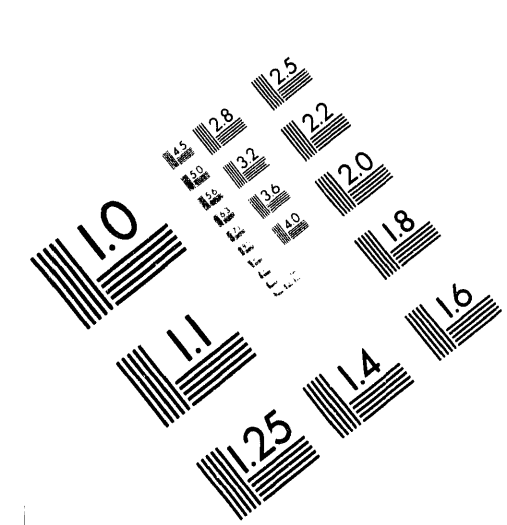

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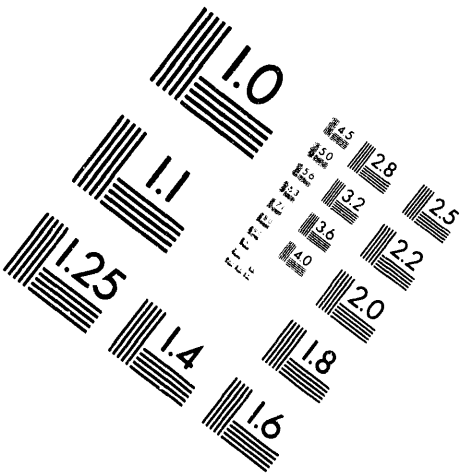

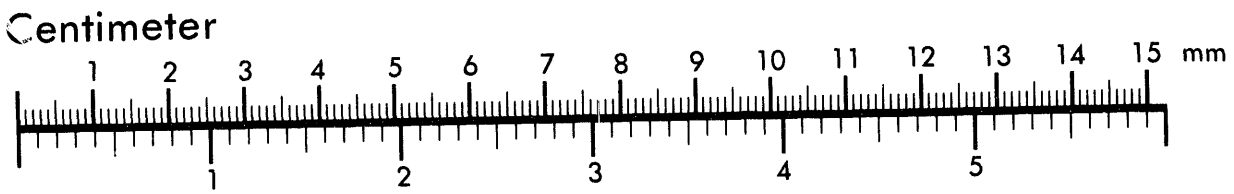

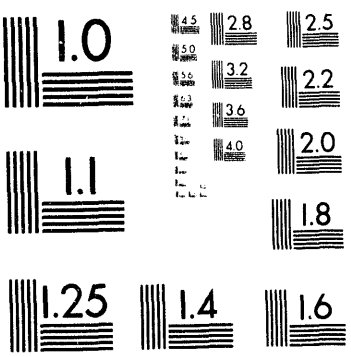

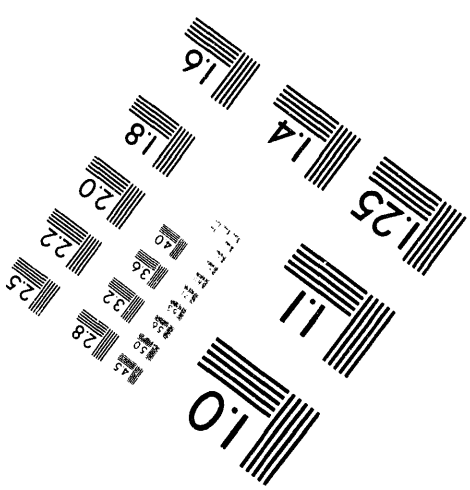

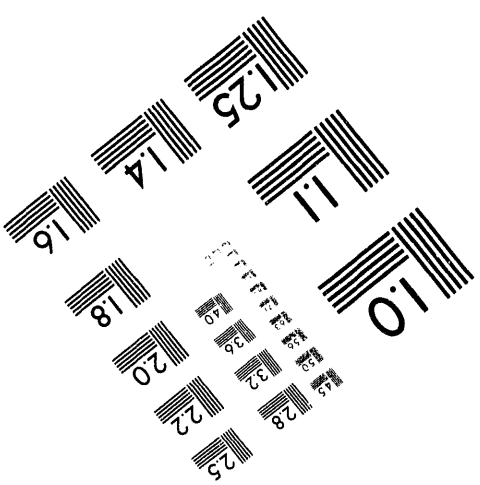

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ROLE OF IMPLANTATION-INDUCED DEFECTS IN SURFACE-ORIENTED DIFFUSION OF FLUORINE IN SILICON

