HTML ABSTRACT + LINKS

JOURNAL OF APPLIED PHYSICS VOLUME 95, NUMBER 3 1 FEBRUARY 2004

Effect of near-surface band bending on dopant profiles in ion-implanted silicon

Michael Y. L. Jung, Rudiyanto Gunawan, Richard D. Braatz, and E. G. Seebauer[a)]
Department of Chemical Engineering, University of Illinois, Urbana, Illinois 61801

(Received 1 October 2003; accepted 11 November 2003)

Recent experimental work has demonstrated the existence of band bending at the Si–SiO_2 interface after ion implantation. The present work employs *FLOOPS*-based numerical simulations to investigate the effects this bending can have upon dopant profiles that evolve during transient enhanced diffusion in post-implant annealing. In the case of boron, band bending induces significant junction deepening because the near-interface electric field repels charged interstitials from the interface. Band bending also provides a mechanism to explain the pile-up of electrically active boron within ~1 nm of the interface. The results suggest that conflicting literature regarding the capacity of the interface to absorb interstitials can be rationalized by a modest inherent absorbing capability coupled with band bending. © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1638621]

I. INTRODUCTION

Transient enhanced diffusion (TED) of ion-implanted dopants in silicon has attracted a great deal of study over the last three decades[1–4] because TED plays a significant role in limiting the shallowness of *pn* transistor junctions in advanced microelectronic devices.[5] Interstitial atoms generated by implantation serve as the primary mediators of TED. Trapping or absorption of these interstitials by larger defects such as dislocation loops, interstitial clusters, and nearby surfaces or interfaces therefore affects the magnitude of TED and the shape of the resulting dopant profile. As junction depths become progressively shallower because of device scaling, the importance of surfaces and interfaces in controlling such phenomena becomes correspondingly greater.

The ability of these structures to absorb interstitials is incompletely understood, however. There is general agreement that atomically clean surfaces absorb interstitials very efficiently, so practical ion implantation technology employs a "screen oxide" overlayer of SiO_2 to mitigate loss of dopant from the bulk. However, the literature has reported both significant[6–8] and negligible[9,10] absorption rates for mobile interstitial atoms at Si–SiO_2 interfaces. Law, Haddara, and Jones have attempted to reconcile these results with a kinetic model based on di-interstitial recombination,[11] but the model does not explain dose loss data or boron pile-up near the interface. Clarifying this issue is becoming increasingly important so that process simulators[3,12] can incorporate suitable boundary conditions for designing post-implant annealing processes. Up to now, simulators have proven inadequate for even qualitative predictions of phenomena such as dopant pile-up at the interface.[13]

The present work focuses on an overlooked facet of interstitial absorption at interfaces: their ability to support electrically active defects. It is well known that atomically clean Si surfaces support electrically charged defects that induce near-surface band bending on the order of 0.5 eV.[14] Recent experimental work in this laboratory[15] has demonstrated band bending of comparable magnitude at the Si–SiO_2 interface after ion bombardment at energies of a few hundred electron volt. The experiments showed that band bending persists for all annealing times and temperatures of interest in conventional implantation technology.

TED tends to be most pronounced for doping with boron, and in this case the band bending sets up a near-interface electric field pointing into the bulk. Interstitial atoms of B and Si are positively charged under these conditions,[16–19] so the field tends to repel the interstitials from the interface. In fact, rough calculations suggest[15] that the field is sufficiently strong to virtually stop the motion of positively charged B and Si interstitials toward the interface. (An analogous effect would be observed for negatively charged defects diffusing in *n*-type material.) The opposing field can transform the interface from a significant sink into a good reflector, which has the net effect of deepening the underlying junction.

This laboratory has recently developed a model for dopant diffusion and activation based on rigorous systems-based analysis.[20–24] The present work employs profile simulations using that model together with the experimentally determined interface Fermi level position[15] to quantify junction deepening and to investigate related effects. The results reveal that interface band bending can deepen the junction. Band bending also provides a mechanism to explain the pile-up of electrically active boron within ~1 nm of the interface. The results suggest that conflicting literature regarding the capacity of the interface to absorb interstitials can be rationalized by a modest inherent absorbing capability coupled with band bending.

II. MODEL

A. Simulation method

Calculations were performed using the profile simulator *FLOOPS 2000* (by Mark E. Law of the University of Florida and Al Tasch of the University of Texas/Austin).[25] This

[a)]Author to whom correspondence should be addressed; electronic mail: eseebaue@uiuc.edu

 © 2004 American Institute of Physics

Downloaded 10 Aug 2007 to 130.126.226.215. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

simulator solves the coupled mass balance equations for B and Si interstitials, immobile substitutional B, and clusters. These equations have the general form for species j

$$\frac{\partial \mathrm{N}_j}{\partial t} = -\frac{\partial J_j}{\partial x} + G_j, \tag{1}$$

where N_j denotes concentration and G a net generation rate. The flux J comprises of Fickian and electromigration terms

$$J_j = -D_j \frac{\partial \mathrm{N}_j}{\partial x} + z\mu_j \mathrm{N}_j \mathcal{E}(x), \tag{2}$$

$$\mathcal{E}(x) = -\frac{\partial \Psi}{\partial x}, \tag{3}$$

with z denoting the charge on the species j. The parameter μ represents the mobility, which can be approximated by Einstein's relation $\mu = qD/kT$, where q denotes electron charge, k Boltzmann's constant, and T temperature. Interstitial clusters are assumed to be immobile. Solution of Poisson's equation gives the electrostatic potential Ψ and determines electric field $\mathcal{E}$. The local charge neutrality assumption employed in some earlier works[26] fails in space charge regions. *FLOOPS* was implemented with the kinetic rate expressions and parameters reported in Ref. 24. Simulation results were compared to experimental data reported previously[24] for Si wafers implanted with B at 0.60 keV with a fluence of 2×10^{15} ions/cm^2 at 0° tilt. The heating program was a conventional "spike anneal" described in Ref. 24, with heating rates varying from 75 to 350 °C/s.

