Invited paper

Properties and benefits of fluorine in silicon and silicon-germanium devices

Peter Ashburn and Huda A. W. El Mubarek

Abstract— This paper reviews the behaviour of fluorine in silicon and silicon-germanium devices. Fluorine is shown to have many beneficial effects in polysilicon emitter bipolar transistors, including higher values of gain, lower emitter resistance, lower 1/*f* noise and more ideal base characteristics. These results are explained by passivation of trapping states at the polysilicon/silicon interface and accelerated break-up of the interfacial oxide layer. Fluorine is also shown to be extremely effective at suppressing the diffusion of boron, completely suppressing boron transient enhanced diffusion and significantly reducing boron thermal diffusion. The boron thermal diffusion suppression correlates with the appearance of a fluorine peak on the SIMS profile at approximately half the projected range of the fluorine implant, which is attributed to vacancy-fluorine clusters. When applied to bipolar technology, fluorine implantation leads to a record f_T of 110 GHz in a silicon bipolar transistor.

Keywords— bipolar transistor, boron diffusion, fluorine, passivation of interface states, polysilicon emitter.

1. Introduction

Over the past few years there has been considerable interest in the behaviour of fluorine in silicon and silicon-germanium devices. This interest initially arose from the use of a BF_2^+ implant for shallow junction formation [1–3]. In bipolar technologies, a BF_2^+ implant was also used to create p-n-p polysilicon emitters and this led to a study of the behaviour of fluorine in polysilicon emitters [4]. This work showed that fluorine influenced a number of key bipolar transistor parameters, including gain [4], base current [5] and $1/f$ noise [6, 7]. More recently, research has focussed on the effect of fluorine on boron diffusion and it has been shown that fluorine suppresses boron transient enhanced diffusion [8, 9] and increases boron activation in silicon [8]. It has also been shown that fluorine decreases boron thermal diffusion in both silicon [10] and silicon-germanium [11, 12].

Recently fluorine implantation has been applied to MOS transistors to reduce boron diffusion in critical areas of the source and drain [13, 14]. Liu *et al.* [13] used a $1 \cdot 10^{15}$ cm^{-2} fluorine implant to create a super halo for both 50 nm n- and p-channel transistors. The fluorine-assisted halo process resulted in reduced junction capacitance and an improved $I_{on} - I_{off}$ trade-off. Fukutome *et al.* [14] used a $5 \cdot 10^{14} - 2 \cdot 10^{15}$ cm^{-2} fluorine implant prior to the p-channel extension implant to minimise the diffusion of boron in the extension. The fluorine implant led to dramatically improved threshold voltage roll-off characteristics without any degradation of drive current in sub-50 nm p-channel MOSFETs. Scanning tunnelling microscopy was used to show that the improvement was due to a reduction of the overlap length, for example from 13 to 7 nm in 40 nm gate length p-channel MOSFETs. Finally, Kham *et al.* [15] applied fluorine implantation to silicon bipolar technology to reduce the diffusion of the base and as a result have delivered a silicon bipolar transistor with a record f_T of 110 GHz.

In this paper, we review the properties and benefits of fluorine in silicon and silicon-germanium devices. We concentrate on fluorine behaviour in bipolar technology, beginning with a study of fluorine in polysilicon emitters and progressing to an investigation of the effects of fluorine on boron diffusion in silicon and silicon-germanium.

2. Effect of fluorine in polysilicon emitters

Fluorine exhibits a variety of interesting behaviour when implanted into the polysilicon emitter of a bipolar transistor. Figure 1 illustrates the effect of fluorine on the common emitter current gain, when 50 keV, $1 \cdot 10^{16}$ cm^{-2} fluorine is implanted into half of each wafer and annealed for 15 min at 850°C (Fig. 1a) or 120 min at 850°C (Fig. 1b) in nitrogen. For the short anneal, Fig. 1a shows that the fluorine implant leads to a higher gain, whereas for the long anneal, Fig. 1b shows that it leads to a lower gain. Thus fluorine gives radically different behaviour for low and high thermal budget anneals.

Figure 2 shows that the effect of fluorine on gain is due to a change in base current rather than a change in collector current. It also shows that for short drive-in times fluorine gives a lower base current (and hence a higher gain), while for long drive-in times it gives a higher base current than the control devices. The same trend is seen for devices given an HF etch (Fig. 2a) and an RCA clean (Fig. 2b) prior to polysilicon deposition, though the cross-over of the two curves occurs at longer times for the RCA clean than the HF etch.

