

## Heat Treatment of Amorphous and Polycrystalline Silicon Thin Films with H<sub>2</sub>O Vapor

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Changes in electrical and optical properties induced by heat treatment with H<sub>2</sub>O vapor at 350 °C are reported for laser-induced amorphous silicon, low pressure chemical vapor amorphous silicon (LPCVD a-Si) and laser crystallized polycrystalline silicon films. The dark conductivity was reduced and the photoconductivity was increased by the heat treatment for these films. The optical absorption in the photon energy range lower than 1.5 eV was reduced for the a-Si films. The optical band gap was slightly increased from 1.48 eV to 1.51 eV for the LPCVD a-Si. The increase in hydrogen concentration was less than  $2 \times 10^{20} \text{ cm}^{-3}$  after the treatment. These results show that the heat treatment with H<sub>2</sub>O vapor reduces the defect density in the silicon films with a small amount of hydrogen incorporation.

KEYWORDS: LPCVD a-Si, Laser crystallization, Photoconductivity, Optical absorption, Hydrogen concentration

We have recently reported that a heat treatment at around 300 °C with H<sub>2</sub>O vapor improves the electrical characteristics of polycrystalline silicon thin film transistors (poly-Si TFTs).<sup>1)</sup> The threshold voltage is reduced as a result of the reduction of the densities of trapped states and fixed oxide charges. Moreover, the treatment makes the subthreshold slope in the transfer characteristics steep and increases the carrier mobility. These results show that the density of trap states of the SiO<sub>2</sub>/poly-Si interface is reduced. Moreover, they indicate a possibility of improvement of the electrical properties of silicon films by the heat treatment with H<sub>2</sub>O vapor.

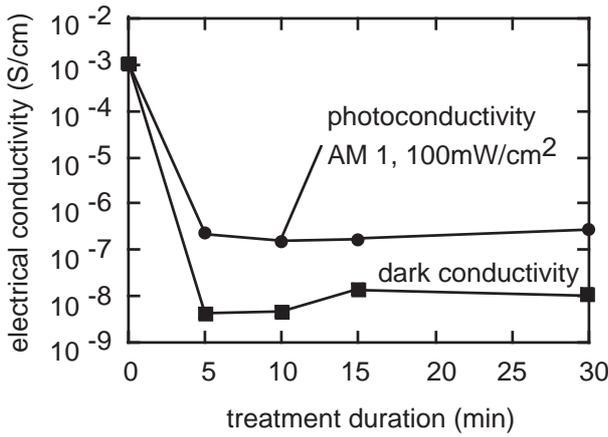
In this paper, we demonstrate the reduction of defects in amorphous and polycrystalline silicon films by the heat treatment with H<sub>2</sub>O vapor. Changes in dark and photo conductivity of the films are reported. Changes in optical absorption spectra at the wavelength range between visible and infrared are also presented to discuss the optical band gap and silicon bonding network.

Amorphous silicon films of 10 nm and 50 nm thicknesses were formed on quartz substrates by dissociation of Si<sub>2</sub>H<sub>6</sub> gas at 430 °C using the low pressure chemical vapor deposition (LPCVD) method. The 10-nm thick amorphous silicon films were melted by the XeCl excimer laser irradiation with a wavelength of 308 nm, a pulse width of 30 ns and a pulse energy of 240 mJ/cm<sup>2</sup> in vacuum at a room temperature to form amorphous state with a very high defect density ( $10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$ ).<sup>2)</sup> Polycrystalline silicon films were also fabricated using the 50-nm-thick the amorphous silicon films formed on quartz substrates by the XeCl excimer laser heating with a pulse energy of 280 mJ/cm<sup>2</sup> in vacuum at room temperature. The average crystalline grain size was 80 nm. For infrared transmission spectra measurements, amorphous silicon films were formed by LPCVD on a silicon substrate coated with 100-nm-thick thermally grown SiO<sub>2</sub> films. Laser crystallization was also carried out for the samples. The samples were placed on a heater plate, whose temperature was maintained at 350 °C. The heat treatment was carried out in a quartz bell-jar filled with H<sub>2</sub>O vapor at almost one atmospheric pressure ( $\sim 10^5 \text{ Pa}$ ). The electrical conductivity was measured in the dark and under an illumination of air-mass 1 (AM-1) with an intensity of 100 mW/cm<sup>2</sup>. The spectra of op-

