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Boron-enhanced diffusion of boron from ultralow-energy boron implantation.

A. Agarwal, D. J. Eaglesham, H.-J. Gossmann, L. Pelaz, S. B. Herner, D. C. Jacobson
Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey, 07974

T. E. Haynes
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Yu. E. Erokhin
Eaton Corporation, 55 Cherry Hill Drive, Beverly, Massachusetts 01915

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BORON-ENHANCED-DIFFUSION OF BORON FROM ULTRA-LOW-ENERGY BORON IMPLANTATION

Aditya Agarwal*[1,2], D. J. Eaglesham[1], H.-J. Gossmann[1], L. Pelaz[1], S. B. Herner[1],
D. C. Jacobson[1], T. E. Haynes[2], and Yu. E. Erokhin[3]

[1]Bell Laboratories, Lucent Technologies, Murray Hill NJ 07974
[2]Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[3]Eaton Corporation, 108 Cherry Hill Drive, Beverly MA 01915

*Present address: Eaton Corporation, 55 Cherry Hill Drive, Beverly MA 01915;
E-mail: aagarwal@bev.etn.com

We have investigated the diffusion enhancement mechanism of BED (boron-enhanced-diffusion), wherein the boron diffusivity is enhanced three to four times over the equilibrium diffusivity at 1050°C in the proximity of a silicon layer containing a high boron concentration. It is shown that BED is associated with the formation of a fine-grain polycrystalline silicon boride phase within an initially amorphous Si layer having a high B concentration. For 0.5 keV B^+, the threshold implantation dose which leads to BED lies between 3×10^{14} and of 1×10^{15} cm^{-2}. Formation of the shallowest possible junctions by 0.5 keV B^+ requires that the implant dose be kept lower than this threshold.

INTRODUCTION

It is currently projected that 0.07 μm technology will require junction depths, x_j, ≈ 30 nm (1). This places severe restrictions on the amount of enhanced diffusion which can be tolerated if dopants are to be introduced by ion implantation. We recently demonstrated that transient enhanced diffusion (TED) of B marker layers from Si$^+$ implants is virtually eliminated at ultra-low-energies (ULE) of 1 keV or less (2). This reduction is both expected and easily understood if the surface is considered to be a sink for interstitials. In that case, the closer the implantation-induced excess interstitials are located to the surface the fewer hops they will make before reaching the surface and being annihilated (2). Since boron diffusion is mediated by interstitials, the diffusivity enhancement is proportional to the total number of interstitial hops during annealing and thus decreases as well (2). The initial assumption that the surface is a perfect sink has

also been verified by comparing experimental data with Monte-Carlo and continuum simulations for different surface-sink conditions (2).

In the case of B^+ implants however, enhanced diffusion is observed at energies as low as 0.5 keV (3). This diffusion enhancement, which is in addition to the standard concentration dependence (4), is observed even from evaporated B layers and has been called BED, or *boron-enhanced*-diffusion (3). In this paper, we further investigate the BED phenomenon. We demonstrate that BED is driven by interstitials produced during annealing of the boron-containing silicon layer when the boron dose exceeds a threshold that corresponds to both amorphization during implantation and silicon boride phase formation during annealing. We also discuss the limit on ULE B^+ implant doses which is implied by these findings.

