

Characterization of the Interface between Plasma-Oxidized SiO₂ and Crystalline Silicon by Cathodoluminescence Spectroscopy (CLS)

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1. Introduction

We report on studies of Si-SiO₂ structures by low-energy cathodoluminescence spectroscopy (CLS) [1]. For these heterostructures with 5 nm thick oxides, the Si-SiO₂ interface was formed by 300°C remote plasma-assisted oxidation (RPAO), and the remainder of the SiO₂ component of the heterostructure was formed by 300°C remote plasma enhanced chemical vapor deposition (RPECVD) [2]. The work includes studies of i) as-deposited films, ii) films annealed at 400°C and 900°C, and iii) films subjected to post-deposition, and post-annealing hydrogenation.

2. Experimental Procedures

The films were prepared on hydrogen-terminated ~10 ohm-cm boron-doped p-Si(100) substrates. The Si-SiO₂ structures were formed by a two-step plasma process: i) RPAO to form the interface and grow ~0.5 - 0.6 nm of SiO₂; and ii) RPECVD to deposit the bulk oxide film, for a total SiO₂ thickness of ~5 nm [2]. CLS studies were carried out at room temperature with electron beam energies between 0.6 keV and 4.5 keV and beam currents of 1-4 μA on a spot approximately 100 μm in diameter. After exposure to an electron beam fluence an order of magnitude higher than used for obtaining the spectra presented in this paper, there was no

meV resolution using a Ge detector for the infrared, and a S-20 photocathode for visible-to-ultraviolet spectral range.

3. Results

CLS spectra of the as-prepared plasma-deposited 50 Å film appear in Fig. 1 as a function of electron energy (0.6 to 4.5 keV), and therefore surface penetration depth. For a beam energy of 1.0 keV, one estimates a mean penetration depth of about 30 Å [3]. The spectra were taken with beam current decreasing with increasing voltage to maintain a constant excitation power, and a nearly constant electron-hole pair generation rate. For intermediate beam energies, 1.5 and 2.0 keV, a prominent feature is observed at 1.9 eV. For lower beam energies, 0.6 and 1.0 keV, this 1.9 eV decreases in intensity, and a new feature emerges at about 2.7 eV. At higher energies, 3.0 and 4.5 keV, i) the 1.9 eV peak remains, ii) the 2.7 eV peak is not observed, and iii) there is an additional spectral peak at 3.4 eV that is most evident as a distinct feature for the 4.5 keV excitation.

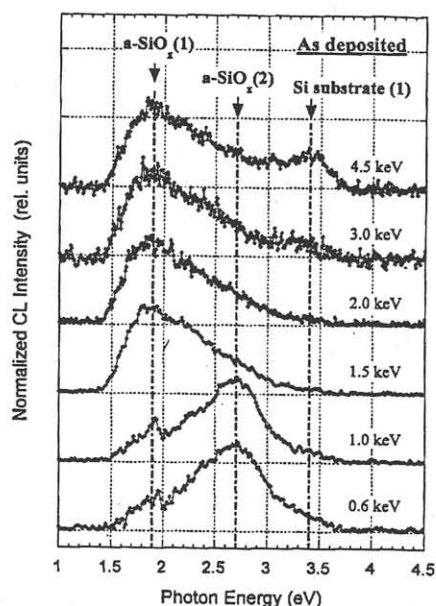


Fig. 1 CLS spectra recorded with an S-20 phototube.

observable spectroscopic or visual e-beam damage. The luminescence was recorded with a monochromator set to ~50

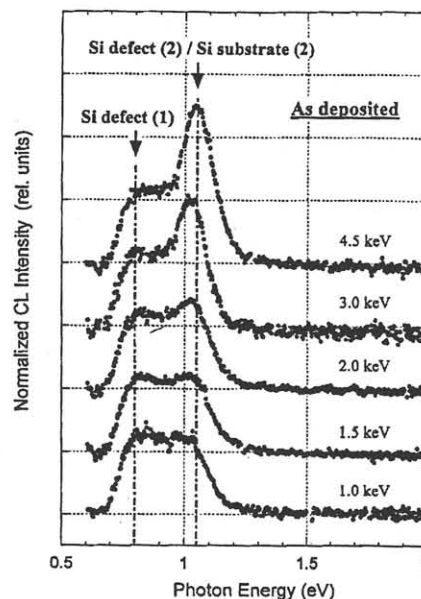


Fig. 2 CLS spectra recorded with a Ge detector.

In the infrared spectral range (Ge detector) shown in Fig. 2, two luminescence features were detected at ~0.8 eV and at ~1.0 eV over the entire range of excitation energies. The relative intensity of 1.0 eV peak increases with increasing excitation energy, indicating one component associated with the bulk Si and a component associated with the interfacial layer and oxide film.