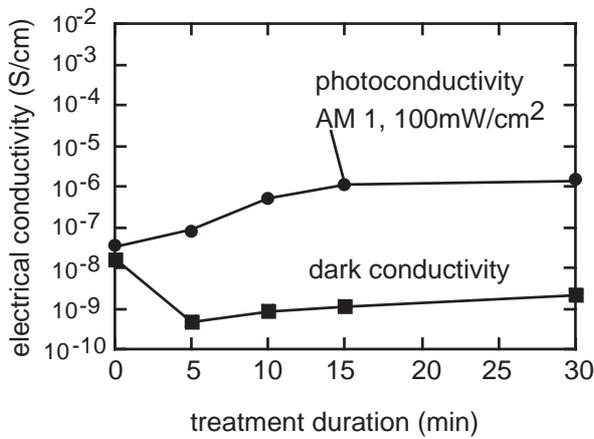
tical absorption were measured using an optical spectrometer. Infrared absorption spectra were also measured using Fourier transform infrared spectroscopy (FTIR).

Figure 1 shows changes in the dark conductivity and photoconductivity as functions of the duration of the heat treatment with H<sub>2</sub>O vapor at 350 °C for 10-nm-thick laser amorphized silicon films (a) and 50-nm-thick LPCVD a-Si films (b). Before the treatment, the laser amorphized silicon films had a high dark electrical conductivity ( $\sim 10^{-3} \text{ S/cm}$ ) because of a high variable range hopping conduction associated with a high defect density ( $\sim 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$ ).<sup>2)</sup> No photo conductivity was observed due to the detection limit under the high dark conductivity. The dark conductivity was reduced to the order of  $10^{-9} \text{ S/cm}$  by the treatment for 5 min, as shown in Fig. 1(a). On the other hand, the photoconductivity increased and it was almost  $10^2$  times higher than the dark conductivity for the treatment longer than 5 min. The as-deposited LPCVD a-Si films had a rather low dark electrical conductivity  $\sim 10^{-8} \text{ S/cm}$  but a very low photoconductivity. The dark conductivity was slightly reduced to  $10^{-9} \text{ S/cm}$  by the heat treatment and the photoconductivity increased to  $\sim 10^{-6} \text{ S/cm}$  for the 15 min treatment, as shown in Fig. 1(b). The laser crystallized Si films had a low photoconductivity because of defects caused by very rapid quenching at a rate of  $\sim 10^8 \text{ K/s}$ .<sup>3)</sup> The dark conductivity was slightly reduced to  $10^{-7} \text{ S/cm}$  and the photoconductivity was increased to  $\sim 10^{-5} \text{ S/cm}$  by the treatment for 10 min, as shown in Fig. 2.

Figure 3 shows the optical absorption spectra of (a) the laser amorphized films and (b) LPCVD a-Si films as fabricated and treated for 15 min at 350 °C, respectively. The laser amorphized silicon films had a high optical absorption coefficient in the photon energy range below 1.5 eV because of the large localized defect density.<sup>4)</sup> The heat treatment markedly reduced the optical coefficient in the low photon energy range, as shown in Fig. 3(a). The optical energy gap was estimated with the relation of  $(\alpha h\nu)^{0.5}$  vs  $h\nu$ . It increased from 1.41 eV (as fabricated) to 1.55 eV. The Urbach tail width was reduced from  $190 \pm 15 \text{ meV}$  to  $50 \pm 5 \text{ meV}$ , which was estimated from the slope of the optical absorption spectra in the low photon energy range.<sup>5)</sup> The LPCVD a-Si also had an appreciable optical absorption in the photon energy range below 1.5 eV because of defects in the films. The heat treatment also re-



(a)



(b)

Fig. 1. Dark and photoelectrical conductivities as functions of the duration of the heat treatment. Photoconductivity was measured under illumination of AM-1 with an intensity of 100 mW/cm<sup>2</sup>. The heat treatment was carried out at 350°C with H<sub>2</sub>O vapor for (a) 10-nm-thick laser a-Si and (b) 50-nm-thick LPCVD a-Si films.

