



Reduction of defects of polycrystalline silicon thin films by heat treatment with high-pressure H₂O vapor

T. Sameshima^{a,*}, K. Sakamoto^a, K. Asada^a, M. Kondo^b,
A. Matsuda^b, S. Higashi^c

^a*Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei, Tokyo 184-8588, Japan*

^b*Electrotechnical Laboratory, Ibaraki 305-8568, Japan*

^c*SEIKO Epson Corporation, Nagano 392-8502, Japan*

Abstract

An improvement of electrical properties of pulsed laser crystallized silicon films was achieved by simple heat treatment with high-pressure H₂O vapor. The electrical conductivity of $7.4 \times 10^{17} \text{ cm}^{-3}$ phosphorus-doped 50-nm-thick pulsed laser crystallized silicon films was markedly increased from $1.6 \times 10^{-5} \text{ S/cm}$ (as crystallized) to 2 S/cm by heat treatment at 270°C for 3 h with $1.25 \times 10^6 \text{ Pa}$ H₂O vapor because of reduction of density of defect states localized at grain boundaries. Spin density was reduced from $1.7 \times 10^{18} \text{ cm}^{-3}$ (as crystallized) to $1.2 \times 10^{17} \text{ cm}^{-3}$ by heat treatment at 310°C for 3 h with $1.25 \times 10^6 \text{ Pa}$ H₂O vapor. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Reduction of defects in silicon films at low temperatures is important for a variety of applications in many devices, such as thin-film solar cells as well as thin-film transistors (TFTs). Hydrogenation using hydrogen plasma or a hydrogen radical has been widely investigated for the reduction of defects and improvement of device characteristics [1,2]. We have proposed simple heat treatment with H₂O vapor at approximately 300°C . Heat treatment has reduced the densities of trapped states and fixed

* Corresponding author. Tel.: + 81-42-388-7436; Fax: + 81-42-388-7436.

E-mail address: tsamesim@cc.tuat.ac.jp (T. Sameshima).

oxide charges in SiO_2 as well as in SiO_2/Si interfaces and has increased the lifetime of minority carriers [3,4]. This is an advantage for fabrication of electronic devices using minority carriers such as solar cells.

In this paper, we apply heat treatment with high-pressure H_2O vapor for improvement of polycrystalline silicon films fabricated by pulsed laser crystallization which is a method for low temperature formation of crystalline materials to quality for photovoltaic devices. Changes in the electrical conductivity caused by reduction of the density of localized defect states are presented for lightly phosphorus-doped silicon films. Change in the spin density is also reported. Reduction of the density of defect states by heat treatment with high-pressure H_2O vapor is discussed.

2. Experimental

50-nm-thick amorphous silicon films undoped and phosphorus doped with a density of $7.4 \times 10^{17} \text{ cm}^{-3}$ were formed on glass substrates using low-pressure chemical vapor deposition (LPCVD) and ion implantation methods. The samples were placed in a vacuum chamber, which was evacuated by a turbo-molecular pump to a level of $1 \times 10^{-4} \text{ Pa}$ for laser irradiation. Polycrystalline silicon films were fabricated by 28-ns pulsed XeCl excimer laser heating. Multiple-step-laser energy irradiation was carried out. Laser energy density was increased from 160 mJ/cm^2 (crystallization threshold) to 400 mJ/cm^2 in a 20 mJ/cm^2 step. Five pulses were irradiated at each laser energy density step. Samples were then placed into a pressure-proof stainless-steel chamber using a metal seal. Pure water was also added into the chamber. The chamber was then placed on a heater to heat samples at $190\text{--}310^\circ\text{C}$. The water evaporated during heating and the gas pressure increased. After heat treatment, Al electrodes were formed on phosphorus-doped polycrystalline films to measure change in the electrical conductivity with heat treatment conditions with H_2O vapor. The spin density was also measured by the electron spin resonance (ESR) microwave absorption method for undoped polycrystalline films formed by laser irradiation before and after heat treatment.

