Si interstitial contribution of F+ implants in crystalline Si

Citation for published version (APA):
López, P., Pelaz, L., Duffy, R., Meunier-Beillard, P., Roozeboom, F., Tak, van der, K., Breimer, P., Berkum, van, J. G. M., Verheijen, M. A., & Kaiser, M. (2008). Si interstitial contribution of F+ implants in crystalline Si. *Journal of Applied Physics*, *103*(9), Article 093538. https://doi.org/10.1063/1.2917297

DOI:
10.1063/1.2917297

Document status and date:
Published: 01/01/2008

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Download date: 04. Oct. 2023

JOURNAL OF APPLIED PHYSICS **103**, 093538 (2008)

Si interstitial contribution of F$^+$ implants in crystalline Si

Pedro López,[1,a)] Lourdes Pelaz,[1] R. Duffy,[2] P. Meunier-Beillard,[2] F. Roozeboom,[3]
K. van der Tak,[4] P. Breimer,[4] J. G. M. van Berkum,[4] M. A. Verheijen,[4] and M. Kaiser[4]
[1]*Departamento de Electricidad y Electrónica, Universidad de Valladolid, Campus Miguel Delibes s/n, 47011 Valladolid, Spain*
[2]*NXP Semiconductors Research, Kapeldreef 75, 3001 Leuven, Belgium*
[3]*NXP Semiconductors Research, High Tech Campus 4, 5656AE Eindhoven, The Netherlands*
[4]*Philips Research Laboratories Eindhoven, High Tech Campus 11, 5656AE Eindhoven, The Netherlands*

(Received 26 October 2007; accepted 5 March 2008; published online 13 May 2008)

The F effect in crystalline Si is quantified by monitoring defects and B diffusion in samples implanted with 25 keV F$^+$ and/or 40 keV Si$^+$. We estimate that about +0.4 Si interstitials are generated per implanted F$^+$ ion, in agreement with the value resulting from the net separation of Frenkel pairs. For short annealings, B diffusion is lower when F$^+$ is coimplanted with Si$^+$ than when only Si$^+$ is implanted, while for longer annealings, B diffusion is higher. This is consistent with a lower but longer-lasting Si interstitial supersaturation set by the additional defects generated by the F$^+$ implant. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2917297]

I. INTRODUCTION

In the fabrication of ultrashallow *p*-type junctions in complementary metal oxide semiconductor technology, B$^+$ has been traditionally coimplanted with F$^+$ because of the technological advantage of using BF$_2^+$. More recently, specially designed cocktail implants combine separate B$^+$ and F$^+$ implants in preamorphized Si to optimize the junction formation.[1] It has been clearly demonstrated that the presence of F inside the recrystallized layer strongly reduces B diffusion.[2,3] This beneficial effect has been related to the formation of F-vacancy complexes (F$_n$$V_m$) during solid phase epitaxial regrowth of the preamorphized layer, acting as annihilation centers for Si interstitials (I's) released from end of range (EOR) defects, reducing Si I's supersaturation, and thus, B diffusion.

The mechanisms governing F behavior in crystalline Si (*c*-Si) and its effect on B diffusion have not been fully elucidated yet. There is not even an agreement about a possible beneficial effect of F$^+$ implantation in *c*-Si. Some experiments indicate that medium energy F$^+$ implants cause B transient enhanced diffusion (TED) although less than that caused by equivalent Si$^+$ or Ne$^+$ implants.[4] Other studies with high energy F$^+$ implants have reported a B diffusion even lower than equilibrium in the vacancy-rich region of the damage profile,[5] but this also occurs for other high energy ion implants.[6] Park *et al.* showed that annealed B profiles of nonamorphizing BF$_2^+$ implants are shallower than the equivalent B implants but they have a higher electrical resistivity.[7] The clarification of the role of F in *c*-Si is important because sometimes, amorphization should be avoided due to the excessive leakage caused by residual EOR defects or because the imperfect recrystallization degrades device performance, as it occurs in thin fin field effect transistor structures.[8] The aim of this work is to elucidate the role of the F$^+$ coimplantation on B diffusion in *c*-Si.

