

## Defect Reduction in Polycrystalline Silicon Thin Films at 150 °C

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We report defect reduction in 50-nm-thick laser-crystallized polycrystalline silicon (poly-Si) films by a combination of hydrogen plasma at 100 W for 5 s at room temperature with  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor heat treatment at 150 °C for 6 h. The present treatment increased the photoconductivity to  $1 \times 10^{-3}$  S/cm for undoped poly-Si films under the illumination of 532 nm light at 100 mW/cm<sup>2</sup>. It also increased the electrical conductivity to 30 S/cm for  $2 \times 10^{19}$  cm<sup>-3</sup> phosphorus-doped poly-Si films. Those values were comparable to those for samples treated with  $1.3 \times 10^6$  Pa H<sub>2</sub>O vapor heat treatment for 3 h at 260 °C. Hydrogen concentration increased from 1.6 to 5.4 at. % as hydrogen plasma duration increased from 5 to 120 s. It was decreased by subsequent H<sub>2</sub>O vapor heat treatment at 150 °C, and ultimately ranged from 1.1 to 4.5 at. %. Hydrogen atoms play a catalytic role in the dissociation of H<sub>2</sub>O molecules at 150 °C. © 2010 The Japan Society of Applied Physics

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### 1. Introduction

Defect reduction in silicon films at low temperatures is important for various applications in electronic devices, for example, thin film transistors (TFTs) and thin film solar cells. Hydrogenation using hydrogen plasma or hydrogen radicals has been widely investigated for defect reduction and improvement of device characteristics.<sup>1-6</sup> The density of defect states in polycrystalline silicon (poly-Si) films is well reduced by hydrogenation above 200 °C. Heat treatment with high-pressure H<sub>2</sub>O vapor has also been developed.<sup>7,8</sup> Electrical active defects located in poly-Si and SiO<sub>2</sub> have been well reduced by heat treatment at approximately 260 °C. The threshold voltage is reduced by decreasing the densities of trapped states and fixed oxide charges in SiO<sub>2</sub> as well as in SiO<sub>2</sub>/Si interfaces for poly-Si TFTs.<sup>9</sup> On the other hand, a low processing temperature of about 150 °C has recently been demanded in order to fabricate poly-Si TFTs on plastic films, because plastic has a low glass transition temperature of, at most, 150 °C.<sup>10</sup> However, high-pressure H<sub>2</sub>O vapor heat treatment is insufficient to reduce defect states at a low temperature of 150 °C because of a low reaction rate. A defect reduction technology should be developed for very low processing temperature.

In this paper, we report a method of defect reduction in laser-crystallized poly-Si films at 150 °C. We propose a combination of hydrogen plasma at room temperature with high-pressure H<sub>2</sub>O vapor heat treatment at 150 °C. We demonstrate effective reduction in the density of defect states by increasing the photoconductivity of undoped poly-Si films and increasing the electrical conductivity of doped poly-Si films. We also report the precise analysis of Si-H formation caused by plasma hydrogenation and the annihilation of Si-H bonds by H<sub>2</sub>O vapor heat treatment.

### 2. Experimental Procedure

Undoped and  $2 \times 10^{19}$  cm<sup>-3</sup> phosphorus-doped amorphous silicon films with a thickness of 50 nm were formed on quartz substrates by the sputtering method. The silicon films were crystallized at room temperature by irradiation with a XeCl excimer laser at a wavelength of 308 nm with a pulse width of 30 ns at 300 mJ/cm<sup>2</sup>. The crystalline volume ratio was estimated to be 0.8 from the analysis of optical

