Two-color optical technique for characterization of x-ray radiation-enhanced electron transport in SiO₂

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Damage enhanced electron transport, across thin oxides in x-ray irradiated Si/SiO₂ samples, was measured via a contactless two-color laser technique. This method involves two steps: (1) optically stimulated electron injection into the oxide and (2) detection of transport, trapping, and recombination rates using time-dependent electric-field-induced second-harmonic generation arising from charge separation at the interface. Measured electron transport rates across an irradiated oxide are found to be substantially higher in comparison to unirradiated oxides. This effect is attributed to the presence of x-ray irradiation-induced defects that act as intermediate trapping sites facilitating enhanced electron tunneling through the oxide. The possible nature of the radiation-induced trapping sites is discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1534904]

I. INTRODUCTION

Carrier movement (injection, transport, tunneling, and recombination) and charge trapping in gate oxides are essential factors in understanding semiconductor device performance and degradation, especially in a radiation environment. In addition to the population of precursor defects with trapped charge and the possible generation of new traps, x-ray irradiation also may influence the carrier dynamics at interfaces. It has been shown recently that high doses of ionizing radiation in thin oxides (40–60 Å) may cause radiation-induced leakage current (RILC). The conduction mechanism in RILC as well as in stress-induced leakage current (SILC) has been attributed to neutral oxide defects, which mediate electron tunneling across the oxide.

Presently, characterization of radiation damage in Si/SiO₂ systems is usually accomplished with electrical methods such as capacitance–voltage and current–voltage measurements. The second-harmonic generation (SHG) technique can be used as an alternative optical method for damage studies, and has been used to provide additional insight into radiation damage in ultrathin oxides. These measurements were based on the detection of time-dependent electric-field-induced second-harmonic (EFISH) signals originating from the Si/oxide interface. The electric field across the interface was created in this previous work by an 800 nm Ti:Sapphire laser via generation of electron–hole pairs in the silicon and subsequent multiphoton injection of electrons into the oxide. For oxide thicknesses below ~100 Å, the injected electrons can reach the free surface of the oxide and become trapped at the surface by the high electron affinity of ambient oxygen molecules, while most holes remain in the vicinity of the interface in the Si. In our earlier studies, we observed a pronounced effect in radiation-damaged samples. When the laser beam was blocked for several tens of seconds after a long laser illumination time and then unblocked, the observed SHG signal, which is a measure of the electric field at the interface, was greatly reduced in intensity before starting to rise again. This is in contrast to the unirradiated samples, where no reduction in intensity was observed. We attributed this effect to radiation-induced trap centers. These trap centers facilitate the transport of electrons and the subsequent recombination of charged carriers, which results in a decrease in the measured SHG signal, indicating a lessened electric field at the interface.

In this work, we describe a two-color optical technique, based on time-dependent electric-field-induced SHG, for direct measurements of changes in electron transport characteristics due to x-ray irradiation in thin oxides. The main advantage of employing a two-color laser technique is that it allows us to separate the SHG process (probe) and the carrier injection (pump) process experimentally. This scheme allows us to monitor the electric field at the interface using the SHG signal whether the pump laser is on or off. We apply this method to characterize the radiation response of a 42 Å SiO₂ film on Si(100) more fully than possible with single-laser techniques. We find that the detrapping rate of a surface charge in the x-ray irradiated devices is much higher than that of unirradiated devices. We hypothesize that the radiation-enhanced transport discussed in this article is of a similar origin as RILC measured by conventional electrical methods.

II. EXPERIMENTAL DETAILS

Our experimental approach (see Fig. 1) involves the application of a widely tunable (1–6 eV), 1 kHz repetition rate, high intensity (>5 μJ/pulse) optical parametric generator (OPG) source as an injection (pump) laser, and a 76 MHz...
The samples were cut from a wafer of thermally grown 42 Å SiO₂ film on Si(100) produced by Lucent Technologies. The irradiation was carried out with a 10 keV x-ray source, at a dose rate of ~1 krad(SiO₂)/s. Since the samples had no gate, they were irradiated without electrical bias.

