Depth-resolved detection and process dependence of traps at ultrathin plasma-oxidized and deposited SiO_2/Si interfaces

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(Received 25 February 2000; accepted 28 February 2000)

Low-energy electron-excited nanoluminescence spectroscopy reveals depth-resolved optical emission associated with traps near the interface between ultrathin SiO_2 deposited by plasma-enhanced chemical vapor deposition on plasma-oxidized crystalline Si. These near-interface states exhibit a strong dependence on local chemical bonding changes introduced by thermal/gas processing, layer-specific nitridation, or depth-dependent radiation exposure. The depth-dependent results provide a means to test chemical and structural bond models used to develop advanced dielectric-semiconductor junctions. © *2000 American Vacuum Society*. [S0734-211X(00)10803-0]

I. INTRODUCTION

As microelectronic dimensions decrease into the nanometer regime, device designers require new materials and processes to achieve higher performance. A key element in such performance is the control of localized states at the semiconductor–insulator interface. However, state-of-the-art interface state densities realized with larger scale devices become more difficult to achieve since reduced thermal budget and higher dielectric strength films are required to minimize chemical degradation and quantum-mechanical tunneling, respectively. The realization of sub-$10^{10}\,cm^{-2}$ interface state densities with such new materials and preparation techniques depends on a fundamental understanding of the chemical bonding between atoms in the last few monolayers of the dielectric–semiconductor interface. More specifically, minimization of localized electronic states requires optimizing the number of bonds and their geometric constraints within the transition region between dissimilar materials.

It is now possible to detect electronic trap states within thin dielectric films and their interfaces with semiconductors. Using low-energy electron beams to generate a depth-dependent cascade of minority carriers and localized recombination as a function of incident beam energy, one can measure energies within the band gaps of these materials, their relative densities, and, most importantly, their dependence on local chemical composition and bonding by *in situ* processing. This technique has provided evidence for such localized states arising from a variety of extrinsic phenomena in a wide array of materials systems. Besides the Si/SiO_2 interface,[1–3] these include: metal-induced/III–V compound interface states,[4–6] dislocations,[7] interdiffusion,[8] and new phase formation at heterojunctions.[9] These studies show that extrinsic phenomena associated with altered bonding and composition can introduce electronic states deep within the band gaps of semiconductors and dielectrics at their interfaces.

II. EXPERIMENT

Over the past few years, Professor Gerry Lucovsky and his research group at North Carolina State University have described a set of advanced growth and processing techniques for preparing ultrathin SiO_2/Si interfaces with low thermal budget, low interface state densities, and reduced tunneling.[10] These world-class science and engineering achievements represent a benchmark for advancing interface dielectric technology in microelectronics and guiding industry efforts with fundamental atomic-scale understanding.

For the low-energy electron-excited nanoluminescence (LEEN) spectroscopy technique used to probe such interfaces, a glancing incidence electron beam with energies ranging from hundreds to thousands of volts provides a depth-dependent source of minority carriers. Recombination of free electrons and holes generated by this beam results in emission corresponding to transitions involving band edges and deep levels as well as transitions across the various band gaps. An optical train collects the emitted light from the irradiated sample inside an ultrahigh vacuum (UHV) chamber and transmits it through a monochromator to one of several photodetectors used to detect radiation from the near infrared to the ultraviolet. Updated descriptions of the LEEN spectroscopy technique and the depth dependence of the electron beam excitation appear elsewhere.[11,12]

III. RESULTS

In order to prepare SiO_2/Si interfaces with a minimum thermal budget and high electrical quality, the Lucovsky group at NCSU has developed a hybrid process that employs a deposited oxide rather than high-temperature oxidation and diffusion to form desired dielectric thicknesses. In order to achieve state-of-the-art interface state densities, the initial monolayer consists of a high-quality plasma oxide monolayer. A remote plasma-enhanced chemical vapor deposition (RPECVD) provides the subsequent dielectric layers. Subsequent annealing and hydrogenation steps further lower the interface state densities. The depth-dependent LEEN spectra

