

Mechanisms of Enhanced Radiation-Induced Degradation Due to Excess Molecular Hydrogen in Bipolar Oxides

X. J. Chen, *Student Member, IEEE*, H. J. Barnaby, *Senior Member, IEEE*, B. Vermeire, *Member, IEEE*, K. Holbert, *Senior Member, IEEE*, D. Wright, R. L. Pease, *Fellow, IEEE*, G. Dunham, *Member, IEEE*, D. G. Platteter, *Senior Member, IEEE*, J. Seiler, *Member, IEEE*, S. McClure, *Member, IEEE*, and P. Adell, *Member, IEEE*

Abstract—Bipolar junction test structures packaged in hermetically sealed packages with excess molecular hydrogen (H_2) showed enhanced degradation after radiation exposure. Using chemical kinetics, we propose a model that quantitatively establishes the relationship between excess H_2 and radiation-induced interface trap formation. Using environments with different molecular hydrogen concentrations, radiation experiments were performed and the experimental data showed excellent agreement with the proposed model. The results, both experimentally and theoretically, showed increased radiation induced degradation with H_2 concentration, and device degradation saturate at both high and low ends of H_2 concentrations.

Index Terms—Bipolar oxide, gated bipolar devices, hydrogen, interface traps, radiation-induced.

I. INTRODUCTION

HYDROGEN, in one form or another, plays a crucial role in the reliability of modern silicon devices. Whether radiation- or stress-induced, the degradation in integrated circuit (IC) performance has always been closely associated with the ability of hydrogen to affect the density of structural defects in silicon devices. The most important and direct cause of device and circuit performance degradation is the generation of radiation- or stress-induced interface traps (N_{it}) at the Si/SiO₂ interface. These interface defects can cause threshold voltage shifts, subthreshold stretch-out, increased off-state leakage, and 1/f noise in metal-oxide-semiconductor field effect transistors (MOSFETs), as well as gain degradation and increased junction leakage in bipolar junction transistors (BJTs). Interface traps are most commonly identified with P_b centers, silicon dangling bonds at the Si/SiO₂ interface. These structural defects can trap

and de-trap carriers, thereby exchanging charge with the underlining silicon and deleteriously impacting the electrical characteristics of the device. Radiation-induced interface trap formation is commonly described as a two-stage transport process [1], which is closely associated with hydrogen concentration and transport in the oxide of the silicon device. In this process, holes, generated by ionizing radiation, transport through the oxide and react with an impurity to generate hydrogen ions, or protons (H^+). A fraction of these released protons transport to the Si/SiO₂ interface and react with hydrogen passivated silicon dangling bonds to create interface traps.

Physical processes relating hydrogen species to interface defect formation have been studied extensively in the past, especially mechanisms for H^+ transport [2], [3] and molecular hydrogen (H_2) passivation of silicon dangling bonds [4]. Molecular hydrogen is used extensively in semiconductor manufacturing to create Si-H bonds at the Si/SiO₂ interface, thus reducing the trap densities associated with dangling Si bonds. However, a handful of past studies have shown that excess H_2 in a radiation environment can actually increase the density of radiation-induced interface traps [5]–[7]. In their 1988 paper, Kohler *et al.* reported that high concentrations of H_2 trapped inside hermetically sealed packages accelerate the total dose degradation of CMOS devices and circuits [5].

Recently, Pease and others [8] showed that Analog Devices' linear bipolar temperature transducers in flat-packs degraded significantly more than the same parts packaged in TO-52 cans in response to ionizing radiation. The difference was attributed to the considerably higher molecular hydrogen (H_2) content in the gas ambient within the flat-packs, which was determined through residual gas analysis (RGA) to be 0.6%. No detectable levels of H_2 were measured in the TO-52 cans. These studies strongly suggest that the impact of H_2 on radiation response is not correlated to a particular technology (i.e., bipolar or CMOS), but is rather a more general signature of the complex relationship between molecular hydrogen and ionizing radiation damage in semiconductor materials.

In this paper, we present data that further illustrate the strong dependence of radiation response on the ambient H_2 concentration. These data, obtained from measurements on bipolar devices, provide new insights into the mechanisms relating molecular hydrogen to radiation sensitivity. Furthermore, a model is presented which expands upon past modeling efforts to characterize the complex processes related to interface trap buildup at Si/SiO₂ interfaces. The proposed model with the support of the

Manuscript received July 20, 2007; revised September 26, 2007. This work was supported in part by NASA's Jet Propulsion Laboratory with funding from the NASA Electronics Parts Program (NEPP) and by the Air Force Office of Scientific Research with funding from the MURI Program.

X. J. Chen, H. J. Barnaby, B. Vermeire, K. Holbert, and D. Wright are with Arizona State University, Tempe, AZ 85287 USA (e-mail: j.chen@asu.edu).

R. L. Pease is with RLP Research, Los Lunas, NM 87031 USA (e-mail: rpease@rlpresearch.com).

G. Dunham, D. G. Platteter, and J. Seiler are with NAVSEA Crane, Crane, IN 47522 USA (e-mail: gdunham@atd.crane.navy.mil; Platteter@atd.crane.navy.mil; seiler.john@atd.crane.navy.mil).

S. McClure and P. Adell are with the Jet Propulsion Laboratory, Pasadena, CA 91109 USA (e-mail: steven.s.mcclure@jpl.nasa.gov; philippe.c.adell@jpl.nasa.gov).

Digital Object Identifier 10.1109/TNS.2007.909708

experimental data, provide a simple 1-D quantitative description of the relationship between H_2 concentration and interface defect buildup during irradiation.