EXPERIMENTAL AND RESULTS

Enhanced diffusion has been quantified using the method of embedded B marker layers
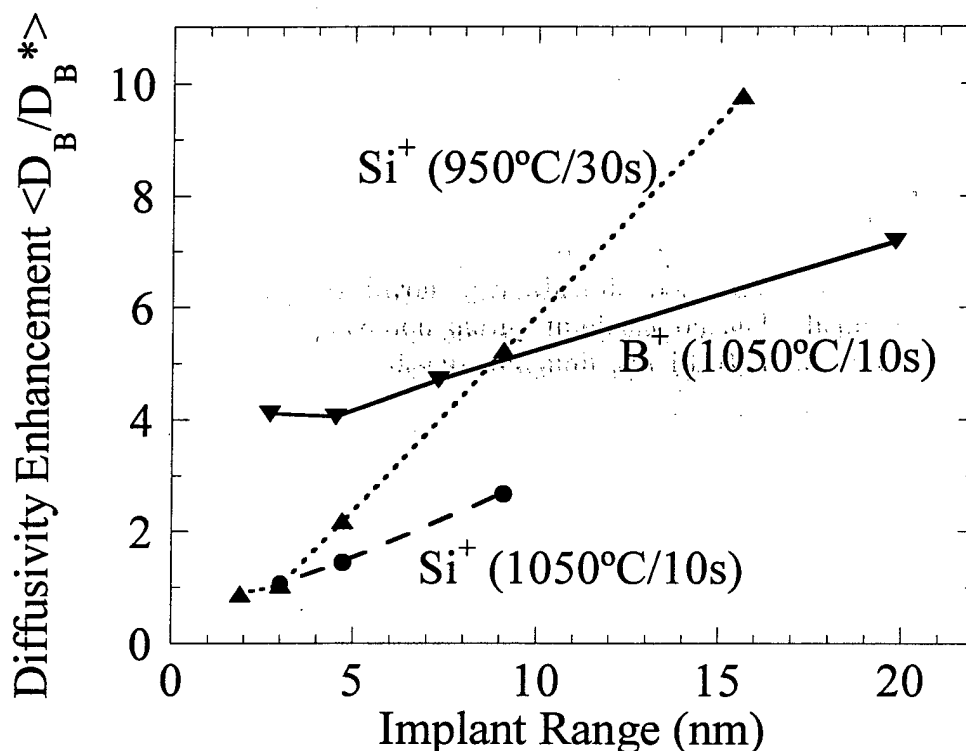

Figure 1. Summary of diffusivity enhancement data for ULE Si^+ and B^+ implants from References 1 and 2, respectively. The Si^+ dose of $10^{14}/cm^2$ was implanted at 0.5, 1, 2, 5 or 10 keV for 950°C/30s annealing, or at 1, 2, and 5 keV for 1050°C/10s annealing; The B^+ dose of $10^{15}/cm^2$ was implanted at 0.5, 1, 2, and 5 for 1050°C/10s annealing.
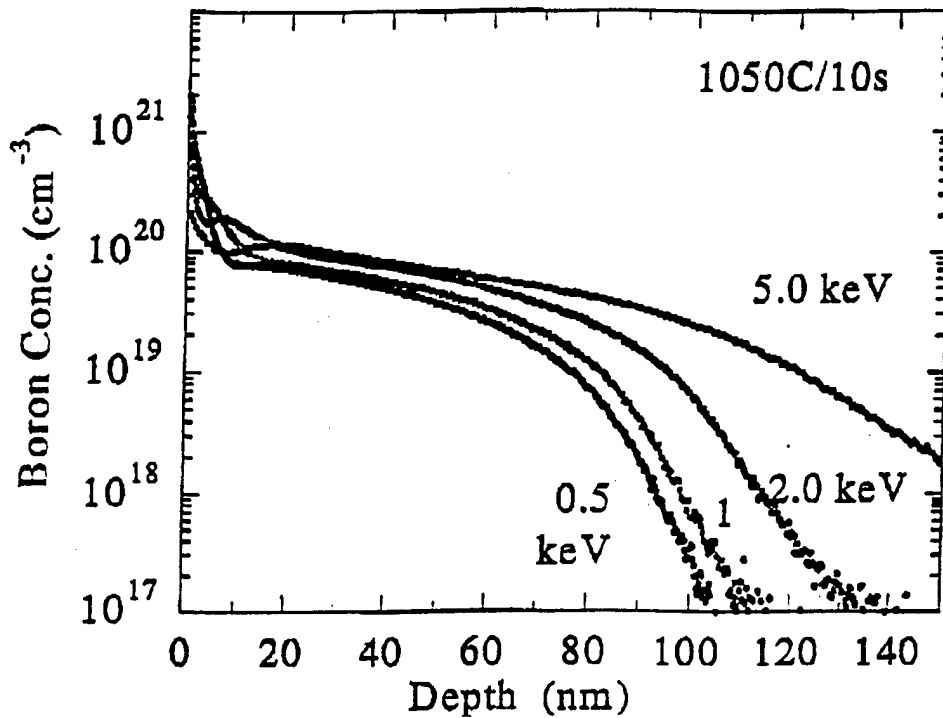
Figure 2. SIMS profiles comparing diffusion of 1×10^{15} cm^{-2} B implanted at 5, 2, 1, and 0.5 keV at from 1050°C/10 s annealing (After Ref.3).

