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Stress in Pulsed-Laser-Crystallized Silicon Films

Seiichiro HIGASHI, Nobuyuki ANDO[1], Koichi KAMISAKO[1] and Toshiyuki SAMESHIMA[1]

Base Technology Research Center, Seiko Epson Corp., 3-3-5 Owa, Suwa, Nagano 392-8502, Japan
[1]*Department of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan*

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Stress in pulsed-laser-crystallized silicon films was investigated using high-resolution Raman scattering measurements. Film stress was evaluated based on the peak shift of transverse optical (TO) phonon of crystalline silicon in Raman scattering spectra. The tensile stress in laser-crystallized 50-nm-thick silicon films on glass substrates increased from 3.5×10^8 Pa to 9.7×10^8 Pa as the film deposition temperature increased from 200°C to 480°C. The peak shift of laser-crystallized microcrystalline silicon (μc-Si) films revealed that the tensile stress introduced by laser irradiation was 2.3×10^8 Pa at most. These results indicate that the strong tensile stress is introduced by the silicon film deposition rather than by the pulsed-laser crystallization. Also, the authors demonstrate that pulsed-laser crystallization maintains the existing stress at the growth initiation sites in the bottom region of silicon films.

KEYWORDS: polycrystalline silicon, thin-film transistors, laser crystallization, stress, Raman scattering

1. Introduction

Pulsed-laser irradiation of a silicon thin film induces local heating followed by extremely fast melting and crystalline growth. Because of the localized nature and short duration of the heat treatment, pulsed-laser crystallization is an effective low-temperature process and enables us to use low-deformation-point substrates such as glass. Currently, this technology is widely applied in low-temperature fabrication of large-area electronic devices such as solar cells and polycrystalline silicon thin-film transistors (poly-Si TFTs).[1–3]

In general, thin films on foreign substrates are subjected to stress introduced by heat treatment, although this depends on factors such as treatment conditions, film thickness, and type of substrate. It has been reported that epitaxially grown silicon films on single-crystal sapphire substrates sustain compressive stress,[4] and it is well known that pulsed-laser crystallized silicon films on glass substrates sustain tensile stress.[5,6] Since several authors have reported that strained silicon films have poor electrical characteristics compared to that of stress-free bulk silicon,[7,8] it is important to control the film stress to realize high-quality silicon films. In this paper, the authors report the basic understanding of stress in pulsed-laser-crystallized silicon films. We also clarify that strong tensile stress is introduced by silicon film deposition rather than by pulsed-laser crystallization of the films. Moreover, we demonstrate that pulsed-laser crystallization maintains the existing stress at the growth initiation sites in the bottom region of silicon films.

2. Experiments

Amorphous silicon (a-Si) films, 50 nm thick, were deposited on quartz substrates using low-pressure chemical vapor deposition (LPCVD) through decomposition of Si_2H_6 gas at 425°C and 480°C [Fig. 1(a)]. Microcrystalline silicon films, 50 nm thick, were also deposited using plasma-enhanced chemical vapor deposition (PECVD) at 200°C and 300°C through decomposition of SiH_4 gas by a remote-type hydrogen plasma excited with 2.45 GHz microwaves at 40 W input power [Fig. 1(a)].[9] The typical grain diameter of the μc-Si was 20 to 30 nm. These films were placed in a 2×10^{-4} Pa vacuum chamber and were irradiated by a 28-ns-pulsed XeCl excimer laser through a quartz window. Laser irradiation was started from 160 mJ/cm^2 and the laser energy density increased stepwise at increments of 40 mJ/cm^2. Five pulses were irradiated at each step. Figure 2 is an example of a 425°C-deposited and laser-crystallized Si film observed by bright-field plan-view transmission electron microscopy (TEM). As seen in the figure, laser-crystallized Si films had an average grain size of 56 nm under 320 mJ/cm^2 laser irradiation conditions, and the grain size was increased up to about 100 nm by higher laser energy irradiation. Stokes Raman scattering spectra associated with the TO phonon of crystalline silicon were measured at room temperature. An argon ion laser beam of 496.5 nm with a diameter of 0.05 cm was used for the probe light and a 1000 mm focal length double monochromator was used to analyze the Raman scattering spectra with a high resolution of 0.15 cm^{-1}. The absolute wave number was calibrated using an emission line from the probe argon ion laser at 514 cm^{-1}, as seen in the inset of Fig. 4. By comparing the peak wave number of the TO phonon obtained from silicon films (ω) and that obtained from a stress-free single-crystal bulk silicon (ω_c), the strength of stress was estimated according to the equation below.[10]

