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Ultra Shallow Junctions I

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Strengths and Limitations of the Vacancy Engineering Approach for the Control of Dopant Diffusion and Activation in Silicon

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ABSTRACT

The fabrication of highly doped and ultra-shallow junctions in silicon is a very challenging problem for the materials scientist. The activation levels which are targeted are well beyond the solubility limit of current dopants in Si and, ideally, they should not diffuse during the activation annealing. In practice, the situation is even worse and when boron is implanted into silicon excess Si interstitial atoms are generated which enhance boron diffusion and favor the formation of Boron-Silicon Interstitials Clusters (BICs). An elegant approach to overcome these difficulties is to enrich the Si layers where boron will be implanted with vacancies before or during the activation annealing. Spectacular results have been recently brought to the community showing both a significant control over dopant diffusion and an increased activation of boron in such layers. In general, the enrichment of the Si layers with vacancies is obtained by Si^+ implantation at high energy. We have recently developed an alternative approach in which the vacancies are injected from populations of empty voids undergoing Ostwald ripening during annealing. While different, the effects are also spectacular. The goal of this work is to establish a fair evaluation of these different approaches under technologically relevant conditions. The application domains of both techniques are discussed and future directions for their development/improvement are indicated.

INTRODUCTION

Dopant diffusion and activation phenomena in silicon both involve point defects. For boron, diffusion occurs by pairing a B atom with a silicon interstitial atom (Is) and consequently, the diffusivity of boron is directly proportional to the concentration of Is in the region. Transient Enhanced Diffusion (TED) of boron, a technologically undesirable effect, is often observed when annealing of B implanted silicon [1] [2]. This behavior is due to the large supersaturations of Is which evolve in time and space during the Ostwald ripening of Is clusters, {113} defects and then dislocation loops [3]. The limited activation of boron often observed after such annealing, at concentration values well below its solid solubility limit, is also due to the

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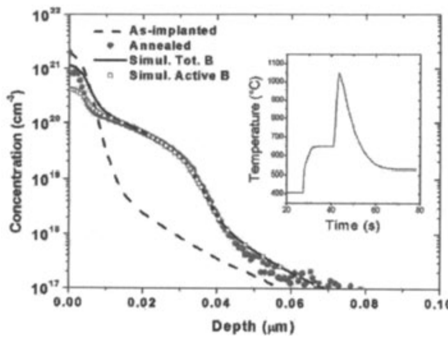
interaction of boron atoms with Is in large supersaturations which favour the formation of immobile, electrically inactive, small B_nSi_m clusters (BIC's) [4]. Recent strategies for attaining the required high activation levels are aimed at either "breaking" these BIC's while limiting boron diffusion for example using very high temperature annealing for a very short time, or at forming highly doped but metastable layers by Solid Phase Epitaxy (SPE). However both approaches have their limits. TED of boron greatly increases the junction depths even during "spike" or "flash" annealing ([5], Fig. 1) while boron deactivation occurs during high temperature annealing of SPE regrown layers [6].



Fig; 1 : Comparison between experiments and simulations for boron implanted at 0.5 keV with a dose of 1.10^{15} /cm^2 and spike annealed at 1050°C. Enhanced boron diffusion occurs even for such short annealing times. Insert is the temperature profile used for annealing (after ref. 1).

An elegant approach to overcome these difficulties is to enrich the Si layers where boron will be implanted with vacancies before or during the activation annealing. Spectacular results have been recently brought to the community showing both a significant control over dopant diffusion and an increased activation of boron in such layers. In general, the enrichment of the Si layers with vacancies is obtained by Si^+ implantation at high energy. We have recently developed an alternative approach in which the vacancies are injected from populations of empty voids undergoing Ostwald ripening during annealing. While different, the effects are also spectacular.

It is the goal of this paper to review the results found in the literature and as well as our own results and to provide a fair evaluation of different vacancy engineering methods in view of fabricating improved ultra-shallow p+/n junctions under technologically relevant conditions in bulk and SOI wafers.

