The Structure of SiO$_2$, its Defects and Radiation Hardness

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Abstract

We review our understanding of the structure of amorphous SiO$_2$ and the role of processing in inducing defect precursors. Five potential sources of positive trapped oxide charge and two of negative trapped charge are described. The most studied of these is the positively charged oxygen-vacancy center. Ionizing radiation is found to be ~ 1000 times less efficient than particle radiation in creating this defect. Various processing induced precursors of the defect and their transformation by radiation are discussed in detail. Macroscopic structural modifications induced by very large radiation doses (10^9 rad) are also discussed. Ionizing radiation is also found to be ~ 1000 times less efficient than particle radiation in inducing these modifications.

I. INTRODUCTION

The radiation sensitivity of amorphous (a-) SiO$_2$ films used in microelectronics technology has been known for a long time to depend upon processing steps used in their production [1]. However, a microscopic identification of the defects responsible for radiation induced electrical charge has been largely lacking due to the difficulty in performing spectroscopic measurements such as electron spin resonance (ESR) on thin films where the sample volumes that can be handled will necessarily be small (say ~ 3 x 10^{-6} cm^{-3} for a 100 nm thick film on a Si substrate). In the early 1980's, various authors were able to study paramagnetic defect and electrical charge creation in a-SiO$_2$ induced by particle [2] and ionizing [3] radiation. Here, however, the defect densities induced were very large so as to render the paramagnetic defects visible by ESR and consequently, substantially larger than the levels normally of interest for radiation sensitivity specialists. In these studies, the radiation induced trapped charge was primarily positive and, consistent with the observation of paramagnetic oxygen-vacancy centers which are expected theoretically [4] to be positively charged, attributed to them. The correlation was not confirmed absolutely in all cases [2]. More recently, etchback defect profiling and dose dependent growth studies on paramagnetic and electrically charged defects induced by energetic (16.7 eV) photons have clearly evidenced the fact that oxygen-vacancy centers cannot be the sole source of radiation induced positive charge in a-SiO$_2$ [5,6]. There is also a growing wealth of information [7,8] which suggests that the origin of radiation induced negative trapped charge should be addressed. Traditionally, negatively charged centers were observed primarily in high OH containing a-SiO$_2$ and so neglected for low OH containing oxides of the kind usually found as gate oxides in metal oxide semiconductor field effect transistors (MOSFET's).

In this paper we review the state of the art of our knowledge of intrinsic point defects in a-SiO$_2$. The microscopic structure of the defects, as determined through measurements such as ESR, and their associated charge state are discussed. Macroscopic structural modifications induced by radiation are also discussed. Since we also wish to concentrate upon the role of processing in radiation sensitivity, we begin by reviewing our understanding of the fundamental network structure of a-SiO$_2$ and how processing may induce variants in it.
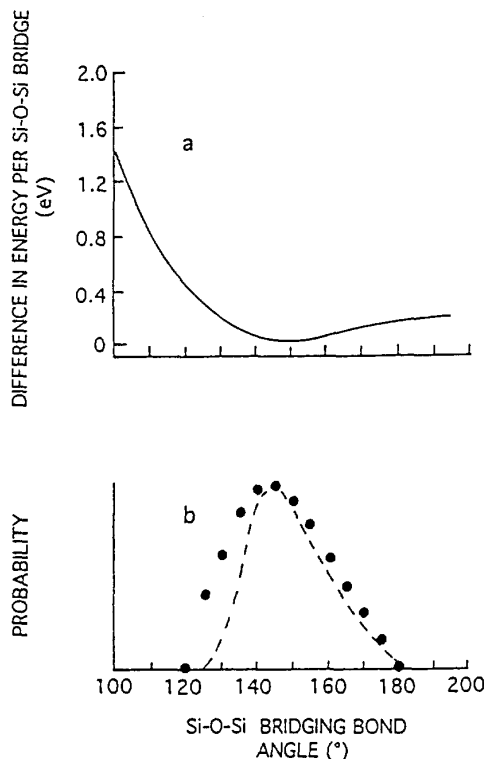

Figure 1. a) The calculated Si-O-Si bond energy as a function of bond angle [9] and b) the measured bond angle distribution (●) X-rays (--) nuclear magnetic resonance [10].