II. EXPERIMENTAL PROCEDURE

In our experiments, two B doped layers were grown by chemical vapor deposition at depths of 120 and 440 nm to act as diffusion markers. B peak concentration was low, approximately 2.5×10^{18} cm^{-3}, to minimize the formation of boron interstitial clusters (BICs). Two different nonamorphizing F fluences (1×10^{14} and 5×10^{14} cm^{-2}) were chosen to analyze the effect of the amount of damage and F fluence on B diffusion. F$^+$ was implanted at 25 keV whose mean projected range (R_p) ($\sim$56 nm) is located close to the position of the shallow B spike. A 40 keV 5×10^{13} cm^{-2} Si$^+$ implant, whose R_p is similar to that of the F$^+$ implants, was also performed alone or combined with one of the two F$^+$ implants to study the effect of F with additional damage. A sample with no implants was used as a reference for equilibrium B diffusion. All samples were annealed at 850 °C for 18, 180, or 1800 s. Secondary ion mass spectrometry (SIMS) was used to analyze B and F profiles and transmission electron microscopy (TEM) to detect the presence of extended defects.

III. RESULTS AND DISCUSSION

SIMS B profiles for the samples implanted with F$^+$, Si$^+$, and F$^+$ plus Si$^+$ after annealing at 850 °C for 18 s are plotted in Fig. 1. We observe that F$^+$ implants alone lead to enhanced B diffusion compared to equilibrium, which indicates that a F$^+$ implant generates a Si I's supersaturation, as previously reported.[4] However, for this short annealing, B diffusion is reduced when a F$^+$ implant is added to the Si$^+$ implant, compared to the samples that are only implanted with Si$^+$. This reduction is observed in both B spikes and for the two F$^+$ fluences but it is clearer for the lower F$^+$ fluence. When 10^{14} cm^{-2} F$^+$ is coimplanted with Si$^+$, B diffusivity in the deep B spike is about 0.6 times that obtained in the sample implanted only with Si$^+$. The situation changes as the annealing proceeds, as we can see in the SIMS profiles plotted in Fig. 2 corresponding to 180 s annealings. For the lower F$^+$

[a)] Author to whom correspondence should be addressed. Electronic mail: pedrol@ele.uva.es.

0021-8979/2008/103(9)/093538/4/$23.00

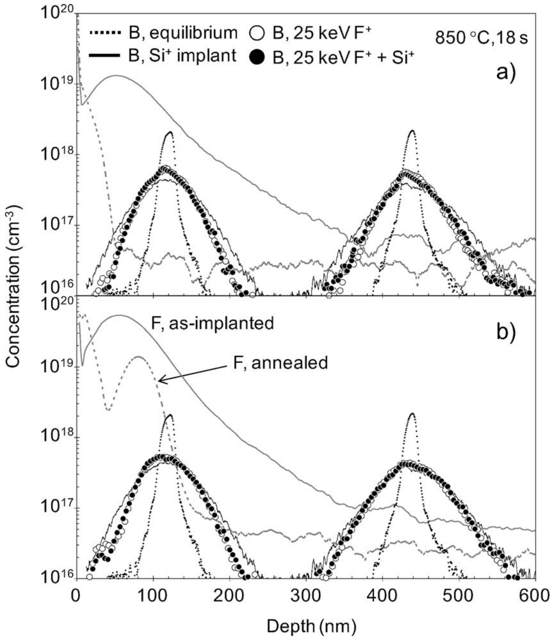

FIG. 1. B SIMS profiles after annealing at 850 °C for 18 s in the samples implanted with 5×10^{13} cm^{-2} 40 keV Si$^+$ (solid black line), 25 keV F$^+$ (open symbols), or coimplanted with Si$^+$ and F$^+$ in the same conditions (solid symbols). Two F fluences were implanted: (a) 10^{14} cm^{-2} F$^+$ and (b) 5×10^{14} cm^{-2} F$^+$. The diffused B profiles in equilibrium conditions (dotted black line) are plotted for comparison. The as-implanted and annealed F profiles for both implants are also shown (solid and dotted gray lines).

fluence, the advantage of F$^+$ coimplantation is no longer observed and a higher B diffusion appears when F$^+$ and Si$^+$ are coimplanted compared to the sample only implanted with Si$^+$ (approximately 1.7 times higher). At this time, samples implanted with 5×10^{14} cm^{-2} F$^+$ (alone or coimplanted) present similar B diffusion to the one implanted only with Si$^+$. The B SIMS profiles for 1800 s (not shown) are similar to those at 180 s.

