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Photoluminescence of Plasma Enhanced Chemical Vapor Deposition Amorphous Silicon Oxide with Silicon Nanocrystals Grown at Different Fluence Ratios and Substrate Temperatures

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Near-infrared photoluminescent dynamics of thermally annealed Si-rich SiO_x films grown by plasma enhanced chemical vapor deposition at different substrate temperatures and N_2O/SiH_4 fluence ratios are studied. The size of nanocrystallite Si (nc-Si) critically depends on the density of oxygen atoms in a Si-rich layer when the N_2O/SiH_4 ratio is smaller than 4; that is, it significantly increases at low N_2O/SiH_4 ratios. Deposition at a high N_2O/SiH_4 ratio strongly reduces the density of nc-Si and degrades the luminescence at 700–800 nm since the density of oxygen atoms is sufficient in the reaction of nc-Si with silicon atoms and formation of a stoichiometric SiO_2 matrix. Under a high RF power condition, the increasing substrate temperature usually inhibits the precipitation of nc-Si since high-temperature growth facilitates stochiometric SiO_2 deposition. The disappearance of visible PL reveals the complete regrowth of a stoichiometric SiO_2 matrix around a nanocrystallite Si cluster after annealing. The results of the transient luminescent analysis of Si-rich SiO_x samples corroborate well with the observed values and reveal a lifetime of 43 µs under an optimized nc-Si precipitation condition of 1100°C annealing for 3 h.
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KEYWORDS: Silicon nanocrystals, photoluminescence, plasma enhanced chemical vapor deposition, Si-rich silicon dioxide, lifetime

1. Introduction

Photoluminescent (PL) of nanocrystalline silicon (nc-Si) structures have been comprehensively investigated since the first report on the luminescence of porous Si.[1)] The optical gain observed in silicon dioxide waveguides with buried silicon nanocrystals further initiates the potential applications of all Si-based optoelectronic integrated circuits.[2)] Up to now, several methods, which include plasma-enhanced chemical vapor deposition (PECVD),[3)] electron-beam evaporation,[4)] cosputtering[5)] and Si ion implantation,[6–8)] have been used to synthesize Si-rich SiO_x layers and to precipitate nc-Si. The most intriguing method is the PECVD deposition associated with subsequent heat treatment, since it enables the easy deposition of a Si-rich SiO_x film with a sufficiently high density of excess Si atoms by controlling the fluence of reactive gases. However, there are few studies on the correlation between the N_2O/SiH_4 fluence ratio and the substrate temperature for optimum nc-Si precipitation. In this work, the near-infrared continuous-wave (CW) and time-resolved (TR) PL spectroscopes are employed to study the effects of the substrate temperature and N_2O/SiH_4 fluent ratio on the PL intensity and lifetime of PECVD-grown, thermally annealed Si-rich SiO_x film with buried nc-Si.

2. Experimental

Si-rich SiO_x films with a thickness of about 100 nm were deposited on (100)-oriented n-type Si substrates with resistivities of 4–7 Ω·cm using a conventional high-density PECVD system at a pressure and a forward RF power of 50 mTorr and 200 W, respectively. The samples were prepared at different gas mixtures and substrate temperatures. Gas mixtures with a constant SiH_4 flucence of 30 sccm and various N_2O flucences (from 90 to 180 sccm) were used. The substrate temperature was changed from 100 to 350°C. The detailed processing conditions are shown in Table I. The Si-rich SiO_x samples were encapsulated by annealing in a quartz furnace with N_2 atmosphere at 1100°C from 1 to 5 h to induce precipitation of nc-Si. The thickness of a Si-rich SiO_x sample containing nc-Si structures was determined by α-step measurement after etching. Room-temperature CWPL measurement with a pumping source, a He–Cd laser, at a wavelength and an average power intensity of 325 nm and 5 W/cm^2, respectively, was carried out with a photon-counting system, which includes a fluorescence spectrophotometer (Jobin Yvon, TRIAX-320) with a wavelength resolution of 0.06 nm and a photomultiplier (Jobin Yvon, Model 1424M). In a TRPL experiment, a SiO_x film was pumped using a Q-switched YAG laser (Continuum, NY 60) at 355 nm and a repetition rate of 1 Hz. The pumping pulse width and pulse energy were 60 ps and 0.5 mJ, respectively. A PL signal was detected using a single-grating monochromator with a near-infrared photomultiplier tube and recorded using a sampling scope (Lecroy, Model LT372 with a resolution of 2 ns).[9)] A TRPL trace, $I_{PL}(t)$, was resolved to extract the PL lifetime using a deconvoluted equation,

Table I. N_2O flucences, SiH_4 flucences and substrate temperatures of different samples.