II. EXPERIMENTAL DETAILS AND RESULTS

Experiments were performed at NAVSEA Crane and Arizona State University (ASU) to explore the effects of the in-package H_2 gas content on the total dose and dose rate response of bipolar devices. The devices are gated lateral pnp (GLPNP) bipolar junction transistors integrated onto a test chip. By utilizing the gate terminal, the GLPNP device has proven to be a simple and effective test structure for studying radiation-induced defects in bipolar devices [9]–[11]. The GLPNP devices were fabricated by National Semiconductor in a split wafer lot with variations in the final passivation [9]. The wafers were processed with no final passivation and with silicon carbide, phosphorous doped glass, and the standard passivation, silicon nitride (Si_3N_4) over p-glass. The oxide thickness and gate area of the devices are $\sim 1.2 \mu m$ and $\sim 1440 \mu m^2$, respectively.

The first experiment, performed at NAVSEA Crane, was designed to explore the response of sealed and unsealed test transistors and compare to results for parts exposed in a 100% H_2 environment during irradiation. Parts with no passivation (NP) were selected for this set of tests. All parts were irradiated in a Co-60 source at a dose rate of 26 rad/s to a total dose of 30 krad(SiO_2). The pre-irradiation and post-irradiation electrical measurements performed on the GLPNP transistors were device current-voltage (I - V) characterization obtained with the gate sweep and subthreshold sweep techniques described below. For the base current vs. gate voltage (gate sweep or GS) measurements, the base current was monitored with a HP4156 parameter analyzer while the gate was swept in 1 V steps from 30 V to -100 V. During the GS tests, the GLPNP transistors were biased in the forward active mode during measurement as the gate voltage was varied, with collector, base, and substrate grounded and the emitter voltage fixed at 0.5 V. For the subthreshold I - V measurements, the GLPNP transistor is treated as a pMOSFET, the gate was swept from 10 V to -100 V in 1 V steps; the emitter (source) was biased at -0.1 V and collector (drain) and base were grounded. All measurements were made at room temperature. The gate sweep results from this experiment are shown in Fig. 1. The data prior to radiation exposure are shown as black circles. The black squares represent the post 30 krad(SiO_2) data of unsealed devices exposed in open air ($<0.0001\%$ H_2). The black diamonds are post 30 krad(SiO_2) data for sealed devices. The H_2 content within the sealed package was determined through RGA to be 1.3%. The black triangles are post 30 krad(SiO_2) data for unsealed devices soaked in 100% H_2 for 7 days before irradiations. As described in [9], [12], the change in peak base current amplitude is proportional to the buildup in radiation induced traps (N_{it}) at the oxide/active base interface. Thus, the data reveal a monotonic increase in N_{it} as a function of the ambient H_2 concentration during irradiation.

To model the mechanisms of radiation-induced interface trap enhancement due to molecular hydrogen, more data points were needed. Thus, additional radiation experiments were performed at Arizona State University with an array of ambient molecular hydrogen concentrations. NP parts were again selected, and 1%,

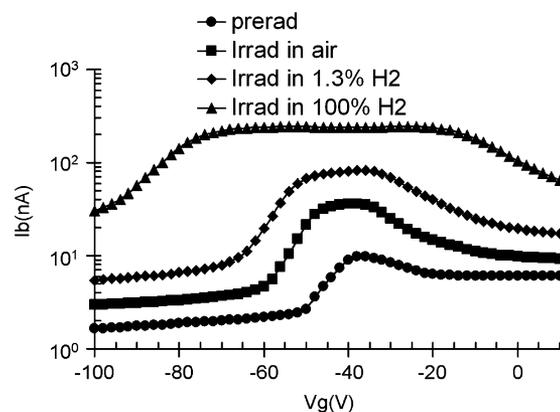


Fig. 1. Irradiation data at dose = 30 krad(SiO_2) for non-passivated GLPNP devices exposed to different H_2 ambient conditions (100% H_2 , 1.3% H_2 (sealed) and open air).



Fig. 2. Glass chamber flange used for soaking and radiation testing of samples in hydrogen environment.

TABLE I
ARRAY OF HYDROGEN CONCENTRATIONS

H_2 (volume percent)	H_2 Partial Pressure (torr)
100%	~ 735
50%	~ 365
10%	76
1%	7.6
0.10%	0.76
0.01%	0.076
0.0001% (in air)	0.000076

100% H_2 data points were recollected to compare with the previous data set. To store and test samples in different H_2 environments, a glass chamber flange (Fig. 2) was specially crafted.

During each experiment, four devices were sealed inside the chamber. After a vacuum of 10^{-5} torr was reached inside, a steady stream of pure hydrogen gas was pumped into the chamber, reaching the desired partial pressure and concentration. Table I lists the hydrogen concentrations used.

To ensure complete saturation of H_2 in the device samples, the devices were soaked in the chamber for 48 hours before radiation exposure. According to the analysis of hydrogen diffusion covered in Section IV, it takes approximately 8 to 10 hrs for H_2 to completely saturate the devices. The devices, while remaining in the H_2 chamber, were exposed to a total dose of

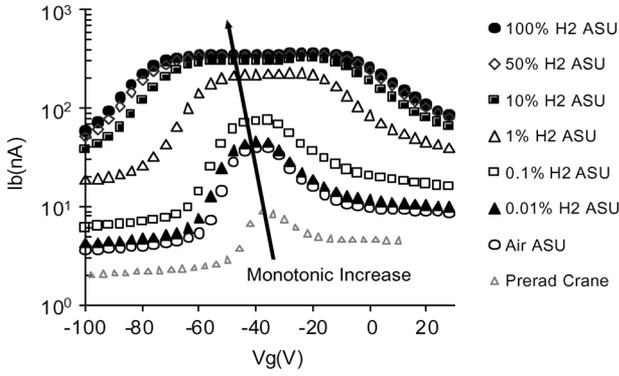


Fig. 3. Gate sweep results from experiments performed at both ASU and Crane showing monotonic increase in base current peak, which indicates increase in interface trap density.

