Characterization of X-Ray Radiation Damage in Si/SiO$_2$ Structures Using Second-Harmonic Generation

Z. Marka, S. K. Singh, W. Wang, S. C. Lee, J. Kavich, B. Glebov, S. N. Rashkeev, A. P. Karmarkar, R. G. Albridge, S. T. Pantelides, R. D. Schrimpf, D. M. Fleetwood, and N. H. Tolk

***Abstract*—We report the first application of second-harmonic generation (SHG) measurements for the characterization of X-ray radiation damage in Si/SiO$_2$ structures. The main advantage of this experimental technique is that it is noninvasive, contactless, and sensitive to the electric field at the interface. Interaction of intense 800 nm femtosecond laser pulses with Si/SiO$_2$ structures results in electron-hole pair creation in the Si, multiphoton carrier injection and second-harmonic generation. The time-dependent second-harmonic (doubled frequency) signal is a measure of the dynamic electric field at the interface. This dynamic field is created and altered by unequal electron-hole injection into the oxide, trapping/detrapping of charges, and carrier recombination processes. We find that the SHG response from Si/SiO$_2$ samples before and after X-ray irradiation is significantly different. Thus, SHG is a promising technique for the characterization of radiation damage in Si/SiO$_2$ structures. In particular, SHG is especially useful in characterizing damage in ultrathin oxide layers, for which conventional electrical measurements may not be sufficiently sensitive to the kinds of defects observable via optical methods.**

I. Introduction

PRESENTLY, characterization of traps due to radiation damage in Si/SiO$_2$ systems is usually accomplished with traditional electronic methods such as capacitance-voltage (*C-V*) and current-voltage (*I-V*) measurements [1]. Noninvasive, contactless alternative characterization techniques can provide additional insight into radiation damage. For example, electron paramagnetic resonance (EPR) has been employed with much success, and has been used to identify several types of oxide and interface traps [2], [3]. However, EPR can only be used to study particular paramagnetic defects. Optical methods, such as second-harmonic generation [4], can potentially provide a more versatile alternative for studying trapping and detrapping phenomena. In this work we show that extending the application of SHG measurements to X-ray irradiated structures can provide new information about radiation-induced damage in thin oxides.

Manuscript received July 25, 2000. This work was supported in part by the U.S. Air Force Office of Scientific Research through the Multi-Disciplinary University Research Initiative program Grant F-49620-99-1-0289 and by the Office of Naval Research.

Z. Marka, S. K. Singh, W. Wang, J. Kavich, B. Glebov, S. N. Rashkeev, R. G. Albridge, and N. H. Tolk are with the Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235 USA (e-mail: {norman.tolk; shailesh.k.singh}@vanderbilt.edu).

S. T. Pantelides is with the Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235 USA, and the Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA (e-mail: pantelides@vanderbilt.edu).

S. C. Lee, A. P. Karmarkar, R. D. Schrimpf, and D. M. Fleetwood are with the Department of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, TN 37235 USA (e-mail: dan.fleetwood@vanderbilt.edu; schrimpf@vuse.vanderbilt.edu).

Publisher Item Identifier S 0018-9499(00)11255-9.

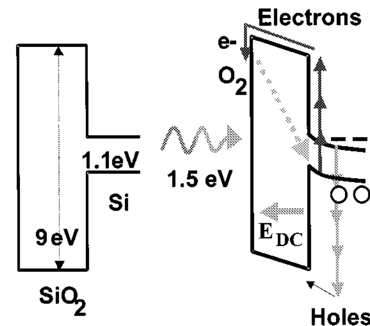

Fig. 1. Interaction of 800 nm laser light with Si/SiO$_2$ interface.

In recent years the SHG technique has been shown as a sensitive, new probe of the Si/SiO$_2$ interface [5]. The technique selectively probes regions of broken symmetry, such as surfaces, interfaces and defects. In addition, the second-harmonic signal is very sensitive to changes in the magnitude of the electric field across interfaces. Therefore, it can be used to study dynamical processes involving the separation of charges [6]. The laser used to generate second-harmonic signal in these studies has exclusively been in the 700–900 nm wavelength range. In the system depicted in Fig. 1, a bare oxide on a Si wafer, the laser irradiation serves a threefold purpose: 1) generation of electron-hole pairs in the Si, 2) injection of electrons to the oxide surface, and 3) the generation of the second-harmonic signal. The first two processes create a photo-excited time-dependent electric field at the interface due to the separation of the electrons and holes. This time-dependent electric field induced second-harmonic (EFISH) signal from Si/SiO$_2$ can be described in general by

$$I^{2\omega}(t) = \left|\chi^{(2)} + \chi^{(3)}E(t)\right|^2 (I^{\omega})^2,$$

where

I^{ω} and $I^{2\omega}(t)$	are the intensities of the fundamental and the time-dependent SHG beams,
$\chi^{(3)}$	is the third-order nonlinear susceptibility,
$\chi^{(2)}$	is the effective second order susceptibility from all other sources, and
$E(t)$	is a quasi-static electric field [7].