	A2	A7	A8	A9	A12	A13	A14	A17
N_2O (sccm)	90	120	150	180	120	120	120	120
SiH_4 (sccm)	30	30	30	30	30	30	30	30
Temp. (°C)	100	100	100	100	200	250	300	350

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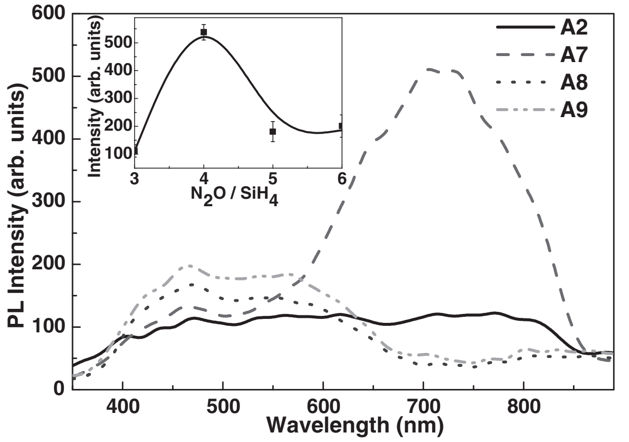

Fig. 1. PL spectra of 3-h-annealed Si-rich SiO_x films fabricated by PECVD with different N_2O/SiH_4 ratios. The inset shows the peak intensity as a function of the N_2O/SiH_4 ratio.

$$I_{\mathrm{PL}}(t) = \int_{-\infty}^{\infty} \sum_{n=1}^{k} I_n \exp\left(-\frac{t'}{\tau_n}\right) \cdot I_{\mathrm{Laser}}(t - t')\,dt',$$

where I_n and τ_n are the intensity and lifetime of the nc-Si.

3. Results and Discussion

3.1 *Effect of N_2O/SiH_4 ratio on density of nc-Si in PECVD-grown Si-rich SiO_x film*

After a Si-rich SiO_x film PECVD-grown at a constant substrate temperature of 100°C, a constant SiH_4 fluence of 30 sccm, and a N_2O/SiH_4 ratio of 4 was annealed at 1100°C for 3 h, a maximum PL intensity at a wavelength of 728 nm was observed (Fig. 1). An optimum N_2O fluence was found at 120 sccm, as shown in the inset of Fig. 1. The excess Si density of the PECVD-grown Si-rich SiO_x film is proportional to the density of nc-Si and the SiH_4 fluence. However, as the N_2O/SiH_4 ratio increases from 4 to 6, the density of nc-Si buried in the PECVD-grown Si-rich SiO_x film decreases and the PL intensity at 400–700 nm increases. The effects of the N_2O/SiH_4 ratio and the evolution of radiative centers buried in the SiO_x structure are seldom addressed. A sufficient amount of oxygen atoms, generated from the N_2O gas, completely reacts with Si atoms, generated from the SiH_4 gas, to deposit a stoichiometric SiO_2 film. After thermal annealing, oxygen-related defects, such as a neutral oxygen vacancy defect[10–12] (NOV, denoted as $O_3{\equiv}Si{-}Si{\equiv}O_3$), are activated. In a previous study,[10] NOV defects attributed to the displacement of oxygen atoms from the stochiometric SiO_2 matrix by the bombardment of Si ions, were usually observed in a Si-ion-implanted Si-rich SiO_2 film. In our experiment, the enhanced PL intensity at the wavelength of 455 nm is attributed to the NOV defect in the SiO_2 matrix fabricated using a sufficient N_2O fluence (N_2O/SiH_4 ratios > 5). This indicates that the growth of the stochiometric SiO_2 matrix at high N_2O/SiH_4 ratios is preferred. On the other hand, for the samples with N_2O/SiH_4 ratios of 5 or larger, the PL intensity at a wavelength of 750 nm is not enhanced, since a complete reaction with oxygen and Si atoms causes few excess Si atoms to hardly precipitate nc-Si.

