Phosphorus diffusion in isoconcentration backgrounds under inert conditions in silicon

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The diffusivity of phosphorus in isoconcentration backgrounds under inert conditions in silicon is investigated. Phosphorus is implanted at low dose into silicon wafers that are constantly doped with arsenic and boron. These samples are annealed to remove any damage. Secondary ion mass spectroscopy (SIMS) measurements are taken of these as-implanted samples. The wafers are then diffused at both 900 and 1100 °C for 60 and 30 min, respectively. The wafer profiles are then measured using SIMS. The diffusivity of phosphorus is measured for five different dopant concentrations. The results show that a double-negative interstitial component of phosphorus is needed to adequately model the data. Also, the heavily doped boron sample shows a significantly retarded diffusivity at 1100 °C which suggests phosphorus-boron pairing or significant strain effects on diffusion.

Phosphorus diffusion modeling in silicon is a difficult and controversial topic.[1–11] The "kink and tail" effect observed in phosphorus diffusion does not lend itself to simple treatment. Because phosphorus is often used in conjunction with arsenic to form lightly doped drain devices, it is important to understand its diffusion behavior in a heavily doped background concentration. To investigate this behavior, a series of experiments have been carried out to measure the diffusivity of phosphorus in constant doped arsenic and boron wafers.

This study looks at low-dose phosphorus diffusion in isoconcentration backgrounds. Isoconcentration backgrounds are important because the diffusivity of the phosphorus does not depend on the depth into the wafer. This technique was first used to investigate arsenic diffusion by Masters and Fairfield.[12] Given the known anomalies with phosphorus, an isoconcentration study is essential when examining its diffusion. This experiment utilized ten Czochralski wafers with five different doping levels. Six arsenic-doped wafers were used with two of each of the following constant concentrations of arsenic: 3×10^{19}, 1×10^{19}, and 2×10^{14} cm^{-3}. Four boron-doped wafers were used with two of each of the following boron concentrations: 4×10^{20} and 3×10^{19} cm^{-3}. All of the wafers were Czochralski material with $\langle100\rangle$ orientation. A 120 Å oxide was grown on all of the wafers. Phosphorus was then implanted through the oxide at 150 keV energy and 5×10^{13} cm^{-2} dose. The wafers were then annealed at 850 °C for 50 min in nitrogen to anneal out any damage. The wafers were then halved and secondary ion mass spectroscopy (SIMS) measurements were performed with a CAMECA 4F using a 14.5 keV Cs+ beam on one section of the wafers in order to obtain the initial profile before the main diffusion. Five of the sections, each with a different background doping were then diffused at 900 °C for 60 min in nitrogen and five others, each with a different background doping, were diffused at 1100 °C for 30 min in nitrogen. These profiles were then measured with SIMS. Using the initial and the final SIMS profile, the diffusivity of the phosphorus was determined by using the SUPREM IV process simulator.

Figure 1 shows the diffusivity of phosphorus at 900 °C plotted versus n/n_i, where n is the electron concentration and n_i is the intrinsic electron concentration. This plot shows that diffusivity behaves parabolically with concentration which strongly suggests the presence of a double-negative interstitial component in the phosphorus diffusion. Figure 2 shows the diffusivity of phosphorus at 1100 °C plotted versus n/n_i. This plot also suggests a parabolic dependence, but could also be described adequately with a linear relationship. Since at 1100 °C there is a small variation in the value of the electron concentration, it is difficult to distinguish between the parabolic and linear dependence with any confidence. The value of the diffusivity at 1100 °C at the heaviest p-type doping will be discussed later.

A doubly negative defect state was first suggested by Chiu and Ghosh[13] for arsenic diffusion in silicon. Fair[14] first suggested the use of the double-negative component to phosphorus diffusion, as shown in

$$D_{\mathrm{P}} = D^0 + D^-\left(\frac{n}{n_i}\right) + D^{--}\left(\frac{n}{n_i}\right)^2. \tag{1}$$

D_{P} is the diffusivity of phosphorus and D^0, D^-, and D^{--} are the neutral, negative, and double-negative components of its diffusion. The normalized electron concentration is given by n/n_i. The results presented in this study tend to support this conclusion, based on the parabolic nature of the curve, especially at 900 °C.