B. Charge statistics

To solve Eqs. (1)–(3) for the mobile species requires knowledge of the charge states available to these species as well as their "ionization levels"—values of the Fermi energy for which the majority charge state changes. Neither the stable charges states nor the ionization levels are definitively known for the key species B_i and Si_i.

The most likely charge states for interstitial boron in p-type Si are B_i^+ and B_i^-; experimental work[27] coupled with discrete Fourier transform (DFT) investigations[19,28] suggests that neutral B_i° at room temperature exhibits "negative-U" behavior that destabilizes this species compared to the charged forms. The room temperature behavior does not preclude the dominance of B_i° at higher temperatures, however; the details of negative-U behavior could in principle alter as temperature rises and the band gap shrinks. Indeed, Sharp *et al.*[29] and Uematsu[30] have satisfactorily fitted diffusion data for boron using the neutral state. We have found by dopant profile simulations detailed elsewhere[31] that the negative-U behavior probably persists, but this conclusion was not strong enough to preclude B_i° entirely. Thus, in the present work both $+/-$ and $+/0$ transitions were considered.

The most likely charge states for Si interstitials in p-type Si are less well established from the literature. The primary candidates are Si_i^{++}, Si_i°, and Si_i^-; Si_i^+ is destabilized by negative-U behavior.[28] We have deduced with considerable confidence from profile simulations[31] that only the $++/0$ transition needs to be considered.

The available literature for the ionization levels of B_i and Si_i provides incomplete guidance for the values to use. For B_i, Harris, Newton, and Watkins[27] interpreted photogenerated signals from deep level transient spectroscopy in terms of a donor $(+/0)$ level close to the conduction band minimum E_c at $E_c - 0.13$ eV and a lower-lying acceptor level $(0/-)$ at $E_c - 0.45$ eV. These results gave evidence of negative-U behavior, and by the theory of Van Vechten[32] and Van Vechten and Thurmond[33] suggest an effective ionization level E^*_{Bi} for the $(+/-)$ transition at $E_c - 0.29$ eV. However, the $(+/0)$ and $(0/-)$ levels almost certainly shift with respect to each other as the temperature increases,[33] since the ionization entropies for donor and acceptor levels differ. Ionization levels for donors tend to track the valence band as the band gap shrinks, while the levels for acceptors track the conduction band. Moreover, Hakala, Puska, and Niemenen[19] reported ionization levels from DFT results that confirmed the negative-U property, but gave ionization levels at 0 K in with poor agreement with Harris *et al.*[27]

For Si, no experimental work exists concerning ionization levels. Computational results from Lee, Lee, and Chang[16] and for the $(++/+)$ and $(+/0)$ transitions based on DFT suggest that the ionization levels differ considerably for the three different site configurations available to Si_i. During high-temperature diffusion, more than one configuration is probably sampled with high frequency. The appropriate effective ionization level $E^*_{\mathrm{Si}_i}$ to use for the $(++/0)$ transition therefore becomes unclear.

Given this uncertain state of affairs, we have treated the effective ionization levels E^*_{Bi} and $E^*_{\mathrm{Si}_i}$ as adjustable parameters to fit the experimental profiles. The optimized values for E^*_{Bi} and $E^*_{\mathrm{Si}_i}$ are 0.33 ± 0.05 and 0.12 ± 0.05 eV above the valence band maximum E_v, respectively. For ease of implementation and following the spirit of the phenomenology used here, these values were assumed to be independent of temperature.

For computational tractability, the mass balance equations of Eq. (1) were set up to track the total concentration of each type of defect (including all charge states) rather than each charge state. Such an approach requires the assumption that defects reach their thermodynamically appropriate charge states on a time scale that is fast compared with defect motion and reaction. This assumption has long been employed in the modeling of defects in Si, for example in diffusion by the Bourgoin mechanism[34] wherein charge state changes even during the course of an individual diffusive hop. To give a specific example of how the mass balance equations were formulated, we take the case of interstitial boron, assumed to exist as B_i^+ and B_i^- species. The transient mass balance for total B_i becomes

$$\frac{\partial B_i}{\partial t} = \frac{\partial B_i^+}{\partial t} + \frac{\partial B_i^-}{\partial t}. \tag{4}$$

Assuming that intrinsic diffusivities of B_i^+ and B_i^- are equal, Eq. (4) can be combined with Eqs. (1)–(3) to become

