Confirmation of a Predictive Process Dependent Model of Oxide Charging

J.F. Conley, Jr.
Dynamics Research Corporation, 19545 NW Von Neumann Dr., Suite 130, Beaverton, OR, 97006
Tel: 503/690-1570 x6115, FAX: 503/690-1517, jconley@stt3.com

The concept of building in reliability (BIR) has been gaining attention in the semiconductor industry. Full realization of BIR, in our view, will require the development of physics-based models of the effects of process parameter variations on reliability mechanisms and subsequent incorporation of these models into predictive semiconductor TCAD tools. Last year at this conference [1], a physics-based model of charge trapping in "intrinsic" SiO_2 was introduced and its potential predictive power demonstrated on a limited array of oxides. (By "intrinsic" it is meant that trapping due to extrinsic contaminants is insignificant.) Here, work is presented that confirms the validity of the model's parameters and shows that the model is predictive for a variety of oxides. In addition, very preliminary results are presented that address the equilibrium kinetics assumptions that were made in order to calibrate this model.

The oxide charging model first presented last year (fully described in [1]) is based on statistical thermodynamics and electron spin resonance (ESR) measurements of the oxygen-vacancy-related point-defects known as E' centers. (E' centers, shown as an inset in Fig. 2, are the dominant hole trapping defect in thermally grown SiO_2 films.) It was found that the density of bridging O-vacancies (herein E'-precursors) in SiO_2 can be modeled by minimizing the Gibb's free energy. The density of E'-precursors present in an oxide film after a dominant high temperature step (defined here as the step that determines final E'-precursors density) is thus described by,

$$[E']_{precursor} = A\, e^{-\Delta H/kT_{max}}, \qquad (1)$$

where A is a constant, ΔH is the formation enthalpy, k is Boltzmann's constant, and T_{max} is the maximum temperature that the oxide experiences. Rearranging (1), it is found that

$$\ln[E'] = \ln(A) - (\Delta H/k)(1/T_{max}). \qquad (2)$$

Eqn. (2) indicates that if one were to process oxides at a variety of temperatures, activate the E' centers in each oxide, and then plot ln[E'] vs. 1/T for each T_{max}, one should get a straight line, the slope of which would yield ΔH, the intercept A. (By activate, it is meant that the E'-precursors are placed in a positively charged and paramagnetic, i.e. ESR active, state.) The model was experimentally calibrated with a set of oxides that were grown at a *single* temperature, deposited with poly-Si, and then subsequently annealed at a higher temperature followed by a rapid pull from the furnace in order to "quench" in the equilibrium defect density. (By equilibrium, it is meant that a steady-state of E'-precursor generation and annihilation is approached, beyond which a *net* generation of E'-precursors does not occur. It was shown that the equilibrium concentration of E'-precursors is dependent on process conditions, mainly temperature.) A plot of ln[E'] vs. 1/T revealed a straight line and it was found that $\Delta H = 1.5$ +/- 0.1eV and $A = 4.8 \times 10^{18}$.

In this summary, a similar experiment is performed on a very different set of oxides. These 45nm dry O_2 oxides, as seen in Fig. 1, were *grown at several temperatures*, deposited with poly-Si, and annealed for 30 min in N_2 at the oxidation temperature, again followed by a rapid pull from the furnace to quench in the equilibrium defect density at the anneal temperature. To activate E' centers, the oxides were then flooded with holes using a vacuum-ultraviolet hole injection technique (see [1]). Note that no new E' centers are created during this process, only pre-existing E' precursors are activated. Fig. 2, shows a plot of $\ln[N_{ot}]$ vs 1/T for the array of oxides in Fig. 1. ($[N_{ot}]$, the number of oxide trapped holes, was determined from the mid-gap shift of high frequency CV measurements, see [1].) From the slope of the straight line one can extract a formation enthalpy of approximately 1.5 +/- 0.1 eV, within experimental error equal to the value obtained previously.

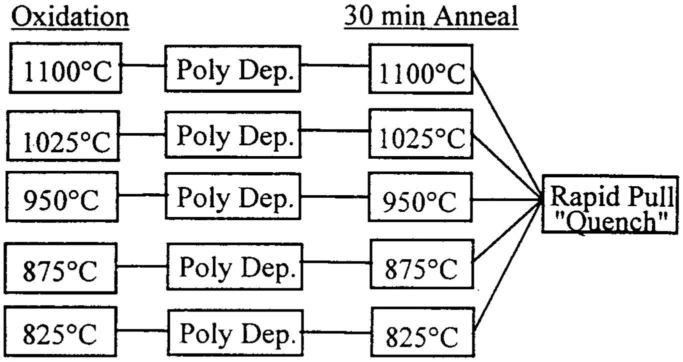

Fig. 1: Oxide array used for Fig. 2.