III. DETECTION OF CARRIER MOVEMENT VIA THE OPTICAL PUMP–PROBE TECHNIQUE

In materials with inversion symmetry, such as Si, all components of the second-order susceptibility tensor vanish. Therefore, the SH signal from the interface of Si and SiO₂ is dominated by the interface μ(2) term, where the symmetry is broken. There is also some minor contribution from electric quadrupole and magnetic dipole terms. However, when an electric field is present across the interface, the magnitude of the electric-field-induced SH signal may become several times greater than the signal in the absence of electric fields. This electric field may be time dependent, and is a measure of the carrier separation across the interface. The time-dependent EFISH signal can be described in general by

$$I^{\text{EFISH}}(t) = |\chi^{(2)} + \chi^{(3)}(I(t))|^2 (I^{\text{PUMP}})^2,$$

where I^{\text{PUMP}} and I^{\text{EFISH}}(t) are the intensities of the fundamental and the time-dependent SH beams. χ^{(3)} is the third-order nonlinear susceptibility, χ^{(2)} is the effective susceptibility from all other sources (mostly the interface term), and E(t) is a quasistatic electric field. In Si/SiO₂, for thin oxides (below 100 Å), the SH signal is dominated by charge separation due to the trapping of photogenerated electrons at the oxide surface by the ambient oxygen. Therefore, E(t) is a measure of the accumulated oxide surface electron density (n_e). The density of filled electronic trap states can be given through the solution of the rate equation:

$$\frac{dn_e}{dt} = \left(n_{0e} - n_e\right)/\tau_\text{PUMP} + \left(n_{0e} - n_e\right)/\tau_\text{PROBE} - n_e/\tau_\text{DETRAP},$$

where n_{0e} describes the initial number of unfilled electronic traps. The rate constant 1/τ_\text{PUMP} gives the injection rate due to the pump beam (actually the rate of filling of the surface electron traps) that is a combination of injection, transport, and trapping probabilities; while 1/τ_\text{PROBE} describes the injection rate due to the probe beam that is negligible (1/τ_\text{PROBE} ≪ 1/τ_\text{PUMP}). The time constant τ_\text{DETRAP} is determined by detrapping from surface traps, transport (tunneling) through the oxide, and recombination near the interface. In our experiments, we find that this time constant is significantly lowered for x-ray irradiated samples.

Figure 2(a) shows a schematic overview of the laser pulse time structure in our experiment, when both lasers are operating. The delay between the high intensity pump and lower intensity probe lasers is not specified in these experiments. The electric field across the interface (upper trace) can greatly increase when a pump pulse hits the sample. This transient behavior was observed previously and was attributed to screening, the separation of electrons and holes in the Si under the influence of an inherent fixed oxide charge. After each pump pulse hits the sample, a small portion of the

The repetition rate Ti:Sapphire laser at 800 nm (this laser is also the seed for the OPG) as an SHG probe laser. The peak intensity (3.3 GW/cm²) and duty factor (a shutter is used to decrease the duty factor) of the probe laser are lowered such that this beam gives a minimal contribution to charge carrier injection and therefore to charge separation with its subsequent electric field. The p-polarized probe beam is incident at 45° on the sample. A polarizer selects the p component of the reflected beam, and we use a set of low-pass and band-pass filters to separate out the second-harmonic (SH) beam. A small portion of the fundamental beam is diverted through another shutter and a doubling crystal in order to detect any fluctuations in the fundamental laser beam. The two beams then are brought together and we use a single photomultiplier tube (PMT) to detect the SH signal. We verified that no fundamental beam photons reach the photodetector, and no additional SH field is created by the filters, at these intensities. A signal generator with a frequency of 0.5 Hz is used to trigger the two shutters (the shutter controlling the beam incident on the sample is set to open for 0.125 s; the reference shutter is closed during this time) and it also gives a trigger to the photon counter. We count with a 100 ms gate for both the reference and signal beams; there is a 300 ms delay between them. The OPG pump beam at 540 nm is diverted to the sample at close to normal incidence at peak intensities of ~50 GW/cm², and we use a camera to insure that the pump (~150 μm diameter spot size) and probe beams (~25 μm diameter spot size) overlap on the sample. Since we are studying very slow processes, on the order of hundreds of seconds, we did not make an effort to specify the time difference between the pump and probe laser beams. Therefore, our experimental approach cannot be regarded as a true pump–probe method, but as a two-color laser technique.

An additional advantage of this experimental method is the wide wavelength tunability of the OPG, which gives us the possibility of studying a variety of interfaces and carrier injection processes. Wavelength-dependent studies of carrier injection processes may show thresholds in injection rates and, therefore, can become a useful tool in determining band offsets at interfaces. (Such measurements were performed on Si/SiO₂ interfaces, and the results will be presented elsewhere.)