The explanation for the lower values of base current at short anneal times is passivation of dangling bonds at the polysilicon/silicon interface by the fluorine. This is illustrated in Fig. 3, where dangling bonds are passivated by the formation of Si-O-F and Si-F complexes [16]. With the passivation of these dangling bonds, recombination of minority carriers at the interface is reduced and conse-

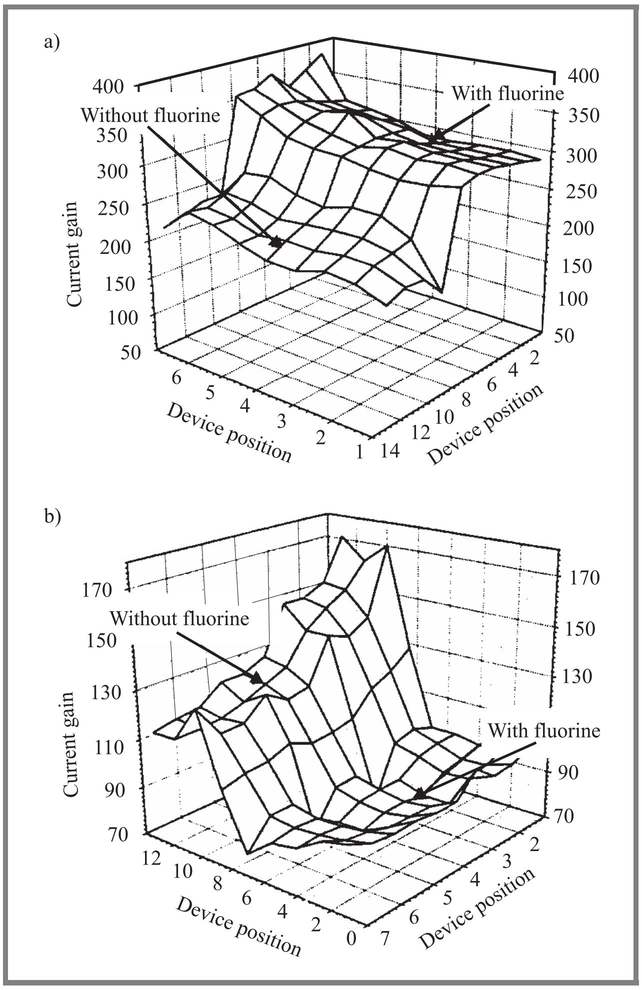

Fig. 1. The 3D plot of polysilicon emitter bipolar transistor gain measured across a wafer. The wafer had a 50 keV, $1 \cdot 10^{16}$ cm^{-2} F^{+} implant into half of each wafer and the wafers were given the following anneals: (a) 15 min at 850°C; (b) 120 min at 850°C. *After Moiseiwitsch et al. [4] © IEEE.*

quently the base current decreases. The explanation for the higher values of base current at long anneal times is the effect of fluorine in enhancing the break-up of the native oxide layer at the polysilicon/silicon interface [17]. This is shown in Fig. 4, which shows cross-section transmission electron microscopy (TEM) micrographs of polysilicon emitters without and with a fluorine implant. Figure 4a shows the situation for the control device without a fluorine implant and it can be seen that no regrowth of the polysilicon has occurred. In contrast for the fluorine implanted device in Fig. 4b, the interfacial oxide layer has broken up and the bottom part of the polysilicon layer has epitaxially regrown. Detailed experiments [18] have shown that fluorine increases both the interfacial oxide break-up and the polysilicon regrowth rate.

Fluorine has additional benefits in polysilicon emitter bipolar transistors, including reduced $1/f$ noise [6] and improved base current ideality [5]. The improved $1/f$ noise occurs because the fluorine breaks up the interfacial oxide layer, which is a source of noise in polysilicon emitters. The improved base current ideality is shown in Fig. 5a, where it can be seen that the ideality factor improves from 1.51 to 1.26 as a result of the fluorine implant. This improvement arises because the fluorine passivates interface states at the oxide/silicon interface where the emitter/base depletion region intersects the surface oxide, as shown in Fig. 5b. To reach the oxide/silicon interface, the fluorine has diffused through the polysilicon emitter and the screen oxide during the emitter anneal. This is possible because fluorine diffuses extremely rapidly in polysilicon [19] and silicon dioxide.

