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C.L. Claeys, G.J. Declerck, R.J. van Overstrateten. Correlation between the diffusion of borons atoms and the growth kinetics of oxidation-induced stacking faults. *Revue de Physique Appliquée*, 1978, 13 (12), pp.797-801. 10.1051/rphysap:019780013012079700 . jpa-00244549

HAL Id: jpa-00244549

<https://hal.science/jpa-00244549>

Submitted on 1 Jan 1978

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CORRELATION BETWEEN THE DIFFUSION OF BORONS ATOMS AND THE GROWTH KINETICS OF OXIDATION-INDUCED STACKING FAULTS

C. L. CLAEYS, G. J. DECLERCK and R. J. VAN OVERSTRAETEN

K.U. Leuven, E.S.A.T. Laboratory Kardinaal Mercierlaan 94, B-3030 Heverlee, Belgium

Résumé. — Cet article traite en détail l'influence d'une diffusion de Bore sur l'évolution des défauts d'empilement, formés au cours d'une oxydation à haute température. Utilisant comme source de diffusion un oxyde silox dopé de Bore, on a étudié la longueur des défauts d'empilement en fonction du temps de diffusion. Cette expérience a été répétée à 1 150 °C dans une atmosphère respectivement azote, oxygène et Chlore (oxydation C33). La proportion molaire de diborane au silane est prise comme paramètre. Pour quelques expériences une source de diffusion B_2O_3 a aussi été utilisée. Les résultats peuvent être expliqués si l'on suppose que la diffusion de Bore est partiellement contrôlée par un mécanisme de diffusion *interstitialcy*. Pour les expériences dans une atmosphère de Chlore on doit tenir compte des réactions à l'interface Si-SiO₂. Les résultats obtenus sont discutés et comparés avec ceux de la littérature.

Abstract. — The influence of a boron diffusion on the growth kinetics of oxidation-induced stacking faults is investigated in detail. Using a boron doped silox oxide as a diffusion source, the OSF length is studied as a function of drive-in time for an anneal at 1 150 °C in respectively an inert, an oxygen and a chlorine containing ambient (C33-oxidation). In these experiments, the molar ratio of diborane to silane is used as a parameter. For some experiments, a planar B_2O_3 -diffusion source is used. To explain the different experimental results, the assumption of a fractional interstitialcy diffusion mechanism for the boron diffusion is used. For the experiments in a chlorine containing atmosphere, the chlorine reaction at the Si-SiO₂ interface has to be taken into account. The obtained results are compared with the results reported in the literature.

1. Introduction. — The break-through of VLSI in the field of analog signal processing and imaging circuits, requires large electrically active regions free of crystalline defects. A strong relationship between oxidation-induced stacking faults (OSF's) and yield hazards in bipolar, MOS and CCD integrated circuits has been reported by several investigators [1-3]. It has been demonstrated that in the case of Charge-Coupled Devices, the correspondence between crystalline defects and dark current non-uniformities can be as high as 95 % [4]. Due to the impact of crystalline defects on the electrical performance of the devices, it is very important to understand the nucleation and the growth of these defects.

Since the initial observation by Thomas [5] of oxidation-induced stacking faults in mechanically damaged silicon, the nucleation of OSF's has been studied in detail. The nucleation can be due to residual surface damage [6], surface contamination [7], surface reactions with hydrofluoric acid [8] and grown-in defects [9]. Both the length and the concentration of the stacking faults can be influenced by a preoxidation ion implantation step [10-11]. Dependent on the source of the OSF nuclei, one can differentiate between surface, bulk and process-induced stacking faults [10]. Several models have been proposed to explain the nucleation of the OSF's [12-14].

Dependent on the oxidation atmosphere (dry, wet or a chlorine containing ambient), the stacking

faults can grow or shrink as a function of temperature [15, 16]. The annihilation of the stacking faults can be achieved by a high temperature anneal in an inert or a chlorine containing ambient. Preoxidation gettering techniques on the back-side of the wafer (POGO techniques) are also very effective to suppress the OSF growth [17, 18].