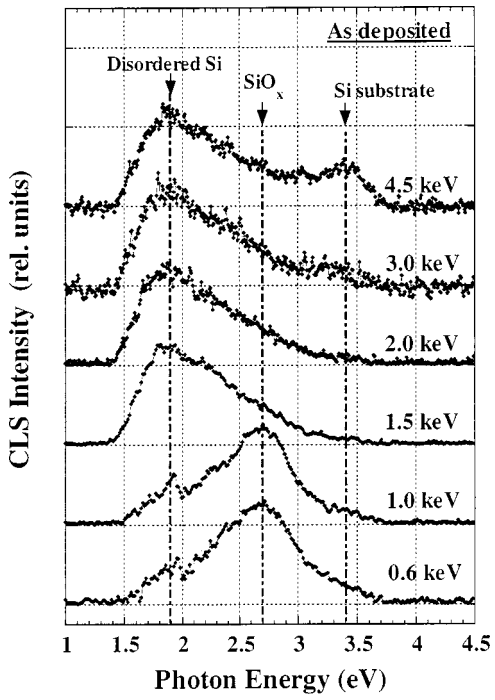

FIG. 1. Depth-dependent localized states at ultrathin (5 nm) SiO_2/Si interface formed by this low-thermal-budget process. As the incident electron beam energy increases, minority carrier recombination is centered initially in the SiO_2, then the interface region, and finally the Si substrate (see Ref. 1).

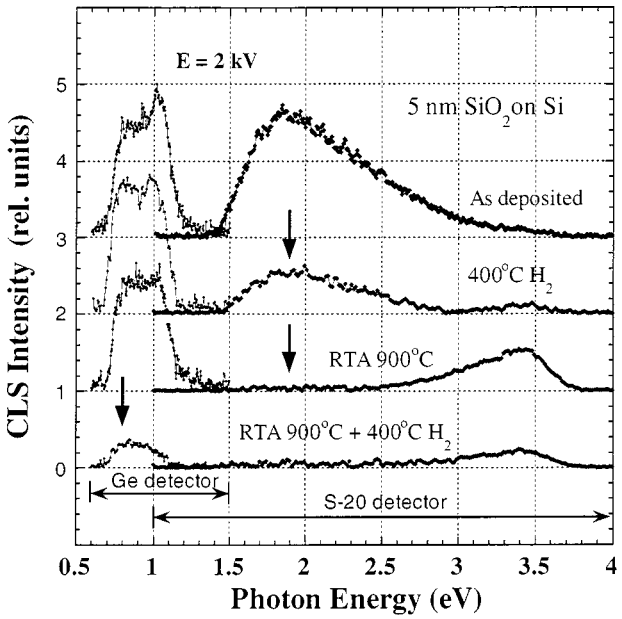

FIG. 2. Process-dependent localized states at ultrathin (5 nm) SiO_2/Si interface. The combination of 900 °C RTA plus 400 °C under hydrogen ambient appears to reduce the trap emissions almost completely (see Ref. 1).

illustrate the presence of such electronic traps, their location at different depths within the SiO_2 and Si layer structure, and their changes with processing. Figure 1 illustrates depth-dependent localized states at ultrathin (5 nm) SiO_2/Si interface formed by this low-thermal-budget process. As the incident electron beam energy increases, minority carrier recombination is centered initially in the SiO_2, then the interface region, and finally, the Si substrate. The ~1.9–2 eV emissions appear strongest at incident beam energies corresponding to depths close to the SiO_2/Si interface. The 2.7 eV peak appears strongest for depths within the SiO_2 overlayer. A peak emerges at 3.4 eV with increasing incident beam energy, corresponding to depths beyond the interface, i.e., in the Si substrate.

These trap emissions exhibit strong changes in intensity with thermal and chemical processing. Figure 2 illustrates such effects for a sequence of process treatments on an as-deposited 5 nm SiO_2/Si junction similar to that in Fig. 1. Figure 2 illustrates the changes in the optical emissions following: (i) 400 °C annealing under a H ambient, (ii) a 900 °C rapid thermal anneal (RTA), and (iii) a 900 °C RTA followed by a 400 °C post-metallization anneal. Both the 400 °C anneal and the 900 °C anneal result in reduced interface state emission. The combination of high-temperature RTA followed by low-temperature anneal under hydrogen ambient exhibits emissions only from the Si indirect band gap (1.1 eV) and a higher lying bulk Si transition at 3.4 eV.