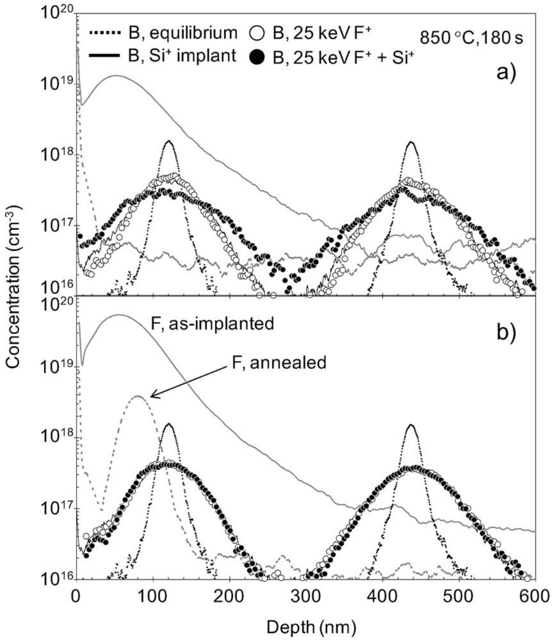

FIG. 2. B SIMS profiles after annealing at 850 °C for 180 s in the samples implanted with 5×10^{13} cm^{-2} 40 keV Si$^+$ (solid black line), 25 keV F$^+$ (open symbols), or coimplanted with Si$^+$ and F$^+$ in the same conditions (solid symbols). Two F fluences were implanted: (a) 10^{14} cm^{-2} F$^+$ and (b) 5×10^{14} cm^{-2} F$^+$. The diffused B profiles in equilibrium conditions (dotted black line) are included. The as-implanted and annealed F profiles are also plotted (solid and dotted gray lines).

The as-implanted and annealed F SIMS profiles are also plotted in Figs. 1 and 2 for 18 and 180 s annealings, respectively. Only the shallow B spike is initially covered by F and a significant fraction of F is lost upon annealing. For the higher F$^+$ implant fluence, there is a F peak located around R_p that remains long. For the 10^{14} cm^{-2} F$^+$ implant, only 24% of F fluence is retained after 18 s annealing and it is located very close to the surface. It has almost completely outgassed after 180 s. Since F rapidly outdiffuses, and theoretical calculations indicate that the F–B interaction is weak,[3] it is unlikely that the immobilization of B atoms by F is responsible for the reduction of B diffusion. It is worthy to note that less B diffusion is observed in the shallow B spike (initially covered by F) than in the deepest one but this also happens for the Si$^+$ implant. This behavior could be explained by the temporal immobilization of B due to the formation of BICs in the damaged region of the F$^+$ or Si$^+$ implants,[9] which reduces the amount of B available for diffusion. The additional damage cascades generated by the F$^+$ coimplantation with Si$^+$ would favor BIC formation in the shallow B spike, and thus, a reduction in B diffusion. In fact, Park *et al.* reported a significantly lower effective solubility of B in BF_{+}^{2} implants compared to equivalent B$^+$ implants.[7] In our experiment, since B concentration is low, only a small B fraction is expected to be in BICs and they would easily dissolve at 850 °C. In any case, the deep B spike is not covered by F or by the implant damage (no BICs are formed) and it also undergoes a reduced B diffusion for short annealing times in samples coimplanted with F$^+$ and Si$^+$ compared to those only implanted with Si$^+$. Therefore, F has a nonlocal effect on B diffusion, which may be attributed to a modification in the Si I's supersaturation set by the defect evolution.

In the sample implanted only with Si$^+$, no defects are observed in TEM images (not shown) after annealing at 850 °C for 18 s. It is known that a 5×10^{13} cm^{-2} 40 keV Si$^+$ implant produces small Si I's clusters and {113} defects that set a high Si I's supersaturation but quickly dissolve.[10] TEM images of the sample coimplanted with Si$^+$ and 10^{14} cm^{-2} F$^+$, included in Fig. 3, show a high defect density after 18 s annealing. After 180 s annealing, most defects have dissolved and only a few {113} defects are visible [Fig. 3(b)]. TEM analysis of the sample implanted with 5×10^{14} cm^{-2} F$^+$ reveals a large number of {113} defects and dislocation loops for 18 s annealing [Fig. 3(c)]. After 1800 s annealing, many dislocation loops still remain [Fig. 3(d)].