$$\omega = \omega_c + 5.2 \times 10^{-9} P.$$

Here, P (Pa) is the strength of the stress. When the stress is compressive, P is positive, and when the stress is tensile, P is negative.

In order to evaluate crystalline characteristics, reflectivity spectra in the ultraviolet (UV) region were measured. A distinct peak around 270 nm (E_2 peak), which is associated with crystalline Si structures, was observed in the spectra. By fitting the spectra with the mixed amorphous and crystalline structures, the crystalline to amorphous phase volume ratio was obtained.

3. Results and Discussions

Figure 3 shows the (a) peak wave number and (b) full width at half maximum (FWHM) of the crystalline TO phonon band as a function of laser energy density. Four kinds of 50-nm-thick silicon films, described previously, were examined. The peak wave number of the crystalline TO phonon

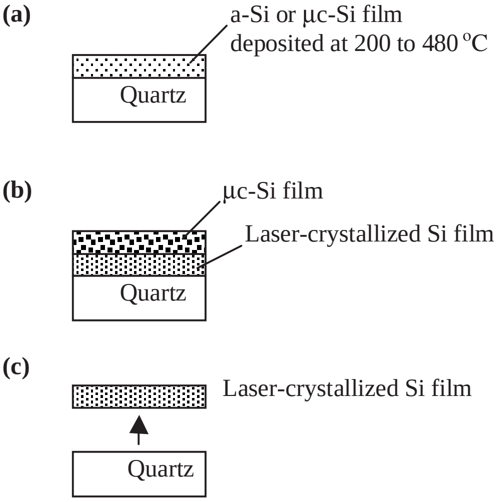

Fig. 1. Three different sample structures (a) to (c) used in the experiments.

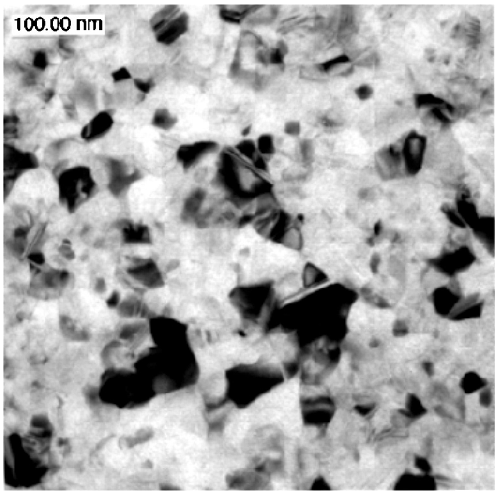

Fig. 2. Bright-field plan-view TEM image of a laser-crystallized 50-nm-thick silicon film. Stepwise irradiation was carried out to an energy density of 320 mJ/cm^2.