0018–9499/00$10.00 © 2000 IEEE

Previous studies indicate that the EFISH signal in Si/SiO_2 structures is due to a large time-dependent electric field created at the interface caused by charge separation. After creation of electron-hole pairs, the electrons are injected to the oxide via a three-photon process [7]. Due to their high mobility, the electrons find their way to the surface and are trapped at the surface by the high electron affinity of oxygen molecules. Experiments performed in vacuum and then at increasing O_2 partial pressures showed that ambient oxygen is the main source of electron traps for studies performed at atmosphere and at room temperature [8], [25]. Devices were not exposed to ionizing radiation in these studies, but all insulating surfaces are known to have high densities of these kinds of surface states. The injection of holes into the oxide using 800 nm laser light would require a four-photon process, and hole mobility in SiO_2 is much lower than electron mobility [9]. Therefore most holes remain in the vicinity of the interface in the Si, in contrast to the electrons, which are free to move to the surface of SiO_2. A time-dependent quasistatic electric field $(E(t))$ is created by the competition between electron injection into the oxide, trapping/detrapping at the surface, and recombination of trapped and transporting electrons and holes at the Si/SiO_2 interface, giving a rising EFISH signal until equilibrium is reached and a steady signal is observed.

The time-dependent EFISH signal is highly oxide thickness dependent. It has been observed that, as the oxide thickness increases, the steady- state second-harmonic signal decreases with a characteristic length of 3.5 nm [8], [25]. The SHG signal observed for thick oxides (>10 nm) is mostly attributed to the $\chi^{(2)}$ time-independent (bulk and interface) contributions. The increasing sensitivity of SHG with decreasing oxide thickness is aligned with the trend of decreasing oxide thickness in modern microelectronics technologies, and in contrast to the decrease in sensitivity of traditional electrical techniques with decreasing oxide thickness.

Based on the above discussion, it seems reasonable to apply the SHG technique to study the radiation damage process in Si/SiO_2 systems. We have done this for thin (~6.5 nm) and thicker (~33 nm) oxides. For the thin oxides, the signal is mostly due to electric fields created by the charge separation caused by surface trapped electrons, as illustrated above in Fig. 11. During X-ray irradiation, precursor defects are populated with trapped charge, and/or new defects are created within the oxide and at the interface. We can study the interactions of these new and pre-existing traps with the transporting and surface-trapped electrons. For thicker oxides (>10 nm) the photoinjected electrons cannot reach the surface [8], [25], and therefore they do not contribute to the SHG signal, which is preferentially time-independent. However, if any small time-dependency is observed, it can be attributed to changes in the electric field at the interface due to trapping and detrapping of carriers, e.g., at O vacancies in the SiO_2 near the Si/SiO_2 interface [2], [3]. Below we evaluate SHG signals from irradiated and unirradiated oxides.

II. Experimental Details

We carried out SHG measurements on two different Si/SiO_2 samples. The first sample, provided by Lucent Technologies,

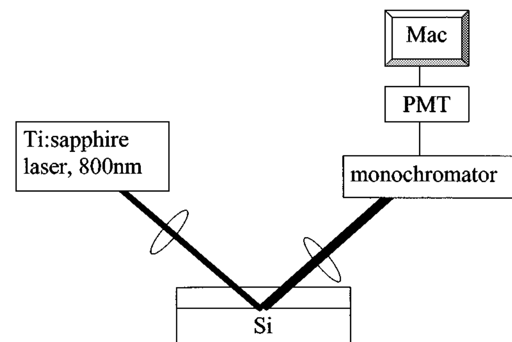

Fig. 2. Experimental setup for SHG measurements.

has a 6.5 nm thermally grown oxide layer on Si and was annealed in a H_2 atmosphere. The SHG experiments were carried out on a contactless (i.e., nongated) sample. However, for *C-V* measurement we deposited a 1 mm diameter Al dot on the oxide and metallized the backside with Al to form a capacitor structure. The second sample has a 33 nm oxide layer grown on n-type Si. The Al-gate was formed by evaporating 1 μm of aluminum through a shadow mask with a 1 mm diameter [10]. To ensure that ohmic contact was made to the substrate, 50 nm of Ti and 250 nm of Au were evaporated onto the backside of the wafers. The sample sizes were generally in the 1 cm by 1 cm range. For SHG measurements, we used spots at least 1 mm away from the Al-gate.

