Infrared spectroscopic analysis of an ordered Si/SiO_2 interface

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Infrared spectroscopy is used to compare the Si/SiO_2 interfaces created by thermal oxidation of a standard Si(100) substrate and of an ordered, (1×1) Si(100) substrate. The thermal oxides (approximately 25 Å) examined in this study are etched in dilute hydrofluoric acid and the resulting films analyzed spectroscopically. The behavior of the dominant optical phonon modes as a function of film thickness provides strong evidence that the ordered Si(100) substrate provides a template for an Si/SiO_2 interface with a higher degree of homogeneity in the Si–O bonding environment of the intervening substoichiometric SiO_x layer than does the standard Si(100) substrate. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1644030]

The interface between the crystalline Si(100) substrate and the amorphous SiO_2 gate oxide is both essential to the performance of microelectronic devices and poorly defined from a structural point of view. Studies have shown that the electrical properties of the ultrathin SiO_2 layers required for current device dimensions depend critically on the quality of this Si/SiO_2 interface.[1–6] Since formation of a thin layer of interfacial SiO_2 is often unavoidable even when a different high-κ material is used for the gate dielectric, control and understanding of this interfacial oxide phase will remain an important issue even in future devices.

There is no long-range order apparent in the Si/SiO_2 interface formed by thermal oxidation of Si after standard wafer-cleaning protocols.[7–10] However, it has been shown that modification of the wafer-preparation protocol produces an ordered (1×1) Si(100) surface that leads to an ordered Si/SiO_2 interfacial phase.[11–15] Ion beam analysis (IBA) detected that Si atoms in the interfacial oxide are in registry with the (1×1) Si(100) surface, in contrast with the disordered interfaces detected by IBA for all other interfacial oxides studied. This result is consistent with high-resolution transmission electron microscopy (HRTEM) detection of aligned bonds between the oxide and Si(100) at the interface, with very reduced step density, for oxides grown on this (1×1) substrate. Finally, as reported in Ref. 11, IR spectroscopy provides complementary evidence of unique homogeneity of SiO_x bonding at this ordered interface; the details of the IR analysis are presented herein.

IR spectroscopy has been used previously to investigate changes in the structure of a high-quality thermal SiO_2 layer close to the Si/SiO_2 interface.[16] In that study, a ~30 Å SiO_2 layer was gradually thinned down to ~6 Å in dilute hydrofluoric acid (HF), and the dominant optical phonon modes of the SiO_2 film monitored as a function of film thickness. Careful analysis of the SiO_2 thickness-dependent frequency shift of these phonons shows that the main cause of changes in the IR spectrum of SiO_2 near the Si/SiO_2 interface is substoichiometric SiO_x $(x<2)$ within ~6 Å of that interface.

In the present work, we apply this same spectroscopic approach to probe the interfacial oxide phase of an SiO_2 film grown on an ordered (1×1) Si(100) template by comparison with a control oxide grown on a standard substrate. We show that the presence of an ordered interfacial SiO_2 phase on (1×1) Si(100) correlates with a narrower region of substoichiometric oxide. This result not only supports the picture of an ordered interfacial oxide phase generated from previous studies, but also provides evidence that ordering of the Si/SiO_2 interface allows a more abrupt transition between the fully stoichiometric SiO_2 and the underlying Si(100) substrate.

The SiO_2 layers analyzed herein were grown by rapid thermal oxidation on both ordered (1×1) and control Si(100) substrates. The resulting oxide layers, approximately 25 Å thick, are referred to hereafter as the ‘‘ordered interfacial oxide’’ and ‘‘control oxide,’’ respectively. Preparation of the ordered (1×1) Si(100) template is described in detail elsewhere.[11–15] Briefly, a critically modified sequence of SC-1 clean [H_2O:H_2O_2:NH_4OH (4:1:1)], HF etch [49% HF_{aq}] and SC-2 clean [H_2O:H_2O_2:HCl (4:1:1)] is followed by a 60 s etch in 49% $HF_{(aq)}$:CH_3OH (1:9) and a final methanol rinse. The control template is prepared via a conventional RCA clean of SC-1 followed by SC-2, with a final etch in 49% $HF_{(aq)}$ only. IR spectroscopic analysis was carried out on two wafers of each type of oxide.

Each oxidized wafer was cut into 0.6 in.×0.75 in. pieces for IR analysis. The pieces were first cleaned in a 4:1 mixture of H_2SO_4:H_2O_2 (30%) to remove surface hydrocarbon contamination, then immersed via a custom-made Teflon™ holder into dilute hydrofluoric acid (~0.05% HF) and withdrawn for analysis at varying time intervals. Each sample was briefly rinsed in deionized water and dried with com-

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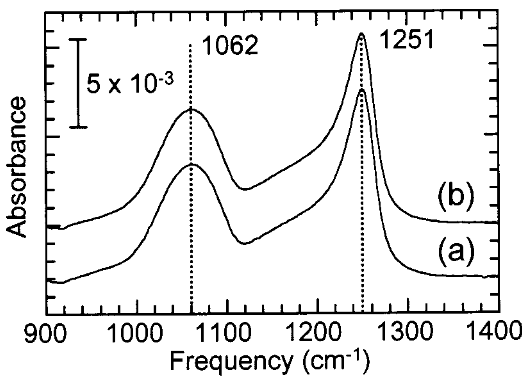

FIG. 1. Grazing-incidence infrared spectra of the dominant TO and LO phonon modes for 25 Å thermal SiO_2 grown on (a) an ordered Si(100) template prepared as described in the text and (b) a control template that received only a standard RCA clean.

