Influence of UV irradiation and RTA process on optical properties of Si implanted SiO₂

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ABSTRACT
Si ion implantation was widely used to synthesize specimens of SiO₂ containing supersaturated Si and subsequent high temperature annealing induces the formation of embedded luminescent Si nanocrystals. In this work, the potentialities of excimer UV-light (172 nm, 7.2 eV) irradiation and rapid thermal annealing (RTA) to enhance the photoluminescence and to achieve low temperature formation of Si nanocrystals have been investigated. The Si ions were introduced at acceleration energy of 180 keV to fluence of 7.5 x 10¹⁶ ions/cm². The implanted samples were subsequently irradiated with an excimer-UV lamp. After the process, the samples were rapidly thermal annealed before furnace annealing (FA). Photoluminescence spectra were measured at various stages at the process. We found that the luminescence intensity is strongly enhanced with excimer-UV irradiation and RTA. Moreover, effective visible photoluminescence which is not observed with a simple FA treatment, is found to be observed even after FA at 900 °C, only for specimens treated with excimer-UV lamp and RTA. Based on our experimental results, we discuss the effects of excimer-UV lamp irradiation and RTA process on Si nanocrystals related photoluminescence.

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1. INTRODUCTION

After first reports on room temperature visible photoluminescence from porous silicon in the early 1990s [1, 2], great interest in the optical properties of Si nanocrystals embedded in SiO₂ has grown over the last decade [3-5] because of their potential applications toward Si-based integrated optoelectronic devices. The attention to this material is greatly increased due to the observation of light amplification in Si nanocrystals [6] and the application for nonvolatile memory [7]. One of the most promising approaches, compatible with modern microelectronic device fabrication techniques, to produce Si nanocrystals may be ion implantation technique. This technique has the advantage that a given number of proper ions can be easily placed at a controlled depth and distribution by changing the fluences and acceleration energies [8, 9].

It is well known that Si ion implantation into SiO₂ and subsequent high temperature annealing (more than 1000 °C) induce the formation of luminescent Si nanocrystals. The photoluminescence peaking in the near infrared or visible spectrum (between 1.4 eV and 1.8 eV) is evidently related to implant Si nanocrystals formed by decomposition of the SiOₓ phase and aggregation with high temperature annealing [10-14]. It is also shown that the photoluminescence is enhanced with annealing in forming gas ambient to induce hydrogen passivation [15-19]. Although a considerable amount of research has been extensively performed by many researchers, the detailed mechanism responsible for this photoluminescence is still unclear.

The photoluminescence arising from Si nanocrystals in SiO₂ has been attributed by some investigations to simple quantum confinement, while others have concluded that surface states present in the interfacial layer (including some types of defects) between the Si nanocrystals and the surrounding oxide matrix (localized surface states) play an important role in the emission process. In this work, the potentialities of excimer UV-light irradiation and rapid thermal annealing (RTA) processes combined with conventional furnace annealing (FA) for enhancement of the photoluminescence intensity and for achievement low temperature (below 1000 °C) formation of luminescent Si nanocrystals in SiO₂ have been investigated.

2. EXPERIMENTAL

The samples used were prepared by implanting Si⁺ ions into oxidized commercial Si
epitaxial layers (10 Ωcm, 10 μm) grown on p+-type Si wafers (Sb-doped) with a resistance of around 0.01 Ωcm (P on P⁺, oxide thickness of around 500 nm). The Si ions were introduced at acceleration energy of 180 keV with the fluence 7.5 x 10¹⁶ ions/cm² with a beam current of 300 μA (current density of about 15 μA/cm²). The expected depth profiles of the implanted Si were estimated using TRIM [20] and found to be distributed in near Gaussian profiles with a peak depth around 300 nm from surface.

The implanted samples were subsequently annealed at 900 °C or 1050 °C in a flowing N₂ atmosphere for 4 hours using a conventional tube furnace. Some of the samples were UV-light (172 nm, 7.2 eV, Ushio, excimer UV lamp unit, Xe2* type) irradiated for 2 hours with power density of 50 mW/cm² in vacuum, or rapidly thermal annealed at 1050 °C in N₂ atmosphere for 5 minutes with a rising rate of 50 °C /sec (ULVAC, MILA-3000). Conventional room temperature photoluminescence spectra were measured at various stages of the processing. A He-Cd laser (325 nm, 3.82 eV) was used as the excitation source and the luminescence was detected by a cooled photomultiplier tube (Hamamatsu, R-943-02) employing the photon counting technique.

