

Physically Based Predictive Model of Oxide Charging

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Abstract

A combination of statistical thermodynamics and electron spin resonance (ESR) measurements of defects known as E' centers is used to develop a physically based predictive model of oxide charging. It is found that this model is in excellent agreement with experimental data.

Introduction

With the inadequacies of testing-in-reliability becoming increasingly apparent, the microelectronics industry is continuing its journey toward the building-in-reliability (BIR) approach of assuring reliability [1-4]. As Jim McPherson mentioned in his keynote presentation [5], everyone has their own notion of what BIR means. To us, BIR means coming up with alternatives to end-of-line testing. One alternative is to establish links between processing parameters and future wear-out mechanisms. Ideally, one should then be able to confidently adjust the appropriate process parameters to avoid reliability problems. Full realization of this BIR approach will require physically based models of the effects of process variations on reliability mechanisms and incorporation of these models into predictive TCAD tools [6,7]. In this paper, we apply this notion of BIR to metal/oxide/silicon (MOS) field-effect-transistor (MOSFET) gate oxide reliability.

For MOS gate oxides, it is known that the threshold voltage shifts and decreased channel conductance that limit the performance and reliability of MOSFETs are due to charge trapping at point defects in the bulk of the SiO₂ and at its interfaces with Si. Although charge trapping in SiO₂ and the Si/SiO₂ interface has been studied for nearly 30 years, to the best of our knowledge, there are still no physically based predictors of oxide charging. In order to develop a *physically based* model of gate oxide reliability, it will be necessary to use characterization tools capable of providing not only electrical but also chemical and structural information about electrically active point defects and the effects that process variations have on them. The only technique capable of providing the necessary chemical and structural information is electron spin resonance (ESR) [8-10]. ESR measurements provide information about the density and structure of defects that are in a paramagnetic state (that is with net unpaired electrons). Since trapping sites, by definition, will capture either electrons and/or holes, appropriate excitation into a paramagnetic state should allow ESR detection of virtually all relevant (electrically active) defects in MOS systems. The sensitivity of ESR measurements approaches that of electrical measurements (10¹⁰/cm²), allowing correlations to be established between defects and electrical behavior. In this paper, we combine ESR measurements of defects known as E' centers with statistical thermodynamics to create a physically based model of bulk charging in MOS gate oxides. After a rudimentary discussion of ESR measurements, a description of E' centers, and discussion of the statistical thermodynamics equations used in this study, we will discuss the experimental data obtained, propose a model of charging based on this data, and finally, successfully test this model.

Electron Spin Resonance

A simple schematic of an ESR spectrometer is shown in Fig. 1. The sample under test is placed at the center of a microwave cavity and then simultaneously exposed to a large (~3500G) static magnetic field of amplitude, H, perpendicular to a small oscillating magnetic field of frequency, ν . An unpaired electron will either line up with or oppose the magnetic field, H. As shown in Fig. 2, the situation is analogous to that of a compass needle. Under the influence of the Earth's magnetic field (approximately 0.5G), the compass needle will swing around to line up with magnetic north. In a poorly constructed compass, one with no damping mechanism, the needle will buildup momentum and continue to swing around past north, slowing down and eventually stopping to swing back. Without any damping, the needle would oscillate indefinitely. The situation is similar at the defect except that the electron will precess in three dimensions and can either precess with or against the field. Shown in Fig. 3, the difference in energy of an electron precessing with and against the field depends on the field strength, $\Delta E = g\mu_B H$, where g is the ESR g-value (a dimensionless factor, close to 2.0 in these systems) and μ_B is the Bohr magneton. In an ESR measurement, the field, H, is slowly swept until the splitting between the energy levels of the electron is equal to the energy supplied by the oscillating field, $E = h\nu$ where h = Planck's constant. (In practice, it is much easier to vary the magnetic field that it is to vary the microwave frequency.) At this point, the spin resonance equation,

$$h\nu = g\mu_B H, \quad [1]$$

is satisfied and resonant transitions will be induced between the two spin states of the electron. Since, at room temperature, there are slightly more electrons precessing in the low energy state than in the high energy state, a net absorption of microwave magnetic power by the sample can be detected. By comparing the power absorption in the sample to that in a carefully characterized "spin" standard, one can calculate the density of the paramagnetic defects in the sample.

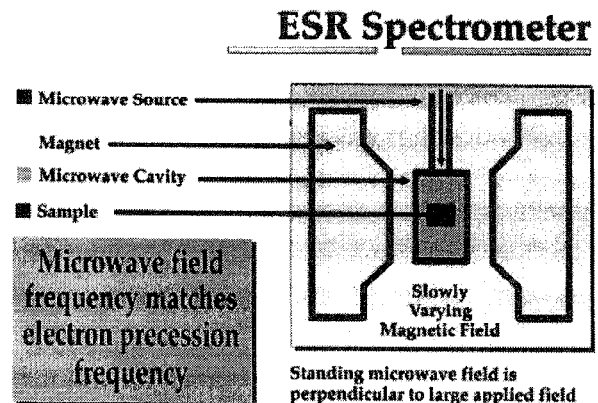


Fig. 1: Simple schematic of an ESR spectrometer.