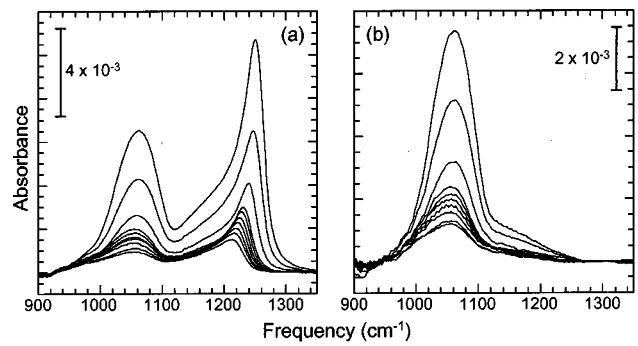

FIG. 2. Infrared spectra of SiO_2 films on an ordered substrate, acquired after successive etching of an initial 25 Å SiO_2 film. The spectra in (a), acquired at grazing incidence, show both the TO and LO phonon modes. The normal-incidence spectra in (b) show only the TO mode and were used to calculate film thickness.

pressed N_2 gas prior to spectroscopic analysis.

IR spectra were acquired with two Nicolet Fourier transform infrared spectrometers (Magna series) equipped with thermoelectrically cooled DTGS detectors, one for grazing (22°) incidence and one for normal incidence. All spectra were ratioed to a spectrum of a hydrogen-terminated sample from the same wafer, prepared by stripping the entire thermal oxide with 49% HF. The normal incidence spectra, which access only the parallel-oriented TO modes, were used to determine film thickness for each sample piece, since previous work[16] demonstrated good agreement between thickness as measured by integrated area of the TO peak and thickness determined from XPS measurements.

The infrared spectra of the initial 25 Å oxide layers are presented in Fig. 1. Comparison of spectra of the ordered [Fig. 1(a)] and the control [Fig. 1(b)] oxide reveals no detectable difference between the two. Specifically, both oxides exhibit a TO peak frequency of 1062 cm^{-1} and an LO peak frequency of 1251 cm^{-1}, both typical frequencies for a thermally grown SiO_2 layer. The peak shapes also appear identical, with the same full width at half-maximum (FWHM) (50 cm^{-1} for the LO, 79 cm^{-1} for the TO). In short, examination of the signatures of Si–O bonding in the complete 25 Å oxides provides no information about differences at the respective Si/SiO_2 interfaces, since the spectroscopic signature of the bulk of this film overwhelms any signature of the interface. This is consistent with the IBA and HRTEM results of Refs. 11–15, which similarly detected identical oxide characteristics for both ordered and control oxides in the stoichiometric phase above the interfacial oxide region.

Differences between the interfacial regions of oxides grown on the two substrates are, however, apparent upon examination of sequentially thinned oxide layers from each. A sample data set—in this case, for the oxide grown on the ordered substrate—is shown in Fig. 2. The set of thickness-dependent grazing incidence spectra [Fig. 2(b)] display a characteristic redshift of both the LO and TO modes with decreasing film thickness, a redshift previously determined[16] to result primarily from substoichiometric oxide at the Si/SiO_2 interface. Plots of TO and LO peak frequencies as a function of film thickness, for both the ordered (solid triangles) and the control (open circles) substrates, are summarized in Fig. 3.

The redshift of the LO peak frequency [Fig. 3(a)] does not differ significantly between the two substrates. However, the TO peak frequency [Fig. 3(b)] exhibits markedly different behavior for films grown on the ordered versus the control substrate. Specifically, for film thicknesses under 10 Å, the TO frequency for SiO_2 grown on the ordered substrate plateaus around 1056 cm^{-1}, while the TO frequency for the film on the control substrate continues to decrease down to 1051 cm^{-1}. While this difference is small in absolute frequency (5 cm^{-1} for the thinnest films obtained), it is both significant (peak frequencies are determined to within only 1 cm^{-1}) and consistent over the full range of the thinnest films studied. Furthermore, this effect is a large percentage of the total TO shift (nearly 50% of the 12 cm^{-1} shift for the control oxide).

