

# Preliminary investigation of the kinetics of postoxidation rapid thermal anneal induced hole-trap-precursor formation in microelectronic SiO<sub>2</sub> films

J. F. Conley, Jr.<sup>a)</sup>

*Dynamics Research Corporation, Commercial Systems, 19545 NW Von Neumann Drive, Beaverton, Oregon 97006*

P. M. Lenahan

*The Pennsylvania State University, Department of Engineering Science and Mechanics, University Park, Pennsylvania 16802*

W. F. McArthur

*Dynamics Research Corporation, Commercial Systems, 3725 Talbot Street Box 130, San Diego, California 92106*

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Measurements of the growth of  $E'$  center precursor and hole trap precursor densities versus postoxidation anneal time show that both approach saturation values and that the approach to these values is more rapid at higher temperatures. Our results, at least qualitatively, show that a kinetic component can be added to a predictive thermodynamics-based model of oxide hole trapping. The results also indicate quite strongly that a thermodynamics approach to oxide hole trap precursor modeling is appropriate, i.e., the relevant defect densities approach thermodynamic equilibrium or quasiequilibrium in reasonable times. © 1998 American Institute of Physics.

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The use of semiconductor technology-computer-aided-design (TCAD) software tools to aid the design of integrated circuits promises significant potential savings in time and cost. Successful TCAD tools will require predictive physically based models of the effects of process variations on semiconductor device performance and reliability. In metal/oxide/semiconductor field-effect transistors, the dominant semiconductor technology, performance, and reliability are known to be dominated by thin oxide films and their interfaces with Si. Recently, we introduced a quantitative and process dependent model which allows prediction of radiation induced oxide charge density ( $[N_{ot}]$ ) in thin film SiO<sub>2</sub> via computation of  $E'$ -precursor density.<sup>1-3</sup> This “ $E'$  model” is based on the thermodynamic properties of vacancies in a solid and the widely corroborated observation that  $E'$  centers (O vacancies) dominate hole trapping in a wide variety of thermally grown SiO<sub>2</sub> films.<sup>4-13</sup> (The structure of the  $E'$  center, shown as an inset in Fig. 2, consists of a hole trapped at an oxygen vacancy site.) Our earlier work demonstrated that temperature is a dominant process variable in determining  $E'$  and hole trap precursor density in “intrinsic” (clean) SiO<sub>2</sub>.  $E'$  precursor density was found to be exponentially dependent on the final maximum process temperature

$$[E']_{\text{precursor}} = A^* \exp(-\Delta H_f/kT), \quad (1)$$

where  $[E']_{\text{precursor}}$  is the density of  $E'$  precursors,  $A$  is a constant ( $A \sim 5 \times 10^{18}/\text{cm}^2$  for the oxides used in this investigation. In general,  $A$  will depend weakly on oxide thickness and process parameters.),  $\Delta H_f$  is a formation enthalpy,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature. It

was determined that  $\Delta H_f = 1.5 \pm 0.1$  eV,<sup>1-3</sup> a result generally consistent with theoretical studies.<sup>14-16</sup> Note that *accurate* calculation of the formation energy of a vacancy is difficult; the results generally can only be considered estimates.<sup>17</sup>

Equation (1) was calibrated using arrays of poly-capped oxides which were annealed for 30 min in  $N_2$  at temperatures higher than the oxidation temperature and then rapidly pulled from the furnace. It was necessary to assume that the 30 min anneal time would allow  $E'$ -precursor density to approach thermodynamic equilibrium and that the rapid pull step would quench this quasiequilibrium density of  $E'$ -precursors into the SiO<sub>2</sub>. Although these kinetics assumptions proved to work splendidly for the arrays of oxides in those studies,<sup>1-3</sup> it was recognized that time at a given anneal temperature would determine the MOS system's approach to equilibrium  $E'$ -precursor density. One would expect that the approach to equilibrium would follow  $(Dt)^{1/2} \approx l_c$ , where  $D$  is an activated diffusion coefficient,  $t$  is time, and  $l_c$  is a characteristic length. In this study, we have begun to investigate the kinetics of  $E'$ -precursor formation during post-oxidation high temperature anneals to provide initial estimates of the times required for MOS systems to approach equilibrium at various temperatures.

