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ABSTRACT

The diffusion of Sb and B markers has been studied in vacancy supersaturations produced by MeV Si implantation in float zone (FZ) silicon and bonded etch-back silicon-on-insulator (BESOI) substrates. MeV Si implantation produces a vacancy supersaturated near-surface region and an interstitial-rich region at the projected ion range. Transient enhanced diffusion (TED) of Sb in the near surface layer was observed as a result of a 2 MeV Si^+, $1\times10^{16}/cm^2$, implant. A 4× larger TED of Sb was observed in BESOI than in FZ silicon, demonstrating that the vacancy supersaturation persists longer in BESOI than in FZ. B markers in samples with MeV Si implant showed a factor of 10× smaller diffusion relative to markers without the MeV Si^+ implant. This data demonstrates that a 2 MeV Si^+ implant injects vacancies into the near surface region.

INTRODUCTION

Growing interest in diffusion and TED of dopants has led to a great deal of study of point defects in silicon. However, the focus of most studies has been interstitial type defects, primarily because interstitials have been shown to be responsible for the TED of ion implanted B and P during integrated circuit processing, while much less emphasis has been placed on the study of vacancies. There are several methods for creating interstitial supersaturations of known concentrations in silicon and of analytically quantifying them. For instance, medium-energy ion implantation injects excess interstitials in numbers roughly equal to the total number of implanted ions.[1] These excess interstitials coalesce into elongated {311} defects, which are visible in transmission electron microscopy (TEM) such that the number of interstitials can be measured. TED of B and P, which are interstitialcy diffusers whose diffusivity is proportional to the concentration of Si self-interstitials, has been observed as a result of the evaporation of these {311} defects.[2]

To fully understand interstitial interactions and dopant diffusion in silicon a better understanding of interstitial-vacancy and dopant-vacancy interactions is also needed. To study vacancy interactions, better methods to prepare and characterize vacancy supersaturations in silicon are required. Thermal nitridation has been shown to create vacancy supersaturations of the order of 3-5 times the equilibrium concentration (C_V^{eq}) of vacancies at temperatures ranging from 800° to 900°C.[3] When compared to the supersaturation of excess interstitials that are created by ion implantation, this supersaturation of vacancies is not very large. Furthermore, the temperature range over which these supersaturations can be achieved is limited to the temperatures at which nitridation is possible. The ability to produce and control larger vacancy supersaturations is desirable in order to improve the sensitivity to detect and measure all the possible vacancy interactions that can take place and their degree of importance.

High-energy, high-dose self-ion implantation in silicon has been shown to produce large vacancy-rich regions near the silicon surface that can extend a micron or so into the bulk.[4,5] This can be explained by considering the profiles of interstitial and vacancy point defects created by ion-atom collisions. During ion implantation, both vacancies and interstitials are created in pairs as implanted ions collide with silicon lattice atoms. This results in a distribution of vacancies and interstitials within the implanted layer. The recoil distribution (interstitial distribution) is shifted slightly deeper into the bulk relative to the vacancy distribution, due to the forward momentum of the implanted ion. The spatial separation between the interstitial and vacancy distribution increases with increasing ion energy. In low and medium ion implantation, the spatial separation is small, so during the early stages of annealing the interstitial distribution recombines with the vacancy distribution leaving only excess atoms (interstitial) corresponding to the number of implanted ions. However, for MeV implantation the spatial separation between the distributions is large enough that after recombination there is a net point defect distribution of excess vacancies over interstitials near the surface and a corresponding region of excess interstitials near the ions range, R_p. We propose to exploit this vacancy-rich region to control vacancy supersaturation and extend studies of diffusion and point defect interaction to large vacancy concentrations.