The effect of post-deposition annealing under different ambients has been measured and spectra obtained with the S-20 phototube and Ge-detector are given in Fig. 3. The top two traces indicate the effects of the 400°C forming gas anneal. These spectra, taken at an excitation energy of 2.0 keV after the anneal reveal only small changes in the relative intensities of the 0.8 and 1 eV bands, but a pronounced decrease in the broad band at 1.9 eV. Additionally, the intensity remains relatively unchanged for the 3.4 eV transition after the anneal.

Rapid thermal annealing (RTA) in Ar at 900°C caused the band at 1.9 eV to vanish below the level of detection. The 900°C anneal enhances the 3.4 eV feature, but does not change the relative intensity of the 0.8 and 1 eV bands. In addition, the features at 0.8 and ~1 eV decrease significantly after being subjected to an RTA at 900°C followed by hydrogenation at 400°C. Relative to the 900°C anneal spectra, the intensity of the 3.4 eV band also decreases.

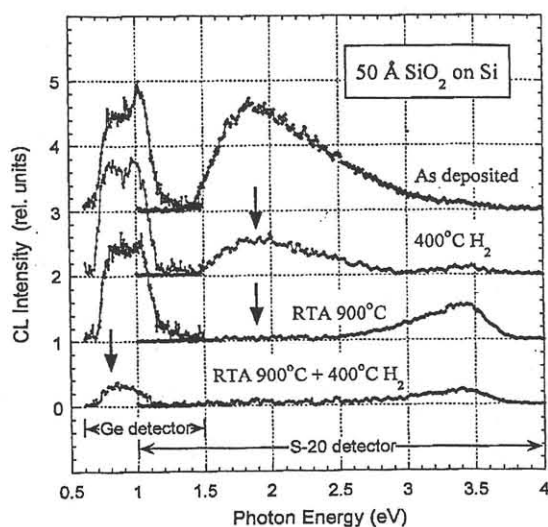


Fig. 3. CLS spectra as a function of annealing.

4. Discussion

The CLS studies have identified five distinct spectral features at 0.8 eV, ~1 eV, 1.9 eV, 2.7 eV and 3.4 eV. At first sight it is tempting to interpret these features in terms of defect luminescence bands previously identified in irradiated quartz, silica glass, thermally grown silicon dioxide, and oxidized porous silicon [4-7]. However, since the most dramatic changes in the CLS spectra occur after the combined 900°C RTA and 400°C rehydrogenation, it is more instructive to compare these results with annealing studies on similarly-prepared Si-SiO₂ interfaces that have relied on other characterization procedures [8].

Based on the energy dependence of the CLS as shown in Figs. 1-3, the following assignments are proposed. The 0.8 eV feature and the 1 eV feature, are assigned to interfacial Si-atom dangling bond defects with different numbers of Si and O atoms back-bonded to the Si atom the dangling bond. These assignments are based on the photon energy of the luminescence [9], and are consistent with the changes in the

concentration of these defects after a 900°C RTA. The 900°C RTA by itself will remove H-atoms from the dangling bonds increasing CLS; however, following an anneal in a H-containing ambient the dangling bond CLS is reduced by H-atom attachment. The 0.8 eV dangling bond is assigned with a Si atom that has three Si-nearest neighbors, whereas for the 1 eV defect the Si atom with the dangling bond has O-nearest neighbors as well [10,11]. The 1 eV band also contain an additional substrate contribution; e.g., from disorder-induced near-band edge luminescence.

The features at 1.9 and 2.7 eV are assigned to luminescent transitions involving an as yet unspecified suboxide bonding defect in the transition region *near* the grown interface. Based on the electron energy dependence, the 1.9 eV feature is located closer to the interface than the 2.7 eV feature. Since both of these bands are removed completely after 900°C annealing, the assignments are consistent with significant suboxide reductions found by other characterization methods [8]. Finally, the 3.4 eV peak corresponds to a substrate bulk resonance associated with the lowest direct band-gap in crystalline Si. The CLS peak is at essentially the same energy as the sharp feature in the imaginary part of the dielectric constant, ϵ_2 , which is due to optical transitions in the Brillouin zone between G and L along the L direction [12].

In summary, the CLS study has provided depth-resolved information relative to interfacial transition regions and interface bonding defects which complement the results of other studies. In particular, this information is important in helping identify local bonding environments which contribute to electronically-active defects at Si-SiO₂ interfaces. Therefore, such direct detection of deep electronic defect levels can help guide further development of low defect semiconductor-dielectric interfaces.

Acknowledgments

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