A model of hole trapping in SiO_2 films on silicon

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We demonstrate that hole trap densities and hole trapping in SiO_2 films on silicon can be predicted quantitatively using a physically based model of intrinsic oxide trapping centers. © *1997 American Institute of Physics.* [S0021-8979(97)00810-4]

I. INTRODUCTION

There is now a movement within the microelectronics industry called building in reliability (BIR).[1] BIR involves identifying those device processing parameters that are involved in device failure phenomena and adjusting these parameters in ways that ameliorate or eliminate the failures. In principle this approach is extremely appealing, but in order for full realization physically based models of the effects of processing parameters on reliability limiting mechanisms must be developed.

The microelectronics industry is dominated by metal–oxide–silicon field effect transistor (MOSFET) technology. The performance and reliability of these devices are limited by hole traps within the gate oxide and interface traps at the gate oxide/silicon substrate boundary.[2] Despite the enormous amount of time and effort devoted to the Si/SiO_2 system over the past 30 years, no quantitative physically based predictor of either oxide hole trapping or interface trap creation has been developed.

In this article we demonstrate that quantitative physically based predictions can be made by combining simple statistical mechanics calculations with a knowledge of relevant defect structures obtained through electron spin resonance (ESR). ESR measurements have the sensitivity and analytical power to identify and provide a quantitative measure of the defects responsible for both oxide hole trapping and Si/SiO_2 interface traps. Indeed two decades of ESR studies have lead to a first order understanding of both Si/SiO_2 interface traps and oxide hole traps.[3]

II. EXPERIMENTAL DETAILS AND ANALYSIS

We use the standard approach of statistical mechanics[4,5] to calculate the density of oxygen vacancies in MOSFET oxides, calibrate the parameters of the expression with ESR measurements and then test the validity of calibrated (quantitative) expression on several oxide films. We find quite good correspondence between the calibrated expression and our experimental results.

Our ESR measurements were made at room temperature using Bruker Instruments 200 series x-band ESR spectrometers with 300 series bridges, TE_{104} double microwave cavities, and calibrated weak pitch spin standards. The measurements allowed $\pm$ 10% relative accuracy in paramagnetic defect density measurements; absolute accuracy is good to slightly better than a factor of 2. Our electrical, capacitance versus voltage measurements of oxide trapped charge were made at 1 MHz and utilized a mercury probe.

The statistical mechanics arguments that we use in our analysis are quite similar to those proposed several years ago in the pioneering study of Ohmameuda *et al.*[6] Although their study did not involve any ESR measurements and involved considerably more limited electrical measurements than does the work reported herein, their calculated estimates of relevant ESR E' defect parameters are in excellent agreement with our ESR results. Their electrical measurements, though considerably more limited in scope are also consistent with those reported herein.

Our analysis involves a paramagnetic oxide defect called the E' center. E' centers are holes trapped in oxide oxygen vacancies. Some time ago, Lenahan and Dresserdorfer established that, for reasonably high-quality device structures, MOS oxide trapped holes and E' density were approximately equal, have essentially identical spatial distributions through the oxide, have virtually identical annealing characteristics, and that the densities can be altered in identical manners by some simple process variations.[7,8] The results and conclusions of that early study have been confirmed and extended by later investigations including those of Miki *et al.*[9] Takahashi *et al.*,[10] Lipkin *et al.*,[11] Awazu, Watanabe, and Kawazoe,[12] and Kim and Lenahan.[13]

From these earlier spin resonance studies we conclude that E' centers dominate the hole trapping of high-quality SiO_2 films on silicon. We, in addition, utilize the observation of Conley *et al.*[14] that the most important E' variant (sometimes called E'_γ) has a hole capture cross section of $\simeq 3 \times 10^{-14}$ cm^2.

A consideration of the basic principles of statistical thermodynamics tells us that equilibrium occurs when the Gibbs free energy G of a solid is minimized.[4,5]

It can be shown that, for the simplest cases, the minimization of Gibbs free energy leads to an equilibrium density of vacancy sites given by

$$n = Ne^{\Delta S_f/k - \Delta H_f/kT}, \tag{1}$$

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where ΔS_f represents the nonconfigurational entropy contribution per defect site, ΔH_f represents the enthalpy of formation of a defect site, k is the Boltzmann constant, and N represents the density of available sites. For the purposes of this discussion, the important points here are that the nonconfigurational entropy contribution is large and essentially temperature independent and that ΔH_f essentially represents the increase in system energy caused by vacancy creation of an unstressed lattice site minus the strain energy lost by removal from a compressed SiO_2 matrix. (This reduction in ΔH_f would be a strain energy $\sim P\,dV$ caused by the effective volume change caused by the removal of the atom from its particular location.)

As pointed out by Ohmameuda *et al.*,[6] this strain energy reduction will be greatest for sites near the Si/SiO_2 boundary, this energy contribution should amount to several tenths of an electron volt.[6] One thus expects and finds[8] that the E' centers are primarily located close to the Si/SiO_2 boundary.