An important difference between F$^+$ implantation in amorphous Si (a-Si) and c-Si is that in a-Si, some vacancies (V's) can be retained into the lattice as F_nV_m complexes while excess Si atoms are swept to the surface during regrowth, resulting in a net excess vacancy contribution associated to the presence of F. In c-Si, I's and V's are created in pairs, plus one additional excess Si interstitial per implanted ion if this becomes substitutional (not likely in the case of F).[11] If F_nV_m complexes are formed, the amount of excess

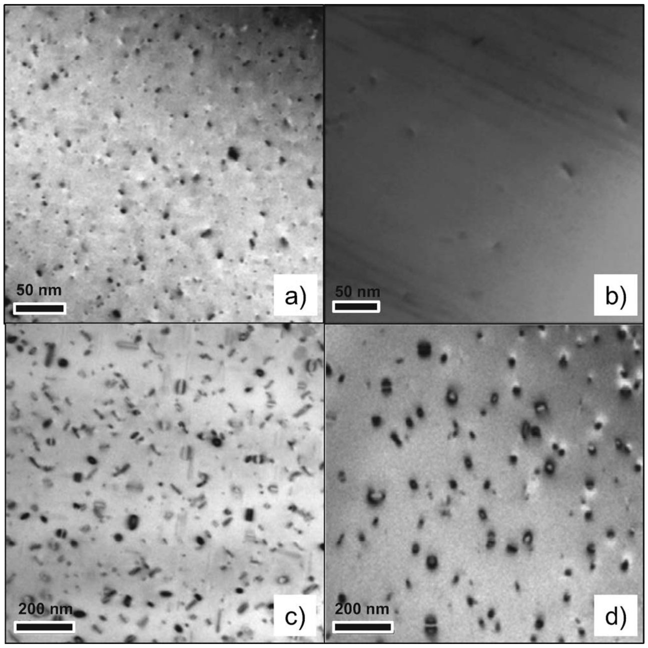

FIG. 3. [(a) and (b)] Plan-view TEM images for 10^{14} cm^{-2} 25 keV F$^+$ plus 5×10^{13} cm^{-2} 40 keV Si$^+$ after annealing at 850 °C for 18 and 180 s, respectively. [(c) and (d)] Plan view TEM images for 5×10^{14} cm^{-2} 25 keV F after annealing at 850 °C for 18 and 1800 s.

Si I's per F atom would correspond to the number of V's retained per F atom (m/n). Frenkel pairs can be locally separated due to the momentum transfer of the energetic incoming ions, and a vacancy-rich region is created near the surface and a Si self-interstitial-rich region deeper.[12] In the Si interstitial-rich region, F_nV_m complexes are not likely to survive because the excess Si I's will easily recombine them[3] and F would outdiffuse or segregate to extended defects. A chemical role of F could be derived from the trapping of Si I's in F_nI_m complexes,[13] although theoretical calculations indicate that F and Si I's are not strongly bound.[3] Some authors suggested the modification of Si self-interstitial defect stability,[14] while others indicated that F did not have an effect on defect evolution.[15] In any case, a change in defect stability or the temporary trapping of Si I's would alter B diffusion during the transient period (while defects or complexes exist), but once defects had been completely annealed out and all Si I's were released, the overall B diffusion should correspond to the excess Si I's generated independently of the stability of defects or complexes where they may have been temporarily stored.[16] An additional contribution of F could be attributed to its transport capability of point defects. If the dominant diffusing species were interstitial F (F_i),[3] F would only transport itself and the implanted ion would outdiffuse without altering the damage balance associated with the Frenkel pair separation. Nevertheless, if the F_i-interstitial pair $(F_i\text{-}I)$ significantly diffused as it has been recently suggested,[17] the presence of F would favor the removal of Si I's, leaving excess V's behind. The contrary would hold if the main diffusing species were the F_i-V pair.

