

Heat Treatment of Amorphous and Polycrystalline Silicon Thin Films with High-Pressure H₂O Vapor

Toshiyuki SAMESHIMA, Mitsuru SATOH, Keiji SAKAMOTO, Kentaro OZAKI and Keiko SAITOH
Tokyo University of Agriculture and Technology, Tokyo 184-8588, Japan

(Received May 11, 1998; accepted for publication June 1, 1998)

Changes in electrical and optical properties induced by heat treatment with high-pressure H₂O vapor are discussed for low pressure chemical-vapor deposited amorphous silicon (LPCVD a-Si) and laser-crystallized polycrystalline silicon films. Heat treatment at 190°C with $\sim 1 \times 10^6$ -Pa-H₂O vapor reduced the dark conductivity to $\sim 10^{-11}$ S/cm and increased the photoconductivity to $\sim 10^{-7}$ S/cm. The photoconductivity was also increased for laser-crystallized polycrystalline silicon films. Optical absorption in the photon energy range lower than 1.5 eV was reduced for the a-Si films. Heat treatment at 190–270°C resulted in a minimal change in optical band gap, which was 1.50 ± 0.02 eV for the LPCVD a-Si. The increase in hydrogen concentration was less than 2×10^{20} cm⁻³ after the treatment for the amorphous and polycrystalline silicon films. These results show that the heat treatment with high-pressure H₂O vapor can reduce the defect density in the silicon films at low temperatures.

KEYWORDS: LPCVD a-Si, laser crystallization, photoconductivity, optical absorption, hydrogen concentration

1. Introduction

Reduction of defects in silicon films at low temperatures is important for a variety of applications in many devices, for example, thin film transistors (TFTs) and thin film solar cells. For example, hydrogenation using hydrogen plasma or a hydrogen radical has been widely investigated for the reduction of defects and improvement of device characteristics.^{1–11)} We have proposed simple heat treatment with H₂O vapor at approximately 300°C.¹²⁾ Heat treatment improves the electrical characteristics of polycrystalline silicon thin film transistors (poly-Si TFTs). The threshold voltage is reduced as a result of the reduction of the densities of trapped states and fixed oxide charges in SiO₂ as well as in SiO₂/Si interfaces. Moreover, we have recently demonstrated a possibility in the reduction in defects in amorphous silicon and polycrystalline silicon films by applying heat treatment with H₂O vapor at 350°C at one atmospheric pressure.¹³⁾

In this paper, we discuss electrical and optical properties of low-pressure chemical vapor deposited amorphous silicon (LPCVD a-Si) and laser-crystallized polycrystalline silicon films when they are heated with high-pressure H₂O vapor at low temperatures. Changes in dark conductivity and photoconductivity of the films caused by heat treatment at from 190 to 270°C shows a reduction in the density of defect states in silicon films at low temperatures. Changes in optical absorption spectra between visible and infrared wavelength ranges are also presented to discuss the optical band gap as well as the silicon bonding network.

2. Experimental

50-nm-thick amorphous silicon films were formed on quartz substrates by dissociation of Si₂H₆ gas at 430°C using the LPCVD method. 50-nm-thick polycrystalline silicon films were fabricated on quartz substrates by crystallization of the amorphous silicon films by heating with the XeCl excimer laser at a wavelength of 308 nm, a pulse width of 30 ns and a pulse energy of 220 mJ/cm² in vacuum at room temperature. The average crystalline grain size was 40 nm. For infrared transmission spectra measurements, the amorphous silicon films were formed by LPCVD on a silicon substrate

coated with 100-nm-thick thermally grown SiO₂ film. Laser crystallization was also performed on the Si/SiO₂/Si samples. Hydrogenated amorphous silicon films fabricated by plasma CVD at 300°C were used to compare their optical properties to that of LPCVD a-Si treated with the present annealing method.

