

## Pulsed Laser Annealing of Thin Silicon Films

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The 30 ns pulsed XeCl excimer laser annealing of silicon films with an average thickness of 2.2 nm formed on quartz substrates is reported. Crystallization occurred at laser energies between 150 and 170 mJ/cm<sup>2</sup>. Raman scattering spectra revealed the mixed states of small crystalline grains, and nanocrystalline and disordered amorphous regions. The amorphization of the silicon films was observed for laser irradiation above 180 mJ/cm<sup>2</sup>. Photoluminescence was observed around at approximately 3 and 2 eV from 18 to 130 K for the films annealed at 260 °C for 3 h in 1.3 × 10<sup>6</sup> Pa H<sub>2</sub>O vapor after laser irradiation at 170 mJ/cm<sup>2</sup>. [DOI: 10.1143/JJAP.45.2437]

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### 1. Introduction

The pulsed laser crystallization of silicon has been precisely studied.<sup>1–7)</sup> Laser-induced melting followed by solidification has been analyzed. Pulsed-excimer-laser crystallization has been widely applied to the formation of polycrystalline silicon films for the fabrication of polycrystalline-silicon thin-film transistors (poly-Si TFTs) at low processing temperatures.<sup>8–15)</sup> The formation of crystalline silicon films with thicknesses from 20 to 100 nm has been established by pulsed-laser crystallization. A high crystalline volume ratio and crystalline grains with excellent properties have been obtained. Pulsed-excimer-laser irradiation is also an interesting method for the crystallization of very thin films because of the high optical absorption coefficient of silicon and the rapid heating of thin silicon films. The formation of small crystalline grains with low-dimensional quantum effect properties is expected. However, few research studies of the laser crystallization of very thin silicon films have been carried out.<sup>16)</sup>

In this paper, we report the pulsed XeCl excimer laser annealing of silicon films with an average thickness of 2.2 nm formed on glass substrates. The physics of the laser crystallization of the thin silicon films is discussed. The structural properties are also discussed. Ultraviolet-light-induced photo luminescence is also reported.

### 2. Experimental

Undoped amorphous silicon films were formed on quartz glass substrates at 300 °C by 13.56-MHz-RF plasma-enhanced chemical vapor deposition (PECVD) using SiH<sub>4</sub> gas. Average film thickness was determined from deposition rate and the optical reflectivity of the sample surface at 800 nm because the reflectivity was markedly increased by thin-silicon-film deposition. The film surface was also observed by atomic force microscopy (AFM). The samples were irradiated with a 308 nm pulsed XeCl excimer laser at room temperature in vacuum at different laser energies. Raman scattering was measured for structural analysis using a probe laser light at 514.5 nm with a 4 mW power and a 10 μm diameter. The defect passivation of the thin films was carried out. The silicon surface was coated with 76 nm SiO<sub>x</sub> films using thermal evaporation. The samples were then heated at 260 °C with 1.3 × 10<sup>6</sup> Pa H<sub>2</sub>O vapor for 3 h in order to oxidize disordered states and reduce the density of defects in

the silicon films.<sup>17,18)</sup> Photo luminescence spectra were measured at 18–300 K by He–Cd laser excitation with 10 mW.

### 3. Results and Discussion

Figure 1 shows AFM photographs of the silicon surface of as-deposited amorphous silicon films (a) and the same films laser-annealed at 170 mJ/cm<sup>2</sup> (b). Although the average film thickness was estimated as 2.2 nm by optical measurement, many silicon domains were observed for the as-deposited films as shown in Fig. 1(a). Their sizes ranged from 10 to 40 nm and their heights ranged from 1 to 7 nm. After laser irradiation, the size of the silicon domains was slightly reduced. Their heights remained unchanged, as shown in Fig. 1(b). The results of AFM indicate that there was no significant movement of silicon atoms during and after laser irradiation, although agglomeration of silicon on quartz substrates was reported in the case of the laser-induced melting of silicon.<sup>19)</sup> Similar distributions of silicon domains were observed at other points for the present as-deposited and laser annealed films. Figure 2 shows the Raman Stokes spectra of the initial amorphous silicon films and the same films laser-annealed at different laser energies. Although the initial film only had a broad peak from 400 to 500 cm<sup>-1</sup>, a small and sharp peak associated with the TO phonon of crystalline silicon appeared at approximately 515 cm<sup>-1</sup> for laser irradiation at 150 mJ/cm<sup>2</sup>. The intensity of the crystalline-silicon TO phonon peak increased and the intensity of the amorphous-silicon broad band decreased as laser energy density increased from 150 and 170 mJ/cm<sup>2</sup>. On the other hand, crystalline TO phonon peak intensity markedly decreased for laser irradiation at 180 mJ/cm<sup>2</sup> and the intensity of the amorphous broad band increased. These results show that the silicon films were crystallized by laser irradiation from 150 to 170 mJ/cm<sup>2</sup>, and that they were amorphized by laser irradiation above 180 mJ/cm<sup>2</sup>.

