

# EFFECT OF LASER ON FORMATION OF Ge NANOCRYSTALS EMBEDDED IN SiO<sub>2</sub>

V. Ho,<sup>1</sup> W.K. Choi,<sup>1,2</sup> C.L. Heng<sup>2</sup> and V. Ng<sup>1</sup>

<sup>1</sup> Microelectronics Laboratory, Department of Electrical and Computing Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117576

<sup>2</sup> The Singapore-MIT Alliance, 4 Engineering Drive 3, Singapore 117576

Received: June 20, 2001

**Abstract.** We investigate the possibility of using laser for the synthesis of Ge nanocrystals in the co-sputtered Ge + SiO<sub>2</sub> samples. The laser annealed samples, that were sputtered with  $\geq 4$  cm<sup>2</sup> of Ge attached to the target, exhibited a Raman peak at  $\sim 290$  cm<sup>-1</sup>. The peak sharpened as the laser beam exposure time increased. However, the peak position was significantly lower than the position of bulk Ge (300 cm<sup>-1</sup>) peak. It is possible that a structural change in the Ge nanocrystals or stress in the films has caused the peak position to be lower than the bulk Ge value. The photoluminescence (PL) intensity of the laser annealed samples was also considerably weaker as compared to samples that were synthesized by rapid thermal annealing.

## 1. INTRODUCTION

The discovery of luminescence from porous silicon in 1990s has created tremendous interests in nanocrystals synthesized from Group IV semiconductors such as Si and Ge. The quantum confinement effect enables indirect bandgap semiconductors to become more efficient light emitters. It is basically due to the potentials in optoelectronic applications that research on Ge nanocrystals embedded in a silicon oxide matrix was originated [1]. It should be pointed out that, however, there are also reports of using Ge nanocrystals in silicon oxide as non-volatile memories [2,3].

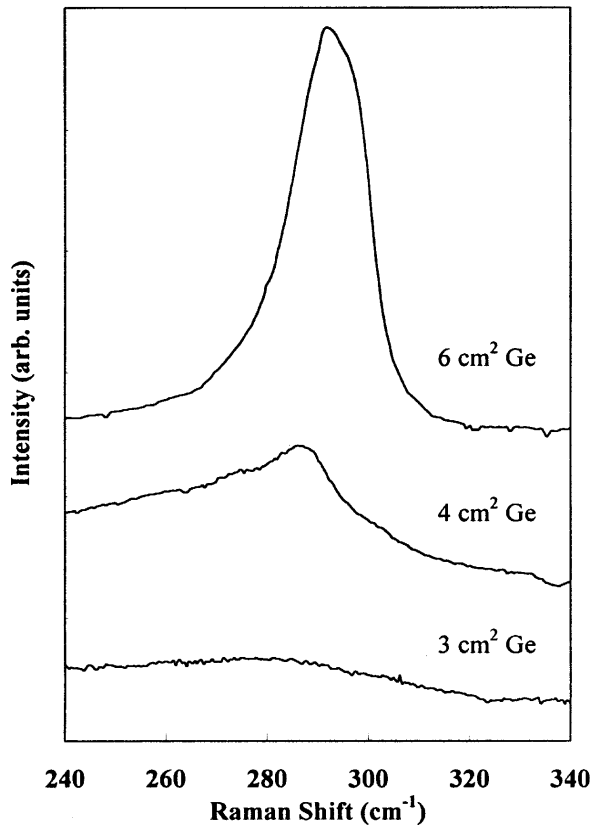
Ge nanocrystals may be synthesized by anodic etching, ion implantation, co-sputtering and cluster beam methods. The synthesis of Ge nanocrystals often involves annealing at elevated temperatures for more than 30 minutes [4,5]. We have synthesized Ge nanocrystals using rapid thermal annealing (RTA) by changing the RTA temperature ( $T_p$ ) from 600 to 1000 °C or RTA duration ( $t_p$ ) from 0 to 300 s [6-8]. We have shown recently the Raman results of as-prepared and rapid thermal annealed co-sputtered Ge+SiO<sub>2</sub> films with different Ge concentrations [9]. For films that were sputtered with  $\sim 1$  cm<sup>2</sup> of Ge

attached to the sputtering target, the Ge peak (at  $\sim 300$  cm<sup>-1</sup>) was absent regardless of the different RTA conditions used in the synthesis of Ge nanocrystals. For films sputtered with 3 cm<sup>2</sup> of Ge, Raman peak can be observed when  $T_p$  was increased from 600 to 900 °C for 300 s. When the Ge attached to the sputtering target was further increased to  $\geq 4$  cm<sup>2</sup>, a Raman peaks was observed even from the as-prepared samples at  $\sim 290$  cm<sup>-1</sup>. This seems to suggest that Ge nanocrystals were present even in the as-prepared films. Note that for samples sputtered with  $>4$  cm<sup>2</sup> of Ge, the oxide films became unstable when annealed. This is manifested either as bubbling at the film surface, peeling off or discoloration of film. Thus, a critical Ge concentration (i.e. 3 cm<sup>2</sup> of Ge attached to the sputtering target) exists in the synthesis of Ge nanocrystals in SiO<sub>2</sub> matrix under the present RTA conditions.

