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Luminescent Si Nanocrystals Synthesized by Si Ion Implantation and Reactive Pulsed Laser Deposition: The Effects of RTA, Excimer-UV and E-Beam Irradiation

T. S. Iwayama, T. Hama

***Abstract*—**Si ion implantation was widely used to synthesize specimens of SiO_2 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 10^{16} ions/cm^2. 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 is found to be observed even after FA at 900 ^oC, only for specimens treated with excimer-UV lamp and RTA. We also prepared specimens of Si nanocrystals embedded in a SiO_2 by reactive pulsed laser deposition (PLD) in an oxygen atmosphere. We will make clear the similarities and differences with the way of preparation.

***Keywords*—**Ion implantation, photoluminescence, pulsed laser deposition, rapid thermal anneal, Si nanocrystals.

I. Introduction

AFTER 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 decade [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_2 using ion implantation [7], [8]. 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 [9], [10]. Nowadays, it is well known that Si ion implantation into SiO_2 and subsequent high temperature annealing (more than 1000^{o}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_x phase and aggregation with high temperature annealing [7], [8], [11], [12]. The PL arising from implanted Si nanocrystals in SiO_2 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 (7.2 eV), e-beam irradiation and rapid thermal annealing (RTA) to enhance the PL and to achieve low temperature formation of Si nanocrystals have been investigated. Together with, we prepared specimens of Si nanocrystals embedded in a SiO_2 by reactive pulsed laser deposition (PLD) in an oxygen atmosphere. We will make clear the similarities and differences with the way of preparation.

T. S. Iwayama is with the Department of Physics, Aichi University of Education, Kariya, Aichi 448-8542, Japan (Phone: +81-566-26-2637; Fax: +81-566-26-2637; e-mail: tiwayama@auecc.aichi-edu.ac.jp).

T. Hama is with the School of Electrical and Computer Engineering, Kanazawa University, Kanazawa, Ishikawa 920-1192, Japan (e-mail: hama@se.kanazawa-u.ac.jp).

II. Experiment Procedures

The samples used were prepared by implanting Si^+ ions into oxidized Si epitaxial layers (10 Ω cm, 10 μm) grown on p^+-type Si wafers (Sb-doped) with a resistance of around 0.01 Ω cm (P on P^+, oxide thickness of around 500 nm). The Si ions were introduced at acceleration energy of 180 keV with the fluence 7.5x10^{16} ions/cm^2 with a beam current of 300 μA (current density of about 15 μA/ cm^2). The expected depth profiles of the implanted Si were estimated using TRIM [13] and found to be distributed in near Gaussian profiles with a peak depth around 300 nm from the surface. The implanted samples were subsequently annealed at 1050^{o}C or 900^{o}C in a flowing N_2 atmosphere for 4 hours using a conventional tube furnace. Some of the samples were UV-light (172 nm, 7.2 eV, Xe_2^*) irradiated for 2 hours with power density of 50 mW/ cm^2 in vacuum (Ushio, excimer UV lamp unit), or rapidly thermal annealed at 1050^{o}C in N_2 atmosphere for 5 minutes with a rising rate of 50^{o}C /sec (ULVAC, MILA-3000). We also investigated electron-beam (e-beam) irradiation effects on samples, by using e-beam gun with acceleration energy of 10 keV and beam current of 3 μA.

We also prepared Si nanocrystals embedded in a SiO_2 by reactive pulsed laser deposition (PLD) in an oxygen atmosphere. Si sub-oxide (SiO_x, $0<x<2$) films were firstly

deposited on Si wafers, by using conventional PLD system with 2nd-harmonic YAG laser (532nm, 10Hz, 80J/cm^2) under controlled low oxygen pressure (0.4Pa – 1.2Pa). Duration time for PLD was kept for 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. After deposition of SiO_x films on Si wafer in the oxygen ambient, the SiO_x films were annealed for 4 hours at 1050^{o}C in N_2 atmosphere to induce the formation of Si nanocrystals.

Conventional room temperature photoluminescence spectra were measured at various stages of the processing. A He-Cd laser (325 nm, 3.82 eV, 20mW) was used as the excitation source, and the photoluminescence was focused to spectrograph and detected by a cooled photomultiplier tube (Hamamatsu, R-943-02), employing the photon counting technique.

III. Results

It is well known that Si ion implantation into SiO_2 and subsequent high temperature annealing (more than 1000^{o}C) induce the formation of embedded luminescent Si nanocrystals by decomposition of supersaturated 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.

