

Free carrier optical absorption used to analyze the electrical properties of polycrystalline silicon films formed by plasma enhanced chemical vapor deposition

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Abstract

The electrical properties of (400) oriented polycrystalline silicon films fabricated at 300°C by 100-MHz plasma enhanced chemical vapor deposition from gaseous mixture of SiF₄/H₂/SiH₄ are reported. A double layered structure of phosphorus-doped poly-Si/H/F film (200 nm)/undoped poly-Si/H/F film was adopted to research the changes in electrical properties in the doped layer induced by the undoped layer thickness. The carrier mobility in the crystalline grain of the doped layer, analyzed by free carrier optical absorption, increased from 10 to 35 cm²/Vs as the undoped film thickness increased from 0 to 1000 nm. The carrier density in the crystalline grain was 2.5 × 10²⁰ cm⁻³ for each sample. The grain properties in the doped layer improved as the undoped film thickness increased. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polycrystalline silicon films (poly-Si) fabricated at low temperatures (< 400°C) are important for device applications such as solar cells and thin film transistors. Plasma enhanced chemical vapor deposition (PECVD) has the advantage of uniform film formation over a large area at a low temperatures. The poly-Si/H/F films fabricated at low temperatures (≤ 300°C) from SiF₄/H₂ mixing gases using very high frequency PECVD were reported to have large grain sizes (> 100 nm in diameter) and a high electron mobility (~ 10 cm²/Vs) [1–4]. The analysis of free carrier optical absorption gives the carrier mobility and density in the crystalline grain, because free carrier optical absorption occurs via the excitation induced by the electrical

field of incident photons, followed by energy relaxation in the crystalline grains [5–10]. Besides, electrical conductivity is analyzed with electrons traversing crystalline grains and grain boundaries. It depends on the grain boundary properties.

In this paper, we have reported the electrical properties at the leading surface region of film growth using a doped poly-Si/H/F film/undoped poly-Si/H/F film double-layered structure with different undoped film thickness. Also, in order to reduce defect states in the crystalline grain and grain boundary, a XeCl excimer laser was irradiated. The electrical properties after laser irradiation were discussed.

2. Experiment

The poly-Si/H/F films were formed on quartz glass by 100-MHz plasma enhanced chemical vapor deposition from SiF₄ and H₂ mixing gases, as reported [1,2]. Small amounts of SiH₄ were added to the mixing gases to increase growth rate. The (400) oriented phospho-

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rus-doped films were fabricated at 300°C, 20 W and $\text{SiF}_4/\text{H}_2/\text{SiH}_4 = 60/3.0/0.1$ sccm. The PH_3 gas concentration was used between 0.2 and 40 000 ppm. In order to investigate the electrical properties in the doped layer which are dependent on underlying film thickness, we adopted a double-layered structure. The top P-doped layer thickness was 200 nm. The bottom undoped layer thickness was varied from 0 to 1000 nm. The free carrier optical absorption was measured using conventional Fourier transform infrared spectroscopy (FTIR Bomem MB-100) between 400 and 4000 cm^{-1} . The carrier mobility and density in the crystalline grains were obtained by best fitting of experimental and calculation reflective spectra. These samples were irradiated by a 28-ns-pulsed XeCl excimer laser from the top region at room temperature and 1×10^{-4} Pa. Multiple step laser energy irradiation was carried out. The laser energy density was increased from 160 to 550–600 mJ/cm^2 in 40- mJ/cm^2 steps. Five pulses were irradiated at each laser energy density step.

3. Results and discussion

The carrier mobility in the crystalline grain (μ_{FCA}) of doped layer was analyzed by free carrier optical absorption. The μ_{FCA} increased from 10 to 35 cm^2/Vs as the undoped poly-Si/H/F film thickness increased from 0 to 1000 nm. The crystalline grain properties improved as the undoped film thickness increased. The μ_{FCA} for a 1000-nm undoped film thickness was close to the carrier mobility of doped single crystalline silicon. A good quality crystalline film was grown on the thick undoped film. Fig. 1(a) shows that μ_{FCA} depended on temperature and that of $5 \times 10^{20} \text{ cm}^{-3}$ doped poly-Si films annealed at a laser energy density of 360 mJ/cm^2 . The μ_{FCA} of poly-Si/H/F double-layered structures decreased by $\sim 1 \text{ cm}^2/\text{Vs}$ for each sample as the temperature increased from room temperature (RT) to 200°C. Besides, the μ_{FCA} value of the laser crystallized silicon film was higher than that of the poly-Si/H/F double-layered structure and decreased by $\sim 5 \text{ cm}^2/\text{Vs}$. The reduction of carrier mobility is an effect of carrier scattering caused by lattice vibration. This result indicates that crystalline grains for doped poly-Si/H/F have density defects compared with laser crystallized silicon films. Fig. 1(b) shows the changes in μ_{FCA} depending on the temperature after laser irradiation. The μ_{FCA} values increased in the case of thin undoped film thickness. Even after laser irradiation, μ_{FCA} for each sample didn't decrease as the temperature increased, in comparison with laser crystallized silicon films shown in Fig. 1(a). The defects in the crystalline grain remained even after laser irradiation. The crystalline volume fraction at the top surface of the doped poly-Si/H/F film was analyzed from an E_2 peak height of approximately 276 nm, because the E_2 peak gives the crys-