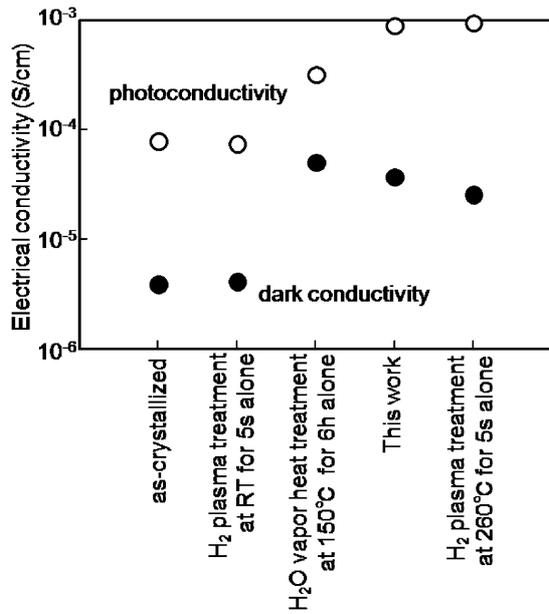
reflectivity spectra in the ultraviolet region.<sup>11</sup> The undoped and doped silicon films were treated at room temperature by hydrogen plasma generated by the application of a 13.56 MHz RF power of 100 W to parallel plate electrodes for 5 to 120 s with a hydrogen gas pressure of 20 Pa. The silicon films were subsequently heated at 150 °C with  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor for 6 h. Photoconductivity was measured for undoped silicon films under the illumination of light from a second-harmonic neodymium-ion-doped yttrium aluminium garnet (Nd<sup>+</sup>:YAG) laser at 532 nm with an intensity of 100 mW/cm<sup>2</sup>. The electrical conductivity of phosphorus-doped silicon films was also measured. We measured a resonant peak intensity of Si-H molecular vibration ranging from 1800 to 2400 cm<sup>-1</sup> by a Raman scattering measurement method. Secondary ion mass spectrometry (SIMS) was used in order to determine the hydrogen concentration for films treated with hydrogen plasma for 120 s. That concentration was applied to the calibration of the Raman scattering intensity of Si-H molecular vibration.

### 3. Results and Discussion

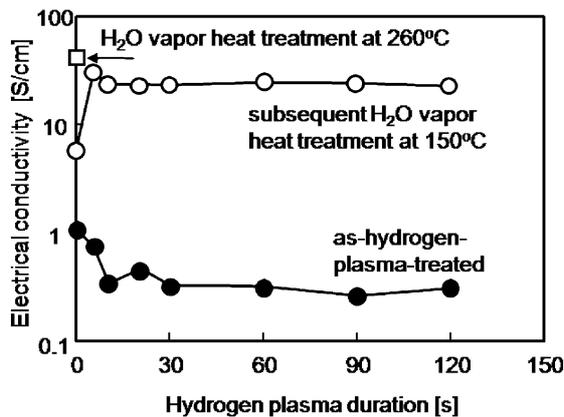
Figure 1 shows the dark conductivity and photoconductivity for undoped silicon film samples treated with the combination of hydrogen plasma at room temperature for 5 s with  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor at 150 °C for 6 h. Hydrogen plasma at room temperature for 5 s alone,  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor heat treatment at 150 °C for 6 h alone and  $1.3 \times 10^6$  Pa H<sub>2</sub>O vapor heat treatment at 260 °C for 3 h alone were also carried out for comparison. The photoconductivity was markedly increased from  $8.0 \times 10^{-5}$  (as crystallized) to  $1.0 \times 10^{-3}$  S/cm under the illumination of 532 nm light at 100 mW/cm<sup>2</sup> by the present method. It was higher than those for samples treated with hydrogen plasma at room temperature for 5 s alone ( $7.4 \times 10^{-5}$  S/cm), and with  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor at 150 °C for 6 h alone ( $3.2 \times 10^{-4}$  S/cm). It was close to that for the sample treated with  $1.3 \times 10^6$  Pa H<sub>2</sub>O vapor at 260 °C for 6 h alone. This result indicates that the recombination probability of photo-induced electron and hole carriers was greatly decreased by the present method at 150 °C.

Figure 2 shows changes in the electrical conductivity of the phosphorus-doped silicon films as a function of the duration of hydrogen plasma treatment at room temperature. The electrical conductivity of as-crystallized silicon films

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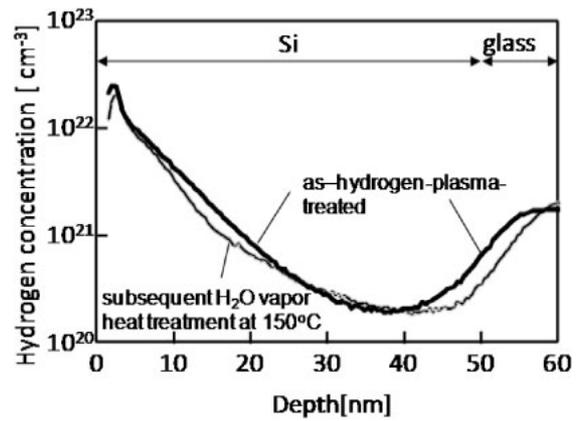