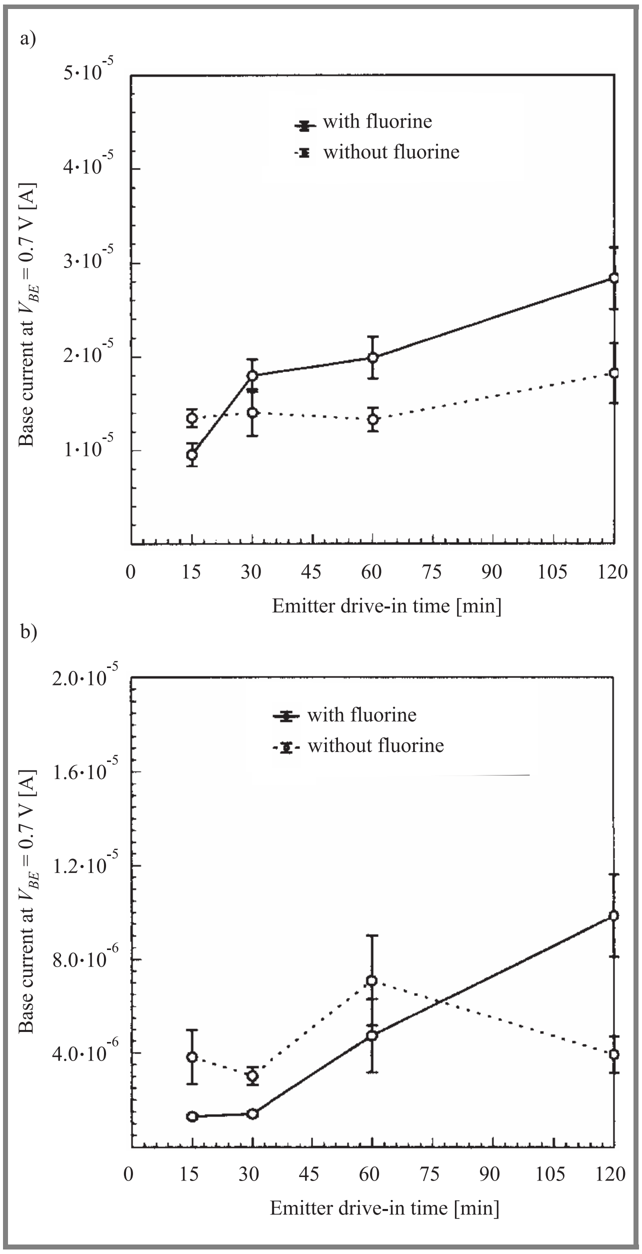

Fig. 2. Common emitter current gain as a function of emitter anneal time at 850°C for wafers given different wet chemical treatments prior to polysilicon deposition: (a) HF etch; (b) RCA clean. *After Moiseiwitsch et al. [4] © IEEE.*

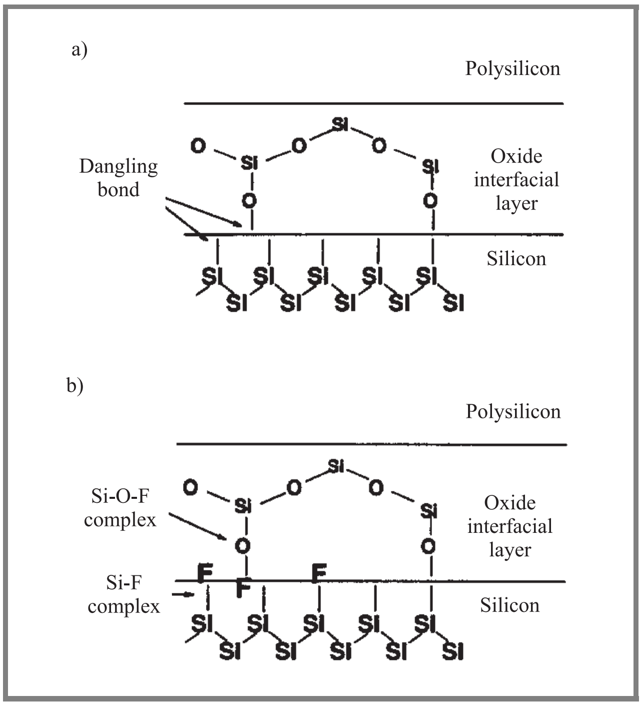

Fig. 3. Schematic illustration of the polysilicon/silicon interface showing the passivation of dangling bonds by fluorine as a result of the formation of Si-O-F and Si-F complexes: (a) interface in the absence of fluorine; (b) interface in the presence of fluorine. *After Moiseiwitsch et al. [4] © IEEE.*