II. THE STRUCTURE OF a-SiO$_2$

It is generally accepted that a-SiO$_2$ is composed of SiO$_4$ tetrahedral building blocks which are interlinked with Si-O-Si bridging bond angles, θ. Since the structure is non-

crystalline one anticipates a variety of possible angles. In Figure 1a we show the calculated [9] bond energy as a function of bridging bond angle, θ. One observes that over a substantial range of angles ($120° \leq \theta \leq 180°$) there is very little variation in the bond energy leading us to assume that independent of any purely geometrical consideration, the amorphous SiO_2 network contains not a variety but rather a continuous range of θ. This assumption is confirmed by the results of measurements of bond angle distributions in bulk a-SiO_2 samples [10] as shown in figure 1b. It is important to note from Figure 1b that bond angles not having the energy minimizing value of ~ 144° exist and that therefore we must anticipate the presence of strained bonds even in the network which we consider to be "regular, relaxed" a-SiO_2. The radiation response of the strained bonds, we will see, is not necessarily identical to that of the unstrained bond.

In dealing with point defects, we need not in general go beyond nearest neighbour bonding considerations. It is instructive, however, to examine how the bonds configure themselves in the extended network. We know that the linked SiO_4 tetrahedra arrange themselves in rings, an example of a regular ring is shown in Figure 2. Generally, the rings are neither planar nor regular. The rings may twist and buckle so as to try to minimize the bond energy (Figure 2b) at the same time taking account of physical constraints imposed by the geometry of their immediate environment and space filling requirements. Such constraints then lead us to anticipate, naturally, the presence of a continuum of bridging bond angles such as the distribution shown in Figure 1b.
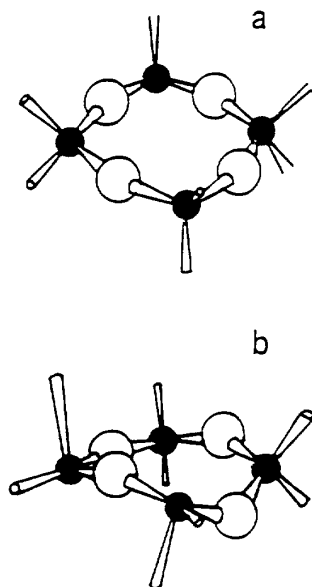

Figure 2. a) A schematic diagram of a planar, regular 4 membered ring b) the same ring puckered so as to reduce the bridging bond angle to the optimum value of 144°.

Having discussed the basic structure of the a-SiO_2 network and before specifically discussing defects, we examine possible modifications other than in the bond angle distribution, which might be induced by processing. In particular, we examine two extremes which are used in microelectronics, oxides produced in the presence of water vapour (high OH containing) and those produced in very dry O_2 (low OH containing). The former oxide is usually found in inter-device isolation applications whilst the latter is used for MOSFET gate oxides. In high OH containing oxide the OH levels may attain 1200 ppm by weight, they are incorporated into the network in bonds which terminate one of the SiO_4 tetrahedral bonds generally leading to mechanical (and radiation) softening of the network.

$$O_3{\equiv}Si\text{-}O\text{-}Si{\equiv}O_3 + H_2O \rightarrow 2\ O_3{\equiv}Si\text{-}OH \qquad (1)$$
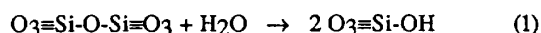
At the other extreme, oxidation in a dry O_2 atmosphere possibly coupled with inert atmosphere annealing post-oxidation, may result in slight sub-stoichiometry and the formation of oxygen deficient structures :
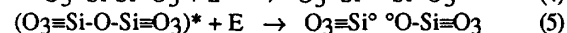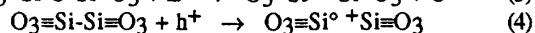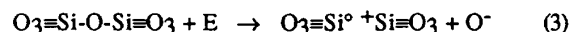
$$O_3{\equiv}Si\text{-}O\text{-}Si{\equiv}O_3 \rightarrow O_3{\equiv}Si\text{-}Si{\equiv}O_3 + O{\uparrow} \qquad (2)$$
$$\text{reduction}$$
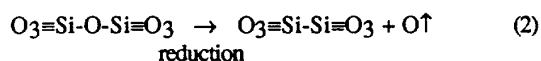
Both structures, indicated by Equations 1 and 2, must be considered defective.