The samples were irradiated using a 10-keV X-ray source up to a total dose of 7.6 Mrad (SiO_2). The dose rate used in this experiment was ~1 krad(SiO_2)/s. For the samples without gate electrodes, the samples were irradiated without electrical bias. For 33 nm oxide samples, biased irradiation was also performed to observe the correlation between the changes in *C-V* (capacitance-voltage) characteristics and SHG signals due to irradiation. A positive bias of 5 V was applied to the gate of the dot capacitor with the backside of wafer grounded. Standard high-frequency (100 kHz) *C-V* measurements [1] were performed before and after irradiation for the gated devices.

The SHG experiments reported here were performed using a 6 W Verdi pumped Mira Ti : sapphire laser (manufactured by Coherent) at 800 nm (1.5 eV). According to the company specifications, the laser delivers ~150 fs FWHM pulses with repetition rate of 76 MHz and average power of around 600 mW. These high intensity short pulses combined with the high repetition rate allow us to achieve a good signal-to-noise ratio while avoiding significant steady-state heating of the sample [11]–[13]. The beam is focused to an approximately 40 μm beam waist diameter ($2w_0$) spot size, corresponding to 10 GW/cm^2 peak intensity. Under these conditions and by attaching the sample to an aluminum block, which acts as a heat sink, we estimate that the steady-state temperature increase in the sample is considerably less than 30 K and it does not play a significant role in these measurements [14]. The fundamental beam is horizontally polarized and hits the sample at a 45 degree angle of incidence (Fig. 2). A neutral density filter is positioned in the beamline for studies performed at decreased power. The reflected fundamental and SHG signals are collected by another lens, and a monochromator is used

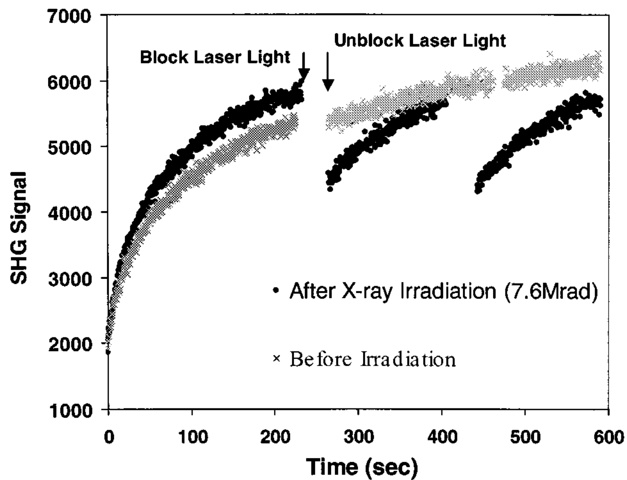

Fig. 3. Example of SHG signal versus time for 6.5 nm H_2 annealed oxide before and after irradiation.

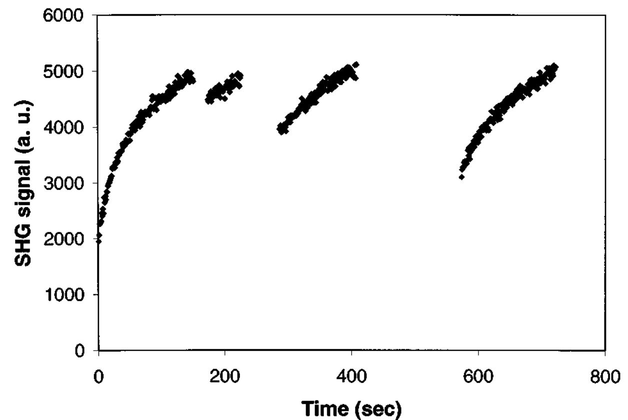

Fig. 4. Example showing the decrease in the second-harmonic level as longer and longer blocking times are applied for 6.5 nm H_2 annealed oxide. Laser power is 580 mW.

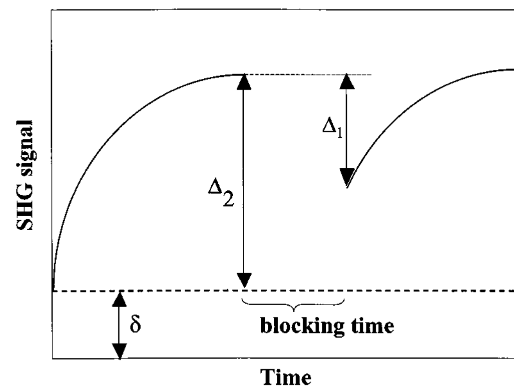

Fig. 5. Definition of Δ_1 and Δ_2.