Cs. Szeles[1*], B. Nielsen[1], P. Asoka-Kumar[1], K.G. Lynn[1], M. Anderle[2], T.P. Ma[3], and G.W. Rubloff[4+]

[1]*Department of Physics and Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973, USA*
[2]*Istituto per la Ricerca Scientifica e Tecnologica, Divisione di Scienza dei Materiali, 38050 Povo, Italy*
[3]*Department of Electrical Engineering, Yale University, New Haven, CT 06520, USA*
[4]*IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598, USA*

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ABSTRACT

The annealing behaviour open-volume defects introduced in Si(100) crystals during fluorine implantation and their role in the surface-oriented diffusion of F impurities were investigated by variable-energy positron beam depth profiling. The defects become mobile and undergo recovery at temperatures well below the onset of fluorine diffusion at 550 °C as seen by secondary ion mass spectroscopy (SIMS). The results suggests that after irradiation and annealing the F occupies substitutional sites to which positrons are insensitive. The anomalous F diffusion seen in SIMS has been explained through a two-step diffusion mechanism, in which the diffusion kinetics is determined by dissociation of the substitutional F into an interstitial F and a vacancy, followed by their rapid diffusion to the surface.

INTRODUCTION

Incorporation of a small, controlled amount of fluorine (F) near the SiO_2/Si interface significantly improves the reliability of metal-oxide-semiconductor (MOS) devices [1]. The understanding of F diffusion, interactions with lattice defects, and the mechanism behind reliability enhancement has not yet been achieved. Fluorine redistribution during post-implantation annealing drastically deviates from simple diffusion in Si. F atoms are immobile below 500 °C both in crystalline and amorphous Si. For F doses below the amorphization threshold ($1x10^{15}$ F^+cm^{-2}) a strong surface-oriented diffusion was observed. F migrates to the surface and leaves the Si in the 550-800 °C temperature range [2,3]. The F diffusion is more complicated for doses above the amorphization threshold [2]. The implantation damage is known to have a strong effect on the migration of dopants during annealing, causing anomalous enhanced transient diffusion [4], and suggesting that the lattice defects created during F implantation could be responsible for the surface-oriented diffusion of F in Si.

Here we have examined the behaviour of implantation-induced *open-volume* lattice defects and their role in the surface-oriented diffusion of F during post-implantation annealing for F dose below the amorphization threshold. The F migration was followed by secondary ion mass spectroscopy (SIMS) and thermal desorption spectroscopy (TDS) [3]. The annealing of lattice defects was monitored by the variable-energy positron beam depth-profiling technique [5].

EXPERIMENTAL

B doped *p*-type 0.8-2.0 Ωcm, P doped *n*-type 0.8-2.0 Ωcm, and As doped n^+ <0.002 Ωcm Si(100) Czochralski (CZ) wafers were used in this study. The samples were implanted with 30 keV F^+ ions to a dose of $1x10^{13}cm^{-2}$. Samples were annealed for periods of 30 minutes in the 50-750 °C temperature range in a purified He atmosphere. The SIMS depth profiles were recorded with a Cs^+ primary ion beam. TDS was performed with a quadrupole mass

* On leave from the Department of Nuclear Chemistry, Eötvös University, Budapest, Hungary
+ Present address: Center for Advanced Electronic Materials Processing, North Carolina State University, Raleigh, NC 27695