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FIG. 1. Experimental setup.
electrons will cross the interface, transport through the oxide to the surface, and get trapped by the ambient oxygen. This will result in a cumulative increase in the field across the interface until a saturation level is reached. The actual saturation level is determined by a combination of factors including the number of available surface traps thickness dependent transport and oxide band bending. The probe laser itself has a minimal contribution to this cumulative process, since its low photon energy would require a higher-order multi-photon electron injection into the oxide for which the probability is exceedingly low.

The following experimental procedure was used in the measurements presented here:

1. Initially, the pump laser was off and the probe laser measured a constant background SH signal from the sample. After turning on the pump beam, a fast rise in the probe signal was observed, indicating that electrons were injected into the oxide, transported to the surface and trapped by the ambient oxygen [Fig. 2(b)]. The holes remained at the interface thus resulting in an electric field arising from charge separation. The solution of Eq. (2) is an exponential rise to a maximum which under the conditions of $1/\tau_{PUMP} \gg 1/\tau_{DETRAP}$ becomes

$$n_e(t) = n_{0e} \exp(-t/\tau_{DETRAP}).$$

2. After the signal reached a saturation level, corresponding to the complete filling of all surface electronic traps, the pump beam was blocked and the probe SHG signal decreased. In this case, the surface trapped electrons transported back to the interface to recombine with the holes remaining at the interface [dotted line in Fig. 2(b)]. Since now $1/\tau_{PUMP} = 0$ and $1/\tau_{DETRAP} \gg 1/\tau_{PROBE}$. only the third term in Eq. (2) is present, and $n_e(t=0) = n_{0e}$. therefore, the solution becomes a simple exponential decay for $n_e(t)$:

$$n_e(t) = n_{0e} \exp(-t/\tau_{DETRAP}).$$

Figure 3 shows a simulation of a pump–probe type experiment based upon Eqs. (1)–(4). First, the high intensity pump laser light fills up the surface traps with electrons up to the saturation level, and then the pump is blocked in order to monitor the electron transport process back to the interface via the probe laser beam. As shown next, these simulation results are qualitatively identical with our experimental data.

In this work, we used 540 nm (2.3 eV) pump laser light. Since the difference between the Si valence band and SiO$_2$ conduction mobility band is approximately 4.3 eV, the electron injection from Si into the oxide requires at least a two-photon process. Our goal in this study was to elucidate the recombination of the transporting electrons with the holes at the interface while the pump laser is blocked. In fitting our EFISH data, we used a relative phase of 0° between the two susceptibility components, $\chi^{(2)}$ and $\chi^{(3)}$ terms, of Eq. (1). Simulations of the influence of the relative phase showed that our data could only be fitted adequately with a phase shift term of at most 40°. This uncertainty introduces less than 10% error into the value of the fitted $\tau_{DETRAP}$, which does not affect the conclusions drawn next.

### IV. RESULTS AND DISCUSSIONS

Figure 4 compares time-dependent pump–probe type EFISH measurements performed on irradiated [15 Mrad (SiO$_2$)] and nonirradiated Si/SiO$_2$ samples with 42 Å oxides. Electron tunneling across a nonirradiated oxide at this thickness has a very low probability; it only becomes significant below thicknesses of $\sim$30 Å. In both irradiated and nonirradiated samples, the electric field increases rapidly after the pump laser is turned on. This is explained by multi-photon selective injection of electrons into the oxide (for the 540 nm probe beam it is a two-photon process), while the
holes remain at the interface. For the nonirradiated sample, the EFISH signal stays at a constant saturation level after the pump laser is blocked, indicating that the electrons in the surface traps have a long lifetime. In contrast, the electric field across the x-ray irradiated sample decreases steadily, implying that the trapped electrons tunnel back to the interface and recombine with the holes, thereby decreasing the electric field. This suggests that the x-ray irradiation increases the rate of electron transport through the oxide. Systematic dose dependent measurements were not carried out on these samples, but we have seen similar time-dependent behavior (shown in Fig. 4) for similar samples irradiated up to 2 Mrad (SiO$_2$) and also 20 Mrad (SiO$_2$) doses via a 10 keV x-ray source.

Additionally, Fig. 4 shows that the steady-state SHG signal, while the pump laser is on, is greater for the irradiated oxide sample. This suggests an increased electric field at the interface, possibly due to the creation of additional electron trapping sites in the oxide by x-ray irradiation, in addition to the original surface electron traps present in nonirradiated samples. Alternatively, x-ray irradiation could generate additional traps on the oxide surface, e.g., by cracking organic molecules, which may be present as impurities. However, we always maintained maximum cleanliness of samples and did not observe variation in the signal levels for oxides treated with differing cleaning agents (e.g., deionized water or methanol). Moreover, our data indicate that the newly created oxide traps are neutral electron traps, since the background SHG signal before turning on the pump laser was unaltered by x-ray damage.