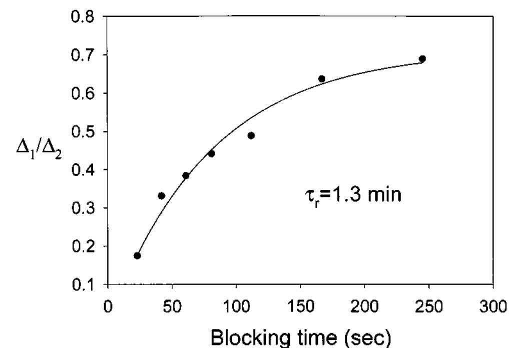

Fig. 6. Recombination time of surface electrons with holes at the interface for X-ray damaged [7.6 Mrad (SiO_2) dose] 6.5 nm H_2 annealed oxide sample.

to separate these two beams. The SHG signal at 400 nm is detected by a photomultiplier and measured with a 1 s temporal resolution by a photon counter.

We have done the SHG measurements on the samples at several different new spots to check spot-to-spot reproducibility on the sample. However, we repeated all measurements with another sample irradiated up to the same X-ray dosage. In all cases shown here, the results are reproducible to within experimental error from spot-to-spot on a given sample, and from different samples from the same wafer.

III. Second Harmonic Generation Measurements on Thin Oxides

On the 6.5 nm oxide samples we investigated the recombination of surface trapped electrons with holes at the interface. The experiment focused on observation of changes in the SHG signal for alternating periods of laser illumination and dark conditions. This measurement sequence is useful for studying the buildup and decay of the EFISH signal under varying conditions. In Fig. 3 we plot a characteristic example of SHG signal versus time for 6.5 nm H_2 annealed sample before and after irradiation to a dose of 7.6 Mrad(SiO_2). The signal does not start at the zero level, showing that there exists a time-independent $\chi^{(2)}$ contribution. The monotonically rising SHG signal with increasing exposure time indicates the creation of an increasing electric field at the interface. This increase in magnitude is evidently due to photo-induced electron transport to the surface of the oxide. As shown in Fig. 3, after a long laser illumination time we blocked the laser beam (dark condition) for several tens of seconds and then unblocked the beam and started to record the SHG signal again. Both before and after the dark condition, the laser hits the same spot on the sample. These blocking measurements are not affected by the minor temperature change in the sample, because under the laser parameters applied here we do not observe a difference in SHG signal intensity due to local sample heating. We observed a pronounced effect on the radiation-damaged sample: when we unblock the laser beam, the SHG signal is initially greatly reduced in intensity and starts rising again. For the control, unirradiated sample, we do not observe any change in the SHG intensity after several tens of seconds of dark condition. This illustrates the sensitivity of the EFISH signal to radiation damage in the SiO_2.

We observed that, the longer the laser is blocked, the greater is the drop in the SHG signal (Fig. 4). Therefore, we carried out systematic measurements at increasing blocking times. To quantify our results we introduced the factor Δ_1/Δ_2 (Fig. 5), which describes the relative change in the SHG intensity before and after the dark condition. As mentioned previously, the observed second-harmonic signal always has a time-independent $\chi^{(2)}$ contribution besides the time dependent electric-field induced part. This level is denoted by δ on Fig. 5; the SHG signal after unblocking the laser can drop at most to this minimum constant level. Fig. 6 plots the quantity Δ_1/Δ_2 versus blocking (or dark) time. This data was deduced from a single blocking time

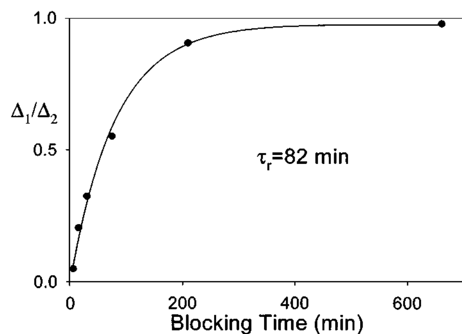

Fig. 7. Recombination time of surface electrons with holes at the interface for nonirradiated 6.5 nm H_2 annealed oxide sample.

experiment, such as shown on Fig. 4, taken continuously on the same spot between 1 hour 55 minutes to 2 hours 15 minutes after the 7.6 Mrad(SiO_2) X-ray irradiation finished. The data points on Fig. 6 (as well as on Figs. 7 and 9) are the result of single blocking-unblocking measurements. The inherent error in these data points comes only from the error associated with photon counting, which is less than ± 100 counts per second. This would give a maximum of ± 0.05 error bar for Δ_1/Δ_2 data points. By fitting the data on Fig. 6 with an exponential growth to a maximum, we deduce a characteristic (recombination) time $\tau_r = 1.3$ min. This means that, if the dark condition is applied for several minutes, the SHG signal drops down to the minimum level, presumably because of the recombination of electrons trapped at the surface of the SiO_2 with holes at the Si/SiO_2 interface. The data of Fig. 3 therefore suggest that the trapped electrons can transport back across the irradiated oxide much more easily than across the unirradiated oxide.