band decreased as the deposition temperature of the silicon film was increased, and it had no substantial dependence on the laser energy density. Since multiple laser irradiations with increasing laser energy density were performed, the total number of laser shots in the case of 200 and 400 mJ/cm^2 were 10 and 35, respectively. Although greater numbers of laser irradiations were performed in high-laser-energy-irradiated samples, the change in the peak wave number was within 0.3 cm^{-1} in the case of 425°C-deposited films; similar results were observed in other samples. This suggests that change in the peak wave number is independent not only of energy density but also of the number of laser shots. The surface roughness of the laser-irradiated films was examined by atomic force microscopy (AFM). The root-mean-square value of the surface roughness increased from 2.5 to 5.1 nm with increasing laser energy density. Since stepwise laser irradiation was carried out, the surface roughness was low under all laser irradiation conditions. Therefore, stress relaxation induced by surface roughening is not relevant to our experiment. On the other hand, the FWHM of the crystalline TO phonon peak decreased from 9.0 to 5.7 cm^{-1} as the laser energy density increased from 200 to 400 mJ/cm^2 for every sample. These results indicate that increasing the laser energy density and increasing the number of laser shots decrease the disordered amorphous states in the silicon films, but not significantly change stress in the films. A decrease in the peak wave number with increasing deposition temperature of silicon films strongly suggests that significant tensile stress is introduced into the film during its deposition. The tensile stress was estimated based on the difference in the measured TO phonon peak wave number between single crystalline bulk silicon ($\omega_c = 520.03\,\mathrm{cm}^{-1}$ in this measurement) and laser-crystallized silicon films.[10] It increased from 3.5×10^8 to 9.7×10^8 Pa as the silicon film deposition temperature increased from 200 to 480°C.

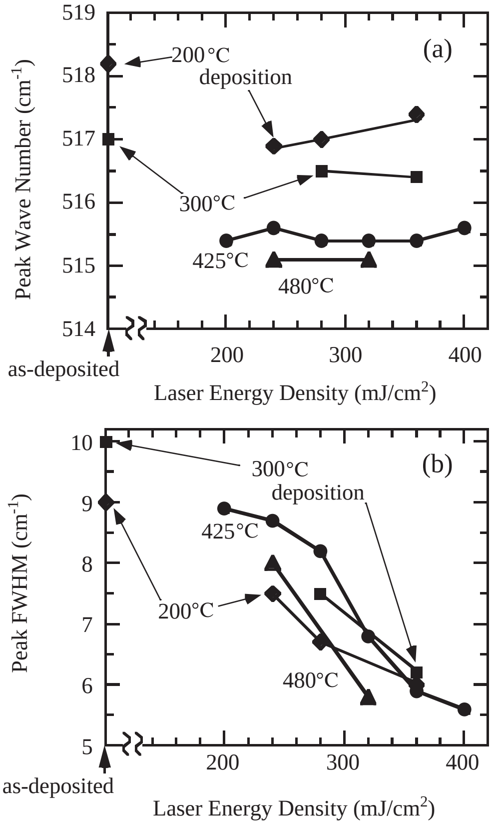

Fig. 3. (a) Peak wave number and (b) FWHM of crystalline TO phonon band as a function of laser energy density. Initial films are formed at different deposition temperatures (200 to 480°C) and crystallized by excimer laser. Sample (a) in Fig. 1 was used for the experiment.

In order to estimate the stress introduced by laser crystallization, the change in the TO phonon peak wave number by laser irradiation to μc-Si was observed. As-deposited μc-Si films have partially crystallized regimes which show the TO phonon peak in Raman scattering spectra. Stress caused by the film formation was obtained from the TO phonon peak wave number of the as-deposited μc-Si films. The peak wave numbers of as-deposited μc-Si films were 518.2 and 517.0 cm^{-1} when the deposition temperatures were 200 and 300°C, respectively. From this peak wave number shift, the tensile stresses introduced by film deposition were estimated to be 3.5×10^8 and 5.8×10^8 Pa, respectively. This means that a higher deposition temperature results in greater tensile stress in silicon films. Pulsed-laser irradiation was performed on these films, and the peak wave number of the TO phonon was measured again. As seen in Fig. 3, the change in the peak wave number caused by laser irradiation was 1.2 and 0.5 cm^{-1} when the deposition temperatures of μc-Si were 200 and 300°C, respectively. This means that the tensile stresses introduced by laser crystallization are estimated to be 2.3×10^8 and 9.6×10^7 Pa, respectively. These results show that stress introduced by film deposition is more significant compared to that introduced by laser crystallization. Stress introduced in a-Si films during deposition was estimated to be at least as high as 7.4×10^8 Pa when the deposition temperature was 480°C, a value much higher than that introduced by laser crystallization.

