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# Optical properties of Si nanocrystals in SiO<sub>2</sub> matrix synthesized by reactive pulsed laser deposition

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**Abstract.** Si ion implantation into SiO<sub>2</sub> is widely used to synthesize specimens of SiO<sub>2</sub> containing supersaturated Si. We also prepared specimens of supersaturated Si in SiO<sub>2</sub> by reactive pulsed laser deposition (PLD) in an oxygen atmosphere. After high temperature annealing of these specimens induces the formation of embedded luminescent Si nanocrystals in SiO<sub>2</sub>. 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  $7.5 \times 10^{16}$  ions/cm<sup>2</sup>. We also prepared Si nanocrystals embedded in a SiO<sub>2</sub> by reactive pulsed laser deposition (PLD) in an oxygen atmosphere by using conventional PLD system with 2nd-harmonic YAG laser (532 nm, 10 Hz, 80 J/cm<sup>2</sup>) under controlled low oxygen pressure. 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 enhanced with excimer-UV irradiation and RTA. Moreover, effective visible photoluminescence is found to be observed even after FA below the annealing temperature at 1000 °C, only for specimens treated with excimer-UV lamp and RTA. We will make clear the similarities of photoluminescence with the way of preparation techniques.

## 1. Introduction

After the first reports on room temperature visible photoluminescence (PL) in the early 1990s [1], [2], great interest in the optical properties of Si nanocrystals has grown over the last few decades [3]-[5] because of their potential applications toward Si-based integrated optoelectronic devices [6]. Our group has focused on the formation of silicon nanocrystals, and developed the first examples of luminescent Si nanocrystals inside of SiO<sub>2</sub> using ion implantation [7]-[10]. This technique has the advantage that a given number of the required ion species can be easily placed at a controlled depth and distribution by changing the fluence and acceleration energies [11], [12]. Nowadays, it is well known that Si ion implantation into SiO<sub>2</sub> and subsequent high temperature annealing (more than 1000 °C) induce the formation of luminescent Si nanocrystals. The PL 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 SiO<sub>x</sub> phase and aggregation with high temperature annealing [7]-[10], [13], [14]. The PL arising from implanted Si nanocrystals in SiO<sub>2</sub> 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



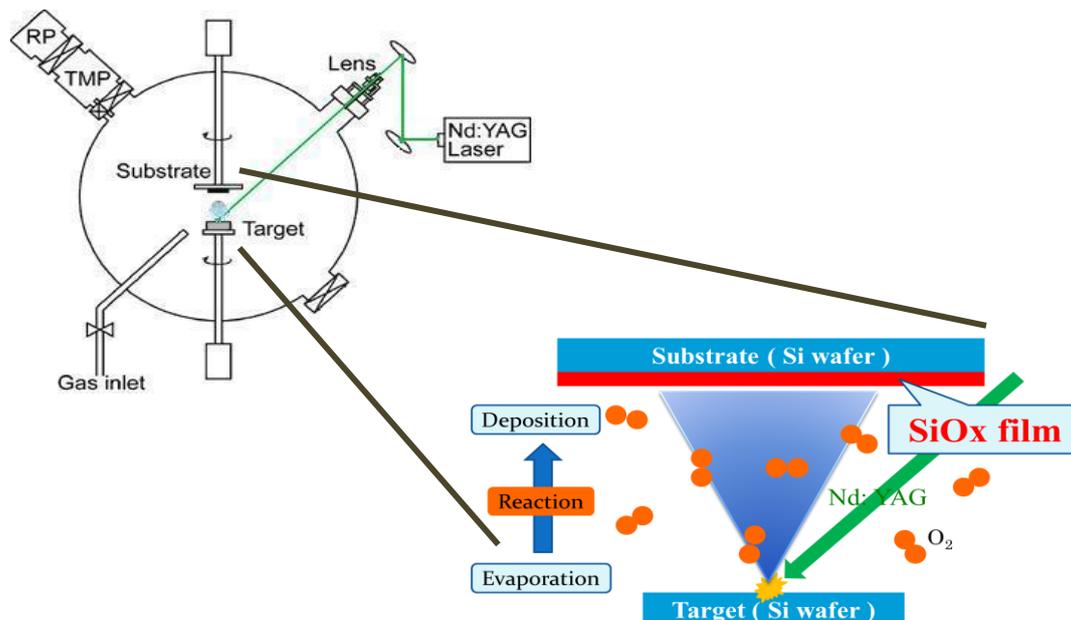
surrounding oxide matrix (localized surface states) play an important role in the emission process. Among various techniques to synthesize Si-rich oxide films, we also employed the technique of reactive pulsed laser deposition (PLD) [15] in a controlled oxygen atmosphere to prepare Si nanocrystals embedded in a  $\text{SiO}_2$ .