The origin of the TO frequency shift is somewhat more straightforward to describe than that of the LO, since the TO is not subject to the same long-range Coulombic interactions that affect both the frequency and the intensity of the LO. We have previously attributed the shift in TO to the growing predominance near the interface of the substoichiometric "TO" mode that appears as a low-frequency (~990 cm^{-1}) shoulder in the infrared spectra of the thinnest films.[16] The inhomogeneous nature of this transition from SiO_2 to SiO_x presumably results in a number of bonding environments with intensity at a range of frequencies below the TO from the purely stoichiometric SiO_2, leading to a TO mode that is broadened to the low-frequency side in the thinnest films. If this picture is correct, then a film with a more homogeneous interface, and hence a smaller array of bonding environments in the substoichiometric layer, might display a smaller TO redshift due to less overlap between the SiO_2 and the SiO_x signatures in this spectral region. Instead, the TO of such a film would evolve more as two discrete modes (the high-frequency SiO_2 TO and the low-frequency SiO_x TO) rather than as a broadening of the original TO peak. While the trend in TO peak width (as measured by FWHM, data not shown) is consistent with this picture (the FWHM grows more dramatically as film thickness decreases for the control versus the ordered oxide), the shift in TO peak frequency is more significant and therefore provides a much more reliable spectroscopic indicator of interface quality.

While LO peak frequency appears less sensitive to interface quality, the behavior of this mode provides qualita-

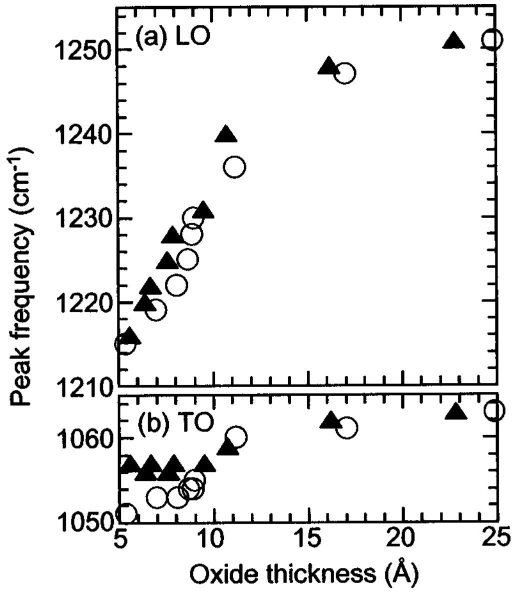

FIG. 3. The peak position of both the (a) LO and (b) TO modes as a function of film thickness for both the ordered (▲) and the control (○) substrate, corresponding in the former case to the spectra in Fig. 2.

tive support for the spectroscopic identification of the ordered interface as a higher quality one. Figure 4 compares the grazing-incidence spectra of two of the thinnest films obtained, one from the control and one from the ordered interfacial oxide. While the relative TO intensity is consistent with the ordered film being slightly thinner than the control film, the LO intensity is greater in the spectrum of the ordered film than in the spectrum of the control film. Although the intensity of the LO mode is not a reliable indicator of film thickness due to effects from the aforementioned Coulombic interactions, these interactions provide qualitative information about film quality. Specifically, film inhomogeneity near the Si/SiO_2 interface effectively screens some of the SiO_2 oscillators from one another, decreasing the Coulombic contribution to the LO intensity. The *higher* intensity of the LO mode in the *thinner* ordered interfacial oxide film therefore supports the picture of this interface as a more abrupt, higher quality one, with less disruption of the final SiO_2 layer by intervening substoichiometric bonding configurations. It is also worth noting that the ordered interfacial oxide appears to have more of a discrete shoulder in the TO region than does the control oxide (arrow in Fig. 4).

In summary, we have shown that IR spectroscopy is sensitive to bonding differences in the interfacial oxide phase at the Si/SiO_2 interfaces created by thermal oxidation of an ordered, (1×1) Si(100) substrate and of a standard Si(100) substrate. Analysis of the IR spectra of the interfacial region provides strong evidence that the ordered interfacial oxide phase results in a more homogeneous Si–O bonding environment in this critical region, the result of a more abrupt transition from SiO_2 to the required substoichiometric SiO_x layer immediately adjacent to the ordered Si substrate. These IR results correlate well with the IBA and HRTEM analysis described in Refs. 11–15. Specifically, the picture derived from those studies, of the registry of atoms in the ordered interfacial oxide phase with (1×1) Si(100) substrates and of the reduced step density at these interfaces, should lead to more homogeneous bonding than in conventional (thus, disordered) interfacial oxide phases. This increased homogeneity of bonding is precisely what the IR results of this study demonstrate. Furthermore, the spectroscopic analysis described herein is both extremely sensitive to differences in bonding environments and relatively inexpensive, making it a promising candidate for comparing the structural differences between any number of gate dielectric interfaces in cases in which these differences lead to changes in electrical behavior.

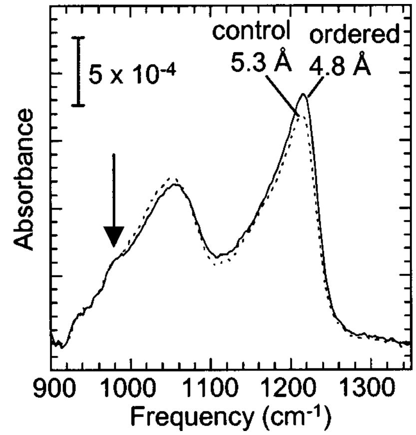

FIG. 4. Comparison of the grazing incidence spectra of a ~4.8 Å film from the ordered interfacial oxide (solid line) and a ~5.3 Å film from the control oxide (dashed line).

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