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Atomistic modeling of F_nV_m complexes in pre-amorphized Si

Pedro Lopez [a,*], Lourdes Pelaz [a], María Aboy [a], G. Impellizeri [b], S. Mirabella [b], F. Priolo [b], E. Napolitani [c]

[a] Departamento de Electricidad y Electrónica, Universidad de Valladolid, Campus Miguel Delibes s/n, 47011, Valladolid, Spain
[b] MATIS CNR-INFM and Dipartimento di Fisica ed Astronomia, Università di Catania, Via S. Sofia 64, 95123 Catania, Italy
[c] MATIS CNR-INFM and Dipartimento di Fisica, Università di Padova, Via Marzolo 8, 35131 Padova, Italy

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ABSTRACT

The co-implantation of F and B in pre-amorphized Si has been proved to be beneficial for the fabrication of ultrashallow junctions due to a remarkable reduction of B diffusion. This is attributed to the presence of fluorine-vacancy (F–V) complexes after regrowth, acting as annihilation centers for Si interstitials. Whereas the resulting F profile in the recrystallized layer can be easily determined by chemical profiling, the vacancy distribution, which has a strong influence on B diffusion, can only be indirectly estimated. In this work, atomistic simulations have been used to analyze several aspects that can affect the efficiency of F–V complexes on Si interstitials annihilation, by considering the effects on B diffusion and the evolution of F profiles. The vacancy content of the complexes, determined by the F/V ratio, and the complex size play an important role on B redistribution. The existence of a recombination barrier for the interaction of a Si interstitial and some F–V complexes, as proposed by theoretical calculations, and its influence on the Si interstitial annihilation efficiency of the complexes are also analyzed.

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1. Introduction

The evolution of complementary metal oxide semiconductor technology has followed the path of device scaling. One of the most difficult challenges in the miniaturization of transistors is the formation of ultrashallow junctions. For p-type junctions, the co-implantation of F^+ and B^+ in pre-amorphized Si followed by the solid phase epitaxial (SPE) regrowth technique can significantly reduce B diffusion, improving junction features [1,2]. The ability of F in reducing B diffusion has been attributed to the existence of fluorine–vacancy (F_nV_m) complexes after the recrystallization of the F-enriched amorphous layer [2]. These complexes represent a reservoir of vacancies (V's) located in the regrown layer that may act as annihilation centers for Si interstitials (I's) released from the end of range defects during subsequent thermal treatments. This hypothesis is supported by the high affinity of F with V's, as indicated by theoretical calculations [3,4] and by the direct transmission electron microscopy (TEM) observation of bubbles in the high concentration region of a F profile [5].

Although nowadays there is an agreement on the role of F_nV_m complexes on B diffusion, little information is available about the characteristics of these complexes. The average ratio between the number of F atoms and vacancies (F/V ratio) in F_nV_m complexes determines the amount of V's that exists along the F profile, which has a direct impact on B diffusion. $F_{3n}V_n$ complexes with n being 1 and/or 2 were proposed by Abdulmalik et al. by means of positron annihilation spectroscopy (PAS), a technique that is sensitive to open volume defects, and secondary ion mass spectrometry (SIMS) characterization of pre-amorphized Si wafers implanted with 10^{15} cm^{-2} F^+ at 10 keV [6]. By estimating the number of F-related traps for Si I's in pre-amorphized samples implanted with F^+, Cowern et al. proposed a F/V ratio of 2:1 or 3:1 [7]. A F/V ratio of 5:1 after SPE, that increased to 8:1 after a Si^+ implant and annealing, was estimated by Boninelli et al. combining TEM analysis and SIMS characterization of pre-amorphized samples implanted with a high F^+ dose [5]. Lopez et al. reported that $F_{2m+2}V_m$ complexes, in which F atoms are decorating the dangling bonds left by the V's, were the most abundant by means of ab-initio calculations of small F_nV_m complexes [4,8].

Using kinetic Monte Carlo (KMC) simulations we have analyzed different aspects related to F_nV_m complexes that can influence their ability to act as annihilation centers for Si I's and to reduce B diffusion.

2. Experiment and simulation description

Our analysis is based on some experimental results reported in Ref. [2]. A dose of 4×10^{14} cm^{-2} F^+ was implanted at 100 keV in a pre-amorphized layer. A molecular beam epitaxy grown B spike, covered by F profile and with a concentration of $\sim 2 \times 10^{18}$ cm^{-3},

* Corresponding author.
E-mail address: pedrol@ele.uva.es (P. Lopez).

