Low Energy Electron-Excited Nanoscale Luminescence: A Tool to Detect Trap Activation by Ionizing Radiation

B. D. White, L. J. Brillson, S. C. Lee, D. M. Fleetwood, R. D. Schrimpf, S. T. Pantelides, Y.-M. Lee, and G. Lucovsky

Abstract—Ultra-thin SiO₂/Si gate dielectric structures exposed to heavy X-ray irradiation exhibit optical emission characteristic of interface traps. Low energy electron-excited luminescence spectroscopy with nanometer-scale depth resolution yields a characteristic spectral energy and excitation depth dependence. Ultra-thin (5 nm) oxide films on Si substrates exposed to 10 keV, 7.6 Mrad(SiO₂) [13.7 Mrad (Si)] X-ray irradiation introduces trap densities on the order of $10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$, localized near the intimate SiO₂-Si interface. This density is consistent with the trapped oxide and interface charge densities expected based on observed capacitance-voltages shifts of thicker oxides, their corresponding charge densities, and the proportionally smaller charge densities expected for the thinner oxide layers in this study.

I. INTRODUCTION

AS MICROELECTRONIC device dimensions are scaled into the deep sub-micron regime, there must be corresponding decreases in the oxide-equivalent thickness of gate dielectrics. In order to avoid the charge tunneling associated with such thin layers, materials with higher dielectric constant K are needed to maintain gate capacitance without further reduction in thickness. In addition, ultra-thin Si-SiO₂ interfaces are needed that form a low interface trap density substrate for these high- K dielectrics. Control of the chemical bonding and defect states in the immediate vicinity of these interfaces includes an understanding of the effect that ionizing radiation has on such defects. As part of our effort to understand the basic atomic-scale mechanisms responsible for the radiation-induced degradation observed in microelectronics, we are using low energy electron-excited nanoscale-luminescence (LEEN) spectroscopy, a very low energy analogue of cathodoluminescence spectroscopy [1], [2]. This technique provides a spectrally-resolved measure of

free carrier recombination, yielding determinations of defect energy levels and relative densities as a function of distance from interfaces on a scale of nanometers. LEEN also enables observation of electronic transitions involving deep traps within wide band gap insulators such as SiO₂ [3]. Such observations are inaccessible by conventional optical techniques. Measurements are performed in ultrahigh vacuum (UHV) to eliminate contamination effects and control interface chemical properties, as measured by surface science techniques. The technique is sensitive to the deep level electronic properties of native defects, impurities, chemically-induced interface traps and interfacial compounds. The depth of free carrier excitation and recombination varies from nanometers to microns as the beam energy varies, thereby discriminating between contributions from different layers of a multi-layer interface [4].

II. EXPERIMENTAL PROCEDURE

The LEEN spectroscopy experiment consists of an electron gun that illuminates a specimen in ultrahigh vacuum (UHV) at glancing incidence (45°). Incident beam currents at 1–4 keV are nominally 1 μA or less. Excitation area is typically $\sim 1 \text{ mm}^2$ or less. UHV conditions are desirable to avoid the deposition of carbon on the surface from decomposing air molecules. Such carbon deposits reduce the optical emission significantly. The impinging electron beam produces a cascade of secondary electrons whose penetration depends strongly upon the initial beam energy E_B . An extrapolated depth-dose curve provides a relation between E_{Beam} and depth of maximum energy loss [4]. For energies of a few keV or less, such depths are in the low nanometer range [5]. Monte Carlo simulations [6] of the electron cascade process confirm such calculations. A CaF₂ collection lens within the chamber relays the light out of the chamber into a monochromator and one of several photodetectors that cover the near IR to UV range. Deflection plates modulate the electron beam so that a lock-in amplifier can filter out any unmodulated background noise. Further details are available in prior publications [5], [7]. Measurements of ultra-thin SiO₂ on Si are particularly challenging not only because of the low film thickness, but also because the indirect gap Si and the amorphous SiO₂ both have relatively weak optical emissions. Nevertheless, the LEEN technique's ability to excite primarily in the region of interest compensates for much of this deficiency. The SiO₂/Si specimens consisted of a 10 Ohm-cm, B-doped p-type (100) Si substrate, an interfacial oxide layer 0.5–0.6 nm thick prepared by remote plasma assisted oxidation, followed

Manuscript received July 24, 2000. This work was supported by the Air Force Office of Scientific Research (Physics and Electronics Directorate (AFOSR/NE) under MURI Grant F49620-99-1-0289.

