealing temperature is raised to 900 °C, the peak begins to broaden again and at 1000 °C, the Raman spectrum is almost like that of the as-sputtered sample.

We have confirmed the amorphous structure of the as-sputtered film by the TEM experiment. Figs. 2 (a) and (b) shows the TEM pictures of samples annealed at 800 and 1000 °C for 300 s, respectively. It can be seen from Fig. 2(a) that the Ge nanocrystals (i.e. the dark patches) are approximately 6 nm in diameter in the SiO_2 matrix. The inset of Fig. 2(a) shows the formation of good nanocrystals, as indicated by the clear lattice fringes. The nanocrystals are almost spherical and are well dispersed in the matrix. Fig. 2(b) shows the Ge nanocrystals with diameters δ = 20-30 nm near the SiO_2/Si interface. Note that the nanocrystals reduce in size (i.e. δ) further away from the interface. A closer examination of the nanocrystals near the interface reveals that the crystals have a multiply twin structure. Similar twin structures have been reported by Oku *et al.* [11].

With the narrowing of the full width at half maximum of the Raman peak in Fig. 1 as T_p increases from 600 ºC to 800 ºC, δ can be deduced to be increasing from the phonon confinement model. This is consistent with the TEM observation that there were no Ge nanocrystals observed in the as-sputtered film and good quality Ge nanocrystals were formed at 800 °C.

Note that at 900 °C and 1000 °C, the Raman spectra of Fig. 1 suggested that the nanocrystals were smaller. The TEM pictures of Fig. 2(b), however, showed that the nanocrystals synthesized at 1000 ºC were bigger than those synthesized at 800 °C.

There are two possible explanations for the contradiction between the Raman and the TEM results. Firstly, Fig. 2(b) shows that defects were common in nanocrystals synthesized at 1000 ºC. The nanocystals, although bigger, were not single crystals. They were polycrystal assemblies with defects at the grain boundaries. The disorder arrangements in the particles may have the effect of altering the phonon dispersion relation in the Ge crystals. The disordered boundaries in the grain may also distort the phonon behaviour, giving rise to the amorphous

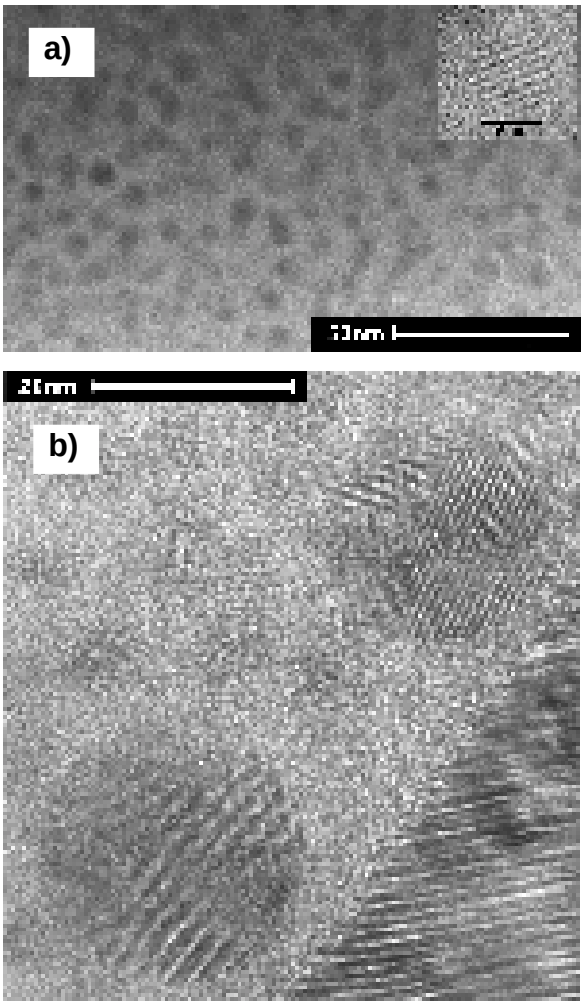

Fig. 2. TEM pictures of co-sputtered Ge+SiO_2 samples RTA at (a) 800 °C and (b) 1000 °C for 300 s.

like hump observed in the samples annealed at 1000 °C. Secondly, the TEM picture of Fig. 2(b) shows a wide distribution of size of the nanocrystals for the sample annealed at 1000 °C. This could also have stretched the Raman spectrum out. In the following paragraphs, the Raman spectra of samples annealed at 800 °C and 1000 °C were fitted with the theoretical model to study the effect of size distribution of the nanocrystals.