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spectrometer in a UHV system [3]. The defect depth profiling was done with a variable-energy monoenergetic positron beam apparatus coupled to a HPGe gamma spectrometer to measure the Doppler broadening of the 511 keV annihilation γ-line as a function of incident positron energy in the 0.1-25 keV range. To assess the broadening the lineshape parameter (S), defined as the ratio of counts in the central region of the 511 keV photopeak to the total counts in the peak, was calculated for each positron energy (E). The S parameter is normalized to the bulk S_b value. To avoid the difficulties involved in the interpretation of S-E curves of multilayered materials [5], the surface oxide was removed by an aqueous HF etch, resulting a chemically stable, temporarily oxidation resistant, hydrogen-terminated Si surface [6].

RESULTS

Fig. 1 shows the behaviour of the SIMS fluorine depth-profile upon annealing. It clearly shows that F migration begins at 550 °C and that the migration is oriented toward the surface. TDS shows the onset of SiF^+ and $SiOF^+$ desorption at the same temperature [3]. The F redistribution pattern was independent of the dopant type or concentration. The detailed discussion of the SIMS and TDS results has been given elsewhere [3].

Fig. 2 shows the behaviour of S parameter versus positron incident energy (S-E) curves upon annealing. For the as-implanted samples the S values are well above the bulk value at low incident positron energies indicating positron trapping at open-volume defects.

Fig. 3 compares the isochronal annealing of the implantation induced defects seen by the positrons and the F diffusion seen by SIMS in the n^+-type sample. The strongest annealing stage of defects is at 400 °C followed by a broad annealing stage in the 450-600 °C temperature where the defect signal completely disappears. The F diffusion stage is centered around 700 °C where most of the open-volume defects have already annealed out.

DISCUSSION

A. Likely Open-Volume Defects after F Implantation

Both single vacancies and self-interstitials are mobile well below room temperature in Si [9]. Strong point-defect diffusion takes place during room temperature irradiations, and for doses below the amorphization threshold ($1 \times 10^{15} cm^{-2}$) the defects retained after F implantation are mostly small associations of point defects, dopants and impurities.

Contrary to monovacancies, divacancies are stable at room temperature and they are readily formed during room temperature ion irradiation of Si [10]. Higher vacancy agglomerates can be also formed by trapping additional vacancies at divacancies. Boron-vacancy pairs dissociate around room temperature, but phosphorus-vacancy and arsenic-vacancy pairs are stable up to 120 - 170 °C in Si [10]. In CZ-grown Si crystals oxygen is by far the most abundant impurity with concentrations typically in the $\sim 10^{18} cm^{-3}$ range, which is well above the dopant concentration in the lightly doped samples (10^{15} - $10^{16} cm^{-3}$). O effectively traps mobile vacancies and divacancies forming O-vacancy pairs and O-divacancy complexes [10,11]. We expect therefore that, beside divacancies, O-vacancy pairs and their small agglomerates will be the predominant open-volume defects present in the lightly doped samples. In the heavily As doped samples As-vacancy pairs are expected to be formed in concentrations comparable to the concentration of O-vacancy complexes.

Little is known about F-vacancy interactions. According to theory [12] F atoms diffuse interstitially in crystalline Si with a migration barrier of ~ 0.7 eV between adjacent tetrahedral positions. For such a low activation energy, however, a migration stage around room temperature would be expected contrary to the diffusion observed above 550°C. This strongly suggests that the F atoms are trapped at lattice defects during implantation. There is a strong evidence for F trapping at extended interstitial-type defects in Si [4], but for doses below the amorphization threshold the concentration of interstitial agglomerates is low. It is unlikely that interstitial-type defects are responsible for the trapping of F atoms. We instead suggest that the F atoms are trapped at vacancies and divacancies during the irradiation.

B. Annealing Behaviour and F Diffusion

It is clear from Fig. 3. that the open-volume defects anneal out below the onset of the F migration at 550°C. This result is in accordance with the general annealing behaviour of divacancies, vacancy-O complexes and vacancy-dopant pairs in CZ Si. Divacancies become

mobile in the 180-230°C temperature range [10] in Si, and anneal forming multivacancy clusters, some of which are stable up to 450°C [13], as well as by trapping at O impurities and dopants. The vacancy-As pair dissociates at 180°C [9]. The vacancy-O pair and the divacancy-O complex are stable up to 350°C [10,11], and anneal through the formation of more complicated multivacancy-multioxygen complexes [11].