**Fig. 1.** Dark conductivity and photoconductivity for undoped silicon films treated with the combination of hydrogen plasma at 100 W at room temperature for 5 s with  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor at 150 °C for 6 h. Hydrogen plasma at room temperature for 5 s alone, heat treatment with  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor at 150 °C for 6 h alone, and heat treatment with  $1.3 \times 10^6$  Pa H<sub>2</sub>O vapor at 260 °C for 3 h alone were also carried out for comparison.



**Fig. 2.** Electrical conductivity of  $2 \times 10^{19}$  cm<sup>-3</sup> phosphorus-doped silicon films as a function of duration of hydrogen plasma treatment at room temperature for samples as-hydrogen-plasma-treated and with subsequent  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor heat treatment at 150 °C for 6 h. The electrical conductivity was also presented for the case of heat treatment with  $1.3 \times 10^6$  Pa H<sub>2</sub>O vapor at 260 °C for 3 h alone.

was only 1 S/cm. Most of the electron carriers generated by phosphorus doping were trapped by electrically active defects located at grain boundaries of poly-Si films. The electrical conductivity was decreased from 0.8 to 0.3 S/cm by hydrogen plasma treatment at room temperature from 5 to 120 s. No effective defect passivation was achieved by hydrogen plasma treatment at room temperature. On the other hand, the electrical conductivity was markedly increased by hydrogen plasma treatment at room temperature followed by  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor heat treatment at 150 °C for 6 h. The highest value was 30 S/cm for the sample treated with hydrogen plasma for 5 s. The electrical conductivity gradually decreased to 20 S/cm as the hydro-



**Fig. 3.** In-depth profiles of hydrogen atoms in poly-Si films treated with hydrogen plasma for 120 s followed by  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor heat treatment at 150 °C for 6 h.

gen plasma duration increased from 5 to 120 s. However, it was only increased to 5.7 S/cm after  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor heat treatment at 150 °C for 6 h alone. These results indicate that hydrogen plasma treatment at room temperature promoted defect passivation by  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor heat treatment at 150 °C. The electrical conductivity obtained by the present method was close to that of 42 S/cm for the sample treated with  $1.3 \times 10^6$  Pa H<sub>2</sub>O vapor at 260 °C for 3 h alone.

The incorporation of hydrogen atoms into silicon films was precisely investigated by SIMS and the Raman scattering method. Figure 3 shows the in-depth profiles of hydrogen atoms in poly-Si films treated with hydrogen plasma for 120 s followed by  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor heat treatment at 150 °C for 6 h. Hydrogen concentrations higher than  $10^{22}$  cm<sup>-3</sup> were observed at the surface region for both samples. The concentration monotonically decreased to  $2 \times 10^{20}$  cm<sup>-3</sup> with increasing depth. An average of 5.4 at. % hydrogen atoms was incorporated into poly-Si films by hydrogen plasma treatment for 120 s. The subsequent  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor heat treatment at 150 °C for 6 h slightly decreased the average amount of hydrogen atoms to 4.5 at. % because of the oxidation process of H<sub>2</sub>O vapor heat treatment.<sup>12)</sup> SIMS measurement also revealed that there was a hydrogen concentration of 1.0 at. % in poly-Si films in the case of hydrogen plasma treatment for 5 s followed by  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor heat treatment at 150 °C for 6 h. Hydrogen atoms were effectively incorporated into poly-Si films during the short plasma treatment. Figure 4 shows Raman scattering spectra of the Si-H molecule vibration from 1800 to 2300 cm<sup>-1</sup> in the cases of hydrogen plasma treatment at room temperature for 5 s (a) and 90 s (b). While as-crystallized silicon films showed no peak, a small peak at around 2000 cm<sup>-1</sup> was observed for the sample treated with hydrogen plasma for 5 s. Si-H bonding was certainly formed by hydrogen plasma treatment at room temperature. The peak at around 2000 cm<sup>-1</sup> means that mono hydride bonding was dominant. The peak intensity was decreased by subsequent  $4.7 \times 10^5$  Pa H<sub>2</sub>O vapor heat treatment at 150 °C for 6 h, as shown in Fig. 4(a). On the other hand, a large peak at around 2100 cm<sup>-1</sup> was observed for the sample treated with hydrogen plasma for 90 s. Similar spectral shapes with a peak at around 2100 cm<sup>-1</sup> were