3. Results and discussion

Fig. 1 shows the electrical conductivity as a function of the heating temperature with $1.25 \times 10^6 \text{ Pa}$ H_2O vapor for 1 and 3 h for samples crystallized at a laser energy density of 400 mJ/cm^2 in vacuum at room temperature. Although, in general, most of phosphorus atoms are incorporated into crystalline silicon lattice sites by pulsed laser-induced melting followed by solidification, the samples just after crystallization had a low electrical conductivity of $1.6 \times 10^{-5} \text{ S/cm}$. This means that the pulsed laser crystallized silicon films had a high density of defect states at deep energy levels near midgap. The defect states localized at grain boundaries and they trapped most of the electrons generated from ionized phosphorus atoms in crystalline grains [5]. The electrical conductivity was markedly increased by heat treatment with high-pressure

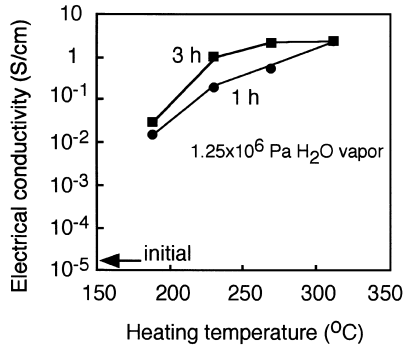


Fig. 1. The electrical conductivity as a function of the heating temperature for treatment with 1.25×10^6 Pa H_2O vapor for 1 and 3 h for $7.4 \times 10^{17} \text{ cm}^{-3}$ phosphorus-doped samples crystallized at a laser energy density of 400 mJ/cm^2 in vacuum at room temperature.

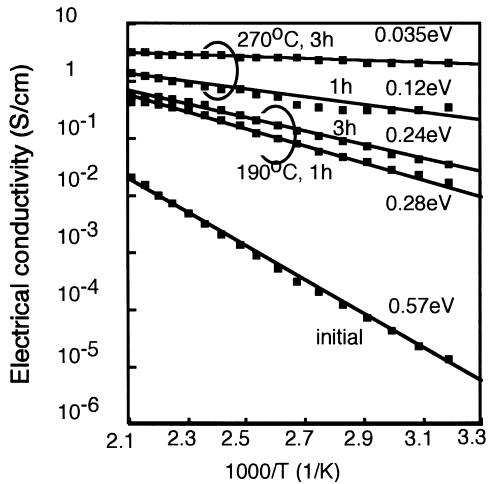


Fig. 2. Changes in the electrical conductivity as a reciprocal function of temperature for initial laser crystallized silicon films and films annealed with 1.25×10^6 Pa H_2O vapor at 190 and 270°C for 1 and 3 h, respectively. the activation energy of the electrical conductivity was also presented for each sample.

H_2O vapor. It increased as the heating temperature increased from 190 to 310°C, as shown in Fig. 1. The electrical conductivity reached a maximum of 2 S/cm for heat treatment at 270°C for 3 h.

Fig. 2 shows changes in the electrical conductivity as a reciprocal function of temperature for initial laser crystallized silicon films and films annealed with H_2O vapor at 190 and 270°C for 1 and 3 h, respectively. The low electrical conductivity of the initial crystallized films increased rapidly with an activation energy of 0.57 eV as the temperature increased. On the other hand, the electrical conductivity increased and the activation energy decreased after heat treatment with high-pressure H_2O

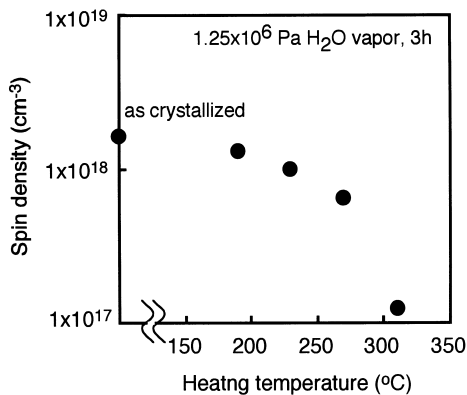


Fig. 3. Spin density obtained by ESR measurements as a function of the heating temperature for treatment with 1.25×10^6 Pa H_2O vapor for 3 h for undoped samples crystallized at a laser energy density of 400 mJ/cm^2 in vacuum at room temperature.