There are a number of experiments that demonstrate the existence of vacancy supersaturations after high-energy self-ion implantation, including positron annihilation spectrometry.[4,5] In addition, {311} defects containing a peak interstitial concentration of approximately $1\times10^{18}/cm^3$ have recently been annihilated by superimposing a 2 MeV Si implant with a dose of $1\times10^{16}/cm^2$, suggesting that the excess vacancy concentration (C_v^{MeV}) produced by this MeV implant may be as large as $10^{18}/cm^3$.[6] In the same work, the same MeV implant induced large enhanced diffusion of MBE-grown Sb markers. Since Sb diffuses primarily by a vacancy mechanism, this is another indicator of a large value of C_v^{Mev}/C_v^{eq}. Other researchers have also used high-energy self-ion implantation to demonstrate a reduction in the TED of implanted boron, consistent with vacancy injection.[7,8] Further evidence of vacancy supersaturations produced by MeV Si implantation is shown in Fig. 1. Figure 1a shows the interstitial type dislocation loops that grow at the original amorphous-crystal interface when a recrystallized a-Si layer was regrown by solid phase epitaxy (SPE) at 600°C then post-annealed at 1000°C for 20 min. Figure 1b shows the same regrown layer with the addition of a 2 MeV Si implant prior to the 1000°C anneal. The MeV Si implant resulted in the annihilation of the defects at the original amorphous-crystal interface. Since these defects are interstitial in nature,

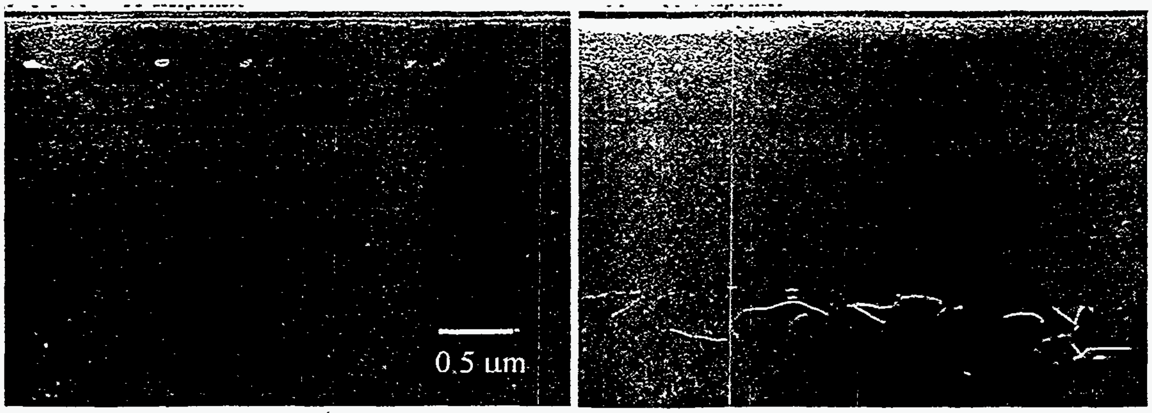

Figure 1a) Interstitial-type defects at the original amorphous crystal interface of a preamorphized layer regrown by SPE and annealed at 1000°C for 20 min, in FZ-Si(100).

Figure 1b) Same preamorphization and SPE as in a), with the addition of a 2 MeV Si^+, $1x10^{16}/cm^2$, implant prior to a 1000°C 20 min anneal.

we attribute their disappearance to recombination with the excess vacancies produced from the MeV Si implant.

The aim of this work is to evaluate MeV Si implantation as a method for injecting a large, and controlled, vacancy supersaturation to study vacancy interactions. The diffusion of Sb and B markers in a vacancy-supersaturated region created by MeV Si implantation was studied. Since Sb diffuses by a vacancy mechanism[9], any enhancement in its diffusivity reflects an enhancement in the vacancy concentration, making the diffusion of Sb an excellent probe for vacancies. Similarly, B diffuses primarily by an interstitial mechanism; the diffusion of boron is used to detect the possible presence of excess interstitials from the MeV Si implant. Using Sb and B markers in this complementary fashion allows us to monitor both vacancy and interstitials supersaturations, and potentially to detect vacancy-interstitial interaction.