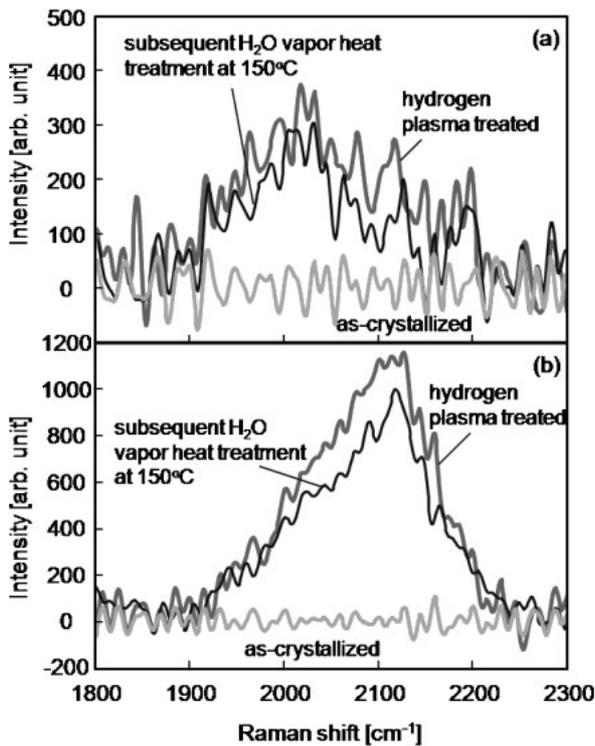


Fig. 4. Raman scattering spectra of Si-H molecule vibration from 1800 to 2400  $\text{cm}^{-1}$  in the cases of hydrogen plasma treatment at room temperature for 5 s (a) and 90 s (b) for samples as-hydrogen-plasma-treated and with subsequent  $4.7 \times 10^5$  Pa  $\text{H}_2\text{O}$  vapor heat treatment at 150 °C for 6 h.

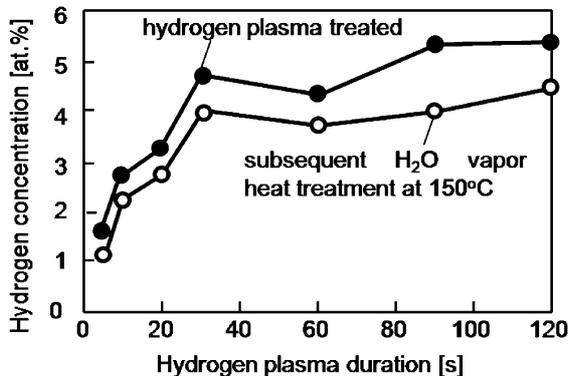


Fig. 5. Hydrogen concentration as a function of hydrogen plasma treatment duration at room temperature for samples treated with hydrogen plasma and then  $4.7 \times 10^5$  Pa  $\text{H}_2\text{O}$  vapor at 150 °C for 6 h.

measured for samples treated with hydrogen plasma longer than 10 s. The peak at around 2100  $\text{cm}^{-1}$  means that most of the Si-H bonds were the dihydride type. The peak intensity was also decreased by subsequent  $\text{H}_2\text{O}$  vapor heat treatment. Figure 5 shows hydrogen concentration as a function of hydrogen plasma treatment duration at room temperature for samples treated first with hydrogen plasma and subsequently with  $4.7 \times 10^5$  Pa  $\text{H}_2\text{O}$  vapor at 150 °C for 6 h. The hydrogen concentration was estimated from the integrated intensity of Raman scattering spectra of the Si-H molecule vibration from 1800 to 2300  $\text{cm}^{-1}$  shown in Fig. 4. The integrated intensity was calibrated by the amount of hydrogen after hydrogen plasma treatment for 120 s obtained by SIMS measurement as reported above. The hydrogen

concentration increased from 1.6 to 5.4 at. % as the hydrogen plasma duration increased from 5 to 120 s. On the other hand, the hydrogen concentration was decreased by subsequent  $\text{H}_2\text{O}$  vapor heat treatment. It finally ranged from 1.1 to 4.5 at. %. The hydrogen concentration of 1.1 at. % after hydrogen plasma treatment for 5 s followed by  $\text{H}_2\text{O}$  vapor heat treatment was almost the same as that directly measured by SIMS presented above. This indicates the total hydrogen concentration and Si-H bonding concentration kept their ratio constant for different durations of hydrogen plasma treatment.