grown by molecular-beam-epitaxy (MBE) (5). In this way the detecting marker is spatially separated from the source of interstitials allowing the diffusivity enhancement and hence the interstitial supersaturation to be quantified unambiguously. The diffusivity enhancement is defined as the time averaged ratio of the observed boron diffusivity, D_B, to the thermal equilibrium diffusivity, D_B^*. A value of 1× means no enhancement. Furthermore, since B diffusion in silicon is mediated by interstitials, the value of D_B/D_B^* also gives the supersaturation ratio of the interstitial concentration relative to its equilibrium value. A value greater than 1 implies interstitial injection.

Figure 1 illustrates the reduction in TED at 950 and 1050°C which accompanies a reduction in the implantation energy down to 0.5 keV for a fixed Si$^+$ dose of 1×10^{14} cm^{-2}. Each data point corresponds to the diffusivity enhancement measured at a buried marker located 150 nm below the surface during annealing following Si$^+$ implantation at energies ranging from 10 to 0.5 keV (2). The data has intentionally been plotted as a function of the projected ion range corresponding to the implantation energy to illustrate the linear dependence of diffusivity enhancement on the distance of the implantation-induced excess interstitials to the surface. From a simple random walk argument the total number of hops made by an interstitial before arriving at the surface is a quadratic function of its initial distance from the surface. Under conditions of perfect
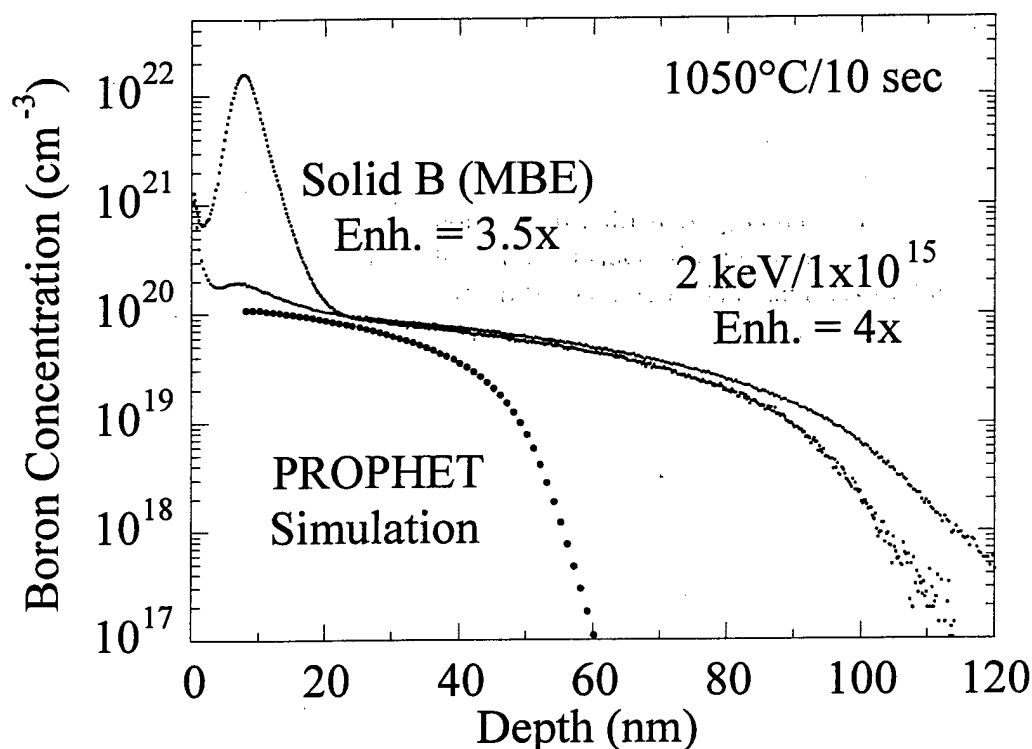
Figure 3.   SIMS profiles comparing diffusion from an evaporated pure-B layer (capped with 10 nm of amorphous Si) with that from a 1×10^{15} cm^{-2}, 2 keV B^{+} implant, after 1050°C/10 s annealing. Also shown for comparison is a simulated diffusion profile which assumes only the standard concentration-dependent diffusivity.

