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Defect Reduction in Polycrystalline Silicon Thin Films by Heat Treatment with High-Pressure H_2O Vapor

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We investigated defect reduction in laser crystallized polycrystalline silicon (poly-Si) films by heat treatment with 1.3×10^6 Pa H_2O vapor. The H_2O vapor heat treatment at 260 °C for 6 h reduced the spin density in laser crystallized poly-Si films from 2.0×10^{18} (initial) to 6.5×10^{16} cm^{-3}. The activation energy of the reaction for defect reduction was 0.26 eV. Photoconductivity under 532 nm light illumination at 100 mW/cm^2 was increased from 2.7×10^{-6} (initial) to 3.3×10^{-5} S/cm by heat treatment for 1 h. The oxygen concentration in the silicon films was increased by 1.1×10^{19} cm^{-3} by heat treatment, although the hydrogen concentration was decreased by 1.4×10^{20} cm^{-3}. This suggests that oxygen atoms have an important role in defect state reduction in polycrystalline silicon films. [DOI: 10.1143/JJAP.46.1286]

KEYWORDS: spin density, laser crystallization, SIMS, ESR, photoconductivity, high pressure H_2O vapor heat treatment

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. For example, hydrogenation using a hydrogen plasma or a hydrogen radical has been widely investigated for defect reduction and device characteristic improvement.[1–6] Heat treatment with high pressure H_2O vapor at approximately 300 °C has also been developed.[7] Electrical active defects in polycrystalline silicon (poly-Si) and SiO_2 have been reduced by heat treatment.[7,8] The threshold voltage is reduced by reducing the densities of trapped states and fixed oxide charges in SiO_2 as well as in SiO_2/Si interfaces for poly-Si TFTs.[9]

In this paper, we report defect reduction in laser-crystallized silicon films by heat treatment with high-pressure H_2O vapor. We show a reduction in the spin density of the silicon films as a function of heating duration and heating temperature. We then report changes in the hydrogen and oxygen concentrations in the silicon films by heat treatment. We also present an increase in photoconductivity by heat treatment. With these results, we discuss the defect reduction mechanism of heat treatment with high-pressure H_2O vapor.

2. Experimental

Amorphous silicon films of 50 nm thickness were formed on quartz substrates by the dissociation of the gas mixture of SiH_4 with H_2 at 200 °C using the plasma-enhanced chemical vapor deposition (PECVD) method at 100 MHz. Secondary ion mass spectrometry (SIMS) measurement revealed that the initial films contained hydrogen atoms at an average concentration of 4.0×10^{21} cm^{-3} and oxygen atoms at an average concentration of 3.0×10^{18} cm^{-3}. 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. The laser energy density was increased stepwise from 130 to 305 mJ/cm^2 in 15 mJ/cm^2 steps. Twenty shots were irradiated at each energy step. The crystalline volume ratio was estimated to be 0.85 by the analysis of optical reflectivity spectra in the ultraviolet region.[10]

The silicon films were treated with 1.3×10^6 Pa H_2O vapor for 10 min, 1 h, 3 h, and 6 h at 260 °C. Heat treatments with 1.3×10^6 Pa H_2O vapor for 3 h were also conducted at 190, 230, 260, and 290 °C. The Raman scattering spectra of phonon peak of the Si–H bonds was measured by a 514.5 nm Ar ion laser probe. The spin density was measured by the electron spin resonance (ESR) microwave absorption in polycrystalline silicon (poly-Si) films before and after H_2O vapor heat treatment. The electrical conductivity was measured in the dark and under the illumination of light from a second harmonic neodymium-ion-doped yttrium aluminium garnet (Nd^+:YAG) laser at 532 nm with an intensity of 100 mW/cm^2. Hydrogen and oxygen concentrations in poly-Si were measured by SIMS before and after heat treatment with high-pressure H_2O vapor.