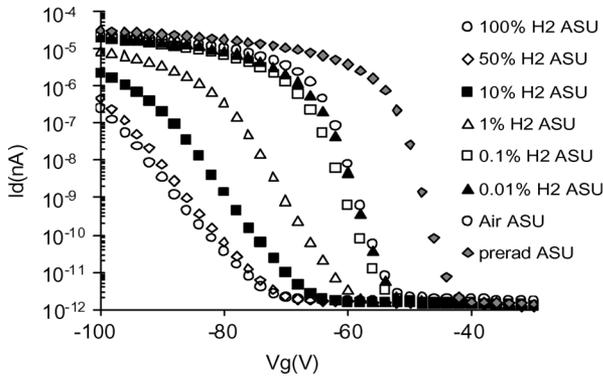


Fig. 4. pMOSFET characteristics from experiments performed at both ASU and Crane showing monotonic increase in subthreshold swing, which indicates increase in interface trap density.

30 krad(SiO₂) of ionizing radiation in a Co-60 Gammacell at a dose rate of approximately 20 rad/s. Immediately after exposure, the devices were removed from the chamber and characterized using the methods discussed above. Due to large volume of the data sets and figure readability issues, Fig. 3 only shows the gate sweep results of the ASU experiments. In Fig. 4, only ASU's subthreshold sweep results are shown.

The monotonic increase in the gate sweep peaks in Fig. 3 clearly indicates an increase of interface trap density with increasing molecular hydrogen concentration. The increase in subthreshold swing in pMOSFET response, shown in Fig. 4, also confirms an increase in interface trap density [13].

Using the simple interface trap estimation method described in [10], [11], the radiation-induced N_{it} density was estimated from the gate sweep results. Fig. 5 is the plot of interface trap density versus the hydrogen concentration in the device oxide during radiation exposure. In Fig. 5, the extracted ΔN_{it} data are shown for experiments performed at both Crane and ASU. The concentrations of H₂ molecules that permeate into the bipolar base oxide are approximated from volume percent to volume density using Henry's Law [14],

$$N_{H_2,ox} = \kappa_{H_2,ox} P_{H_2}, \quad (1)$$

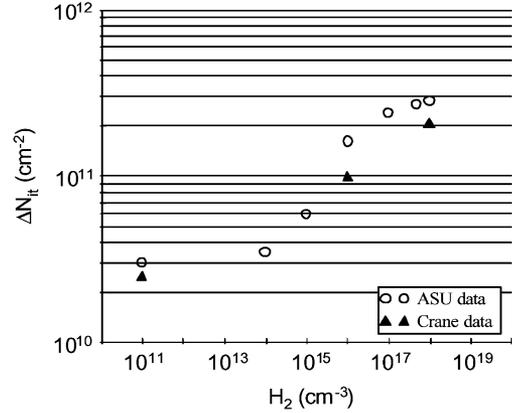


Fig. 5. Estimated radiation-induced interface trap buildup versus molecular hydrogen concentration in the oxide.

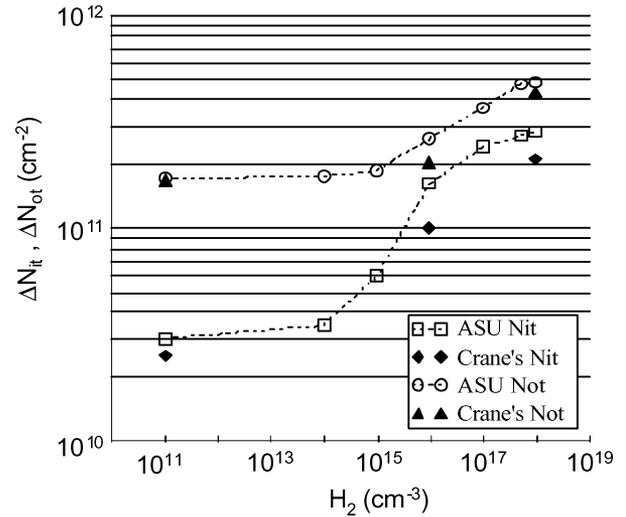


Fig. 6. Estimated radiation-induced oxide trapped charge (N_{ot}) buildup versus molecular hydrogen concentration in the oxide plotted in the same figure with the N_{it} data.

where the solubility of H₂ in oxide, $\kappa_{H_2,ox}$, is approximately $10^{18} \text{cm}^{-3} \text{atm}^{-1}$, and P_{H_2} is the partial pressure of H₂ computed from volume percentage in the ambient. From the plot, we see interface trap density changes the most between H₂ concentrations of 10^{14}cm^{-3} to 10^{17}cm^{-3} , and N_{it} saturation occurs at both high and low concentrations.

Using the subthreshold extraction method [12], [15], the amount of radiation induced oxide trapped charge (N_{ot}) was also extracted and shown in Fig. 6 along with extracted N_{it} data. It is very interesting to note that, similar to the N_{it} data, the radiation induced N_{ot} also increases with H₂ concentration, and saturates at both high and low concentrations of H₂.

In Figs. 5 and 6, there are slight differences in the Crane and ASU experimental data. This is most likely due to the differences in pre-radiation characteristics, radiation source dosimetry, doses rates, and/or characterization environments during the experiments.