recombination at the surface (every interstitial is annihilated the very first time it reaches the surface), the diffusivity enhancement, related to the number of interstitial hops per lattice site, is then expected to have a linear dependence on R_I. Such a linear dependence is observed both 950 and 1050°C (2).

Figure 1 also shows diffusivity enhancements extracted from the profiles shown in Fig. 2 for a fixed B^{+} dose of 1×10^{15} cm^{-2}, implanted at 5, 2, 1, and 0.5 keV, and annealed at 1050°C for 10 s. In contrast to the reduction in enhancement to 1× observed for ULE Si^{+}, a saturation in the reduction of diffusivity enhancement at 4× is seen for B^{+} implanted at 1 and 0.5 keV (Fig.1). Extrapolation of this trend predicts that enhanced diffusion would be observed even if the implantation energy was reduced to a few eV! To establish that the trend exhibited by the B^{+} data can be extrapolated to extremely low energies, we tested for a diffusivity enhancement from an evaporated surface B layer. Evaporated B represents the ultimate limit of ULE implantation since the B atoms arrive at the surface with energies of the order of ≈0.0001 keV, insufficient for Frenkel-pair defect generation. Figure 3 compares diffusion from an evaporated B layer and from the 1×10^{15} cm^{-2}, 2 keV B^{+}-implanted layer shown in Fig.2. The junction depth in the two samples is surprisingly similar even though the evaporated-B sample does not contain
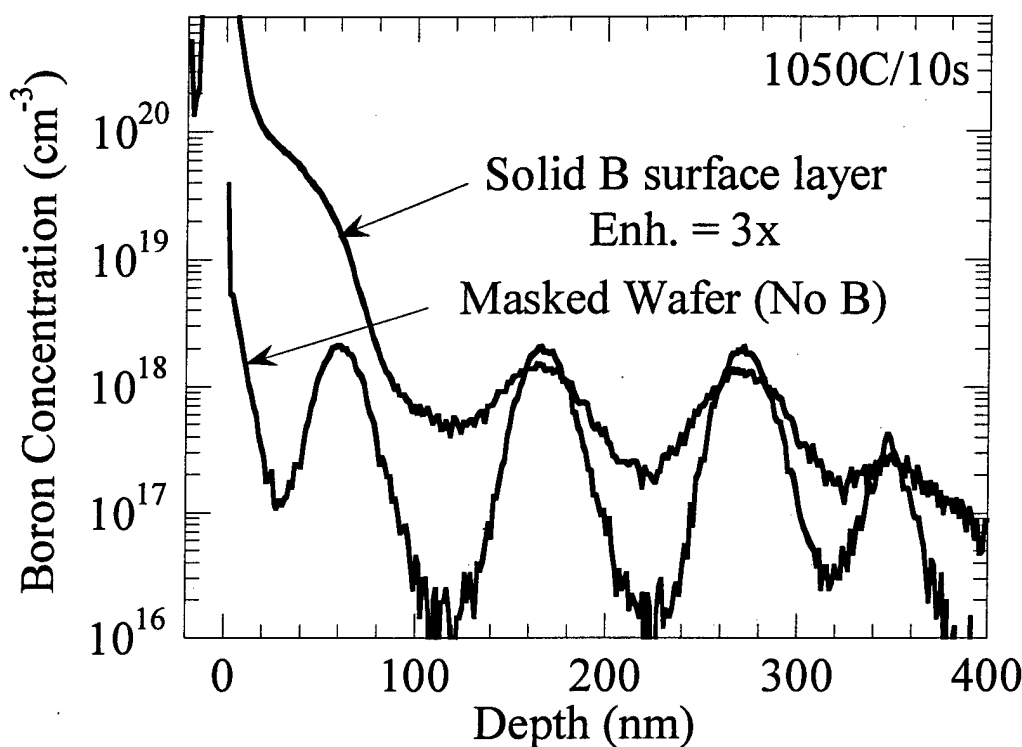
Figure 4.   SIMS profiles comparing diffusion of B markers with and without a layer of pure-B on the surface.