Downloaded 10 Aug 2007 to 130.126.226.215. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

$$\frac{\partial B_i}{\partial t}=D_{B_i}\left[\frac{\partial^2 B_i}{\partial x^2}+\frac{1}{\alpha}\left(\gamma_{B_i}B_i\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial\Psi}{\partial x}\frac{\partial}{\partial x}(\gamma_{B_i}B_i)\right)\right]+G_{B_i}, \tag{5}$$

where $\alpha=kT/q$ and the parameter γ obeys

$$\gamma_{B_i}=\gamma_{B_i^+}-\gamma_{B_i^-}, \tag{6a}$$

with

$$\gamma_{B_i^-}=\frac{B_i^-}{B_i}=\left[1+\frac{1}{g}\exp\left(\frac{E_{B_i^-}-E_F}{kT}\right)\right]^{-1} \tag{6b}$$

and

$$\gamma_{B_i^+}=\frac{B_i^+}{B_i}=\left[1+g\exp\left(\frac{E_F-E_{B_i^+}}{kT}\right)\right]^{-1}. \tag{6c}$$

The parameters $\gamma_{B_i}^+$ and $\gamma_{B_i}^-$ represent the relative fractions of interstitial boron in the positive and negative states, respectively. The degeneracy factor g[32,35] in Eqs. (6b) and (6c) equals unity for the interstitial pair B_i^+ and B_i^- (as well as for B_i° and B_i^{+2}) because there is no difference between the charge states in the number of unpaired electron spins. However, $g=2$ for the interstitial pair B_i^+ and B_i° because B_i° contains an extra unpaired spin compared to B_i^+.

C. Surface boundary condition for the mass balance equations

A central motivation for the present work is the hypothesis that existing data can be better explained by a combination of modest interstitial absorbing properties at the interface coupled in some cases with band bending. This hypothesis requires a functional form for the surface boundary condition of the mass balance equations that permits behavior somewhere along the continuum between a perfect sink and a perfect reflector.

A perfect-sink boundary condition has the form $C_{j,x=0}=0$, while a perfect-reflector condition has the form $-D_j dC_j/dx|_{x=0}=0$. An intermediate condition can be formulated in terms of a fraction f that scales $C_{j,x=0}$ at the surface with respect to the nearby bulk concentration $C_{j,x=\Delta x}$ evaluated at a small distance Δx into the bulk. With $0\leqslant f\leqslant 1$, the surface flux can then be written as

$$\begin{aligned}-D_j\frac{dC_j}{dx}\bigg|_{x=0}&\approx -D_j\frac{\Delta C_j}{\Delta x}\bigg|_{x=0}\\&=-D_j\frac{(C_{j,x=\Delta x}-C_{j,x=0})}{\Delta x}\\&=-D_j\frac{(C_{j,x=\Delta x}-fC_{j,x=\Delta x})}{\Delta x}\\&=-D_j\frac{C_{j,x=\Delta x}(1-f)}{\Delta x}.\end{aligned} \tag{7}$$

A perfect sink boundary condition corresponds to $f=0$, while a perfect-reflector boundary condition corresponds to $f=1$. To give this equation a clearer physical meaning, we can define a parameter $S=1-f$, which can be considered to be an annihilation probability. Equation (7) can then be rewritten as

$$-D_j\frac{dC_j}{dx}\bigg|_{x=0}=D_j\frac{SC_{j,x=\Delta x}}{\Delta x}=k_rC_{j,x=\Delta x}, \tag{8}$$

where $k_r=SD_j/\Delta x$ represents a surface recombination velocity, or equivalently, a surface reaction rate constant.

A variant of this condition has been employed by Vuong *et al.*,[36] who allowed the interstitial annihilation rate to vary with the number of interstitials trapped at the interface. These workers used the equivalent of a simple Langmuir-like model with $S=S_0(1-\theta)^n$, where θ represents the fractional number of trapping sites filled with interstitials, and n is typically a small integer (0, 1, or 2). Nonzero values of n require a separate mass balance equation for the trapping sites in terms of θ. Reference 36 assumes a value of $n=1$, but gives no value for other parameters that enter into k_r. Such values are nearly impossible to predict *a priori*. In the absence of more knowledge regarding interstitial interactions with interfaces, we have chosen to keep the number of parameters and associated mass balances to a minimum. Thus, we chose $n=0$, making S constant.

There is little guidance from the literature regarding what value S should take. During annealing, an interface of Si/SiO_2 typically overlies the diffusing profile. There is conflicting evidence concerning the ability of this interface to absorb interstitials.[2] On one hand, experiments have detected a reduction in size and concentration of {311} defects with increasing proximity to the interface,[8] suggesting that the interface absorbs Si interstitials fairly efficiently. Some doping profile measurements confirm this suggestion,[6] while other experiments point to a similar conclusion for boron.[6,37] On the other hand, Napolitani *et al.*[10] have cited low levels of boron dose loss compared to phosphorous in order to claim that the interface acts as a poor sink for B_i. Moreover, boron segregates above the solid solubility limit on the Si side of the interface,[9,38] indicating that the interface does not absorb B interstitials very well. This body of work also implies that the interface acts as a poor sink for Si interstitials. Indeed, some laboratories[22,39] have successfully applied a no-flux boundary condition at the interface for both B and Si interstitials. Other workers have avoided the issue altogether by simply not reporting the boundary conditions employed in their models.[38,40]

The interface can also act as a source for Si interstitials, injecting them into the bulk during oxidation and leading to oxygen-enhanced diffusion of dopants.[2] Law *et al.*[11] have recognized the ability of the Si/SiO_2 interface to serve as both a source and a sink of Si interstitials, and attempted to reconcile the conflicting observations by employing a model that includes both di-interstitial interstitial injection and a hypothesized surface recombination pathway for di-interstitials. The model can claim some qualitative successes, but does not explain dose loss data or boron pile-up near the interface.