An analysis of the spectra was conducted with three Gaussian components whose peaks located at 460, 500, and 515 cm<sup>-1</sup> associated with TO phonons for amorphous, nanocrystalline and crystalline structures, respectively, as shown in Fig. 3(a).<sup>20,21)</sup> Figure 3(b) shows the normalized total intensities of amorphous, nanocrystalline and crystalline TO phonon bands as functions of laser energy density. The normalized total intensity was the intensity ratio obtained by the integration of each Gaussian component

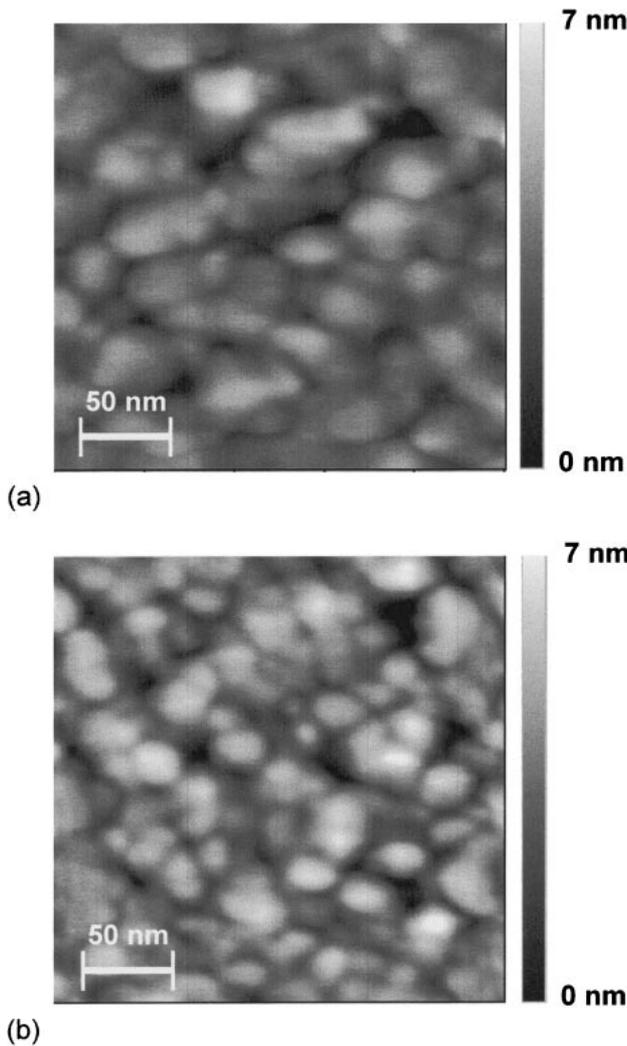


Fig. 1. AFM images of surface of as-deposited silicon film (a) and 170 mJ/cm<sup>2</sup> laser annealed film (b).

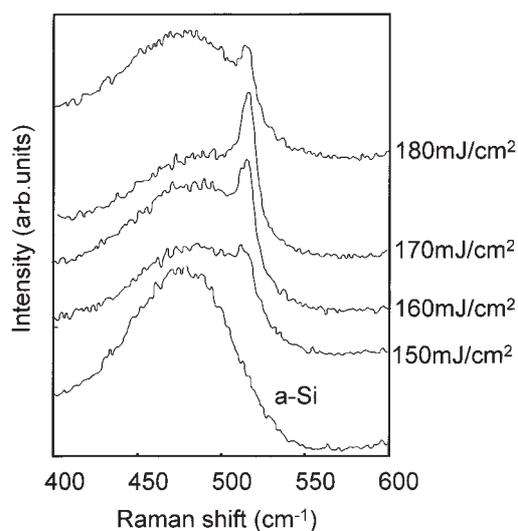


Fig. 2. Raman Stokes spectra initial amorphous silicon films and the same film laser-annealed at different energies.