In this work, synthesized Si-rich oxide films in both way (ion implantation and reactive-PLD) were subsequently treated with irradiated with an excimer-UV lamp (172 nm, 7.2 eV) and/or rapid thermal annealing (RTA) to enhance the PL and to achieve low temperature formation of Si nanocrystals. After the process, the samples were annealed by using conventional tube furnace (FA). Photoluminescence spectra were measured at various stages at the process. We found that the luminescence intensity is enhanced with excimer-UV irradiation and RTA. Moreover, effective visible photoluminescence is found to be observed even after FA below the annealing temperature at 1000 °C, only for specimens treated with excimer-UV lamp and RTA. We will make clear the similarities of photoluminescence with the way of preparation techniques.

## 2. Experimental procedures

The samples used were prepared by implanting  $\text{Si}^+$  ions into oxidized Si epitaxial layers (10  $\Omega$  cm, 10  $\mu$  m) grown on  $\text{p}^+$ -type Si wafers (Sb-doped) with a resistance of around 0.01  $\Omega$  cm (P on  $\text{P}^+$ , oxide thickness of around 500 nm). The Si ions were introduced at acceleration energy of 180 keV with the fluence  $7.5 \times 10^{16}$  ions/ $\text{cm}^2$  with a beam current of 300  $\mu$  A (current density of about 15  $\mu$  A/ $\text{cm}^2$ ). The expected depth profiles of the implanted Si were estimated using TRIM [16] and found to be distributed in near Gaussian profiles with a peak depth around 300 nm from the surface.

We also prepared Si-rich oxide films by reactive pulsed laser deposition (PLD) in an oxygen atmosphere. Si sub-oxide ( $\text{SiO}_x$ ,  $0 < x < 2$ ) films were firstly deposited on Si wafers, by using conventional PLD system with 2nd-harmonic YAG laser (532 nm, 10 Hz, 80 J/ $\text{cm}^2$ ) under controlled low oxygen pressure (0.4 Pa – 1.2 Pa), as shown in Figure 1. Duration time for PLD was varied from 0.5 to 2 hours, and the distance between the target and the substrate was kept 5 cm. During the PLD, both the target and the substrate were rotated to avoid damage and obtain uniformity.



**Figure 1.** Experimental set-up to synthesize Si-rich oxide films by reactive pulsed laser deposition (PLD) in an oxygen atmosphere.

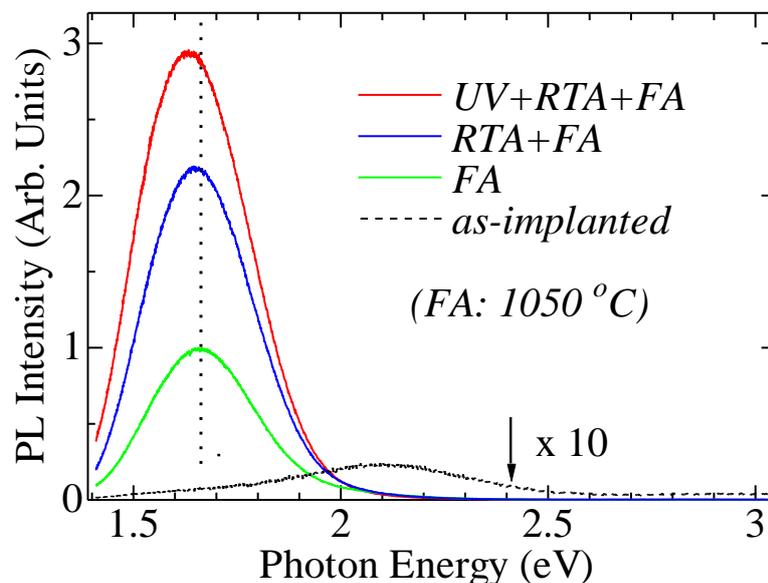
Prepared  $\text{SiO}_x$  film samples in both way were subsequently annealed at 1050 °C or below 1000 °C in a flowing  $\text{N}_2$  atmosphere for several hours using a conventional tube furnace to induce the formation of Si nanocrystals. Some of the samples were excimer-UV light (172 nm, 7.2 eV,  $\text{Xe}_2^*$ ) irradiated for 2 hours with power density of 50 mW/cm<sup>2</sup> in vacuum (Ushio, excimer UV lamp irradiation unit), or rapidly thermal annealed at 1050 °C in  $\text{N}_2$  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, 20 mW) was used as the excitation source, and the photoluminescence was focused to spectrograph via an optical fibre and detected by a cooled photomultiplier tube (Hamamatsu, R-943-02), employing the photon counting technique.

