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APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 8 23 FEBRUARY 2004

Enhanced formation of luminescent nanocrystal Si embedded in Si/SiO_2 superlattice by excimer laser irradiation

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(Received 12 September 2003; accepted 19 December 2003)

The effect of excimer laser annealing on the formation of luminescent nanocrystal Si (nc-Si) embedded in Si/SiO_2 superlattice is investigated. An amorphous Si/SiO_2 superlattice consisting of 20 periods of 2 nm thin Si layers and 5 nm thin SiO_2 layers was deposited on Si using electron cyclotron resonance plasma-enhanced chemical vapor deposition. Excimer laser annealing alone did not result in any nc-Si luminescence even at an energy density sufficient to melt the Si layers. However, if the nc-Si is preformed by a thermal anneal, subsequent excimer laser annealing will result in a threefold increase of the nc-Si luminescence intensity. The temperature dependence of the nc-Si luminescence spectrum, lifetime, and intensity indicates that excimer laser annealing activates luminescent nc-Si by removing defects and amorphous regions in thermally crystallized Si layers without significant changes in the size or shape of nc-Si. © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1650037maximum]

Ever since the report on the luminescence of porous Si by Canham,[1] the study of luminescent nanocrystalline Si (nc-Si) has been an extremely active field of research.[2] With steady advances, there now have been reports of optical gain in nc-Si,[3] as well as in light-emitting diodes with very low turn-on voltage and high efficiency at room temperature.[4,5] Of the many possible methods of producing nc-Si, precipitating them from a SiO_x $(x<2)$ matrix by a high temperature anneal has proven to be a successful method of preparing a dense array of robust, well-passivated nc-Si in a manner that is compatible with standard Si processing technology.[3,5–7] One drawback of this method, however, is that both the nucleation rate and the growth rate of the nc-Si are determined by supersaturation. This leads to difficulty in controlling the size and the density of nc-Si separately since increasing the supersaturation of Si in the original SiO_x matrix leads to formation of larger nc-Si rather than formation of a denser array of small nc-Si.[8]

An interesting alternative is crystallization of Si/SiO_2 superlattices with nm-thin amorphous Si (a-Si) layers, since for these, the size and density can be controlled independently by varying the thickness of the Si layers.[9–12] A serious drawback of this method, however, is that such nm-thin a-Si layers are very resistant to crystallization due to strain, and can require crystallization temperatures as high as 1300 °C.[13,14] This is not only undesirable from a processing point of view, but also can lead to breakup and agglomeration of the Si layers, and lead to larger nc-Si size and a strong decrease in nc-Si luminescence efficiency.[12]

Thus, reduction of such a large thermal budget is an important goal in nc-Si research. Recently, there has been a report that nc-Si formation can be achieved at much lower temperatures by using an SiO/SiO_2 superlattice.[15] Another promising alternative is an excimer laser anneal (ELA), since excimer lasers with sufficient energy density can nearly instantaneously crystallize or even melt a thin layer of Si at ambient processing temperatures.[16,17] In this letter, we report the effect of ELA upon the formation of luminescent nc-Si in an a-Si/SiO_2 superlattice deposited on Si. We find that ELA alone cannot form luminescent nc-Si even when the energy density is sufficient to melt the Si layers. When combined with a thermal anneal, however, it increases the nc-Si luminescence intensity threefold. The temperature dependence of the nc-Si luminescence spectrum, lifetime, and intensity indicates that excimer laser annealing activates luminescent nc-Si by removing defects and amorphous regions in thermally crystallized Si layers without significant changes in the size or shape of nc-Si.

a-Si/SiO_2 layers with 2 nm thin a-Si layers and 5 nm thin SiO_2 layers were deposited on Si using electron cyclotron resonance plasma-enhanced chemical vapor deposition of SiH_4 and O_2. The microwave power was 400 W, and the deposition temperature was 450 °C. After deposition, the samples underwent (a) a thermal anneal at 1100 °C for 1 h in vacuum only; (b) a thermal anneal as before followed with ELA with three shots of a 30 ns, 308 nm XeCl excimer laser at room temperature with power densities ranging from 250 to 500 mJ cm^{-2}; (c) or ELA with three shots of an excimer laser at 500 mJ cm^{-2} only. Following treatment, all samples were hydrogenated by a 1 h anneal at 700 °C in a forming gas environment to passivate defects and enhance nc-Si luminescence. Transmission electron microscopy analysis confirmed that the layers were preserved in all cases (data not shown).