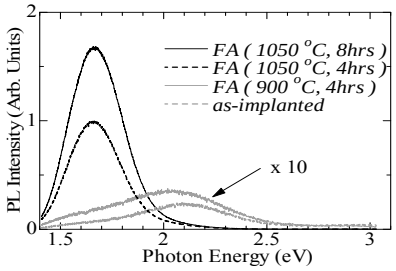

Fig. 1 PL spectra of a sample implanted to a fluence of 7.5×10^{16} Si ions/cm^2. The implanted sample was furnace annealed at 950 ^{o}C or 1050 ^{o}C for the times indicated in the figure

We will first show typical photoluminescence spectra obtained after FA at 1050^{o}C in a flowing N_2 atmosphere for several hours. The photoluminescence spectra of ion-implanted samples after annealing using a conventional furnace are shown in Fig. 1. Hereafter, all of the photoluminescence intensities are normalized to the luminescence of specimens formed after FA at 1050^{o}C for 4 hours without rapid thermal annealing, i.e., only conventional FA. The photoluminescence spectrum after FA at 900^{o}C is also shown. It is clear that the luminescence intensity grows as the annealing time increases and the peak energies of the luminescence spectra are independent of the annealing time after annealing at 1050^{o}C. It is noted that only a very weak photoluminescence was obtained after FA at 900^{o}C. The peak height of this photoluminescence band is at a similar level to that of an as-implanted sample and is related to defect generated during ion implantation.

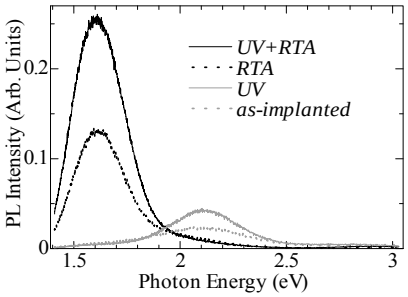

Fig. 2 PL spectra of samples implanted to fluence of 7.5×10^{16} Si ions/cm^2. Samples were treated with UV-excimer light for 2 hours and/or RTA for 5 minutes at 1050 ^{o}C. A PL spectrum before some treatments is also indicated in the figure for comparison

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 and increase with UV-light irradiation. Moreover, the luminescence peak around 2.1 eV was quenched and a new band located around 1.6 eV appears after RTA.

Samples with/without UV-irradiation and RTA treatment were further treated using the conventional furnace. The results for the photoluminescence measurements of samples after FA at 1050^{o}C in a flowing N_2 atmosphere for 4 hours are shown. It is clear that the luminescence intensity with RTA treatments was enhanced and is twice as high as the intensity for samples without RTA. 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.

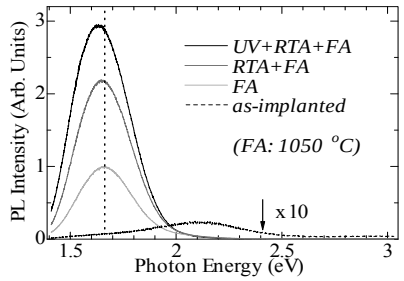

Fig. 3 PL spectra of samples implanted to a fluence of 7.5×10^{16} Si ions/cm^2, obtained after various steps. Excimer-UV irradiation and rapid thermal annealing conditions are similar to those in upper figure. Samples were finally annealed using a conventional furnace at 1050 ^{o}C for 4 hours. Each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

Low temperature annealing effects of UV-irradiated samples using a conventional furnace have been investigated. New additional shoulders of spectra located around 1.7 eV appear without quenching of the defect-related peak. This means that UV-irradiation before FA is not effective for FA at 900^{o}C and there is even generation of defects with UV-light irradiation, in this case. 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 N_2 atmosphere for 4 hours are shown in Fig. 4. The photoluminescence spectrum after only FA at 1050°C is also shown. 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.