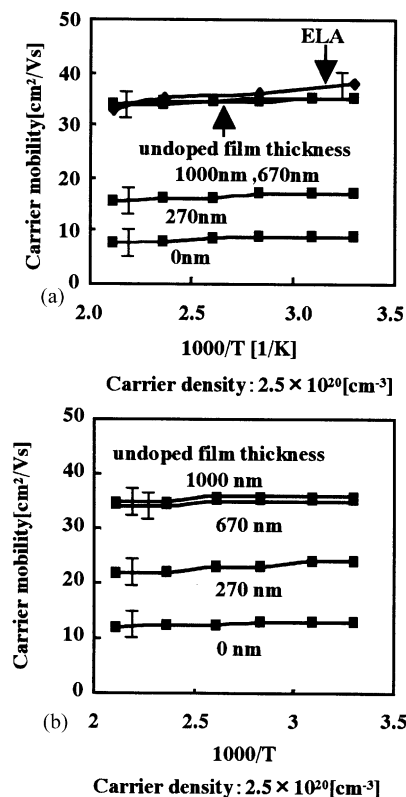


Fig. 1. (a) Changes in carrier mobility in the crystalline grain as a function of temperature and XeCl excimer laser annealed silicon film. (b) Changes in carrier mobility in the crystalline grain as a function of temperature after laser irradiation.

talline state at a surface region 10 nm deep due to a large optical absorption for silicon ($\sim 10^6 \text{ cm}^{-1}$). It increased from 0.3 to 0.7 for each sample after laser irradiation. The value of single crystalline silicon is 1 and amorphous silicon is 0. In spite of the equal crystalline volume fractions at the surface region for each sample, μ_{FCA} values were different, as shown in Fig. 1(a,b). This result reveals the distribution of crystalline states in the vertical direction of doped poly-Si/H/F.

In order to estimate grain boundary properties of doped poly-Si films/H/F, we adopted the ratio of σ_{grain} to σ_{eff} ($\sigma_{\text{grain}}/\sigma_{\text{eff}}$). The σ_{grain} value is electrical conductivity in the crystalline grain. It was calculated by $en_{\text{FCA}}\mu_{\text{FCA}}$, where e is the electrical primitive charge and n_{FCA} is the carrier density in the crystalline grain. The n_{FCA} value was analyzed at approximately $2.5 \times 10^{20} \text{ cm}^{-3}$ for each sample. It did not change as temperature increased before and after laser irradiation. The σ_{eff} value is the effective conductivity measured by electrical measurement with aluminum gap electrodes with a length of 6 mm and an applied voltage of 1 V. In Fig. 2, the ratio before and after laser irradiation in the case of 0 and 1000-nm undoped film thickness are shown. The ratio depended on tempera-

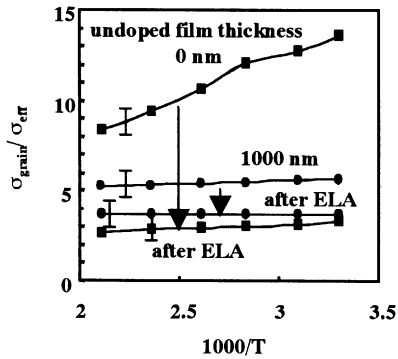


Fig. 2. The ratio of σ_{grain} to σ_{eff} ($\sigma_{\text{grain}}/\sigma_{\text{eff}}$) as a function of temperature before and after laser irradiation.