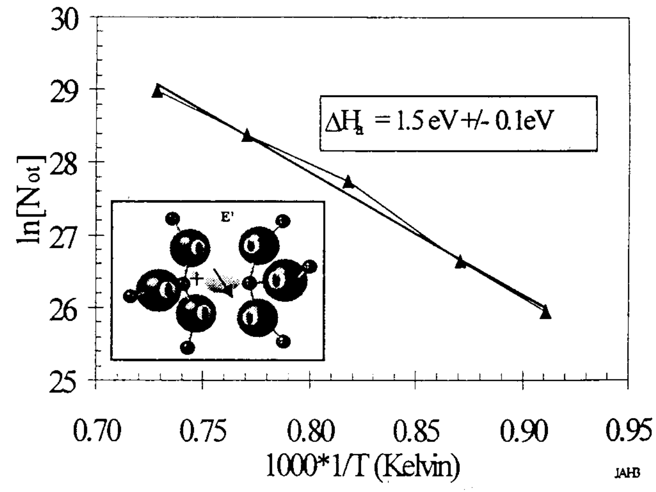

Fig. 2: Plot of ln[Not] vs. 1/T for the array of oxides shown in Fig. 1.

As discussed in [1], combination of the extracted values of ΔH_a and A with E' distribution and σ_h (ESR measurements indicate that E' centers are found predominantly within 10nm of the Si/SiO_2 interface and $\sigma_h \cong 3 \times 10^{-14}$ cm^2) allows prediction of mid-gap voltage shift from

$$\text{Predicted } \Delta V_{mg} = (1/C_{ox}) \bullet [E']_{precursors} \bullet (1-e^{-\sigma h \bullet \eta}) \; ;$$
$$= (1/C_{ox}) \bullet A e^{-\Delta Ha/kTmax} \bullet (1-e^{-\sigma h \bullet \eta}) \qquad (3)$$

where η is the hole fluence.

Figs. 3 and 4 confirm the predictive capability of this ΔV_{mg} model. In each case, identical model parameters to those listed above are used. The only difference is in T_{max} which is assumed to be equal to the highest processing temperature that the oxide experienced.

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Fig. 3 shows predicted ΔV_{mg} (Eqn. 3) and CV measurements of ΔN_{ot} vs. VUV induced hole fluence for SIMOX buried oxide films from two vendors. The SIMOX oxide films received a final anneal at 1320°C and it was assumed that $T_{max} = 1320°C$.

Fig. 4 shows predicted (Eqn. 3) and extracted approximate ΔV_{mg} of several *fully processed* NMOS and PMOS devices that were irradiated with ^{60}Co gamma rays to doses up to 1.2 Mrad. The 15 nm gate oxides of these devices were grown at 875°C in dry O_2 and were not exposed to temperatures higher than the 875°C oxidation temperature. It was assumed that $T_{max} = 875°C$.

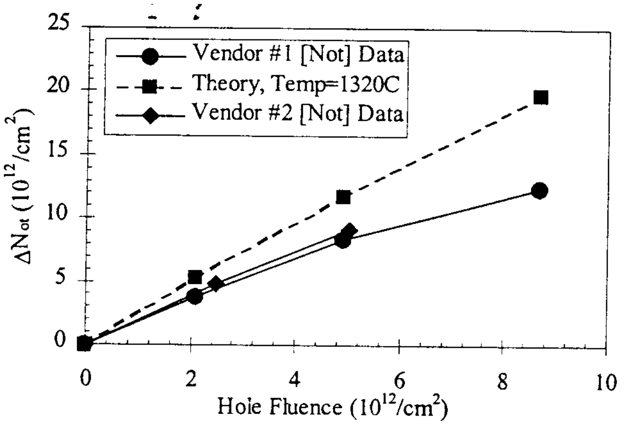

Fig. 3: Plot of experimental and theoretical ΔN_{ot} vs. hole fluence for SIMOX buried oxides.

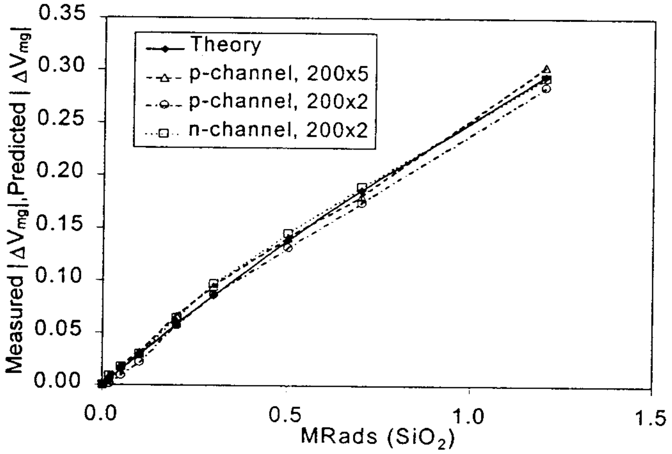

Fig. 4: Plot of experimental and theoretical ΔV_{mg} vs. Mrads ^{60}Co for NMOS and PMOS transistors.

