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Accurate Determination of the Intrinsic Diffusivities of Boron, Phosphorus, and Arsenic in Silicon: The Influence of SiO_2 Films

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Accurate determination of the intrinsic diffusivities of boron (B), phosphorus (P), and arsenic (As) in silicon (Si) is reported. We show that the differences in the B, P, and As diffusivities reported in the previous works arise from whether SiO_2 films existed on the Si sample surfaces. Impurity diffusion near the Si surface without SiO_2 is affected by oxidation of Si even in the nominally inert atmosphere, which has unavoidable residual oxygen background due to the open furnace. On the other hand, a surface SiO_2 film of ~20 nm thickness prepared before the diffusion annealing is sufficient to block further oxidation of Si, i.e., truly intrinsic diffusivities of impurities have been obtained from samples having surface oxide layers.
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KEYWORDS: boron, phosphorus, arsenic, diffusion, silicon, SiO_2 films, secondary ion mass spectrometry

1. Introduction

Fundamental understanding of the impurity diffusion in Si is crucial for accurate modeling of the ultra-shallow junction formation in the next generation process simulators.[1] Modeling of the time-dependent processes, e.g., transient enhanced diffusion (TED), oxidation enhanced diffusion (OED), etc., involves the intrinsic diffusivities as the most important reference parameters. Therefore, accurate determination of the intrinsic diffusivities of impurities such as boron (B), phosphorus (P), and arsenic (As) is technologically important for the development of reliable diffusion simulators. However, previously reported values of "intrinsic" diffusivities of B, P, and As in Si do not agree with each other and the origin of this discrepancy has been unknown.[2–6] Much debate has been devoted on the importance of placing the diffusion species away from the Si surface, e.g., new "intrinsic" diffusivities of B were reported by monitoring the diffusion of buried B layers recently[3] whose values were different from those established for more than 30 years.[2] However, we find that those different diffusivities of B, P, and As can be separated clearly into two groups depending on the existence of the surface SiO_2 layers regardless of whether diffusion takes place from the surface or from the buried region.

The present work reports the precise measurement of the B, P, and As diffusivities in Si with and without ~20-nm-thick SiO_2 films on the surface. Such thin oxide cannot stress the diffusion region of Si sufficiently to make the experimentally measured diffusivities different. The concentrations of impurities are kept below the intrinsic carrier concentrations at diffusion-annealing temperatures, i.e., diffusion takes place in the intrinsic Si having the Fermi level approximately in the middle of the band gap. The diffusion-annealing atmosphere is flowing gas of 99.999% semiconductor grade argon (Ar). Therefore, diffusivities of the impurities in Si under such intrinsic and inert condition should not differ depending on the existence of such thin layers of SiO_2 on the Si surface. However, our experiment reproduced previously reported experimental results very well; the absolute values of diffusivities of B, P, and As as a function of temperatures were categorized into clearly separated two groups depending on the existence of the SiO_2 films on the sample surface. By inspection, we conclude that the diffusivities of impurities in the samples without surface oxides were affected by the excess Si interstitials generated by the oxidation of the Si surface. Therefore, truly intrinsic diffusivities of B, P, and As have been obtained with the Si samples having ~20 nm of the SiO_2 films.

2. Experimental Procedure

Samples employed in this study have been prepared as follows. $^{11}B^+$, $^{31}P^+$, and $^{75}As^+$ ions were implanted into p-type 12-in. Si(100) wafers of the sheet resistance 10–15 Ω·cm having thermally-grown SiO_2 films of ~20 nm in thickness. All the ions were implanted into the Si bulk region through the surface oxide. Implantation energies were 40, 120, and 180 keV, and doses were 2.0×10^{13}, 2.1×10^{13}, and 1.5×10^{13} cm^{-2}, for B, P, and As, respectively. Each wafer after implantation was annealed at 950 °C for 30 min in order to remove damages that would cause TED.[7–9] Then wafers were cut into 5×10 mm^2 pieces and two groups of samples were prepared from each wafer. One group is so-called "samples with SiO_2" that maintained the ~20 nm surface oxide during the following diffusion annealing. The other group is "sample without SiO_2" whose surface oxides were removed by hydrofluoric acid treatment before the diffusion annealing. The diffusion annealing for both sets of samples took place at 800–1050 °C for 0.25–84 h in a resistively heated furnace. Semiconductors processing grade quartz tube was employed for maintaining the sample as clean as possible. Diffusion annealing was conducted under flowing 99.999% Ar of the flow rate 1.2 l/min. The depth profiles of B, P, and As were determined by secondary ion mass spectrometry (SIMS). Primary ions used in SIMS were $O_2{}^+$ with the acceleration energy 5.5 keV for ^{11}B profiling, and Cs^+ with the energies of 14.5 keV (5 keV) for ^{31}P (^{75}As) profiling. The impurity profiles