vapor. This means that the free carrier density increased after heat treatment. ESR measurements were conducted to measure the spin density for undoped silicon films laser crystallized at 400 mJ/cm^2 before and after heat treatment with high-pressure H_2O vapor. Fig. 3 shows the spin density as a function of heating temperature for heat treatment with 1.25×10^6 Pa for 3 h. The initial films crystallized at 400 mJ/cm^2 had a high spin density of $1.7 \times 10^{18} \text{ cm}^{-3}$ caused by a number of dangling bonds localized at grain boundaries. The spin density was reduced to $1.2 \times 10^{17} \text{ cm}^{-3}$ by heat treatment as the heating temperature increased to 310°C . The dangling bond was effectively eliminated by heat treatment with high-pressure H_2O vapor.

From the results of Figs. 1–3, heat treatment with H_2O vapor made the defects electrically inactive and changed localized electron states to extended states. Defect states localized at grain boundaries for laser crystallized silicon films was reacted by H_2O molecules incorporated into silicon films. H_2O molecules coming at defect sites would be chemically dissociated with the help of heating energy. The dangling bonds of silicon atoms were probably eliminated through formation of Si–O, Si–OH or Si–H bondings.

We analyzed changes in the electrical conductivity of polycrystalline films using a statistical thermodynamical analysis program [5]. We introduced a Gaussian-type energy distribution of density of defect states in the band gap at grain boundaries. Phosphorus dopant atoms were assumed to be distributed uniformly in silicon films. Electron carriers are generated from the phosphorus dopant atoms via their ionization, whose probability is determined with the Fermi–Dirac statistical distribution function. Free carriers are trapped by the localized defect states and the defects are charged negatively. The Fermi energy level is determined by the statistical thermodynamical conditions keeping the charge neutrality among the densities of ionized dopant atoms (N_d), defect states charged negatively with electron carriers (X_d) and free carriers (n), $N_d = n + X_d$, in the whole region including crystalline grains and grain boundaries. However, the density of ionized donors is larger than that of the free electrons in

crystalline grains because some electrons produced from doped phosphorus atoms are trapped at grain boundaries. This space-charge effect in crystalline grains causes the band bending and results in the potential barrier at grain boundaries. We also introduced scattering effects due to dopant ions, lattice vibration and disordered states at grain boundaries, which reduces the carrier mobility [6,7]. Heat treatment with high-pressure H_2O vapor was introduced by the assumption that H_2O molecules were incorporated into the films with a diffusion constant. The H_2O flux is assumed to distribute according to the complementary error function. The density of the defect states at a film depth is assumed to be reduced in proportion to a reaction probability and a density of H_2O molecules incorporated in the films. Through fitting process between temperature dependence of calculated and experimental conductivities for initial as-crystallized case, the energy level and its width of defect states were determined as 0.2 eV above the midgap and a width of 0.4 eV. Fitting calculated activation energies to experimental one gave the H_2O flux, the reaction probability and the H_2O diffusion coefficient. The value of H_2O flux \times reaction probability increased from 5.3×10^{13} to $8.3 \times 10^{13} \text{ cm}^{-3} \text{ s}^{-1}$ as the heating temperature increased from 190 to 310°C. The H_2O diffusion coefficient also increased from 3×10^{14} to $6 \times 10^{14} \text{ cm}^{-3} \text{ s}^{-1}$ as the heating temperature increased from 190 to 310°C.