3. Results and Discussion

Figure 1 shows the Raman scattering spectra of hydrogenated amorphos silicon (a-Si:H) films as-deposited and annealed for 3 h in 1.3×10^6 Pa H_2O vapor at 260 °C (a) and of poly-Si films as-crystallized and annealed for 3 h in 1.3×10^6 Pa H_2O vapor at 260 °C (b). A broad peak around 2000 cm^{-1} produced by the Si–H phonon was observed for the a-Si:H films. This result shows that the a-Si:H films fabricated by PECVD contain a substantial amount of hydrogen atoms as Si–H bonding. The peak intensity of Si–H slightly decreased after the high pressure H_2O vapor heat treatment, as shown in Fig. 1(a). This indicates that hydrogen atoms are partially released from the silicon films during H_2O vapor heat treatment. On the other hand, no Si–H peak was observed in poly-Si films as-deposited and annealed for 3 h in 1.3×10^6 Pa H_2O vapor at 260 °C, as shown in Fig. 1(b) because the Raman scattering intensities were lower than the detection limit. Most of hydrogen atoms were evaporated and released from the films during laser crystallization, because the films were heated to a high temperature and melted by laser irradiation.

Figure 2 shows the in-depth profiles of hydrogen (a) and oxygen (b) atoms in poly-Si films as-crystallized and treated for 3 h at 260 °C with 1.3×10^6 Pa H_2O vapor. A substantial amount of hydrogen atoms still remained after laser heating and crystallization, as shown in Fig. 2(a). Heat treatment

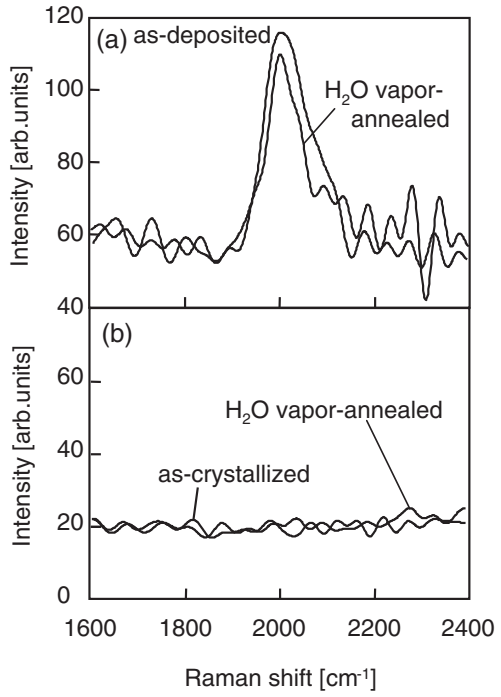

Fig. 1. Raman scattering spectra of a-Si:H films as-deposited and annealed for 3 h in 1.3×10^6 Pa H_2O vapor at 260 °C (a) and poly-Si films as-crystallized and annealed for 3 h in 1.3×10^6 Pa H_2O vapor at 260 °C (b).