### 3. Results

It is well known that Si ion implantation into  $\text{SiO}_2$  and subsequent high temperature annealing (more than 1000 °C) induce the formation of embedded luminescent Si nanocrystals by decomposition of supersaturated  $\text{SiO}_x$ . The peak energy of photoluminescence is close to 1.7 eV for extreme low fluence implanted samples, but is slightly shifted to lower energies side with increase in implanted ion fluence.

We first investigated the effects of excimer UV-light irradiation and RTA on the photoluminescence. The photoluminescence spectra of samples after treated using the conventional furnace at 1050 °C in a flowing  $\text{N}_2$  atmosphere for 4 hours are shown in Figure 2. UV-light irradiation (172 nm, 7.2 eV) was carried out for 2 hours in vacuum. It is clear that the luminescence intensity with RTA treatments was enhanced and is twice as high as the intensity for samples without RTA.

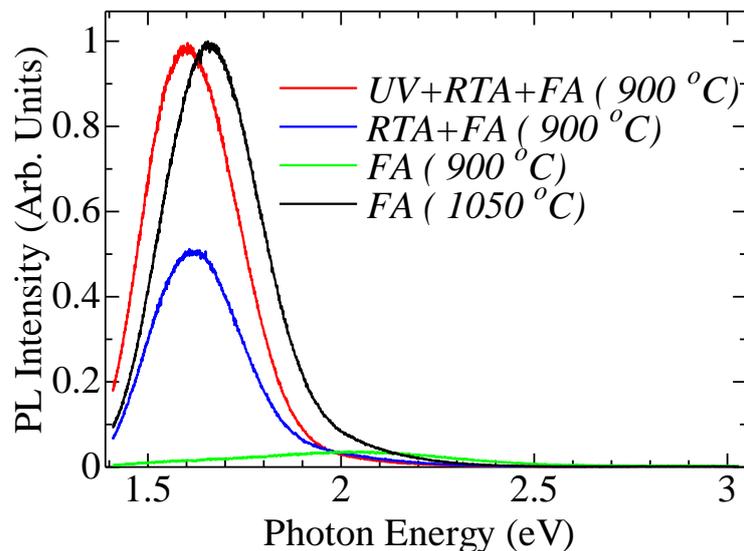


**Figure 2.** PL spectra of samples implanted to a fluence of  $7.5 \times 10^{16}$  Si ions/cm<sup>2</sup>, obtained after various steps. Samples were treated with excimer-UV light for 2 hours and/or RTA for 5 minutes at 1050 °C. Samples, except as-implanted, were finally annealed using a conventional tube furnace (FA) at 1050 °C for 4 hours.

Moreover, the enhancement is three times for samples treated with both UV-light and RTA. It is also noted that the peak energies of the photoluminescence shift to the lower energy side with increasing photoluminescence intensity.

Low temperature annealing effects of UV-irradiated samples using a conventional furnace have been also investigated. 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  $\text{N}_2$  atmosphere

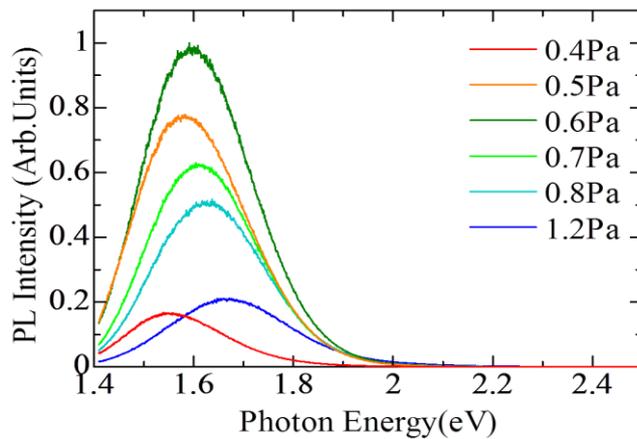
for 4 hours are shown in Figure 3. The photoluminescence spectrum after only FA at 1050 °C is also shown for comparison. It is clear that sufficient luminescence intensity can be obtained even after FA at 900 °C, combined with both UV-irradiation and RTA. The luminescence intensity reaches the same level as that obtained after the FA process at 1050 °C which is twice as high as that with RTA only.