Samples were placed into a pressure-proof stainless-steel chamber with a volume of 60 cm³ using a metal seal.¹⁴⁾ Pure water was also put into the chamber, which was then placed on a heater plate to heat samples at 190°C, 230°C and 270°C. The H₂O evaporated during heating and the gas pressure increased. The heat treatment with H₂O vapor at almost one atmospheric pressure ($\sim 10^5$ Pa) was also carried out for comparison with the high-pressure H₂O vapor heating. The electrical conductivity was measured in the dark and under an illumination of air-mass 1 (AM-1) with an intensity of 100 mW/cm². The optical absorption spectra were measured using an optical spectrometer.¹³⁾ Infrared absorption spectra were also measured using Fourier transform infrared spectroscopy (FTIR).

3. Results and Discussions

Figure 1 shows changes in the dark conductivity and photoconductivity as a function of the duration of the heat treatment in H₂O vapor with a pressure of 8.4×10^5 Pa at 270°C for 50-nm-thick LPCVD a-Si films. Dark conductivity was reduced from 10^{-8} S/cm (as-fabricated) to approximately 10^{-11} S/cm by the heat treatment longer than 1 h and photoconductivity was increased to approximately 10^{-7} S/cm. This result shows that electrical properties of amorphous silicon can change remarkably by heat treatment; therefore we set the heating duration to 1 h.

Figure 2 shows changes in dark conductivity and photoconductivity caused by heat treatment for 1 h at different temperatures of 190°C, 230°C and 270°C as functions of the H₂O vapor pressure for 50-nm-thick LPCVD a-Si films. For each heating temperature, the dark conductivity was reduced to approximately 10^{-11} S/cm. Although a H₂O vapor pressure higher than 1×10^6 Pa was necessary to reduce the dark conductivity to $\sim 10^{-11}$ S/cm for the treatment at 190°C, 4×10^5 Pa was sufficient to reduce the dark conductivity to

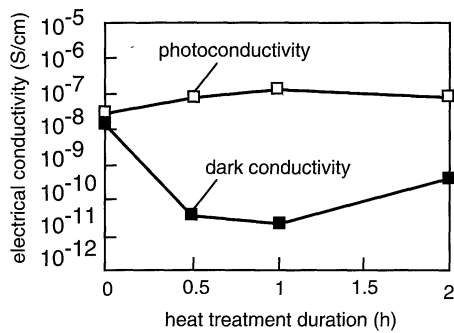


Fig. 1. Dark and photoelectric conductivities of 50-nm-thick LPCVD a-Si films as functions of the heat treatment duration. Photoconductivity was measured under illumination of AM-1 with an intensity of 100 mW/cm². Heat treatment was carried out at 270°C with 8.4 × 10⁵-Pa-H₂O vapor.

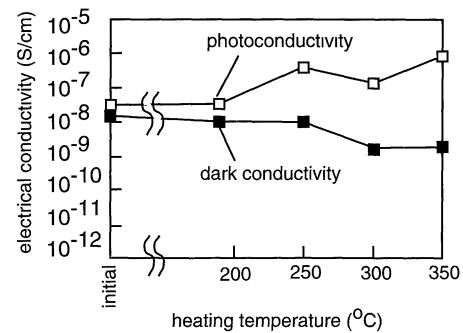


Fig. 3. Changes in dark and photo-electrical conductivities of 50-nm-thick LPCVD a-Si films caused by the heat treatment for 1 h in H₂O vapor at one atmospheric pressure as functions of heating temperature. Photoconductivity was measured under illumination of AM-1 with an intensity of 100 mW/cm².

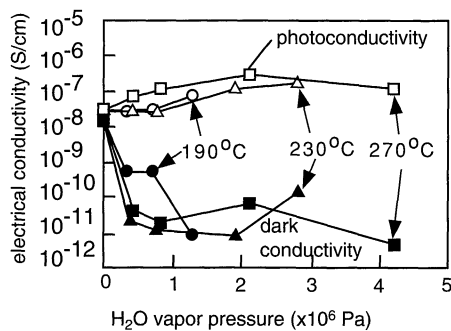


Fig. 2. Changes in dark and photo-electrical conductivities of 50-nm-thick LPCVD a-Si films caused by the heat treatment in H₂O vapor for 1 h at 190°C, 230°C and 270°C as functions of H₂O vapor pressure. Photoconductivity was measured under illumination of AM-1 with an intensity of 100 mW/cm².