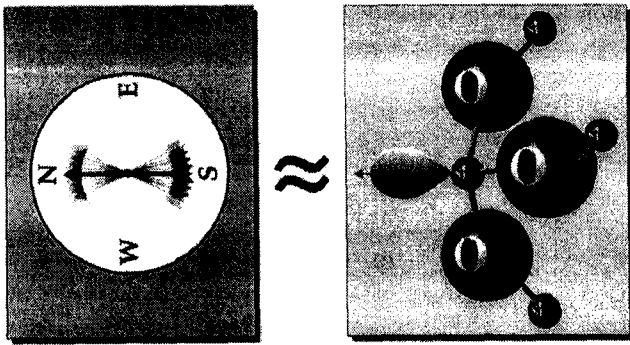


Fig. 2: Analogy between a compass and a defect in a magnetic field.

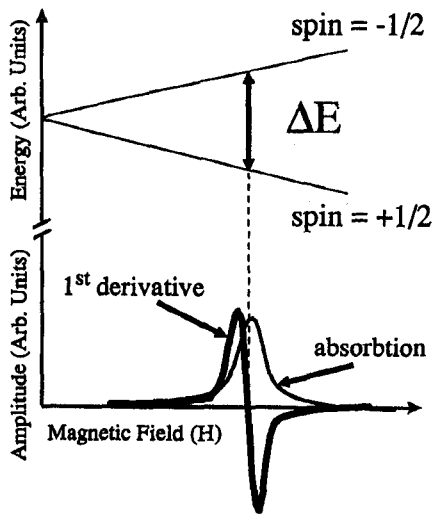


Fig. 3: Simplest case energy levels for an unpaired electron in a magnetic field.

Q: The g-value is the ratio between the frequency at which the resonance occurs to what?

A: Rearranging Eqn. 1, it is seen that $g = h\nu/\mu_B H$. Thus, the g-value is the ratio between the magnetic field and microwave frequency at which the resonance occurs multiplied by Planck's constant and divided by the Bohr magneton. Since the defect's local environment superimposes local fields on the external field, it changes the effective field that the electron sees. Thus, the g-value contains information about the structure of the defect. The g-value can sometimes serve as a fingerprint for previously identified defects. (Much more information about defect structure can be gleaned from nuclear hyperfine interactions, but they are not important for this study as hyperfine information about E' centers has been obtained previously.)

A typical simple ESR spectra is shown in Fig. 3. The detected signal is actually the first derivative of the absorption instead of the absorption itself, a side effect of the lock-in technique used to improve signal to noise. The ESR spectra in Fig. 4 show that it is generally necessary to somehow activate the defects, in this case with VUV radiation, before they can be detected with ESR.

Q: Are there other ways of activating the defects?

A: Yes. For example, various defects can also be activated in SiO₂ by high and low field stressing, gamma irradiation, and hot carrier stressing. See [8] and [9] for a review.

Q: Could you apply electrical stress via the poly-gate, etch off the poly, and then make ESR measurements of defect density?

A: Yes, assuming a large enough density of paramagnetic defects were activated, that also work.

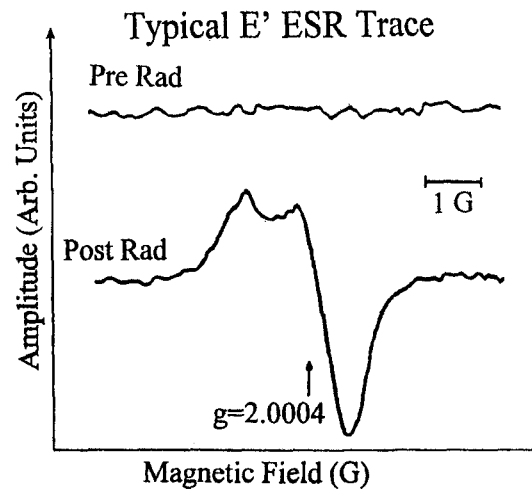


Fig. 4: Typical ESR spectra of a thermal oxide (a) before and (b) after irradiation. E' centers are generated at $g=2.0004$.