3. RESULTS AND DISCUSSION

It is well known that Si ion implantation into SiO₂ and subsequent high temperature annealing (more than 1000 °C) induce the formation of embedded luminescent Si nanocrystals by decompose of supersaturated SiOₓ. The peak energy of photoluminescence is close around 1.7 eV for extreme low fluence implanted samples, but is slightly shifted to lower energies side with increasing in implanted ion fluences [21]. Si implantations with the fluence of 7.5 x 10¹⁶ ions/cm² correspond to relatively lower case.

We will firstly show typical photoluminescence spectra obtained after FA at 1050 °C in a flowing N₂ atmosphere for several hours. The photoluminescence spectra of ion implanted samples after annealed with conventional furnace are shown in fig.1. Hereafter, all of the photoluminescence intensities are normalized with the luminescence of specimen after FA at 1050 °C for 4 hours without rapid thermal annealing, i.e., only conventional FA. The photoluminescence spectrum after FA at 900 °C is also shown in the figure. It is clear from the figure that the luminescence intensity grows as the annealing time increases and the peak energy of the luminescence spectra are independent of the annealing time after annealing at 1050 °C. It is noted that only a very weak photoluminescence was obtained
after FA at 900 °C. As shown in the figure, peak height of this photoluminescence band is at a similar level that of as-implanted sample, which is related to defect generated with ion implantation.

We also investigated the effects of excimer UV-light irradiation and RTA on the photoluminescence. The photoluminescence spectra of samples are shown in fig.2. UV-light irradiation (172 nm, 7.2 eV) was carried out for 2 hours in vacuum. The intensities of luminescence peaked around 2.1 eV increase with UV-light irradiation. Moreover, the luminescence peaked around 2.1 eV quenched and new band located around 1.6 eV appears with RTA.

Samples with/without UV-irradiation and RTA treatment were further treated with conventional furnace. The results for the photoluminescence measurements of samples after FA at 1050 °C in a flowing N₂ atmosphere for 4 hours are shown in fig.3. It is clear from the figure that the luminescence intensity with RTA treatments enhanced twice as high as samples without RTA. Moreover, the enhancement comes to three times for sample treated with both UV-light and RTA. It is also noted that the peak energies of the photoluminescence shift to lower energy side with increasing photoluminescence intensity.

Low temperature annealing effects of UV-irradiated samples with conventional furnace have been investigated. The results for the photoluminescence measurements of sample after FA at 900 °C in a flowing N₂ atmosphere for 4 hours are shown in fig.4. New additional shoulders of spectra located around 1.7 eV appear without quenching of defect related peak. It is clear from the figure that no difference was observed in samples with/without UV-irradiation and without RTA. It means that UV-irradiation before FA is not effective for FA at 900 °C, even generation of defects with UV-light irradiation, in this case. This situation is similar to that observed with FA at 1050 °C.

We also combined the process of RTA before low temperature FA. The results for the photoluminescence measurements of samples after FA at 900 °C in a flowing N₂ atmosphere for 4 hours are shown in fig.5. The photoluminescence spectrum after only FA at 1050 °C is also shown in the figure. It is clear from the figure that sufficient luminescence intensity can be obtained even after FA at 900 °C, combined with both UV-irradiation and RTA. The luminescence intensity achieves to the same level as that of after the FA process at 1050 °C or twice as high as that with RTA only. It is also clear from the figure that the peak energy of photoluminescence band shifts around 0.1 eV towards
lower side compared to that of 1050 °C FA sample.

Firstly, we discuss the enhancement of the photoluminescence with RTA prior to FA. For the case embedded Si nanocrystals, the luminescence intensity is determined by the number of optimally-sized Si nanocrystals and their luminescence efficiency [22]. In forming the luminescent Si nanocrystals in a SiO₂ matrix, decomposition, segregation, diffusion, nucleation, aggregation, growth and crystallization processes are clearly important. The implanted Si ions will initially form SiOₓ or to a lesser extent, Si aggregates. With such a short time RTA, of course, the diffusion of implanted Si is limited. As a result of diffusion limited segregation, a number of small aggregates will be formed and they act as a nucleation point.

Here we discuss drastic enhancement with excimer-UV light irradiation and RTA prior to FA. After ion implantation, a lot of defects are introduced in SiO₂ layer. In case for Si-implanted samples, Si-rich type defects and oxygen-deficiency centers (ODCs) seems to be dominant and optically active [10, 23, 24]. The luminescence band peaked around 2.1 eV observed in as-implanted samples, shown in fig.2, is believed to be assigned to Si-rich defects in SiO₂ [10, 11]. This luminescence intensity evidently increased with UV-light irradiation, as shown in fig.2. UV irradiation induces the bond-breaking of Si-Si or Si-O. ODCs have optical absorption band peaked at 7.6 eV, and the band tail extend to 7.2 eV correspond to the emission energy from excimer-UV lamp. As a result of UV irradiation, we can expect the defect generation.