The oxides used in this study were grown on 38–62  $\Omega$  cm (100) Si substrates to approximately 50 nm in dry O<sub>2</sub> at 875 °C. Following deposition of 180 nm of poly-Si, oxides were then rapid thermal annealed (RTA) for either 3, 30, 200, or 300 s at either 950, 1050, or 1100 °C in dry N<sub>2</sub> followed by a rapid pull (see Fig. 1). The rapid pull was performed in order to “quench” in the quasiequilibrium defect density at the anneal temperature.<sup>18</sup> The poly-Si layer was removed before any measurements were taken. Electron spin resonance (ESR) measurements of  $[E']$  density were determined on a state of the art Bruker Instruments ESP

<sup>a)</sup>Electronic mail: jconley@stt3.com

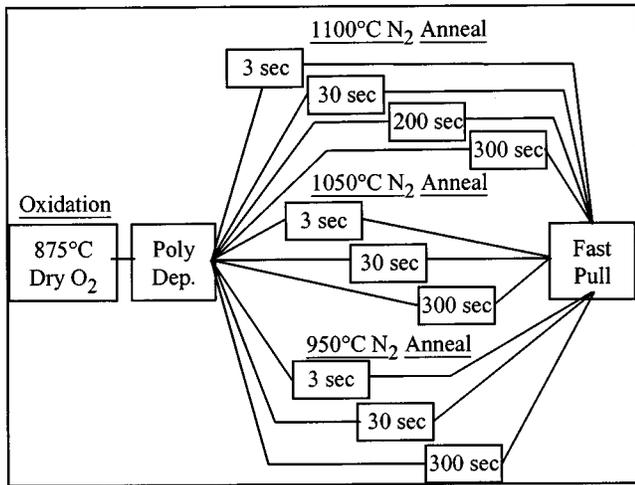


FIG. 1. Oxide array used for Figs. 2 and 3.

300E spectrometer by comparison with a calibrated “weak-pitch” spin standard. Absolute accuracy of spin densities is estimated to be better than a factor of 2; relative accuracy is  $\pm 10\%$ . Oxide trapped charge density,  $[N_{ot}]$ , was determined from the midgap shift of high frequency (100 kHz) capacitance versus voltage measurements performed with a HP 4284A and a Hg probe. For the extraction of  $[N_{ot}]$ , we assumed that the defects are near the Si/SiO<sub>2</sub> interface. During the high temperature postoxidation RTAs there will likely be some buildup of defect precursors near the poly-Si gate interface; this would result in a shift in the defect precursor centroid. However, the shift in the charge centroid would be somewhat less as hole injection is performed under positive gate bias.

Samples of oxide from each RTA combination (time and temperature) from the array of oxides shown in Fig. 1 were flooded under bias with approximately  $8.6 \times 10^{12}$  holes/cm<sup>2</sup> using a vacuum-ultraviolet hole flooding technique described elsewhere.<sup>1,19</sup> (Oxide hole flooding serves to fill existing  $E'$  precursors and render them ESR detectable and electrically active; several studies have shown that the formation of additional  $E'$  precursors does not occur at this dose level.<sup>19,20</sup>) ESR measurements of  $[E']$  and CV measurements of  $[N_{ot}]$  were then obtained on all samples. In Fig. 2, the density of  $E'$  centers,  $[E']$ , versus anneal time is plotted for the 950,