A low PL intensity of around 750 nm was obtained for the sample fabricated with a N_2O/SiH_4 ratio < 4. The size of nc-Si buried in the Si-rich SiO_x film depends on the density of oxygen atoms in the Si-rich SiO_x film. Nc-Si larger than 5 nm can be observed in the Si-rich SiO_x film prepared with small N_2O fluences (N_2O/SiH_4 ratios < 4). In addition, the small N_2O/SiH_4 ratio cannot produce the stoichiometric SiO_2 matrix due to the insufficient density of oxygen atoms. It induces an imperfect quantum confinement effect in the SiO_2 matrix, resulting in the suppression of the PL radiating from nc-Si. The PL intensities at 455 nm for the NOV defect and 750 nm for nc-Si in the sample prepared with a N_2O/SiH_4 ratio of 3 are observed to be lower than those of the sample prepared with a N_2O/SiH_4 ratio of 4. As shown in Fig. 1, the enhanced PL intensity in the visible range, attributed to oxygen-related defects, and the highest PL intensity in the near-infrared range, attributed to nc-Si, were observed in the sample with the N_2O/SiH_4 ratio of 4.

This indicates that at a suitable N_2O/SiH_4 ratio, not only the highest density of excess Si atoms, resulting in a large amount of nc-Si, but also the stoichiometric SiO_2 matrix, resulting in a better quantum confinement between nc-Si and the SiO_2 matrix, can be obtained. Therefore, the N_2O/SiH_4 ratio should be well controlled.

3.2 *Effect of substrate temperature on density of excess Si atoms and nc-Si*

In general, a stochiometric SiO_2 film is grown using a PECVD system at a substrate temperature and an RF power of 350–400°C and 700–900 W, respectively. However, a nearly stochiometric SiO_2 film can be grown at an RF power as low as 200 W in our case. Typically, a further reduction in either substrate temperature or RF power results in an evident phase separation between Si and SiO_2 during deposition. The two different methods are potentially applicable to the fabrication of a Si-rich SiO_x film with a high excess Si density. Previously, the substrate temperature was maintained at 350–400°C, and the RF power was decreased to <50 W for preparing a Si-rich SiO_x film.[2,3] Nonetheless, the effect of reducing the substrate temperature at a given RF power on the excess Si density of the PECVD-grown Si-rich SiO_x film was seldom discussed. By increasing the substrate temperature from 100 to 350°C, the PL spectra of Si-rich SiO_x films PECVD-grown at an RF power of 200 W are shown in Fig. 2. The peak PL intensity shows a distinct decreasing trend with increasing substrate temperature. The near-infrared PL is mainly due to the quantum confinement effect of the nc-Si cluster, whereas the defect-related visible PL can hardly be obtained in the PECVD-grown Si-rich SiO_x film.

After annealing, Ma *et al.* also observed the Si nanoparticles embedded in a Si-rich SiO_2 film deposited at a substrate temperature between 30 and 450°C.[13] The highest density of nc-Si was found in the Si-rich SiO_2 film deposited at a low substrate temperature of 30°C, which was attributed to the enhanced phase separation between Si and SiO_2 during low-substrate-temperature deposition at a high RF power in the PECVD chamber.[14] Obviously, a low-substrate-temperature deposition that facilitates the generation of nonstoichiometric SiO_2 was revealed in our experiment. The slightly increasing PL at 455 nm in the Si-rich SiO_x film deposited at such a low substrate temperature was also observed due to dense oxygen-related NOV defects.