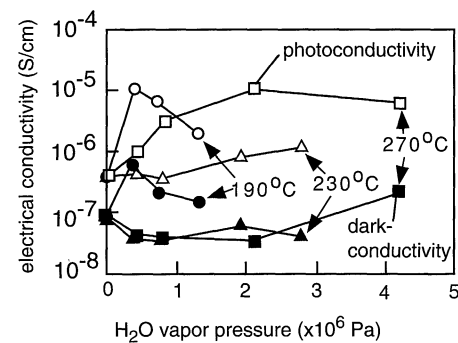


Fig. 4. Changes in dark and photo-electrical conductivities of 50-nm-thick laser-crystallized silicon films caused by the heat treatment in H₂O vapor for 1 h at 190°C, 230°C and 270°C as functions of H₂O vapor pressure. Photoconductivity was measured under illumination of AM-1 with an intensity of 100 mW/cm².

~10⁻¹¹ S/cm for the heat treatment at 230 and 270°C. These results show possible defect reduction for silicon films even at the low temperature of 190°C by heat treatment with high pressure H₂O vapor. The photoconductivity was increased to approximately 10⁻⁷ S/cm for each heating temperature case. The highest photoconductivity, 2.5 × 10⁻⁷ S/cm, was obtained by the 270°C treatment.

The heat treatment with H₂O vapor at one atmospheric pressure was also applied to LPCVD a-Si films in order to compare the heat treatment with high-pressure H₂O vapor. Figure 3 shows that the dark conductivity was reduced to 2 × 10⁻⁹ S/cm and the photoconductivity increased to 1 × 10⁻⁶ S/cm as the heating temperature increased to 350°C. Although a high photoconductivity/dark conductivity ratio was obtained for heating temperatures higher than 300°C, the dark conductivity was not reduced lower than 10⁻⁹ S/cm at any heating temperatures. In contrast, a reduction of the dark conductivity to ~10⁻¹¹ S/cm was achieved by the heat treatment at 190°C with high-pressure H₂O vapor as shown in Fig. 2.

Figure 4 shows changes in dark conductivity and photoconductivity for the laser-crystallized polycrystalline films caused by the heat treatment for 1 h at different temperatures of 190°C, 230°C and 270°C as functions of H₂O vapor pressure. For every heating temperature, the dark conductivity was slightly reduced to 10⁻⁷–10⁻⁸ S/cm. The ratio of photoconductivity/dark conductivity was increased by the heat

treatments. The highest ratio of 3 × 10² was obtained by the 270°C-heat treatment. These results show that reduction in defect density can be achieved for poly-Si by heat treatment with high-pressure H₂O vapor at temperatures of 190–270°C.

Figure 5 shows the optical absorption spectra of LPCVD a-Si films as fabricated and treated for 1 h at 190°C, 230°C and 270°C in H₂O vapor at pressures of 7.1 × 10⁵–8.4 × 10⁵ Pa. The LPCVD a-Si exhibited a substantial optical absorption in the photon energy range below 1.5 eV because of large band tail states. Heat treatment at every temperature reduced the optical coefficient in the low photon energy range, as shown in Fig. 5. The optical energy gap was estimated using the relationship of (αhν)^{0.5} vs hν. The optical band gap was 1.50 eV for as-fabricated films. The optical band gap hardly changed with a measurement error of ±0.02 eV when the samples were heated with the high-pressure H₂O vapor at temperatures 190–270°C.