VACANCY ENGINEERING USING Si^+ IRRADIATION

A bit of History

The concept of "point defect imbalance" due to ion implantation has been introduced decades ago based on single collision arguments. Indeed, when the nuclear energy transfer between a moving atom or ion and a target atom is larger than a certain threshold a Frenkel pair is created. The vacancy (V) stays where the collision took place while the recoiling atom moves further as an interstitial (I). When the energy transfer is small (typically < 1 keV), the recoiling

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atom gains a small momentum and thus their "exchange angle" is large and they may move in almost every direction. This argument was used by Brinkman in the 50's to predict the structure of low energy sub-cascades i.e., the formation of zones consisting of a vacancy-rich core surrounded by an interstitial-rich shell (7). Alternatively, when the energy transfer is much larger, the "exchange angle" is small and recoiling atoms predominantly moves along the direction of the impinging particle. It has been suspected for long that, in this case, the concentration of vacancies and interstitials in the target should not be constant along the depth but instead should show enrichment of vacancies close to the surface and of interstitials deeper in the target. However, this finding could not be demonstrated until Monte Carlo simulations of the slowing down process of ions into materials and that the effect of the subcascades created by the recoiling target atoms was included. This happened when TRIM was rendered available to the community in 1984 (8). It took another couple of years for the computers to become powerful enough so that information about a possible point defect imbalance could be extracted from the simulation of the slowing down of several tens of thousand of incident ions. This was done for the first time by Holland et al. in 1991 (9) and, although the profiles were still very noisy, the concept of vacancy engineering was introduced as well as the possible benefits for the fabrication of shallow junctions. Two years later, Laanab et al. used the same type of calculation to explain the origin of the interstitials defects found after annealing of amorphous layers created by ion implantation and known as "End of Range" (EOR) defects (10).

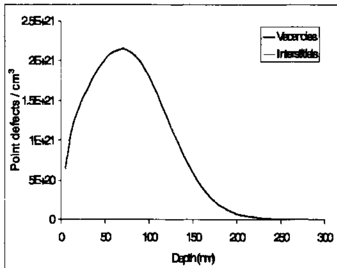

Fig. 2a: Depth distributions of vacancies and interstitials after a 150 keV Ge^+ implantation into silicon (from TRIM)

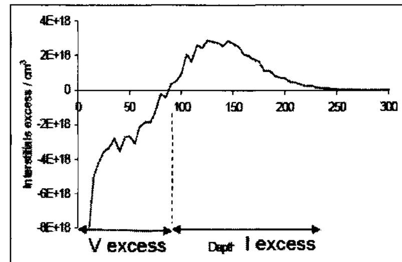

Fig. 2b: Depth distribution of Vs and Is "in excess" after the same implant.

We have plotted in Fig 2, the result of the simulation of a Ge^+ implantation at 150 keV in silicon. On the left, we have plotted both the vacancy and the interstitial profiles obtained by averaging the results over 500 000 ions. These profiles cannot be distinguished one from the other by eye. However, when subtracting one from the other, a profile showing an excess of vacancies close to the surface and an excess of interstitials close the end of range can be evidenced. In general, the vacancy-rich profile exhibits two components, a very steep high concentration region at the surface and a plateau extending further down to a depth approximately equal to that corresponding to the maximum of both the vacancy and the interstitial profiles. The first one is due to the fact that there is simply no silicon before the surface and that the corresponding Is are "missing". Only vacancies mostly originating from primary knock out collisions are left in this region. The plateau found deeper is due to generation of high energy recoiling atoms in this region which preferentially propagate in directions close

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to that defined by the incident ions i.e., towards greater depths, leaving behind their corresponding vacancies. Finally, the width of this plateau increases with the incident energy of the ions. For very high energies, the V-rich region can be displaced towards greater depth leaving an almost defect-free surface region because only "electronic" collisions take place at the beginning of the slowing down of the ions.

In all cases, assuming that, after ion implantation at room temperature in silicon, a "vacancy-rich region exists close to the surface" deserves discussion. It must be kept in mind that, in most practical cases, the concentrations of point defect "in excess" one can calculate weights for only 10^{-4} to 10^{-2} of the total concentrations of point defects created by the implantation. Thus, manipulating such numbers requires a good understanding of the physical meaning and final impact of the parameters injected into the simulation. Moreover, the regions showing an excess of vacancies or an excess of interstitials can "transform" into vacancy-rich or interstitial-rich regions only if the total recombination of Vs and Is takes place at every depth where they are created during implantation or annealing. At room temperature, this can occur within "dilute" cascades where Vs and Is are almost randomly distributed. Single Vs and Is being not stable at RT in Si, they diffuse until they recombine either to form Vn and In (with n>2) or annihilate, the latter phenomenon being favored within dilute cascades. Such cascades result from the interaction of "light" ions with silicon, light meaning low mass and high energy as in the LSS theory.