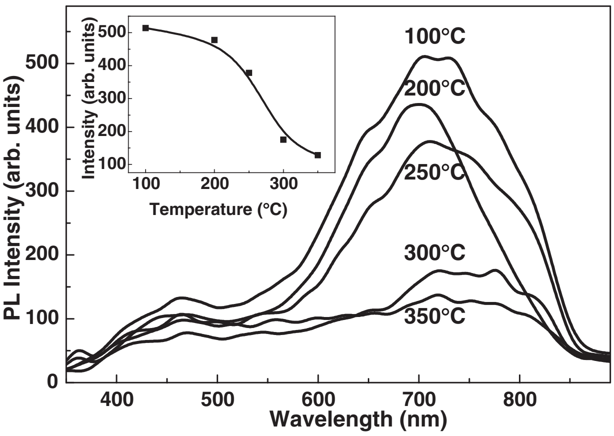

Fig. 2. Room-temperature PL spectra of annealed Si-rich SiO_x films fabricated by PECVD with different substrate temperatures from 100 to 350°C. The inset shows the peak intensity as a function of substrate temperature.

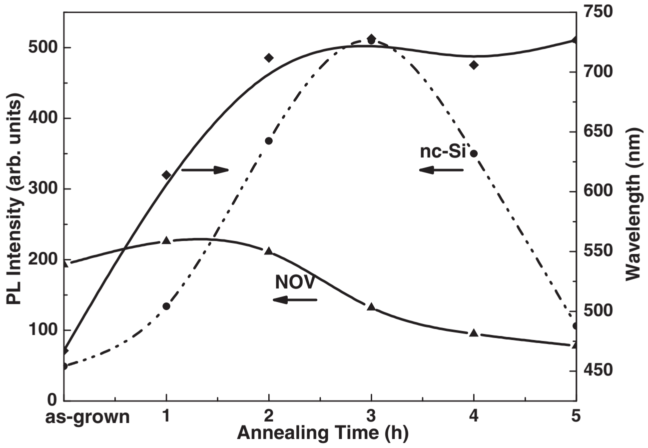

Fig. 4. Peak PL intensities of NOV defect and nc-Si, and peak wavelength of nc-Si as a function of the annealing time.

Thus, a low substrate temperature is required for depositing a SiO_x film with a high excess Si density when the RF power of the PECVD system used is high. The peak PL at a wavelength between 703 and 728 nm is contributed by nc-Si with a diameter ranging between 3.5 and 3.8 nm. A nearly stoichiometric SiO_2 matrix prevents the formation of a large-size precipitate of mobile Si atoms, which increases the density of small-size nc-Si. Under a high RF power condition, a high substrate temperature is detrimental to the formation of nc-Si, since it favors stochiometric SiO_2 deposition.

3.3 *Effect of annealing time on size and PL lifetime of nc-Si*

The annealing-time-dependent PL spectra of sample A7 with the highest density of excess Si atoms are shown in Fig. 3. The optimum annealing time for the precipitation of nc-Si is 3 h, corresponding to the peak wavelength of 703 nm. The PL at a wavelength of 455 nm for the as-grown sample A7 is attributed to the NOV defect. After annealing at 1100°C for 1 h, the sample A7 has the maximum PL intensity of the NOV defect. In comparison, the optimized annealing time for the PECVD-grown SiO_x sample is similar to that (1.5 h) for the multienergy Si-ion-implanted SiO_2 sample reported previously.[15–17] Moreover, the NOV intensities of both the PECVD-grown and Si-ion-implanted SiO_2 samples decrease after annealing at 1100°C for 2 h. As the annealing time increases to 5 h, the peak intensity of the NOV defect rapidly decreases since most of the NOV defects are annealed in a high-temperature environment. In addition, the peak wavelength is redshifted from 455 to 727 nm due to the precipitation of nc-Si, as shown in Fig. 4. This indicates that the increase in PL intensity at a wavelength of 600 nm is attributed to small-size nc-Si. After 1-h annealing, the excess Si atoms rapidly precipitate into small-size nc-Si. Moreover, nc-Si is enlarged due to the accumulation of small-size nc-Si after a long thermal annealing time of up to 3 h. An obvious redshift of the peak PL wavelength is also found after annealing times of 1 to 3 h. However, as the annealing time increases to 5 h, a small redshift is observed due to large-size nc-Si. On the other hand, the variations in the PL intensities of NOV and nc-Si as a function of annealing time are shown in Fig. 4. The intensities of nc-Si were determined at a wavelength of 703 nm. The optimized annealing time for nc-Si is 3 h and the intensity of nc-Si decreases by a factor of 5 as the annealing time increases to 5 h due to the reaction of nc-Si with mobile oxygen atoms resulting in the regrowth of SiO_2 matrix.