Figure 6 shows the optical absorption spectra of laser-crystallized silicon films as fabricated and treated for 1 h at 190°C, 230°C and 270°C in H₂O vapor at pressures of 7.1 × 10⁵–8.4 × 10⁵ Pa. The laser-crystallized silicon films had rather low-optical absorption at a photon energy lower than 2.5 eV because of the indirect band structure compared with those of LPCVD a-Si. The absorption spectra showed nearly the same photon energy dependence for samples as fabricated and treated with high-pressure H₂O vapor. These results show

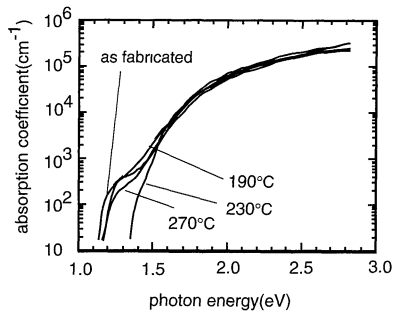


Fig. 5. Optical absorption spectra before and after the heat treatment for 50-nm-thick LPCVD a-Si films. Heat treatments were carried out for 1 h at 190°C with 7.1×10^5 -Pa-H₂O vapor, 230°C with 7.8×10^5 -Pa-H₂O vapor and 270°C with 8.4×10^5 -Pa-H₂O vapor, respectively.

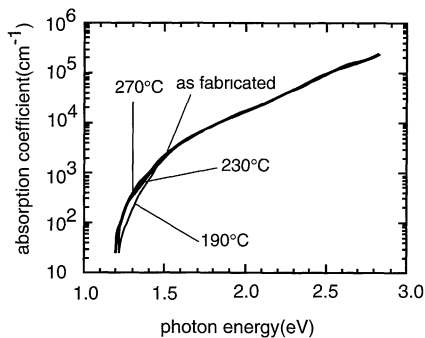


Fig. 6. Optical absorption spectra before and after heat treatment for 50-nm-thick laser-crystallized silicon films. Heat treatments were carried out for 1 h at 190°C with 7.1×10^5 -Pa-H₂O vapor, 230°C with 7.8×10^5 -Pa-H₂O vapor and 270°C with 8.4×10^5 -Pa-H₂O vapor, respectively.

that the present heat treatment does not change the bulk structure so much in these conditions although the heat treatment with high-pressure H₂O vapor has a high-oxidation effect.¹⁴⁾

The electrical and optical results shown in Figs. 1–6 indicate that the heat treatment can reduce localized defect states in the band gap for the amorphous and polycrystalline silicon films. The reduction of the optical absorption coefficient in the low-photon energy region (< 1.5 eV) of the LPCVD a-Si films means that the heat treatment reduced the density of the band tail states. The weak bonds broke as a result of the reaction with H₂O incorporated into the film. Then the silicon bonds were terminated by hydrogen atoms or oxygen atoms provided from the H₂O. 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 caused by the heat treatment may suggest that the density of dangling bonds also was reduced. The dangling bonds were terminated by hydrogen atoms or oxygen atoms provided from the H₂O incorporated into the film during annealing. The high-pressure H₂O vapor effectively helped the reaction between weak bonds (or dangling bonds) and H₂O at the low temperature of 190°C so that very low dark conductivity $\sim 10^{-11}$ S/cm was achieved, although the reaction between weak bonds (or dangling bonds) and H₂O can occur in the case of heat treatment in H₂O vapor at one atmospheric pressure at higher temperatures.¹³⁾

In order to determine the concentration of the hydrogen

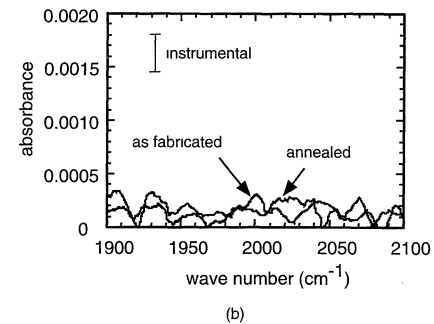
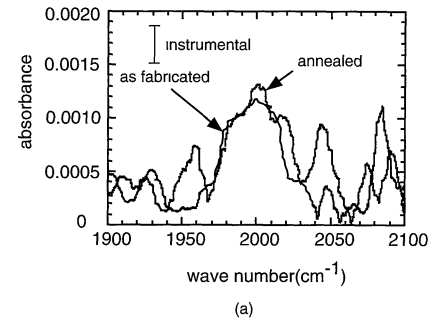


