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# Activation of boron and phosphorus atoms implanted in polycrystalline silicon films at low temperatures

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**Abstract**

Phosphorus atoms implanted in laser crystallized polycrystalline silicon films were activated by a heat treatment in air at 260 °C for 1, 3 and 24 h. Analysis of ultraviolet reflectivity of phosphorus-doped silicon films implanted by ion doping method at 4 keV revealed that the thickness of the top disordered layer formed by ion bombardment was 6 nm. It is reduced to 4 nm by a 3 h heat treatment at 260 °C by recrystallization of disordered region. The electrical conductance of silicon films implanted increased to $1.7\times10^5$ S/sq after 3 h heat treatment.


*Keywords:* Ion doping; Impurity activation; Low temperature

## 1. Introduction

The formation of polycrystalline silicon films on cheep substrates such as glass has been important for device application such as thin film transistors (TFTs) and solar cells. Many technologies have been reported for the formation of polycrystalline silicon films at low processing temperature [1–10]. Usually, the silicon films doped by ion doping need be annealed at high temperature above 300 °C for the activation of impurity atoms and for recrystallizing the disordered amorphous region formed by ion bombardment. It is important for TFT fabrication at low temperature to activate impurity atoms in order to form source and drain regions in such crystallized silicon films.

In this paper, we report the development of dopant activation and carrier generation when polycrystalline silicon films implanted with phosphorus atoms are heated at 260 °C in air.

## 2. Experimental

50-nm-thick nondoped amorphous silicon films are deposited on glass substrates by plasma enhanced chemical vapor deposition. These films are crystallized at room temperature in vacuum of $\sim3\times10^{-6}$ Torr by irradiation with a pulsed XeCl excimer laser (pulse width of 30 ns, energy density of 380 mJ/cm$^2$). Phosphorus atoms are then implanted into these laser-crystallized silicon films at room temperature at 10 keV and 4 keV. The phosphorus concentration is $1.0\times10^{14}$ cm$^{-2}$ by ion doping. The samples are then treated in air for 1, 3 and 24 h at 260 °C.

After the heat treatment, the crystalline volume ratio to the whole at the region 10-nm deep from the surface is estimated from the analysis of the optical reflectivity spectra in the ultraviolet region. For the estimation of the crystalline volume ratio, we use the peak at around 276 nm ($E_2$ peak), which is caused by the large joint density of states at the X point in the Brillouin zone of crystalline silicon, while there is no peak for amorphous silicon. Raman scattering spectra are also used in order to investigate the crystalline properties. A laser with wavelength of 514.5 nm is used; the spot measures 0.75 μm in diameters. The electrical conductivity is also measured with Al gap electrodes formed by thermal evaporation.

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## 3. Results and discussion

The crystalline volume ratio can be estimated from the optical reflectivity spectra in the ultraviolet region. We used a numerical calculation program with Fresnel coefficients including interference effect of silicon films on glass substrate. We calculated the crystalline fraction $x$ assuming the reflectivity $r$ to be $r=xr_c+(1-x)r_a$, where $r_c$ is the reflectivity of crystalline Si and $r_a$ the reflectivity of amorphous Si. The crystalline volume ratio was $x$=0.93 for as laser-crystallized silicon films. Fig. 1a shows the reflectivity spectra in UV range taken from silicon films implanted at 4 (Fig. 1a) and 10 keV (Fig. 1b). Thick lines presented the experimental spectra, the fine lines the calculated data. The analysis of the spectra reveals that the sample structure of as-implanted films changes to a double layer consisting of a 6-nm-thick disordered top layer and a 42-nm-thick bottom poly-Si layer as shown in Fig. 1a. After annealing for 3 h, the structure is changed to 4-nm-thick disordered top layer and a 44-nm-thick bottom poly-Si layer. The recrystallization occurred therefore in 2 nm. Since the top disordered layer is very thin because of the low implantation energy, ultraviolet (UV) light can therefore reach the crystalline layer. We can therefore obtain the information about the crystalline properties of the top disordered layer as well as of the bottom crystalline layer and analyze the UV reflectivity spectra using simulation. The crystalline volume ratios for such a double layer $x$ is estimated by analysis of the reflectivity. The analysis results are shown in Table 1. The crystalline ratio $x$ of as-implanted films were $x$=0.3 and $x$=0.9 for the top disordered and the bottom crystalline layer, respectively. After 3 h annealing, the values changed to $x$=0.4 (top disordered layer) and $x$=0.9 (bottom crystalline layer). The decrease of the volume and the increase of the crystalline volume ratio $x$ of top disordered layer occurs because the recrystallization occurs from the bottom crystalline layer acting as a crystalline seed. On the other hand, in the case of 10 keV shown in Fig. 1b, the as-implanted sample structure is a double layered structure consisting of a 19-nm-thick disordered top layer and a 30-nm-thick bottom poly-Si layer, because phosphorus atoms were concentrated within 20 nm from the surface as determined by secondary ion mass spectrometry (SIMS). The crystalline phase in the volume within 20 nm from the surface is destroyed by the ion bombardment. After annealing, the sample structure is changed to 16-nm-thick disordered top layer and a 32-nm-thick bottom poly-Si layer. In the 10 keV case, a 3-nm disordered layer was recrystallized by 3 h annealing. The crystalline volume ratio of as-implanted at 10 keV was very low and is $x$=0.14. The crystalline volume ratio increased to $x$=0.35 after heat treatment in air at 260 °C for 3 h.

Table 1
Crystalline volume ratio $x$ of as-implanted and annealed silicon films

| Implanted energy (keV) | | $x$ before anneal | $x$ after anneal |
|---|---|---|---|
| 4 | bottom layer | 0.9 | 0.9 |
| | top layer | 0.3 | 0.4 |
| 10 | | 0.14 | 0.35 |

Phosphorus atoms were implanted at 4 and 20 keV.