Since ESR measurements require no physical contact with the sample under test, the ESR test structure can be minimally processed. The test structure generally used for ESR measurements of MOS materials is the 0.4 x 2 cm SiO₂/Si sandwich shown in Fig. 5. Two advantages of testing minimally processed structures are: (1) since no process steps are required beyond the step of interest, close correlation can be made between the process step of interest and its effects on device characteristics and (2) they allow for short loop experiments. (Note: it has been shown by workers in the radiation effects community that measurements on MOS capacitors correlate well with measurements on fully processed transistors [11].)

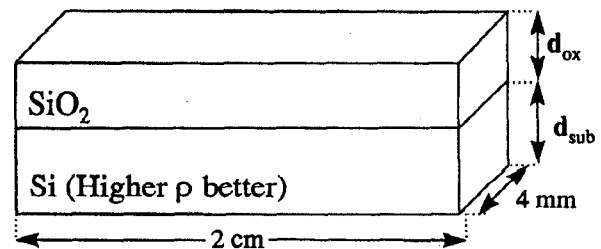


Fig. 5: Schematic of a typical ESR test structure.

Q: You have at the bottom of Fig. 5 that higher ρ Si is better. What does that mean?

A: A higher resistivity (ρ) Si is better for ESR measurements because conductive material degrades the sensitivity of ESR measurements via decreased microwave cavity quality factor, Q , where $Q = 2\pi(\text{maximum microwave energy stored in the resonator})/(\text{energy dissipated per cycle})$. We prefer to have material of at least 10-20 $\Omega\text{-cm}$; 100-200 $\Omega\text{-cm}$ is very good. When necessary, we can also work with lower resistivity material if we first thin the Si substrate by about 80%. (The actual amount of thinning for a given sample depends on the resistivity.) Thinning is more time-consuming but possible. For the same reason just discussed, any gate metal is usually removed prior to any data acquisition.

Q: What oxide thickness is suitable?

A: In principle, assuming that the defect density is above the detection limit (see next paragraph), we can make ESR measurements on oxides of any reasonable thickness.

The detection limit of conventional ESR measurements approaches that of standard MOS "electronic" measurements (i.e. $\approx 10^{10}$ defects/cm²) allowing for correlation of specific defects with specific electrical behavior.

Previous ESR Results: E' Centers

Perhaps the greatest advantage of ESR measurements is that they have already provided a first order understanding of charge trapping in intrinsic SiO₂ thin films. In the early '80s, ESR studies of thermally grown SiO₂ on Si by Lenahan and Dressendorfer [12-14] demonstrated a rough one-to-one correspondence between the density of hole traps and the density of defects known as E' centers. The precursor of the E' defect, shown in Fig. 6, is a weak Si-Si bond at the site of an oxygen

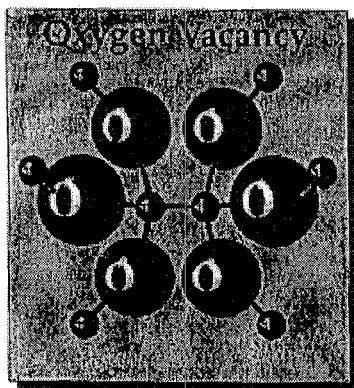


Fig. 6: "Ball and stick" schematic of an oxygen vacancy E' precursor.

vacancy. An E' center is created when a hole becomes trapped at the oxygen vacancy. Shown in Fig. 7, the ESR active part of the defect consists of an unpaired electron localized in an sp³ orbital on a single trivalent Si atom that is backbonded to three O atoms. The electrically

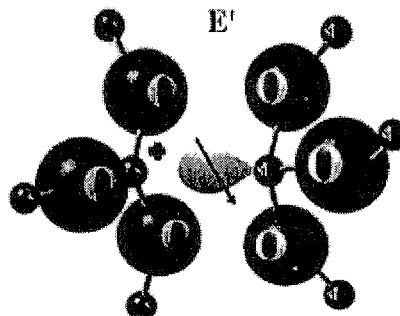


Fig. 7: "Ball and stick" schematic of an E' center, a hole trapped at an oxygen vacancy.

detected positive charge is localized on the Si atom opposite the oxygen vacancy. A typical ESR trace of the E' center is shown in Fig. 4. It has a lineshape with two peaks on the low field side (characteristic of a randomly oriented axially symmetric defect) and a zero-crossing g -value in the range of $g=2.0004$ - 2.0006 . As mentioned earlier, defects generally cannot be observed in as-grown thermal SiO₂. As previously mentioned, they usually must first be activated, in this case by VUV irradiation.

Q: Why is the defect called E'?

A: It was first studied in bulk α -quartz in 1956 by Weeks [15] who originally thought it was an electron trap. The "E" stands for electron and the ' is the occupancy of the orbital. Even though it turned out to be a hole trap, the nomenclature has remained.