The best fit, neutral, single-negative, and double-negative interstitial components of phosphorus diffusion, are shown in Table I for both 900 and 1100 °C. These diffusivity components are essentially those reported by Fair, with an enhancement to the double-negative component in order to fit the heavily doped arsenic samples. Fair used the Boltzmann–Matano analysis of heavily doped phosphorus diffusion to extract diffusion values, which is difficult to compare to the isoconcentration measurements due to the nonequilibrium diffusion exhibited by heavily
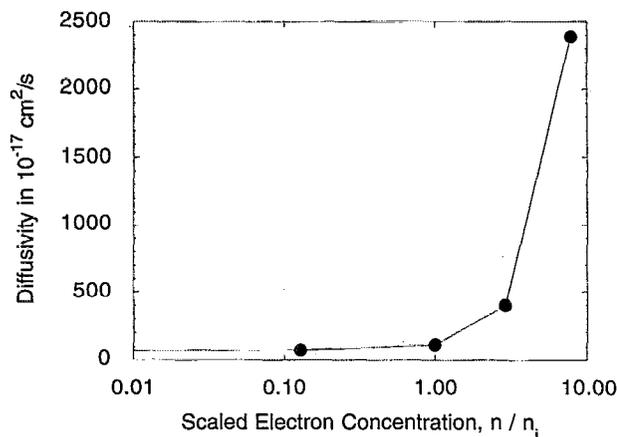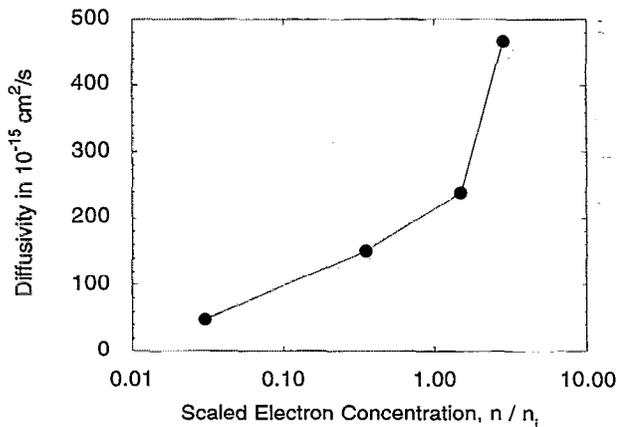
FIG. 1. Phosphorus diffusivity at 900 °C vs the normalized electron concentration in silicon.

TABLE I. Best-fit charged defect diffusivity components.

Component	900 °C $(10^{-17}$ cm^2/s	1100 °C $(10^{-15}$ cm^2/s
Neutral	73.3	143
Negative	2.93	9.31
Double-negative	37.3	36.4

doped phosphorus. The low concentration value of the diffusivity were extracted by Fair using lightly doped samples, and this is why the values agree in this regime. At higher n-type concentrations, however, a large value of the double-negative component was required to fit the diffusivity.

More interesting, however, is the diffusivity of phosphorus in the 4×10^{20} cm^{-3} boron-doped sample at 1100 °C. The reported diffusivity cannot be explained with Eq. (1), since the value is approximately 1/3 of the value found with a 3×10^{19} cm^{-3} boron doping. For heavy p-type backgrounds, the doping should be constant. This same effect has also been reported by Fahey.[15] There are two possible explanations for the phenomena. First, the phosphorus could be pairing with the background boron, which could retard the diffusion of the phosphorus.[16] The

second explanation is that the large boron concentration strains the crystal and effectively reduces the lattice constant.[17] This would reduce the number of interstitials and thereby the diffusivity of the phosphorus. Further investigations are necessary to clarify this phenomena.

The data presented here give support for the double-negative component of phosphorus diffusion. Plots of diffusivity versus electron concentration show a definite parabolic dependence at 900 °C and a possible one at 1100 °C. The diffusivity components that best fit the given experimental data are identical to Fair's except that a higher double-negative component is needed to explain the diffusion in the heavily doped arsenic wafers. A significantly smaller diffusivity is reported at 1100 °C in the 4×10^{20} cm^{-3} boron-doped wafers than explained by current models. These phenomena could be explained due to either phosphorus-boron pairing or strain effects due to the heavy boron doping.

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FIG. 2. Phosphorus diffusivity at 1100 °C vs the normalized electron concentration in silicon.