Silicon films are melted by laser irradiation and crystalline growth starts from the growth initiation sites in the film. Although the stress introduced by laser crystallization is small, silicon films have significant tensile stress after laser crystallization. Tensile stress in the silicon films is introduced by heat treatment during a-Si film deposition, and this stress remains even after the laser crystallization of the silicon films. This suggests that the extremely fast crystalline growth induced by laser irradiation maintains the existing stress at the growth initiation sites in the bottom region of the film. In order to demonstrate this idea, the authors performed a laser crystallization experiment using double-layer silicon films, as shown in Fig. 1(b). Amorphous silicon films, 50 nm thick, were formed on quartz substrates at 425°C by LPCVD and crystallized using an excimer laser. Then TO phonon spectra of these laser-crystallized silicon films were measured by Raman scattering measurement. On these laser-crystallized silicon films, 60-nm-thick μc-Si films were deposited at 200°C using the PECVD method mentioned before. As shown in Fig. 3(a), μc-Si films deposited at 200°C have weaker tensile stress than laser-crystallized LPCVD silicon films deposited at 425°C. Since the TO phonon spectra of these double-layer silicon films are a mixture of each layer's spectrum, by subtracting the initial TO phonon spectra of the bottom-layer silicon films, one can obtain TO phonon spectra of the top-layer silicon films. Since the scattered light from the bottom layer is absorbed by the top layer, the intensity of the bottom-layer spectrum was corrected by considering the absorption by the top-layer μc-Si film. The reflectivity spectrum of the μc-Si film was measured and the crystalline volume ratio was obtained by analyzing the spectrum with a mixed structure of amorphous and crystalline silicon. Based on this analysis, the absorption by the top-layer μc-Si film was estimated. An example of this analysis is shown in the inset of Fig. 4. These layered silicon films were irradiated by an excimer laser, and the change in the peak wave number of the top-layer silicon film were analyzed. Figure 4 shows the change in the peak wave number of the top-layer silicon films as a function of irradiated laser energy density. Before laser irradiation, the top-layer μc-Si film showed TO phonon peak at 518.3 cm^{-1}, which was almost the same as that of the single-layer μc-Si film deposited at 200°C [see Fig. 3(a)]. After laser irradiation, little change in the peak wave number of top-layer μc-Si film was observed when the laser energy density was less than 200 mJ/cm^2. Under this condition, crystalline growth seems to start in the μc-Si film, which does not result in a significant stress in the film because the initial stress at the growth initiation site is small. However, the peak wave number suddenly decreased to 516.7 cm^{-1} by irradiating at a laser energy density of 240 mJ/cm^2 and it decreased further by increasing the laser energy density. The change in peak wave number of TO phonon Raman scattering spectra of the top layer was larger than that of the laser-crystallized single-layer μc-Si films formed at the same substrate temperature of 200°C, which was 517.1 cm^{-1} [indicated by (A) in Fig. 4]. By increasing the laser energy density, the peak wave number of the top-layer silicon film decreased to 515.5 cm^{-1}, which is almost same as the peak wave number of the bottom-layer silicon film [indicated by (B) in Fig. 4]. This result indicates that the existing stress in the bottom layer was spread to the top layer by melting the upper layer μc-Si film and starting the crystalline growth from the strained bottom-layer silicon bondings. Stress introduced at the substrate and the a-Si hetero interface during deposition of the initial a-Si film seemed to spread to the top layer by laser-induced melt and crystalline growth. If the crystalline growth was indeed initiated from the bottom-layer silicon film, we may observe