In the face of this complicated literature, we treated S as a free parameter to be matched to experiment.

Downloaded 10 Aug 2007 to 130.126.226.215. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

D. Surface boundary conditions for Poisson's equation

For the interface, the following two boundary conditions for Poisson's equation were employed for comparison with each other

$$\text{Flat band:} \quad \Psi(x=0,t)=\Psi_s, \tag{9}$$

$$\text{Band bending:} \quad \Psi(x=0,t)=E_v(T)/q+(0.5\ \text{eV})/q. \tag{10}$$

For the flat band condition, the local carrier concentration in the bulk adjoining the surface determines the electrostatic potential Ψ. For the band bending condition, the interface Fermi energy rests 0.5 eV above the valence band maximum E_v, independent of time and temperature.

This latter condition represents an approximation for computational convenience; experiments show[15] that the degree of band bending actually varies with both time and temperature. Just after implant and before annealing, E_f lies 0.40 $\pm$0.02 eV above E_v. Two distinct kinetic regimes characterize the subsequent evolution of band bending. Between roughly 300 and 500 °C, the band bending increases to 0.56 eV, following first order kinetics with a rate constant $k_{\text{low}}=(2.4\times 10^{1\pm 0.1}\ \text{min}^{-1})\exp(-0.20\pm 0.02\ \text{eV/kT})$. Above roughly 750 °C, the band bending decreases to zero, again with first order kinetics and a rate constant $k_{\text{high}}=(4.9\times 10^{3\pm 0.1}\ \text{min}^{-1})\exp(-0.89\pm 0.02\ \text{eV/kT})$. A typical "spike" annealing program first subjects the interface to about 0.5 min of treatment near 600 °C, during which time the band bending evolves slightly upward with a time constant of 0.7 min. The program then employs a rapid ramp up to roughly 1050 °C, followed by immediate quenching back to room temperature. The main spike has a full width at half maximum on the order of 5 s, which is negligibly small compared to the time constant of 0.7 min for band bending disappearance at 1050 °C. Thus, during a typical annealing program the band bending is about 0.50 eV near the top of the spike where most diffusion takes place.

Note that with the high implantation levels assumed here, the host silicon has reached a state of degenerate doping. No corrections were made for such effects in the modeling. Also, the calculated space charge regions are very narrow: on the order of 1 nm. There is a mean electric field assumption that tacitly underlies the simulations; that is, a space charge region is assumed to be well defined and uniform everywhere on the surface. It may be asked whether this assumption properly applies in the presence of the high doping concentrations after implantation. As an example, Lu *et al.*[41] have shown that at carrier concentrations significantly above $10^{18}\ \text{cm}^{-3}$ in GaAs, optical photoreflectance spectra at the E_0 transition disappear. This phenomenon was attributed to spatial fluctuations in the depth of the space charge region, which becomes comparable to random variations in the spacing of dopant atoms. Thus, the one-dimensional continuum treatment employed here should be considered as an approximation. Possible charge compensation due to ion-geneated defects is not considered either. However, these various approximations are unlikely to change the qualitative effects of surface band bending; indeed, the dopant pile-up effects to be described below accord well in their spatial extent with those reported by Shima *et al.*[9]

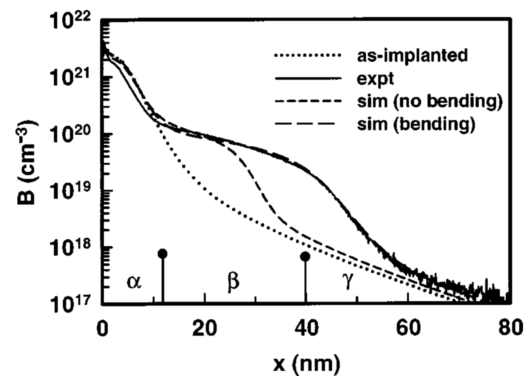

FIG. 1. Simulation fits to a typical experimental TED profile. Three regions (α,β,γ) are labeled for convenience of description in the text. Combination of a surface sink with $S=2\times 10^{-5}$ and band bending yields good fit to experiment, mimicking an essentially perfect reflecting boundary condition for interstitials. The sink condition alone results in a much poorer fit with a shallower junction.

III. RESULTS AND DISCUSSION

A. Profile shape and junction depth

Figure 1 shows simulated boron profiles in comparison with a typical experiment. The figure indicates that incorporation of band bending in concert with a best-fit value of $S=2\times 10^{-5}$ for both B_i and Si_i matches the experimental profile quite well—the only significant difference being a small difference in the width of the profile in the high-concentration α region near the surface. Matches of similar quality were obtained for other experimental data at different peak temperatures and ramp rates.

Figure 1 also shows that exclusion of band bending effects greatly degrades the quality of the fit, mainly due to substantially reduced TED. Increasing the value of S even in the presence of band bending leads to a similar result. However, the combination of band bending and modest-sink boundary conditions yields an effective boundary condition for interstitials that is almost perfectly reflecting. A primary effect of band bending is therefore to increase junction depth.