The model used here was based on that proposed by Campbell and Fauchet [7]. According to this model (we termed it Theory (1)), the first order Raman spectrum, $I(\omega)$, is given by

$$I(\omega) = \int \frac{d^3q\,|C(0,\boldsymbol{q})|^2}{[\omega - \omega(\boldsymbol{q})]^2 + (\Gamma_0 / 2)^2}, \qquad (1)$$

where $\omega(\boldsymbol{q})$ is the phonon dispersion curve; Γ_0 is the natural line width; $\boldsymbol{q}_0 = 0$ for first-order Raman scattering; and the integration is performed over the entire Brillouin zone.

Note that when construct the Raman curve using Eq. (1), the confinement function $W(\boldsymbol{r},L)$ has to be specified. Campbell and Fauchet [7], in their calculation of the Raman lineshape, have proposed three different types of confinement functions. By comparing the calculated Raman spectra with the experimental results, they concluded that the Gaussian confinement function is the most suitable one for semiconductor microcrystallites. Therefore, we have chosen $W(\boldsymbol{r},L)$ as

$$(\boldsymbol{r},l) = \exp\left(-\frac{8\pi^2 r^2}{L^2}\right) \qquad (2)$$

and as a result

$$|C(0,\boldsymbol{q})|^2 = \exp\left(-\frac{q^2L^2}{16\pi}\right). \qquad (3)$$

Note that Eq. (3) can be written as $\exp(-\alpha r^2/L^2)$ [12]. The value of α can then be used to fit the model to the data.

Note that, however, in the present work, α was not used for the fitting. The value of α was fixed to $8\pi^2$ following that used by Campbell and Fauchet [7]. The size distribution profile obtained from the TEM pictures was used together with Eq. (1) to yield

$$I(\omega) = \int \rho(L)dL \times \int \frac{d^3q\,|C(0,\boldsymbol{q})|^2}{[\omega - \omega(\boldsymbol{q})]^2 + (\Gamma_0 / 2)^2}, \qquad (4)$$

where $\rho(L)$ is the size distribution of the sample. It should be pointed out that this model (i.e. Theory (2)) was also used by Gonzalez et al [8] and Bottani et. al. [9]. Note that this means that the theoretical Raman spectrum was superimposed onto the experimental data with no additional curve fitting algorithm.

Fig. 3(a) shows the theoretical plots of the Raman spectra and the experimental data for sample annealed at 800 °C. The dash line was obtained by using the Raman spectrum of the single size crystal (Eq. (1)) while the full line was modeled by using Eq. (4). It is clear that Eq. (1) alone does not give a good fit to the experimental data as compared to Eq. (4). The inclusion of the size distribution has allowed the lower wavenumber to be accounted for as well. However, the higher wavenumber could not be satisfactorily accounted for by both Eqs (1) and (4). In fact, looking at Fig. 3, the size variations in nanocrystals never produce a Raman blueshift.