As the stacking faults are bounded by (111) Frank partial dislocations, the growth of the faults is due to the climb of the partials. This climb mechanism involves the emission of vacancies or the absorption of interstitials. The degree of disturbance of the equilibrium concentration of vacancies and interstitials near the surface is influenced by the diffusion of impurities like e.g. phosphorous, boron or arsenic. This means that the growth kinetics of the OSF's will also be influenced by the diffusion of impurity atoms. This paper describes in detail the influence of the diffusion of boron atoms on the growth and the annihilation kinetics of oxidation-induced stacking faults.

2. Experimental procedure. — The wafers used in these experiments are 6-10 Ω cm, 2 inch, (100) oriented n-type silicon grown by the Czochralski technique. Wafers with a lot of grown-in defects and without surface damage are selected. To obtain stacking faults, these wafers are oxidized in wet oxygen at 1 150 °C.

This step results in OSF's with a bulk type nature. By careful handling and processing, the nucleation of surface stacking faults is further avoided. After stripping the oxide layer, the OSF's are revealed by using a Wright etch [19].

The structures, used in the different experiments, are shown in figure 1. A sandwich layer of 3 000 Å boron doped and 3 000 Å undoped CVD-silicon-dioxide is deposited at 425 °C, after removing the wet oxide layer. By using different molar ratio's of diborane to silane, a range of samples with different boron concentrations is obtained. For some experiments, a planar B_2O_3 -diffusion source at 910 °C and 1 010 °C is used. The diffusion of the boron atoms is carried out at 1 150 °C either in nitrogen, oxygen or in a chlorine containing oxidizing ambient. The chlorine atmosphere is provided for by adding 0.2 % 111-trichloroethane (referred to as C33) to the oxidizing ambient. Any C33 concentration corresponds to a three times higher concentration of HCl-gas [20]. The wafers are inserted in the hot zone of the diffusion furnace under an oxygen ambient.

FIG. 1. — The different structures, used in the experiments to study the influence of a boron diffusion on the OSF growth kinetics.

After dissolving the oxide layer, the wafers are preferentially etched for 5 min. To enable a comparison with the *classical* OSF growth kinetics, control wafers with the initial wet oxide layer also receive the same drive-in steps. The classical growth kinetics corresponds with the growth behaviour, observed when there is no influence of indiffusing boron atoms.

3. Experimental results. — The experimental observation that during the diffusion of boron atoms, an interaction exists between oxidation-induced stacking faults and indiffusing atoms, has first been reported by Ravi [21]. He observes that annealing oxidized and boron diffused wafers, results in a redistribution of the boron concentrated at the fault. The further

diffusion of boron atoms creates an undersaturation of vacancies near the fault, forcing the Frank partials to climb. It has to be remarked that for his experiments, Ravi [21] uses thin foils which affects the possibility of an unfaulting reaction. However, no systematic analyses of the stacking fault length is presented.

In a first set of our experiments, the molar ratio of diborane to silane during the silox deposition is taken constant and equal to 0.03. The stacking fault length, measured as a function of drive-in time, is given in figure 2. for a drive-in at 1 150 °C either in a nitrogen, an oxygen or in a 0.2 % C33 atmosphere.

FIG. 2. — Relationship between the OSF length and the drive-in time for a drive-in at 1 150 °C respectively in nitrogen, oxygen and 0.2 % C33. The dashed curves represent data for samples without boron, corresponding with the classical OSF growth behaviour.

The dashed curves correspond with the classical OSF's behaviour and have previously been discussed in detail by the authors [16]. The distribution of the OSF's, after a 3 h nitrogen anneal of a wafer with a boron doped diffusion layer, is shown in figure 3a. As can be seen, the size of the OSF's is not uniform across the wafer, pointing to a bulk type nature of the stacking faults. A more detailed photograph of the stacking faults is represented in figure 3b. The plotted OSF length always corresponds with the longest stacking fault on the wafer. One notices from figure 2 that the indiffusing boron atoms enhance the OSF growth under oxidizing conditions and retard the shrinkage of the OSF's during a nitrogen anneal. It seems that for long diffusion times, the shrinkage rate of the OSF's under a nitrogen atmosphere, decreases to a small value. This leads to a nearly constant OSF length.

