A New Technique for Low Concentration Diffusion of Boron into Silicon

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The commonly employed method for the low concentration diffusion of boron into silicon from a doped-oxide source has a difficulty in reproducibility of the result, which strongly depends on the low level source deposition. To obtain a surface concentration of $10^{16}$ cm$^{-3}$, for instance, the B$_2$O$_3$ source in the CVD glass film should be doped to such a low concentration as 0.01 mole %. Moreover, some redistribution of boron in silicon due to the out-diffusion does occur during the drive-in step in the oxygen ambient.

The present paper proposes a new technique for doped-oxide diffusion of boron into silicon, which provides a controlled surface concentration over a wide range of $10^{15}$ to $10^{20}$ cm$^{-3}$. The principle is based on our finding that if the deposited boro-silicate film is heat-treated in an NH$_3$ gas ambient prior to the drive-in step the transfer of boron into silicon is greatly suppressed. The effect of the NH$_3$ heat-treatment on the concentration of diffused boron in silicon is well controlled by both the temperature and the time of the heat-treatment. In addition, an undoped SiO$_2$ film overdeposited on the source film functions as a mask against the NH$_3$ ambient so that local diffusions of boron to high and low concentrations can be simultaneously performed from a single source film. Figure 1 schematically shows the new process, where a part of the undoped SiO$_2$ film overdeposited is windowed to exposure the SiO$_2$-B$_2$O$_3$ film to the NH$_3$ ambient.

The doped-oxide films were deposited on n-type silicon wafers of (111) orientation from the vapor phase of SiH$_4$, B$_2$H$_6$, and O$_2$ at a temperature of 400$^\circ$C. The thickness and B$_2$O$_3$ concentration of the film were about 0.1 μm and 1 - 12 mole %, respectively. The NH$_3$ heat-treatment was...
carried out at a temperature between 700 and 1000°C for 30–60 min, and the drive-in step at 1000–1200°C in N₂ was followed. Figure 2 is an experimental result of high and low concentration diffusion of boron into silicon from an NH₃ treated borosilicate glass film which was locally covered with an undoped SiO₂ film as in Fig. 1. The cross-sectional view of the diffused region explicitly reveals the difference in depth and concentration of diffused boron between the covered and uncovered regions. In Fig. 3 is shown the surface concentration of diffused boron in silicon as a function of the concentration of B₂O₃ in the source borosilicate glass for different NH₃ heat-treatments. The NH₃ heat-treatment remarkably suppresses the boron concentration in silicon which can be controlled by the time and temperature of the treatment. For the surface concentrations below $10^{16} \text{ cm}^{-3}$, the source oxide film doped with 1.1 mole % of B₂O₃ were subjected to prolonged high-temperature NH₃ treatments.

The profiles of the diffused boron concentration in silicon, which were observed by the SIMS technique, were found to be in good agreement with the complementary error functions, suggesting no redistribution of boron in silicon due to the out-diffusion during the drive-in step. As is seen in Fig. 3, the dependence of the diffused boron concentration in silicon on the B₂O₃ concentration in the source oxide is weakened by the NH₃ heat-treatment. This fact provides an advantage over the conventional doped-oxide diffusion technique, that fluctuation of the B₂O₃ concentration in the source glass has little effect on the uniformity and reproducibility of the resulting boron concentration in silicon. The transfer of boron through the interface between doped oxide and silicon may be the rate-determining process for the suppressed diffusion in the drive-in step.

The potential application of the new technique for the boron diffusion will be found in the integrated circuit process, especially by the use of simultaneous formation of high and low resistivity regions.