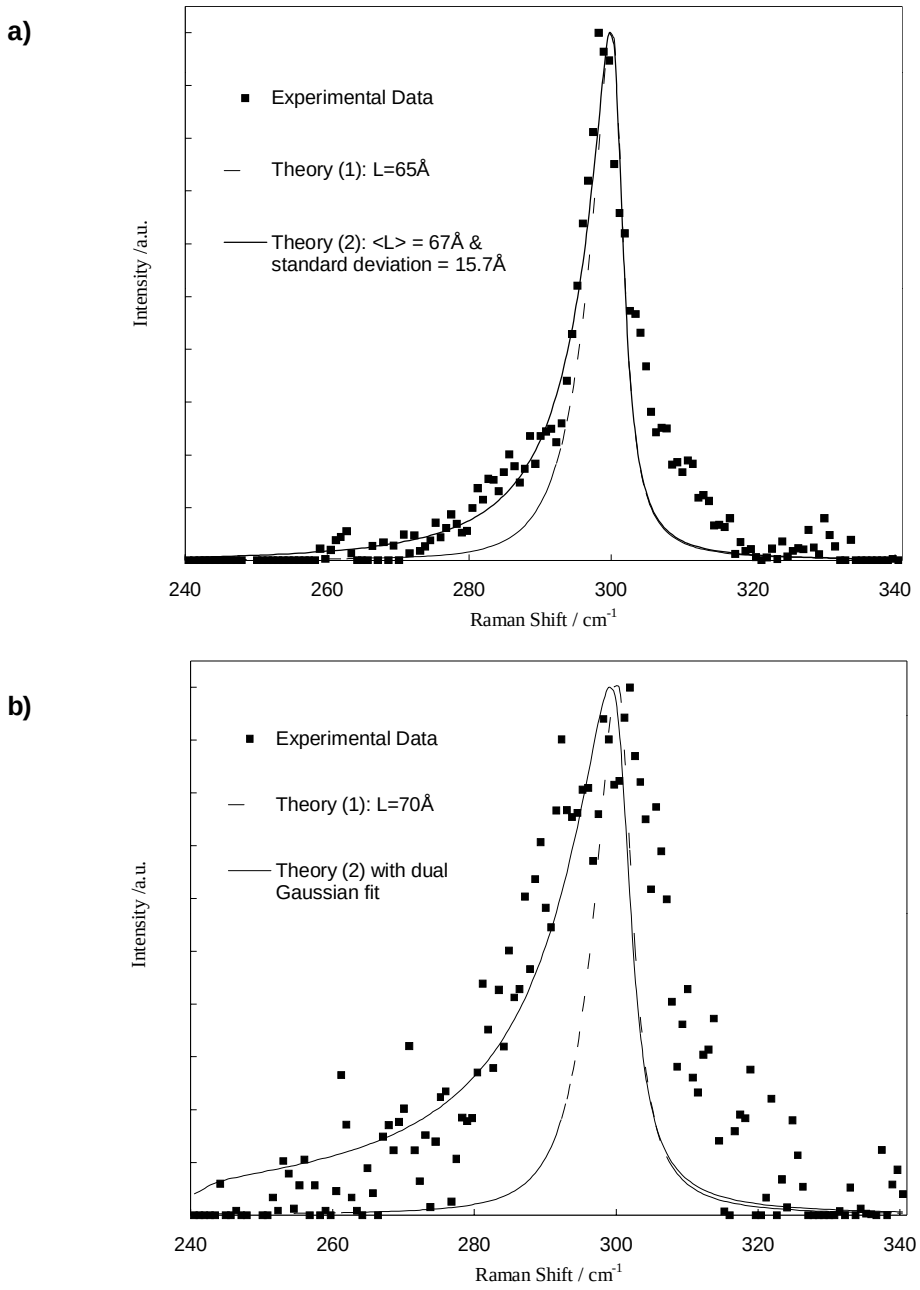

Fig. 3. The theoretical and experimental Raman spectra for Ge nanocrystals rapid thermally annealed at (a) 800 °C and (b) 1000 °C.

The experimental and theoretical Raman results for sample annealed at 1000 ºC are shown in Fig. 3(b). Note that the considerable scatter in the experimental data is caused by the difficulty in the determination of the nanocrystal size accurately in the 1000 °C annealed sample. Nevertheless, similar observations as described in the previous paragraph equally applied to Fig. 3(b). Again, the higher wavenumber portion could not be fully modeled by both Eqs. (1) and (4).

Fujii et al. [1] have suggested that the disagreement between the theoretical and experimental Raman peak frequencies, especially at the high frequency sides, may be due to compressive stress exerted on the Ge nanocrystals by the SiO_2 matrix. Our model does not include the effect of compressive stress experienced by Ge nanocrystals. This may be the reason that poor agreement is obtained at the high frequency sides of our results shown in Fig. 3.

4. CONCLUSIONS

We have adopted a modified phonon confinement model that takes into account of the size distribution of Ge nanocrystals for the construction of the theoretical Raman curve. The TEM results were used in the determination of the size distribution for samples annealed at 800 and 1000 °C. We compare the Raman characteristics constructed based on theories (1) and (2) to the experimental data. We found that the agreement between the theoretical Raman spectra, calculated using the pure phonon confinement model (i.e. theory 1), and the experimental spectra, is not good. There is a good agreement between the theoretical Raman spectra, calculated using the model that takes into account size distribution, and the experimental data at the lower frequency side. The agreement between the theoretical and experimental data at the high frequency side is, however, not satisfactory. The effect of compressive stress exerted by the SiO_2 network on the Ge nanocrystals was suggested as a possible reason for the poor agreement between the theoretical and experimental Raman results at the high frequency sides.

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