any implant damage which could lead to TED.   The enhancement for evaporated B is 3.5×.

The observation of enhanced diffusion for evaporated B suggests that there is another source of interstitials in the sample with evaporated B. This hypothesis was directly confirmed using MBE-grown boron markers separated from an evaporated surface boron layer. Figure 4 compares diffusion of boron markers in samples with and without a pure B layer on the surface. It is clear from the data in Fig.4 that marker diffusion is enhanced in the sample with the surface B. This implies that the surface B layer produces an interstitial supersaturation in the near-surface bulk during annealing. Evaporated surface layers containing 10% B and 1% B were also grown on marker layer samples for comparison with the 100% B layer. The same enhancement was observed for the 10% B layer as for the 100% B surface layer, but there was no enhancement for the layer containing only 1% B (Fig.5), indicating (a) that there exists a threshold concentration for the BED effect and (b) that the enhancement factor is independent of the boron concentration above this threshold (6). It should also be noted that the evaporated layer containing 1% B grew epitaxially, as indicated by *in situ* RHEED, while the layers with larger B concentrations were amorphous.
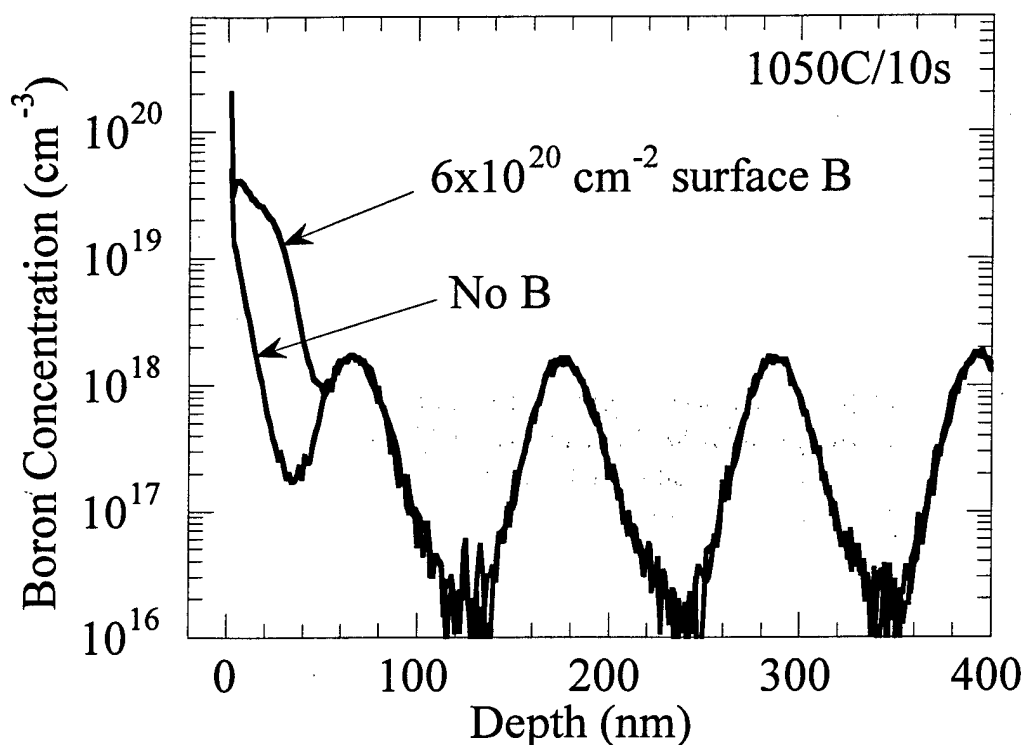
Figure 5.   SIMS profiles comparing diffusion of B markers with and without 6×10^{20} cm^{-3} B on the surface.