For an anneal in 0.2 % C33, the curves for samples with and without boron are falling together. This is only so for the small molar ratio of diborane to silane used in this experiment. By using a higher molar ratio

FIG. 3a. — The distribution of the OSF's, after a 3 h N_2 anneal of a wafer with a boron diffused layer.

FIG. 3b. — A more detailed photograph of some of the OSF's on the wafer of figure 3a. The longest OSF length is 12 μ .

of diborane to silane, the shrinkage of the OSF's is retarded. Another C33 concentration in the oxidizing ambient also separates both curves. However to explain the different experimental results, it is important to take the total amount of indiffusing borons atoms into account as a parameter.

In order to investigate the influence of the in-going boron atoms on the OSF growth kinetics more in detail, experiments are performed with different molar ratio's of diborane to silane. Experimental data of the OSF length as a function of drive-in time are given in figure 4 and figure 5 for an anneal at 1150 °C respectively in nitrogen and oxygen. These experi-

FIG. 4. — The OSF length *versus* drive-in time for an anneal at 1150 °C in nitrogen. The molar ratio of diborane to silane is used as a parameter.

FIG. 5. — The OSF length as a function of drive-in time for an oxygen anneal at 1150 °C. The molar ratio of diborane to silane is used as a parameter.

ments are performed on wafers with a longer wet oxidation time than used for the experiments reported in figure 2, resulting in a greater initial OSF length. One notices that the molar ratio of diborane to silane has a great influence on the growth and the annihilation kinetics of the stacking faults. In a nitrogen atmo-

sphere, the shrinkage of the OSF's slows down with increasing molar ratio of diborane to silane. For a constant molar ratio of diborane to silane, the shrinkage rate decreases with increasing drive-in time. This is in agreement with the trend reported in figure 2. For a drive-in in oxygen, a small molar ratio of diborane to silane is already sufficient to strongly increase the OSF growth rate. The influence of the used molar ratio of diborane to silane is less pronounced than for the experiments with a nitrogen anneal.

Some experiments are performed with a planar B_2O_3 -source respectively at 910 °C and 1010 °C for 20 min. After the various drive-in steps, the same trend in stacking fault length *versus* diffusion time, as reported in figure 2, is found.

4. Discussion. — The growth of the stacking faults is due to the climb mechanism of the Frank partials, which involves the emission of vacancies or the absorption of interstitials. Originally, Sanders and Dobson [22] proposed a growth mechanism of the stacking faults, based on an undersaturation of vacancies near the surface. However, in order to explain the phenomenon of the oxidation-enhanced diffusion (OED), Hu [23] assumes that the growth of the OSF's is due to the absorption of interstitials. The incompleteness of the oxidation process results in a supersaturation of interstitials near the surface. Our previously reported results on the influence of phosphorous diffusion on the growth kinetics of oxidation-induced stacking faults, also point to a growth mechanism based on the absorption of interstitials [24]. An interstitial model can also explain the growth behaviour of the OSF's in a chlorine containing oxidizing atmosphere.

As the growth of the stacking faults is enhanced during a boron diffusion in an oxidizing ambient, the indiffusing boron atoms must increase the concentration of interstitials near the surface. This can be explained by assuming that in an oxidizing atmosphere, the boron diffusion has a dominant interstitialcy component. This is in agreement with the oxidation enhanced diffusion of boron, reported by Hu [25]. In order to explain the increase in diffusion enhancement with decreasing temperature, Antoniadis *et al.* [26] also propose a fractional interstitialcy mechanism for the boron diffusion under oxidizing conditions.