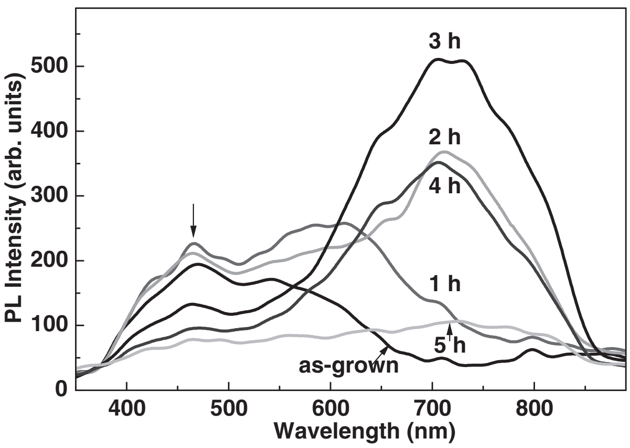

Fig. 3. PL spectra of as-grown sample A7 after annealing at 1100°C for 1–5 h.

The PL lifetimes of sample A7 for the annealing times of 1, 2, and 3 h are 27, 39, and 43 μs, respectively, and the PL decayed spectra are shown in Fig. 5. The calculated size of nc-Si buried in the Si-rich SiO_x film grown under the conditions of sample A7 is around 3.7 nm. In comparison, Brongersma *et al.*[11] formed Si nanocrystals (diameter, 2–5 nm) by Si ion implantation and thermal annealing at 1100°C, and the room-temperature lifetime of Si nanocrystals with a PL wavelength of about 710 nm is similar to our result. Moreover, the decayed lifetime of nc-Si embedded in the sample A7 after annealing for 3 h ($\tau_{\text{nc-si}} = 43\,\mu s$) is very close to that obtained from the plot (lifetime τ vs λ_{PL}) given by Garcia *et al.*[18]

4. Conclusions

The CWPL and TRPL properties of thermally annealed PECVD-grown nc-Si samples that show luminescence in the

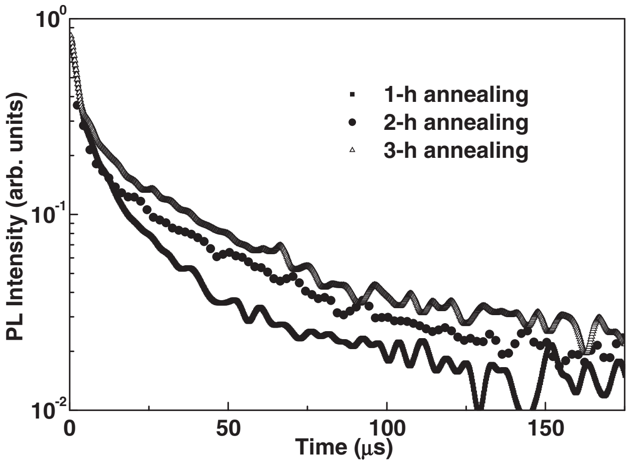

Fig. 5. Time-resolved PL traces of sample A7 after annealing at 1100°C for 1, 2, and 3 h.

near-infrared spectrum are studied. The optimum annealing time at a temperature of 1100°C and the N_2O/SiH_4 ratio are 3 h and 4, respectively. The optimum processing substrate temperature is determined to be 100°C according to the substrate-temperature-dependent spectra. As the N_2O/SiH_4 ratio < 4, the size of nc-Si buried in the Si-rich SiO_x film depends on the density of oxygen atoms in the Si-rich SiO_x film, and the low N_2O/SiH_4 ratio causes an imperfect quantum confinement effect in the SiO_2 matrix, resulting in the suppression of the PL radiating from nc-Si. At a N_2O/SiH_4 ratio > 4, the intensity between 700 and 800 nm is much weak because a sufficient amount of oxygen atoms completely reacts with silicon atoms to generate a SiO_2 film, and the amount of excess Si is too low to precipitate nc-Si. The normalized TRPL traces of samples with an optimum N_2O/SiH_4 ratio and an optimum processing substrate temperature, after annealing at 1100°C for 1, 2, and 3 h are 27, 39, and 43 μs, respectively.

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