SIMS and Raman scattering measurements revealed that many hydrogen atoms were incorporated into silicon by hydrogen plasma treatment at room temperature. Although dangling bonds in poly-Si films would be terminated by hydrogen incorporated into the films, the high Si-H concentration shown in Figs. 3–5 indicates that many silicon bonds were broken by hydrogen atoms and mono hydride or dihydride bonds were formed. There would be new dangling bonds produced by hydrogen attack because of the lack of thermal energy assistance. The dangling bonds probably kept the photoconductivity for undoped poly-Si and conductivity for phosphorus-doped poly-Si low. These were still in non-thermal equilibrium states just after hydrogen plasma treatment at room temperature. The high-pressure vapor heat treatment at 150 °C for 6 h decreased the hydrogen concentration by 1 at. % at most, as shown in Fig. 5. Si-H bonds were oxidized by  $\text{H}_2\text{O}$  molecules incorporated into poly-Si films. The authors believe that hydrogen atoms in poly-Si played a catalytic role in the dissociation of  $\text{H}_2\text{O}$  molecules at 150 °C because of the high electro affinity of hydrogen. Si-H bonds were probably broken by oxygen atoms dissociated from  $\text{H}_2\text{O}$  molecules. Si-OH or  $\text{SiO}_2$  bonds were then formed. Dangling bonds were also terminated by OH or oxygen atoms. Those reactions probably rendered poly-Si films close to the thermal equilibrium state.

#### 4. Conclusions

A combination of hydrogen plasma treatment at room temperature with high-pressure  $\text{H}_2\text{O}$  vapor heat treatment at 150 °C was investigated in order to reduce defect states of 50-nm-thick poly-Si films formed by pulsed XeCl excimer laser irradiation at 300  $\text{mJ}/\text{cm}^2$ . The photoconductivity of undoped silicon films was increased to  $1 \times 10^{-3}$  S/cm under the illumination of 532 nm light at 100  $\text{mW}/\text{cm}^2$  by 13.56 MHz RF hydrogen plasma at 100 W in 20 Pa for 5 s followed by  $4.7 \times 10^5$  Pa  $\text{H}_2\text{O}$  vapor at 150 °C for 6 h, whereas that of as-crystallized films was only  $8.0 \times 10^{-5}$  S/cm. The electrical conductivity of  $2 \times 10^{19}$   $\text{cm}^{-3}$  phosphorus-doped poly-Si films was markedly increased to 30 S/cm by hydrogen plasma treatment at room temperature for 5 s followed by  $4.7 \times 10^5$  Pa  $\text{H}_2\text{O}$  vapor at 150 °C for 6 h, while it was slightly decreased to 0.8 S/cm from that of the as-crystallized sample, 1 S/cm. SIMS and Raman scattering measurements revealed that the hydrogen concentration increased from 1.6 to 5.4 at. % as the hydrogen plasma treatment duration increased from 5 to 120 s. On the other hand, the hydrogen concentration was decreased by subsequent  $\text{H}_2\text{O}$  vapor heat treatment at 150 °C for 6 h. It ranged from 1.1 to 4.5 at. %. These were far from a thermal equilibrium state in spite of formation of many Si-H bonds by

hydrogen plasma treatment at room temperature. Hydrogen atoms in poly-Si would play a catalytic role in the dissociation of H<sub>2</sub>O molecules at 150 °C incorporated during H<sub>2</sub>O vapor heat treatment. Si–H bonds were probably broken by oxygen atoms dissociated from H<sub>2</sub>O molecules. Si–OH or SiO<sub>2</sub> bonds were then formed. Dangling bonds were also terminated by OH or oxygen atoms. Those reactions probably rendered poly-Si films close to the thermal equilibrium state.

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