To quantify this difference in recombination rates, we repeated the blocking time experiment for a control, unirradiated 6.5 nm H_2 annealed sample. As we stated earlier, there is no observable change in the SHG signal when dark condition of the order of tens of seconds is applied. We found that we have to block the laser for several tens of minutes in order to see a significant drop in the SHG level. The characteristic recombination time for this nonirradiated sample is $\tau_r = 82$ min., as seen in Fig. 7.

When we performed the blocking time experiment at several hours after X-ray irradiation we observed that the drop in the SHG signal is smaller for the same length of dark condition applied, as illustrated in Fig. 8. Systematic measurements were carried out to deduce the characteristic decay time of the effect. We measured the drop in the SHG level for a constant (102 seconds) blocking time at increasing times after the end of X-ray irradiation. Fig. 9 plots the relative change in SHG intensity versus time after irradiation. These data points were deduced from single blocking experiments, such as shown on Fig. 8, taken on different spots on the sample at different times after X-ray irradiation. By fitting the data with a simple exponential decay curve we found a characteristic decay time $\tau_d = 103$ minutes. We could not observe any significant change in the SHG level after blocking and unblocking the laser at 10 hours after irradiation, showing the complete loss of the enhancement in electron transport across the SiO_2. We would like to note here that preliminary experiments performed on 6.5 nm as-deposited

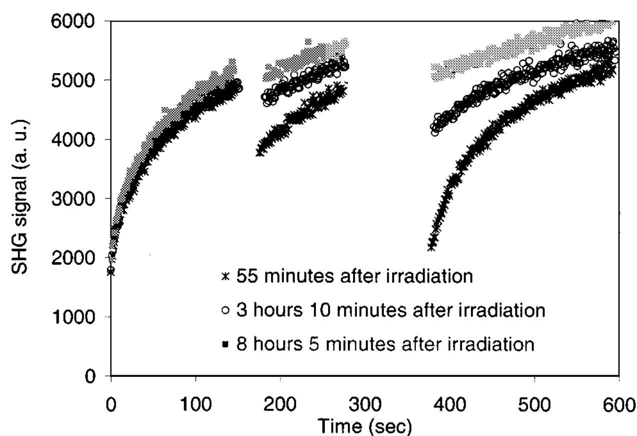

Fig. 8. Time-dependent SHG signal at different times after irradiation of the sample [7.6 Mrad (SiO_2), 6.5 nm H_2 annealed oxide]. The laser was blocked at 150 seconds for 27 seconds and then blocked again at 175 seconds for 102 seconds. Each of the three traces shown here corresponds to measurements at a different spot on the sample.

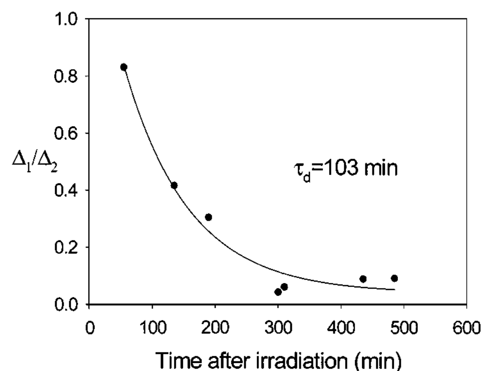

Fig. 9. Characteristic time for the decay of the observed recombination effect.

oxide sample (no H_2 anneal treatment) show that this characteristic decay time is of the order of days in this case. For example, four days after irradiation we still observed a 20 percent change in the SHG level after the laser was unblocked. This difference in response between as-processed and H_2 annealed samples suggests a key role for hydrogen in the above experiments.

We evaporated Al contact onto these very thin samples for the purpose of *C-V* measurements. We did not find any significant shift in the *C-V* curves due to 7.6 Mrad (SiO_2) irradiation, which is not surprising because of the known radiation hardness of ultrathin oxides [15]. This emphasizes the utility of SHG for studying radiation damage in ultrathin oxides.