The role of E' centers in thin film SiO₂ was determined in a series of ESR studies by Lenahan *et al.* [12-14,16]. In Fig. 8, it is seen that there is a rough one to one correspondence between E' centers and trapped positive charge generated by varying doses of ionizing radiation [14]. Fig. 9 shows that E' centers and trapped positive charge have roughly the same isochronal annealing characteristic [14]. Finally, in Fig. 10, it is seen that both E' centers and trapped positive charge have roughly the same electron capture cross section when oxides are injected with electrons via UV exposure [16]. The role of E' centers as the dominant charge trap in thermal SiO₂ is well established; these results have been independently confirmed by a number of different groups around the world [17-22].

It is important to note, however, that E' centers will probably only dominate charge trapping in intrinsic oxides. We define intrinsic to mean that no impurity content significantly alters charge trapping. In fact, we believe that a test to determine whether an oxide is intrinsic or not would be to determine whether or not the oxide exhibited a one to one correlation between E' and positive charge.

We develop a predictive model of oxide charging by combining ESR measurements E' centers with statistical thermodynamics.

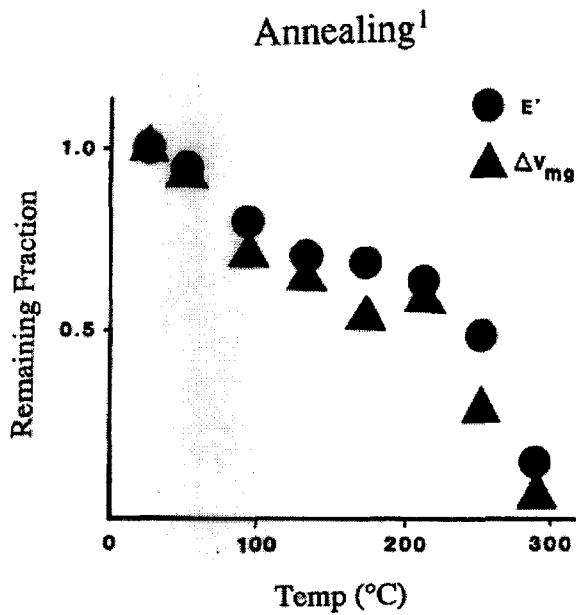


Fig. 8: Plot of E' center and trapped positive charge density in thermal SiO vs. γ -irradiation dose. (From Lenahan and Dressendorfer [14].)

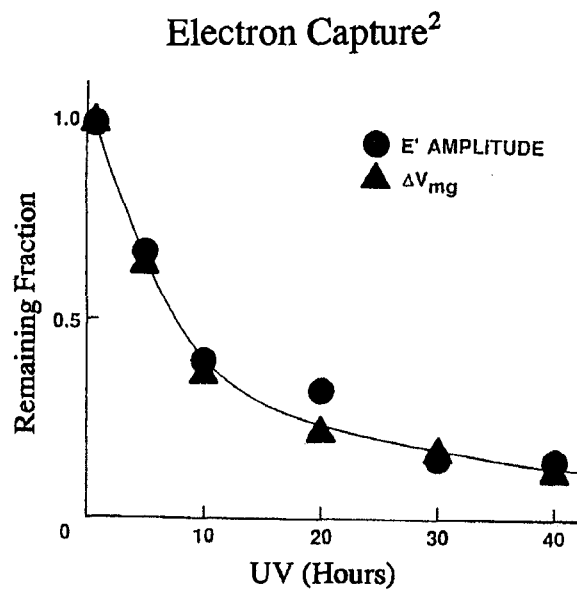


Fig. 10: Plot of E' center and trapped positive charge density in thermal SiO₂ vs. UV injected electron fluence. (From Kim and Lenahan [15].)

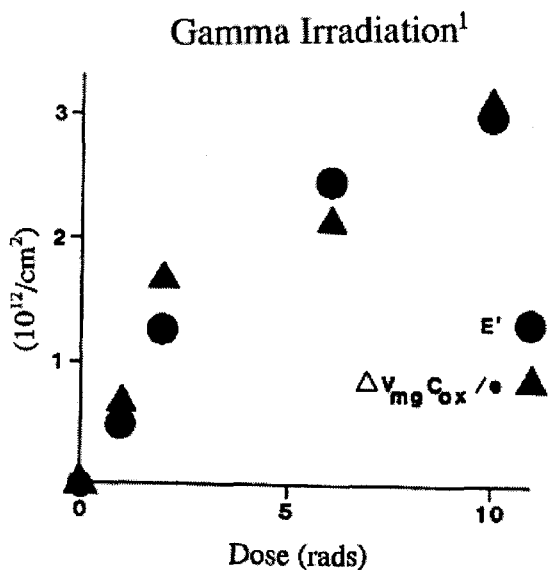


Fig. 9: Plot of E' center and trapped positive charge density in thermal SiO vs. isochronal annealing temperature. (From Lenahan and Dressendorfer [14].)