After the anneals photoluminescence (PL) spectra were obtained using the 477 nm line of an Ar laser as the excitation source, a grating monochromator, an InGaAs photomul-

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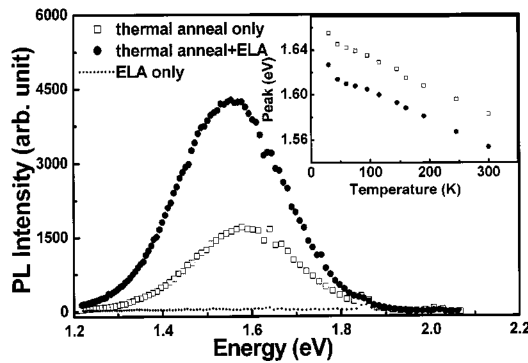

FIG. 1. Room-temperature PL spectra of samples that underwent a thermal anneal only; a thermal anneal followed by a ELA with power density of 500 mJ cm^{-2}; ELA only. All samples were hydrogenated by a 1 h anneal at 700 °C in a forming gas environment to passivate defects and enhance nc-Si luminescence. The inset shows the temperature dependence of the peak position.

tiplier tube, and the lock-in technique. The nominal pump power was about 2 W cm^{-2}. Low-temperature PL spectra were obtained using a closed-cycle He cryostat, and time-resolved luminescence decay traces were obtained using a digitizing oscilloscope. All spectra were corrected for system response.

Figure 1 shows room-temperature PL spectra of the samples. The inset shows the temperature dependence of the peak position. We observe no luminescence from the film that underwent ELA only. The sample that underwent thermal annealing only shows a Gaussian-shaped PL peak centered near 1.6 eV that is typical of nc-Si luminescence. Subsequent ELA increases the overall PL intensity such that after being irradiated with an energy density of 500 mJ cm^{-2}, the PL intensity had increased threefold. Samples with lower laser energy density displayed smaller enhancement of the PL intensity (data not shown). The redshift of the PL peak due to ELA, however, amounts to 30 meV only. Furthermore, ELA does not affect the full width at half maximum (FWHM) of the PL peak either, since they are ~270 meV for both films. We note that the peak PL energy of 1.6 eV agrees well with reported values from other similarly sized nc-Si/SiO_2 superlattices that were formed from either SiO/SiO_2 (Ref. 15) or a-Si/SiO_2 superlattices.[12]

Figure 2(a) shows the temperature dependence of the integrated PL intensities of the sample that underwent thermal annealing only and the sample that underwent thermal and ELA with an energy density of 500 mJ cm^{-2}. We find that in both cases, the PL intensity initially increases, and then decreases with an increase in temperature.

The PL decay traces were nonexponential, but can be described well by a stretched exponential of the form $\exp[-(t/t_0)^{\beta}]$, where t_0 is the effective lifetime. The temperature dependence of the effective lifetimes is shown in Fig. 2(b). We find that ELA does not affect the lifetime. In both cases, the lifetime continues to decrease with an increase in temperature from 2 ms to 70 μs.

In describing nc-Si luminescence, a model that was proposed by Calcott *et al.*[18] has recently been confirmed to agree well with both theoretical and experimental results.[19,20] In this model, the luminescence is ascribed to recombination of strongly localized excitons whose levels are split by ex-

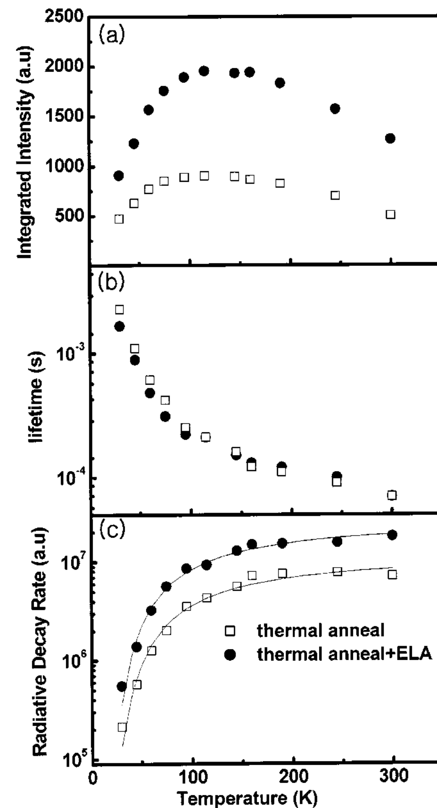

FIG. 2. Temperature dependence of the integrated PL intensities of the sample that underwent a thermal anneal only and the sample that underwent a thermal anneal and ELA with energy density of 500 mJ cm^{-2}. (b) Temperature dependence of the effective lifetimes measured at emission wavelength of 730 nm. (c) Temperature dependence of the radiative decay rates (given in arbitrary units) obtained by dividing the PL intensities given in (a) by the luminescence decay times given in (b). The solid curves are the result of fitting the radiative decay rates using a model proposed by Calcott *et al.* (Ref. 18).

change energy into a forbidden (dark) triplet state with radiative rate R_T and an allowed (bright) singlet state Δ above the triplet state with radiative rate R_S. The total radiative decay rate then can be written as the result of a thermal equilibrium between the two levels as

$$R_R = \frac{3R_T + R_S \exp(-\Delta/kT)}{3 + \exp(-\Delta/kT)}. \quad (1)$$

Figure 2(c) shows the temperature dependence of the radiative decay rates (given in arbitrary units) obtained by dividing the PL intensities given in Fig. 2(a) by the luminescence decay times given in Fig. 2(b),[12,20] and the fit to the data using Eq. (1). We find that in both cases, the radiative decay rates increase by a factor of ~40 with an increase in temperature, and that both can be fitted well by assuming Δ of 12 meV, in good agreement with previously published results.[20]