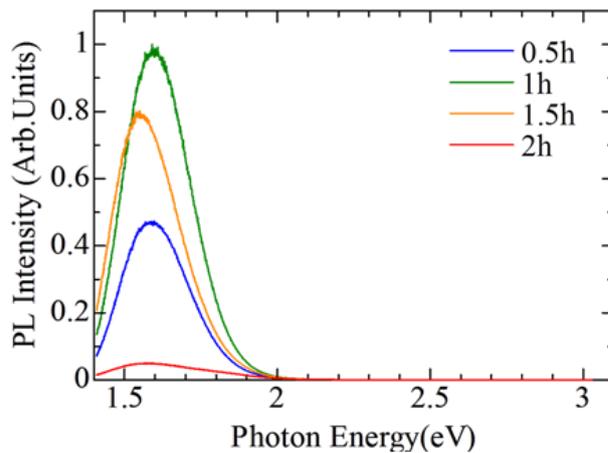
**Figure 3.** PL spectra of samples implanted to a fluence of  $7.5 \times 10^{16}$  Si ions/cm<sup>2</sup>, obtained after various steps. Samples were treated with excimer-UV light for 2 hours and/or RTA for 5 minutes at 1050 °C. Samples, except FA (1050 °C), were finally annealed using a conventional tube furnace (FA) at 900 °C for 4 hours.

We also prepared Si nanocrystals embedded in a SiO<sub>2</sub> by reactive pulsed laser deposition (PLD) in controlled oxygen atmosphere. Si sub-oxide (SiO<sub>x</sub>, 0 < x < 2) films were firstly deposited on Si wafers, by using conventional PLD system with 2nd-harmonic YAG laser (532 nm, 10 Hz) under controlled low oxygen pressure (0.4 Pa – 1.2 Pa). After deposition in the oxygen ambient, the SiO<sub>x</sub> films were annealed for 4 hours at 1050 °C in N<sub>2</sub> atmosphere to induce the formation of Si nanocrystals. The photoluminescence spectra of samples produced with PLD at various oxygen pressure after FA at 1050 °C in a flowing N<sub>2</sub> atmosphere for 4 hours are shown in Figure 4. It is clear that photoluminescence intensity increases with increasing oxygen gas pressure, and then decrease. The maximum photoluminescence intensity can be obtained with oxygen pressure of 0.6 Pa. Peak energies of the photoluminescence are also affected by ambient oxygen pressure. These features are almost consistent with those obtained from ion implanted samples.

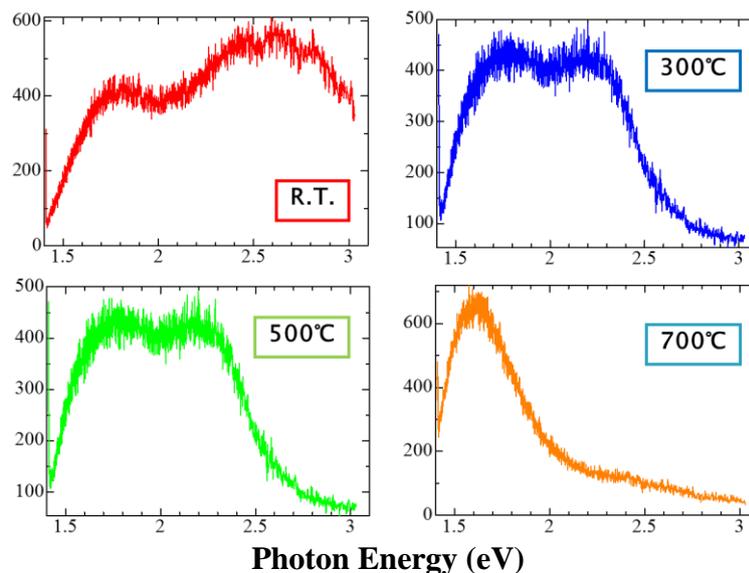
We also show in Figure 5 the photoluminescence spectra of samples with different duration time for PLD, from 0.5 to 2.0 hours after FA at 1050 °C for 4 hours. It is also clear that duration time for PLD affects photoluminescence intensity. The intensity increases with increasing duration time and the maximum photoluminescence intensity can be obtained with 1 hour ablation. We also investigated the possibility to obtain Si nanocrystals directly in as-deposited samples, by increasing the substrate temperature up to 700 °C. The results are shown in Figure 6. In all cases, Si nanocrystals related weak peak around 1.6 eV is observed. But only for the samples at 700 °C, defect related peak [17] above 2.0 eV almost disappeared. We expect the possibility to obtain Si nanocrystals directly without FA annealing above these temperature. We will try it for the near future. We also found that all of these samples show photoluminescence around 1.6 eV after FA at 1050 °C, as shown in Figure 7.