III. ANALYTICAL MODEL

One of the most widely accepted models for interface trap formation was originally proposed by McLean [1] and later refined by Rashkeev in [16]. In this 1-D model, electron-hole pairs are generated by radiation in the oxide, and after surviving recombination, a fraction of holes transport through the oxide. The hole generation, recombination, and transport processes in the oxide can be coupled in the continuity equation:

$$\frac{\partial p}{\partial t} = \dot{D}k_g f_y - \frac{\partial f_p}{\partial x}. \quad (2)$$

In (2), p is the hole concentration (cm^{-3}), f_p is the hole flux ($\text{cm}^{-2}\text{s}^{-1}$), \dot{D} is the radiation dose rate, k_g is the dose to concentration conversion factor, and f_y is the hole yield [16]. Based on data from biased irradiation experiments [3], radiation-induced interface trap formation depends on a positively charged species, which is now widely accepted to be protons. Protons, generated from hole-assisted reactions during irradiation, transport to the Si/SiO₂ interface and react with passivated silicon dangling bonds (P_b centers) to form interface traps. Similar to (2), the proton continuity equation can be expressed as

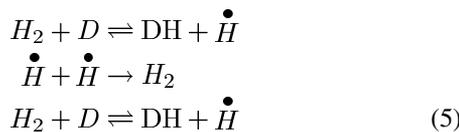
$$\frac{\partial H^+}{\partial t} = N_{\text{DH}}\sigma_{\text{DH}}f_p - \frac{\partial f_{H^+}}{\partial x}, \quad (3)$$

where H^+ is the proton concentration (cm^{-3}), f_{H^+} is the proton flux ($\text{cm}^{-2}\text{s}^{-1}$), N_{DH} is the concentration of hydrogen-containing defect centers (DH), and σ_{DH} is the capture cross-section of holes reacting with the DH centers (cm^2) [16]. The interface trap formation rate is related to proton flux through the equation

$$\frac{\partial N_{\text{it}}}{\partial t} = (N_{\text{Si-H}} - N_{\text{it}}(t))\sigma_{\text{it}}f_{H^+} - \frac{N_{\text{it}}(t)}{\tau_{\text{it}}}, \quad (4)$$

where $N_{\text{Si-H}}$ is the surface concentration of passivated dangling bonds (cm^{-2}), σ_{it} is the proton capture cross-section (cm^2), and τ_{it} is the interface trap lifetime used here to account for N_{it} annealing [16].

Based on our experimental results and the model presented in [1], [16], we propose a model that describes interface trap formation as a function of the H_2 present during radiation exposure. In this model, as depicted by the cartoon in Fig. 7, molecular hydrogen, after reaching an equilibrium concentration in the oxide, reacts with process-related neutral oxide defects (D) at room temperature prior to and during irradiations through the equilibrium reactions:



where $\dot{\text{H}}$ is a hydrogen radical. The reactions in (5), can be reduced to the single reaction,

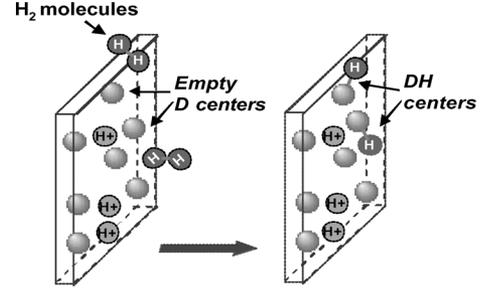
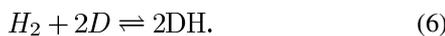


Fig. 7. Cartoon shows the reaction between molecular hydrogen and vacancy defects in the oxide.

This reaction produces hydrogen containing defects (DH) in the oxide bulk that react with radiation-induced holes to form protons for N_{it} generation.

Using chemical kinetics, we can establish a relationship between excess H_2 concentration and DH centers produced in the oxide by writing the equilibrium reaction rate (k_{eq}) for (6) as

$$k_{\text{eq}} = \frac{(N_{\text{DH}})^2}{(N_{\text{H}_2})(N_D)^2}, \quad (7)$$

where N_{DH} , N_{H_2} , and N_D are concentrations of reactants and products. In our model, it is assumed that the sum of all defects with and without a captured hydrogen atom is a constant, N_o . Therefore, the density of neutral and hydrogen containing defects can be related as

$$N_D = N_o - N_{\text{DH}}. \quad (8)$$

After simple algebraic manipulations, N_{DH} can be expressed in terms of H_2 concentration in the oxide as,

$$N_{\text{DH}} = \frac{N_o \sqrt{k_{\text{eq}}} (N_{\text{H}_2})^{\frac{1}{2}}}{1 + \sqrt{k_{\text{eq}}} (N_{\text{H}_2})^{\frac{1}{2}}}. \quad (9)$$

Solving (2)–(4) with assumptions of steady state and no interface dangling bond saturation or annealing, we can express ΔN_{it} in terms of hydrogen defect centers, DH, in the oxide as,

$$\Delta N_{\text{it}} = N_{\text{DH}} \left(\sigma_{\text{DH}} N_{\text{SiH}} \sigma_{\text{it}} \dot{D} k_g f_y t_{\text{ox}}^2 \Delta t / 2 \right) \quad (10)$$

and using the relationship between N_{DH} and excess H_2 density in (9), the radiation induced interface trap density can now be expressed as,

$$\begin{aligned} \Delta N_{\text{it}} &= \frac{N_o \sqrt{k_{\text{eq}}} (N_{\text{H}_2})^{\frac{1}{2}}}{1 + \sqrt{k_{\text{eq}}} (N_{\text{H}_2})^{\frac{1}{2}}} \\ &\times \left(\sigma_{\text{DH}} N_{\text{SiH}} \sigma_{\text{it}} \dot{D} k_g f_y t_{\text{ox}}^2 \Delta t \right) / 2 \\ &= \kappa \frac{k_1 (N_{\text{H}_2})^{\frac{1}{2}}}{1 + k_2 (N_{\text{H}_2})^{\frac{1}{2}}}. \end{aligned} \quad (11)$$

Using the optimized Levenberg Marquardt method [17], the model in (11) is fitted to the experimental data. The results are shown in Fig. 8.