with the wave number. The normalized total intensity for the crystalline TO phonon band increased from 0.03 to 0.08 as laser energy increased from 150 to 170 mJ/cm<sup>2</sup>, as shown in

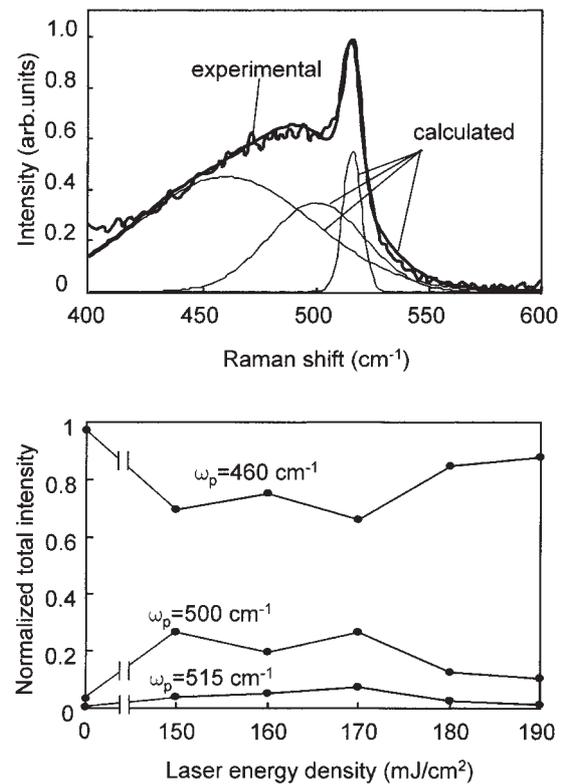


Fig. 3. Analysis of TO phonon band using three Gaussian curves with peaks at 460, 500, and 515 cm<sup>-1</sup> for 170 mJ/cm<sup>2</sup> laser irradiation (a). The sum spectrum of the three Gaussian components is also shown. (b) Normalized total scattering intensity of each Gaussian component as functions of laser energy density.

Fig. 3(b). This means that laser irradiation at 170 mJ/cm<sup>2</sup> resulted in only an 8% crystallization region. The normalized total intensity of the nanocrystalline TO phonon band increased to 0.2–0.26 for laser energy densities from 150 to 170 mJ/cm<sup>2</sup>. On the other hand, The normalized total intensity of the amorphous TO phonon band significantly remained 0.65–0.7 for laser energy densities from 150 to 170 mJ/cm<sup>2</sup>. According to many previous reports, silicon films formed on quartz substrates are rapidly melted by pulsed-laser irradiation when the silicon surface is heated above the melting point.<sup>16)</sup> The molten region extends in the deep silicon region when the latent heat energy of 4171 J/cm<sup>3</sup><sup>22)</sup> for melting is given by laser energy. After the termination of laser irradiation, molten silicon solidifies to crystalline states through cooling by heat diffusion into the underlying quartz substrates. Silicon films crystallize well and a high crystalline volume ratio of 0.9 is obtained for thicknesses from 20 to 50 nm.<sup>23,24)</sup> The normalized total intensity of the crystalline TO phonon band revealed that the crystalline region was only 8% of the present films. The low crystalline volume ratio of the present films was interpreted as that crystalline grain growth was limited by a small film thickness because the surface energy of small crystalline grains was high. The high surface energy reduced the probability of crystalline grain growth.

According to Iqbal and Veprék, TO phonon peak wave number decreases as crystalline grain size decreases from that of crystalline silicon bulk, 520 cm<sup>-1</sup>, because of significant damping lattice vibration.<sup>20)</sup> The TO phonon peak wave number at 515 cm<sup>-1</sup> observed in this work is