III. POINT DEFECTS

A. The Oxygen-Vacancy Center

The most studied intrinsic defect in a-SiO_2 is the positively charged, oxygen-vacancy center [4] : $O_3{\equiv}Si°$ $^+Si{\equiv}O_3$ The reason for this is that the ESR of the paramagnetic site ($O_3{\equiv}Si°$) is readily observable at room temperature and insensitive to its immediate environment (no major lineshape sensitivity, no major enhancement of the relaxation rate, ...). As mentioned in the previous section, there is now good reason to believe that this defect is not necessarily the major source of positive fixed oxide charge induced by radiation. However, since it is the most studied and perhaps the most understood, we will review it extensively. We discuss three possible creation mechanisms :

$$O_3{\equiv}Si\text{-}O\text{-}Si{\equiv}O_3 + E \rightarrow O_3{\equiv}Si° {}^+Si{\equiv}O_3 + O^- \qquad (3)$$
$$O_3{\equiv}Si\text{-}Si{\equiv}O_3 + h^+ \rightarrow O_3{\equiv}Si° {}^+Si{\equiv}O_3 \qquad (4)$$
$$(O_3{\equiv}Si\text{-}O\text{-}Si{\equiv}O_3)^* + E \rightarrow O_3{\equiv}Si° \ °O\text{-}Si{\equiv}O_3 \qquad (5)$$

where ( )* infers that the bond is strained. In Equations 3 and 5 we use E to symbolize a source of energy which may be either particle or ionizing radiation. Note that in Equation 5 the initial product of radiation induced bond scission is the simultaneous production of two paramagnetic defects one being oxygen-vacancy "like" because it lacks the positively charged complement. Before discussing the defect creation
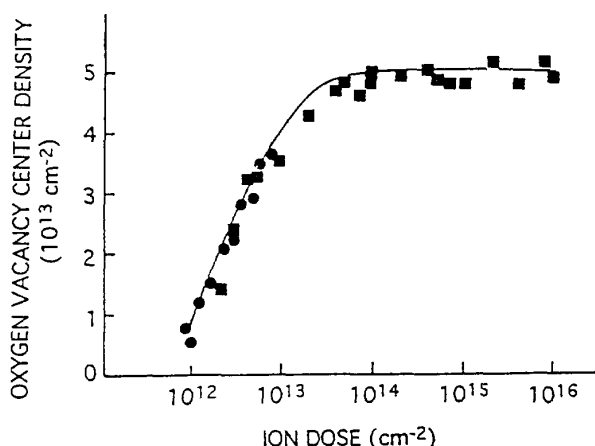
2100 eV in nuclear displacement processes (both O and Si atoms).

Figure 3. Ion implantation induced growth of the oxygen-vacancy center density in a-SiO$_2$ films as a function of dose of 30 keV N$^+$ ions.
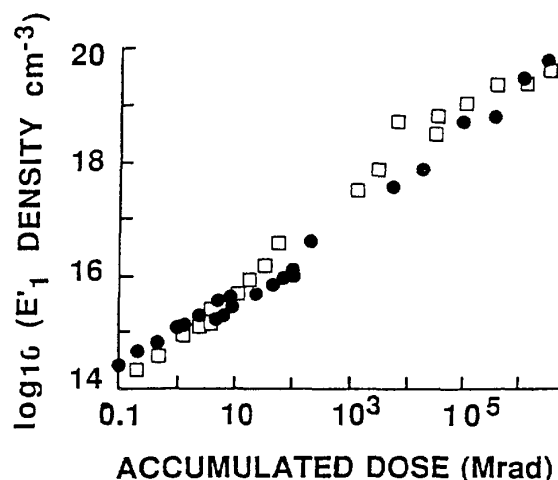

Figure 4. Growth of the paramagnetic oxygen-vacancy (E'$_1$) defect density as a function of ionizing radiation dose. Filled symbols, low OH oxide, open symbols, high OH oxide.

mechanisms in detail, it is clear from Equations 4 and 5 that their relative importance in radiation sensitivity will depend upon the numbers of neutral oxygen-vacancies (O$_3\equiv$Si-Si$\equiv$O$_3$) and strained bonds ((O$_3\equiv$Si-O-Si$\equiv$O$_3$)*) present prior to irradiation. We see immediately, then, a potential source for processing induced differences in radiation sensitivity.

If we consider primarily particle radiation, then the displacement of a bridging oxygen atom results from a simple nuclear shock. Figure 3 shows the growth of the oxygen-vacancy defect density in thin films of a-SiO$_2$ implanted with 30 keV N$^+$ ions. The observed curve, showing a saturation phenomena corresponding to a volume defect density $\sim 2 \times 10^{19}$ cm^{-3}, is common for all ions dissipating their energy in the form of nuclear displacement [11]. It can be modeled using an equation of the form :

$$\rho = \rho_0 \eta_c (1 - \exp(- [\eta_a + \eta_c]D))/(\eta_a + \eta_c) \qquad (6)$$

where ρ is the defect density, D the ion dose, η_a a cross section for defect annihilation and η_c, a cross section for defect creation. ρ_0 is a saturation density of defects "creatable". This model allows not only for implantation induced defect creation but also for some annihilation. Analysis of the low dose behaviour (dρ/dD | D → 0) and comparison with the results of calculation of total oxygen atom displacement based on TRIM-89 [12] suggests that one stable paramagnetic oxygen-vacancy center is created for 37 expected oxygen displacements in the radiation cascade. This result demonstrates that most of the oxygen-vacancies created in the cascade must self-anneal. On the basis of these numbers one can show that the creation of one stable paramagnetic defect requires the deposition of approximately