ture for the 0-nm undoped film thickness, and decreased from 13.6 to 8.4 as the temperature increased. This is the effect of increasing of the thermal carrier crossing the grain boundary. After laser irradiation, that decreased from 3.3 to 2.66. Both the crystalline grain and grain boundary properties were effectively improved by laser irradiation, as shown in Figs. 1 and 2. For the 1000-nm undoped film thickness, before laser irradiation, the ratio showed 5.68 to 5.23, and after laser irradiation, it showed 3.73 to 3.67 as the temperature increased. The ratio dependence on temperature didn't change drastically in comparison with the case of the 0-nm undoped film thickness before laser irradiation. The increasing thermal carriers crossing the grain boundary were lower than that of the 0-nm undoped film thickness. The crystalline grain properties were barely improved, as shown in Fig. 1, but grain boundary properties were improved by laser irradiation, as shown in Fig. 2. For poly-Si films/H/F double-layered structure, grain and grain boundary properties improved as undoped film thickness increased. Using σ_{eff} and σ_{grain} , the average energy barrier height at the grain boundaries (ΔE) were roughly estimated by $\sigma_{\text{eff}} = \sigma_{\text{grain}} \exp(-\Delta E/kT)$, where k and T are the Boltzmann constant and the absolute temperature, respectively. The average energy barrier height at RT decreased from 52 to 34 meV for the 0-nm undoped film thickness before and after laser irradiation. On the other hand, it decreased from 68 to 31 meV for the 1000-nm undoped film thickness [7,11]. Also, the effective carrier mobility of electrical current (σ_{eff}), which traverses the grain boundary, was calculated by $en_{\text{eff}}\mu_{\text{eff}}$. The effective carrier density (n_{eff}) was given approximately the same value as $2.5 \times 10^{20} \text{ cm}^{-3}$ of n_{FCA} . The μ_{eff} value increased from 0.9 to 4.5 for the 0-nm undoped film thickness and from 4 to 9 for the 1000-nm undoped film thickness [7].

4. Summary

We investigated the electrical properties of doped poly-Si/H/F/undoped poly-Si/H/F double-layered

structure fabricated by 100-MHz plasma enhanced chemical vapor deposition. The carrier mobility in the crystalline grain (μ_{FCA}) increased from 10 to 35 cm^2/Vs as the undoped film thickness increased from 0 to 1000 nm. A good quality crystalline grain was grown on thick undoped film. The μ_{FCA} for each sample decreased by $\sim 1 \text{ cm}^2/\text{Vs}$ as the temperature increased from room temperature to 200°C before and after laser irradiation. The defects in the crystalline grain remained for each sample even after laser irradiation, in comparison with that of the laser crystallized silicon film because the μ_{FCA} of the laser crystallized silicon film was higher and decreased by $\sim 5 \text{ cm}^2/\text{Vs}$. The grain boundary properties of doped poly-Si films were estimated by the ratio of electrical conductivity in the crystalline grain to effective conductivity ($\sigma_{\text{grain}}/\sigma_{\text{eff}}$). The ratio depended on temperature for the 1000-nm undoped film thickness, showed 5.68 to 5.23 before laser irradiation. After laser irradiation, it showed 3.73 to 3.67. The average energy barrier height decreased from 52 to 34 meV. The ratio of temperature dependence did not change more drastically than for that of the 0-nm thickness of undoped film before and after irradiation. The thermal carrier increased by less than for the 0-nm film thickness. The grain and grain boundary properties improved as the undoped film thickness increased.

References

- [1] T. Kamiya, K. Nakahata, K. Ro, C.M. Fortmann, I. Shimizu, to be published in Mater. Res. Soc. Symp. Proc. (1999).
- [2] T. Kamiya, K. Nakahata, K. Ro, C.M. Fortmann, I. Shimizu, Jpn. J. Appl. Phys. 38 (1999) 5750.
- [3] T. Kamiya, K. Nakahata, A. Miida, C.M. Fortmann, I. Shimizu, Thin Solid Films 337 (1999) 18.
- [4] K. Nakahata, A. Miida, T. Kamiya, C.M. Fortmann, I. Shimizu, Thin Solid Films 337 (1999) 45–50.
- [5] H. Engstrom, J. Appl. Phys. 51 (1980) 5245.
- [6] M. Born, E. Wolf, Principals of Optics Chap. 1 and 13, Pergamon, New York, 1974.
- [7] T. Sameshima, K. Saitoh, N. Aoyama, S. Higashi, M. Kondo, A. Matsuda, Jpn. J. Appl. Phys. 38 (1999) 1892.
- [8] T. Sameshima, K. Saitoh, M. Sato, A. Tajima, N. Takashima, Jpn. J. Appl. Phys. Lett. 36 (1997) L1360–L1363.
- [9] T. Sameshima, Mat. Res. Soc. Symp. Proc. 536 (1999) 427–438.
- [10] T. Sameshima, K. Saito, N. Aoyama, M. Tanda, M. Kondo, A. Matsuda, S. Higashi, Technical Digest of the Int. Photovoltaic Solar Energy Conf, Sapporo, Japan, 1999, p. 211.
- [11] F. Le Bihan, B. Fortin, H. Lhermite, O. Bonnaud, D. Briand, in: H.P. Strunk, J.H. Werner, B. Fortin, O. Bonnaud (Eds.), Polycrystalline Semiconductors III, Scitec Publications, Zuerich-Uetikon, 1994, p. 379.