Local introduction of new chemical species near the dielectric-semiconductor junction represents another avenue to improve electrical properties. In particular, nitridation is expected to decrease tunneling across the ultrathin dielectric since the dielectric constant of silicon nitride ($\epsilon/\epsilon_0 = 7.5$) exceeds that of SiO_2 ($\epsilon/\epsilon_0 = 4.2$). Nitrogen atoms near the SiO_2/Si interface can also help reduce dangling bond densities since the nitrogen-to-oxygen ratio can be adjusted on a layer-by-layer basis to satisfy both valence and bond geometric constraints at the last few monolayers of the interface. Such nitrided layers can also improve resistance to hot electron degradation and increase device oxide breakdown voltage.[13] Figure 3 illustrates spectra acquired from structures prepared via remote plasma assisted oxidation to produce one monolayer of SiO_2, a second monolayer on nitrided SiO_2 via remote plasma-assisted nitridation (RPAN), followed by deposition of 5 nm of SiO_2 via remote RPECVD. The spectra of the nitrided interface include features at 0.8, 1.05, 2.0, 2.7, and 3.4 eV, similar to the SiO_2/Si specimens without nitridation. The process dependence of the RPAN SiO_2/Si exhibits significant differences versus the same structure without the nitrided monolayer. Interface-sensitive (~1 keV) LEEN spectra show that a 900 °C RTA reduces the oxide-related emission at 2.7 eV but does not remove the broad ~2 eV peak due to Si microstructure or defects. The substrate-sensitive (~3 keV) LEEN spectra in Fig. 3 show that the 900 °C RTA does in fact reduce ~2 eV emission well below the interface. However, the ~2 eV peak does not decrease as much as it does with the RTA anneal in SiO_2/Si without N. This peak persists to some extent even with a combination of 900 °C plus 400 °C ''post-metallization'' anneals. Such differences show the sensitivity of interface trap structures to single nitrided monolayers.

A major concern for any advanced dielectric–semiconductor interface is the introduction of new trap states due to irradiation, either by cumulative x-ray, high-energy

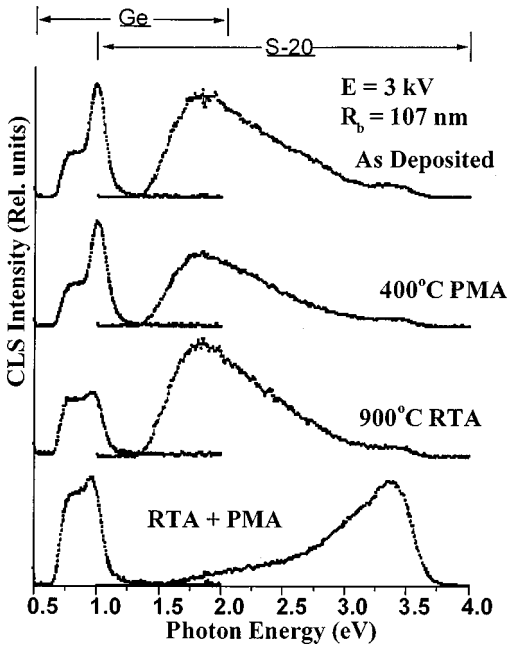

FIG. 3. Evolution of the as-deposited nitrided SiO_2–Si interface with the same excitation energy. Processing does not remove the ~2 eV luminescence band vs the interface without nitridation (see Ref. 3).

electron, or nuclear particle doses, or a combination of such extrinsic effects with electric fields during normal device operation.[14] LEEN spectroscopy of ultrathin SiO_2/Si junctions before and after irradiation with 10 keV x rays for a total dose of 10 Mrad (SiO_2) or 18 Mrad (Si) reveals a pronounced increase in emission in the energy range from 1.5 to above 2 eV. Figure 4(a) illustrates depth-dependent spectra analogous to those of Fig. 1 for the as-deposited SiO_2/Si junction. A similar junction after x ray irradiation [Fig. 4(b)] exhibits comparable depth-dependent features and the addition of new emissions at 1.5–2 eV for incident beam energies corresponding to the near-interface region. The intensity of this emission is not apparent at lower energies (0.5–1 keV) corresponding to the oxide overlayer or higher energies (3–4 keV) corresponding to the Si substrate. Other than the x-ray irradiation, the two specimens shown in Fig. 4 are identical.