Statistical Thermodynamics:
Discussion of Gibb's Free Energy

From statistical thermodynamics [23-25], it is known that equilibrium in solids is determined by minimizing the Gibb's free energy, $G=H-TS$, which is a balance between the enthalpy (H) and entropy (S) of a solid at a given temperature (T). The enthalpy term is $H = E + PV$, where E is the energy of the bonds and PV is a pressure-volume work term. In order to remove an atom from a solid, one must supply enough energy to break its bonds. The entropy, S, involves two terms, a non-configurational term and a configurational term. The configurational term is $S_c = k \ln(W)$, where W is the number of distinct ways of arranging the vacancies, $W = N! / ((N-N_v)! N_v!)$, where N is the total number

of lattice sites and N_v is the number of vacancies. (Using Stirling's approximation, $\ln(N!) = N \ln(N) - N$.)

For a small number of vacancies, the increase in configurational entropy more than overcomes the increase in enthalpy causing the Gibb's energy to decrease; thus a modest number of vacancies will be thermodynamically stable. In the case of SiO₂, because O atoms have only two bonds vs. the Si atom's four bonds it takes less energy to create O vacancies than Si vacancies.

When the Gibb's free energy is minimized, in the simplest cases, the concentration of vacancies [N_v] in thermodynamic equilibrium will be,

$$[N_v] = A e^{-\Delta H_a / kT} \tag{2}$$

(the higher the temperature, the greater the vacancy concentration) where ΔH_a is the activation enthalpy of vacancy formation. The effects of non-configurational entropy along with the total number of lattice sites are incorporated in the constant, A. Rearranging Eqn. 2, it is found that

$$\ln[N_v] = \ln(A) - (\Delta H_a) / k (1/T). \tag{3}$$

Assuming that the dominant hole trap in SiO₂ is due to E' centers, O vacancies, we can replace [N_v] in Eqn. 3 with [E'] and plot $\ln[E']$ vs. $1/T$ and compare with $\ln[N_{ot}]$ vs. $1/T$. The slope of these plots (shown in Figs. 13 and 14) will allow extraction of an activation enthalpy for E' precursor (O vacancy) formation. This activation enthalpy can then be used to predict the equilibrium number of E' centers that will be present after a high temperature step. When combined with E' distribution and hole capture cross section, σ_h , one should be able to predict mid-gap voltage shifts (shown in Fig. 15).

Experimental Plan

In order to make this experiment reasonable, we had to begin with some assumptions. First of all, we assume that the charge trapping is primarily determined by a dominant high temperature step. This turned out to be valid. For the present, we ignore anneal ambients, plasma processes, pre-oxidation issues, etc.

With the decision to focus on a dominant high temperature step, we decided to investigate an array of oxides grown at one temperature and then subsequently annealed at a variety of temperatures. (The oxides were provided by Navy Research and Development (NRAD).) The array of oxides used in this study is shown in Fig. 11. First, on all wafers, dry oxides were grown at 825°C and then deposited with poly. Sets of oxides were then subsequently annealed for 30 min in N₂ at either 825°C, 875°C, 950°C, 1025°C, or 1100°C. The oxides were then rapidly pulled from the furnace in order to “quench-in” the equilibrium density of defects present at the anneal temperature. We realize that rapid pulling is not done with commercial oxides. but if the samples were pulled out too slowly, equilibrium might be established at a lower temperature. At the lower temperature there would be, presumably, a lower density of defects which would cause us to over-estimate the activation enthalpy. Our second assumption is that the oxides have been annealed long enough to come to equilibrium at the anneal temperature. Our third assumption is that the ramp down is rapid enough not to allow the system to come into equilibrium at a lower temperature. We believe that these also turned out to be reasonable assumptions. As discussed later, we will need to closely investigate the assumptions we make about kinetics in the future.

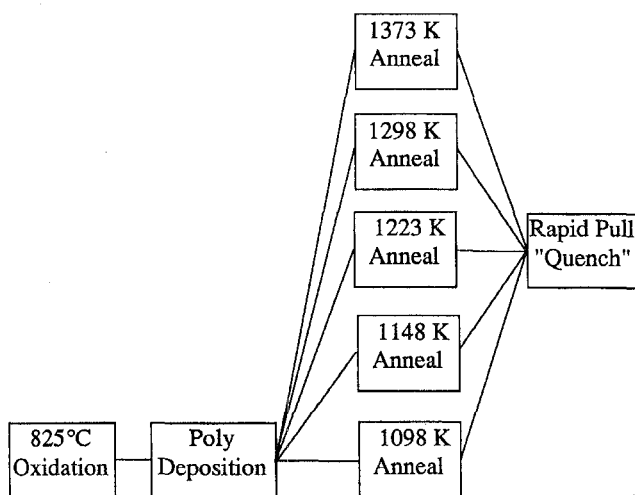


Fig. 11: Experimental array of samples used in this study.