The above results have demonstrated that, for the H_2 annealed 6.5 nm oxides, the recombination time is close to two orders of magnitude lower for the X-ray damaged sample than for unirradiated samples (1.3 min vs. 82 min). This implies that, for the irradiated sample, a significantly faster "channel" is opened up for recombination of surface electrons. The defects responsible for this channel apparently anneal at room temperature on a timescale of the order of hours, based on the observed decay of the recombination effect with time. In thin oxides, this sort of annealing time is consistent with the rate at which trapped positive charge in the oxide is completely annealed by tunneling

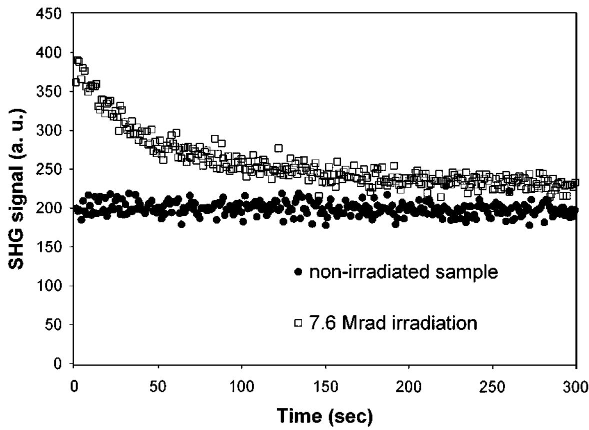

Fig. 10. Time-dependent SHG signal for 33 nm thick oxide sample before and after irradiation. Laser power is 340 mW.

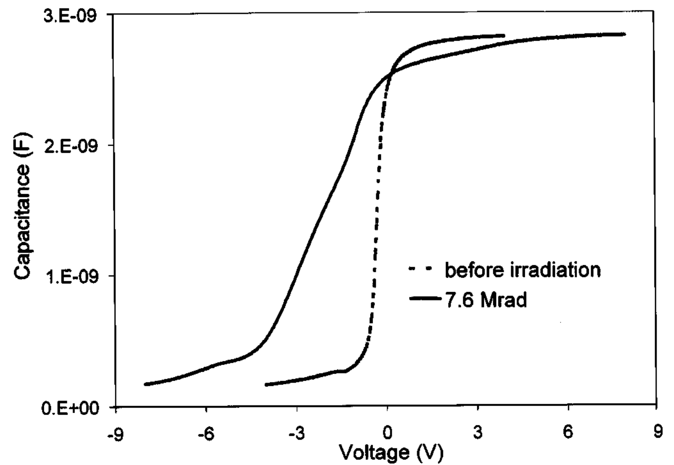

Fig. 11.

electrons [15], leading to the formation of dipoles in the insulator [16]–[19]. Thus, defects associated with radiation-induced trapped positive charge like E' centers [2], [3] are natural candidates for the defects responsible for the changes in the EFISH signal. Indeed, both E'_γ and E'_δ centers are known to be reactive with hydrogen [20], making this connection quite plausible. Moreover, the E'_δ center is known to exist in the bulk of the SiO_2, and to have a short lifetime after radiation exposure. Indeed, Warren *et al.* have measured characteristic decay rates in the E'_δ center in thicker oxides [21] that are quite similar to the decay rates we observe here. The microstructure of the E'_δ is still controversial [22], but it is known to be associated with an O vacancy in SiO_2. Thus, the E'_δ center is an especially appealing candidate for the defect responsible for the EFISH signal observed here. However, the above-noted sensitivity to hydrogen may also be consistent with other defects like the hydrogen bridge (essentially a hydrogen atom in an oxygen vacancy), which has been implicated in stress-induced leakage current in thin SiO_2 [23]. Additional studies are required to determine the microstructure of the defects responsible for the changes in the EFISH signal for the thin oxides.

IV. Second Harmonic Generation Measurements on Thick Oxides

We investigated the differences in the second-harmonic signal from a 33 nm thick oxide sample before and after irradiation. We observed a low level of SHG signal in these samples. As mentioned in the introduction, for oxide thickness greater than 10 nm the SHG signal is mostly due to the low-level time-independent bulk and interface $\chi^{(2)}$ contributions. This fact actually is advantageous, since if any small time-dependence in the SHG is observed it can be attributed to radiation-induced interface and oxide traps [1], since the electrons can no longer reach the surface. The laser is still generating electron-hole pairs and the carriers can be injected into the near-interfacial oxide and get trapped. This can produce a time-dependent electric field and consequently a time-dependent EFISH signal.

Fig. 10 shows the SHG signal versus time for a 33 nm thick oxide sample before and after X-ray irradiation to 7.6 Mrad(SiO_2). The main difference is observed in the first 100 seconds after the laser illumination started. The nonirradiated sample gives a time-independent second harmonic signal, mostly due to bulk and interface $\chi^{(2)}$ contributions. On the other hand, the X-ray damaged sample shows a time-dependent feature: the signal starts out high, and then it decays to a steady state level. Decrease in the EFISH level indicates a decreasing electric field at the interface. We also performed *C-V* measurements before and after irradiation on the same 33 nm oxide sample. Fig. 11 plots these *C-V* curves, showing a significant shift for the X-ray damaged case. The shift to negative voltages and the stretchout in the curve are consistent with radiation-induced oxide- and interface-trapped charge. In particular, the presence of trapped holes near the Si/SiO_2 interface makes it very natural for electrons excited during the SHG measurements to be captured by the holes [19], [24], leading to their annihilation or their compensation by nearby electron trapping, and thus a reduction in the field near the interface and the resulting EFISH signal in Fig. 10. Thus, in the future, it may be possible to use SHG to assist in the characterization of trapped positive charge annealing in irradiated Si/SiO_2 structures.