We have also observed the production of emission features by the electron beam used for LEEN spectroscopy.[15] Such defect emission can be produced with doses several times larger than used in one spectral scan. However, the defect creation is cumulative so that one must take care to minimize any multiple scans of the same sample surface area. Although not presented here, the creation of new states at the SiO_2/Si interface appears strongest for energies around 2 keV. Significantly, extended exposure of these specimens to a 3 keV electron beam does not introduce any new defect emission.[15]

IV. DISCUSSION

Figure 1 shows that a number of different deep levels reside in the dielectric overlayer, at the dielectric interface with the Si and below the interface in the Si. It is possible to distinguish between such states due to their different energies and their intensity variations as a function of excitation depth. This depth resolution is enabled by the extremely short diffusion length of minority carriers generated by the low-energy incident electron beam. As a result, it is possible to assign particular transition energies to specific layers of the interface structure and, in principle, identify specific bond defects and their locations.

Hence, the 2.7 eV emission localized within the dielectric agrees closely with the $E2'$ defect known to exist within SiO_2 and believed to arise from Si–O–Si bridge bond de-

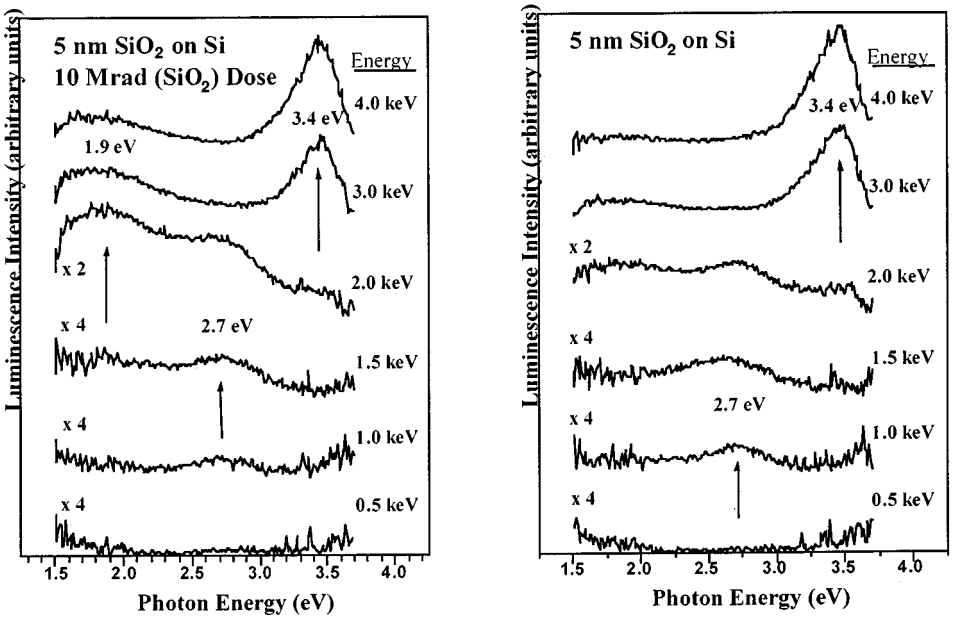

FIG. 4. Effect of irradiation on localized states. Here, x-ray doses of 10 Mrad (SiO_2) produced increases in emission at ~1.9 eV (see Ref. 15).

fects. Likewise, the 1.9 eV emission has been associated with suboxide bonding in the transition region between SiO_2 and Si. Such defects are expected to decrease in number as the interface becomes more abrupt and such transition regions are minimized. Likewise, the 0.8 eV emission has been associated with Si dangling bonds, and its decrease with hydrogenation is consistent with hydrogen termination of such bonds after the post-metallization anneal.[2]

