Abstract.
We report activation of silicon implanted with phosphorus atoms by heat treatment at 350°C. The sheet resistance was reduced to 950 Ω/sq heat treatment for 24 h for samples implanted at 10 keV with a concentration of 5×10^{14} cm^{-2}. Compared with the sheet resistance obtained by laser annealing, ratios of conductance increase were estimated to be 0.21. It was close to a recrystallization ratio of 0.20 obtained by analysis of optical reflectivity spectra. In contrast, the sheet resistance decreased only to 2200 Ω/sq for samples implanted at 70 keV with 5×10^{14} cm^{-2}. Ratios of conductance increase were 0.06. It was lower than that in the case of 10-keV implantation. On the other hand, the recrystallization ratio for samples implanted at 70 keV was 0.25, which was comparable to that in the case of 10-keV implantation.

Introduction

Activation of silicon implanted with phosphorus atoms is an essential process technology for fabrication of field effect transistors, bipolar transistors and thin film transistor (TFT). Furnace and flash lamp heating have been used for the purpose. In general, a high heating temperature above 800°C has been used for activation and recrystallization of the disordered region caused by ion implantation [1]. On the other hand, a processing temperature lower than 400°C has been required in order to fabricate TFTs over a large glass substrates with a low heat proof. A simple furnace heating lower than 400°C has been already applied for TFT fabrication. It has been also believed that the activation ratio is low about 2% and the recrystallization ratio is also low in the case of the low temperature heat treatment. On the other hand we have reported that the activation ratio depends on a condition of ion implantation, and that there can be a condition for achieving an activation ratio much higher than 2% in the case of 300°C-heat treatment of polycrystalline silicon [2].

In this paper, we report behaviors of activation and recrystallization of silicon implanted with phosphorus atoms by heat treatment at different temperature in the case of phosphorus ion implantation to the single crystalline silicon. We especially concentrate investigation of heat treatment of the samples at 350°C. We discuss the ratios of activation and recrystallization as functions of phosphorus energy and its concentration.

Experimental

The ion implantation of phosphorus atoms was conducted for p-type silicon substrates with a resistivity of 3~10 Ω cm. Acceleration energies were 10 and 70 keV. Concentrations were 5×10^{14}, 1×10^{15}, and 2×10^{15} cm^{-2}. The samples implanted at 10 and 70 keV with 1×10^{15}-cm^{-2} phosphorus atoms were heated at 300, 400, 500, 600 and 800°C for 1h by a furnace. Heat
treatment was also carried out at 350°C from 15 min to 24 h for samples implanted at 10 and 70 keV with concentrations of $5 \times 10^{14}$, $1 \times 10^{15}$, and $2 \times 10^{15} \text{ cm}^{-2}$. The sheet resistance was measured using a four-point-probe measurement system.

Optical reflectivity spectra were measured between 250 and 1100 nm by a conventional spectrometer. The optical reflectivity spectra were analyzed by a numerical calculation program, which was constructed with the optical interference effect for a structure of air/seven Si layers/Si-substrate [3]. The optical reflectivity at the sample surface depends on the complex refractive indexes of Si. Using the effective dielectric model, the complex refractive index $\tilde{n}$, with a crystalline volume ratio, $X$, was determined by combination of the crystalline refractive index $\tilde{n}_c$ with amorphous refractive index $\tilde{n}_a$ [4] as, $\tilde{n} = X \tilde{n}_c + (1 - X) \tilde{n}_a$ (1). The values of the parameters of thickness and the crystalline volume ratio were changed for each seven doped layer for calculation of the reflectivity. Most possible in-depth distribution of the crystalline volume ratio was obtained by fitting calculated reflectivity spectra to the experimental ones.

Results and discussion

Figure 1 shows the sheet resistance as a function of the heating temperature of samples implanted at 10 and 70 keV with $1 \times 10^{15} \text{ cm}^{-2}$ phosphorus atoms. The figure 1 also represents the sheet resistance for samples as implanted and laser annealed using 940-nm semiconductor laser at 70 kW/cm² for 2.6 ms by arrows. We believe the samples were completely activated by the semiconductor laser annealing [5]. The sheet resistance decreased as the heating temperature increased for samples implanted at 10 and 70 keV. It decreased to 135 $\Omega$/sq at a heating temperature above 500°C, which was the same of that annealed by the semiconductor laser for samples implanted at 10 keV. On the other hand, it decreased to 80 $\Omega$/sq at a heating temperature of 800°C, which was higher than 70 $\Omega$/sq obtained by semiconductor laser annealing for samples implanted at 70 keV. The high sheet resistance of 80 $\Omega$/sq suggests that the activation ratio was lower than 1 for samples implanted at 70 keV even in the case of 800°C-heat treatment.