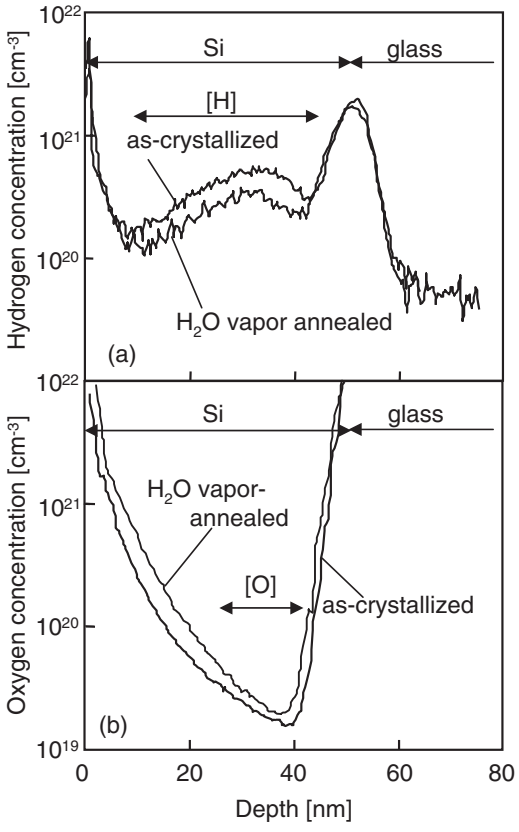

Fig. 2. In-depth profiles of hydrogen (a) and oxygen (b) atoms in poly-Si films as-crystallized and treated for 3 h at 260 °C with 1.3×10^6 Pa H_2O vapor. The average concentration was estimated between 10 and 45 nm for hydrogen and between 25 and 42 nm for oxygen, as shown by arrows.

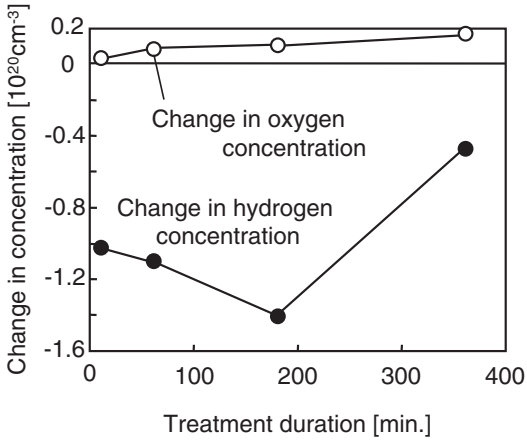

Fig. 3. Changes in average concentrations for hydrogen and oxygen atoms as functions of duration of heat treatment with 1.3×10^6 Pa H_2O vapor at 260 °C.

with 1.3×10^6 Pa H_2O vapor at 260 °C for 3 h slightly reduced the hydrogen concentration. A high oxygen concentration was observed in the surface region for the as-crystallized silicon films. We considered that a thin oxide layer was formed during the experimental process and that the oxide layer caused oxygen contamination during the measurement of in-depth profiles. Heat treatment with 1.3×10^6 Pa H_2O vapor at 260 °C for 3 h slightly increased the oxygen concentration in contrast to the change in hydrogen concentration. We measured changes in the average concentrations of hydrogen in the depth from 10 to 45 nm and for oxygen in the depth from 25 to 42 nm in the as-crystallized and annealed films with high-pressure H_2O vapor. The depth regions for the average concentrations were determined by avoiding noises near the surface and the bottom interface, as shown in the depth profiles in Fig. 2.

Figure 3 shows the changes in the hydrogen and oxygen concentrations as a function of the duration for heat treatment with 1.3×10^6 Pa H_2O vapor at 260 °C. The change in hydrogen concentration was negative for heat treatment from 10 min to 6 h. This indicates that the hydrogen concentration was decreased by 5.0×10^{19}–1.4×10^{20} cm^{-3} by H_2O vapor heat treatment. In contrast to the hydrogen concentration, the oxygen concentration slightly increased by 3.6×10^{18}–1.1×10^{19} cm^{-3}. Oxygen atoms were incorporated into the silicon films by H_2O vapor heat treatment. The SIMS measurement accuracies were 2.0×10^{19} cm^{-3} for hydrogen atoms and 3.0×10^{18} cm^{-3} for oxygen atoms. These results indicate that oxygen atoms have an important role in defect state reduction in laser-crystallized silicon films.

Figure 4(a) shows the spin density as a function of the duration of heat treatment with 1.3×10^6 Pa H_2O vapor at 260 °C. The films as-crystallized at 305 mJ/cm^2 had a high spin density of 2.0×10^{18} cm^{-3} owing to the dangling bonds localized at grain boundaries.[8] The spin density was reduced to 5.0×10^{17} cm^{-3} by 10 min heat treatment. It was further reduced to 6.5×10^{16} cm^{-3} by increasing the treatment duration to 6 h. The dangling bonds were effectively passivated by heat treatment with high-pressure H_2O vapor. The spin density decreased similar to the exponential decay with a single time constant of approximately 110 min, as