Finally, the concentration of this vacancy excess is proportional to the ion dose, but a threshold dose exists above which the silicon turns amorphous. At room temperature, silicon amorphization by light ions is much less efficient than by heavy ions, again because of enhanced recombination of Is and Vs within the dilute cascades. This trade-off between amorphization dose and high vacancy concentration can be optimized and this has been recently discussed in details by Cowern et al. [11].

All these characteristics, a high energy, a low mass and a high defect annihilation rate, favorable to the formation of large enough regions containing relatively high concentrations of vacancies, explain why most if not all the studies reported so far use Si^+ ion implantations at room temperature to produce these vacancy-rich regions. Unfortunately, we suspect that several of the results reported in the past made use of Si doses equal or above the amorphization dose.

Literature review

One of the first conclusive reports of the effect of Si^+ irradiation onto boron diffusion has been published by Raineri in 1991 [12]. In this paper, it is shown that a minimum dose of 5.10^{13} Si^+/cm^2 at 1 MeV is required to almost suppress the diffusion of boron implanted at 10 keV and at low dose and during annealing at 900°C for 10s. It is to be noticed that the maximum concentration of boron involved in this experiment was quite small ($<10^{18}/cm^3$). In 1999, Venezia et al. [13] have shown that the "famous" TED seen from the evolution of lightly doped B-marker layers ($<2.10^{18}/cm^3$) and related to the dissolution of {113} defects could be suppressed when the structure was previously irradiated with 1 MeV. From these experiments it was concluded that the Is emitted by the defects were recombining with the vacancies in excess in the region. However, the dose used in this experiment was dangerously high (10^{16} Si^+/cm^2) and we doubt that part of the silicon matrix was not amorphized by this Si implant. Interestingly, in 2003, Neijim et al. [14] have shown that not only TED but also "regular", equilibrium, diffusion could be suppressed by pre-irradiating silicon with Si ions at 1 MeV. From this

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experiment, it can be concluded that the enrichment of the region with Vs results in a lowering of the concentration of Is in the same region, below the equilibrium concentration Ci*. In 2002, Shao et al. [15] have shown that the surface region is less damaged (measured by RBS) after a sequential implantation with 500 keV Si+ and 2 keV B+ than after a 2 keV B+ implantation alone. From this results, it was inferred that BIC's already form at room temperature and that immediately after Si+ irradiation, Vs are available and prevent the formation of BICs when boron is implanted later.

More recently, Cowern and co-workers have studied the activation of boron in such V-rich layers [11, 16] after isochronal anneals. They have shown for the first time that for the same annealing conditions, the activation rate of boron was an increasing function of the irradiation dose. Another important result from their work is that for sufficiently high Si irradiation doses, the activation of boron can be as good after a 600°C than after a 1000°C annealing. Unfortunately, the benefit of this irradiation reduces for increasing temperature and after annealing at 1000°C, the effect of Si irradiation is marginal.

Finally, it is interesting to know whether this approach is suitable to increase the sheet resistivities attainable in SOI layers. Indeed, carrier mobilities are often reduced in SOI layers and this could be compensated by increasing the doping levels. Actually, an answer to this question cannot be simply found in the literature. For the materials scientist, the idea of "isolating" the vacancy-rich region from the Is-rich region found immediately below it is tempting as it could prevent possible recombinations between the two antinomic species. Again, controversial results can be found in the literature [17, 18] which focus only on the behavior of boron diffusion in these SOI layers. As we will show it later in this paper, diffusion in SOI layers is mostly governed by trapping at the Si/SiO_2 interfaces and a clear demonstration of the usefulness of this "barrier" was still lacking.

Experimental details

In our experiments, bulk and SOI (70/140 nm) wafers were implanted at RT with 250 keV Si^+ at doses up to $1.10^{15}/cm^2$ i.e., below the amorphization dose. Fig. 3 shows the depth distribution of excess point defects created by this irradiation. For a dose of $1.10^{15}/cm^2$, there exists a plateau extending from the surface and towards a depth of about 300 nm within which the concentration of excess Vs is relatively constant at $1.10^{19}/cm^3$. The total number of Vs available in the region is thus about $3.10^{14}/cm^3$ in the bulk Si wafers.After this irradiation step, B was implanted at 3 or 0.5 keV for doses ranging from $1.10^{14}/cm^2$ to $3.10^{15}/cm^2$. Finally, samples from these wafers were annealed by RTA for 10 s or by spike annealing at 800 or 1000°C under nitrogen gas. The samples were analyzed by TEM, SIMS, Hall effect or Scanning Capacitance. We report below a selection of important and representative results.