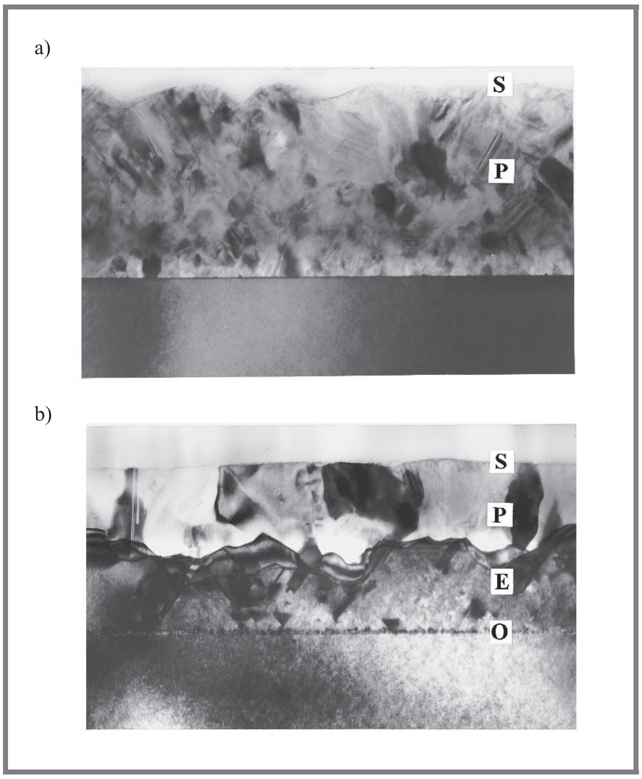

Fig. 4. Cross-section TEM micrographs of polysilicon emitters without and with a fluorine implant: (a) no fluorine implant and anneal of 480 min at 850°C; (b) 50 keV, $1 \cdot 10^{16}$ cm^{-2} F implant and anneal of 240 min at 850°C. *After Moiseiwitsch et al. [17] © AIP.*

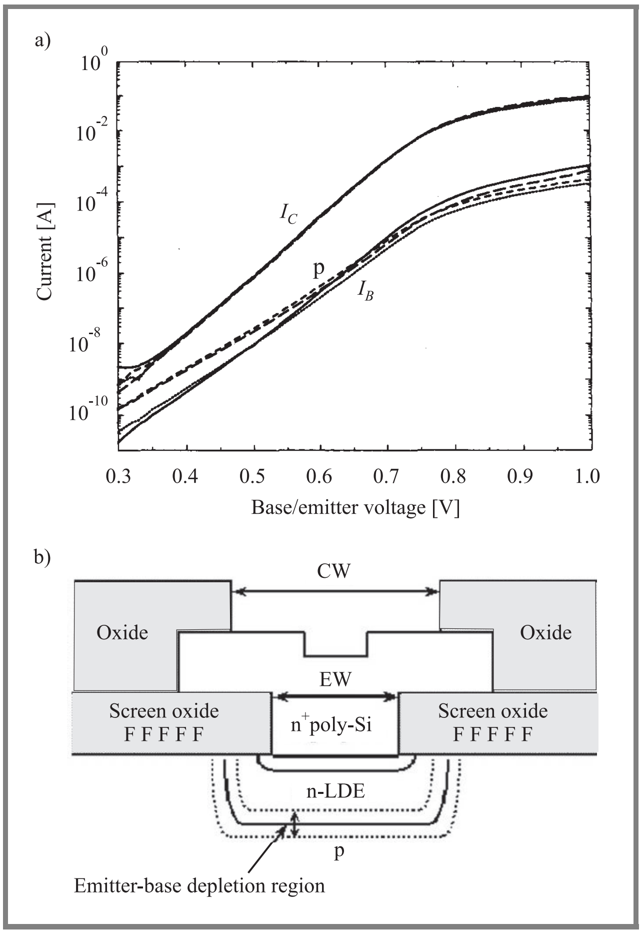

Fig. 5. Gummel plots of fluorine implanted and control polysilicon emitter bipolar transistors (a). The solid lines show fluorine-implanted transistors and the dashed lines show transistors without a fluorine implant. Schematic cross-section of the polysilicon emitter (b) showing the location of passivating fluorine at the interface between the screen oxide and the silicon wafer. *After Moiseiwitsch et al. [4] © IEEE.*

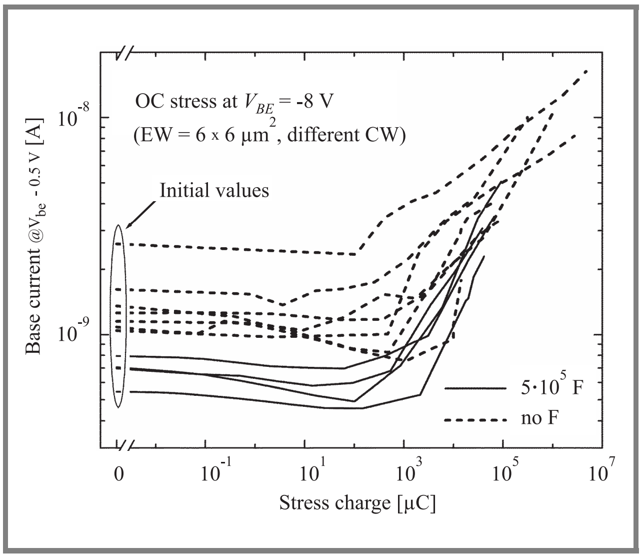

Fig. 6. Base current (at 0.5 V) as a function of stress charge in polysilicon emitter bipolar transistors with and without a fluorine implant. *After Sheng et al. [20] © IEEE.*

