THE EFFECT OF THE OXIDE NETWORK STRUCTURE ON THE IRRADIATION BEHAVIOR OF SiO_2 FILMS ON SILICON

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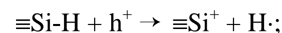
Ionizing irradiation (X-rays, γ-rays, VUV light) generates positive charge in Si/SiO_2 structures used in Si devices that affects their characteristics. The oxide charge has usually been attributed to hole trapping at oxygen vacancies where one of the two neighboring Si atoms become positively charged and the other one has an unpaired electron (dangling bond) which is ESR-active (E'-center). However, the oxide charge is usually larger than the integrated concentration of E'-centers. (1) It has been suggested that intrinsic hole trapping (i.e. not associated with E'-centers) may be due to $d\pi-p\pi$ orbitals (2) or polarons (1) which are closely tied to the structure of the non-crystalline oxide. Even the E'-centers and other network defects are closely tied to the details of the oxide structure and the nature ofSi-O bonds.

Thermally grown SiO_2 films used in Si devices are non-crystalline (nc), i. e. without long-range-order (LRO). However, they have a high degree of short-range-order due to the practically invariant nature of the $SiO_{4/2}$ units (the O-Si-O bond angles are 109°), As the concentration of broken bonds in un-irradiated oxides is less than $\sim 10^{14}$ cm^{-3}, the degree of **bond-ordering** (BO) is also high. This type of nc-structure has been designated as **vitreous** (v). (3) The lack of LRO in v-SiO_2 is due to the flexibility of the Si-O bonds that is shown by the small variation of their energy (< ~ 0.15 eV) with the Si-O-Si bond angles (ϕ) in the range of ~120° to ~180° (4) which is the typical distribution of ϕ in v-SiO_2. However, the energy increases sharply for ϕ < 120°, reaching ~0.4 eV at ~110°; these bonds can be considered as *strained*. As ϕ decreases, the bond length increases. It follows that the proportion of strained bonds increases with increasing oxidation or annealing temperature.

We suggest that intrinsic hole trapping (i.e. without E'-centers) can occur in ring configurations in the oxide which are connected to the network by strained long bonds with ~120°>ϕ >~109°. The long bond prevents the de-localization of the $d\pi$-$p\pi$ orbitals which are very sensitive to local configurations. The bond energy of these configurations is between ~ 0.15 and ~0.4 eV. This model is different from the polaron model (1) which is based on essentially ionic Si-O bonds, even though, in reality, such bonds are predominantly covalent.

We have determined the activation energy of generating oxide charge by irradiation from published data (5) and, depending on the temperature range, found ~0.15 and ~ 0.5eV for VUV irradiation (see Fig.) as well as ~0.18 eV for x-ray irradiation; these values indicate that strained bonds are involved. Most of the oxide charge reported in Ref. 5 is not associated with E'-centers, indicating intrinsic hole trapping. Another possibility is the dissociation of SiH groups at configurations with strained Si-O bonds:



$$\equiv Si\text{-}H + h^+ \rightarrow \equiv Si^+ + H\cdot;$$

the H atoms then form H_2 molecules or SiOH groups.

This model is different from that in Ref. 5 where the positive charge was assigned to protons linked to O atoms by hydrogen-bonds, especially in Si-O-Si configurations with very large ϕ; the origin of protons was not discussed there.

In conclusion, the over-all oxide network structure plays a more important role in the irradiation behavior of v-SiO_2 films on silicon than network defects (e.g. oxygen vacancies).

Acknowledgment. This work was supported by the Defense Threat Reduction Agency, Washungton, DC.

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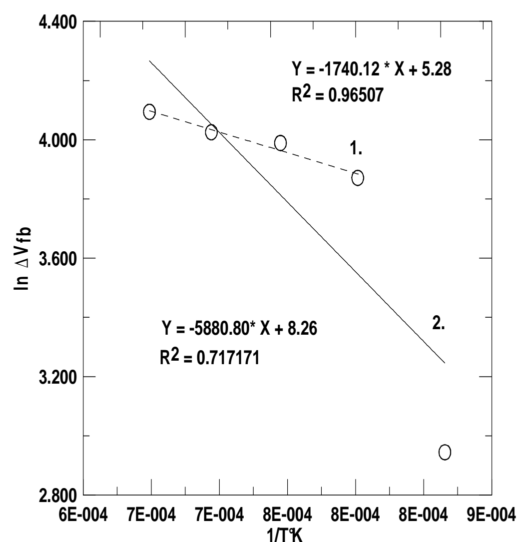

Positive oxide charge generated by VUV irradiation given by the flat-band voltage shift of the C-V curve, ΔV_{fb}, as a function of the reciprocal absolute processing temperature (from data in Ref. 5) Curves 1 and 2 give 0.15 and 0.5 eV activation energies, respectively.