B. Dopant pile-up

A considerable body of literature data suggests that boron can exhibit apparent "uphill diffusion" behavior.[9,13,42–45] In some cases, pile-up has been observed in the vicinity of a surface or interface,[9,42,44] sometimes within 1 nm of the surface. Such peaks impose a severe test of secondary-ion-mass spectroscopy (SIMS). Wang *et al.* concluded that their observed pile-up was an artifact,[46] probably caused by surface oxygen. However, Shima *et al.*[9] employed SIMS conducted from the front and back sides of implanted specimens to conclude that the pile-up observed in their data within 0.6 nm of the surface was genuine. Such effects have been suggested to result from implantation-induced gradients in interstitial concentration due to localized interstitial clustering or

Downloaded 10 Aug 2007 to 130.126.226.215. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

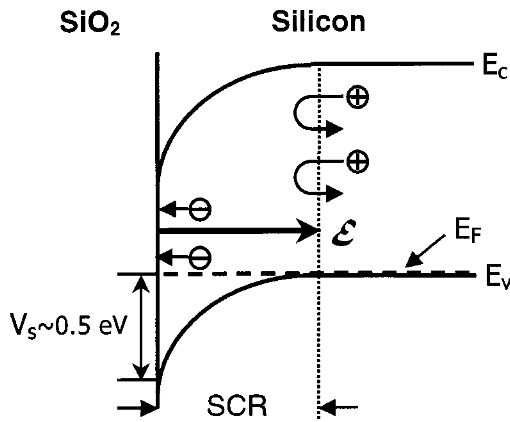

FIG. 2. Schematic potential energy diagram for electrons in *p*-type silicon. Defects at the Si/SiO_2 interface absorb positive charge from the underlying bulk, creating a narrow space charge region, and a corresponding electric field $\mathcal{E}$ that points into the bulk. The field repels positively charged interstitials. Interstitials created from clusters sufficiently close to the surface can be negatively charged (or neutral), however, because of the local position of the Fermi level near midgap. These interstitials move with ease toward the surface.

related effects.[13] However, process simulators have been unable to reproduce surface or interface pile-up effects based on this picture.[9]

Our simulations indicate that pile-up can indeed take place, and highlights a new mechanism to show how it happens. During annealing, interstitials of boron and silicon are liberated from clusters. The Fermi level within the 20% of the space charge region closest to the interface lies sufficiently high above the valence band maximum that locally created boron interstitials take on a negative charge, rather than positive. (The ionization level used here is at $E_v + 0.33\,\mathrm{eV}$.) In a similar way, silicon interstitials take on a neutral, rather than positive, charge. The electric field shown in Fig. 2 pulls the boron interstitials quite strongly toward the surface, while the neutral silicon interstitials diffuse toward the surface uninhibited. Boron interstitials moving toward the surface can be sequestered in the lattice by kick-in reactions, however. Silicon interstitials suffer such sequestration less often because the lattice consists many of Si with only about 1% boron. Thus, the silicon interstitials are much more sensitive to the presence of the surface sink than boron interstitials, and the silicon interstitial concentration decreases substantially. Boron that kicks into the lattice is therefore much more likely to remain there in electrically active form, instead of being converted back to interstitial form by silicon interstitials.

Figure 3 illustrates these effects. Boron piles up within 0.4 nm of the interface; the distance compares favorably with the 0.6 nm observed by Shima *et al.*[9] Figure 3 shows that no pile-up occurs if the boron interstitial charge state varies $+/0$ instead of $+/-$. Note that when pile-up takes place, the profile for total boron actually exhibits two maxima: a sharp one at the interface and a much broader one 1.5–2 nm deeper. Substitutional boron increases monotonically toward the interface and reaches concentrations near $10^{21}\,\mathrm{cm}^{-3}$—well above the solubility limit. If this region is not consumed by subsequent silicidation steps during contact formation, the

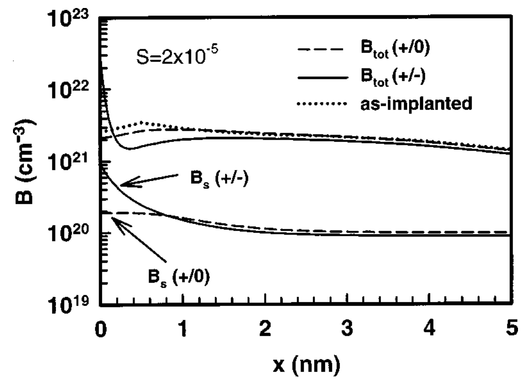

FIG. 3. Comparison of simulated profiles of substitutional boron and total boron within 5 nm of the interface for two different possible charge populations of boron interstitials: $+/0$ and $+/-$. For the $+/-$ case, dopant pile-up at the interface occurs, with substitutional boron concentrations near the interface elevated by a factor of 5.

pile-up presumably has favorable consequences for contact resistance.

Figure 4 contrasts near-surface boron profiles for cases in which band bending is turned on and off. Pile-up occurs only in the presence of band bending, and concentrations of both substitutional and total boron reach interface concentrations nearly an order of magnitude above the flat-band case.