In order to quantify the Si interstitial damage produced by the F$^+$ implant and its net contribution to B diffusion, we have determined from TEM images (according to the quantification method described elsewhere)[18–20] that approximately 2×10^{14} Si I's/cm^2 are stored in the {113} defects and dislocation loops for the 25 keV 5×10^{14} cm^{-2} F$^+$ implant after 18 s annealing (typical error is 20%). The defects observed in TEM images at short times (when defects have ripened enough to be visible but before a significant part of them has dissolved) give an estimate of the initial amount of defects. This value is a lower limit since some defects may not be visible or may have already dissolved. Thus, we experimentally estimate that around 0.4, Si I's per implanted F$^+$ ion are stored in defects. An estimate of the effective number of Si I's can also be derived from diffusion experiments when TED is complete. For the longest annealing time analyzed (defects are completely dissolved), the averaged value of the B diffusivity multiplied by time (which is proportional to the time integrated free Si interstitial concentration) in the deep B spike for the 25 keV 10^{14} cm^{-2} F$^+$ implant alone is about 0.7 times that of the 40 keV 5×10^{13} cm^{-2} Si$^+$ implant, while for the F$^+$ and Si$^+$ coimplantation, this value is equal to 1.7 times that of the Si. Therefore, the contribution of this F$^+$ implant (whose R_p is similar to that of the Si$^+$ implant) is about 0.7 times that of the Si$^+$ implant, although the F$^+$ implant fluence is double the Si fluence. Considering that the effective $+n$ factor for the Si$^+$ implant is approximately +1.3,[12] this indicates that the number of effective Si I's per implanted F$^+$ ion in c-Si is about +0.5, which is significantly lower than unity. Theoretical calculations reveal that F prefers to remain interstitial rather than to occupy a substitutional position,[11] which explains this low value, and why F$^+$ implants produce less TED than similar Si$^+$ or Ne$^+$ implants.[4]

Kinetic Monte Carlo simulations of the 25 keV F$^+$ implant reveal that once the Frenkel pairs have locally recombined, there are approximately 0.4 Si I's per implanted F$^+$ ion in the interstitial-rich region, in good agreement with the values estimated experimentally. Therefore, the net separation between Si I's and the corresponding V's resulting from the F$^+$ implant in c-Si accounts for the presence of Si interstitial-type defects and the measured enhanced B diffusion. This also indicates that F_i has no significant transport capability of additional point defects. Although we cannot rule out a chemical role of F stabilizing extended defects, the additional damage created by the F$^+$ coimplant with Si$^+$ also contributes to the formation of a larger defect density, favoring their growth by the capture of emitted Si I's and setting a lower Si I's supersaturation responsible for the reduced B TED for short annealing times. The coimplantation of Si$^+$ and the lower F$^+$ fluence causes a higher B TED for longer annealings because more Si I's (those generated by both Si$^+$ and F$^+$ implants) have contributed to it. The samples implanted with a higher F$^+$ fluence (5×10^{14} cm^{-2}) do not show more B diffusion than that implanted only with Si$^+$, even for the longest analyzed annealing (1800 s), in spite of the much larger effective Si interstitial fluence contribution for the F$^+$ implant [$\sim2\times10^{14}$ cm^{-2} for F$^+$ (0.4× implant fluence) versus $\sim6.5\times10^{13}$ cm^{-2} for Si$^+$ (1.3× implant fluence)] because many I's still remain stored in stable dislocation loops[21] and have not effectively contributed to enhance B diffusion.

IV. CONCLUSIONS

In summary, from TEM images and B diffusion experiments, we have estimated that approximately +0.4 Si *I*'s are generated per implanted 25 keV F^+ ion, in good agreement with the value resulting from the net separation of Frenkel pairs. Although other effects cannot be completely ruled out, the overall resulting effect of F on B diffusion can be explained on the basis of the defect evolution. The additional Si *I*'s generated by F^+ coimplants contribute to the formation of a larger amount of more stable extended defects, which set a lower but longer-lasting Si interstitial supersaturation. As a result, at short annealing times a reduction of B diffusion is observed, but if the annealing is complete (which is desirable to reduce junction leakage), B diffusion is enhanced by the additional F^+ implant. Our results clearly indicate that F^+ coimplantation with Si^+ (or normally B^+ implant) in *c*-Si causes additional Si interstitial defects and it has an overall negative effect on junction formation.

ACKNOWLEDGMENTS

This work has been funded by the Spanish DGI under Project No. TEC2005–05101 and the JCyL Consejería de Educación y Cultura under Project No. VA070A05.