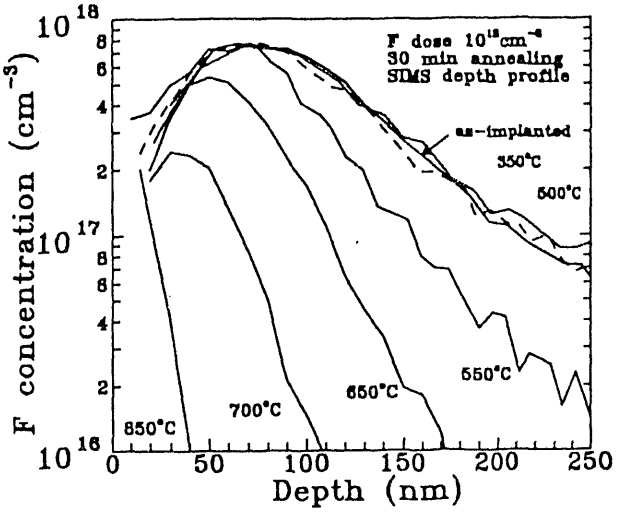

Fig. 1. The behaviour of the SIMS F depth distribution in Si implanted with 1×10^{13}cm^{-2} F ions, upon isochronal annealing for 30 minutes at the indicated temperatures [3].

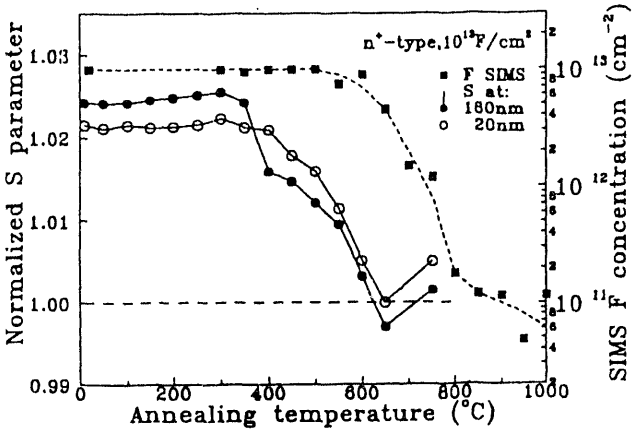

Fig. 3. The *S* parameter at 20 nm and 160 nm *vs.* annealing temperature for the n^+-type sample implanted with 1×10^{13}cm^{-2} F^+ ions. The amount of F retained in Si after annealing is also shown for comparison (dashed curve, right axis) [3]. The curves are only guides to the eye.