If the creation of oxygen-vacancy centers via nuclear displacement is "self-explanatory" the same cannot be said for the case of ionizing radiation. The exact mechanism leading to oxygen displacement in the unstrained bond (Equation 3) remains unclear although it is generally believed that it involves the non-radiative relaxation of self-trapped excitons. This means that cross-bandgap excitations such as electron-hole (e-h) pairs which result in O displacement must lose their energy first by a cascade process which terminates in the formation of the self-trapped exciton.

In Figure 4 we show the radiation induced oxygen-vacancy center creation curve as a function of dose (in rad(SiO$_2$)) for low OH and high OH containing a-SiO$_2$. Most of the data was obtained for bulk samples. In the low dose regime the equations governing the growth of the defect density are :

$$\rho_{low\ OH} = 3.2 \times 10^{11} D^{0.58} \text{ cm}^{-3}$$

$$\rho_{high\ OH} = 2.9 \times 10^{10} D^{0.77} \text{ cm}^{-3} \qquad (7)$$

where D is the radiation dose in rad. From these results we conclude that the order of magnitude of the energy dissipated in ionizing processes for the creation of one stable oxygen-vacancy defect is $\sim 2 \times 10^6$ eV. This is approximately 1000 times larger than the energy required in nuclear displacement processes. Assuming the energy necessary to create an e-h pair in a-SiO$_2$ is ~ 18 eV [13] then, crudely, one stable oxygen-vacancy defect is created for every 5.5×10^4 e-h pairs. By analogy with the nuclear displacement result, assuming we observe only 1/37 of all displaced oxygens then we conclude that it requires ~ 1500 e-h pairs be created per displaced oxygen. This result suggests that relatively few of

the e-h pairs created in a radiation cascade actually lead to self-trapped exciton generation followed by displacement of a network oxygen atom. Finally, we note from Figure 4 that there appears to be the beginning of a defect saturation at densities ~ 10^{20} cm^{-3} for radiation doses approaching 10^6 Mrad. These doses are largely in excess of those generally of interest in radiation sensitivity studies.
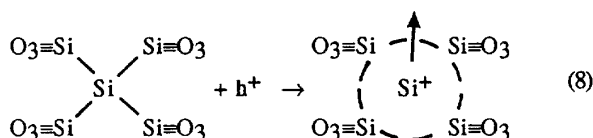
Little can be said at the present time about the efficiency of charged oxygen-vacancy defect creation following equations 4 and 5 since, amongst other things, the precursor densities depend upon the processing conditions.

B. Other sources of positive trapped charge

As mentioned previously, the most studied positively charged intrinsic defect is the oxygen-vacancy center discussed at length in the previous section. In the present section we discuss other potential sources of positive trapped oxide charge.

B.1. Oxygen-Vacancy Complexes

There is growing evidence [14,15] that oxides that have become slightly sub-stoichiometric due to processing during production (for example, Separation by IMplantation of OXygen, SIMOX, films) or post-oxidation annealing, contain oxygen-vacancy/Si complexes. One such complex which has been studied spectroscopically and which may lead to positive fixed oxide charge formation and paramagnetism by hole trapping is :

$$O_3 \equiv Si \diagdown Si \equiv O_3 \quad O_3 \equiv Si \overset{\uparrow}{\diagup\!\!\!\diagdown} Si \equiv O_3$$
$$Si + h^+ \rightarrow \left(Si^+ \right) \quad (8)$$
$$O_3 \equiv Si \diagup Si \equiv O_3 \quad O_3 \equiv Si \diagdown \diagup Si \equiv O_3$$

where the paramagnetic spin is delocalized over the five Si's. Note that the central Si is initially tetrahedrally co-ordinated as in pure Si. The precursor center (left hand side of Equation 8) may also be viewed as a multiple (4) oxygen-vacancy. The paramagnetic defects (denoted E'$_\delta$) have been observed following hole injection and trapping in SIMOX and other silicon on insulator structures [14] as well as in hole injected high temperature/inert atmosphere annealed thermal oxides. They are also observed, but with greater difficulty, following X or γ irradiation. The latter result is assumed to be due to the fact that the positively charged defect (right hand side of Equation 8) once formed by hole trapping, has a large cross section for electron capture so that in a radiation cascade, the defect may be created and "simultaneously" eliminated. Irradiations in the presence of an electric field minimize electron-hole pair recombination at defects by sweeping the high mobility electrons away from the holes as the pairs form. Such experiments have not yet been performed on these defects to our knowledge. No dose dependent creation kinetics for these defects have been reported either.