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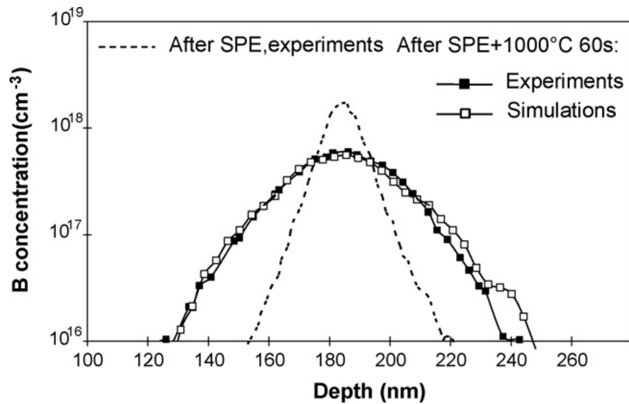

Fig. 1. Experimental and simulated B profiles after SPE and annealing at 1000 °C for 60 s in equilibrium conditions. The experimental B distribution after SPE is also shown, taken from Ref. [2].

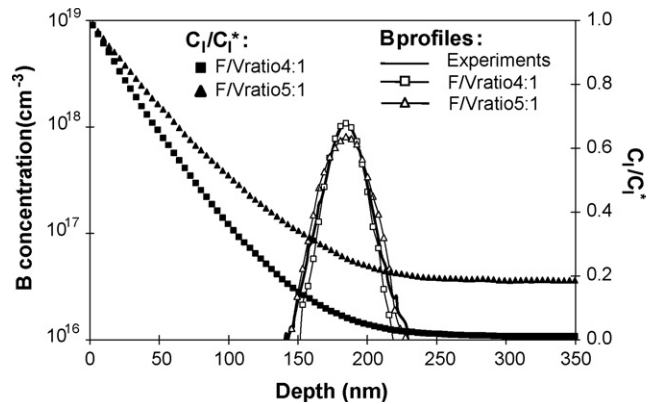

Fig. 2. Simulated B profiles (open symbols) and Si I's undersaturation (C_I/C_I^*) (solid symbols) after SPE and 1000 °C 60 s anneal in samples containing V's distributions that represent the V's stored in F_nV_m complexes with a F/V ratio of 4:1 (squares) and 5:1 (triangles). The experimental B profile after SPE and 1000 °C 60 s anneal is included for reference (solid line).

was used as a diffusion marker. A carbon-rich layer was inserted between the F profile and the end-of-range (EOR) damage to act as a barrier for Si I's injected from the residual defects during annealing. In these conditions the only source of Si I's is the surface, which sets the equilibrium Si I's concentration at the annealing temperature. After regrowth at 700 °C an additional anneal at 1000 °C for 60 s was used to observe B diffusion and the evolution of F profile.

Simulations are performed using the atomistic simulator DADOS, based on the KMC approach [9]. We consider that the surface acts as a perfect sink for point defects. Si I's and V's are thermally generated from the surface at a rate determined by the annealing temperature and the equilibrium values reported by Bracht et al. [10]. In Fig. 1 we have plotted the experimental and simulated B profiles after SPE and 1000 °C 60 s anneal in equilibrium conditions (without F or V's) as a reference.

In our simulations we use the experimental B and F profiles after SPE as initial profiles and we simulate the 1000 °C anneal. The capture volume of F_nV_m complexes is determined only by the number of V's they contain, the F atoms being located within the volume defined by the V's. F_nV_m complexes dissolution takes place by the emission of V's and F atoms from the complexes, according to their binding energies, and by the recombination of a vacancy by a free Si interstitial. We assume a migration energy for F diffusion of 0.4 eV as estimated from ab-initio calculations [4], being F evaporated when it reaches the surface.

3. Results

The F/V ratio in F_nV_m complexes can be roughly estimated by considering a V profile, which represents the V's stored in the complexes. This profile is obtained by scaling the experimental F profile after SPE by the factor corresponding to the F/V ratio until the simulation results fit the experimental B distribution. The excess of V's introduced in this way acts as recombination centers for the Si I's injected from the surface. We have analyzed several F/V ratios, including those proposed in literature for other experiments [5–8], but in our case we obtain the best results in terms of B diffusion for F/V ratios of 4:1 and 5:1.

In Fig. 2 we show the experimental B profile after annealing and those obtained in our simulations considering the F/V ratios 4:1 and 5:1. For F/V = 4:1 our results slightly underestimate B diffusion, which indicates that the number of V's considered is too high. For F/V = 5:1 we obtain more B diffusion than in experiments. The Si interstitial undersaturation as a function of depth is also shown in the figure. This is calculated as the number of Si interstitial hops in these simulations, which is proportional to the concentration of free Si I's, divided by the number of Si interstitial hops in equilibrium conditions. The Si interstitial concentration presents the equilibrium value at the surface, since the surface generates Si I's at the equilibrium rate, but a strong gradient is observed as they diffuse into the bulk due to their recombination with V's. The interstitial undersaturation at the location of the B marker depends on the V dose existing in the sample, causing a different amount of B diffusion as it can be seen for the two F/V ratios simulated.