Two other literature reports confirm the observations and explanations we have offered. Pao, Hierl, and Cooper[47] observed near-surface pile-up of beryllium in *p*-type GaAs during diffusional broadening of layers doped via molecular beam epitaxy. These workers did little modeling, but explicitly attributed the pile-up to surface band bending effects, which are very difficult to avoid with GaAs. The postulated mechanism differed from that presented here, however. Beryllium was said to pile up near the outer reaches of the surface space charge region due to bottlenecking of charged mobile beryllium by a repulsive electric field. We indeed observe such repulsion at the edge of the space charge region, but the repulsion leads to increased junction depths, not pile-up. Pile-up originates instead from the interplay of B and Si interstitials through kick-in and kick-out, together with charge state statistics that change close to the surface.

Privitera *et al.*[48] and Mannino[49] observed near-surface pile-up of B implanted into Si at lower doping levels (near

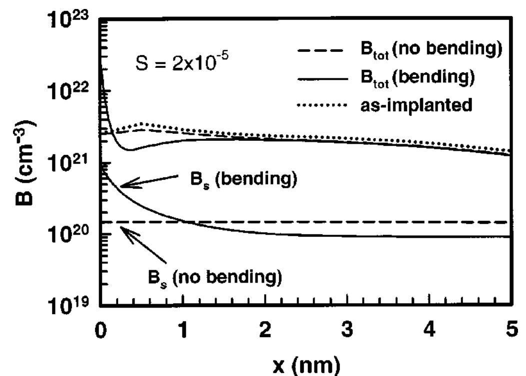

FIG. 4. Comparison of simulated boron profiles within the first 5 nm of the interface in the presence and absence of band bending. (B_i varies as $+/-$).

Downloaded 10 Aug 2007 to 130.126.226.215. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

$2\times10^{18}\,cm^{-3}$) than reported here. Pile-up was observed, however, only when the surface was exposed to plasma-based ion bombardment before annealing. The authors postulated with little evidence that plasma-generated bulk damage accounts for the pile-up. However, the pile-up depth was much narrower than the quoted plasma damage depth. We suggest instead that the pile-up resulted from plasma-induced oxygen removal that left a nearly atomically clean surface (or a damaged $Si-SiO_2$ interface) during annealing, leading to band bending.

C. Relation to boride enhanced diffusion

Boride enhanced diffusion (BED)[50,51] represents an enhancement of boron TED sometimes observed for very high-dose, low-energy implants. The enhancement has been attributed to Si interstitial injection into the bulk from a surface silicon boride phase, and to a boron flux[52] from the high boron concentration gradient near the surface. However, neither of these mechanisms explains dopant pile-up near the interface.

Our results suggest an alternate mechanism that explains BED behavior: band bending. Both Agarwal *et al.*[50] and Cowern *et al.*[51] observed formation of a surface silicon boride phase SiB_y in connection with BED. Silicon boride is a ceramic that can exist in several phases such as SiB_4, SiB_6, SiB_{6-x}, SiB_{6+x}, and $Si_{11}B_{31}$.[53] Thus, when the boride forms there is no longer a single $Si-SiO_2$ interface near the surface but possibly two separate interfaces of $Si-SiB_y$ and SiB_y-SiO_2. Electrically active defect states could easily exist at either interface, leading to band bending and therefore to increased levels of TED and dopant pile-up as described above. The band bending induced by the boride could conceivably be larger or exist under a broader range of processing conditions than bending in the absence of boride, thereby making TED and dopant pile-up appear more pronounced for high-dose, low-energy conditions.

D. Other Influences on interface band bending

The results reported here were based upon experiments in which band bending was measured in ultrahigh vacuum after implantation. Band bending can still exist under other processing conditions, however. For example, annealing is sometimes performed in a gas ambient that contains trace amounts of oxygen (~a few tens of ppm).[54] The oxygen promotes the growth of SiO_2; oxide growth generates on the order of $10^{12}\,cm^{-2}$ electrically active interface states[55,56] while it occurs. (These states disappear when the oxygen flow stops under annealing conditions.) To our knowledge, the band bending has not been measured under conditions that typify annealing, but the magnitude is probably comparable to that assumed in the present work. Dispensing with a screen oxide does not significantly change the situation; an atomically clean Si(100) surface still supports band bending on the order of 0.4 eV.[15,57–59]

IV. CONCLUSION

The present paper quantitatively confirms via modeling the qualitative prediction made elsewhere[15] that near-surface band bending can increase transistor junction depth during processing. The results have also identified another consequence of such band bending: the pile-up of dopant at the interface. Such pile-up has proven elusive to measure quantitatively because of the severe strains put upon existing methods for metrology. The situation has been clouded by lack of a firm theoretical underpinning to explain this effect. The present paper offers such an underpinning, and in the meantime helps to reconcile conflicting literature regarding the annihilation probability for interstitials at $Si-SiO_2$ interfaces. Experiments in which band banding is present will exhibit much lower annihilation probabilities than experiments at flat band. Clearly, band bending needs to be monitored during experiments aimed at determining the annihilation probabilities. The present work helps to deconvolute these effects, and thereby offers by best estimates yet for the general magnitude of these probabilities. The numbers are rather small—on the order of 10^{-5}.

ACKNOWLEDGMENTS

This work was supported by NSF (CTS 98-06329 and CTS 02-03237) and by International Sematech.