B.2. Strained Bond Related Centers

Three more defects which can be expected to be positive trapped charge centers have been suggested, two have been identified spectroscopically by ESR and one has been proposed on the basis of calculation. All three defects involve strained bonds and unlike the bond scission process shown in Equation 5 which results in the creation of two paramagnetic defects, here we consider the effects of strained bonds (with or without scission) and the trapping of radiation generated holes. Since we know that the regular "relaxed" a-SiO$_2$ network contains strained bonds (section I.) such defects may be regarded to some degree as intrinsic. Furthermore, since the degree of strain present in the network may conceivably depend upon processing conditions (in particular, near the Si/SiO$_2$ interface) the number of these defects present may be considered to be process dependent. The two defects which have been studied by ESR, in bulk a-SiO$_2$, are the self-trapped holes denoted STH1 and STH2 [16]. A hole is assumed to localize at a strained bond either on the bridging oxygen (STH1) or between two bridging oxygens associated with the same SiO$_4$ tetrahedron (STH2). A schematic representation of the two types of defect is presented in Figure 5. We note that since STH2 requires two bridging oxygens in strained bonds, we would expect to observe less of these than the STH1 defects which require only one. In Figure 6 we show data obtained by ESR on bulk a-SiO$_2$ samples exposed to X irradiation at 77 K [16]. One indeed observes, numerically less STH2 defects than STH1. We also observe, in Figure 6, that both types of defects appear to anneal out in the bulk at temperatures ≤ 200 K where one also measures an increased rate of annealing of the positive fixed oxide charge in low temperature irradiated MOSFET's (Figure 6). Note that in this figure the absolute scale is not important, only the observation that a bump appears in the oxide charge curve which corresponds with the annealing out of trapped hole related defects. Whether or not
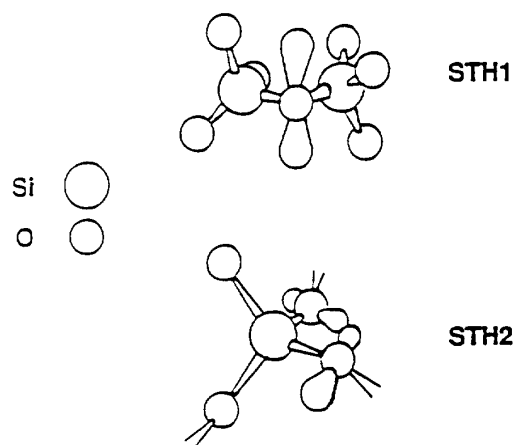
Figure 5. A schematic representation of the self-trapped hole centers STH1 and STH2 [16]. The holes are trapped on strained Si-O-Si bonds.

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these defects are significant sources of positive charge at room temperature in MOSFETS will depend upon the possibility that they may be stabilized to higher temperatures by very severely strained bonds. This will again depend upon processing.

Finally, in discussing sources of positive trapped charge we consider the case of the scissioned strained bond. Unlike the simple scission suggested by Equation 5 which results in the production of two paramagnetic centers, hole trapping on the oxygen related center may occur. Whether or not this is the driving mechanism for scission or the trapping occurs once the Si-O bond is ruptured is of little importance :

$$(O_3 \equiv Si\text{-}O\text{-}Si \equiv O_3)^* + h^+ \rightarrow O_3 \equiv Si^\circ \ ^+O\text{-}Si \equiv O_3 \qquad (9)$$
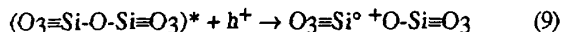
Note that calculations [17] suggest that the positively charged defect is stable. The resultant complementary pair of defects is positively charged and paramagnetic. However, to date, no ESR data has been reported which clearly identifies the paramagnetic part of such a defect. This result may not be significant if we recall that the ESR active part of the defect ($O_3 \equiv Si^\circ$) is relatively insensitive to its immediate environment and the defect would therefore be indistinguishable from the usual oxygen-vacancy center.