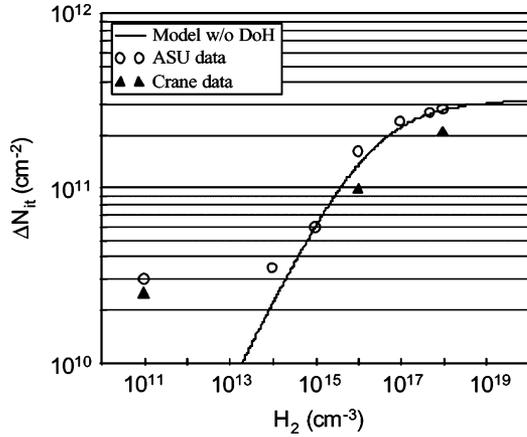


Fig. 8. Fit of model described by (11) to data obtained from the experiments.

From Fig. 8, one finds the model fits the data well for high hydrogen concentrations 10^{15}cm^{-3} (0.1%) to 10^{18}cm^{-3} (100%). However, for low levels of H_2 , 10^{14}cm^{-3} (0.01%) and in open air, 10^{11}cm^{-3} , the model deviates from the experimental data. This lack of agreement is most likely due to the fact that at low H_2 levels, N_{it} formation is no longer strongly dependent on excess H_2 , but on pre-existing hydrogen defects already present in the oxide. A simple calculation reveals that if all of the H_2 in ambient air (10^{11}cm^{-3}) are used, with an oxide thickness of $1\ \mu\text{m}$, a maximum of 10^7cm^{-2} interface traps would be formed, a level which cannot be detected in our measurements.

Since irradiation of devices in air ambient still generates moderate amount of interface traps through the mechanisms described by (2)–(4), to make the chemical kinetics model stand, the pre-existing defects could be considered as defects of a different species, and we denote these as D_oH defects. It is possible that, even though chemically different, these defects can also react with radiation-induced holes to generate protons necessary for interface trap formation. By taking the pre-existing D_oH defects into account, the model in (10) is modified into:

$$\Delta N_{\text{it}} \approx \kappa \left(N_{\text{D}_o\text{H}} + \frac{k_1 (N_{\text{H}_2})^{\frac{1}{2}}}{1 + k_2 (N_{\text{H}_2})^{\frac{1}{2}}} \right). \quad (12)$$

The modified model in (12) is again fitted to the experimental data, and the results are shown in Fig. 9.

IV. ANALYSIS OF DIFFUSION KINETICS

The model presented in this paper is based on equilibrium reactions of molecular hydrogen and oxide defects in the sample devices. Since a saturated molecular hydrogen concentration was used in our experiments, the dynamic impact of H_2 diffusion is omitted. However, to ensure the equilibrium concentrations of H_2 were reached in the experiments, a simple study of molecular hydrogen diffusion through the device oxide was carried out. Using the theory of gas diffusion in solids, a simple calculation was made to estimate the time required for molecular hydrogen to fully saturate the device oxide. Assuming constant source diffusion, that is the hydrogen gas concentration in the ambient does not change appreciably as H_2 diffuses into the

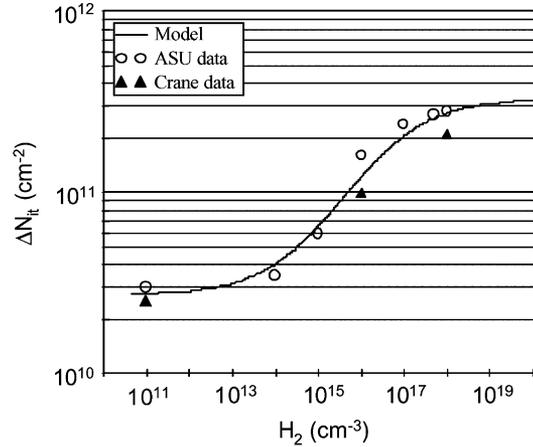


Fig. 9. Fit of model described by (12) to data obtained from the experiments.

device, and that there is a negligible amount of H_2 initially in the device, we can solve the 1-D diffusion equation [18]:

$$\frac{\partial N_{\text{H}_2}}{\partial t} = D_{\text{H}_2,\text{ox}} \frac{\partial^2 N_{\text{H}_2}}{\partial x^2} \quad (13)$$

using the assumed boundary conditions. $D_{\text{H}_2,\text{ox}}$ is the diffusion constant of H_2 in the oxide, and N_{H_2} is the hydrogen gas concentration. The solution [19],

$$N_{\text{H}_2}(x, t) = N_{\text{H}_2,\text{surface}} \operatorname{erfc} \left(\frac{x}{2\sqrt{D_{\text{H}_2,\text{ox}}t}} \right), \quad (14)$$

shows the relationship between H_2 concentration, time, and the position in the horizontal direction. Fig. 10 plots the concentration of H_2 as a function of both time and distance. The diffusion constant $D_{\text{H}_2,\text{ox}}$ in SiO_2 has been calculated by several studies [20]–[24], the range of $D_{\text{H}_2,\text{ox}}$ is from 10^{-9} to $10^{-11}\text{cm}^2\text{s}^{-1}$ depending on the type of the oxide and the existence of pressure gradient in the oxide. Deposited oxides with the presence of pressure gradient are argued to have a higher diffusion constant [24]. Since the oxide in these bipolar devices is composed of both thermally grown and deposited oxides [9], and there is an established H_2 partial pressure gradient in the device during the experiments, the value of $D_{\text{H}_2,\text{ox}}$ is therefore obtained from [20], which is approximately $10^{-9}\text{cm}^2\text{s}^{-1}$.