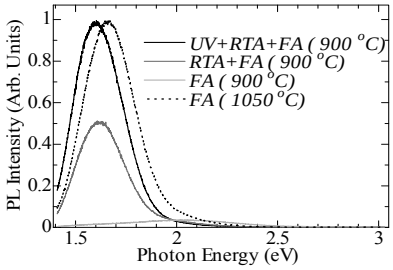

Fig. 4 PL spectra of samples implanted to a fluence of 7.5×10^{16} Si ions/cm^2, obtained after various steps. UV irradiation and RTA conditions are similar to those in previous figures. All samples were finally annealed using a conventional furnace at 900 °C or 1050 °C for 4 hours. Each annealing or irradiation history is indicated in the figure

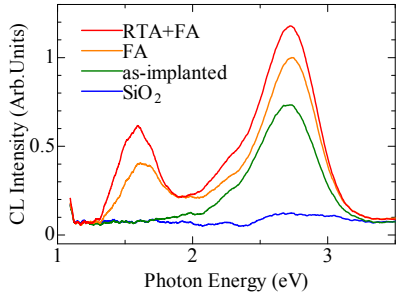

Fig. 5 CL spectra of samples implanted to a fluence of 7.5×10^{16} Si ions/cm^2, obtained after various steps. Similarity rapid thermal annealing conditions, annealing all samples using a conventional furnace at 1050°C for 4 hours

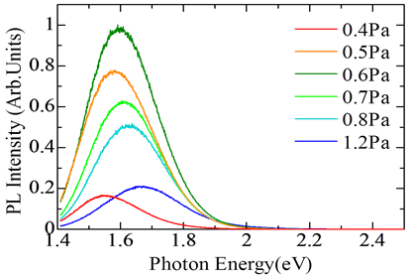

Fig. 6 PL spectra of samples produced with PLD techniques. The pressure of oxygen during ablation is indicated in the figure

We also investigated e-beam irradiation effects, and obtained photoluminescence and cathode luminescence spectra. It is not shown here, but we found that the photoluminescence intensity enhanced with e-beam irradiation, similar to that with UV irradiation. The results for the cathode luminescence measurements of samples after FA and RTA in a flowing N_2 atmosphere are shown in Fig. 5. It is clear from the figure that two main peaks appear in luminescence spectra. One peak located around 2.7eV is originate to some types of defects [14]. Another peak located around 1.6eV originates to Si nanocrystals, similar to that obtained by photoluminescence measurements.

We prepared Si nanocrystals embedded in a SiO_2 by reactive pulsed laser deposition (PLD) in an oxygen atmosphere. Si sub-oxide (SiO_x, $0<x<2$) films were firstly deposited on Si wafers, by using conventional PLD system with 2nd-harmonic YAG laser (532nm, 10Hz) under controlled low oxygen pressure (0.4Pa – 1.2Pa). After deposition in the oxygen ambient, the SiO_x films were annealed for 4 hours at 1050 °C in N_2 atmosphere to induce the formation of Si nanocrystals. The photoluminescence spectra of samples produced with PLD are shown in Fig. 6. 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 0.6Pa. Peak energies of the photoluminescence are also affected by ambient oxygen pressure. These features are almost consistent with those obtained from ion implanted samples.

IV. Discussion

First, we discuss the enhancement of the photoluminescence with RTA prior to FA. For the case of embedded Si nanocrystals, the luminescence intensity is determined by the number of optimally-sized Si nanocrystals and their luminescence efficiency [15]. In forming the luminescent Si nanocrystals in a SiO_2 matrix, decomposition, segregation, diffusion, nucleation, aggregation, growth and crystallization processes are clearly important. The implanted Si ions will initially form SiO_x 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.

Next we discuss the drastic enhancement obtained with excimer-UV light irradiation and RTA prior to FA. After ion implantation, a lot of defects are introduced into the SiO_2 layer. For Si-implanted samples, Si-rich type defects and oxygen-deficiency centers (ODCs) seem to be dominant and optically active [7], [14], [16]. The luminescence band peak at around 2.1 eV observed in as-implanted samples (shown in Fig. 2) is believed to be assigned to Si-rich defects in SiO_2 [7], [8]. This luminescence intensity evidently increased with UV-light irradiation, as also shown in Fig. 2. 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 1minute. 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, and these new Si aggregates and generated defects act as nucleation points (defect-initiated nucleation).

Now, 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_x occurs at a temperature above 1000°C [17]. As shown in Fig. 4, we observed photoluminescence even after FA at 900°C. 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_x is 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. 4. In the model proposed by the present authors for the luminescence from Si nanocrystals in SiO_2 [14], 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_2 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 Nano crystal formation with 900°C FA than that with 1050°C FA, a simple quantum confinement model will not be acceptable based on the present experimental results.

V. 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_2. 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 similar luminescence can be obtained from samples produced with PLD techniques in oxygen ambient. Moreover, both the peak energies and intensities depend on the pressure of oxygen during PLD. The maximum photoluminescence intensity can be obtained with oxygen pressure of 0.6Pa.

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