We have discussed five defects which may be considered to be sources of radiation induced, trapped positive charge in a-SiO$_2$. Four of the defects have been identified spectroscopically and there are strong grounds to believe that the fifth defect exists. A word of caution is required at this point. Starting ten years ago and until recently it was

Figure 6. Isochronal annealing of the self-trapped hole density and positive fixed oxide charge in a-SiO$_2$ films initially irradiated at 77K using X-rays. (■) STH1, (●) STH2, (▲) positive fixed oxide charge.

generally believed that the positively charged oxygen-vacancy was the sole source (or major source) of trapped positive charge in irradiated a-SiO$_2$. Now we are discussing at least five potential sources. We may still be, therefore, some considerable way from completely cataloguing all of the possible positively charged defects.

C. Negative Trapped Charge

It is reasonable to say that the most common model for radiation induced, trapped negative charge concerns hydroxyl groups incorporated into the a-SiO$_2$ network. These species result from the presence of water vapour or hydrogen in the growth atmosphere [18]. Transformation of the neutral defect is assumed to arise by electron trapping :

$$O_3 \equiv Si\text{-}OH + e \rightarrow O_3 \equiv Si\text{-}O^- + H\uparrow \qquad (10)$$

The hydrogen released during the trapping of the electron is, furthermore, potentially hazardous because of subsequent gettering of passivating hydrogen at the Si/SiO$_2$ interface leading to interface state creation :

$$Si_3 \equiv Si\text{-}H + H \rightarrow Si_3 \equiv Si^\circ + H_2 \qquad (11)$$

The use of multiple walled oxidation furnaces and ultra-dry oxygen sources considerably reduces the hazards associated with hydrogen in MOSFET gate oxides. The problem remains, however, for thick (field) oxides used for interdevice isolation (LOCalized Oxidation of Silicon, LOCOS) which must be grown in a wet atmosphere because of the high oxidation rates required to obtain thick oxides in a reasonable time. The problem of hydrogen incorporation is also expected to exist for deposited oxides which may be obtained via chemical vapour deposition using SiH$_4$/N$_2$O or Si(OC$_2$H$_5$)$_4$ O$_2$ chemistries.

Recent radiation sensitivity studies [7,8] on buried oxide layers (SIMOX) and on dry, thermal oxides subjected to high temperature anneals in an inert atmosphere have provided clear evidence for the presence of radiation induced, negative trapped charge in dry oxide. Negative charge trapping due to processes such as those described by Equation 10 are, of course, excluded for the dry oxide case. In ultra-dry oxides it is not impossible to imagine a certain substoichiometry so that one can anticipate the presence of neutral oxygen-vacancies ($O_3 \equiv Si\text{-}Si \equiv O_3$). Calculations [19] have indicated that whereas we generally expect the neutral oxygen-vacancy to be a hole trap, it may also trap electrons leading to a negatively charged state in the SiO$_2$ bandgap about 1 eV below the conduction band edge :

$$O_3 \equiv Si\text{-}Si \equiv O_3 + e \rightarrow O_3 \equiv Si\text{-}^\circ\text{-}Si \equiv O_3 \qquad (12)$$
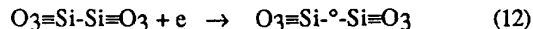
The negatively charge defect center is also paramagnetic although, to date, there have been no reports of the observation of the ESR associated with the defect.
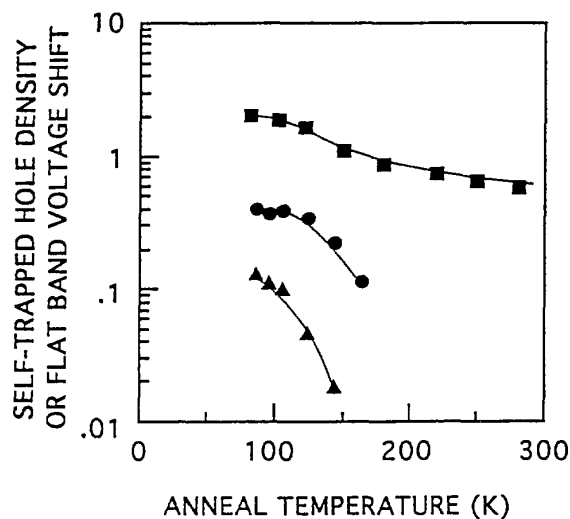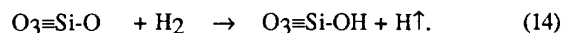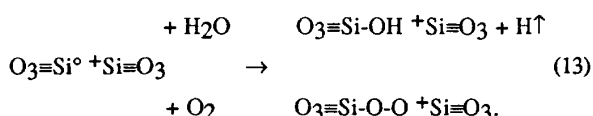
We have reached the point, microscopically, where two sources of negative trapped charge have been identified. The reason for such a small number is perhaps not that others do not exist but that, until recently, their presence was unexpected. As with the case of the many sources of positive fixed oxide charge, it would not be surprising if, in the years to come, a whole family of previously unknown negatively charged centers was revealed.