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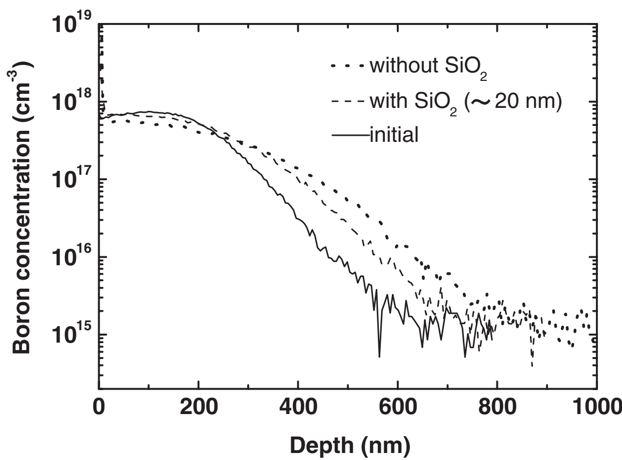

Fig. 1. Boron concentrations as a function of the depth determined by SIMS. The solid curve represents the initial profile before diffusion annealing but after 950 °C for 30 min annealing to complete TED. Dashed and dotted curves are boron profiles in samples with and without SiO_2 films, respectively, after diffusion annealing at 900 °C for 12 h. The profile in the sample with SiO_2 is shifted by −20 nm, the thickness of SiO_2 film.

determined by SIMS after the 950 °C annealing to complete TED were taken as the initial profiles for our diffusion experiments. In order to obtain the diffusivity for a given temperature, the initial profile was broadened using single diffusivity as a fitting parameter until the broadened profile matched with the experimentally obtained SIMS profile after annealing.

3. Results and Discussion

Figure 1 shows the SIMS depth profiles of ^{11}B before and after diffusion annealing at 900 °C for 12 h. The diffusion in the "sample without SiO_2" was larger than that in the "sample with SiO_2". This tendency was consistently observed for different diffusion temperatures and also for P diffusion. Figures 2 and 3 show the B and P diffusivities as a function of temperature, respectively. Different diffusivities were obtained between "samples with SiO_2" and "samples without SiO_2" for both B and P diffusion in Si. For "samples without SiO_2", we found the growth of SiO_2 of ~3 nm thickness after the annealing. This growth is attributable to very small amount of oxygen that existed in the "inert" atmosphere in spite of our best effort to avoid leaking oxygen into the furnace by flowing ultra-pure Ar gas continuously. We considered that this entered oxygen grow the SiO_2 film on the Si surface. Then, Si interstitials were emitted from SiO_2/Si interface into Si substrate. The emitted Si interstitials enhance B diffusion, which is well-known as OED.[10–12] In other words, OED of B and P was observed in the "samples without SiO_2". On the other hand, the thickness of SiO_2 films was not changed after diffusion annealing of the "samples with SiO_2". The SiO_2 films clearly prevented oxygen from reaching the SiO_2/Si interface and therefore OED was avoided successfully. Thus, truly intrinsic diffusivities are obtained from the "samples with SiO_2" and they are represented by

$$D_B = (9.07^{+28.9}_{-7.07}) \times 10^{-2} \exp\left[-\frac{(3.23 \pm 0.15)\,\text{eV}}{kT}\right] \text{cm}^2/\text{s} \quad (1)$$

for B diffusivities D_B in Si and

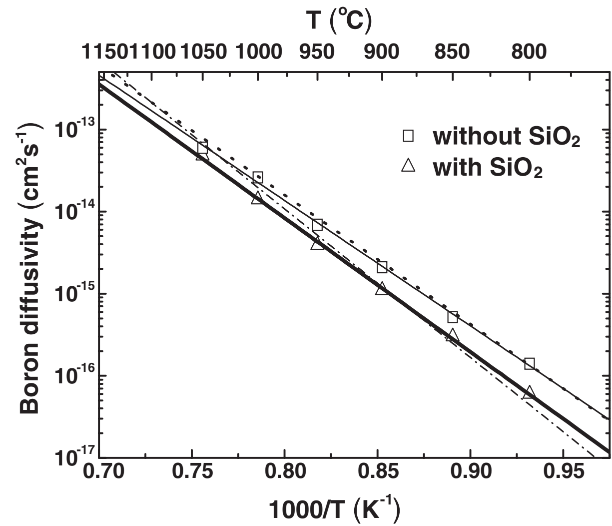

Fig. 2. Temperature dependence of B diffusivities in samples with (open triangle) and without (open square) SiO_2 films. The bold and thin solid lines show Arrhenius fitting to the data. The previously reported data in ref. 2 (dashed line) and in ref. 3 (dotted line) are shown for comparison.