V. Summary and Conclusions

We have shown that second-harmonic generation is a very useful technique for characterizing X-ray radiation damage in Si/SiO_2 structures. Intense ultrafast laser pulses were used to create electron-hole pairs, to preferentially inject electrons into the oxide, and to study the interaction of charges with the traps created during X-ray irradiation. The method measures the electric field across the interface, which is the result of unequal charge distribution in the structure. We performed time-dependent measurements, which provided dynamical information about trapping, detrapping, and recombination processes in Si/SiO_2. The technique was used to characterize damage in a thin (6.5 nm, H_2 annealed) and a thicker (33 nm) oxide sample. In both cases, when irradiated and unirradiated samples were compared, we observed significant differences in the time-dependent SHG signal.

Since the second-harmonic signal is significantly thickness dependent we obtained different information from the two different oxides studied. In case of the thin oxide (6.5 nm) we measured the rate of recombination of surface-trapped electrons

with holes at the interface. This characteristic recombination time was measured to be $\tau_r = 1.3$ min for the damaged sample and $\tau_r = 82$ min for the unirradiated sample. We also observed that the differences in the SHG behavior of the irradiated and nonirradiated samples decay with increasing time after irradiation, with a characteristic timescale of decay $\tau_d = 103$ min in samples that received a H_2 anneal during device processing. These defects are apparently much more stable in devices that have not received a H_2 anneal. The nature of the defects that lead to this response is unknown, but the decay of this effect is similar to the timescale at which E'_δ centers have been observed to anneal in previous work [21]. However, other O vacancy-related defects and hydrogen impurity centers in SiO_2 are also plausible candidates for causing this response.

Measurements (both SHG and *C-V*) performed on the thicker (33 nm) oxides indicated the presence of positive trap charge in the oxide due to X-ray irradiation, as expected.

For ultrathin oxides the SHG technique was found to detect significant changes in the characteristics of the samples after irradiation that *C-V* methods could not. Studies of ultrathin oxides have gained importance over the past decade due to the trend of using thinner and thinner gate oxides. We present here the first application of the second-harmonic generation technique to the study of radiation effects in oxides. We believe that this can become a quantitative method through proper calibration and will thereby be useful in determining defect densities. The strength of this technique is that it readily yields dynamical information on defect/trap relaxation/trapping times. These timescales can be important in determining the nature of the defect/trap created during X-ray irradiation. This information about relaxation times for defects in the bare oxides cannot be obtained in any other way that we know of.

The second-harmonic measurement requires no contacts, it is nondestructive and is easily applicable for both thin and thick oxides. We conclude that SHG is a valuable tool to assist in the analysis of radiation effects in the Si/SiO_2 system.

ACKNOWLEDGMENT

The authors would like to thank B. K. Choi for experimental assistance. They also would like to thank I. C. Kizilyalli and P. K. Roy at Lucent Technologies for providing the 6.5-nm oxide samples.

REFERENCES

[1] P. S. Winokur, J. R. Schwank, P. J. McWhorter, P. V. Dressendorfer, and D. C. Turpin, "Correlating the radiation response of MOS capacitors and transistors," *IEEE Trans. Nucl. Sci.*, vol. 31, p. 1453, 1984.

[2] P. M. Lenahan and P. V. Dressendorfer, "Hole traps and trivalent Si defects in irradiated MOS devices," *J. Appl. Phys.*, vol. 55, p. 3495, 1984.

[3] W. L. Warren, M. R. Shaneyfelt, J. R. Schwank, D. M. Fleetwood, P. S. Winokur, R. A. B. Devine, W. P. Maszara, and J. B. McKitterick, "Paramagnetic defect centers in irradiated BESOI and SIMOX buried oxides," *IEEE Trans. Nucl. Sci.*, vol. 40, pp. 1755–1764, 1993.

[4] J. F. McGilp, "A review of optical second-harmonic and sum-frequency generation at surfaces and interfaces," *J. Phys. D: Appl. Phys.*, vol. 29, p. 1812, 1996.

[5] G. Lüpke, "Characterization of semiconductor interfaces by second-harmonic generation," *Surf. Sci. Rep.*, vol. 35, p. 75, 1999.