We define the ratio of conductance increase $C$ by sheet resistance obtained by laser annealing $R_{\text{laser}}$ divided by that obtained by heat treatment with a furnace $R$ as, $C = R_{\text{laser}} / R$ (2). Figure 2 shows the $C$ value as a function of the heating temperature for samples implanted at 10 keV.
and 70 keV. The C value increased to almost 1 as the heating temperature increased above 500°C for samples implanted at 10 keV. On the other hand, it increased to 0.86 at most when the heating temperature increased to 800°C for samples implanted at 70 keV. The C value for samples implanted at 70 keV was lower than that for samples implanted at 10 keV at every heating temperature.

Figure 3 shows the sheet resistance as a function of the heating duration at 350°C for samples implanted at 10 keV (a) and 70 keV (b) with 5×10¹⁴, 1×10¹⁵ and 2×10¹⁵ cm⁻² phosphorus atoms. The sheet resistance decreased as the heating duration increased for both samples implanted at 10 and 70 keV. It was reduced to 950, 892 and 904 Ω/sq by heat treatment at 350°C for 24h for the sample implanted at 10 keV with 5×10¹⁴, 1×10¹⁵ and 2×10¹⁵ cm⁻², respectively. On the other hand, it was decreased to 2200, 2300 and 1700 Ω/sq at most by heat treatment at 350°C for 24h for the sample implanted at 70 keV with 5×10¹⁴, 1×10¹⁵ and 2×10¹⁵ cm⁻², respectively. Figure 4 shows the C value as a function of the heating duration for samples implanted at 10 keV (a) and 70 keV (b) with different phosphorus concentrations. The C value increased as the heating duration increased. Moreover, the C value was high when phosphorus concentration was low. The highest C value was 0.21 obtained when the sample
implanted at 10 keV with $5 \times 10^{14}$-cm$^{-2}$-phosphorus atoms was heated for 24 h. The $C$ value was 0.11 for sample implanted at 10 keV with $2 \times 10^{15}$-cm$^{-2}$-phosphorus atoms. Samples implanted at 70 keV had $C$ values lower than that for samples implanted 10 keV for every doping concentration. The highest $C$ value was 0.06 for sample implanted at 10 keV with $2 \times 10^{15}$-cm$^{-2}$-phosphorus atoms. It was lower than the lowest value in the case of heat treatment for 24h for sample implanted at 10 keV with $2 \times 10^{15}$-cm$^{-2}$-phosphorus atoms. The results of Fig.4 clearly indicate that the activation ratio of phosphorus atoms was high for low energy implantation.

Figure 5(a) shows optical reflectivity spectra for samples as-implanted at 70 keV with $1 \times 10^{15}$-cm$^{-2}$-phosphorus atoms and heated at 500 and 800oC for 1h. The as-implanted sample had a broad spectrum in the ultraviolet region with no $E_1$ or $E_2$ peak. Its spectrum also had two peaks in the visible and infrared regions. The optical reflectivity spectrum shows that a disordered amorphous surface layer was formed by ion implantation as shown in the inset, and that there was an interference effect induced by the amorphous/crystalline structure in the visible and infrared regions. Heat treatment at 500oC for 1h caused change in the spectrum in the visible and infrared regions. On the other hand, there was no $E_1$ or $E_2$ peak yet. It means that crystallization proceeded from the deep region, but that the surface region was still in the amorphous state. The optical reflectivity spectrum almost the same as single crystalline one was obtained by heat treatment at 800°C for 1h. The disordered amorphous surface region was recrystallized by the treatment. Figure 5(b) shows the crystalline volume ratio as a function of the depth from the top surface, obtained by analysis of optical reflectivity spectra shown in Fig. 5(a). The top 20 nm region was completely amorphized and underlying region were partially amorphized to a depth of 150 nm by the ion implantation at 70 keV with $1 \times 10^{15}$-cm$^{-2}$-phosphorus atoms. Heat treatment at 500°C for 1h caused recrystallization in the partially amorphized region. But the top surface was still in amorphous state. Heat treatment above 600°C caused recrystallization in the ion implantation region including the surface region. We estimated the effective amorphized thickness $A$ obtained by integration of $X$ as a function of depth as,

$$A = \int_0^\infty (1 - X) dx$$

(3), where $x$ is the depth. Figure 6 shows the $A$ values as a function of the heating temperature applied to samples implanted at 10 and 70 keV with $1 \times 10^{15}$-cm$^{-2}$-phosphorus atoms. The $A$ value was 26 nm for as implanted at 10 keV. It decreased to zero as the temperature for heat treatment increased above 500°C. On the other hand, the $A$ value was large of 110 nm for as implanted at 70 keV. It decreased to zero as the temperature for heat treatment increased above 600°C. The recrystallization ratio $R_e$ was defined as

$$R_e = 1 - A / A_{as implanted}$$

where $A_{as implanted}$ is the effective amorphized thickness for samples.