As shown from Fig. 10, for an H_2 ambient concentration of 10^{16}cm^{-3} , it takes approximately 11 hrs to reach full saturation in the GLPNP devices with an oxide thickness of $1\ \mu\text{m}$. Dynamic experiments were also performed at ASU to study the out diffusion of H_2 through these device structures [25]. The details of the experiments are not covered in this paper, however the results of those experiments showed that H_2 saturated in these devices can be fully diffused out within the same time range. From the results of these calculation and experiments, it may be safe to assume that an equilibrium H_2 concentration is reached before the 48-hour soaking time.

The simple dynamic study of H_2 diffusion discussed above does not capture the effect of materials surrounding the oxide of the bipolar device. The metal contacts and interconnects, and particularly passivation layers deposited on top of the oxide can

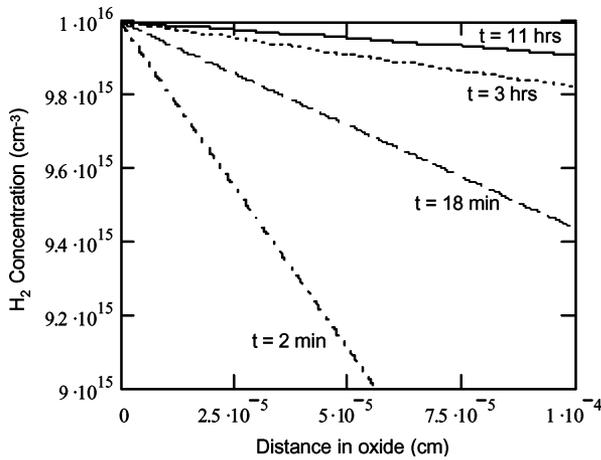


Fig. 10. Plot of molecular hydrogen concentration vs. time and distance in the oxide.

have a significant impact on the diffusion of hydrogen in the device since the diffusion constants for these materials are very different from the device oxide. Since the devices used in this study do not have a passivation layer, and H_2 can easily diffuse into the oxide from large areas uncovered by metal contacts and interconnects in these devices, the results of the calculations using simple oxide H_2 diffusivity agrees well with experimental results in [25]. However, when dealing with H_2 diffusion processes in complex device structures that includes passivation layers and multiple layers of interconnects, one must take into account the H_2 diffusivities in those materials as well.

V. DISCUSSION

The experimental data suggest and the model appears to confirm that chemical reactions are taking place between molecular hydrogen and oxide defects during radiation exposure; however, there is conflicting evidence on the chemical and physical structures of the defects involved. Previous studies, based on quantum mechanical calculations of bonding energies [26], [27] and experimental techniques such as Electron Spin Resonance [28], [29], have identified several oxide defect candidates that are most likely involved with radiation-induced interface trap formation. The most common defects, the oxygen vacancies (stress Si-Si bonds) and silicon dangling bonds (E' centers) in the oxide can bond with hydrogen to form a Si-H bonds. Another defect, the non-bridging oxygen (NBO) center, is a broken Si-O-Si bond with the oxygen attached to only one silicon and had been shown to bond with hydrogen to form an OH group [27]. From experimental data [30], [31], the E' centers can readily react with molecular hydrogen to form Si-H bonds at room temperature. However, according to quantum mechanical calculations, the NBO is energetically favored to dissociate H_2 to form a Si-OH bond at room temperature [6], [7], [26]. The conflicting studies make distinguishing the type of defect that reacts with H_2 in our devices difficult. Nevertheless, since the experiments performed in this study were all done at room temperature, it is reasonable to assume that one of these defects readily reacts with molecular hydrogen in our test devices. From

the theoretical analysis, we see that at much lower H_2 concentrations, there is still a moderate amount of interface trap formation after irradiations. This also raises the question of how different, chemically, do the pre-existing defects compare with the defects that react with molecular hydrogen. In the model, it was assumed that the pre-existing defects are chemically and physically different than H_2 reacting defects.

From the view point of bipolar device operations, the oxide trapped charge (N_{ot}) buildup due to excess H_2 shown in Fig. 6 plays a significant role in bipolar device gain degradation. As thoroughly studied in the past [32], [33], the positive oxide charge can change the surface potential in the active base region of the device surface, and thus modulating carrier concentrations and changing recombination current in the base. The change in base current due to recombination will result in gain variation of the bipolar device.

From defect formation mechanism point of view, the N_{ot} data is also significant because it reveals some insight into the type of defects that react with H_2 in these devices. Since the radiation-induced oxide trapped charge also increases the same way as interface traps, it suggests that defects involved with oxide trapped charge buildup are likely reacting with molecular hydrogen. Shaneyfelt *et al.* [30], from their biased irradiation experiments, suggested a hole-trapping/hydrogen transport (HT)² model to explain how some interface traps are formed in a process closely correlated to hole trapping and N_{ot} formation. That is, the protons released for N_{it} generation could come from the hole trapping defect sites in the oxide. Several studies have been done to investigate the energetics of reactions between molecular hydrogen and hole trapping defect centers to generate H-complexed defects in the oxide and the subsequent reactions of proton generation from these defects [26], [27], [34]. According to the most recent study in [34], molecular hydrogen can react at either E' centers or oxygen vacancies, the latter being the precursors of E' centers and are abundant in device oxides [34], [35]. Prior to radiation exposure, H_2 reacts most likely at the oxygen vacancy location to generate Si-H H-Si defects with the Si atoms. During radiation exposure, proton release and neutral hydrogen bridge (Si-H-Si) formation is energetically favored over neutral hydrogen release and charged hydrogen bridge formation, from the reaction between radiation induced holes and the Si-H H-Si defects. The protons released from this reaction would then go on to form excess interface traps. It is possible that either a hole trapping E' center can be generated from the neutral hydrogen bridge or the hydrogen bridge itself can act as a deep hole trap [34], which can be detected as a oxide trapped charge. In either case, the formation of the hydrogen bridge can lead to excess oxide trapped charge observed in the experimental results.