B. D. White is with the Department of Electrical Engineering, Ohio State University, Columbus, OH 43210 USA (e-mail: whiteb@ee.eng.ohio-state.edu).

L. J. Brillson is with the Department of Electrical Engineering and the Department of Physics, Ohio State University, Columbus, OH 43210 USA (e-mail: brillson@ee.eng.ohio-state.edu).

S. C. Lee, D. M. Fleetwood, and R. D. Schrimpf are with the Department of Electrical and Computer Engineering, Vanderbilt University, Nashville, TN 37235 USA (e-mail: ron.schrimpf@vanderbilt.edu).

S. T. Pantelides is with the Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235 USA (e-mail: pantelides@vanderbilt.edu).

Y.-M. Lee and G. Lucovsky are with the Department of Physics, North Carolina State University, Raleigh, NC 27695 USA (e-mail: Gerry_Lucovsky@ncsu.edu).

Publisher Item Identifier S 0018-9499(00)11258-4.

Fig. 1. Low energy electron-excited nanoscale spectroscopy of ultra-thin SiO_2/Si interfaces as a function of increasing excitation energy and penetration depth. At low energies, excitation occurs primarily in the oxide and exhibits a pronounced peak at 2.7 eV. At higher energies a new feature appears at 1.9 eV that is associated with the Si interface. Higher excitation energy produces emission at 3.4 eV associated with the bulk Si [3]. All spectra are normalized to their largest peak feature.

by a 5.0 nm remote plasma enhanced chemical vapor deposition (RPECVD) carried out at 300°C [8]. The aim of this low thermal budget process developed by the North Carolina State University group is to minimize any chemical reactions or interdiffusion that would otherwise result from a high temperature oxidation process. X-ray irradiation was performed at Vanderbilt University with a 10 keV X-ray source. Irradiated and un-irradiated specimens from the same wafer were then mailed to Ohio State University for the LEEN studies reported here.

III. ULTRA-THIN SiO_2/Si INTERFACES

We have used LEEN spectroscopy to measure deep-level defects at Si/SiO_2 interfaces. These studies provide a clear determination of defect energies and relative densities within the ultra-thin (5 nm) oxide films on Si substrates, electronic states due to suboxide bonding with the monolayer transition region separating the SiO_2 and Si, as well as dangling bond defects at the interface on the Si side of the interface. Fig. 1 illustrates optical spectra acquired with a set of different incident E_B from the 5 nm-thick oxides on Si [3]. At low E_B , a prominent feature appears at 2.7 eV along with a weak shoulder feature at 1.9 eV. Spectral features at these energies have been reported previously from cathodoluminescence spectroscopy measurements, albeit for thick film or bulk SiO_2 [9]–[11]. With increasing E_B , the

Fig. 2. Evolution of defect emission bands versus processing treatments, for the same 2.0 keV LEEN excitation energy [3]. Spectral intensities between the two detectors are not normalized, but for each detector the relative intensities of the series of samples directly reflect the luminescence efficiency. A dramatic decrease in defect density is observed at 1.9 eV upon annealing at 900°C. Further processing reduces the trap-related features even further.

2.7 eV feature decreases and the 1.9 eV increases as the penetration depth increases. These spectra reveal the depth variation of such defect features near interfaces. An additional feature at 3.4 eV can be attributed to emission from the bulk substrate. The increase and decrease of these features are consistent with the calculated depths of excitation. Additional emissions (not shown) are detectable in the near IR, specifically a near band edge-related feature at 1.05 eV and 0.8 eV. The latter “ P_b ” center has been modeled based on electron paramagnetic resonance studies as a “dangling bond” defect in which an unpaired electron resides on a Si atom, backbonded to three other Si atoms at the $\text{Si}-\text{SiO}_2$ interface [12]. The broad feature at 1.9–2.0 eV has been attributed to $\alpha\text{-SiO}_x$ bonding environments, interface microstructure, or associated point defects of the otherwise crystalline substrate [9]. Broad features peaking at 1.9 eV or above are also reported for porous and hydrogenated amorphous Si films [13]. The 2.7 eV feature has been reported previously in crystalline SiO_2 , amorphous SiO_2 , SiO_x , and SiO_x at thermally-grown SiO_2 –Si interfaces. It is associated either with self-trapped excitons, two-fold coordinated Si, or O vacancies. This E' center represents the most important trap center in silicon oxides and has been modeled to involve an unpaired electron localized on a Si atom back-bonded to three O atoms [12]. The 3.4 eV emission corresponds to bulk Si transitions and provides a means to normalize the spectral intensities of the near-interface features [14]. Fig. 1 indicates that the 2.7 eV and 1.9 eV emissions originate from the oxide region within the film and near the interface respectively.