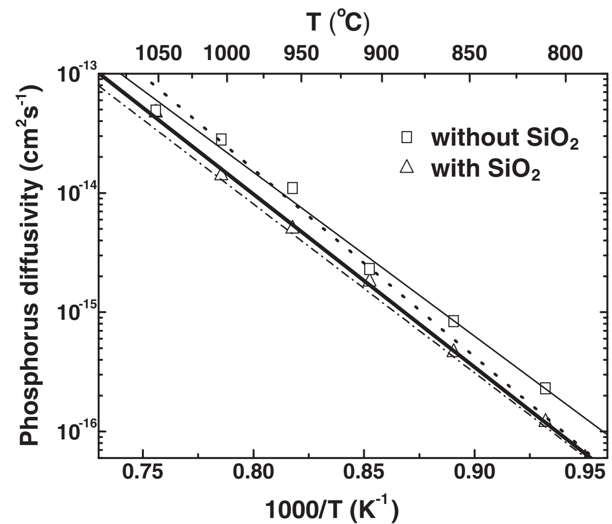

Fig. 3. Temperature dependence of P diffusivities in samples with (open triangle) and without (open square) SiO_2 films. The bold and thin solid lines show Arrhenius fitting to the data. The dotted and dashed lines are after refs. 3 and 4, respectively, for comparison.

$$D_P = (3.86^{+12.1}_{-2.74}) \times 10^{-3} \exp\left[-\frac{(2.88 \pm 0.15)\,\text{eV}}{kT}\right] \text{cm}^2/\text{s} \quad (2)$$

for P diffusivities D_P in Si.

In order to emphasize the importance of our experimental results, we show in Figs. 2 and 3 the diffusivities reported in the previous works.[2–4] In ref. 4, the sample surface was covered with thermally-grown oxide and their P diffusivities are practically the same with our data with the "samples with SiO_2". The diffusivities of ref. 3, where the samples are presumed to have no oxide at the surface, are comparable with our results with the "samples without SiO_2". Therefore, our results are fully consistent with the previously published data and explain the origin of the discrepancies between two groups of data sets.

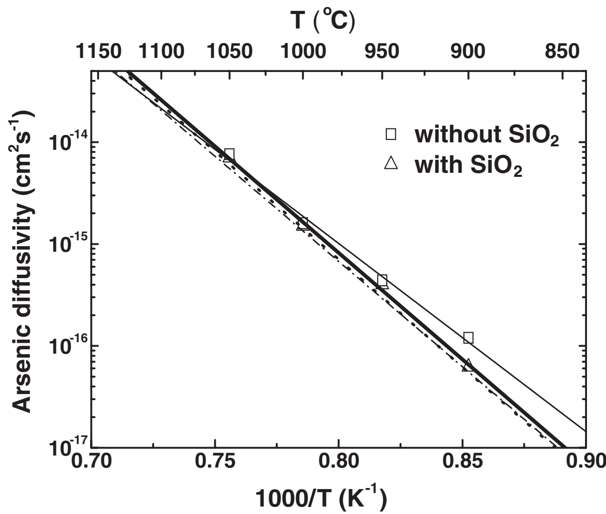

Fig. 4. Temperature dependence of As diffusivities in samples with (open triangle) and without (open square) SiO_2 films. The bold and thin solid lines show Arrhenius fitting to the data. The dotted and dashed lines are after refs. 5 and 6, respectively, for comparison.

To complete the picture, we show the As diffusivity as a function of temperature in Fig. 4. As expected, much smaller difference between the diffusivities of "samples with SiO_2" and "samples without SiO_2" was observed, because As diffusion in Si occurs not only via Si self interstitials but also via vacancies with comparable contribution.[13–15] Therefore, As diffusion in Si is less affected by OED compared to B and P diffusion in Si. Nevertheless, the diffusivities of the "samples without SiO_2" are larger than those of the "samples with SiO_2". Therefore, we determined the intrinsic As diffusivities in Si from the "samples with SiO_2" as

$$D_{\mathrm{As}} = (44.0^{+656}_{-41.4})\exp\left[-\frac{(4.15 \pm 0.30)\,\mathrm{eV}}{kT}\right]\mathrm{cm^2/s}. \quad (3)$$

As can be seen in Figs. 2–4, the difference of the diffusivities between the samples with and without SiO_2 became larger with decreasing temperatures. This tendency was observed for all the impurities, B, P, and As, and is explained by the following reason. The ratio between the concentration of Si interstitials generated via oxidation and that in thermal equilibrium is larger at lower temperatures and hence the diffusion enhancement by the oxidation, which is described by the ratio, becomes larger.[16] Therefore, the diffusion enhancement observed in "samples without SiO_2" becomes larger at lower temperatures. This difference between the two samples is smaller in As diffusion, to which both Si interstitials and vacancies contribute, and little difference was observed at higher temperatures.

4. Conclusions

The intrinsic diffusivities of B, P, and As in Si have been determined precisely. The present work shows clearly that the large "intrinsic" diffusivities previously reported for samples without surface oxide layers were in fact affected by OED. On the other hand, a surface SiO_2 films of ~20 nm thickness prepared before the diffusion annealing block further oxidation of Si successfully. Therefore, reliable intrinsic diffusivities of impurities have been obtained from samples having surface oxide layers.

Acknowledgments

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