[1] R. B. Fair, J. J. Wortman, and J. Liu, J. Electrochem. Soc. **131**, 2387 (1984).
[2] P. M. Fahey, P. B. Griffin, and J. D. Plummer, Rev. Mod. Phys. **61**, 289 (1989), and references within.
[3] P. A. Stolk, H.-J. Gossman, D. J. Eaglesham, D. C. Jacobson, C. S. Rafferty, G. H. Gilmer, M. Jaraiz, J. M. Poate, H. S. Luftman, and T. E. Haynes, J. Appl. Phys. **81**, 6031 (1997), and references within.
[4] G. Mannino, P. A. Stolk, N. E. B. Cowern, W. B. de Boer, A. G. Dirks, F. Roozeboom, J. G. M. van Berkum, P. H. Woerlee, and N. N. Toan, Appl. Phys. Lett. **78**, 889 (2001).
[5] R. B. Fair, *Rapid Thermal Processing* (Academic, San Diego, 1993).
[6] N. E. B. Cowern, D. Alquier, M. Omri, A. Claverie, and A. Aejim, Nucl. Instrum. Methods Phys. Res. B **148**, 257 (1999).
[7] H.-H. Vuong, C. S. Rafferty, S. A. Eshraghi, J. Ning, J. R. McMacken, S. Chaudhry, J. McKinley, and F. A. Stevie, J. Vac. Sci. Technol. B **18**, 428 (2000).
[8] A. Agarwal, H.-J. Gossman, D. J. Eaglesham, L. Pelaz, D. C. Jacobson, T. E. Haynes, and Yu. E. Erokhin, Appl. Phys. Lett. **71**, 3141 (1997).
[9] A. Shima, T. Jinbo, N. Natsuaki, J. Ushio, J.-H. Oh, K. Ono, and M. Oshima, J. Appl. Phys. **89**, 3458 (2001).
[10] E. Napolitani, A. Carnera, E. Schroer, V. Privitera, F. Priolo, and S. Moffatt, Appl. Phys. Lett. **75**, 1869 (1999).
[11] M. E. Law, Y. M. Haddara, and K. S. Jones, J. Appl. Phys. **84**, 3555 (1998).
[12] S. Chakravarthi and S. T. Dunham, J. Appl. Phys. **89**, 3650 (2001).
[13] S. C. Jain, W. Schoenmaker, R. Lindsay, P. A. Stolk, S. Decoutere, M. Willander, and H. E. Maes, J. Appl. Phys. **91**, 8919 (2002) and references within.
[14] M. McEllistrem, G. Haase, D. Chen, and R. J. Hamers, Phys. Rev. Lett. **70**, 2471 (1993).
[15] K. Dev, M. Y. L. Jung, R. Gunawan, R. D. Braatz, and E. G. Seebauer, Phys. Rev. B **68**, 195311 (2003).
[16] W.-C. Lee, S.-G. Lee, and K. J. Chang, J. Phys.: Condens. Matter **10**, 995 (1998).
[17] G. D. Watkins, Phys. Rev. B **12**, 5824 (1975).
[18] W. Windl, M. M. Bunea, R. Stumpf, S. T. Dunham, and M. P. Masquelier, Phys. Rev. Lett. **83**, 4345 (1999).
[19] M. Hakala, M. J. Puska, and R. M. Niemenen, Phys. Rev. B **61**, 8155 (2000).

Downloaded 10 Aug 2007 to 130.126.226.215. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp