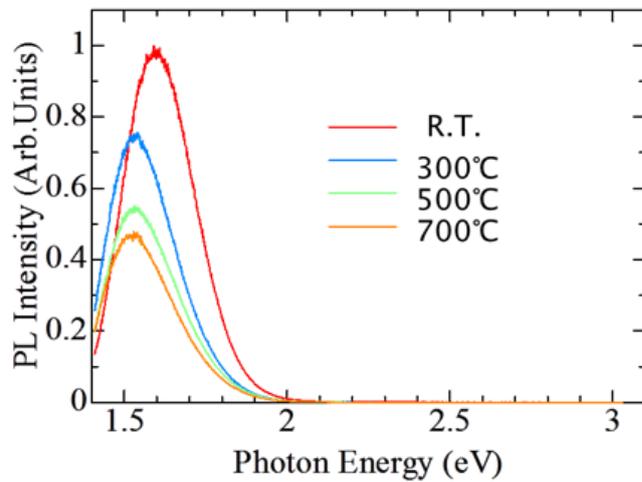
**Figure 4.** PL spectra of samples produced with PLD techniques. The pressure of oxygen during ablation is indicated in the figure. Samples were finally annealed using a conventional tube furnace (FA) at 1050 °C for 4 hours. Duration time and substrate temperature were kept 1 hour and R.T., respectively.



**Figure 5.** PL spectra of samples produced with PLD techniques. Duration time for PLD was varied from 0.5 to 2 hours. Samples were finally annealed using a conventional tube furnace (FA) at 1050 °C for 4 hours. Oxygen pressure and substrate temperature during PLD were kept at 0.6 Pa and R.T., respectively.