Experimental Details

The ESR measurements in this study were performed at room temperature on an Bruker Instruments X-band spectrometer. Spin densities and zero-crossing *g*-values were determined using a TE₁₀₄ “double” resonant cavity and a calibrated “weak pitch” spin standard. This setup allows for an accuracy in determination of defect density of better than a factor of two in absolute number and a relative accuracy between similar measurements of 10%.

The high frequency (1 MHz) CV measurements in this study were performed room temperature with a Boonton capacitance bridge and a Leighton mercury probe.

Before any measurements were taken, the samples were cut into 0.35 cm x 2 cm rectangular bars (see Fig. 5) and the poly Si layer was removed.

Q: How do you remove the poly?

A: We do a wet chemical etch.

Q: Won't that affect the gate oxide?

A: Perhaps it might affect the first 10 or 20 or 30Å. But since the oxides are 450Å and E' centers are mainly generated within 100Å of the Si/SiO₂ interface we don't think this will affect our results.

Q: Do you use a special etch which is selective to poly and not SiO₂? How do you do that?

A: Etch recipe:

1) Mix 45 g KOH, 40 ml DI H₂O, and 20 ml isopropanol (isopropanol reduces the SiO₂ etch rate without significantly impairing the Si etch rate).

2) Heat to 80°C.

3) Place samples in bath and stir gently for approximately 6-8 minutes.

Experimental Data

The first step of the experiment is to activate the E' centers. It must be emphasized that we are only *activating* them because, at low radiation doses [26], all we are doing is populating pre-existing vacancies, we are *not* creating new oxygen vacancies. The way we activate the E' centers is by injecting holes via vacuum ultraviolet (VUV) illumination in combination with positive corona ions. A schematic of this apparatus is shown in Fig. 12. First, the samples are placed under a candelabra of very sharp needles which generate ions via corona discharge [27]. These corona ions drift to the surface of the oxide to form an immobile sheet of charge on our “gateless” samples. They allow us to create a uniform bias, transparent gate over the large surface area of our samples.

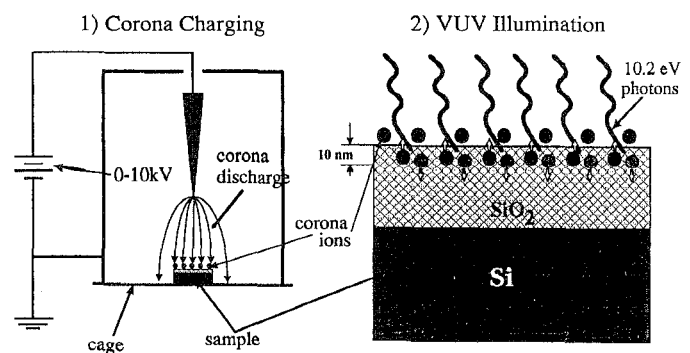


Fig. 12: Schematic of corona biasing and VUV hole injection apparatus

Q: What is the electric field in the oxide?

A: The field used is typically in the range of 1-3 MV/cm.

Next, the sample is placed in a vacuum chamber. There, 10.2 eV VUV photons are strongly absorbed within the top 100 Å of the oxide where they create electron hole pairs. Under the influence of the positive field, the holes are swept across the oxide to the interface where they become trapped at E' centers; electrons escape to the surface where they neutralize the positive corona ions. By measuring with a Kelvin probe the charge on the surface of the oxide before and after the VUV exposure, we can calculate the injected hole fluence from $C_{ox}\Delta V=Q$. Using this method, approximately 1×10^{13} holes / cm² are injected into oxides grown at each temperature. ESR and CV measurements are then made on the samples.

Looking first at the ESR results, a plot of $\ln[E']$ vs. $1/T$ is shown in Fig. 13. The E' density generated at each temperature falls on a straight line. From the slope of this line and Eqn. [3], we extract an activation enthalpy for E' center formation of $\Delta H_a = 1.5 \pm .1$ eV.

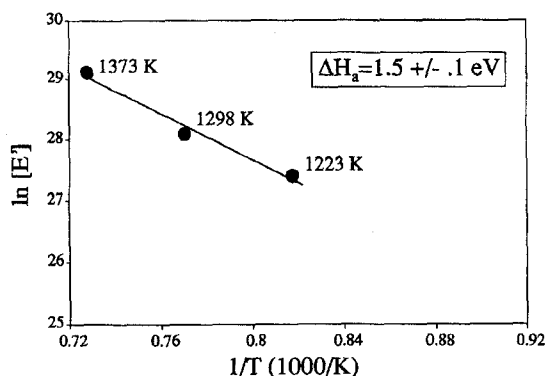


Fig. 13: Plot of $\ln[E']$ vs. $1/T$ for oxides flooded with $\sim 1 \times 10^{13}$ holes/cm²

Next, we look at high frequency CV measurements of the same oxide samples. Shown in Fig. 14, the CV results reveal that the density of trapped holes generated at each temperature also falls on a straight line when $\ln[N_{ot}]$ is plotted vs. $1/T$. Again, from the slope of this line and Eqn. [3], an activation enthalpy for oxide trapped charge is calculated to be $\Delta H_a = 1.5 \pm .1$ eV.