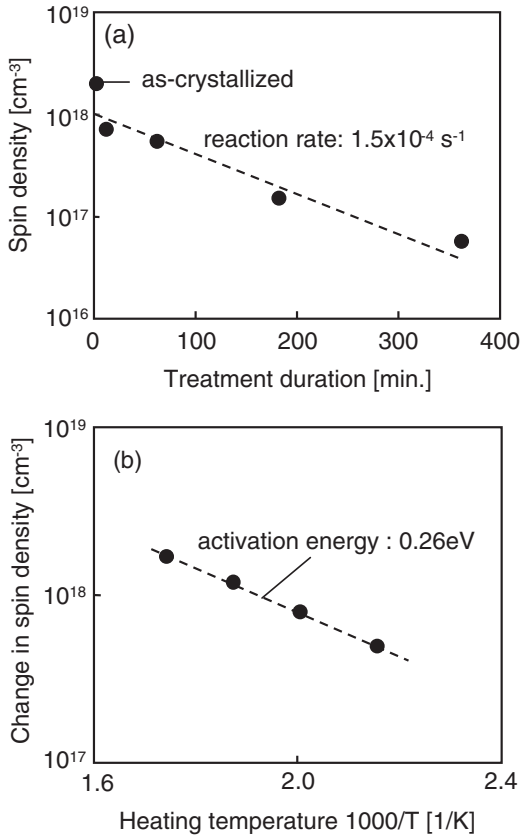

Fig. 4. Spin density as a function of duration of heat treatment with 1.3×10^6 Pa H_2O vapor at 260 °C (a) and change in spin density by heat treatment at 1.3×10^6 Pa H_2O vapor for 3 h as a function of heating temperature. The dashed lines indicate the calculated decay of the spin density with a reaction rate of 1.4×10^{-4} s (a) and an activation energy of 0.26 eV (b).

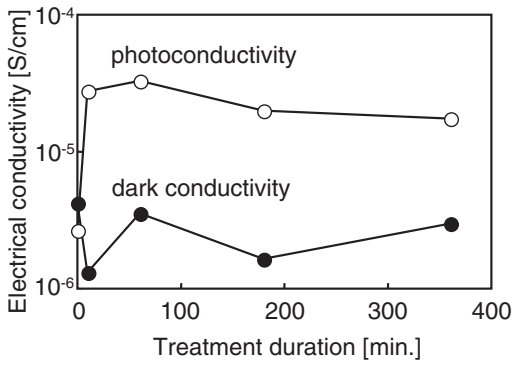

Fig. 5. Changes in dark conductivity and photoconductivity as functions of the duration of heat treatment with 1.3×10^6 Pa H_2O vapor at 260 °C for poly-Si films. The photoconductivity was measured under the illumination of light from a second-harmonic Nd^+:YAG laser at 532 nm at 100 mW/cm^2.

shown in Fig. 4(a). This indicates that defect reduction is governed by the pseudo-first-order reaction between the densities of dangling bonds and H_2O molecules incorporated into the silicon films. Figure 4(b) shows the change in spin density by heat treatment with 1.3×10^6 Pa H_2O vapor for 3 h as a function of heating temperature. The change in spin density was obtained by subtracting the spin density after H_2O vapor annealing from the initial spin density. The change in spin density increased as the heating temperature increased. This indicates that heat treatment at a high temperature effectively reduces the spin density. The change in spin density decreased similar to a single exponential decay, as shown in Fig. 4(b). The single exponential decay indicates that reduction rate of the spin density is proportional to the spin density.