EXPERIMENT

Diffusion markers were prepared by a sequence of amorphizing implants followed by dopant implantation and SPE as follows. Wafers were preamophized with a dual Si ion implant of 70 and 140 keV, both to a dose of $6\times10^{14}/cm^2$ at 77 K. Ion channeling measurements confirmed that the amorphous layer was continuous to the surface and 3000 Å thick. Diffusion markers of Sb, (290 keV $1.8\times10^{13}/cm^2$) or B (30 keV $1.8\times10^{13}/cm^2$), were then implanted into the amorphous layer. The implant energies were chosen to place the markers and the damage from the implant well within the amorphous region. These doses produce a peak concentration of 2×10^{18} atoms/cm^3 for both Sb and B. The substrates were then regrown by SPE at 600°C for 1 hour in 1 atm of Ar (4% H_2). These preamorphization and SPE steps were performed to reduce the channeling tail and to place the dopants on substitutional sites with minimal diffusion. A portion of each sample was then implanted with 2 MeV Si ions to a dose of $1\times10^{16}/cm^2$. This implant was done at an elevated temperature of 300°C to prevent amorphization and promote local recombination of defects. The portions of the samples that were not implanted with 2 MeV Si^+ ions will be referred to as reference samples. The marker samples were then annealed at 1000°C for 20 min or at 800°C for 15 min in Ar (4% H_2). Sb and B concentration profiles were analyzed by secondary-ion mass spectrometry (SIMS). Diffusivities were measured by fitting the diffused profiles with a diffusion simulator.

These experiments were performed in BESOI material as well as in FZ silicon. The buried oxide in the BESOI is intended to be a barrier to the possible back diffusion of silicon interstitials from R_p of the MeV implant. In a recent experiment, enhanced diffusion of MBE-grown B markers was observed as a result of a MeV Si implantation[6], suggesting that the deep interstitials may influence near surface diffusion unless some such barrier is provided. Interstitials have been shown to have a very small diffusivity in SiO_2,[10] so the buried oxide in the BESOI should act as an effective barrier. In addition, positron annihilation spectroscopy data has shown that the vacancy supersaturations created by MeV implantation exist for longer times and at higher temperatures in BESOI than they do in FZ or Czochralski (Cz) silicon.[11] The BESOI substrate consisted of 5000 Å Cz-Si(100) on a 4500 Å oxide. The energy of the MeV Si implant was chosen to put R_p (~2 μm) well beyond the buried oxide in the BESOI.

RESULTS

Figure 2 shows SIMS concentration profiles for Sb markers in FZ-Si(100). The initial profile of the regrown Sb marker is included in the figure. The reference Sb marker annealed at

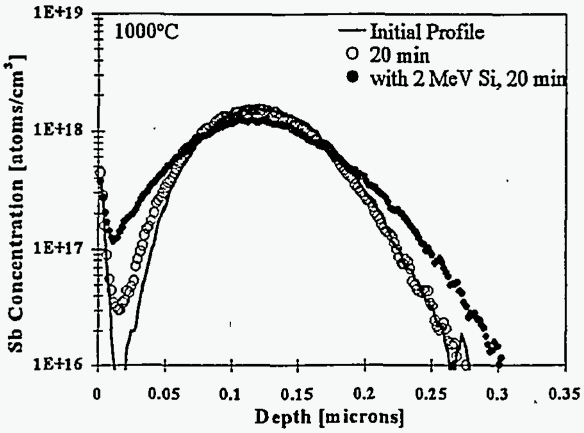

Figure 2. Sb concentration profile in FZ-Si(100) of initial Sb marker, annealed at 1000°C for 20 min, and implanted with MeV Si^+ prior to 20 min anneal at 1000°C.

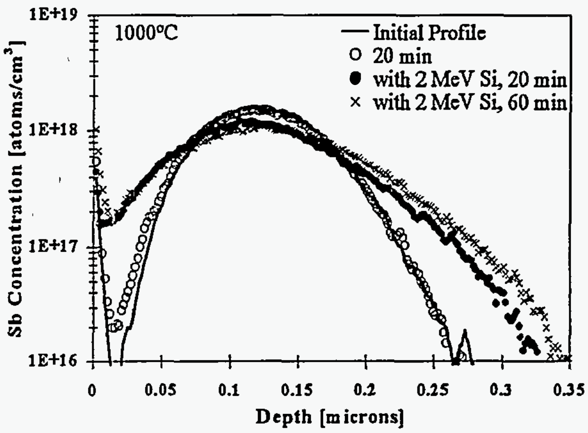

Figure 3. Sb concentration profile in BESOI of initial Sb marker, annealed at 1000°C for 20 min, implanted with MeV Si^+ prior to 20 min anneal at 1000°C, and implanted with MeV Si^+ prior to 60 min anneal at 1000°C.