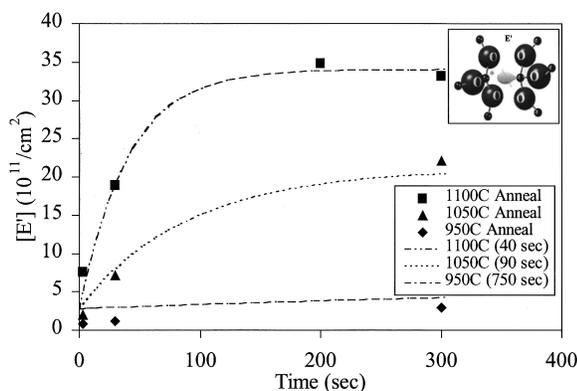


FIG. 2. Plot of  $[E']$  (symbols) and theory as calculated from Eq. (3) (dashed lines) vs anneal time for oxides grown at 875 °C and subsequently annealed at  $T_{\text{anneal}}$  equal to either 950, 1050, or 1100 °C.

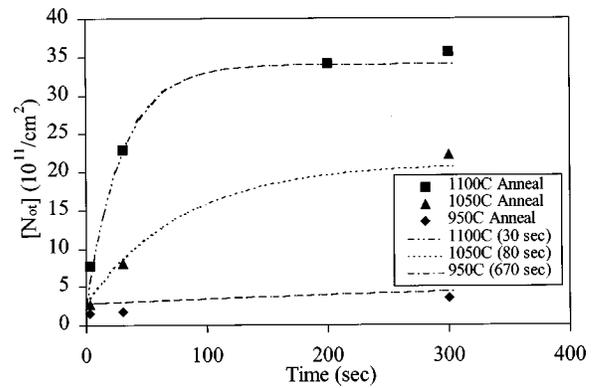


FIG. 3. Plot of  $[N_{ot}]$  (symbols) and theory as calculated from Eq. (3) (dashed lines) vs anneal time for oxides grown at 875 °C and subsequently annealed at  $T_{\text{anneal}}$  equal to either 950, 1050, or 1100 °C.

1050, and 1100 °C annealed oxides. In Fig. 3, the density of oxide hole traps,  $[N_{ot}]$ , versus anneal time is plotted for the same oxides.

From Figs. 2 and 3, we note that: (1) At each anneal combination,  $[E']$  is approximately equal to  $[N_{ot}]$ . (Note that the extremely close agreement between absolute densities here may be fortuitous since ESR defect density estimates have an absolute precision of only a little better than a factor of 2; the relative correspondence, however, is not fortuitous as relative ESR precision is approximately  $\pm 10\%$ .) This validates the basic assumption that  $E'$  centers dominate hole trapping in these oxides. (2) Initially at each anneal temperature, longer anneal times result in higher  $E'$  density; at short times,  $E'$ -precursor formation is a function of time. (3) For the 1100 °C annealed oxides, both  $[E']$  and  $[N_{ot}]$  approach saturation within 300 s;  $E'$ -precursor density eventually saturates as the system approaches thermodynamic equilibrium at the anneal temperature. (4) The measured saturation density of  $[E']$  and  $[N_{ot}]$  generated in the oxides annealed for 300 s at 1100 and 1050 °C agrees extremely well with the thermodynamic equilibrium density predicted by<sup>1-3</sup>

$$[E'](\eta) = [E']_{\text{precursor}}(1 - e^{-\sigma \cdot \eta}), \quad (2)$$

where  $[E']_{\text{precursor}}$  is given by Eq. (1) with  $T$ =the absolute anneal temperature, the hole capture cross section of  $E'$  centers,  $\sigma$ , is  $3 \times 10^{-14}$  cm<sup>2</sup>, and  $\eta$  is the hole fluence (in this case  $\sim 8.6 \times 10^{12}$ /cm<sup>2</sup>). This excellent agreement further validates the predictive power of the  $E'$  model. (5) Close inspection of Figs. 2 and 3 reveals that the time to approach equilibrium is temperature dependent.