Fig. 7. Infrared absorption spectra before and after heat treatment for (a) LPCVD a-Si film and (b) laser-crystallized silicon films. Heat treatment was carried out for 1 h at 270°C with 2.1×10^6 -Pa-H₂O vapor. Experimental error bars are presented in the figures.

atoms in the LPCVD a-Si and laser-crystallized films, optical absorption spectra were measured around 2000 cm⁻¹ using FTIR. As-deposited LPCVD a-Si had a small absorption peak associated with Si-H stretching vibration modes with a hydrogen concentration of 1.5 at. %. The film treated with 2.1×10^6 -Pa-H₂O vapor at 270°C for 1 h had almost the same absorption spectrum as that of as-fabricated film within the measurement limit, as shown in Fig. 7(a). The measurement limit gave an increment of the hydrogen concentration of less than ~ 0.4 at. % ($\sim 2 \times 10^{20}$ cm⁻³). The fact that the LPCVD a-Si films maintained a low optical band gap after the treatment of the present annealing method also indicates incorporation of a low amount of hydrogen and oxygen atoms,¹⁵⁾ although the oxygen concentration could not be measured because of the intermediate SiO₂ layer. Hydrogen or oxygen atoms dissociated from H₂O would only have the role of terminating the dangling bonds. The as-fabricated laser-crystallized films had no Si-H absorption. There was no increase in the Si-H absorption peak within the detection limit after heat treatment at 270°C, as shown in Fig. 7(b). No increase of Si-H absorption was also observed after the heat treatment at 190°C and 230°C for samples of LPCVD a-Si and laser-crystallized silicon films. The 2.1×10^6 -Pa-H₂O vapor heating at 270°C for 1 h was applied to hydrogenated amorphous silicon thin films deposited by plasma CVD in order to investigate the influence of heating with high-pressure H₂O vapor to the silicon-hydrogen alloying system with a high concentration of hydrogen by measuring changes in optical absorption spectrum, as shown in Fig. 8. Although the absorption coefficient was reduced by the heat treatment at a low photon energy region, it was not substantially changed at photon energy higher than 1.7 eV. No change in the optical band gap, 1.67 eV, was observed. These results indicate that the heat treatment under conditions presented in this paper may incorporate hydrogen or oxygen with a small amount (at most $\sim 2 \times 10^{20}$ cm⁻³) re-

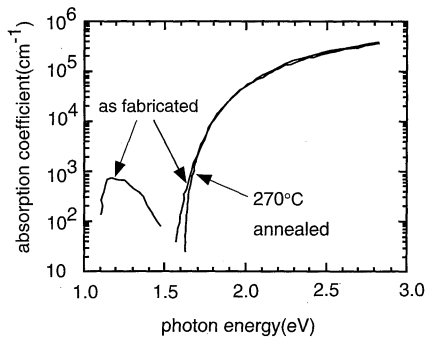


Fig. 8. Optical absorption spectra before and after heat treatment for 75-nm-thick hydrogenated amorphous silicon films. Heat treatments were carried out for 1 h at 270°C with 2.1×10^6 -Pa- H_2O vapor.

not seriously change the silicon bonding structure or the Si-H bonding structure. The results obtained in this paper suggest that the present simple heat treatment with high pressure H_2O vapor may be attractive for defect reduction of silicon films with various optical band gaps, which are useful as photo-voltaic materials. It would be also useful for the reduction of the defect density in the silicon films for TFT fabrication processing at low temperatures.