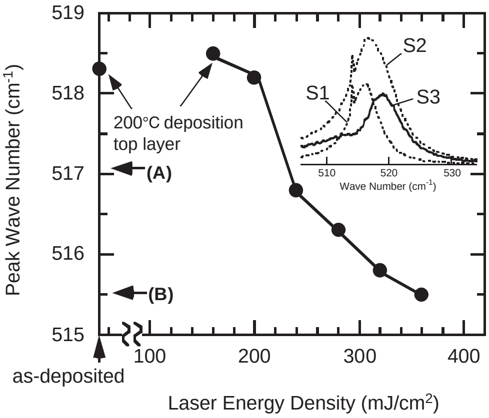

Fig. 4. Change in peak wave number of crystalline TO phonon band of top layer silicon films as a function of laser energy density [sample (b) in Fig. 1 was used for the experiment]. Inset shows an example of Raman scattering spectra obtained from (S1) bottom-layer sample, (S2) double-layer sample and (S3) calculated top-layer spectrum. A peak at 514 m^{-1} is the emission line from the probe argon ion laser. Peak wave numbers of (A) 200°C-deposited and laser-crystallized single-layer silicon film and (B) 425°C-deposited and laser-crystallized single-layer silicon film are indicated.

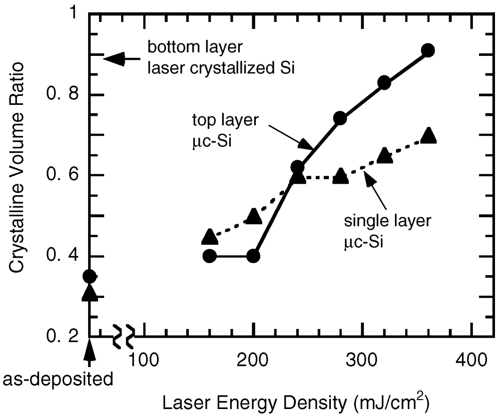

Fig. 5. Change in crystalline volume ratio of μc-Si film obtained by analyzing UV reflection spectra as a function of laser energy density [sample (b) in Fig. 1 was used for the experiment]. The solid line shows the case of μc-Si film (60 nm)/laser-crystallized silicon film (50 nm) double-layer structure and dashed line shows the case of single-layer μc-Si film (50 nm).

changes in crystalline characteristics of the top-layer μc-Si film. The crystalline volume ratio near the surface region was evaluated using UV reflection spectrum analysis. Since UV reflection provides information on crystalline properties of the surface region of only 10 to 20 nm, this measurement is not affected by the bottom layer. First, the UV reflection spectrum of the laser-crystallized silicon film (50 nm) was measured, and the crystalline volume ratio was estimated to be 0.89. Then the crystalline volume ratio of the μc-Si film (60 nm) deposited on the laser-crystallized Si film (50 nm) (double-layer structure) and single-layer μc-Si film (50 nm) were measured at different laser irradiation energy densities. Results are shown in Fig. 5. The crystalline volume ratio of the single-layer μc-Si film increased linearly with increasing laser energy density, but it was less than 0.7. On the other hand, in the case of the double-layer structure, the crystalline volume ratio of the top-layer μc-Si film abruptly increased when a laser energy higher than 200 mJ/cm^2 was irradiated. This change in the crystalline volume ratio agrees well with the abruptly increasing stress in the top layer μc-Si film, which is shown in Fig. 4. The crystalline volume ratio finally reached 0.91, which was almost the same as that of the bottom-layer laser-crystallized 50-nm-thick silicon film. From this result, the authors confirmed that crystalline growth was initiated from the bottom-layer laser-crystallized silicon film. From these results, we can conclude that stress in the laser-crystallized films is controlled by the stress at the growth initiation sites in the bottom region of the films.