VI. CONCLUSION

Radiation experiments were performed on gated bipolar test structures to study the effect of molecular hydrogen on the radiation response of these devices. The experimental results show a monotonic increase in radiation-induced interface traps as well as oxide trapped charge with increasing molecular hydrogen concentration in the ambient during irradiations. Using chemical kinetics and previously developed models

for interface trap formation, a model is proposed to describe the relationship between interface trap formation and excess molecular hydrogen concentration in gaseous ambient during radiation exposure. This model has been proposed to at the very least qualitatively describe the reactions between molecular hydrogen and oxide defects to form interface traps in a semiconductor device. This first order model provides a good fit to the data obtained from the experiments. From the analysis of the correlation between radiation-induced interface traps and oxide trapped charge, the oxide defects that most likely react with H₂ to form excess interface traps are suggested to be oxygen vacancies, the E' center precursors in the oxide.

ACKNOWLEDGMENT

The authors are grateful to Kitt Reinhardt of AFOSR for his support, and Marty Shaneyfelt, Ron Schrimpf, Sokrates Pantelides, and Dan Fleetwood for stimulating discussions.

REFERENCES

- [1] F. B. McLean, "A framework for understanding radiation-induced interface states in SiO₂," *IEEE Trans. Nucl. Sci.*, vol. NS-27, no. 6, pp. 1651–1657, Dec. 1980.
- [2] N. S. Saks and D. B. Brown, "Interface trap formation via the two-stage H⁺ process," *IEEE Trans. Nucl. Sci.*, vol. 36, no. 6, pp. 1848–1857, Dec. 1989.
- [3] P. S. Winokur and H. E. Boesch, Jr., "Interface-state generation in radiation-hard oxides," *IEEE Trans. Nucl. Sci.*, vol. NS-27, p. 1647, 1980.
- [4] K. L. Brower, "Kinetics of H₂ passivation of P_b centers at the (111) Si-SiO₂ interface," *Phys. Rev. B*, vol. 38, pp. 9657–9666, 1988.
- [5] R. A. Kohler, R. A. Kushner, and K. H. Lee, "Total dose radiation hardness of MOS devices in hermetic ceramic packages," *IEEE Trans. Nucl. Sci.*, vol. 35, no. 6, pp. 1492–1496, Dec. 1988.
- [6] B. J. Mrstik and R. W. Rendell, "Si-SiO₂ interface state generation during X-Ray irradiation and during post-irradiation exposure to a hydrogen ambient," *IEEE Trans. Nucl. Sci.*, vol. 38, no. 6, pp. 1101–1110, Dec. 1991.
- [7] R. E. Stahlbush, A. H. Edwards, D. L. Griscom, and B. J. Mrstik, "Post-irradiation cracking of H₂ and formation of interface states in irradiated metal-oxide-semiconductor field-effect transistors," *J. Appl. Phys.*, vol. 73, pp. 658–667, 1992.
- [8] R. L. Pease, D. G. Platteter, G. Dunham, J. E. Seiler, and S. McClure, "Total dose and dose rate response of an AD590 temperature transducer," in *Proc. Radiation Effects Components and Systems Workshop*, Athens, Greece, 2006.
- [9] R. L. Pease, D. G. Platteter, G. W. Dunham, J. E. Seiler, H. J. Barnaby, R. D. Schrimpf, M. R. Shaneyfelt, M. C. Maher, and R. N. Nowlin, "Characterization of enhanced low dose rate sensitivity (ELDRS) effects using gated lateral PNP transistor structures," *IEEE Trans. Nucl. Sci.*, vol. 51, no. 6, pp. 3773–3780, Dec. 2004.
- [10] D. R. Ball, H. J. Barnaby, and R. D. Schrimpf, "Separation of ionization and displacement damage using gate-controlled lateral PNP bipolar transistors," *IEEE Trans. Nucl. Sci.*, vol. 49, no. 6, pp. 3185–3190, Dec. 2002.
- [11] X. J. Chen, H. J. Barnaby, R. L. Pease, R. D. Schrimpf, D. G. Platteter, and G. Dunham, "Radiation induced base current broadening mechanisms in gated bipolar devices," *IEEE Trans. Nucl. Sci.*, vol. 51, no. 6, pp. 3178–3185, Dec. 2004.
- [12] X. J. Chen, H. J. Barnaby, R. L. Pease, R. D. Schrimpf, D. G. Platteter, M. Shaneyfelt, and B. Vermeire, "Estimation and verification of radiation induced N_{ot} and N_{it} energy distribution using combined bipolar and MOS characterization methods in gated bipolar devices," *IEEE Trans. Nucl. Sci.*, vol. 52, no. 6, pp. 2245–2251, Dec. 2005.
- [13] P. S. Winokur, J. R. Schwank, P. J. McWhorter, P. V. Dressendorfer, and D. C. Turpin, "Corelating the radiation response of MOS capacitors and transistors," *IEEE Trans. Nucl. Sci.*, vol. NS-31, no. 6, pp. 1453–1460, Dec. 1984.