Hot carrier stressing experiments have been carried out on polysilicon bipolar transistors incorporating fluorine and results are shown in Fig. 6. The initial values of base current in all fluorine implanted devices are lower than those of the control devices. In all cases, the base current begins to increase at a stress charge of $10^2 - 10^4$ μC, whether the device is fluorine implanted or not, and then degrades at approximately the same rate with increasing stress charge. Detailed characterisation [20] has shown that benefits achieved by fluorine implantation are robust. This is, there is no evidence that defects passivated by fluorine are reactivated during stressing or that fluorine implantation introduces any additional defects that are activated during stressing.

3. Boron diffusion control using fluorine

Figure 7 shows the effect of fluorine on boron transient enhanced diffusion and boron thermal diffusion in silicon. A boron marker layer was used to monitor boron diffusion and transient enhanced diffusion was created using the damage from a P^+ implant at the same depth as the fluorine implant [9]. The results in Fig. 7a show that the P^+ implant induces considerable transient enhanced boron diffusion as a result of point defects created by the P^+ implant. However, the profile for the sample implanted with P^+ and F^+ indicates that the fluorine has dramatically suppressed the transient enhanced boron diffusion. Furthermore, Fig. 7b shows that the sample implanted with (185 keV, $2.3 \cdot 10^{15}$ cm^{-2}) F^+ shows less diffusion than the unimplanted sample. This is a surprising result, which indicates that the fluorine implant has significantly decreased boron thermal diffusion.

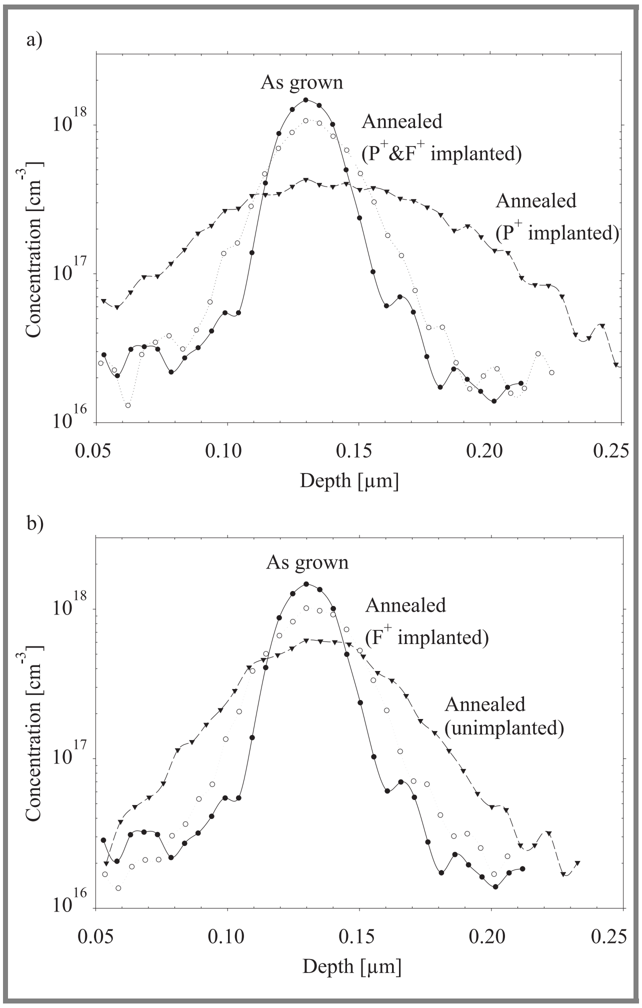

Fig. 7. Boron SIMS profiles of a buried marker layer after anneal for 30 s at 1000°C in nitrogen: (a) samples implanted with P^+ only and with P^+ and F^+; (b) an unimplanted sample and a sample implanted with F^+ only. *After Mubarek et al. [9] © AIP.*