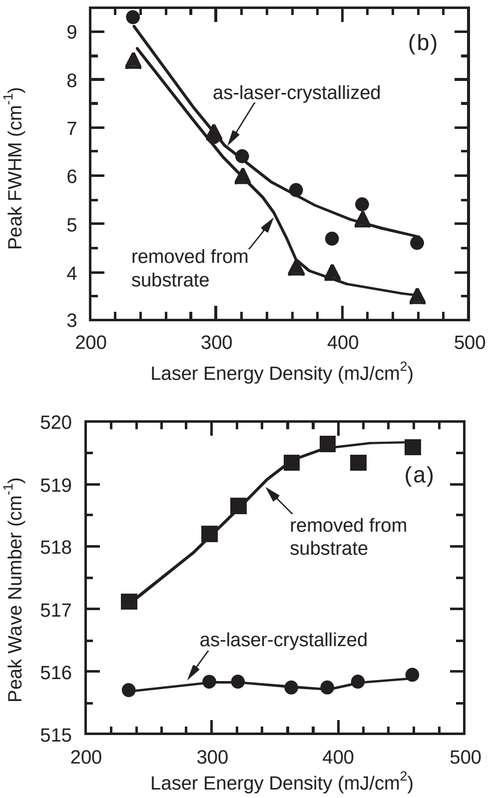

Fig. 6. (a) Peak wave number and (b) FWHM of crystalline TO phonon band as a function of laser energy density before and after removing the silicon films from substrates (sample (c) in Fig. 1 was used for the experiment). Initial films were deposited at 425°C and were crystallized by excimer laser.

If stress in the silicon films originates from the stress at the bottom interface between films and substrates, this stress may be relieved by removing the films from the substrates. As shown in Fig. 1(c), 50-nm-thick silicon films deposited by LPCVD and laser-crystallized were removed from the substrates by etching the SiO$_2$ substrates using HF solution. Figure 6 shows (a) the peak wave number and (b) the FWHM of the crystalline TO phonon band as a function of laser energy density before and after the separation of silicon films from the substrates. Silicon films removed from the substrates showed a much higher TO phonon peak wave number than silicon films on the substrates. The silicon films crystallized at high laser energy density and removed from the substrates showed peak wave numbers of 519.3 to 519.7 cm^{-1}, which were almost the same as that of stress-free bulk silicon (519.7 cm^{-1} in this measurement). This result indicates that tensile stress in laser-crystallized silicon films is completely relieved by removing them from substrates. Although there exists a disordered structure like a grain boundary in the removed laser-crystallized silicon films, stress among the silicon films themselves is quite small, resulting in Raman scattering spectra comparable with those of stress-free single crystalline silicon. The origin of the stress is primarily the hetero interface between the silicon film and substrate. Strong Si-to-Si or Si-to-O covalent bondings may be formed at the interface between substrates and silicon films when silicon films are deposited, and due to the difference in thermal expansion between substrates and silicon films, these bondings are strained after the film deposition. Laser crystallization melts the film and crystalline growth starts from the strained silicon bondings. Therefore, stress at the growth initiation sites is spread over the entire film by crystalline growth, resulting in a significant tensile stress in the entire film. Less change in peak wave number was seen in the films crystallized by low laser energy density and removed from substrates. This may be because the melt depth was small and internal stress introduced in the film by film deposition remains, or because a relatively small grain size contributes to the shift in the peak wave number.$^{11)}$ As seen in Fig. 6(b), by removing the film, the bandwidth of the crystalline TO phonon band decreased and approached that of single crystalline silicon (2.8 cm^{-1} in this measurement). This result suggests that by relieving the tensile stress anchored to the bottom interface, the crystalline quality of laser-crystallized silicon films can be improved.

4. Conclusions

Stress in pulsed-laser-crystallized silicon films was investigated using high-resolution Raman scattering measurements. Tensile stress in the silicon films introduced by laser crystallization was 2.3×10^8 Pa at most, which is small compared to the tensile stress introduced by film deposition, 3.5×10^8 Pa to 9.7×10^8 Pa, as the film deposition temperature increased from 200°C to 480°C. Although stress introduced by laser crystallization is not significant, pulsed-laser-induced crystalline growth maintains the existing stress at the growth initiation sites. This is the reason why laser-crystallized silicon films have significant tensile stress. Since the origin of the tensile stress is the strained bondings at the starting point of crystalline growth in the bottom interface of silicon films and substrates, the stress can be relieved by removing the laser-crystallized silicon films from the substrates.

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