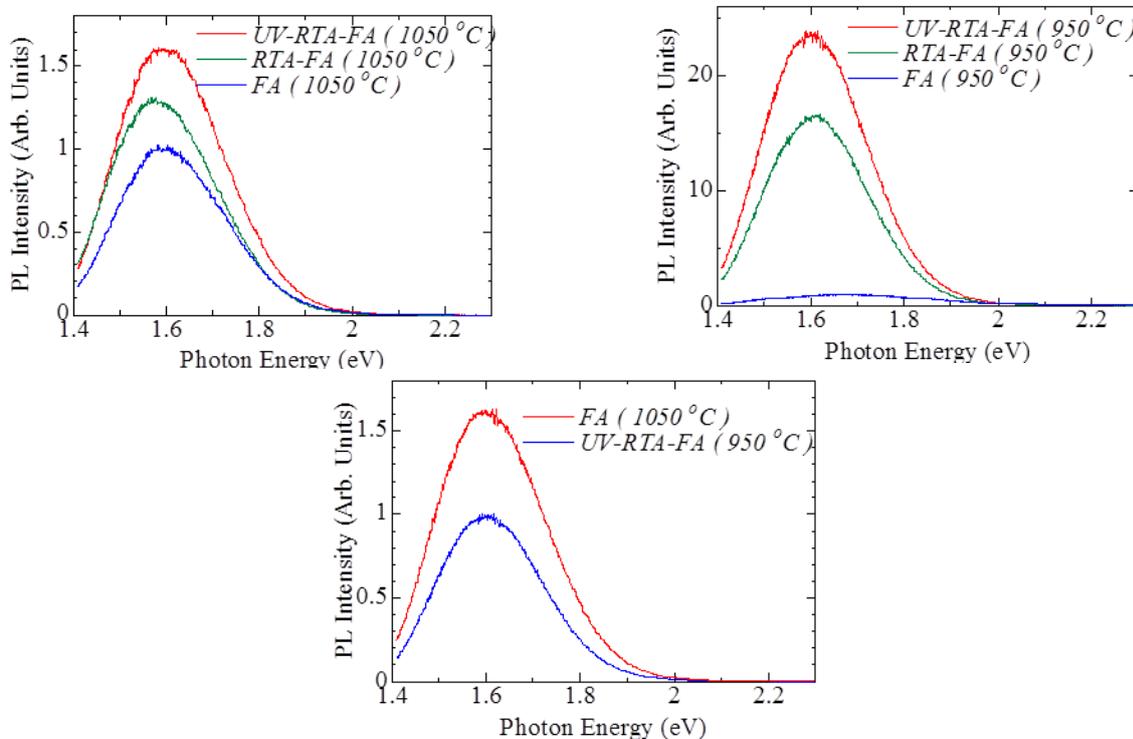


**Figure 6.** PL spectra of samples produced with PLD techniques. Substrate temperature during PLD was varied from R.T. to 700 °C. Samples were not annealed. Oxygen pressure and duration time were kept at 0.6 Pa and for 1 hour, respectively.



**Figure 7.** PL spectra of samples produced with PLD techniques. Substrate temperature during PLD was varied from R.T. to 700 °C. Samples were finally annealed using a conventional tube furnace (FA) at 1050 °C for 4 hours.

Next, we show the results for effects of excimer UV-light irradiation and RTA on the photoluminescence, in case for PLD synthesized Si-rich oxide films. The photoluminescence spectra of samples after treated using the conventional furnace at 1050 °C or 950 °C in a flowing N<sub>2</sub> atmosphere for 4 hours are shown in Figure 8. UV-light irradiation (172 nm, 7.2 eV) was carried out for 2 hours in vacuum. It is clear that the luminescence intensity with RTA treatments was enhanced than that without RTA. Moreover, the enhancement is much higher for samples treated with both UV-light and RTA. In this case, we can obtain sufficient luminescence intensity even after FA at 950 °C, combined with both UV-irradiation and RTA. These features are almost consistent with those obtained from ion implanted samples.



**Figure 8.** PL spectra of samples produced with PLD techniques. Samples were treated with excimer-UV light for 2 hours and/or RTA for 5 minutes at 1050 °C. Samples were finally annealed using a conventional tube furnace (FA) at 1050 °C or 950 °C for 4 hours. Oxygen pressure, duration time and substrate temperature were kept 0.6 Pa, 1 hour and R.T., respectively.

#### 4. Discussion

First, we discuss the enhancement of the photoluminescence with RTA prior to FA. For the case of embedded Si nanocrystals (Si-rich oxide films), the luminescence intensity is determined by the number of optimally-sized Si nanocrystals and their luminescence efficiency [18]. In forming the luminescent Si nanocrystals in a SiO<sub>2</sub> matrix from Si-rich oxide films, decomposition, segregation, diffusion, nucleation, aggregation, growth and crystallization processes are clearly important. The implanted or deposited Si atoms will initially form SiO<sub>x</sub> or to a lesser extent, Si aggregates. With such a short time RTA, of course, the diffusion of Si atoms in SiO<sub>2</sub> matrix is limited. As a result of diffusion-limited segregation, a number of small aggregates will be formed and they act as a nucleation point.

Now we discuss the enhancement obtained with excimer-UV light irradiation and RTA prior to FA. After ion implantation or reactive PLD, a lot of defects are introduced into the Si-rich oxide film layer. In both case, Si-rich type defects and oxygen-deficiency centres (ODCs) seem to be dominant and optically active [8], [17], [19]. The luminescence band peak at around 2.1 eV observed in as-implanted samples (shown in Figure 2) is believed to be assigned to Si-rich defects in SiO<sub>2</sub> [8], [20]. UV irradiation induces the bond-breaking of Si-Si or Si-O. ODCs have an optical absorption band peak at 7.6 eV, and the band tail extends to 7.2 eV corresponding to the emission energy from the excimer-UV lamp. As a result of UV irradiation, we can expect defect generation.