The LEEN spectroscopy technique can monitor the changes in defect properties with different gas and temperature treatments. Fig. 2 illustrates such changes with chemical treatments used to lower the interface trap density. A 400°C H_2 “post

Fig. 3. Depth-resolved spectra of ultra-thin SiO_2/Si interfaces with no irradiation (left), 10 keV X-ray, 7.6 Mrad (SiO_2) irradiation (middle), and 10 keV X-ray, 15.2 Mrad (SiO_2) irradiation (right). All three spectra exhibit peak features at 1.9 eV and 2.7 eV that reach maximum intensity below the free surface. A significant increase in 2.7 eV peak height is apparent at 3 keV for the highest dose. All spectra shown refer to a common intensity scale and directly reflect the relative luminescence efficiency.

metallization anneal" (PMA) in forming gas is intended to passivate Si dangling bonds. A 900°C rapid thermal anneal (RTA) acts to smooth the SiO_2/Si interface and reduce suboxides. A subsequent PMA is intended to replace hydrogen and minimize Si dangling bonds after the RTA. The combination of 900°C plus 400°C H_2 anneal produces interfaces with low interface trap densities in the 10^{10} to 10^{11} cm^{-2} range for the low-energy CLS technique at the Si/SiO_2 interfaces [8]. The pronounced differences between spectra indicate that any electron beam-induced effects are relatively small in comparison with the process-induced features.

IV. IRRADIATED ULTRA-THIN SiO_2/Si INTERFACES

Fig. 3 illustrates the effect of 10 keV, 7.6 Mrad(SiO_2) [13.7 Mrad(Si)] X-ray irradiation on the SiO_2 on Si near-interface region. These samples were grown and processed just as in case of those shown in Fig. 1 for the RTA 900°C + 400°C H_2 case. Fig. 3 illustrates depth-dependent LEEN spectra for specimens before and after irradiation. The increase in 2.7 eV and 1.9 eV emissions in all three spectral sets reaches a maximum between 2 and 3 keV, corresponding to the "buried," i.e., Si/SiO_2 , interface region. No significant changes are evident after just the 7.6 Mrad (SiO_2) irradiation. However, an additional 7.6 Mrad irradiation of this specimen produces a significant increase of the 2.7 eV peak in the 3 keV spectrum. In order to verify that such changes were not due to any artifacts, we performed another set of measurements on these specimens 9–11 days later. These appear in Fig. 4. The spectra shown in both Figs. 3 and 4 are shown with their absolute intensity, corrected only for the spectral response of the optical train. The multiple curves for the same energy in each panel of Fig. 4 illustrate variations ($\sim +8\%$) in spectra from point to point across the surface under identical conditions, separated only

by millimeters or less. Each spectrum is acquired from a fresh spot in order to minimize any electron beam effects. Fig. 4 displays the same spectral features as in Fig. 3. However the relative increase in 2.7 eV emission is now more apparent for the 15.2 Mrad irradiation case than before, increasing relative to the unirradiated case by over 20% for both 3 keV and 4 keV. The 15.2 Mrad panel also indicates somewhat sharper emission spectra at 1.9 eV than in previous spectra, suggesting more than one origin for emission at these energies. Since this excitation occurs near the SiO_2/Si interface in all these spectra, and few if any new point defects are expected to be created by 10 keV X-ray irradiation in the bulk Si, this result suggests that the emissions occur from traps localized near the SiO_2/Si interface. Our initial conclusion is that the post-irradiation peak at 1.9 eV is due to the same defects (presumably NBOHC or P_b centers) as the as-processed interface traps in Fig. 2. This is consistent with a common origin for both irradiation and interface bonding defects, namely Si dangling bonds at the interface. These traps likely result from the migration of H to the interface and its subsequent reaction with Si–H bonds [15]. The post-irradiation peak at 2.7 eV is also consistent with a common origin for irradiation and interface bonding defects, possibly due to electromigration of mobile hydrogen-associated defects within the SiO_2 film and across the Si interface [10]. While previous studies have reported optical emission from defects induced by X-rays in bulk amorphous SiO_2 [16], the LEEN studies reported here appear to be the first to report such X-ray-induced defect emission from SiO_2 –Si interfaces.