The above results confirm that the luminescence we observe is indeed due to nc-Si. It also indicates, however, that ELA alone does not form luminescent nc-Si in 2 nm thin Si layers even though the energy density and the absorption depth are sufficient to fully melt the a-Si layers.[21,22] It may be that a-Si layers are not crystallized due to the presence of SiO_2 layers that prevent propagation of the melt front. Or it may also be that the nc-Si crystallized by ELA is too defective for luminescence even with hydrogenation. In any case,

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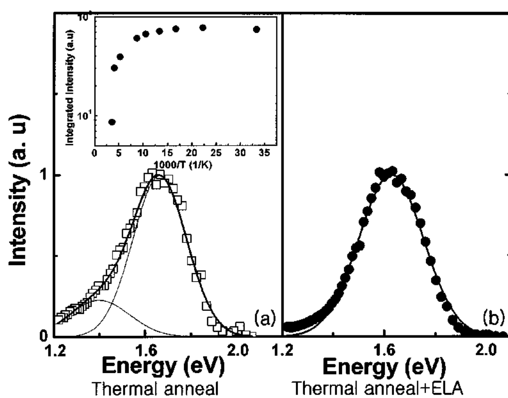

FIG. 3. (a) Normalized low-temperature (30 K) PL spectrum of the sample that underwent a thermal anneal at 1100 °C only. The solid lines are the results of using two Gaussian peaks to fit the PL spectrum. The inset shows the temperature dependence of the intensity of the PL peak centered at 1.4 eV. (b) Normalized low-temperature (30 K) PL spectra of the sample that underwent a thermal anneal followed by ELA with power density of 500 mJ cm^{-2}. The solid line is the best Gaussian fit using a single Gaussian peak centered at 1.6 eV.

Figs. 1 and 2 indicate that forming luminescent nc-Si in nm-thin *a*-Si layers is difficult not only with thermal annealing, but also with ELA as well.

On the other hand, if nc-Si is preformed by thermal annealing, ELA substantially increases the nc-Si PL intensity. The reason for such enhancement can be found in Fig. 3 which shows the low-temperature PL spectra. The PL spectrum of the sample that underwent thermal annealing and ELA remains Gaussian down to 30 K. On the other hand, the PL spectrum of the sample that underwent thermal annealing only shows a pronounced shoulder at lower energies such that an additional Gaussian peak centered at 1.4 eV is necessary to fit the PL spectrum. The temperature dependence of this additional luminescence peak, however, does not match that of the 1.6 eV peak due to nc-Si. As is shown in the inset, it decreases monotonically with an increase in temperature, and drops below the noise level above 200 K.

Such temperature dependence, while unlike that of nc-Si, is similar to that of luminescence of *a*-Si. The peak position of 1.4 eV is in agreement with the reported values for *a*-Si.[23] Thus, we argue that a 1100 °C anneal leaves small regions of the Si layers amorphous and/or heavily defective, and that this amorphous/defective region quenches the nc-Si luminescence by acting as a nonradiative recombination site for excitons. ELA then improves the nc-Si luminescence by removing such regions. Furthermore, since all samples were hydrogenated for optimum luminescence, ELA seems to be more effective at defect removal than hydrogenation alone.

Such defect removal can also be achieved by a higher temperature anneal. Such an anneal, however, not only adds significantly to the thermal budget, but also results in strong redshifting of the luminescence peak by 100 meV or more and a substantial increase of the FWHM of the PL peak.[12] In contrast, the small degree of redshift and the near invariance of the splitting energy and FWHM following ELA indicate that ELA achieves defect removal without significantly changing the size, shape, or size distribution of nc-Si.[2] We note that an analogous situation has been known for some time in ELA of polycrystalline Si, in which ELA, by removing defects and amorphous regions at grain boundaries, greatly improves the electrical qualities without significantly changing the overall microstructure of the film.[24] Thus, the results presented here suggest that while ELA alone cannot form luminescent nc-Si, a low temperature anneal followed by ELA may be an effective method by which to produce small, luminescent nc-Si at a much reduced thermal budget, not only for Si/SiO_2 superlattices, but also for other systems in which nc-Si formation needs to be induced by a high temperature anneal.

In conclusion, we have investigated the effect of excimer laser annealing of a Si/SiO_2 superlattice with nm-thin Si layers. We find that excimer laser annealing alone does not form luminescent nc-Si even when the energy density is sufficient to melt the *a*-Si layers. Combined with a low-temperature thermal anneal, however, excimer laser annealing can be an effective method by which to produce small, luminescent nc-Si at a much reduced thermal budget.

This work was supported in part by the National Research Laboratory project and the National Nuclear Technology Program of the Ministry of Science and Technology of Korea.

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