In order to quantify the kinetics of the approach to equilibrium, we assume that  $E'$ -precursor density must move from equilibrium at the oxidation temperature to an equilibrium at the higher anneal temperature and that this will follow a characteristic temperature dependent time constant,  $\tau$ .  $E'$ -precursor density as a function of time,  $[E'](t)$ , is

$$[E']_{\text{precursor}}(t) = [E']_{\text{Tox}} + ([E']_{\text{Tanneal}} - [E']_{\text{Tox}}) \times [1 - \exp(-t/\tau_{\text{Tanneal}})], \quad (3)$$

where  $[E']_{\text{Tox}}$  is the equilibrium density of  $E'$  at the oxidation temperature,  $[E']_{\text{Tanneal}}$  is the equilibrium density of  $E'$

at the anneal temperature,  $t$  is time, and  $\tau_{\text{Anneal}}$  is the anneal temperature dependent time constant. An equivalent expression can be written for  $[N_{\text{O}}]$ .

For the 1100 °C annealed oxides grown at 875 °C, we rewrite Eq. (3) as

$$[E']_{\text{precursor}}(t) = [E']_{875} + ([E']_{1100} - [E']_{875}) \times [1 - \exp(-t/\tau_{1100})]. \quad (4)$$

(Similar expressions are used for the other anneal temperatures.) Both  $[E']_{875}$  and  $[E']_{1100}$  are calculated directly from Eq. (2), the previous  $E'$  model.<sup>1-3</sup> The dashed lines in Figs. 2 and 3 reveal good agreement for this very simple model; the time constant,  $\tau_{\text{Anneal}}$ , is the only adjusted parameter. Approximately the same time constants produce good fits for both  $E'$  and  $N_{\text{O}}$  at each temperature. Progressively longer time constants are required to model the data at lower temperatures, i.e.,  $\tau_{1100} < \tau_{1050} < \tau_{950}$ .

Recently, a qualitative model based on the kinetics of O diffusion was postulated to predict  $E'$ -precursor formation in annealed oxides.<sup>21</sup> If a *kinetics-based* model (as opposed to a *thermodynamics-based* model) were to accurately describe defect concentration in oxides, one would expect that  $E'$  density would grow continuously with anneal time and would *not* saturate at a thermodynamic equilibrium value. Our finding that  $E'$  density does not continue to grow with anneal time but instead saturates as equilibrium is approached is not consistent with this model. The O diffusion model<sup>21</sup> also has a quantitative problem (see Ref. 22).

The effects of high temperature postoxidation anneals have been studied since the pioneering work of Deal *et al.*<sup>23</sup> In this study, we find that when an oxide is annealed at a temperature higher than that at which it had been previously processed, both  $[N_{\text{O}}]$  and  $[E']$  grow as a function of anneal time until thermodynamic equilibrium is approached, at which point saturation occurs. The saturation density is in excellent agreement with that predicted by Eq. (2), the  $E'$  model of oxide charging.<sup>1-3</sup> These results validate the basic premise of this model: the formation of  $E'$  precursors in SiO<sub>2</sub> is dominated by thermodynamics. We also find that the equilibration time is temperature dependent with the time decreasing as temperature increases. Although further work will be needed to fully characterize the kinetics of the approach of  $E'$ -precursor density to thermodynamic equilibrium and to quantitatively extrapolate these results into the slightly lower temperature regime more typical of state-of-the-art integrated circuit processing, the excellent agreement between Eq. (3) and the data in Figs. 2 and 3 demonstrate how the original model can be extended to include anneal time as a parameter. Knowledge of the effects of both time and temperature will allow predictions of the incremental effects of arbitrary time high temperature anneals on  $E'$ -precursor density, opening the possibility of designing for trade-offs between defect density and dopant profiles, etc., for, e.g.,  $\Delta V_{\text{th}}$  control.<sup>24</sup> Since  $E'$  centers have been shown to dominate hole trapping<sup>4-13</sup> and play a role in interface trap formation<sup>25,26</sup> and are suspected of playing a role in neutral electron trapping<sup>27,28</sup> and time dependent dielectric breakdown (TDDB),<sup>28-30</sup> a predictive knowledge of  $E'$  density may provide a great deal of information about oxide

quality, performance, and reliability without the need for extensive testing.

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