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Response to "Comment on 'A model of hole trapping in SiO_2 films on silicon' " [J. Appl. Phys. 83, 5591 (1998)]

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We disagree with the comment of R. A. B. Devine, W. L. Warren, and S. Karna [J. Appl. Phys. **83**, 5591 (1998)]. © *1998 American Institute of Physics.* [S0021-8979(98)00110-8]

We agree with Devine *et al.*[1] that our recent paper does "constitute a major step toward quantitative prediction of the effects of processing" on metal oxide silicon field effect transistor problems. We disagree with the rest of the comment.

Devine *et al.*[1] repeatedly refer to an activation energy of oxygen vacancy/E' defect creation of 4.49 or 4.5 eV, which they obtain from their expression (3): $(14.6-5.11)/2$. Actually, $(14.6-5.11)/2=4.745$. We use 4.75 eV in our response.

Devine *et al.*[1] direct their criticism of our paper at an assumption which is not in it. They *assume* that, in the absence of a nearby Si/SiO_2 boundary, oxygen vacancy E' defect creation proceeds via $2\text{Si–O–Si}\rightarrow 2\text{Si–Si}+O_2$. Other obvious possibilities exist; for example, Robertson proposes[2] $2\text{Si–O–Si}\rightarrow\text{Si–Si}+\text{Si–O–O–Si}$.

Assuming that the Devine *et al.*[1] reaction is responsible for oxygen vacancy/E' generation (without a Si/SiO_2 interface nearby) Devine *et al.*[1] (imprecisely) compute a lower limit to the enthalpy of defect creation from $(14.6-5.11)/2$. They obtained 14.6 eV from an estimate of the energy required to remove an oxygen atom from SiO_2 (7.3 eV) which is almost certainly wrong. It was obtained from a one line arithmetic calculation involving the formation energy of β-crystobolite.[3] Far more sophisticated (*ab initio*—Hartree-Fock and modified neglect of differential overlap) calculations[4] which include (large) lattice relaxation effects estimate this energy to be $\cong 4$ eV. Using the crudely estimated 7.3 eV, and an O_2 bond energy (5.11 eV), Devine *et al.*[1] compute $[2(7.3)-5.11]/2\text{ eV}=4.5\text{ eV}$, more precisely 4.75 eV, which they argue is impossible to reconcile with our 1.5 ± 0.1 eV.

With the more sophisticated[4] estimate of 4 eV, they would have obtained $[2(4)-5.11]/2=1.45\text{ eV}$, a result within our experimental error. This agreement between our experimental result and "theory" is itself far from definitive. An *accurate* calculation of the formation energy of a vacancy is not straightforward. See Lannoo and Bourgoin, Chap. 6,[5] who comment with regard to comparatively sophisticated calculations: "Considering the very crude approximations which are made in these calculations, *the results can only be considered estimates.*" (emphasis added.)

The most serious shortcoming of the Devine *et al.*[1] 4.5 eV (actually 4.75 eV) is that it is impossible to reconcile with experimental results. E' center/oxygen vacancy defects have been measured in amorphous SiO_2 without Si/SiO_2 interfaces nearby, in large volume ($\sim 1\text{ cm}^3$) samples. E' densities in the range of $\sim 10^{17}/\text{cm}^3$ are typically observed.[6,7] If the Devine *et al.*[1] activation energy were correct, the maximum possible defect density would be, within a few orders of magnitude,[8] the density of available sites ($\sim 10^{22}/\text{cm}^3$) multiplied by $\exp(-4.75\text{ eV}/kT)$, where T represents the temperature in which the defects are quenched. Robertson suggests $T\cong 1500$ K as a reasonable estimate for this temperature.[2] At 1500 K, $\exp(-4.75\text{ eV}/kT)=1\times 10^{-16}$. Thus, the maximum possible defect density would be $\sim 10^6/\text{cm}^3$, approximately *eleven orders of magnitude* below experimental results.

Using the crude bond breaking energy arguments of Devine *et al.*,[1] the oxygen vacancy/E' defect creation mechanism proposed by Robertson[2] would yield a much lower activation energy, because each oxygen vacancy creation event would also yield one peroxy center; thus, $[\text{Si–O–O–Si}]\,[\text{Si–Si}]=[\text{Si–Si}]^2=K[\text{Si–O–Si}]^2$. This reaction and the (not very accurate) bond breaking arguments yield an activation energy under 3 eV even if we utilize (the almost certainly inaccurate) 7.3 eV energy to remove an oxygen from SiO_2. Other possibilities would also yield lower energy estimates.

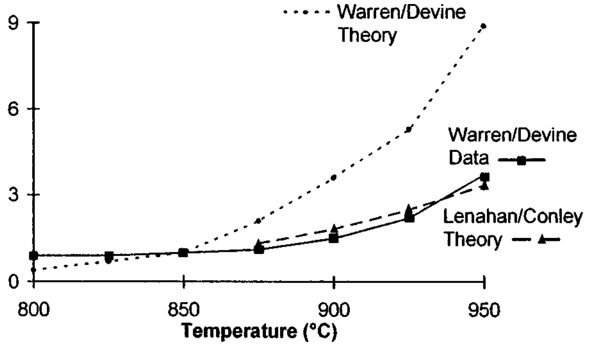

FIG. 1. An illustration of the Warren/Devine (see Ref. 9) "theory" and data as well as a plot of a constant times $\exp(-\Delta H_a/kT)$, where $\Delta H_a=1.5$ eV.

Devine, Warren, and Karna argue that our results could be ‘‘anticipated’’ from recent work of Devine, Warren, and co-workers from which one could further *anticipate* an activation energy of 2.27 eV. This energy is not within our experimental error. Reviewing the Devine and Warren work,[9] we notice that our 1.5 ± 0.1 eV activation energy fits their own data significantly better than their model. In Fig. 1 we replot Devine/Warren and co-workers[9] Fig. (1) using the same scales for theory and experiment. (Their original paper utilized different ordinate axis scales and zeros to compare data and theory.) Furthermore, Devine and Warren *et al.*[9] require oxygen vacancy concentration to vary by *an order of magnitude* over distances as small as 0.1 Å to produce the fit illustrated in Fig. 1 (see Fig. 2 of Ref. 8). Since atomic diameters exceed 1 Å, this is impossible.

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