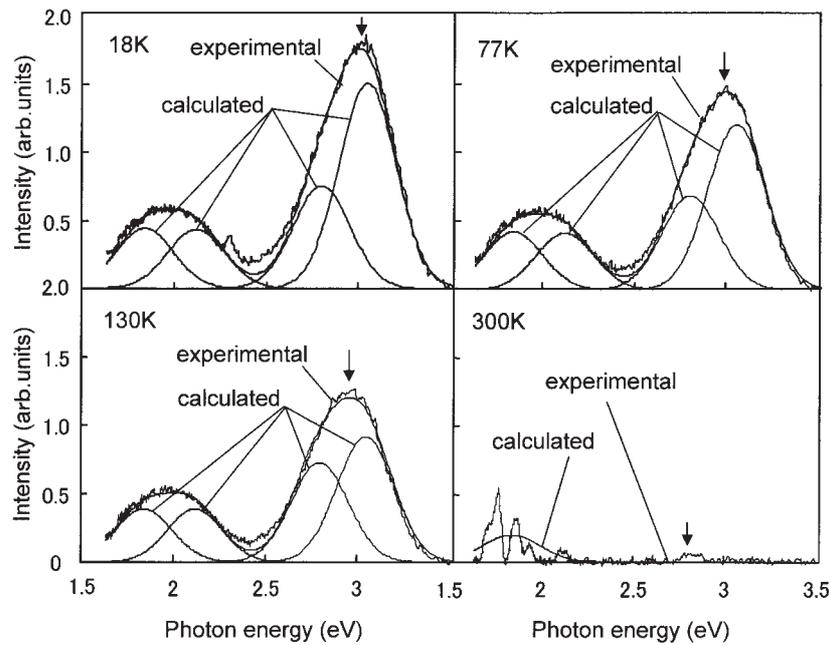


Fig. 4. He-Cd-laser-excited photo luminescence spectra at different temperatures from 18 to 300 K of  $170\text{-mJ/cm}^2$ -laser-annealed films, further annealed at  $260^\circ\text{C}$  for 3 h in  $1.3 \times 10^6\text{-Pa}$   $\text{H}_2\text{O}$  vapor. Four Gaussian components with peak energies at 3.05, 2.80, 2.12, and 1.84 eV, and their sum spectrum are also presented.

caused by crystalline grains with a diameter of about 5 nm. 5-nm-diameter crystalline grains were probably formed by laser irradiation in silicon domains with a height of 5 nm or higher shown in Fig. 1(b). The 8% crystalline region for  $170\text{ mJ/cm}^2$  irradiation suggests that the number of crystalline grains with a diameter about 5 nm was approximately  $4.1 \times 10^{11}\text{ cm}^{-2}$ . In the same manner, we believe that silicon domains thinner than 5 nm gave phonon bands for nanocrystalline clusters approximately  $500\text{ cm}^{-1}$  and for amorphous at around  $460\text{ cm}^{-1}$ .

We previously reported that laser-induced amorphization occurs through the complete melting of silicon films followed by rapid solidification for film thicknesses from 6 to 20 nm.<sup>16)</sup> In the present silicon films, the normalized total intensities of crystalline and nanocrystalline TO phonon bands also decreased to 0.01 and 0.1, respectively, as laser energy density increased to  $190\text{ mJ/cm}^2$ . The observation of the amorphization and crystallization of the silicon films shown in Figs. 2 and 3 indicates that the silicon films melted then solidified on the quartz substrates in the same manner 6–20-nm-thick silicon films. It is interesting that a very thin silicon liquid layer was transiently formed on quartz substrates by laser-induced heating.

Figure 4 shows the photo luminescence spectra at different temperatures from 18 to 300 K of films laser-annealed at  $170\text{ mJ/cm}^2$  and then annealed at  $260^\circ\text{C}$  for 3 h in  $1.3 \times 10^6\text{ Pa}$   $\text{H}_2\text{O}$  vapor. Two important luminescence broad bands were observed at approximately 3 and 2 eV by the He-Cd laser excitation. The peak energy of the high-energy band slightly decreased from 3.0 to 2.8 eV as shown by arrows in Fig. 4 and the peak intensity gradually decreased as temperature increased from 18 to 130 K, then decreased to a very small value at 300 K. The intensity of the peak at approximately 2 eV hardly decreased as temperature increased from 18 to 130 K, then also decreased to a small value at 300 K. The spectral bands were analyzed using Gaussian

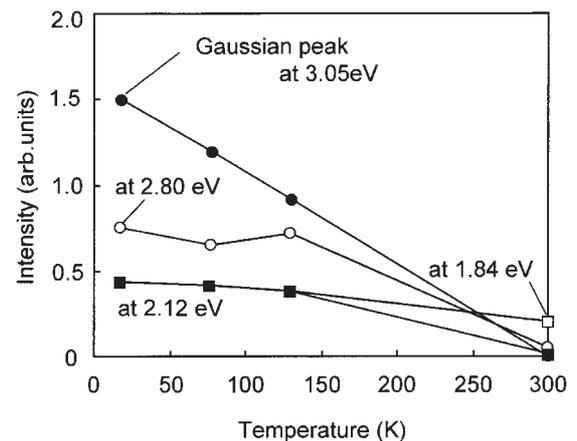


Fig. 5. Intensities of Gaussian peaks at 3.05, 2.80, 2.12, and 1.84 eV as functions of temperature.