[20] M. Y. L. Jung, R. Gunawan, R. D. Braatz, and E. G. Seebauer (unpublished).
[21] M. Y. L. Jung, R. Gunawan, R. D. Braatz, and E. G. Seebauer, J. Electrochem. Soc. **151**, G1 (2004).
[22] R. Gunawan, M. Y. L. Jung, R. D. Braatz, and E. G. Seebauer, J. Electrochem. Soc. **150**, G758 (2003).
[23] R. Gunawan, M. Y. L. Jung, R. D. Braatz, and E. G. Seebauer, J. Process Control **14**, 270 (2003).
[24] M. Y. L. Jung, R. Gunawan, R. D. Braatz, and E. G. Seebauer, J. Electrochem. Soc. **150**, G838 (2003).
[25] See Mark Law: http://www.swamp.tec.ufl.edu.
[26] W. Jüngling, P. Pichler, S. Selberherr, E. Guerrero, and H. W. Pötzl, IEEE Trans. Electron Devices **32**, 156 (1985).
[27] R. D. Harris, J. L. Newton, and G. D. Watkins, Phys. Rev. Lett. **48**, 1271 (1982), and references within.
[28] W. A. Harrison, Phys. Rev. B **57**, 9727 (1998).
[29] I. D. Sharp, H. H. Silvestri, H. Bracht, S. P. Nicols, J. W. Beeman, J. L. Hansen, A. Nylandsted Larsen, and E. E. Haller, Mater. Res. Soc. Symp. Proc. **719**, F433-8 (2002); H. Bracht, H. H. Silvestri, I. D. Sharp, S. P. Nicols, J. W. Beeman, J. L. Hansen, A. Nylandsted Larsen, and E. E. Haller, *Proc. 26th International Conference on the Physics of Semiconductors* (ICPS-26), Edinburgh, July 29–Aug. 2, 2002; paper C3.8 (Institute of Physics, Bristol, UK, 2002).
[30] M. Uematsu, J. Appl. Phys. **82**, 2228 (1997).
[31] M. Y. L. Jung, R. Gunawan, R. D. Braatz, and E. G. Seebauer (unpublished).
[32] J. A. Van Vechten, in *Handbook on Semiconductors*, Vol. 3, edited by S. P. Keller (North Holland, New York, 1980).
[33] J. A. Van Vechten and C. D. Thurmond, Phys. Rev. B **14**, 3539 (1976); **14**, 3551 (1976).
[34] For a review, see D. V. Lang, Annu. Rev. Mater. Sci. **12**, 377 (1982).
[35] P. T. Landsberg, *Recombination in Semiconductors* (Cambridge Press, Cambridge, 1991).
[36] H.-H. Vuong, C. S. Rafferty, S. A. Eshraghi, J. Ning, J. R. McMacken, S. Chaudhry, J. McKinley, and F. A. Stevie, J. Vac. Sci. Technol. B **18**, 428 (2000).
[37] R. B. Fair, IEEE Trans. Electron Devices **20**, 466 (1999).
[38] S. Solmi, F. Baruffaldi, and R. Canteri, J. Appl. Phys. **69**, 2135 (1999).
[39] G. Mannino, S. Whelan, E. Schroer, V. Privitera, P. Leveque, B. G. Svensson, and E. Napolitani, J. Appl. Phys. **89**, 5381 (2001).
[40] See M. Uematsu, J. Appl. Phys. **84**, 4781 (1998) and references within.
[41] C. R. Lu, R. Anderson, D. R. Stone, W. T. Beard, R. A. Wilson, T. F. Keuch, and S. L. Wright, Phys. Rev. B **43**, 11791 (1991).
[42] C. M. Harish, V. Kumar, and A. Prabhakar, Jpn. J. Appl. Phys., Part 1 **31**, 1287 (1992).
[43] M. D. Giles, Appl. Phys. Lett. **62**, 1940 (1993).
[44] H. C.-H. Wang, C. C. Wang, C. S. Chang, T. Wang, P. B. Griffin, and C. H. Diaz, IEEE Electron Devices Lett. **22**, 65 (2001).
[45] R.-D. Chang, H.-P. Chiang, H.-W. Liu, L.-W. Ho, P.-C. Chiang, J.-R. Tsai, and J. Lin, Jpn. J. Appl. Phys., Part 1 **39**, 6136 (2000).
[46] T.-S. Wang, A. G. Cullis, E. J. H. Collart, A. J. Murrell, and M. A. Foad, Appl. Phys. Lett. **77**, 3586 (2000).
[47] Y.-C. Pao, T. Hierl, and T. Cooper, J. Appl. Phys. **60**, 201 (1986); Y.-C. Pao, J. Cryst. Growth **201/202**, 202 (1999).
[48] V. Privitera, F. Priolo, G. Mannino, S. U. Campisano, A. Carnera, G. Arena, and C. Spinella, Appl. Phys. Lett. **71**, 1834 (1997).
[49] G. Mannino, F. Priolo, V. Privitera, V. Raineri, C. Spinella, E. Napolitani, A. Camera, G. Arena, A. Messina, and C. Rapisarda, J. Appl. Phys. **84**, 6628 (1998).
[50] A. Agarwal, H.-J. Gossman, D. J. Eaglesham, S. B. Herner, A. T. Fiory, and T. E. Haynes, Appl. Phys. Lett. **74**, 2435 (1999).
[51] N. E. B. Cowern, M. J. J. Theunissen, F. Roozeboom, and J. G. M. van Berkum, Appl. Phys. Lett. **75**, 181 (1999).
[52] S. T. Dunham, S. Chakravathi, and A. H. Gencer, *Proceedings of the International Electron Devices Meeting*, San Francisco, CA, December 6–9, (IEEE, Piscataway, NJ, 1998).
[53] N. Takashima, A. Noriyuki, Y. Azuma, and J. I. Matsushita, Mater. Res. Soc. Symp. Proc. **604**, 233 (2000).
[54] W. Lerch, M. Glueck, N. A. Stolwijk, H. Walk, M. Schaefer, S. D. Marcus, D. F. Downey, and J. W. Chowe, J. Electrochem. Soc. **146**, 2670 (1999).
[55] A. T. Fiory, J. Zhang, P. Frisella, J. Hebb, and A. Agarwal, *Rapid Thermal and Other Short-time Processing Technologies II*, edited by F. Roozeboom, J. C. Gelpey, M. C. Ozturk, K. Reid, D. L. Kwong, Electrochemical Society Proceedings, Vol. PV2000-9 (Electrochemical Society, Pennington, NJ, 2000) p. 215.
[56] B. J. O'Sullivan, P. K. Hurley, C. Leveugle, and J. H. Das, J. Appl. Phys. **89**, 3811 (2001).
[57] F. J. Himpsel, P. Heimann, T.-C. Chiang, and D. E. Eastman, Phys. Rev. Lett. **45**, 1112 (1980).
[58] F. G. Allen and G. W. Gobeli, Phys. Rev. **127**, 150 (1962).
[59] F. J. Himpsel, G. Hollinger, and R. A. Pollak, Phys. Rev. B **28**, 7014 (1983).

Downloaded 10 Aug 2007 to 130.126.226.215. Redistribution subject to AIP license or copyright, see http://jap.aip.org/jap/copyright.jsp