Recent experiments involving electrical measurement on 40–60 Å metal–oxide–semiconductor (MOS) samples showed that ionizing radiation [starting from a dose of 4 Mrad(Si) arising from 8 MeV electrons] can induce leakage current in these oxides. In these studies, gate current versus gate voltage characteristics were measured and evaluated after electrical stress (causing SILC) as well as after subjecting the sample to irradiation. It was shown that both RILC and SILC have a similar conduction mechanism: Trap-assisted electron tunneling across the oxide. In this previous work, irradiations performed at different gate biases showed the highest induced leakage current when an electric field near zero was applied; the induced leakage decreased with increasing oxide fields. Ceschia et al. suggested that the traps/defects involved in the electron conduction are neutral; however, these defects likely have a positively charged precursor. Candidates for precursor defects include hole traps (such as an $E'$ center, which becomes neutralized after capturing a hole); however, the microscopic character of the traps/defects involved in the process is not yet resolved. It has been suggested that both RILC and SILC originate from the same defect.

A recent study by Lenahan et al. gives strong, but circumstantial, evidence for linking $E'$ centers to oxide leakage currents. They subjected Si/SiO$_2$ samples with a wide range of oxide thicknesses (3.3–45 nm) to vacuum ultraviolet (VUV) radiation from a deuterium lamp (up to 10.2 eV). After VUV illumination, they measured the oxide current via corona ion decay and they also recorded the electron spin resonance signature of the samples. They found a strong correlation between neutral $E'$ center density and oxide current. They argued that neutral $E'$ centers have an important, perhaps dominating, role in SILC and RILC. However, they did not rule out possible roles for other defects.

A competing idea for the microscopic origin of SILC is that the defect responsible for the induced leakage is hydrogen related. Blochl and Stathis have suggested a two-step inelastic tunneling mechanism via a defect, in which voltage greater than the level shift between uncharged and charged states of the defect must be applied. They investigated several different structures via density-functional theory calculations and proposed that the trap mainly responsible for SILC is the neutral hydrogen bridge trap, Si–H–Si. These traps may be connected with RILC in that ionizing radiation can release H from other sites, and this hydrogen may migrate and form neutral bridge traps within the oxide.

We may relate our two-color EFISH measurements to the aforementioned leakage current measurements. For the experiments described here, the pump laser injects electrons into the oxide, which are subsequently trapped at the surface. This creates an electric field across the oxide that is similar to applying a gate voltage across a MOS capacitor. After x-ray irradiation, we detect a time-dependent decrease of the electric field across the oxide, which we attribute to electron transport back to the Si and subsequent recombination with holes remaining at the interface. We attribute our observation of a time-dependent decrease in electric field to a trap-assisted tunneling current, such as is seen in RILC or SILC. We have observed strikingly different electron tunneling characteristics between irradiated and unirradiated oxides. However, since our oxides have no gate electrode, we cannot detect electrical leakage directly. Instead, we measure time-
dependent changes in the electric field across the oxide associated with charge transport and trapping via an optical method, which may be called laser interrogated leakage current (LILC).

We have also studied the long-term time dependence of the observed leakage in our x-ray irradiated samples at a dose of 20 Mrad (SiO₂). Figure 5 shows the 1/τDETAP [Eq. (4)] values (presumably associated with trap-assisted tunneling rates) deduced from our measurements versus time after irradiation. Figure 5 depicts that the rate at which the electrons tunnel back to the interface decreases with time after x-ray irradiation. These rates were several orders of magnitude lower 2–3 days after irradiation. In a previous publication, we suggested that the defects mediating the electron transport across the oxide may anneal at room temperature. In our experiments, the OPG pump laser should not give rise to any significant heating due to its low repetition rate. In addition, we reduced the duty factor of this laser to 0.125 using a shutter. Also, each data point was taken on a fresh spot on the sample, at least 500 μm away from the previous measurement point. With these precautions, we believe laser-heating-induced annealing should not be a significant factor in these experiments.

Riess et al. showed that RILC can be fully annealed thermally in the devices they studied with an activation energy of 1.3±0.2 eV. They interpreted the annealing as the diffusion of hole-related defects that are involved in the conduction mechanism of RILC/SILC. However, in their samples, which were irradiated to the very high dose of 125 Mrad (SiO₂), they needed significantly elevated temperatures (above 200 °C) to completely anneal the leakage. Lena

FIG. 5. Measured detrapping rates on fresh spots on a 42 Å oxide as a function of time past after x-ray irradiation up to 20 Mrad dose. The inset shows an example of an exponential decay fit for obtaining detrapping rates.