components. The spectral bands for every temperature were well fitted by the sum of four Gaussian components with peak energies of 3.05, 2.80, 2.12, and 1.84 eV, and a width of 0.44 eV, as shown in Fig. 4. The results indicate that there were four important direct transition sites. Figure 5 shows the peak intensity of every Gaussian component as a function of temperature. The peak intensity at 3.05 eV linearly decreased to zero as temperature increased from 18 to 300 K, as shown in Fig. 5. On the other hand, the peak intensities of the Gaussian components at 2.80, 2.12, and 1.84 eV were almost constant between 18 and 130 K and decreased markedly as the temperature increased to 300 K.

We surmise that the photo emissions with spectral bands at 2.80, 2.12, and 1.84 eV are attributable to the direct energy transitions in nanocrystalline silicon clusters and small crystalline grains. The three peak energies were probably governed by the quantum size effect of silicon clusters with different sizes. Kanemitsu *et al.* reported photo

luminescence at 2.7 eV from very-small nanocrystalline silicon clusters formed by Si ion implantation in fused silica.<sup>25)</sup> Crystalline silicon with a grain sizes up to 7 nm probably exhibits photo emissions at 2.12 and 1.84 eV, as Mason *et al.* reported for porous silicon.<sup>26)</sup> The wide bandwidth of each Gaussian component (0.44 eV) indicates a strong electron–phonon interaction according to the conventional configurational coordinate model.<sup>27)</sup> The strong electron–phonon interaction results in a high-potential well as a function of coordinates. A high potential well will achieve a strong photoemission associated with the transition from the excited state to the ground states even at a high temperature. This model explains well the almost constant intensity of photo luminescence at 2.80, 2.12, and 1.84 eV between 18 and 130 K, as shown in Fig. 5. However, the intensity of photo luminescence at 3.05 eV decreased as temperature increased. Photo luminescence at 3.05 eV could be caused by SiO<sub>x</sub> regions, which were probably formed through the oxidation of the surface of silicon grains caused by the high-pressure H<sub>2</sub>O vapor heat treatment. Nonradiative energy dissipation associated with Si–O lattice vibration might be significant compared with that associated with silicon grains.

No photoemission was observed for as-laser-annealed films probably due to the high nonradiative energy relaxation caused by significant defect states. Heat treatment at 260 °C for 3 h in  $1.3 \times 10^6$  Pa H<sub>2</sub>O vapor effectively reduced the density of defect sites.

#### 4. Conclusions

We investigated the 308 nm pulsed XeCl-excimer laser annealing of silicon films with an average thickness of 2.2 nm formed on quartz substrates. The silicon films had a domain structure with heights from 1 to 7 nm. Laser induced crystallization occurred at laser energies of 150–170 mJ/cm<sup>2</sup>. Laser induced amorphization was observed for laser irradiation above 180 mJ/cm<sup>2</sup>. An analysis of Raman scattering spectra revealed that there were three TO phonon bands at 460, 500, and 515 cm<sup>-1</sup>. This indicates that the films had disordered amorphous regions, nanocrystalline silicon clusters and 5-nm-diameter crystalline grains. Under laser irradiation at 170 mJ/cm<sup>2</sup>, 66–70% significant amorphous states remained because of the limitation of crystalline growth owing to the small film thickness. Photoluminescence was observed at approximately 3 and 2 eV from 18 to 300 K by He–Cd laser excitation for the films annealed at 170 mJ/cm<sup>2</sup> and heated at 260 °C for 3 h in  $1.3 \times 10^6$  Pa-H<sub>2</sub>O vapor. Photo luminescence spectral bands were analyzed using Gaussian components with peak energies

of 3.05, 2.8, 2.12, and 1.84 eV. The constant intensity of the Gaussian peaks at 2.80, 2.12, and 1.84 eV up to 130 K and the wide bandwidth of 0.22 eV suggest a strong electron–phonon interaction in nano-silicon and small crystalline grains. Photo luminescence at 3.05 eV could be caused by SiO<sub>x</sub> formed at the surface of silicon grains.

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