IV. DEFECT REACTIVATION

Before leaving the subject of point defects induced/revealed by radiation it is important to say a few words about "annealing". As far as paramagnetic defects are concerned, it is generally accepted that they anneal by the trapping of some diffusing molecular species such as O_2 [20], H_2 [21], H_2O [22],...:

$$O_3\equiv Si^\circ \ ^+Si\equiv O_3 \ \rightarrow \ \begin{array}{ll} + H_2O & O_3\equiv Si\text{-}OH \ ^+Si\equiv O_3 + H\uparrow \\ \\ + O_2 & O_3\equiv Si\text{-}O\text{-}O \ ^+Si\equiv O_3. \end{array} \quad (13)$$

$$O_3\equiv Si\text{-}O \ + H_2 \ \rightarrow \ O_3\equiv Si\text{-}OH + H\uparrow. \quad (14)$$

We note that these equations do not account for charge annealing (where relevant) and that therefore we must assume that it comes about through totally independent mechanisms. Since the localized charge for the self-trapped holes, STH1 and STH2 (Figure 6), and the negative oxygen-vacancy center (Equation 12) are also the sources of paramagnetism of these defect centers, they may constitute unique cases in which both paramagnetism and localized charge are expected to anneal out simultaneously (see Figure 6 for example).
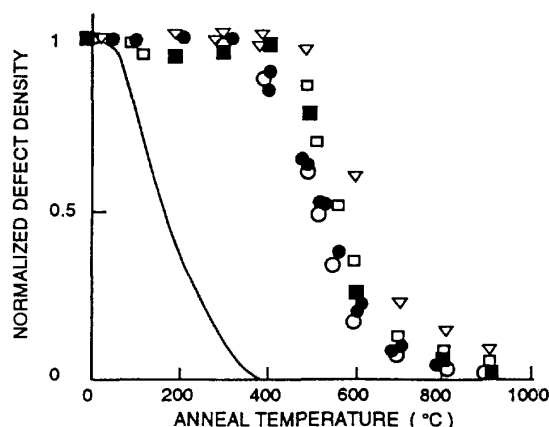

Figure 7. Isothermal annealing of paramagnetic oxygen-vacancy centers created by ion implantation in a-SiO$_2$. Solid line, straightforward annealing. Symbols, defect density after reactivation using small doses of ionizing radiation demonstrating that the defects were only passivated by annealing.

In Figure 7 we reproduce defect reactivation data obtained in a study [6] of the annealing of paramagnetic oxygen-vacancy centers in ion implanted thin films (high OH). In these experiments the samples were first irradiated or ion implanted then the paramagnetic defect density measured. Subsequently the samples were annealed at different temperatures in an inert atmosphere and the defect density remeasured. Finally, the samples were re-irradiated with ionizing radiation but with doses normally too small to create a measurable number of defects (for example, 0.5 Mrad for the case of ^{60}Co γ's). One observes (Figure 7) that whereas the paramagnetism of oxygen-vacancy centers usually anneals out at temperatures in the range ~ 200 - 400°C (solid line) in fact they can be re-activated and are not removed irreversibly unless the anneal temperatures are in excess of 700°C. The explanation of this is that a true "annealing" has not occured but the defects have been passivated (Equation 13) in a reversible manner. The damaged network is only repaired by very high temperature annealing. Technologically, the importance of this result is that as we reduce the thermal budgets used in microelectronics processing we must remain conscious of the fact that certain types of processing generated damage will not be automatically removed during later high temperature stages. This point is particularily relevant in ASIC technology where direct electron beam writing damage induced in dielectrics cannot be permanently removed because the presence of metal interconnects (such as Al) excludes subsequent processing at temperatures higher than about 500°C.

To our knowledge similar reactivation studies have not been carried out for the case of charge annealing. They are, however, extremely important because a) they are needed to complete our physical understanding of the underlying process of low and high temperature defect annealing, and b) they would enable us to fix lower limits to annealing cycles required to "harden" oxides softened during circuit processing. The coupling of such electrical studies with spectroscopic measurements would appear to be essential.