A threshold concentration is also observed in the case of implanted B^+. Figure 6 shows diffusivity enhancement data from 0.5-keV B^+ as a function of implanted dose. As before, each data point corresponds to the enhancement at a boron marker located 150 nm below the surface following implantation at doses from 1×10^{13} to 2×10^{15} cm^{-2}, and 10 s annealing at 1050°C. The diffusivity enhancements from doses of 3×10^{14} cm^{-2} and below are close to 1 (no enhancement), consistent with the reduced TED expected due to the very shallow placement of the implant damage. However, between the doses of 3×10^{14} and 1×10^{15} cm^{-2}, the diffusivity enhancement abruptly increases from approximately 1x to 4x. This increase is due to the onset of the BED effect and the enhancement factor of 4x is consistent with that observed for evaporated B. According to TRIM simulations (7), the peak B concentrations corresponding to the two doses that bracket the increase in enhancement are 1% and 3%. This threshold is also consistent with the evaporated-B threshold concentration of between 1 and 10%.

DISCUSSION

It was previously shown that fairly modest B^+ doses can amorphize the implanted layer at ULE energies, e.g. between 2 and 5×10^{15} cm^{-2} at 2 keV (8). Moreover, once
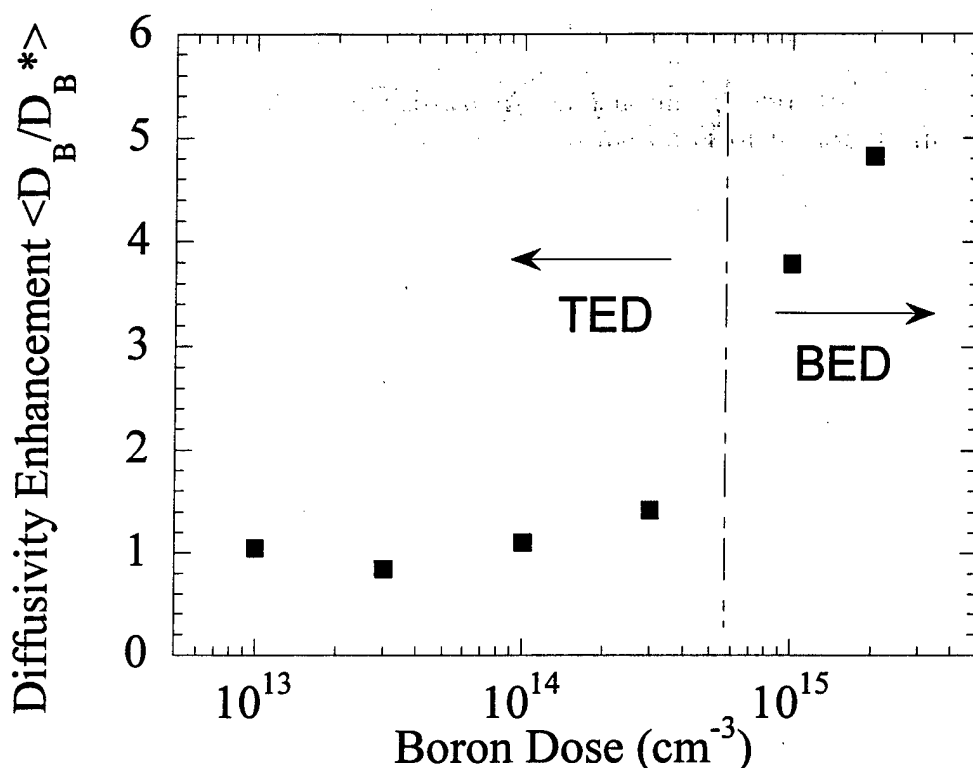
Figure 6.   Diffusivity enhancement from 0.5 keV B^+ implanted at doses from 10^{13} to 2×10^{15} cm^{-2}.