- [14] J. C. Kotz and J. P. T. Treichel, *Chemistry & Chemical Reactivity*. Forth Worth, TX: Saunder College Publishing, 1999.
- [15] R. L. Pease, D. Emily, and H. E. Boesch, Jr., "Total dose induced hole trapping and interface state generation in bipolar recessed field oxides," *IEEE Trans. Nucl. Sci.*, vol. NS-32, no. 6, pp. 3946–3952, Dec. 1985.
- [16] S. N. Rashkeev, C. R. Cirba, D. M. Fleetwood, R. D. Schrimpf, S. C. Witczak, A. Michez, and S. T. Pantelides, "Physical model for enhanced interface trap formation at low dose rates," *IEEE Trans. Nucl. Sci.*, vol. 49, no. 6, pp. 2650–2655, Dec. 2002.
- [17] P. R. Gill, W. Murray, and M. H. Wright, "The Levenberg-Marquardt method," in *Practical Optimization*. London, U.K.: Academic, 1981, pp. 136–137.
- [18] W. Jost, *Diffusion in Solids, Liquids, Gases*. New York: Academic, 1960.
- [19] R. C. Jaeger, *Introduction to Microelectronic Fabrication*, 2nd ed. Englewood Cliffs, NJ: Prentice-Hall, 2002.
- [20] R. W. Lee, R. C. Frank, and D. E. Swets, "Diffusion of hydrogen and deuterium in fused quartz," *J. Chem. Phys.*, vol. 36, pp. 1062–1071, Feb. 1962.
- [21] J. E. Shelby, "Molecular diffusion and solubility of hydrogen isotopes in vitreous silica," *J. Appl. Phys.*, vol. 48, pp. 3387–3394, 1977.
- [22] W. G. Perkins and D. R. Begeal, "Diffusion and permeation of He, Ne, Ar, Kr, and D₂ through silicon oxide thin films," *J. Chem. Phys.*, vol. 54, pp. 1683–1694, 1971.
- [23] G. Schols and H. E. Maes V. J. Kapoor and H. J. Stein, *Silicon Nitride Thin Insulating Films*. Pennington, NJ: Electrochemical Soc., 1983.
- [24] B. J. Fishbein, J. T. Watt, and J. D. Plummer, "Time resolved annealing of interface traps in polysilicon gate metal-oxide-silicon capacitors," *J. Electrochem. Soc.*, vol. 134, pp. 674–681, 1987.
- [25] R. L. Pease, D. G. Platteter, G. Dunham, J. E. Seiler, P. C. Adell, H. J. Barnaby, and X. J. Chen, "The effects of hydrogen in hermetically sealed packages on the total dose and dose rate response of bipolar linear circuits," in *Proc. IEEE Nuclear and Space Radiation Effects Conf.*, Honolulu, HI, 2007.
- [26] A. H. Edwards, "Dissociation of H₂ at silicon dangling orbitals in a-SiO₂: A quantum mechanical treatment of nuclear motion," *J. Non-Cryst. Solids*, vol. 187, pp. 232–243, 1995.
- [27] M. Vitiello, N. Lopez, F. Illas, and G. Pacchioni, "H₂ cracking at SiO₂ defect centers," *J. Phys. Chem.*, vol. A104, pp. 4674–4684, 2000.
- [28] J. F. Conley and P. M. Lenahan, "Room temperature reactions involving silicon dangling bond centers and molecular hydrogen in amorphous SiO₂ thin films on silicon," *Appl. Phys. Lett.*, vol. 62, pp. 40–42, 1993.
- [29] J. F. Conley, P. M. Lenahan, and P. Roitman, "Electron spin resonance study of E' trapping centers in simox buried oxides," *IEEE Trans. Nucl. Sci.*, vol. 38, no. 6, pp. 1247–1252, Dec. 1991.
- [30] M. R. Shaneyfelt, J. R. Schwank, D. M. Fleetwood, P. S. Winokur, K. L. Hughes, and F. W. Sexton, "Field dependence of interface trap buildup in polysilicon and metal gate MOS devices," *IEEE Trans. Nucl. Sci.*, vol. 37, no. 6, pp. 1632–1640, Dec. 1990.
- [31] D. L. Griscom, "Diffusion of radiolytic molecular hydrogen as mechanism for the post-irradiation buildup of interface states in SiO₂-on-Si structures," *J. Appl. Phys.*, vol. 58, p. 2524, 1985.
- [32] S. L. Kosier, R. D. Schrimpf, R. N. Nowlin, D. M. Fleetwood, R. L. Pease, M. Delaus, W. E. Combs, A. Wei, and F. Chai, "Charge separation for bipolar transistors," *IEEE Trans. Nucl. Sci.*, vol. 40, no. 6, pp. 1276–1277, Dec. 1993.
- [33] D. M. Schmidt, A. Wu, R. D. Schrimpf, D. M. Fleetwood, and R. L. Pease, "Modeling ionizing radiation induced gain degradation of the lateral PNP bipolar junction transistor," *IEEE Trans. Nucl. Sci.*, vol. 43, no. 6, pp. 3032–3039, Dec. 1996.
- [34] P. E. Bunson, M. D. Ventra, S. T. Pantelides, D. M. Fleetwood, and R. D. Schrimpf, "Hydrogen-related defects in irradiated SiO₂," *IEEE Trans. Nucl. Sci.*, vol. 47, no. 6, pp. 2289–2296, Dec. 2000.
- [35] W. L. Warren, M. R. Shaneyfelt, D. M. Fleetwood, J. R. Schwank, P. S. Winokur, and R. A. B. Devine, "Microscopic nature of border traps in MOS Oxides," *IEEE Trans. Nucl. Sci.*, vol. 41, no. 6, pp. 1817–1827, Dec. 1994.