1000°C for 20 min shows hardly any diffusion. Its time averaged diffusivity, $\langle D_{Sb}^{Ref}\rangle$, was found to be 2.3×10^{-16} cm^2/s (+ 0.3×10^{-16}, - 2×10^{-16}). The marker implanted with MeV Si ions prior to annealing at 1000°C for 20 min diffused much more than the Sb reference marker. Its time-averaged diffusivity, $\langle D_{Sb}^{MeV}\rangle$, was found to be $4.5\times10^{-15}cm^2/s$ (+/- 0.4×10^{-15}). Therefore, there is at least a 20× enhancement in the average Sb diffusivity, due to the MeV Si implant in FZ silicon. Since Sb is a vacancy diffuser whose diffusivity is proportional to the vacancy concentration, we conclude that there was at least a 20× enhancement in the vacancy concentration as a result of the MeV Si implant when compared to the reference Sb marker: $\langle C_v^{MeV}\rangle/\langle C_v^{Ref}\rangle \geq 20$.

Figure 3 shows the corresponding Sb concentration profiles in BESOI. Again, the reference Sb markers show very little diffusion: $\langle D_{Sb}^{Ref}\rangle = 2.3\times10^{-16}$ cm^2/s ($+0.3\times10^{-16}$,-2×10^{-16}). Similar to the FZ case, the Sb marker implanted with 2 MeV Si ions prior to annealing diffused much more than the reference sample: $\langle D_{Sb}^{MeV}\rangle = 8.6\times10^{-15}$ cm^2/s (+/- 0.6×10^{-15}) in BESOI. So, there was at least a 37× enhancement in the diffusivity of Sb in BESOI, implying that $\langle C_v^{MeV}\rangle/\langle C_v^{Ref}\rangle \geq 37$. The enhancement in Sb diffusivity due to the MeV Si^+ implantation in the BESOI is larger than it is in FZ by almost 2×, suggesting that in the BESOI substrate a larger vacancy supersaturation persists over the duration of the anneal. We attribute this effect to the buried oxide in the BESOI, which can act as a barrier to the back diffusion of excess interstitials that form at the range of the MeV implant.

Also included in Fig. 3 is an Sb marker profile after implantation with 2 MeV Si ions and annealing at 1000°C for 60 min. Comparing the profiles in Fig. 3, we see that the diffusion was larger in the first 20 min of the anneal than it was for the next 40 min. By simulating the evolution of the 20 min profile into the 60 min profile, we obtain an average diffusivity of 2.2×10^{-15} cm^2/s. This is 4 times smaller than the average diffusivity over the first 20 min, clearly indicating that $\langle C_v^{MeV}\rangle$ is decreasing over this time scale and that the diffusion enhancement is transient. This result confirms the first observation of TED of Sb as a result of ion implantation (Ref 6) and extends that result to higher temperatures and to non-MBE grown samples.

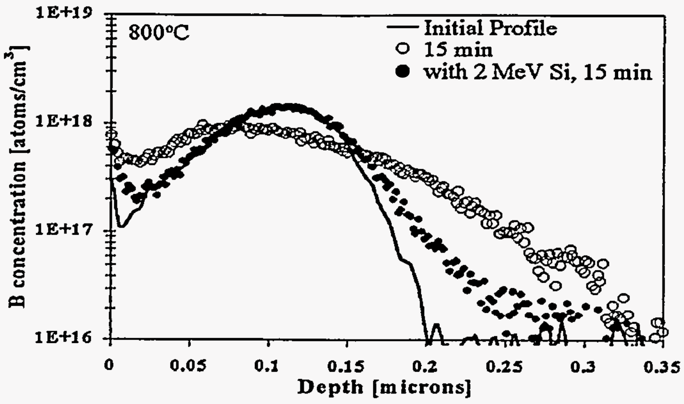

Figure 4. B concentration profile in FZ-Si(100) of initial B marker, B marker annealed at 800°C for 15 min, and B marker implanted with MeV Si^+ prior to 15 min anneal at 800°C.