The difference of these two annealing steps (FA and RTA) is time scale to achieve expected temperature (1050 °C). The former takes around 1hour but the latter takes only 1minute. It means that the surrounding condition will be frozen with RTA process. Bond-breaking of Si-Si or Si-O also induce de-nucleation of Si aggregates formed with ion implantation, and these new Si aggregates and generated defects act as a nucleation points (defect-initiated nucleation).

Now, we discuss the observation of photoluminescence after UV irradiation and RTA and subsequent lower temperature FA. It is well known that the decomposition of SiOₓ occurs at the temperature above 1000 °C [25]. As shown in fig.5, we observed photoluminescence even after FA at 900 °C. There are two possibilities to explain our experimental results. One is due to only the crystallization of implanted Si small aggregates and the annihilation of non-radiative defects. We can exclude this possibility
simply because the sufficient luminescence was not obtained only after FA. The other is due to the decomposition of SiOₓ induced by UV and RTA. The aggregation and crystallization occur with subsequent lower temperature FA.

Finally, we will discuss the difference of peak energies, shown in fig.5. In the model proposed by the present authors for the luminescence from Si nanocrystals in SiO₂ [21, 22], it is considered that the band-gap widening due to the quantum confinement effect plays an essential role in the absorption process of photons and that the interface defect energy states between the Si nanocrystals and the thin SiO₂ layer, for which the energy levels are affected by interactions between clusters, play an essential role in the emission process of photons. If the population of Si nanocrystals is very dense, the nanocrystals interact with each other via the thin intervening oxide and a decrease in the interface energy level should be expected. Based on this model we can easily explain the shift of the luminescence, because samples have more inclusions. As we cannot expect larger Si nanocrystals formation with 900 °C FA than that with 1050 °C FA, simple quantum confinement model will not be acceptable based on present experimental results. Direct confirmation of the correlation between the size distribution of Si nanocrystals with HR-TEM and the luminescence properties is now in progress.

4. CONCLUSION

We have investigated the effects of excimer UV-light irradiation and rapid thermal annealing (RTA) process on the photoluminescence of Si implanted SiO₂. We found that UV and RTA process are effective to obtain luminescent Si nanocrystals, even with low temperature FA (less than 1000 °C). The formation can be explained with bond-breaking, defect generation, de-nucleation, defect-initiated nucleation and frozen of states with excimer-UV light irradiation and RTA.

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References


**Figure captions**

**Fig. 1** Photoluminescence spectra of a sample implanted to a fluence of $7.5 \times 10^{16}$ Si ions/cm$^2$. Implanted sample was furnace annealed at 950 °C or 1050 °C for hours indicated in the figure.

**Fig. 2** Photoluminescence spectra of samples implanted to a fluences of $7.5 \times 10^{16}$ Si ions/cm$^2$. Samples were treated with UV-excimer light for 2 hours and/or RTA for 5 minutes at 1050 °C. A Photoluminescence spectrum before some treatments is also indicated in the figure for comparison.

**Fig. 3** Photoluminescence spectra of samples implanted to a fluence of $7.5 \times 10^{16}$ Si ions/cm$^2$, obtained at various steps. Excimer-UV irradiation and rapid thermal annealing conditions are similar to those in upper figure. Samples were finally annealed with conventional furnace at 1050 °C for 4 hours. Each annealing history is indicated in the figure.

**Fig. 4** Photoluminescence spectra of sample implanted to a fluence of $7.5 \times 10^{16}$ Si ions/cm$^2$, and before and after UV-light irradiated for 2 hours in vacuum. Both of samples were further treated with conventional furnace at 900 °C for 4 hours.

**Fig. 5** Photoluminescence spectra of samples implanted to a fluence of $7.5 \times 10^{16}$ Si ions/cm$^2$, obtained at various steps. Excimer-UV irradiation and rapid thermal annealing conditions are similar to those in upper figures. All of samples were finally annealed with conventional furnace at 900 °C or 1050 °C for 4 hours. Each annealing or irradiation history is indicated in the figures.
Fig. 1
Fig. 2
PL Intensity (Arb. Units)

Photon Energy (eV)

UV + RTA + FA
RTA + FA
FA
as-implanted

(FA: 1050 °C)

x 10

Fig. 3
Fig. 4
Fig. 5