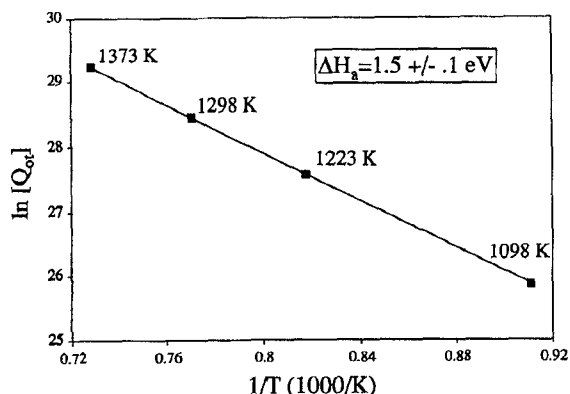


Fig. 14: Plot of $\ln[N_{ot}]$ vs. $1/T$ for oxides flooded with $\sim 1 \times 10^{13}$ holes/cm²

Formulation of Model

This activation enthalpy extracted for the ESR measurements and the CV measurements is nearly identical, $\Delta H_a = 1.5 \pm .1$ eV, confirming the validity of the approach, and an earlier calculation [25]. A question that naturally arises is: What good is an activation enthalpy for E' precursor formation? Well, by combining our extracted activation energy with the distribution and hole capture cross section, σ , of the E' centers, we can predict the mid-gap voltage shift, ΔV_{mg} , from

$$\Delta V_{mg} = (q/C_{ox}) \cdot [E']_{sat} \cdot (1 - e^{-\sigma \cdot \eta}), \tag{4}$$

where q is the electronic charge, C_{ox} is the geometric capacitance of the oxide, $[E']_{sat}$ is the saturation density of E' centers calculated from ΔH_a and replacing $[N_v]$ with $[E']_{sat}$ in Eqn. 2, and η is the hole fluence. (ESR measurements indicate that E' centers are found predominantly within 10nm of the Si/SiO₂ interface and $\sigma \approx 3 \times 10^{-14}$ cm²; parameters ΔH_a and σ were chosen within the limits of error of the spin resonance measurements to fit the experimental data.)

Test of Model

Finally, to test the predictive capability of this model, we attempt to predict, for the same series of oxides, the mid-gap voltage shift vs. hole fluence, η . In Fig. 15 we plot capacitance vs. voltage measurements of mid-gap voltage shift and theoretical calculations from Eqn. 4 of mid-gap voltage shift vs. hole fluence. Excellent quantitative agreement between the theoretical predictions and the experimental results is obtained, verifying the validity of the approach and the equations.

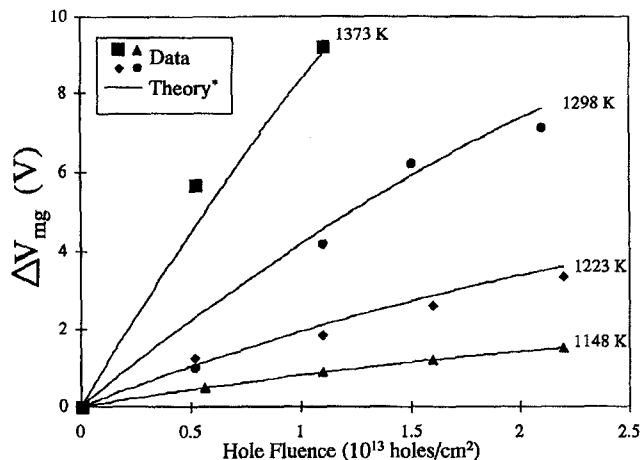


Fig. 15: Plot of experimental and theoretical ΔV_{mg} vs. hole fluence.