We have also measured the diffusion of B markers in order to determine whether the MeV implant is also injecting interstitials in the near surface. Concentration profiles for B markers with and without a 2 MeV Si^+ implant annealed at 800°C for 15 min are shown in Fig. 4. In contrast to the case of Sb, we see that the reference B marker has diffused much more than the B marker implanted with MeV Si ions prior to annealing. We obtain $\langle D_B^{Ref} \rangle = 2.2\times10^{-14}$ cm²/s and $\langle D_B^{MeV} \rangle = 2.2\times10^{-15}$ cm²/s (+/- 0.3×10^{-14}). Comparing these values to intrinsic boron diffusion at 800°C, 4.5×10^{-17} cm²/s, we see that for the reference B marker there is approximately a 500× enhancement, while for the MeV Si implanted B marker the enhancement is only approximately 50×. We attribute these enhancements in B diffusivity to residual interstitials remaining at the position of the original amorphous-crystal interface after SPE regrowth (see Fig. 1). Preamorphization and subsequent SPE regrowth have previously been shown to enhance the diffusion of boron for amorphization conditions similar to ours.[12] Nevertheless, the 2 MeV Si implant has resulted in a reduction in the diffusion of the B marker as compared to the reference B marker: $\langle D_B^{MeV} \rangle / \langle D_B^{Ref} \rangle = 0.1$. This reduction is attributed to the excess vacancies produced by the MeV implant and their recombination with the SPE-induced interstitials and suggests that if there is any interstitial injection from the MeV implant at the depth of the B profile, it is vastly overwhelmed by the vacancy injection.

B markers with and without MeV Si implantation have also been annealed at 1000°C for 20 min. At that temperature, we observe very little enhancement relative to equilibrium B diffusion in the absence of the MeV implant, and evidence of a slight reduction following MeV implantation. So we conclude that at this temperature, vacancy injection dominates over interstitial injection at the marker depth.

It should be mentioned that the measured diffusivity for the reference Sb markers annealed at 1000°C for 20 min was reduced by 10× as compared to the intrinsic diffusivity of Sb at 1000°C: $D_{Sb}^{Ref} = 2.3\times10^{-16}$ cm²/s and $D_{Sb}^{eq} = 2.3\times10^{-15}$ cm²/s at 1000°C. We attribute this to residual interstitials from the SPE trapping or recombining with vacancies in the near surface region. Since all of the Sb markers were prepared under the same conditions, and we are directly comparing the effects of MeV implanted markers to markers that did not have the MeV implant, our conclusions regarding diffusion enhancements and vacancy injection due to MeV implantation are still valid.

CONCLUSIONS

The diffusion of Sb and B markers has been measured in regions of vacancy supersaturation created by 2 MeV Si ion implantation. Sb diffusion was studied as a probe for vacancies, and B diffusion was studied as a probe for interstitials. TED of Sb was observed at

1000°C in markers implanted with MeV Si ions relative to unimplanted markers. The enhancement decreases for longer times at 1000°C, indicating that the concentration of vacancies was decreasing with time. Based on these measurements we estimate that the 2 MeV Si, $1\times10^{16}/cm^2$, produces a time averaged vacancy supersaturation, $<C_V^{MeV}>/<C_V^{Ref}>$, of at least 37× in the first 20 min of the 1000°C anneal in BESOI, that decreased to less than 10× by 60 min. Such large vacancy supersaturations have not been observed previously at this temperature. At the same time, the MeV Si^+ implant did not contribute to the enhancement of B markers. In fact, at 800°C, the MeV implant dramatically reduced the B diffusion, confirming that the excess vacancies produced by the MeV Si implant can reduce the concentration of residual interstitials in the near surface region. We believe that MeV Si implantation can be used as a "tool" for injecting a controlled concentration of excess vacancies. Such methods may ultimately enable independent control of interstitial and vacancy concentrations, making it possible to design experiments that could measure interstitial-vacancy recombination rates, unambiguously determine diffusion mechanisms for dopants, and determine equilibrium concentrations of point defects.

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