V. MACROSCOPIC CHANGES

For radiation sensitivity studies one is usually interested in what one may call the "low dose regime" in which point defect densities increase linearily with accumulated radiation dose. There are, however, situations in which one needs to understand the behaviour of the oxide in the very high dose regime where macroscopic structural changes may be induced. Two examples are a) through field oxide implants for the production of recessed wells and b) very high energy particle tracks. In the former case, for example, the implantation of 900 keV P$^+$ ions through a field oxide of say 580 nm to a dose of 10^{13} cm^{-2} results in the deposition of 8 x 10^{22} eV cm^{-3} in the form of ionization and 4 x 10^{23} eV cm^{-3} in the form of nuclear displacement in the oxide. In terms of radiation dose, these correspond tho 1300 Mrad and 6500 Mrad respectively. At such high

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accumulated doses into displacement one must consider that every Si-O bond in the network has been broken at least once and that in consequence the initial internal ring structure (section I) has been totally modified. Indeed, at such high dose levels one observes a radiation induced compaction that results in an increase in density of ~ 3% in the network, clearly emphasising an internal structural modification. We will not go into the possible physical nature of the internal structural changes here. We do note, however, that electrical breakdown field measurements [23] on films which have received similar particle radiation doses and then been annealed at 900°C for 30 minutes demonstrate that the oxide has been substantially weakened, this is shown in Figure 8 [23]. We re-iterate the important fact that the data were obtained on post-implantation annealed samples, this demonstrates that high temperature annealing does not recover the initial structure of the oxide film. Detailed analysis shows that similar macroscopic effects can result from ionizing radiation although, as in the case of point defect generation, the process is again ~ 1000 times less efficient requiring ~6 x 10^{12} rad. Such accumulated dose levels are seldom encountered.

Another special case should be mentioned which concerns very fast ions which form particle tracks. In this case, because of the very high density of energy deposited in the form of ionization, one may reach a situation in which
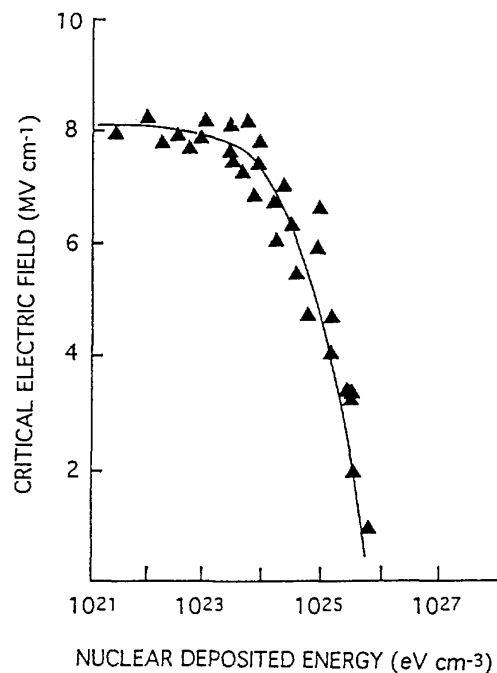
essentialy all the Si-O bonds in the particle track are ionized [24]. The resultant effect is an instantaneous softening/melting of the network which can lead to rearrangement of the bonding configuration on cooling, this is again evidenced by the degree of densification. This case is extreme given the doses involved, it is not generally relevant in sensitivity studies.

VI. CONCLUSIONS

We have reviewed the state of the art of our understanding of the microscopic structure of defects revealed by irradiation of a-SiO$_2$. We have elucidated five defects which are possible sources of positive fixed oxide charge and two which are sources of negative charge. It is very unlikely that this list is complete and time will surely reveal other defects yet unanticipated. A study of the microscopic structure of the defects leads to a natural explanation of where processing used in film manufacture intervenes and enhances the probability of finding certain types of defects. The most commonly observed defect, and the most understood, remains the oxygen-vacancy center, it is produced ~ 1000 times more efficiently by particle radiation than by ionizing radiation (per eV deposited in the amorphous network).

Many questions remain open concerning the behaviour of defects and in particular, that of reactivation following low temperature annealing. It would appear fundamental to combine electrical and ESR studies to completely elucidate the mechanisms of annealing/passivation and potential reactivation. Finally, the behaviour of oxides in the very high dose regime is relatively poorly understood. There is clear evidence for macroscopic modifications in the network but little is known about their physical nature. Given the relevance of this effect technologically in the area of high dose implantation for recessed wells, more attention should, perhaps, be paid to it.

VII. ACKNOWLEDGEMENTS

VIII. REFERENCES

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Figure 8. Variation of the electrical breakdown field as a function of nuclear deposited energy in a-SiO$_2$ films through implanted with P, As and B ions. The breakdown field was measured after post-implantation annealing at 900°C for 30 minutes [23].

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