The V profiles associated to the F/V ratios of 4:1 and 5:1 before and after annealing at 1000 °C for 60 s are plotted in Fig. 3. The experimental F profiles are also included for comparison. The initial V distribution used in simulations corresponds to the experimental F profile divided by 4 or 5 according to the F/V ratio. After annealing a large V dose has disappeared from the near surface region (much more than the experimental F profile) due to their annihilation caused by the Si I's flux coming from the surface.

A B diffusion similar to that observed in experiments can be obtained (Fig. 2) by considering the presence of a given amount of initial V's that mirror (with some scaling factor) the F profile. However, the evolution of the V profile shows too much erosion at the surface compared to the experimental F profile (Fig. 3). This observation seems to indicate that to account for the experimental B diffusion and the evolution of F profile, the impact of the inter-

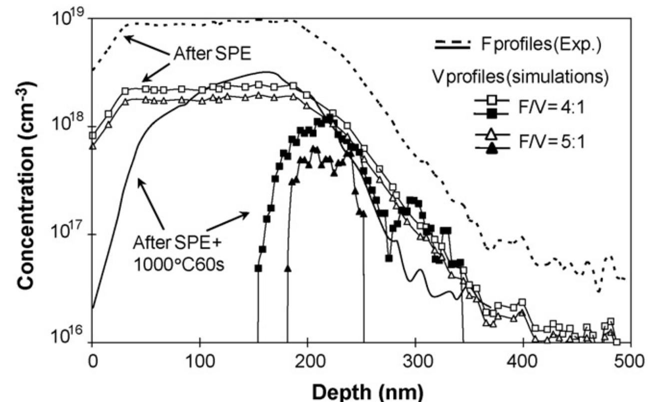

Fig. 3. Simulation results of the evolution during 1000 °C 60 s anneal of the vacancy profile associated to the experimental F profile, considering a F/V ratio of 4:1 (squares) and 5:1 (triangles). The experimental F profiles are also shown (lines) (Ref. [2]). The dashed line and open symbols represent F or V profiles after SPE, respectively, whereas the solid line and solid symbols indicate the profiles after SPE and 1000 °C 60 s anneal.

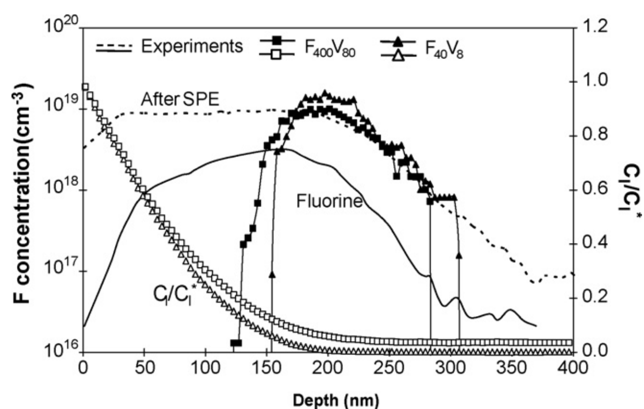

Fig. 4. Simulated F profiles (solid symbols) and Si interstitial undersaturation (C_I/C_I^*) (open symbols) after SPE and 1000 °C 60 s anneal for $F_{400}V_{80}$ (squares) and $F_{40}V_8$ (triangles) complexes. The experimental F profile after SPE (dashed line) and 1000 °C 60 s anneal (solid line) are plotted for comparison, from Ref. [2].

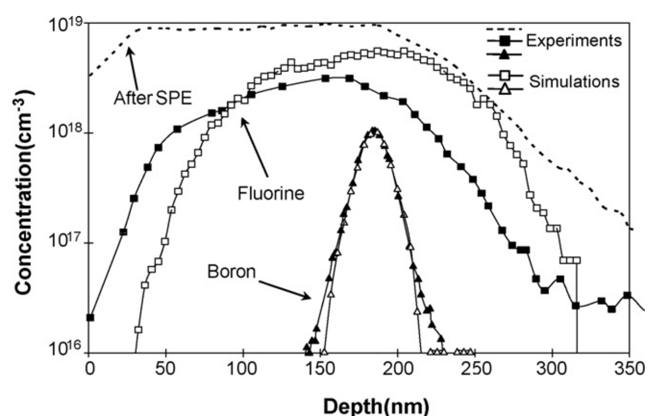

Fig. 5. Simulated F (open squares) and B (open triangles) profiles after SPE and 1000 °C 60 s anneal. The F_nV_m complexes simulated are $F_{100}V_{20}$ keeping a ratio of 5:1. A recombination barrier is considered. The experimental F (solid squares) and B (solid triangles) distributions are also plotted, from Ref. [2]. The dashed line is the experimental F profile just after SPE.