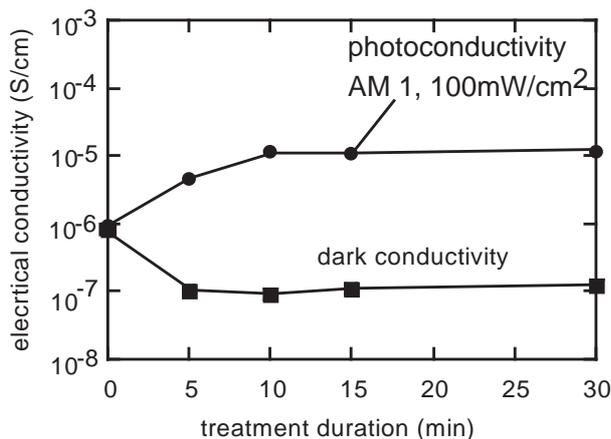
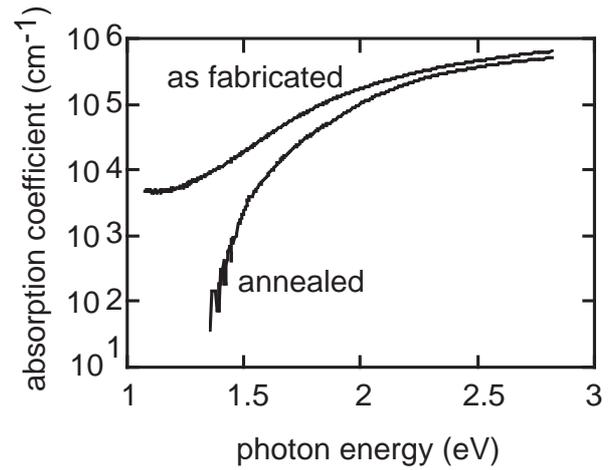
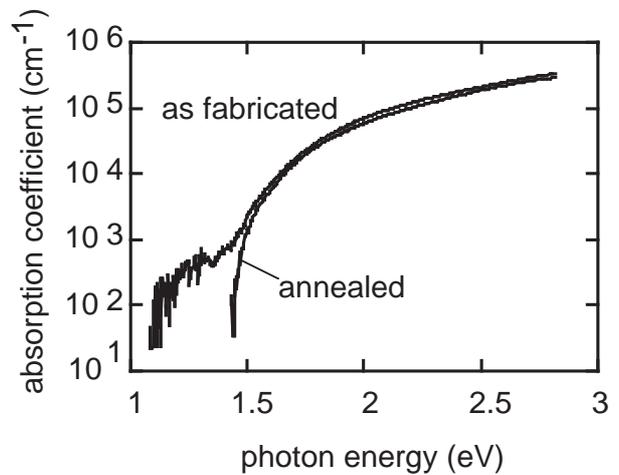


Fig. 2. Dark and photo electrical conductivity as functions of the duration of the heat treatment for 50-nm-thick laser crystallized silicon films.

duced the optical coefficient in the low photon energy range, as shown in Fig. 3(b). The optical band gap was slightly increased from 1.48 eV (as fabricated) to 1.51 eV. The Urbach tail width was reduced from 120±10 meV to 40±4 meV, which was estimated from the slope of the optical absorption



(a)



(b)

Fig. 3. Optical absorption spectra before and after the heat treatment for (a) 10-nm thick laser a-Si and (b) 50-nm-thick LPCVD a-Si films. The heat treatment was carried out at 350°C with H<sub>2</sub>O vapor for 15 min.

spectra in the low photon energy range.

The heat treatment with H<sub>2</sub>O vapor at 350°C resulted in the reduction of dark electrical conductivity, the increase of the photoconductivity and the reduction of the optical absorption coefficient in the low photon energy region, as shown in Figs. 1–3. These results indicate that the treatment reduces the localized defect states in the band gap for the amorphous and polycrystalline silicon films. The reduction of optical absorption coefficient in the low photon energy region (< 1.5 eV) means that the heat treatment reduced the density of band tail states. The weak bonds would be broken as a result of the reaction with H<sub>2</sub>O incorporated into the film with the help of heating the sample to 350°C. Then the silicon bonds would be terminated by hydrogen atoms or oxygen atoms provided from H<sub>2</sub>O. Although the change in the optical absorption spectra in a photon energy range lower than 1.2 eV was not measured because of the detection limit, the increase of photo electrical conductivity by the heat treatment may suggest that the density of dangling bonds also was reduced. The dangling bonds would be also terminated by hydrogen atoms or oxygen atoms provided from H<sub>2</sub>O incorporated into the film during the annealing. In order to determine the concentration of the hydrogen atoms in the LPCVD