Note that with 3 cm<sup>2</sup> of Ge attached to the sputtering target and with the present RTA conditions, the maximum Ge nanocrystal size with good crystallinity that we obtained was approximately 6 nm in diameter ( $\delta$ ). Using transmission electron microscopy, the nanocrystals were found to be evenly distributed in the SiO<sub>2</sub> matrix [8].

---

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



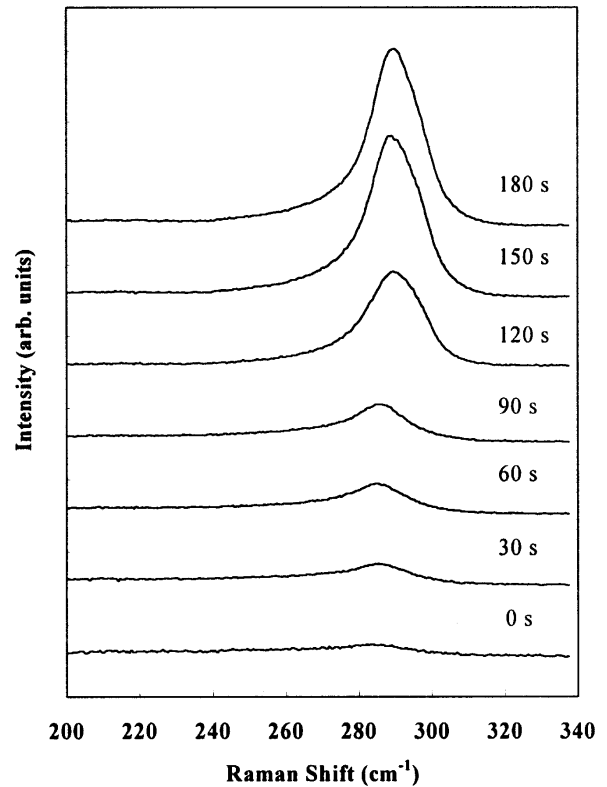
**Fig. 1.** Raman spectra of as-prepared Ge+SiO<sub>2</sub> samples co-sputtered with 3, 4 and 6 cm<sup>2</sup> of Ge.

As pointed out above, a Raman peak was observed from the as-prepared samples sputtered with more than 3 cm<sup>2</sup> of Ge. We suspect that localized thermal heating from the laser beam used in the Raman experiments might have given rise to the peak. In this paper, we investigate the possibility of using laser for the synthesis of Ge nanocrystals in our samples. We also characterize the photoluminescence (PL) response of the Ge nanocrystals synthesized by laser annealing.

## 2. EXPERIMENT

The samples were prepared by co-sputtering a 4" SiO<sub>2</sub> (99.99% pure) target with Ge (<111> orientation) pieces attached. We have sputtered samples with 3, 4 and 6 cm<sup>2</sup> of Ge attached to the sputtering target in Ar at ambient temperature using an Anelva sputtering system (SPH210H). The thickness of the samples was fixed at about 5000 Å.

Raman characterization at room temperature was carried out using a Reinshaw Spectrum 2000 machine with the 633 nm line of a He-Ne laser (power 20 mW) as an excitation source. The PL experiments were carried out using a 369 nm laser source



**Fig. 2.** Effect of laser exposure time on the Raman spectrum of the sample sputtered with 6 cm<sup>2</sup> of Ge.

(power 50 mW) with a 1 nm resolution and a photomultiplier detector.

## 3. RESULTS AND DISCUSSION

Fig. 1 shows the Raman spectra of the as-prepared samples sputtered with 3, 4 and 6 cm<sup>2</sup> of Ge attached to the sputtering target. Note that each spectrum required ~60 s to complete and there may be laser annealing on the three samples during the Raman experiment. This will be discussed later when we investigate the effect of laser exposure time.