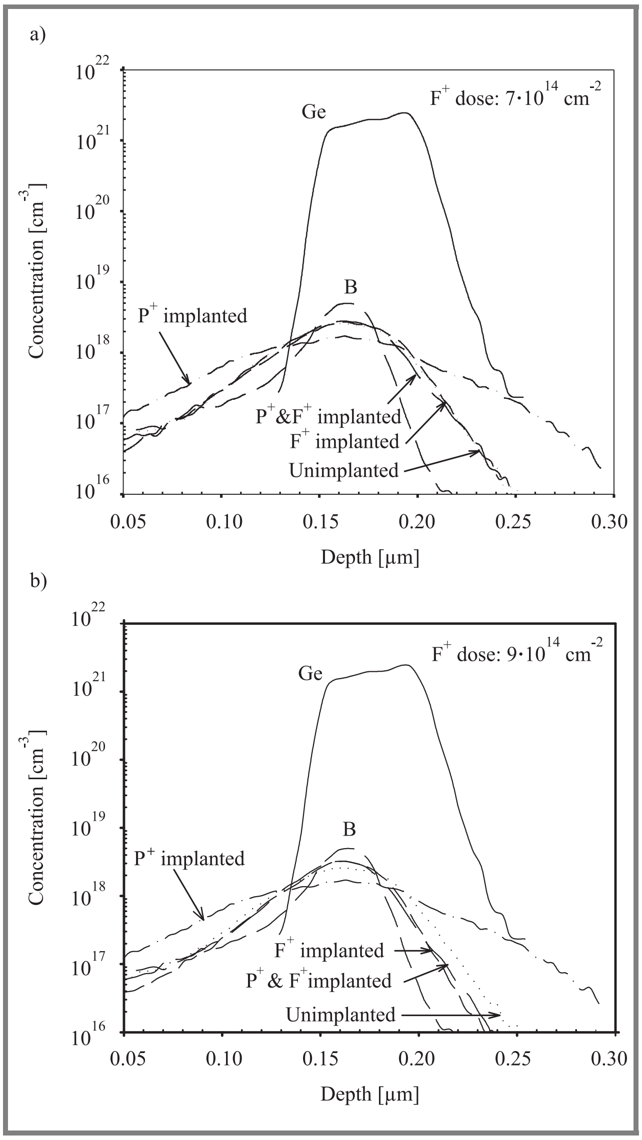

Fig. 8. Boron profiles after anneal for 30 s at 1000°C in nitrogen for samples implanted with P^+ and F^+, P^+ only, F^+ only and for an unimplanted sample. Results are shown for F^+ implantation doses of (a) $7 \cdot 10^{14}$ cm^{-2} and (b) $9 \cdot 10^{14}$ cm^{-2}. *After Mubarek et al. [12] © IEEE.*

Further insight into the effect of fluorine on boron diffusion can be obtained by investigating the effect of the fluorine implantation dose on the diffusion suppression [12]. Figure 8 shows boron secondary ions mass spectroscopy (SIMS) profiles for silicon-germanium samples implanted with P^+ and F^+, P^+ only, F^+ only and for an unimplanted sample. The results in Fig. 8a show that at a F^+ implantation dose of $7 \cdot 10^{14}$ cm^{-2}, the boron profiles for the two F^+ implanted samples are identical to that of the unimplanted sample, indicating that the F^+ implant has completely suppressed boron transient enhanced diffusion. In contrast, Fig. 8b shows that at a F^+ implantation dose of $9 \cdot 10^{14}$ cm^{-2}, the boron profiles for the two F^+ implanted samples show less diffusion than that of the unimplanted sample. This result indicates that the F^+ implant suppresses boron thermal diffusion at this implantation dose. There is therefore a critical F^+ implantation dose, above which boron thermal diffusion is suppressed and below which only boron transient enhanced diffusion is suppressed.