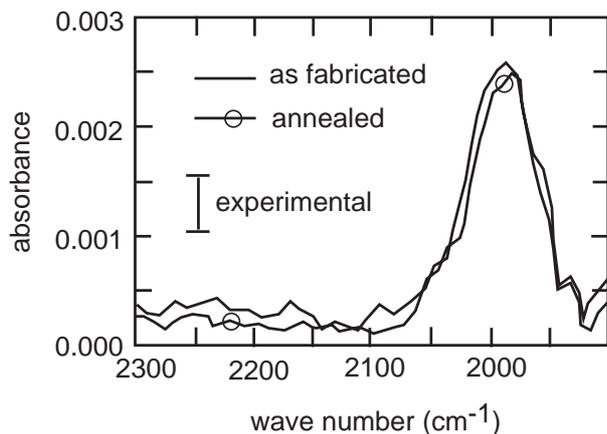


Fig. 4. Infrared absorption spectra before and after heat treatment for the LPCVD a-Si film. The heat treatment was carried out at 350°C with H<sub>2</sub>O vapor for 30 min. An experimental error bar is included.

a-Si and laser crystallized films formed on silicon substrates coated with thermally grown SiO<sub>2</sub>, optical absorption spectra were measured around 2000 cm<sup>-1</sup> using FTIR. As-deposited LPCVD a-Si had a sharp absorption peak associated with Si-H stretching vibration modes with a hydrogen concentration of 2.5 at%. The film treated with H<sub>2</sub>O vapor at 350°C for 30 min had almost the same absorption spectra within the measurement limit, as shown in Fig. 4. The measurement limit gave an increment of the hydrogen concentration of less than ~0.4 at% ( $\sim 2 \times 10^{20}$  cm<sup>-3</sup>). The as-fabricated laser crystallized films had no Si-H absorption. There was no increment in the Si-H absorption peak within the detection limit after the heat treatment. The low hydrogen increments < 0.4 at% indicates that the samples treated by the present annealing method are not like the silicon-hydrogen alloying system with high hydrogen concentration such as hydrogenated amorphous silicon formed by plasma CVD.<sup>6)</sup> The low optical band gap of LPCVD a-Si, 1.51 eV, treated by the present annealing method also indicates a low concentration of hydrogen and oxygen atoms,<sup>7)</sup> although the oxygen concentration could not be measured because of the intermediate SiO<sub>2</sub> layer. Hydrogen or oxygen atoms dissociated from H<sub>2</sub>O would only have the role of terminating the dangling bonds locally. The present heat treatment with H<sub>2</sub>O will be useful for the reduction of the defects in the silicon films for TFT fabrication processing. It would also be attractive for the fabrication of amorphous silicon film with a low optical band gap and low

defect density as photovoltaic materials.

In summary, the heating treatment at 350°C with H<sub>2</sub>O vapor was applied to reduce defects in laser a-Si, LPCVD a-Si and laser crystallized silicon films. The dark conductivity of the laser amorphized silicon films was reduced to 10<sup>-9</sup> S/cm by the treatment for 5 min, although the initial conductivity was very high, ~10<sup>-3</sup> S/cm, because of the high variable range hopping conduction associated with a high defect density ( $\sim 10^{20}$  cm<sup>-3</sup>eV<sup>-1</sup>). The photoconductivity induced by AM-1 illumination with the intensity of 100 mW/cm<sup>2</sup> increased to ~10<sup>-7</sup> S/cm. The heat treatment also reduced the dark conductivity of the LPCVD a-Si films to ~10<sup>-9</sup> S/cm, and increased the photoconductivity to ~10<sup>-6</sup> S/cm, respectively. The optical absorption coefficient was reduced in the photon energy range lower than 1.5 eV by the heat treatment for 15 min for laser amorphized silicon and LPCVD a-Si films. The optical energy gap was increased from 1.41 eV (as fabricated) to 1.55 eV for the laser amorphized silicon films and from 1.48 eV (as fabricated) to 1.51 eV for the LPCVD a-Si films. The Urbach tail width for the LPCVD a-Si films was reduced from 120±10 meV to 40±4 meV. The heat treatment also reduced the dark conductivity of the laser crystallized Si films to ~10<sup>-7</sup> S/cm, and increased the photoconductivity to ~10<sup>-5</sup> S/cm. FTIR measurement revealed that the increment of hydrogen concentration was less than  $2 \times 10^{20}$  cm<sup>-3</sup> after the treatment for the amorphous and polycrystalline films. These results show the heat treatment with H<sub>2</sub>O vapor reduces the defects density in the silicon films and results in silicon films with a low optical band gap with a low hydrogen concentration.

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