Fig. 1 shows that the peak of the sample sputtered with 4 cm<sup>2</sup> of Ge is rather broad and located at ~287 cm<sup>-1</sup>. The peak becomes sharper when the Ge concentration increases to 6 cm<sup>2</sup> and is located at ~292 cm<sup>-1</sup>. Note that the peak position of the high concentration samples is generally located between 285 to 295 cm<sup>-1</sup>. This is significantly lower than the Ge peak position (~300 cm<sup>-1</sup>) quoted in the literature [10]. This suggests that Ge nanocrystals can be formed in samples sputtered with ≥ 4 cm<sup>2</sup> of Ge and with a laser exposure time of ~60 s. This is clearly shown in Fig. 1 that no peak is observed in sample sputtered with 3 cm<sup>2</sup> of Ge. The Ge

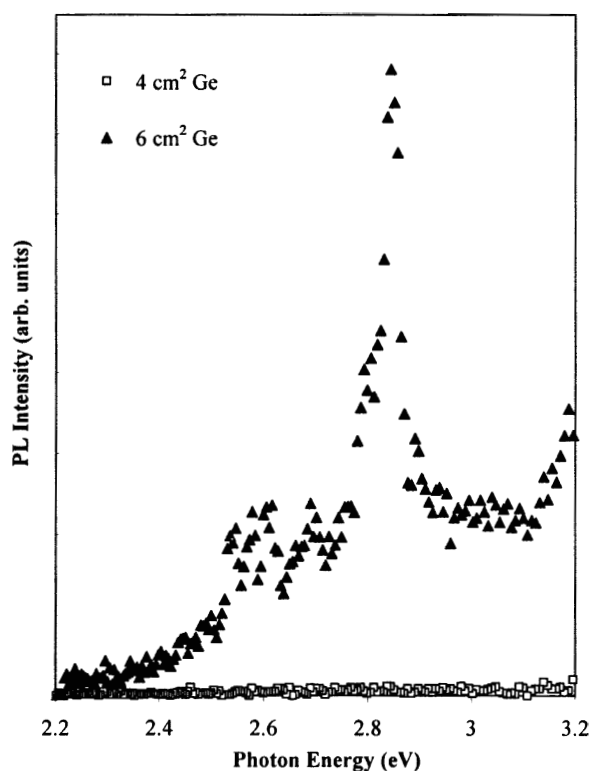
nanocrystal size was determined using the phonon confinement model [6] and was found to be  $\sim 2.2$  nm in diameter for the samples sputtered with  $6 \text{ cm}^2$  of Ge.

Fig. 2 shows the Raman spectra of a sample sputtered with  $6 \text{ cm}^2$  of Ge taken at different laser exposure times. Each spectrum was taken after every 30 s of exposure time. Fig. 2 shows that no peak is observed for the sample that has 0 s of laser exposure. The peak increases in intensity as the laser exposure duration is increased from 30 to 180 s. This is accompanied by a reduction in the full width at half maximum (FWHM) of the peak from  $22.7 \text{ cm}^{-1}$  (at 30 s) to  $16.8 \text{ cm}^{-1}$  (at 180 s). Note that the intensity and FWHM of the Raman spectra do not change much when the exposure time is increased beyond 180 s.

We have ascertained the effect of laser annealing by placing a quartz prism in the path of the laser source to reduce ( $> 95\%$ ) the laser intensity. We observed no Ge peak in the Raman spectrum from a sample prepared in the same run after 180 s of laser exposure. It is also important to point out that, unlike the RTA case, the samples here did not exhibit the bubbling or peeling problems after undergoing prolonged laser exposure. We have, however, observed localized 'black mark' at the film surface at the center of the laser spot.

Fig. 2 shows that there is a shift in the Ge peak position from  $286$  to  $290 \text{ cm}^{-1}$  as the laser exposure time increases from 30 to 180 s. This peak, however, is still significantly lower than the bulk Ge peak position. It is very unlikely that this arises from intermixing between Ge and  $\text{SiO}_2$  [11]. It is possible that a structural change of the Ge nanocrystals or stress in the high Ge concentration films has caused the peak position to be lower than the bulk Ge value. We are currently carrying out TEM experiments on these samples to examine the possible structural changes in the Ge nanocrystals.

Fig. 3 shows the PL spectra of the as-prepared samples shown in Fig. 1. Note that these samples were sputtered with 4 and  $6 \text{ cm}^2$  of Ge attached to the sputtering target, and subjected to 60 s of laser annealing. Fig. 1 shows that the Raman spectrum of the sample sputtered with  $4 \text{ cm}^2$  of Ge to be rather broad. This may indicate the presence of Ge clusters in the film. This may account for the very weak luminescence of this sample shown in Fig. 3. The Raman spectrum of the samples sputtered with  $6 \text{ cm}^2$  of Ge exhibited clear Ge peak (see Fig. 1), which indicates the presence of Ge nanocrystals. This gives rise to a PL peak centered at  $2.84 \text{ eV}$  in



**Fig. 3.** PL spectra of samples sputtered with 4 and  $6 \text{ cm}^2$  of Ge. Note these samples had been laser annealed for  $\sim 60$  s.