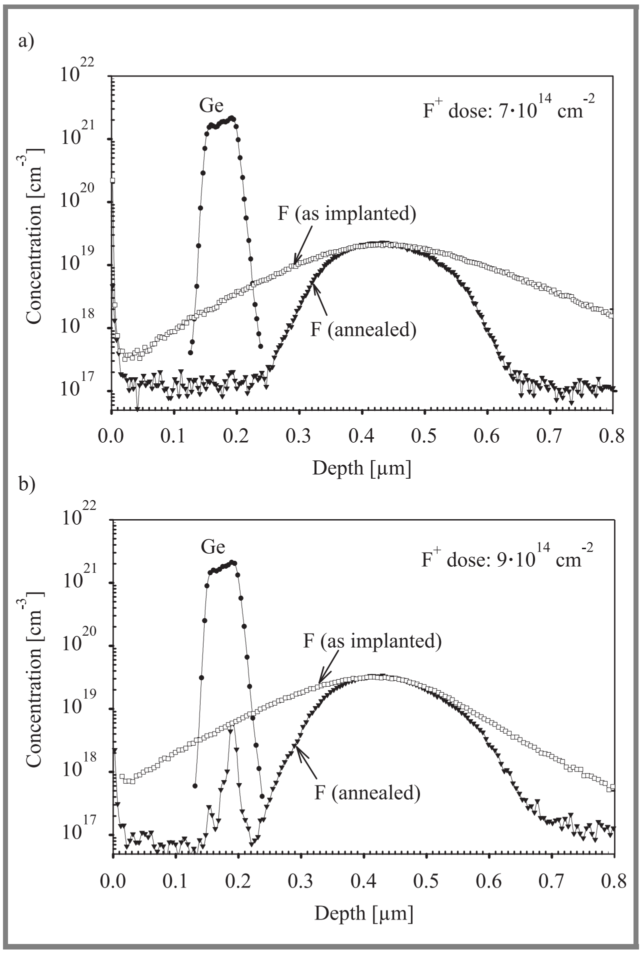

Fig. 9. Fluorine profiles after anneal for 30 s at 1000°C in nitrogen for samples implanted with P^+ and F^+, P^+ only, F^+ only and for an unimplanted sample. Results are shown for F^+ implantation doses of (a) $7 \cdot 10^{14}$ cm^{-2} and (b) $9 \cdot 10^{14}$ cm^{-2}. *After Mubarek et al. [12] © IEEE.*

Insight into the mechanism of boron thermal diffusion suppression can be obtained from the fluorine SIMS profiles of samples implanted with different F^+ doses, as shown in Fig. 9. For a F^+ implantation dose of $7 \cdot 10^{14}$ cm^{-2}, Fig. 9a shows the presence of a broad peak around the range of the fluorine implant, but little fluorine is present in the silicon-germanium layer. In contrast, for a F^+ implantation dose of $9 \cdot 10^{14}$ cm^{-2}, Fig. 9b shows the presence of an additional shallow fluorine peak in the silicon-germanium layer. There is therefore a correlation between the appearance of the fluorine peak in the silicon-germanium layer and the reduction in boron thermal diffusion.

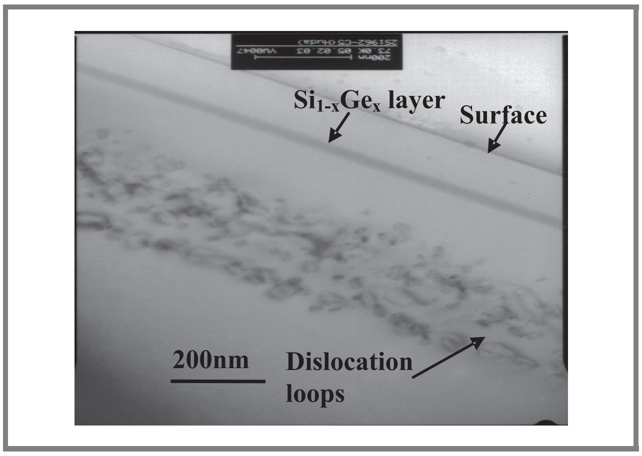

Fig. 10. Cross-section TEM micrograph of a sample implanted with $2.3 \cdot 10^{15}$ cm^{-2} F^+ and annealed at 1000°C for 30 s in nitrogen. *After Mubarek et al. [12] © IEEE.*

Figure 10 shows a cross-section TEM micrograph of the sample implanted with $2.3 \cdot 10^{15}$ cm^{-2} F^+. A band of dislocation loops can be seen extending from a depth of about 0.3 to 0.5 μm, but no defects are visible in the silicon-germanium ($Si_{1-x}Ge_x$) layer. The band of dislocation loops correlates with the broad fluorine peak in Fig. 9, indicating that this peak is due to fluorine trapped at the dislocation loops. The lack of any defect contrast in the $Si_{1-x}Ge_x$ layer indicates that any defects present must be too small to resolve by TEM. The shallow fluorine peak is located in the vacancy-rich region of the fluorine implant damage profile and this leads us to conclude that it is due to fluorine trapped in vacancy-fluorine clusters [12]. This conclusion has been confirmed by point defect injection studies on fluorine implanted samples [21]. The reduction of boron thermal diffusion above the critical fluorine dose is then explained by the action of the vacancy-fluorine clusters in suppressing the interstitial concentration in the silicon-germanium layer. Since boron diffusion is mediated by interstitials, this suppressed interstitial concentration gives reduced boron diffusion.