Anticipating then an oxygen vacancy/E' precursor density of the form

$$n = \alpha e^{-\beta/T}, \tag{2}$$

where the temperature independent constant α is given by $Ne^{\Delta S_f/k}$ and $\beta = \Delta H_f/k$, we may evaluate the relevant ''thermodynamic'' constants by making measurements on devices exposed to various high-temperature anneals. With a knowledge of E' center hole capture cross section[14] and the standard analysis of charge capture in oxide films,[15] we would anticipate that, for a given fluence of holes through the oxides,

$$N_{\text{th}} = \alpha e^{-\beta/T}(1 - e^{-\sigma\eta}), \tag{3}$$

where N_{th} is the density of trapped holes and η is the fluence of holes through the oxide. With α, β, and σ evaluated from spin resonance measurements the expression provides an essentially no adjustable parameter prediction of oxide hole trapping. (Note however that due to the modest absolute precision of ESR measurements the value of α as determined strictly from ESR could be in error by almost a factor of 2.)

We have evaluated the potential validity of Eq. (3) through a series of measurements on MOS oxides subjected to anneals at 875, 950, 1025, and 1100 °C. The oxides were all grown at 825 °C and then a polysilicon gate was deposited. After gate deposition the anneals were carried out for 30 min in a dry N_2 atmosphere. After the anneals the capacitors were rapidly pulled from the furnace in order to ''quench in'' the defect densities at the annealing temperatures.

The poly gate material was removed and the samples were cut into $4 \times 20\ \text{mm}^2$ bars. Two sets of measurements were made on the bars, both after subjecting the oxides to hole flooding with a corona discharge/vacuum ultraviolet light technique described elsewhere.[14] In order to evaluate the E' precursor enthalpy of creation, oxides of the three-higher-temperature annealing samples were each flooded with approximately 2×10^{13} holes/cm^2. From Eq. (2) one sees that the enthalpy could be determined from the slope of a plot of the natural logarithm of E' density versus reciprocal temperature. Such a plot of E' density versus reciprocal absolute temperature is illustrated in Fig. 1; it indicates an activation enthalpy of approximately 1.5 ± 0.1 eV.

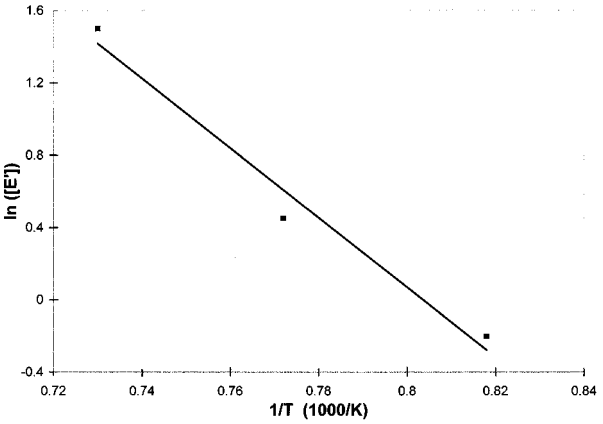

FIG. 1. A plot of the natural logarithm of E' density vs the reciprocal of absolute temperature. (The E' density has been divided by 10^{12}/cm^2.)

To test the predictive capability of Eq. (3), we injected holes into samples subjected to each of the four annealing steps, plotting midgap capacitance versus voltage shifts ΔV_{mg} versus injected hole fluence. Using expression (3) and taking the trapped holes to be close to the Si/SiO_2 boundary, our model predicts midgap shifts of

$$\Delta V_{\text{mg}} = \frac{q\alpha e^{-\beta/T}}{C_{\text{ox}}}(1 - e^{-\sigma\eta}), \tag{4}$$

where q is electronic charge, C_{ox} is oxide capacitance, and all other parameters are as previously defined.

III. CONCLUSIONS

In Fig. 2 we compare the experimental results and the predictions of Eq. (4). The correspondence between prediction and experiment is quite close. This outcome is particularly significant since, to the best of our knowledge, it clearly demonstrates something new and almost certainly useful: a

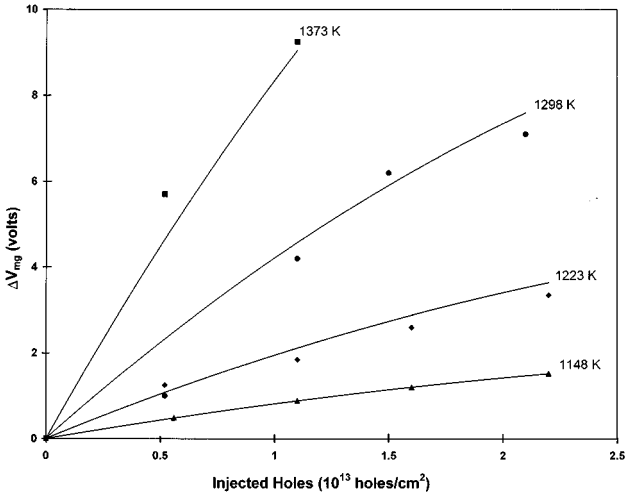

FIG. 2. Plots of ΔV_{mg} vs injected hole fluence for oxides annealed at the indicated temperatures. The solid lines are plots of Eq. (4) for the indicated temperatures.

physically based model that provides quantitative predictions of MOS voltage shifts, which have been verified for a range of oxide process parameters.

A point of additional interest may be that our observations may lead to a straightforward test of MOS oxide quality. The E' center behavior is typical of intrinsic defects;[5] if an oxide were to be microcontaminated, hole trapping would presumably not be predicted from Eq. (4).

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