FIG. 6. (a) Consecutive pump–probe measurements on the same sample spot after 20 Mrad irradiation (42 Å oxide). b) Tunneling rate values vs time after irradiation for the same sample spot compared to data on fresh spots on the sample. These results indicate that electron injection by the pump laser can lead to a faster decay of the radiation-induced leakage.

pared to ours. Additionally, it is also likely that the defect responsible for LILC is hydrogen related. In support of this, our earlier experiments performed on as-processed and H₂ annealed samples suggested that the characteristic decay time for room-temperature annealing is different for the differently treated samples. We note here that the 1.3±0.2 eV activation energy suggested for the thermal annealing of the defects assisting the current leakage in RILC is an easily obtainable electronic energy for both lasers used in our experiments. One must also consider the H-bridge trap suggested by Bleučh and Stathis. According to their calculations, 1.7 eV is required for switching between uncharged/charged states in this defect; this is also easily obtainable with our pump laser.

One way of finding out whether our laser itself gives rise to the observed decrease in the electron tunneling rate with time is to perform consecutive measurements on the same laser spot. Figure 6(a) depicts such a measurement, in which we irradiated the same spot several times on the sample with the pump laser after the probe signal reached a minimum steady-state level. Figure 6(b) shows the tunneling rates for such measurements versus time after irradiation, and compares it with measurements taken on fresh sample spots. Clearly, the continued irradiation by the pump laser on the same spot enhances the decrease in the observed x-ray irradiation effect probably by altering the concentration of irradiation-induced trapping sites.
There are two possible mechanisms to account for our observations of pump–laser-induced reduction of the radiation effect. The first is optically induced local healing of the defect responsible for the leakage in x-ray irradiated samples. Since the laser peak intensities are high and multiphoton processes are possible, the pump laser may break bonds at the defect sites (such as the H-bridge site) and lead to the local relaxation of the structure and consequent removal of the defect.

The other possible mechanism is based on viewing the pump laser as a constant source of injected electrons into the oxide. These electrons can interact with the traps responsible for the radiation-induced effect, giving rise to removal of the trapping site. A similar argument about the impact of electron injection on the time decay of SILC current has been proposed by Cester et al.\textsuperscript{14} When measuring the SILC, the devices are biased at >4 MV/cm and this causes electrons to flow across the oxide. Also, if additional, but nonstressing (orders of magnitudes lower current) current densities were injected, the SILC decreased quickly. These electrons may contribute to the time decay of the SILC, via healing some of the transport-mediating trap sites, thereby decreasing their concentration. In our experiments, the electrons injected by the laser into the oxide from the silicon may act in a similar way.

Data taken consecutively on the same spot investigate the additional effect of optical stimulation and/or the effect of injected electrons on the time decay of the radiation effect. We also observe a decay in the tunneling rates, when fresh spots on the sample are used; this suggests that an additional annealing mechanism exists, which is not stimulated by the laser. The origin of this room-temperature annealing is not yet clear. Since LILC decays with time similarly as observed in RILC and SILC, the defect or defects involved in the enhanced electron transport observed optically (LILC) on x-ray irradiated oxides act in a similar way as the transport-mediating traps responsible for RILC or SILC.

V. CONCLUSIONS

We have developed a contactless two-color optical technique that allows us to monitor carrier transport (injection and tunneling) processes at Si/SiO\textsubscript{2} interfaces. The technique involves application of a high intensity pump laser for injection of electrons into the oxide, while the created electric field caused by the separation of carriers is detected via SHG by a less intense probe laser. We applied this optical method to the study of x-ray-induced defects in a 42 Å SiO\textsubscript{2} film on a silicon substrate. When we compared irradiated and nonirradiated samples, we observed that x-ray damage substantially increased the electron transport rate across the oxide.

We have compared our results to previous electrical observations of RILC and SILC in ultrathin oxides.\textsuperscript{1,2,10} We determined that the electron-tunneling rate decreases with time at room temperature after x-ray irradiation, indicating that the electron transport-mediating traps may be annealed at room temperature. Furthermore, continued exposure to the pump laser also leads to the time decay of the LILC observed in our experiments. We suggest that the defects responsible for these three processes (RILC, SILC, and LILC) share the same origin. It is likely these defects are O vacancies ($E'$ centers) or hydrogen related.

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