4. Application of fluorine diffusion suppression technique in bipolar transistors

The above fluorine diffusion suppression technique has been applied to a double polysilicon silicon bipolar tech-

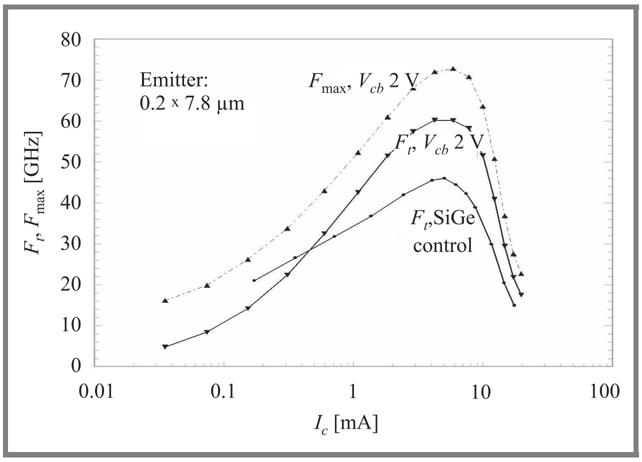

Fig. 11. Effect of a 150 keV, $5 \cdot 10^{14}$ cm^{-2} F$^+$ implant on the f_T and f_{max} of a double polysilicon silicon bipolar transistor. *After Kham et al [15] © IEEE.*

nology in collaboration with ST Microelectronics, Catania, Italy [15]. Figure 11 shows the effect of a 150 keV, $5 \cdot 10^{14}$ cm^{-2} F$^+$ implant on the f_T of a silicon bipolar transistor and it can be seen that fluorine increases the maximum f_T from 46 to 60 GHz. A further improvement in performance can be obtained by scaling the basewidth and optimising the collector doping, while keeping the fluorine implant conditions the same. Results are shown in Fig. 12, where it can be seen that values of peak f_T of 90, 100 and 110 GHz are obtained for collector junction concentrations of 1.2, 2.5 and $5.0 \cdot 10^{17}$ cm^{-2}, respectively. The value of BV$_{ceo}$ at $\sim$ 5 mA collector current varied slightly with collector implant dose, with values around 2.5 V, such that all three variants had Johnson numbers of $\sim$ 250 GHz-V. These values of f_T are the highest ever reported for silicon bipolar transistors.

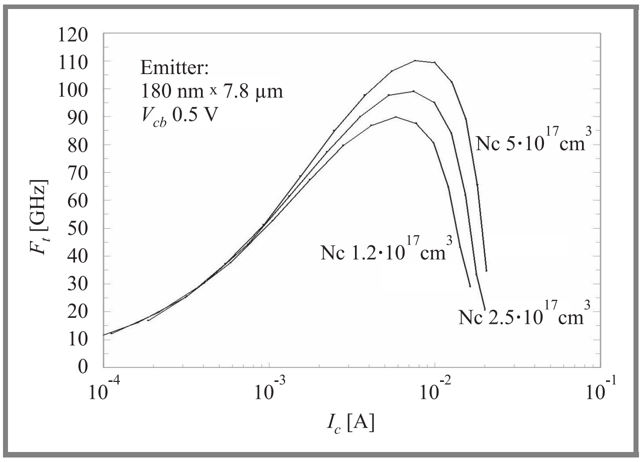

Fig. 12. Values of f_T as a function of collector current for double polysilicon silicon bipolar transistors implanted with 150 keV, $5 \cdot 10^{14}$ cm^{-2} F$^+$ and with different collector profiles. *After Kham et al [15] © IEEE.*

5. Conclusions

A review has been undertaken of the properties and benefits of fluorine in silicon and silicon-germanium devices. Fluorine has been found to exhibit a variety of interesting effects, many of which are beneficial to device performance. When fluorine is implanted into polysilicon emitters, benefits can include higher gain, lower emitter resistance, reduced $1/f$ noise and improved base current ideality. Two conflicting mechanisms have been identified, the first being passivation of interface states by fluorine segregated at the polysilicon/silicon interface and the second being accelerated break up of the interfacial oxide layer. When fluorine is implanted into the collector, a dramatic suppression of boron diffusion is obtained. A critical fluorine dose has been identified, below which fluorine suppresses boron transient enhanced diffusion and above which boron thermal diffusion is also suppressed. This suppression of boron thermal diffusion correlates with the appearance of a fluorine SIMS peak in the silicon-germanium layer that has been attributed to vacancy-fluorine clusters. The reduction of boron thermal diffusion has been explained by the effect of the vacancy-fluorine clusters in suppressing the interstitial concentration in the silicon-germanium layer. When applied to silicon bipolar transistors, fluorine has delivered a record f_T of 110 GHz.

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