[1] E. J. H. Collart, S. B. Felch, H. Graoui, D. Kirkwood, S. Tallavarjula, J. A. Van den Berg, J. Hamilton, N. E. B. Cowern, and K. J. Kirkby, Mater. Sci. Eng., B **114**, 118 (2004).

[2] G. Impellizzeri, S. Mirabella, F. Priolo, E. Napolitani, and A. Carnera, J. Appl. Phys. **99**, 103510 (2006).

[3] G. M. Lopez, V. Fiorentini, G. Impellizzeri, S. Mirabella, and E. Napolitani, Phys. Rev. B **72**, 045219 (2005).

[4] H.-H. Vuong, H.-J. Gossman, C. S. Rafferty, H. S. Luftman, F. C. Unterwald, D. C. Jacobson, R. E. Ahrens, T. Boone, and P. M. Zeitzoff, J. Appl. Phys. **77**, 3056 (1995).

[5] H. A. W. El Mubarek, J. M. Bonar, G. D. Dilliway, P. Ashburn, M. Karunaratne, A. F. Willoughby, Y. Wang, P. L. F. Hemment, R. Price, J. Zhang, and P. Ward, J. Appl. Phys. **96**, 4114 (2004).

[6] V. C. Venezia, T. E. Haynes, A. Agarwal, L. Pelaz, H.-J. Gossmann, D. C. Jacobson, and D. J. Eaglesham, Appl. Phys. Lett. **74**, 1299 (1999).

[7] J. Park, Y.-J. Huh, and H. Hwang, Appl. Phys. Lett. **74**, 1248 (1999).

[8] R. Duffy, M. J. H. Van Dal, B. J. Pawlak, M. Kaiser, B. Degroote, E. Kunnen, and E. Altamirano, Appl. Phys. Lett. **90**, 241912 (2007).

[9] L. Pelaz, M. Jaraiz, G. H. Gilmer, H.-J. Gossman, C. S. Rafferty, D. J. Eaglesham, and J. M. Poate, Appl. Phys. Lett. **70**, 2285 (1997).

[10] D. J. Eaglesham, P. A. Stolk, H.-J. Gossman, and J. M. Poate, Appl. Phys. Lett. **65**, 2305 (1994).

[11] M. Diebel and S. T. Dunham, *Si Front-End Junction Formation Technologies*, MRS Symposia Proceedings No. 717 (Materials Research Society, Pittsburgh, 2002), p. C4.5.1.

[12] L. Pelaz, G. H. Gilmer, M. Jaraiz, S. B. Herner, H.-J. Gossmann, D. J. Eaglesham, G. Hobler, C. S. Rafferty, and J. Barbolla, Appl. Phys. Lett. **73**, 1421 (1998).

[13] R. R. Robison and M. E. Law, Tech. Dig. - Int. Electron Device Meet. **2002**, 883.

[14] F. Cristiano, Y. Lamrani, F. Severac, M. Gavelle, S. Boninelli, N. Cherkashin, O. Marcelot, A. Claverie, W. Lerch, S. Paul, and N. E. B. Cowern, Nucl. Instrum. Methods Phys. Res. B **253**, 68 (2006).

[15] D. F. Downey, J. W. Chow, E. Ishida, and K. S. Jones, Appl. Phys. Lett. **73**, 1263 (1998).

[16] C. S. Rafferty, G. H. Gilmer, M. Jaraiz, D. J. Eaglesham, and H.-J. Gossman, Appl. Phys. Lett. **68**, 2395 (1996).

[17] S. A. Harrison, T. F. Edgar, and G. S. Hwang, Phys. Rev. B **74**, 121201(R) (2006).

[18] D. J. Eaglesham, P. A. Stolk, H.-J. Gossman, and J. M. Poate, Appl. Phys. Lett. **65**, 2305 (1994).

[19] N. Cherkashin, P. Calvo, F. Cristiano, B. de Mauduit, and A. Claverie, *Silicon Front-End Junction Formation-Physics and Technology*, MRS Symposia Proceedings No. 810 (Materials Research Society, Pittsburgh, 2004), p. 103.

[20] J. K. Listebarger, K. S. Jones, and J. A. Slinkman, J. Appl. Phys. **73**, 4815 (1993).

[21] F. Cristiano, J. Grisolia, B. Colombeau, M. Omri, B. de Mauduit, A. Claverie, L. F. Giles, and N. E. B. Cowern, J. Appl. Phys. **87**, 8420 (2000).