In both cases and several not shown, quantitative agreement is obtained between model and measurements, not only for simple test structures, but also for fully processed devices. This agreement verifies the validity of the approach and the equations.

Calibration of Eqn. (2) from the array of oxides in Fig. 1 requires several important, but physically reasonable assumptions. Although the model's success at charging prediction for a variety of oxides strongly suggests that these assumptions are valid collectively, for completeness it is necessary to individually address each assumption. One important assumption concerns the kinetics of equilibrium [1]. It is assumed that E'-precursor density approaches equilibrium during the 30 min post-poly anneal but *not* during the rapid-quench step. If diffusion of Si and O are involved in bringing E'-precursor density into equilibrium, one would expect that during the post-poly anneal, the density of E'-precursors will approach equilibrium at a rate that depends exponentially on the temperature and directly on the square of the oxide thickness.

In order to test this assumption, 45 nm oxides were grown in dry O_2 at 875°C, deposited with poly-Si, and then rapid thermal annealed in dry N_2 at 1100°C for either 3, 30, or 300 sec. One would qualitatively expect that as the number of E'-precursors approaches equilibrium from a low temperature to the higher temperature, the oxides annealed for longer times would exhibit more E'-precursors. Fig. 5 shows a plot of [E'] vs. hole fluence for each anneal. It is seen that our prediction is at least qualitatively correct: more E' centers are activated in the oxides that have been annealed for longer times, an effect that eventually saturates as equilibrium is approached. From these *very preliminary* results (only the three times shown) we estimate that it takes less than 3 min for the 45 nm oxide system approach equilibrium at 1100°C, consistent with our original assumption *for the 1100°C annealed oxides*. However, depending on the activation energy for the diffusion process, the kinetics of equilibrium assumption may or may not be valid for the lowest temperatures. Experiments are currently under way to expand this data set to include the additional temperatures and times necessary to determine the activation energy. This will allow us to determine the circumstances under which the model will be applicable.

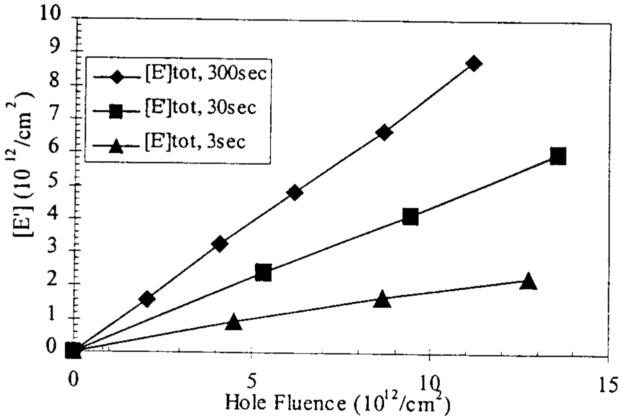

Fig. 5: Plot of [E'] vs. hole fluence for oxides grown at 875°C and then annealed at 1100°C for 3, 30, and 300 sec.

In conclusion, the results presented in this paper strongly support the validity of the materials-based E' model of "intrinsic" oxide charging. The original estimate of the E' precursor formation enthalpy, $\Delta H = 1.5 +/- 0.1$ eV, is confirmed by using a different set of oxides. It is shown that the model quantitatively predicts the density of E'-precursors in oxides processed under a variety of conditions, the only input variable being the maximum temperature that the oxide has experienced. Finally, we have begun to address some of the assumptions that were made to calibrate the model. Very preliminary evidence has been presented that suggests that the original kinetics of equilibrium assumptions are valid.

The fact that the E' Model seems to work for oxide films processed quite differently than thermally grown SiO_2 films and for fully processed devices suggests that temperature is the dominant process variable (i.e. primary determinant) for E'-precursor formation.

The author would like to thank Dr. P.M. Lenahan for many helpful technical discussions and suggestions, Dr. W. McArthur and B. Offord for oxide preparation, Dr. P. Cole for ^{60}Co irradiation data, and B.T. Pomrenke for performing ESR and CV measurements.

[1] J.F. Conley, Jr., P.M. Lenahan, and B.D. Wallace, IEEE 1996 Integrated Reliability Workshop Final Report, IEEE #96TH8215, p. 134-141 (1996).