We assumed that the reduction in dangling bond density was governed by the pseudo-first-order reaction for heat treatment at 190–290 °C; the activation energy was estimated by fitting the single exponential curve to the change in spin density shown in Fig. 4(b). The activation energy E was 0.26 ± 0.1 eV. The activation energy gives the reaction rate constant P in the simple equation $P = A\exp(-E/kT)$, where A is the pre-exponential factor, k is the Boltzmann constant, and T is the absolute temperature for heat treatment. The reaction rate increases with heating temperature. The reaction rate was the reciprocal time constant of the exponential decay of the spin density with time, as shown in Fig. 4. The reaction rate was therefore 1.5×10^{-4} s^{-1} ($= 1/110$ min) for 260 °C treatment with 1.3×10^6 Pa H_2O vapor. The pre-exponential factor A was therefore estimated to be 0.04 s^{-1} using the obtained reaction rates and activation energies. The estimations result in that the spin density I decreased with time t as $I_0\exp\{-0.04\exp(-0.26/kT)t\}$ for heat treatment with 1.3×10^6 Pa H_2O vapor, where I_0 is the initial spin density. The low activation energy allows defect state reduction at a low temperature. However, the pre-exponential factor was low. A long time is necessary for reducing the defect density. The results in Figs. 2–4 suggest that dangling bonds were mainly terminated by the oxygen atoms generated by the dissociation of H_2O molecules. There are possibilities that dangling bonds are well oxidized and oxygen atoms terminate dangling bonds at grain boundaries.

Figure 5 shows changes in dark conductivity and photoconductivity as functions of the duration of heat treatment with 1.3×10^6 Pa H_2O vapor at 260 °C for poly-Si films. The dark conductivity was 1.3×10^{-6}–4.2×10^{-6} S/cm. Although the photoconductivity was very low 2.7×10^{-6} S/cm for the as-fabricated poly-Si films, it was increased to 2.8×10^{-5} S/cm by 10-min-heat treatment. This result shows that the recombination ratio of photo induced carriers was reduced owing to the reduction in defect density in poly-Si films by heat treatment with high-pressure H_2O vapor. The photoconductivity reached a maximum value of 3.3×10^{-5} S/cm and then it slightly decreased to 1.7×10^{-5} S/cm as the treatment duration increased to 6 h. The reduction in photoconductivity during long annealing is strange, because the density of defect states monotonically decreased as the treatment duration increased to 6 h, as shown in Fig. 4. The changes in the optical absorption or quantum efficiency of carrier generation or carrier mobility should be further investigated because the photoconductivity depends on them.

4. Conclusions

Heat treatment with high-pressure H_2O vapor was applied to defect reduction in laser-crystallized poly-Si films. SIMS measurements revealed that the hydrogen concentration was decreased by 5.0×10^{19}–1.4×10^{20} cm^{-3} when 1.3×10^6 Pa H_2O vapor heat treatment at 260 °C was conducted

between 10 minutes and 6 h. On the other hand, the oxygen concentration slightly increased by 3.6×10^{18}–1.1×10^{19} cm^{-3} after H_2O vapor heat treatment. ESR measurements revealed that the spin density of poly-Si films were reduced from 2.0×10^{18} (initial) to 5.0×10^{17} cm^{-3} only by 10 min treatment with 1.3×10^6 Pa H_2O vapor at 260 °C. It was further reduced to 6.5×10^{16} cm^{-3} by heat treatment for 6 h. The activation energy for defect reduction in 1.3×10^6 Pa H_2O vapor was estimated to be 0.26 eV from the change in spin density as a function of heating temperature. The reaction rate was also estimated to be 1.5×10^{-4} s^{-1}. These results indicate the behavior of the change in spin density with time by 1.3×10^6 Pa H_2O vapor heat treatment as $\exp\{-0.04\exp(-0.26/kT)t\}$. The ESR and SIMS results suggest that oxygen atoms terminated dangling bonds and reduced the electrical active defect states in poly-Si films. The photoconductivity induced by 532 nm light illumination with an intensity of 100 mW/cm^2 was increased from 2.7×10^{-6} (initial) to 3.3×10^{-5} S/cm by heat treatment with 1.3×10^6 Pa H_2O vapor at 260 °C for 1 h. The reduction in defect density made the recombination probability of photo induced carriers low and the photoconductivity high.

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