The Behavior of Arsenic in Silicon during Heat-treatment

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Compared with other impurities in silicon, arsenic has the highest solid solubility ($1.5 \times 10^{22}$ atoms/cm$^3$). Arsenic is used extensively as a dopant in silicon device technology because of such a merit. However, when arsenic concentration in silicon reaches $10^{10}$ to $10^{21}$ atoms/cm$^3$, arsenic doped silicon crystal is easily annealed with relatively low temperature (500°C), and its carrier concentration considerably changes. Such crystals can not be effectively used for silicon device fabrication. The second merit of using arsenic as a dopant is that it is not easy for a lattice strain to occur easily at high concentration. This is because the tetrahedral covalent radius of arsenic (1.18 Å) is nearly equal to that of silicon (1.17 Å).

This paper describes experiment aimed at finding the most effective heat treatment to prepare low-defect or no-defect heavily arsenic doped silicon. In this experiment arsenic is doped by diffusion, epitaxial growth, and melt-grown methods. Annealing effect after doping arsenic was investigated by Hall measurement, resistivity measurement, and X-ray double crystal spectrometer. The results of these measurements are as follows. The configuration of arsenic in silicon after doping is independent of doping method and depends on dopant concentration, because the lattice constant of arsenic doped silicon is smaller than that of silicon. After annealing within several minutes at 600 to 1200°C, arsenic is located in crystals so that the lattice constant of arsenic doped silicon is larger than that of silicon, which is comprehensible from Fig.1. Moreover, the difference of diffraction peaks, $\theta$ p-p, of rocking curves from both arsenic doped layer and substrate increases with increasing annealing time and the half width of the curve increases, as shown in Fig.2. This broadening of rocking curve seems to correspond to a kind of diffuse scattering from the surrounding of Bragg point. Then, arsenic is not in normal lattice site and lattice defects are generated gradually. Such a phenomenon is especially remarkable in heavily arsenic doped crystals. After annealing for a long time of several tens hours, rocking curve becomes broader. Similarly, on melt-grown sample with concentration, $6 \times 10^{10}$ atoms/cm$^3$, the changes of lattice constant were investigated by a bending of bi-crystal, silicon intrinsic layer deposited on this sample, as shown in Fig.3, which is same results with Fig.1. But under low temperature (850°C) annealing for an hour, the change of a bending of bi-crystal from convex to concave could not be found out. On the other hand the conductivity after annealing decreases in diffusion sample with $5 \times 10^{20}$ atoms/cm$^3$ but increases in melt-grown sample with $6 \times 10^{10}$ atoms/cm$^3$. These results are shown in Fig.4. Hall mobility decreases with increasing arsenic concentration after doping, and the mobility after annealing doesn't remark-
ably change in diffusion sample but decreases in melt-grown sample. From above results it is considered that configuration of arsenic atom in silicon depends on arsenic concentration in crystals after doping. That is, after annealing in the diffusion sample, heavily arsenic doped, carrier concentration decreases, and in the melt-grown sample, lightly arsenic doped, carrier concentration increases. But the correlation between all data and changes of lattice constant cannot be necessarily explained.

![Graph showing diffraction intensity with labels: Unanneal, Anneal at 700°C for 20 min and 2 hrs.](image)

\[ \Delta \theta \quad \text{sec. of arc} \]

**Fig. 1** The change of rocking curve by annealing.

**Fig. 2** $\theta$-p vs. annealing time at 700°C.

**Fig. 3** The change of curvature by annealing.

**Fig. 4** Annealing effect of Hall data in As doped Si crystals.