Fig. 5 Optical reflectivity spectra for samples as-implanted at 70 keV with $1 \times 10^{15}$-cm$^{-2}$ and heated at 500 and 800°C for 1h (a), and crystalline volume ratio as a function of depth from the top surface, obtained by analysis of optical reflectivity spectra. Inset shown in (a) gives an image of partially crystalline region at surface.
as implanted. Figure 7 shows the $R_e$ value as a function of the heating temperature for samples implanted at 10 and 70 keV. The both samples implanted 10 and 70 keV had similar $R_e$ values for the every heating temperature. The $R_e$ value increased to 1 when the heating temperature increased above 600°C. This result indicates that the recrystallization proceeded in the similar manner on the heating temperature between samples implanted at 10 and 70 keV. This is contrast to the ratio of conductance increase $C$; the ratio of conductance increase of the samples implanted at 10 keV was higher than that of samples implanted at 70 keV, as shown in Fig. 2. There is a possibility of formation of electrical active defect by high energy ion implantation. The defects would trap carriers and reduce the carrier density. The charged defects would also play a role of scattering sites of carriers.

Figure 8 shows the $A$ value as a function of the heating duration at 350°C applied to samples implanted at 10 and 70 keV. The $A$ values were 24, 27 and 29 nm for samples implanted at 10 keV with concentrations of $5 \times 10^{14}$, $1 \times 10^{15}$, $2 \times 10^{15}$ cm$^{-2}$, respectively. The $A$ values were reduced to 19, 23, and 25 nm, respectively, as the duration of heat treatment increased to 24h. On the other hand, the $A$ values were 114, 110 and 124 nm for samples implanted at 70 keV with concentrations of $5 \times 10^{14}$, $1 \times 10^{15}$, $2 \times 10^{15}$ cm$^{-2}$, respectively. The $A$ values were reduced to 84, 94, and 112 nm, respectively, as the duration of heat treatment increased to 24h. Figure 9 shows the recrystallization ratio $R_e$ as a function of the heating duration at 350°C. The $R_e$ value increased to 0.20 as the duration of heat treatment increased to 24h for samples implanted at 10 keV and 5$ \times 10^{14}$ cm$^{-2}$. It decreased to 0.12 as the phosphorus concentration increased to 2$ \times 10^{15}$ cm$^{-2}$. The $R_e$ value was high of 0.25 in the case of heat treatment for 24h for samples implanted at 70 keV because recrystallization proceeded in the deep region. The $R_e$ value was 0.1 for samples implanted at 70 keV with 2$ \times 10^{15}$-cm$^{-2}$-phosphorus atoms. The recrystallization ratio was comparable between samples implanted at 10 and 70 keV for each phosphorus concentration, as shown in Fig. 9.

The results of Figs. 7 and 9 indicate that disordered amorphous region was recrystallized in the similar manner for ion energies of 10 and 70 keV. The on the other hand, the results of Figs. 2 and 4 shows that the electrical conductance of samples implanted at 10 keV was increased by heat treatment much higher than that of samples implanted at 70 keV. Substantial densities of electrically active defects would be formed by high energy ion implantation. The defects would reduce the carrier density and also play a role of scattering sites.
Summary

Activation of silicon implanted with phosphorus atoms was investigated. Phosphorus implantation was carried out at 10 and 70 keV with concentrations 5×10^{14}, 1×10^{15} and 2×10^{15} cm^{-2} to P-type single crystalline silicon. The sheet resistance decreased to 135 and 80 Ω/sq when samples implanted at 10 and 70 keV with a concentration of 1×10^{15} cm^{-2} were heated to 800°C for 1 h. The ratio of conductance increase C was estimated by comparing the sheet resistances with that obtained by laser annealing. The C value for samples implanted at 10 keV was higher than that for samples implanted at 70 keV at every annealing temperature from 300 to 800°C. On the other hand, the recrystallization ratio was similar for the both samples implanted at 10 and 70 keV. It was reached to 1 by furnace annealing at temperature above 600°C for 1 h. The C value also increased as the heating duration increased to 24h for heat treatment at 350°C. It was 0.21 for samples implanted at 10 keV with a concentration of 5×10^{14} cm^{-2}. It decreased to 0.11 as the doping concentration increased to 2×10^{15} cm^{-2}. On the other hand, the C value was 0.06 at most when samples implanted at 70 keV with 5×10^{14} cm^{-2} were heated at 350°C for 24h. It decreased to 0.02 as the doping concentration increased to 2×10^{15} cm^{-2}. The recrystallization ratio Re increased to 0.20 as the heating duration increased to 24h for samples implanted at 10 keV with 5×10^{14} cm^{-2}. It also increased to 0.25 for samples implanted at 70 keV with 5×10^{14} cm^{-2}. The recrystallization ratio did not depend on the implantation energy. However, substantial densities of electrically active defects would be formed by high energy ion implantation. The defects would reduce the carrier density and also play a role of scattering sites.

REFERENCES