Fig. 3. Note that although the PL intensity of the sample sputtered with  $6 \text{ cm}^2$  of Ge is stronger than the sample sputtered with  $4 \text{ cm}^2$  of Ge, the PL intensity of the laser annealed samples is significantly weaker than the RTA samples.

We have reported PL peaks near  $3.0 \text{ eV}$  from our RTA samples [7,8] and concluded that the best PL response was obtained with samples that exhibit uniform nanocrystal size. The origin of the PL for the RTA samples was suggested to be defect-related. The defects may be linked to Ge oxide or suboxides. As the PL peak position of the laser annealed samples is similar to the RTA samples, it is possible that the same mechanism is also responsible for the PL of the laser annealed samples. However, as the PL intensity of the laser annealed samples is significantly weaker than the RTA samples, this may suggest that the species that is responsible for the PL is significantly lower in the laser annealed samples. We plan to carry out X-ray photoelectron spectroscopy (XPS) experiments to estimate the amount of Ge oxide and suboxides in the laser annealed samples.

Note that we have observed that the Raman peak of the laser annealed samples is significantly lower than the RTA samples. If the Ge nanocrystals syn-

thesized via laser annealing is structurally different from that synthesized by RTA, then the weaker PL response may be due to the different structures of the nanocrystals in these samples. Note also that the laser annealed samples were of higher Ge concentration; the weaker PL response may also be due to stress in the higher Ge content in the film. It is, however, clear that Ge nanocrystals formed via laser annealing are not suitable for optoelectronic applications due to the weak PL response.

### 3. CONCLUSIONS

In this paper, we investigated the possibility of using laser for the synthesis of Ge nanocrystals in our samples. We also characterized the PL response of the Ge nanocrystals synthesized by laser annealing. We found that by focusing the laser on the as-prepared samples sputtered with  $\geq 4$  cm<sup>2</sup> of Ge during Raman characterization, a peak at  $\sim 290$  cm<sup>-1</sup> was observed. The FWHM reduced as the laser beam exposure time increased. The existence of the sharp peak suggests possible Ge nanocrystal formation. However, the peak position is significantly lower than the position of bulk Ge peak. It is possible that a structural change of the Ge nanocrystals or stress in the high Ge concentration films has caused the peak position to be lower than the bulk Ge value. The PL intensity of the laser annealed samples was considerably weaker as compared to the RTA samples. As the PL peak of the laser annealed and the RTA samples are very similar to each other, we suggest that defect-related mechanism may be responsible for the PL. We are, however, not able to rule out the effect of structural changes or stress on the PL characteristics of the laser annealed films.

### ACKNOWLEDGMENTS

The authors would like to acknowledge Mr Walter Lim for the assistance in sample preparation, Dr Yu Guangyou of the Physics Department for his assistance in the Raman experiments and Ms K. Chew of the Nanyang Technological University (NTU) for her help in the photoluminescence experiments. We would also like to thank the National Science and Technology Board for a research grant (GR6471) and one of us (C.L.H) to the Singapore-MIT Alliance for a research fellowship.

### REFERENCES

- [1] S.S. Iyer and Y.H. Xie // *Science* **260** (1993) 40.
- [2] S. Tiwari, F. Rana, K. Chan, H. Hanafi, W. Chan and D. Buchanan // *IEDM Tech. Dig.* (1995) 521.
- [3] Y. C. King, T. J. King and C. Hu // *IEDM Tech. Dig.* (1998) 115.
- [4] M. Fujii, S. Hayashi and K. Yamamoto // *Jpn. J. Appl. Phys.* **30** (1991) 687.
- [5] Y. Maeda // *Phys. Rev. B* **51** (1991) 1658.
- [6] W.K. Choi, V. Ng, S. P. Ng and H. H. Thio // *J. Appl. Phys.* **86** (1999) 1398.
- [7] V. Ng, S.P. Ng, H.H. Thio, W.K. Choi, A.T.S. Wee and Y.X. Jie // *Mater. Sci. Eng. A* **286** (2000) 161.
- [8] W.K. Choi, Y.W. Ho, S.P. Ng and V. Ng // *J. Appl. Phys.* **89** (2001) 2168.
- [9] W.K. Choi, V. Ng, Y.W. Ho, T.B. Chen and V. Ho // *Mater. Res. Soc. Symp. Proc.* **638** (2001) F14.1.1.
- [10] Y. Sasaki and C. Horie // *Phys. Rev. B* **47** (1993) 3811.
- [11] D.C. Paine, C. Caragianis, T.Y. Kim, Y. Shigesato and T. Ishahara // *Appl. Phys. Lett.* **60**, 2886 (1992).