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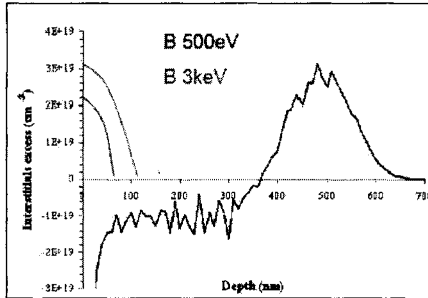

Fig. 3: Depth distribution of excess Vs and Is resulting from the irradiation of silicon with 250 keV Si^+ at a doses of $1.10^{15}/cm^2$

Low Boron concentrations, small thermal budgets

Fig. 4a shows the B SIMS profiles obtained after spike annealing at 800°C of B implanted at 3 keV and with a dose of $1.10^{15}/cm^2$.

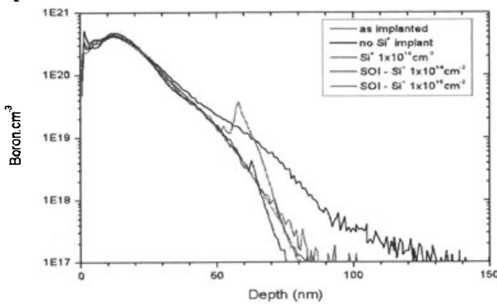

Fig. 4a: SIMS profiles showing the effect of Si irradiation onto diffusion of B implanted at 3 keV $1.10^{15}/cm^2$ and spike annealed at 800°C.

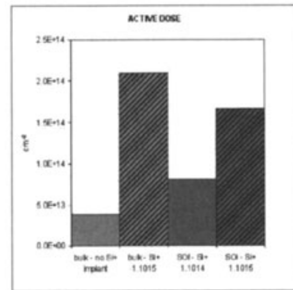

Fig. 4b: Corresponding active doses measured by Hall effect.

Under equilibrium conditions, B should not diffuse for such a small thermal budget. The large diffusion of B evidenced after annealing is due to TED. However, it is clear that Si irradiation with a dose of $1.10^{15}/cm^2$ totally suppresses this diffusion. In the case of the SOI samples, B diffusion is mostly governed by trapping at the SOI interface. After Si irradiation, this trapping is almost suppressed what is an indirect proof that boron diffusivity is extremely small in this SOI layer. Fig. 4b shows the boron active doses we have extracted from Hall measurements on these layers. After such an annealing, only about 4 % of the total B dose implanted in bulk Si is activated. After Si irradiation this activation rate reaches more than 20 % i.e., the injection of vacancies results in a 5 time increase of the concentration of boron atoms sitting on substitutional sites. In SOI, although this effect is somehow reduced, the activation rate can be improved by a factor of 4 when using Si irradiation.

To summarize our results, in the case of boron implanted at relatively low doses and annealed at low temperatures and/or for short times, the effect of Si irradiation is spectacular

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both in bulk and SOI wafers. Boron TED can be suppressed and its activation rate largely increased.

High Boron concentrations, large thermal budgets

Fig. 5a shows the B SIMS profiles obtained after RTA annealing at 1000°C for 10 s of B implanted at 0.5 keV and with a dose of $3.10^{15}/cm^2$. Under equilibrium conditions, B largely diffuses for such a high thermal budget, giving rise to the observed shoulder in the annealed profile. The tail extending towards greater depths is due to B TED. After Si irradiation with a dose of $1.10^{15}/cm^2$, we only note a small reduction of TED. In the case of the SOI samples, B diffusion seems to be reduced but these profiles can be explained by the very large B trapping at the SOI interfaces. After Si irradiation, we do not note any significant reduction of B trapping at the interfaces, an indirect proof that B diffusivity has not been sensibly reduced by the irradiation in these layers.