Figure 2 shows that the optical emission from such defects depends strongly on annealing under different gas ambients. High-temperature RTA at 900 °C appears to minimize emission in the 2 eV spectral range, consistent with a smoothing of the interface.[10] Post-metallization annealing (PMA) at a temperature of 400 °C under a reducing ambient minimizes emission at 0.8 eV attributed to dangling bonds, consistent with reintroducing H at Si bonds originally lost due to the higher temperature anneal. The sequence of high-temperature RTA plus PMA serves to minimize suboxide bonding at the transition layer between SiO_2 and Si, while maintaining the hydrogen needed to passivate Si dangling bonds that result due to the constrained geometry and difference in valence between materials at the interface. This minimal optical emission from trap states coincides with electrical measurements of only $10^{10}-10^{11}$ interface states per cm^2.[10]

Comparison of the LEEN features for structures with versus without an interfacial nitride monolayer between the plasma oxide monolayer and the RPECVD SiO_2 reveals that the process steps optimized for the SiO_2-Si interface are not yet optimized for the nitrided structures. Further optimization will require several parameters to be optimized in combination, including the nitride/oxide stoichiometry, the location of the nitride within the stacked dielectric structure, and the sequence of process conditions. Guiding this process, one needs to include an understanding of the intermediate phase at the transition between the SiO_2 network glass and the crystalline Si that minimizes stress and satisfies local bond constraints.

The effect of x-ray irradiation on the trap emission of SiO_2/Si interfaces shown in Fig. 4 illustrates that such traps are detectable via optical techniques such as LEEN spectroscopy. While the creation of interface states by high energy irradiation is well known, this is perhaps the first time that such states have been observed optically. Furthermore, Fig. 4 illustrates the spatial localization of these traps, namely, at the SiO_2/Si interface.

Radiation is expected to produce traps within the dielectric as well, but for the ultrathin dielectrics studied here, the energy deposited into such thin layers is minimal. The effect of the LEEN beam in producing new defect states is consistent with the effect of x-ray irradiation, which will also produce a cascade of keV energy electrons and holes. The absence of any new defect emission with extended exposure to a 3 keV electron beam suggests that the defect creation requires free electron-hole pairs near enough to the interface to disrupt local atomic bonds. For 3 keV, the pair creation process may occur too far into the Si for significant diffusion of such carriers back to the interface region. The irradiation studies described here suggest that one must use care in probing SiO_2/Si interfaces with electron beams due to their unusually high sensitivity to free carrier generation at the intimate junction. Such effects are not evident for metal–semiconductor or semiconductor heterojunction studies. For the SiO_2/Si interface, electron beam effects may be related to release of hydrogen and dangling bond formation by the additional high-energy carriers. Such electron beam effects may prove useful, particularly with a beam focused laterally on circuit elements by a scanning electron microscope and may provide a new tool for rapidly assessing an interface's resistance to radiation effects.

V. CONCLUSIONS

Electronic states localized at interfaces of ultrathin SiO_2 deposited by low thermal budget techniques on crystalline Si exhibit a strong dependence on local chemical bonding changes introduced by thermal/gas processing, layer-specific nitridation, or depth-dependent radiation exposure. These advanced dielectric-semiconductor structures created by Professor Gerry Lucovsky and his NCSU research group are shown to possess interface states that can be reduced controllably, based on a fundamental understanding of structural and chemical properties on an atomic scale. LEEN spectroscopy reveals depth-resolved optical emission associated with traps near the interface and supports the atomic structure and chemistry models used to achieve these advances in microelectronic device technology.

ACKNOWLEDGMENTS

The authors wish to acknowledge the support of the National Science Foundation (DMR-9711851, Veme Hess) and the Department of Energy (DE-FG0297ER45666, Craig Hartley) (energy-dependent excitation calculations) at Ohio State and by the ONR, SRC, and the NSF Engineering Research Center at North Carolina State University. One of the authors (L.J.B) would like to express his appreciation in working with a scientist and engineer as creative and insightful as Professor Gerry Lucovsky over many years.

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