V. ELECTRON BEAM EFFECTS

We also performed studies of the electron beam itself on the ultra-thin SiO_2/Si interfaces. Fig. 5 shows a series of spectra taken under typical voltage and power conditions as a function

Fig. 4. Depth-resolved spectra of ultra-thin SiO_2/Si interfaces 9–11 days after Fig. 3 measurements with no irradiation (left), 10 keV X-ray, 7.6 Mrad (SiO_2) irradiation (middle), and 10 keV X-ray, 15.2 Mrad (SiO_2) irradiation (right). Different plots for the same energy indicate variations from point to point across SiO_2/Si free surface. All three sets of spectra exhibit peak features at 1.9 eV and 2.7 eV. A clear increase in 2.7 eV peak height is evident at 3 keV for the highest dose. All spectra shown refer to a common intensity scale and directly reflect the relative luminescence efficiency.

Fig. 5. Effect of electron beam exposure on the LEEN spectra. Individual 7 minute scans at 2 keV and 0.5 mW power introduce no new features and less than a 10% decrease in the 2.7 eV relative to 1.9 eV feature heights. All spectra refer to a common scale and directly reflect the photoluminescence efficiency.

of time with the beam focused on the same specimen area. No new spectral features are produced by the electron beam. This

figure also shows that the spectral features change only slowly with time compared with an individual beam scan of 7 min. To emphasize that a change has indeed occurred, however, the spectrum for a new spot taken directly following the 50 minute spectrum is shown for contrast. Overall, the 2.7 eV peak intensity decreases by $\sim 10\%$ relative to the 1.9 eV feature over the span of a single scan. It is important to note that this decrease is opposite to the effect we observe with X-ray irradiation, i.e., the 2.7 eV/1.9 eV ratio increases with X-ray irradiation in these samples. Hence, we conclude that electron beam damage does not play a significant role in the previous experiments.

VI. DISCUSSION: OVERALL EFFECT OF X-RAY IRRADIATION

X-ray irradiation produces a relatively small but significant increase of trap density in the ultra-thin SiO_2/Si specimens. Trap emissions are relatively low both before and after irradiation for the specimens grown by the RPECVD low thermal budget process. Since much larger emissions are observed for specimens before processing, irradiation appears to introduce only small changes of interface traps, on the order of $10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$. This density is consistent with the trapped oxide and interface charge densities expected based on observed capacitance-voltage shifts of thicker oxides, their corresponding charge densities, and the proportionally smaller charge densities expected for the thinner oxide layers [17]. While limited to detecting trap densities at or above this limit for ultrathin SiO_2 on Si, the LEEN technique appears well-suited to observe energies and depth variations of traps activated by X-ray irradiation, especially at high dose levels. For interfaces involving direct gap semiconductors, even higher detection levels are achievable [5]–[7], [18].

VII. CONCLUSION

We have used low energy electron-excited nanoscale luminescence spectroscopy to detect optical emission from defects induced by X-ray irradiation. Further, the depth-dependence of the LEEN spectroscopy technique emphasizes the near-interface nature of the defects and the potential role of electron-hole pairs generated within the Si substrate in generating such defects. The relatively small changes in trap features with irradiation indicate that the ultra-thin dimensions of the gate oxide minimize the creation of new oxide traps induced by X-rays. In general, the LEEN technique can probe such interfaces quite efficiently and is a promising method for use in studying the microstructural defects that lead to radiation damage in microelectronic materials.

ACKNOWLEDGMENT

Conversations with Dr. A. P. Young at Anadigics, Inc. are gratefully acknowledged.