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

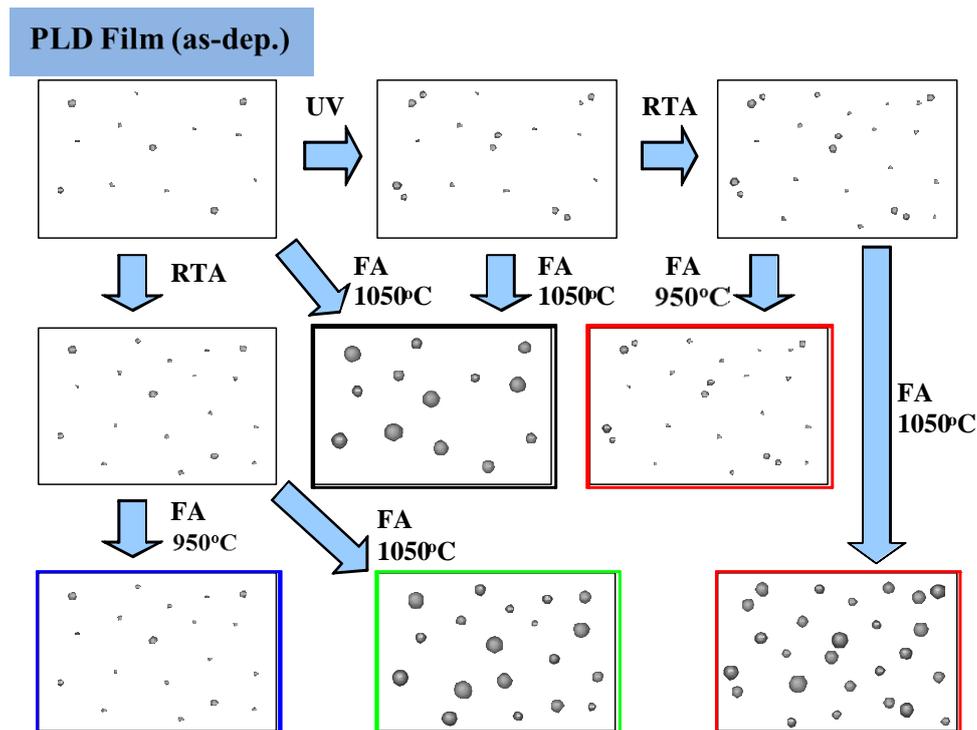
Here, we discuss the effects of photoluminescence after UV irradiation and RTA and subsequent lower temperature FA. It is well known that the decomposition of SiO<sub>x</sub> occurs at a temperature above 1000 °C [21]. As shown in Figure 3 and Figure 8, we observed photoluminescence even after FA at 900 °C (ion-implantation) and 950 °C (PLD). There are two possibilities to explain our experimental results. One is due to the crystallization of implanted Si small aggregates and the annihilation of non-radiative defects. We can exclude this possibility simply because sufficient luminescence was not obtained after only FA. The other possible explanation is that the decomposition of SiO<sub>x</sub> is induced by UV and RTA. The aggregation and crystallization occur with subsequent lower temperature FA. Initial growth of Si nanocrystals was observed in samples prepared with PLD at 700 °C, as shown in Figure 7.

Now, we will discuss the difference of peak energies, shown in Figure 3. In the model proposed by the present authors for the luminescence from Si nanocrystals in SiO<sub>2</sub> [10], 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 SiO<sub>2</sub> layer, for which the energy levels are affected by interactions between clusters, plays 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 lower FA, a simple quantum confinement model will not be acceptable based on the present experimental results.

#### 5. Conclusion

We have investigated the effects of excimer-UV light irradiation and the rapid thermal annealing (RTA) process on the photoluminescence of Si implanted SiO<sub>2</sub> and reactive-PLD produced Si-rich oxide films. We found that UV and RTA process are effective to obtain luminescent Si nanocrystals, even with low temperature FA (less than 1000 °C). Moreover, we obtained intense luminescence with the same way. The formation process of Si nanocrystals with UV, RTA and FA treatments can be

explained with bond-breaking (Si-Si and/or Si-O), defect generation, de-nucleation, defect-initiated nucleation and freezing of states. We also found that the similarities of photoluminescence with the way of preparation techniques. Moreover, both the peak energies and intensities depend on the pressure of oxygen during PLD and the duration time for PLD. The maximum photoluminescence intensity can be obtained with oxygen pressure of 0.6 Pa for 1 hour. We can summarise the results schematically in Figure 9.



**Figure 9.** Schematic illustration of the formation process of silicon nanocrystals in SiO<sub>2</sub> matrix, initially synthesized by reactive pulsed laser deposition.

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