amorphized by B^+, the implanted layer does not regrow as crystalline Si during annealing. Instead, a fine-grain polycrystalline silicon boride phase, identified as SiB_4, is formed (8). The concentrations of implanted B corresponding to the threshold doses for amorphization in that work were estimated to be between 2% and 10%, i.e., similar to the threshold concentration for BED. From these observations, we conclude that the formation of a silicon boride phase in the high boron-concentration silicon layer injects interstitials into the bulk resulting in BED.

It is important to determine precisely what processing conditions lead to BED. There are two physical processes which precede the observation of BED in all of our experiments: creation of an amorphous silicon layer containing a high concentration of boron (either by implantation or by evaporation), and transformation of this amorphous silicon layer to a silicon boride phase during annealing. Strictly speaking, it is possible that both amorphization by boron implantation and the silicon boride phase transformation require different threshold boron doses. In the range of our experiments however, silicon boride phase transformation has only been observed when the layer was initially amorphous, and the two processes appear to have the same threshold. The formation of silicon boride in crystalline silicon has been studied previously by Armigliato, et al. (9). That work showed that precipitation of a silicon boride phase from boron-supersaturated polycrystalline silicon is quite slow, requiring several tens of hours,

even at temperatures as high as 1000°C (9). In contrast, we have observed the formation of silicon boride in amorphized silicon within 10s at 1050°C. This relatively rapid transformation suggests that the kinetic barrier to silicon boride phase formation may be considerably reduced in amorphous silicon as opposed to crystalline silicon. This would provide a natural explanation for our observation that the threshold concentrations for boride phase formation and amorphization coincide. In other words, due to the slow kinetics of the boride phase transformation in crystalline silicon, the boride phase will form during typical anneals if and only if the implanted silicon layer is amorphous.

The implication of these findings for ultra-shallow junction formation is apparent: at ULE energies the B^+ implant dose needs to be smaller than that which will result in amorphization of the implanted layer in order to avoid silicon boride phase formation and BED. We have estimated the threshold doses to achieve amorphization by B^+ ion implantation from a dose-dependence study at 0.5, 2, and 10 keV. At 2 and 10 keV the amorphization threshold doses were between 2 and 5×10^{15} cm^{-2} and 0.8 and 1×10^{16} cm^{-2}, respectively. At 0.5 keV the amorphization dose was confirmed to be between 3×10^{14} and 1×10^{15} cm^{-2} by cross-section transmission electron microscopy. Clearly, the onset of BED corresponds to this threshold (Fig.5). For doses which exceed this threshold, the 4× diffusivity enhancement characteristic of BED at 1050°C means a disastrous doubling of the minimum x_j.

SUMMARY

We have investigated the diffusion enhancement mechanism, BED (boron-enhanced-diffusion), where boron diffusion is enhanced in the proximity of a high-concentration boron-containing layer during annealing. We have shown that the phenomenon is related to the formation of a fine-grain silicon boride phase when annealing an amorphous Si layer which contains a high B concentration. Formation of the silicon boride phase results in injection of interstitials into the silicon bulk. These excess interstitials enhance boron diffusion. The threshold B dose for the BED effect coincides with the amorphization threshold dose. At 0.5 keV the threshold implantation dose which leads to BED lies between 3×10^{14} and 1×10^{15} cm^{-2}. Formation of the shallowest possible junctions by ULE 0.5 keV B^+ requires that the implant dose be kept lower than this threshold.

ACKNOWLEDGEMENTS

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