REFERENCES

- [1] L. J. Brillson, H. W. Richter, M. L. Slade, B. A. Weinstein, and Y. Shapira, "Cathodoluminescence spectroscopy studies of laser-annealed metal-semiconductor interfaces," *J. Vac. Sci. Technol.*, vol. A3, no. 3, pp. 1011–1015, May/June 1995.
- [2] L. J. Brillson and R. E. Viturro, "Low energy cathodoluminescence spectroscopy of semiconductor interfaces," *Scanning Microsc.*, vol. 2, no. 2, pp. 789–799, 1998.
- [3] J. Schäfer, A. P. Young, L. J. Brillson, H. Niimi, and G. Lucovsky, "Depth-dependent spectroscopy defect characterization of the interface between plasma-deposited SiO₂ and silicon," *Appl. Phys. Lett.*, vol. 73, no. 6, pp. 791–793, Aug. 1998.
- [4] T. E. Everhart and P. H. Hoff, "Determination of kilovolt electron energy sissipation vs. penetration distance in solid materials," *J. Appl. Phys.*, vol. 42, no. 13, pp. 5837–5846, Dec. 1971.
- [5] L. J. Brillson, T. M. Levin, G. H. Jessen, and F. A. Ponce, "Localized states in InGaN/GaN quantum well interfaces," *Appl. Phys. Lett.*, vol. 75, no. 24, pp. 3835–3837, Dec. 1999.
- [6] P. Hovington, D. Drouin, and R. Gauvin, "CASINO: A new Monte Carlo code in C language for electron beam interactions—Part I: Description of the program," *Scanning*, vol. 19, pp. 1–14, 1997.
- [7] T. M. Levin, G. H. Jessen, F. A. Ponce, and L. J. Brillson, "Depth-resolved electron-excited nanoscale-luminescence spectroscopy studies of defects near GaN/InGaN/GaN quantum wells," *J. Vac. Sci. Technol.*, vol. B17, no. 6, Nov./Dec. 1999.
- [8] D. R. Lee, C. G. Parker, J. Hauser, and G. Lucovsky, "Reliability of nitrided Si–SiO₂ interfaces formed by a new, low-temperature, remote-plasma process," *J. Vac. Sci. Technol.*, vol. B13, no. 4, pp. 1788–1793, Jul./Aug. 1995.
- [9] M. A. Stevens Kalceff and M. R. Phillips, "Cathodoluminescence microcharacterization of the defect structure of quartz," *Phys. Rev.*, vol. 52, no. 5, pp. 3122–3134, August 1995.
- [10] M. A. Stevens Kalceff, G. J. Thorogood, and K. T. Short, "Charge trapping and defect segregation in quartz," *J. Appl. Phys.*, vol. 86, no. 1, pp. 1–3, July 1999.
- [11] S. W. McKnight and E. D. Palik, "Cathodoluminescence of SiO₂ films," *J. Non-Cryst. Sol.*, vol. 40, pp. 595–603, 1980.
- [12] P. M. Lenahan and J. F. Conley Jr., "What can electron paramagnetic resonance tell us about the Si/SiO₂ system?," *J. Vac. Sci. Technol.*, vol. B16, no. 4, pp. 2134–2153, July/August 1998.
- [13] L. Canham, "Progress toward crystalline-silicon based light-emitting diodes," *Mater. Res. Bull.*, vol. 18, no. 7, pp. 22–28, July 1993.
- [14] H. R. Phillip and E. R. Taft, *Phys. Rev.*, vol. 120, p. 556, 1960.
- [15] S. T. Pantelides, S. N. Rashkeev, R. Buczko, D. M. Fleetwood, and R. D. Schrimpf, "Reactions of hydrogen with Si–SiO₂ interfaces," *IEEE Trans. Nucl. Sci.*, vol. 47, Dec. 2000, to be published.
- [16] L. N. Skuja, A. R. Silin, and A. G. Boganov, "On the nature of the 1.9 eV luminescence centers in amorphous SiO₂," *J. Non-Cryst. Solids*, vol. 63, pp. 431–436, 1984.
- [17] D. L. Griscom, "Optical properties and structure of defects in silica glass," *J. Ceramic Soc. Jpn.*, vol. 99, no. 10, pp. 923–942, Oct. 1991.
- [18] D. M. Fleetwood, D. E. Beutler, L. J. Lorence Jr., D. B. Brown, B. L. Draper, L. C. Riewe, H. B. Rosenstock, and D. P. Knott, "Comparison of enhanced device response and predicted X-ray dose enhancement effects on MOS oxides," *IEEE Trans. Nuc. Sci.*, vol. 35, no. 6, pp. 1265–1271, Dec. 1988.
- [19] A. P. Young and L. J. Brillson, "Luminescence spectroscopy of GaN in the high-temperature regime from room temperature to 900°C," *Appl. Phys. Lett.*, vol. 77, no. 5, pp. 699–701, July 2000.