4. Summary

Heat treatment with high-pressure H_2O vapor at temperatures 190–270°C for 1 h was applied to LPCVD a-Si and laser-crystallized silicon films. The dark conductivity of the LPCVD a-Si films was reduced to 10^{-11} S/cm for heating temperatures ranging from 190 to 270°C. Photoconductivity induced by AM-1 illumination with the intensity of 100 mW/cm^2 increased to $\sim 10^{-7}$ S/cm. The heat treatment also increased the photoconductivity of the laser-crystallized silicon films to $\sim 10^{-5}$ S/cm maximum. The ratio of photoconductivity/dark conductivity was increased to 3×10^2 as the heating temperature was increased to 270°C. The optical absorption coefficient was reduced in the photon energy range lower than 1.5 eV by the heat treatment for LPCVD a-Si

films. The optical energy gap was not changed from the initial value of 1.50 eV within the measurement limit of ± 0.02 eV by the heat treatment at the temperatures from 190 to 270°C for the LPCVD a-Si films. The heat treatment slightly reduced the dark conductivity of the laser-crystallized Si films to 10^{-7} – 10^{-8} S/cm and increased the photoconductivity to $\sim 10^{-5}$ S/cm. FTIR measurement revealed that the increase of hydrogen concentration was less than $2 \times 10^{20} \text{ cm}^{-3}$ after the treatment of the amorphous and polycrystalline films. These results show that heat treatment with high-pressure H_2O vapor reduces the defect densities in the silicon films at the low temperatures $\sim 190^\circ\text{C}$ and does not seriously change Si-Si bonding networks.

Acknowledgements

The authors thanks M. Miyasaka, H. Ohshima, T. Mohri and Professor Saitoh for their support.

- 1) M. Rodder and S. Aur: IEEE Electron Device Lett. **12** (1991) 233.
- 2) R. A. Ditzio, G. Liu, S. J. Fonash, B.-C. Hsieh and D. W. Greve: Appl. Phys. Lett. **56** (1990) 1140.
- 3) I.-W. Wu, A. G. Lewis, T.-Y. Huang and A. Chiang: IEEE Electron Device Lett. **10** (1989) 123.
- 4) K. Baert, H. Murai, K. Kobayashi, H. Namizaki and M. Nunoshita: Jpn. J. Appl. Phys. **32** (1993) 2601.
- 5) T. C. Lee and G. W. Neudeck: J. Appl. Phys. **54**(1983) 199.
- 6) U. Mitra, B. Rossi and B. Khan: J. Electrochem. Soc. **138** (1991) 3420.
- 7) I.-W. Wu, T.-Y. Huang, W. B. Jackson, A. G. Lewis and A. Chiang: IEEE Electron Device Lett. **12** (1991) 181.
- 8) D. Jousse, S. L. Delage and S. S. Iyer: Philos. Mag. B **63** (1991) 443.
- 9) I. Yamamoto, H. Kuwano and Y. Saito: J. Appl. Phys. **71** (1992) 3350.
- 10) M. Okamura, S. Shirai and T. Serikawa: *Ext. Abstr. 1994 Int. Conf. Solid State Devices and Materials, Yokohama, 1994* (Business Center for Academic Societies Japan, Tokyo, 1994) p. 524.
- 11) T. Sameshima, M. Sekiya, M. Hara, N. Sano and A. Kohno: J. Appl. Phys. **76** (1994) 7377.
- 12) N. Sano, M. Sekiya, M. Hara, A. Kohno and T. Sameshima: IEEE Electron Device Lett. **16** (1995) 157.
- 13) T. Sameshima, M. Satoh, K. Sakamoto, A. Hisamatsu, K. Ozaki and K. Saitoh: Jpn. J. Appl. Phys. **37** (1998) L112.
- 14) T. Sameshima and M. Satoh: Jpn. J. Appl. Phys. **36** (1997) L687.
- 15) C. D. Cody, B. Abeles, C. R. Wronki, R. B. Stephens and B. Brooks: Sol. Cells **2** (1981) 227.