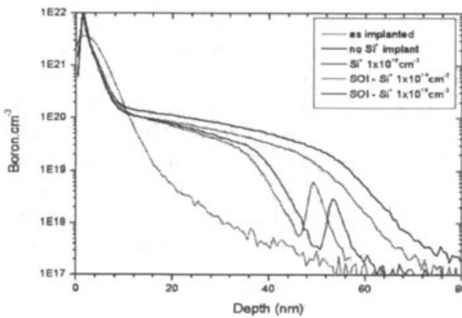

Fig. 5a: SIMS profiles showing the effect of Si irradiation onto diffusion of B implanted at 0.5 keV and with a dose of $3.10^{15}/cm^2$ and during 1000°C, 10 s RTA annealing.

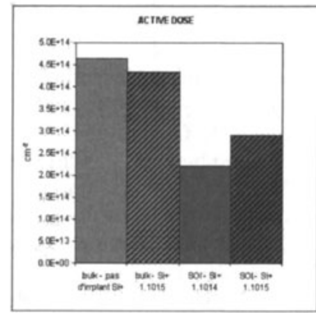

Fig. 5b: Corresponding active doses measured by Hall effect.

Fig. 5b shows the boron active doses we have extracted from Hall measurements on these layers. After such an annealing, about 10 % of the total B dose implanted in bulk Si is activated. After Si irradiation this activation rate is unchanged. In SOI, we only note a slight improvement of the activation rate of boron.

To summarize our results, in the case of boron implanted at high doses and annealed at high temperatures and for long times, the effect of Si irradiation is only marginal both in bulk and SOI wafers.

Conclusions

We confirm here what could be guessed from the literature i.e., that spectacular effects due to Si irradiation are always evidenced when the boron doses are relatively small and/or that the annealing times and temperature are also small. In other words, Vs engineering by Si irradiation is an efficient mean of reducing B diffusion and increasing B activation only if the total number of Is injected during annealing from the B profile is equal or smaller than the total

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number of Vs available in the region. In our experiments (Si^+, 250 keV, $1.10^{15}/cm^2$), the B dose under which these beneficial effects are maximum is limited to $3.10^{14}/cm^2$, significantly lower than the dose targeted by the industry. In SOI, Si irradiation can however be used to compensate the degraded mobility in these layers and drive their sheet resistance back to the value normally obtained in non-irradiated bulk Si wafers.

VACANCY ENGINEERING USING EMPTY VOIDS

Voids i.e., precipitates of vacancies, have been largely used in the past to getter metallic impurities. They are however recent reports suggesting they could also be used for vacancy engineering. Voids are, in general, fabricated by using He implantation followed by some thermal annealing aimed at precipitating He then exodiffusing it from the implanted layer, leaving a population of empty voids behind.

Literature review

One of the first report on the use of empty voids to reduce B diffusion is due to Cayrel et al. [19]. In these experiments, a (very) low dose 5 keV B implant was eventually followed by a high dose 40 keV He implant and the diffusion behavior of boron studied after annealing at 900 and 1000°C. From this experiment, it was shown that B diffusivity could be significantly reduced by the He co-implantation. TEM shows that these layers contain a population of voids of bout 10-20 nm in diameter. From these observations it was concluded, that these voids act as trapping centers for the Is involved in B TED driving B diffusivity back to normal. However, the interpretation of these results is not straightforward as the B profiles overlap with the depth distribution of voids.

More recently, Mirabella and Bruno [20, 21], have refined this experiment by spatially separating the voids from the B profiles. Again, they found a dramatic reduction of B diffusion when He was implanted in the layers. They ascribed this reduced diffusion to the presence of "nano-voids" located between the surface of the wafer and the region where larger voids exists, again acting as "dead sinks" and trapping the Is normally involved in B TED.

However, these experiments are difficult to understand and explain mostly because B and He were implanted together before annealing, He precipitation, the growth of these precipitates, the exodiffusion of He towards the surface take place at the same time as B diffusion and activation. To solve this problem and study the influence of vacancies only on boron diffusion and activation, we have designed a set of experiments in which a controlled supersaturation of vacancies can be maintained constant during annealing of a boron implant. For this purpose, we first fabricate empty voids by helium implantation at 40keV followed by an anneal which is sufficiently energetic to totally desorb helium from the layers. B is then implanted at energies and doses of interest for the fabrication of ultra-shallow junctions into these "void-containing" wafers and its diffusion and activation behaviour are studied in detail [22, 23]. We recall here the main results of these studies..

Characteristics of the populations of voids

Fig. 6 shows the two populations of (empty) voids we have fabricated by annealing the He implanted wafers at either 800°C or 1000°C. The two populations are depth-distributed and

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