[6] W. Wang, G. Lüpke, M. Di Ventra, S. T. Pantelides, J. M. Gilligan, N. H. Tolk, I. C. Kizilyalli, P. K. Roy, G. Margaritondo, and G. Lucovsky, "Coupled electron-hole dynamics at the Si/SiO_2 interface," *Phys. Rev. Lett.*, vol. 81, p. 4224, 1998.

[7] J. G. Mihaychuk, J. Bloch, Y. Liu, and H. M. van Driel, "Time-dependent second-harmonic generation from $Si–SiO_2$ interface induced by charge transfer," *Opt. Lett.*, vol. 20, p. 2063, 1995.

[8] J. Bloch, J. G. Mihaychuk, and H. M. van Driel, "Electron potoinjection from silicon to ultrathin SiO_2 films via ambient oxygen," *Phys. Rev. Lett.*, vol. 77, p. 920, 1996.

[9] R. C. Hughes, E. P. EerNisse, and H. J. Stein, "Hole transport in MOS oxides," *IEEE Trans. Nucl. Sci.*, vol. 22, p. 2227, 1975.

[10] D. M. Fleetwood, P. S. Winokur, L. J. Lorence Jr., W. Beezhold, P. V. Dressendorfer, and J. R. Schwank, "The response of MOS devices to dose-enhanced low-energy radiation," *IEEE Trans. Nucl. Sci.*, vol. 33, p. 1245, 1986.

[11] J. I. Dadap, X. F. Hu, N. M. Russell, J. G. Ekerdt, J. K. Lowell, and M. C. Downer, "Analysis of second-harmonic generation by unamplified, high-repetition-rate, ultrashort laser pulses at Si(001) interfaces," *IEEE Sel. Top. Quantum Electron.*, vol. 1, p. 1145, 1995.

[12] M. Cernusca, R. Heer, and G. A. Reider, "Photoinduced trap generation at the $Si–SiO_2$ interface," *Appl. Phys. B*, vol. 66, p. 367, 1998.

[13] G. Lüpke, D. J. Bottomley, and H. M. van Driel, "Second- and third-harmonic generation from cubic centrosymmetric crystals with vicinal faces: Phenomenological theory and experiment," *J. Opt. Soc. Am. B*, vol. 11, p. 33, 1994.

[14] W. Wang, Ph.D. dissertation, Vanderbilt University, 2000.

[15] J. M. Benedetto, H. E. Boesch Jr., F. B. McLean, and J. P. Mize, "Hole removal in thin-gate MOSFET's by tunneling," *IEEE Trans. Nucl. Sci.*, vol. 32, p. 3916, 1985.

[16] M. Pepper, "Inversion layer transport and the radiation hardness of the Si–SiO2 interface," *IEEE Trans. Nucl. Sci.*, vol. 25, p. 1283, 1978.

[17] A. J. Lelis, T. R. Oldham, H. E. Boesch Jr., and F. B. McLean, "The nature of the trapped hole annealing process," *IEEE Trans. Nucl. Sci.*, vol. 36, p. 1808, 1989.

[18] D. M. Fleetwood, P. S. Winokur, L. C. Riewe, and R. A. Reber Jr., "Bulk oxide traps and border traps in MOS capacitors," *J. Appl. Phys.*, vol. 84, p. 6141, 1998.

[19] D. M. Fleetwood, P. S. Winokur, O. Flament, and J. L. Leray, "Stability of trapped electrons in SiO_2," *Appl. Phys. Lett.*, vol. 74, p. 2969, 1999.

[20] J. F. Conley Jr. and P. M. Lenahan, "Electron Spin Resonance Analysis of EP Center Interactions with H_2: Evidence for a localized EP center structure," *IEEE Trans. Nucl. Sci.*, vol. 42, p. 1740, 1995.

[21] 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, p. 1817, 1994.

[22] J. R. Chavez, S. P. Karna, K. Vanheusden, C. P. Brothers, R. D. Pugh, B. K. Singaraju, W. L. Warren, and R. A. B. Devine, "Microscopic structure of the E'_δ center in a-SiO_2: A 1st principles quantum mechanical investigation," *IEEE Trans. Nucl. Sci.*, vol. 44, p. 1799, 1997.

[23] P. E. Blöchl and J. H. Stathis, "Hydrogen electrochemistry and stress-induced leakage current in silica," *Phys. Rev. Lett.*, vol. 83, p. 372, 1999.

[24] D. M. Fleetwood, "Radiation-induced charge neutralization and interface-trap buildup in metal-oxide-semiconductor devices," *J. Appl. Phys.*, vol. 67, p. 580, 1990.

[25] J. Bloch, J. G. Mihaychuk, and H. M. van Driel, "Time-dependent second-harmonic generation from $Si–SiO_2$ interface induced by charge transfer,", 1996.