The growth rate of the OSF's depends on the amount of in-going boron atoms and will therefore also be influenced by the used diffusion source. In the case of a diffusion from a boron doped CVD- SiO_2 layer, the growth rate will be lower than for a B_2O_3 diffusion source, because of the growth of an interfacial layer of undoped oxide during the anneal in oxygen. This layer acts as a barrier between the B-doped source layer and the silicon [27].

During a nitrogen anneal of boron diffused wafers, the shrinkage of the OSF's is lower than for samples

without a boron doped CVD- SiO_2 source layer. The shrinkage rate decreases with increasing molar ratio of diborane to silane. These results can also be explained by assuming a fractional interstitialcy diffusion mechanism for boron, as such a mechanism increases the concentration of interstitials near the surface and therefore decreases the emission rate of interstitials from the fault site to the surface. It has to be remarked that in these experiments, the boron concentration is low (10^{18} - 10^{19} cm⁻³). For higher boron concentrations, the shrinkage effect is expected to vanish. If the boron concentration is too high, slip dislocations are generated [28] and annihilation of the fault may occur.

Our experimental results are in agreement with the results obtained by Dobson and Filby [29]. They observed the formation of boron precipitates and stacking faults during a boron diffusion. They also noticed a difference between diffusions in thin foils and diffusions in standard wafers. In thin foils, the precipitation of boron is enhanced. The experiments of Ravi [21], carried out with thin foils, also show that during a nitrogen anneal of boron diffused wafers, boron precipitates and stacking faults are formed. However, his assumption that the growth of the stacking faults is due to a vacancy mechanism, is not consistent with our experimental results, neither with recent work by Murarka [30].

Hashimoto *et al.* [31] studied the influence of a boron diffusion on the growth kinetics of OSF's during a nitrogen anneal at 1100 °C. They observe no stacking faults within the diffused layer. To explain this, they propose a model based on the generation of excess vacancies due to the shift of the Fermi-level with the doping concentration. This model is not in agreement with the results reported in this paper.

It should be remarked however that the results of Hashimoto *et al.* [31] are obtained with a much higher boron concentration at the surface (4.3×10^{19} - 2.7×10^{20} cm⁻³) than in our experiments. In the wafer with a boron concentration of 1×10^{20} cm⁻³ they already observe slip dislocations.

To explain the results, obtained with a drive-in under a chlorine containing ambient, one has to take into account the chlorine reaction at the silicon-silicon dioxide interface. In general, the perturbation of the interstitial concentration in equilibrium with the surface is due to

- i) generation of excess interstitials during the oxidation,
- ii) generation of excess interstitials, produced by the indiffusing boron atoms,
- iii) the chlorination reaction at the silicon interface, which results in the formation of Si-Cl bonds. This reaction decreases the concentration of interstitials.

The relative importance of these different components will determine the behaviour of the stacking

fault growth. Although component (i) is always present during an oxidation, the generation of interstitials due to the impurity diffusion can become more dominant for the OSF growth, as is shown by the experiments with a boron diffusion under oxidizing conditions. This is in agreement with our previously reported results on the influence of a phosphorous diffusion on the growth kinetics of the stacking faults [24].

Although the phosphorous experiments are performed with a higher surface concentration, it can be concluded from the comparison of these experiments with those reported in this paper, that for both phosphorous and boron, the interstitialcy diffusion component is very important.

5. Conclusion. — The growth kinetics of stacking faults, generated in silicon during a thermal oxidation, is strongly influenced by the diffusion of boron atoms. It is shown that dependent on both the drive-in atmosphere and the boron concentration in the doped oxide layer, the OSF's can grow or shrink as a function of time during an anneal at 1 150 °C. The experimental results lead to the conclusion that the boron diffusion has an important interstitialcy diffusion component.

Acknowledgment. — G. J. Declerck is indebted to the Nationaal Fonds voor Wetenschappelijk Onderzoek (N.F.W.O.) for his fellowship as *bevoegd verklaard navorser*. The authors would like to thank R. Rooyackers for carrying out the processing steps.

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