stitial flux on the shallow part of F profile should be reduced. One possibility is to consider that $(F_i)_n$ complexes (with no V's) could be very stable (since they survive at 1000 °C for over 60 s) and thus F could remain in the near surface region when all V's have recombined. However, theoretical calculations indicate that the F_i–F_i pair (F_i, interstitial fluorine) is weakly bound or even unbound [3,4]. Another possibility is to reduce the recombination efficiency of F_nV_m complexes favoring that Si I's can reach deeper positions without recombining with V's retained in the shallow part of F profile. This can be achieved by considering larger complexes with a lower effective capture volume or by assuming an energy barrier for the recombination of Si I's and V's in F_nV_m complexes.

The size of F_nV_m complexes has an influence on the erosion of F profile. We have run simulations considering complexes with two different sizes keeping a F/V ratio of 5:1, that provided good results for B diffusion. In both cases the total number of F atoms and V's in the sample is the same: the only difference is the way they are grouped. F profiles and the Si interstitial undersaturation obtained after 1000 °C 60 s anneal are plotted in Fig. 4. A more pronounced erosion on F profile and a steeper gradient in the Si interstitial undersaturation is observed as the complex size reduces. The probability that a diffusing Si interstitial recombines with a V belonging to a F_nV_m complex depends not only on the F and V concentration but also on the actual interaction volume, i.e. the region around the complex in which particles can interact with it. When a F profile is composed by many small F_nV_m complexes the total capture volume of all complexes is much larger than when the same F concentration is distributed in few complexes with a bigger size. As a consequence, the probability of a Si interstitial recombining with a vacancy in a F_nV_m complex decreases as the complex is larger. Boninelli et al. detected by TEM nanobubbles in regrown a-Si when F concentration exceeds 2×10^{20} cm^{-3} [5]. This observation suggests that rather large complexes could be formed. Nevertheless, complexes large enough to be detected by TEM (detection limit in the order of 2 nm in diameter, approximately corresponding to voids with 200 V's) have only been observed for very high F concentrations.

Ab-initio simulations of small F_nV_m complexes reveal that for some stable configurations the recombination of a V belonging to a complex with a free Si interstitial may lead to a higher energy state [4,11]. This implies the existence of an energy barrier for recombination and that these complexes may be stable even in the presence of Si I's. We have explored this idea to analyze in which conditions a barrier for the recombination of Si I's for generic F_nV_m complexes could exist. We have estimated that a barrier may exist if upon V recombination several F atoms are released, that were bound by more than ~2 eV [12]. The mean binding energy per F atom calculated from ab-initio simulations is approximately −1.9 and −2.2 eV for complexes with one or two V's [11]. These data seem to indicate that the F binding energy increases with the number of V's, although it is difficult to extrapolate from just two values. The experimental evolution during annealing at 1000 °C for 60 s of the F profile resulting after SPE reveals that approximately a 20% of F dose remaining after SPE is still retained in the sample [2]. This shows that F_nV_m complexes are quite stable since they are able to survive a long time at 1000 °C. Based on this observation a rough estimate indicates that the binding energy of F in the complexes could be in the order of ~2.8 eV. Therefore, it may not be unlikely that a barrier for recombination exists if several F atoms are left unbound after V recombination.

We have run a simulation assuming that F and V atoms are tightly bound to the complex and that there exist a recombination barrier. We have considered large complexes, $F_{100}V_{20}$, with a F/V ratio of 5:1, since it provides good results in term of B diffusion. As shown in Fig. 5, the simulation results provide a good fit to the experimental B diffusion, improving also the F profile fitting, since the erosion at the surface is not so pronounced.

4. Conclusions

We have analyzed the factors influencing the Si I's recombination efficiency of F_nV_m complexes that are assumed to be present after the regrowth of F-enriched amorphous Si, by considering the effects on B diffusion and the evolution of the F profile. We have shown that the content of V's in the complexes (determined by the F/V ratio) and the complex size influence the free Si interstitial concentration and F and B distribution. Ab-initio calculations of small F_nV_m complexes indicate that some stable configurations may be stable even in the presence of Si I's. We have generalized this idea and we have proposed that a recombination barrier may exist for some strongly bound F_nV_m complexes in which the recombination of a vacancy leaves several F atoms practically unbound.

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