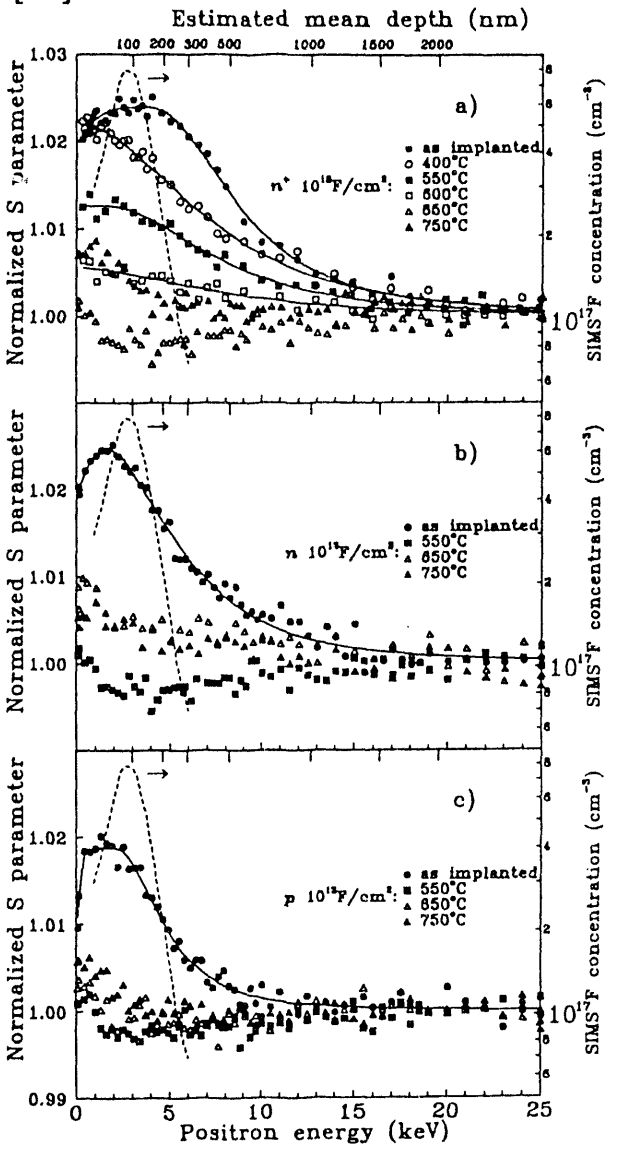

Fig. 2. The *S* parameter *vs.* positron incident energy (*E*) for the n^+ type, b) *n* type, and c) *p* type samples implanted with 1×10^{13}cm^{-2} F^+ ions, after implantation and upon 30 minutes isochronal annealing. The solid curves are model fits to the data [7]. The as-implanted SIMS F depth distribution (dashed curve, right axis) is also shown for comparison.

F atoms may serve as traps for vacancies and divacancies released during the annealing of divacancies, vacancy-O and vacancy-As complexes. However, no indication on the presence of open-volume defects associated with F atoms was found in the samples annealed at 550°C and above. This shows that the vacancy-F complexes are either positively charged or relaxed to configurations which hinders positron trapping. F, however, is expected to be negatively

charged in Si [12] and any vacancy-F complex with at least a vacancy-size open volume is expected to be positron trap. The concentration of F atoms in the implanted range, (1-8) x $10^{17}cm^{-3}$, is well above 5 x $10^{15}cm^{-3}$, the sensitivity limit of the positron technique to vacancies [8]. The absence of positron trapping, therefore, suggests that most of the F atoms are in *substitutional* lattice positions with no open volume associated.

The dissociation of *substitutional* F and the subsequent extremely fast diffusion of the liberated *interstitial* F ($E_a \sim 0.7$ eV [12]) and *vacancy* ($E_a < 0.45$ eV [9]) could explain the *apparent* surface-oriented diffusion of F, seen in the SIMS profiles. Namely, at temperatures above 550°C, interstitial F can reach *both* surfaces of the sample within seconds. The concentration of the mobile F rapidly falls well *below* the sensitivity of SIMS (1 x $10^{15}cm^{-3}$), and becomes evenly distributed throughout the crystal. The concentration profile close to the surface is governed by the F reactions at the Si/SiO_2 interface where, unlike in the bulk, F atoms readily break Si-Si bonds [12]. The desorption of the volatile fluorosilyl (SiF, SiF_2, SiF_3, SiF_4, Si_2F_6) and oxyfluorosilyl (SiOF, $SiOF_2$) products formed in these reactions are observed by TDS [3]. The rate of these reactions is probably much smaller than the F arrival rate explaining the absence of a strong F loss close to the front surface.

CONCLUSIONS

The migration and disappearance of the implantation induced defects, presumably divacancies, vacancy-As pairs, vacancy-O pairs and small multivacancy-oxygen complexes, occur at temperatures *below* the onset of F migration at 550°C in Si. The highly mobile interstitial F relaxes to substitutional position during implantation and annealing, and is immobile below 550°C. The apparent surface-oriented diffusion of F, as seen by SIMS, could be described by a two-step mechanism where dissociation of substitutional F to a vacancy and interstitial F is followed by a very fast migration of these species to the surface.

ACKNOWLEDGEMENT

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