Discussion

The preliminary results of this model are encouraging. Given the dominant temperature step witnessed by an oxide, we quantitatively predicted the mid-gap voltage shift vs. hole fluence. This work has just recently been initiated and the model herein should be viewed as a first-order treatment. Future refinements of the model will begin with addressing the assumptions we have made in this experiment. The most important assumptions to address are those concerning kinetics. We have assumed that 30 min at the anneal temperature is enough time for the oxygen vacancy density to come to thermodynamic equilibrium. We have also assumed that the rapid cooling of the samples

effectively "quenched" in the equilibrium density of vacancies at the anneal temperature. Although these assumptions proved valid for this experiment, they will not be valid for all instances. We will need to perform experiments designed to determine roughly how long the system takes to come to equilibrium at a given temperature. The experiments will probably be based on a model of equilibrium involving the self diffusion of Si and/or O atoms. Once these times are established, we will be able to estimate when the assumptions will hold and when they will not, and perhaps be able to predict the effects of various ramp rates on defect density.

Conclusions

Inspired by the BIR philosophy assuring MOS gate oxide reliability, we have developed a physically based model of oxide charging based on ESR measurements of E' centers and statistical thermodynamics. The predictions of the model are in excellent agreement with the data from the oxides used in this study. These results are particularly significant because they represent, to the best of our knowledge the first physically based model that allows *predictions* of threshold voltage shifts from a process parameter. Future refinements of this model will require a consideration of, among other things, the kinetics of how long it takes E' density to come to equilibrium at a given temperature. Our results confirm the predictions of Evans *et al.* [28] and Lowry *et al.* [29] that ESR may be a viable reliability tool.

Q: When we pull our wafers from our furnace tube we can't change our temperature by more than 7°C/min or the 6" wafers smash in a quartz tube. The point I am trying to make is that at 1100°C, your maximum thermal budget, you are going to have a 30°C anneal, more than 1/2 of your thermal budget is going to be the ramp and the rise in the fall unless you use an RTA system. Did you use an RTA or a furnace?

A: A furnace.

Q: OK. So your results are going to be skewed by that. So you are plotting on your log plots are vs. the peak temperature and not the total thermal budget. So you don't take that into account.

A: Well, a future step in the experiment will be to figure out the kinetics, how long something must be at a certain temperature for equilibrium to be reached.

Q: Right, I was going to ask you that, Are you sure that it is in equilibrium? And if it is, a 20 min ramp or a 20 min fall is going to allow plenty of time if 30 min is plenty of time to equilibrate then it will equilibrate at a lower temperature, so it just doesn't hang together for me.

Q: And the second thing, is 1.5 eV reasonable? Everybody knows what the bond strength of O to Si is. Does 1.5 eV make sense in terms of that? It seems a little low as far as I was concerned.

A: Well, it may seem a little low because these defects are mainly forming near the interface and near the interface there is going to be more stress so there will be a pressure volume or a stress term that will effectively reduce the enthalpy.

Q: Sure, but what is the comparable value in the literature.

A: There is an estimate by Ohmameda *et al.* [25] that it would be about 2 eV in the bulk, decreasing by a few tenths of an eV

toward the interface to about 1.5-1.6 eV at the interface (fairly close to what we saw).

Q: But I would have expected at those temperatures to see bulk defects as well. Even if it is a 2 eV activation energy it doesn't mean it is not going to occur. It is going to be occurring in the bulk as well.

A: Well etchback studies pretty much show that the defects are generated within 100 Å or so of the Si/SiO₂ interface.

Q: I wouldn't have believed that a 0.5 eV difference meant that you couldn't get it in the bulk. After all there are more probabilities, there is more bulk. Anyway just a couple of points.

A: Actually, if you do a calculation for the difference in the equilibrium number of vacancies at T=1000°C [$e^{(-5/kT)}$] you get about a factor of 95 less defects in the bulk of the oxide, defects in the bulk will therefore not significantly alter our result. For the 5×10^{12} defects/cm² detected in our 1100°C annealed oxides, $\sim 5 \times 10^{10}$ /cm² is close to our detection limit.

Q: You mentioned that you look at intrinsic oxides. What if you had a defective oxide with an extrinsic defect say due to contamination, would this show up in your ESR lineshape?

A: Contamination is something we probably could detect. It might very profoundly affect the ESR spectra, an effect we could easily observe. Or it might even replace the ESR spectra. That is, the contaminant might be the dominant hole trap in thermal SiO₂ and the E' centers wouldn't show up at all. It is also possible that the E' spectra might not change at all. In order to observe, for example, transition metal impurities, we would probably have to go to lower temperatures in order to detect them. Other common impurities include P, B, N, and H. Centers coupled to these impurities have all been observed in SiO₂ films on Si. These atoms all have distinct ESR spectra in SiO₂ that contain much information about the defect structure [30-34]

Q: What if you grew an oxide on a Si substrate that had a point vacancy in the Si lattice, a missing Si atom to begin with, a place where you can't bond in the bulk of the Si. How much energy change would that be, that is wouldn't it give a much higher likelihood of a local oxygen vacancy?

A: No, I don't think that vacancies in the Si are going to effect vacancies in the bulk of the oxide.

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