Fig. 2 shows the electrical conductance of silicon films phosphorus implanted at 4 keV and 10 keV with $1.0\times10^{14}$ cm$^{-2}$ as a function of the duration of heating treatments in air. The electrical conductance of the as-implanted films is very low, and about $10^{-9}$ S/sq, for both implantation energies of 4 keV and 10 keV. Such a value means that the implanted phosphorus atoms are not activated and the carrier density in very low. After heat treatment at 260 °C for 1 h, the electrical conductance is markedly increased to $1.7\times10^{-5}$ S/sq. The electrical conductance increased further to $5.4\times10^{-5}$ S/sq after 24 h treatment. A high density of phosphorus atoms existed at the top layer, because

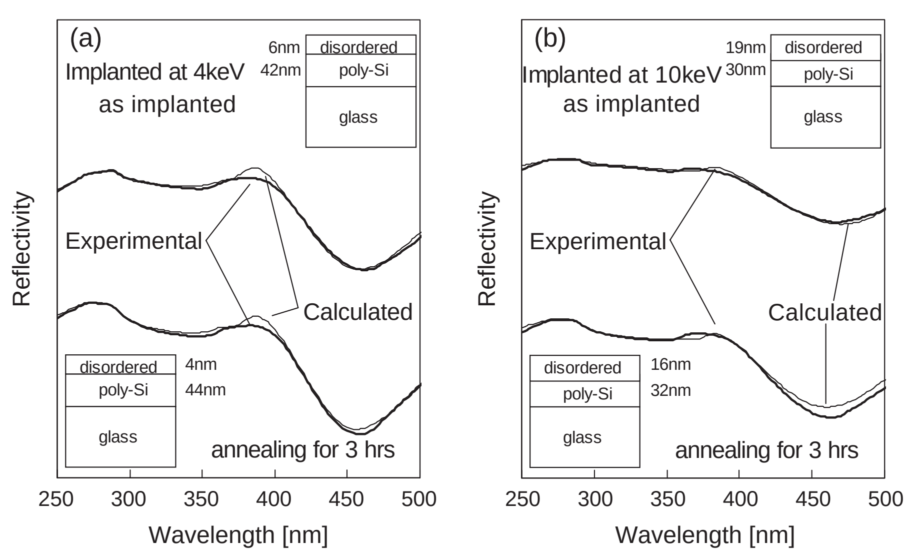


Fig. 1. Optical reflectivity spectra of ultra violet region of samples for as-implanted sample and after annealing for 3 h. (a) An energy for ion implantation is 4 keV; (b) an energy for ion implantation is 10 keV. Calculated spectra are also shown.

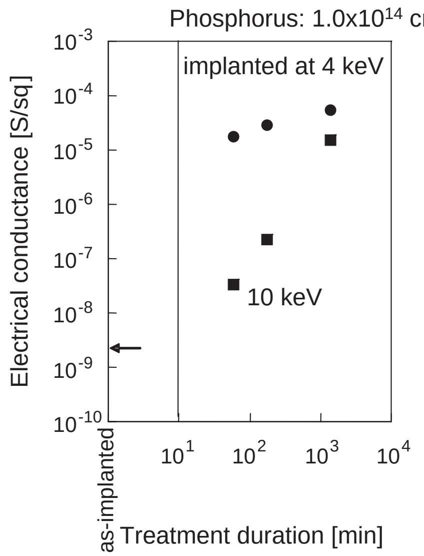


Fig. 2. Electrical conductance of phosphorus-doped silicon films implanted at 4 keV (solid circle) and 10 keV (solid square).

phosphorus atoms of $1.0\times10^{14}$ $cm^{-2}$ were implanted to very shallow region from the surface. The activated phosphorus density in the recrystallized layer in the case of 4 keV was very high. Moreover, the carrier density would be much larger than the defect density in the recrystallization layer. The effective carrier density was high; the electrical conductance also would be high. On the other hand, the electrical conductance of silicon films implanted at 10 keV increased to $3.2\times10^{-8}$ and $2.2\times10^{-7}$ S/sq after heat treatments for 1 h and 3 h, respectively. The activation of the impurity atoms occurs at the recrystallized region. However, the density of the dopant atoms per unit volume at the recrystallized layer is low because the phosphorus atom density per unit volume is low due to large volume implantation of phosphorus atoms. In addition, defect states exist in the silicon films and the trapped carrier density in the recrystallization layer is high. The effective carrier density thus is low, as is the electrical conductance compared with the case of 4 keV implantation. The electrical conductance of silicon films implanted at 10 keV, however, increased to $1.5\times10^{-5}$ S/sq after 24 h heat treatment. Similarly, the conductance for the 4 keV sample after 1 h treatment increased to $1.7\times10^{5}$ S/sq. Long duration annealing resulted in a high electrical conductance of silicon films implanted at 10 keV.

## 4. Conclusions

We report on the activation behavior of phosphorus atoms in laser crystallized silicon films. An areal density of $1.0\times10^{14}$ $cm^{-2}$ phosphorus atoms were implanted by an ion doping method into laser crystallized silicon films. Heat treatment in air for 3 h was carried out to recrystallize the disordered layer formed by ion bombardment and to activate phosphorus atoms. The analysis of UV reflectivity spectra yields a thickness of 6 nm for the formed disordered top silicon layer after ion doping, which is reduced to 4 nm after 3 h heat treatment. The electrical conductance in 4 keV films increases from $\sim10^{-10}$ S/sq to $5.4\times10^{-5}$ S/sq by a 24 h treatment.

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