Calculation gave a high density of defect states $\sim 1 \times 10^{18} \text{ cm}^{-3}$ at the grain boundaries localized electron states generated from phosphorus atoms for as-crystallized films, so that crystalline grains were depleted. Moreover, the potential barrier height at grain boundaries caused by band bending due to ionized donor atoms was 0.3 eV as shown in Fig. 4. The high potential barrier height at grain boundaries resulted in a low free electron density and the low electrical conductivity, as shown in Figs. 1 and 2. The increase of the electrical conductivity resulted from reduction of the density of defect states by heat treatment with high-pressure H_2O vapor. The number of electrons trapped at defect states decreased and the number of free electrons increased so that the Fermi level was shifted toward the conduction band edge and the

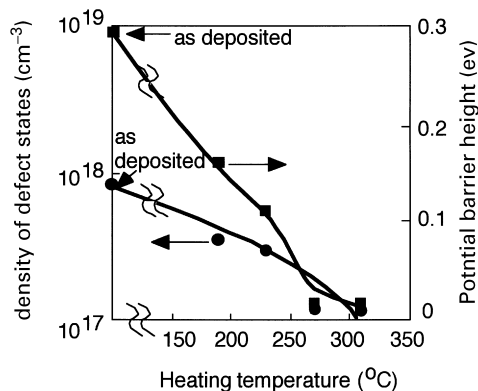


Fig. 4. Calculated density of defect states and potential barrier height as a function of the heating temperature for treatment with $1.25 \times 10^6 \text{ Pa}$ H_2O vapor for 3 h for the phosphorus lightly doped silicon films formed at a laser energy density of 400 mJ/cm^2 .

activation energy was reduced, although the occupation probability of defect states increased according to the shift of Fermi level. Calculation gave a low density of electrically active defect states about 10^{17} cm^{-3} after heat treatment at about 300°C for 3 h at $1.25 \times 10^6 \text{ Pa}$ and allow potential barrier height about 0.02 eV, as shown in Fig. 4. Moreover, the free carrier density and the carrier mobility were estimated to be $2.7 \times 10^{17} \text{ cm}^{-3}$ and about $50 \text{ cm}^2/\text{Vs}$ at room temperature for phosphorus-doped polycrystalline silicon.

The present experimental results revealed that heat treatment at a low temperature of $\sim 300^\circ\text{C}$ with high-pressure H_2O vapor reduced the density of defect states electrically active caused by silicon dangling bonds in the laser-induced crystallized films. This simple treatment needs no vacuum or plasma. The present simple method might be useful for grain boundary passivation of polycrystalline silicon films for fabrication of solar cells at low cost.

4. Summary

We demonstrated grain boundary passivation of polycrystalline silicon films using heat treatment with high-pressure H_2O vapor. Pulsed laser crystallized films 50 nm-thick had a high density of defect states, which trapped most of the electrons generated from phosphorus atoms doped with a density of $7.4 \times 10^{17} \text{ cm}^{-3}$. The electrical conductivity of silicon films was markedly increased from $1.6 \times 10^{-5} \text{ S/cm}$ (as crystallized) to 2 S/cm by heat treatment at 270°C for 3 h with $1.25 \times 10^6 \text{ Pa}$ H_2O vapor. The activation energy of the electrical conductivity was reduced from 0.57 to 0.035 eV according to generation of free carrier associated with defect passivation with hydrogen or oxygen atoms provided by H_2O molecules. The spin density was reduced from $1.7 \times 10^{18} \text{ cm}^{-3}$ (initial) to $1.2 \times 10^{17} \text{ cm}^{-3}$ by heat treatment with $1.25 \times 10^6 \text{ Pa-H}_2\text{O}$ vapor at 310°C for 3 h. Our statistical thermodynamical calculation gave that the potential barrier height at grain boundaries was reduced from 0.3 eV (initial) to 0.02 eV. These results show that simple heat treatment with high-pressure H_2O vapor effectively reduce the density of defect states in laser-crystallized silicon films and improved their electrical properties. The present simple method might be useful for fabrication of polycrystalline silicon solar cells.

Acknowledgements

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