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Structural nature of the Si/SiO₂ interface through infrared spectroscopy

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The spatial variations of the transverse-optic and longitudinal-optic mode vibrations of the bridging oxygen asymmetric stretch have been studied in the region of the SiO₂/Si interface in thermally grown oxides. Comparing the behavior of the two modes it is concluded that vibrational frequency shifts are due primarily to stoichiometry changes and not stress or densification. Fitting to and deconvolution of the measured peak lineshifts as a function of oxide thickness enables us to deduce that the region of stoichiometry variation is ≤ 1.6 nm. © *1996 American Institute of Physics*. [S0003-6951(96)01522-7]

The structure and "width" of the interface between thermally grown, amorphous (a-) SiO₂ films on Si substrates have been the subject of controversy for a considerable time in part due to their technological importance. Many different methods have been used in an attempt to gain some insight into this problem,¹ but its exact nature remains controversial. X-ray photoelectron spectroscopy measurements² have been interpreted as suggesting that various Si oxidation states exist at the Si/a-SiO2 interface corresponding to Si atoms bonded to 1, 2, 3, or 4 O atoms. Such a model is clearly not unreasonable physically, since a transition from the SiO₄ tetrahedron to the SiSi₄ tetrahedron (corresponding to pure Si) must occur somewhere in the so-called interfacial region. The fundamental question is what the width of this transition region is. Infrared absorption associated with O vibrational modes in the a-SiO₂ and Si networks is clearly sensitive to the environment of the oxygen and hence the bonding arrangement. For example, O interstitials in Si, which correspond to bridging oxygens between two Si's, have an absorption mode at 1106 cm^{-1} while in thermally grown a-SiO₂, depending upon film thickness,³ the strongest absorption appears between 1070 and 1090 cm⁻¹ (also a function of growth temperature). The most extensive measurements performed to date¹ concern the variation of the frequency of the transverse-optic mode associated with the asymmetric stretch mode of the O in the Si-O-Si intertetrahedral bridging bond. It was found that the frequency of this mode decreased as the thickness of a-SiO₂ layer decreased and it was concluded that this was not due to variation in stoichiometry (oxygen deficiency) but rather to interfacial strain, which would result from the difference in molar densities of the two networks, $a-SiO_2$ and the underlying Si substrate. In the present work we revisit the problem of infrared absorption in the interfacial region with particular reference to the behavior of both the transverse-optic, TO, and the longitudinal-optic, LO, vibrational modes of the bridging O atoms.

Thin films (<30 nm) of nominally dry a-SiO₂ were grown thermally on Si(100) Czochralski 4 or 8 in. substrates using standard technological methods. Samples 20 and 27 nm thick were grown in dry oxygen at 950 °C while 5-nmthick films were grown at 900 °C using nitrogen dilution of the dry oxygen ambient (to make the oxidation time "controllable"). Infrared absorption measurements were made using a Fourier transform spectrometer (Bruker IFS 66) either with normal incidence (for the study of the TO mode) or at an angle of incidence of 65° in order to study the LO mode.⁴ Background reference samples were obtained by etching off the *a*-SiO₂ film in a commercially available solution of HF acid and NH₄F (Enerlec BE 7:1). In order to study the variation of the position of the LO and TO peaks as a function of oxide thickness, the thermally grown films were systematically etched in increasingly dilute solutions of BE 7:1 (maximum dilution one part by volume BE 7:1 to seven parts of de-ionized water). Infrared spectra were obtained using a resolution of 4 cm⁻¹ and 250 scans to improve the signalto-noise ratio. In all cases film thicknesses were ascertained using a single-wavelength (632.8 nm) ellipsometer assuming the index of the oxide fixed at 1.462. This is an approximation which cannot be circumvented.

In Fig. 1 we show the variation of the position of the peak of the TO and LO vibrational modes associated with the asymmetric stretch of the O in the intertetrahedral Si-O-Si bridge as a function of oxide thickness. We include previously published data on the TO mode variation¹ measured on samples produced by oxidation of Si substrates at 850 °C. The small shift of the TO mode to lower frequencies observed clearly for film thicknesses ~ 20 nm may be attributed to the increased density of the film resulting from the lower oxidation temperature.^{5,6} Our measurements confirm the previous results on the TO mode¹ demonstrating a decrease in mode frequency with decreasing film thickness and show that the same behavior is observed for the LO mode, the overall mode frequency change observed being ~ 37 cm^{-1} for the TO mode and 45 cm^{-1} for the LO mode within the limits of experimental error. Note that the LO and TO mode absorption frequencies were measured on the same samples.

The frequencies of the TO (ω_{TO}) and LO (ω_{LO}) modes of the asymmetric O stretch are given, in the central and noncentral force approximation⁷ by

$$\omega_{\rm TO} = \sqrt{\left[2\left(\alpha \sin^2 \theta/2 + \beta \cos^2 \theta/2\right)/m\right]} \tag{1}$$

and

$$\omega_{\rm LO} = \sqrt{\left[2\left(\alpha \sin^2 \theta/2 + \beta \cos^2 \theta/2 + \gamma^{\rm ss}\right)/m}\right],\tag{2}$$

where θ is the Si–O–Si bridging bond angle, *m* the O atomic mass, α the central force constant, and β the noncentral force constant. γ^{ss} is an electrostatic term which can be expressed as $\gamma^{ss} = \{Z^2/[\epsilon_{\infty}\epsilon_0(2m+M)]\}\rho$. ϵ_{∞} is the relative permittiv-





FIG. 1. The measured infrared absorption peak position as a function of oxide thickness in thermally grown a-SiO₂ on Si. (a) ($\blacklozenge \land \blacksquare$) the TO mode associated with the bridging oxygen asymmetric stretch. (\blacktriangledown) TO mode data from Ref. 1. (b) ($\blacklozenge \land \blacksquare$) LO mode data. The symbols correspond to oxides grown to different initial thicknesses (\blacklozenge) 27 nm, (\land) 20 nm, and (\blacksquare) 5 nm. In both (a) and (b) the (o) points result from calculations.

ity at infinite frequency and ϵ_0 the absolute permittivity of free space, *M* is the atomic mass of Si, and *Z* is an electrical charge related to the movement of the O's. ρ is the mass density of the *a*-SiO₂ network. From experimental infrared measurements of the TO mode frequency in *a*-SiO₂ samples densified plastically⁶ in the bulk form and in thin films densified as a result of growth at different temperatures,⁸ it has been ascertained that the frequency decreases with increasing mass density: $d\omega_{\rm TO}/d\rho = -93$ cm² g⁻¹. To our knowledge there have been no measurements of the variation of $\omega_{\rm LO}$ with density. However, comparison of Eqs. (1) and (2) yields

$$2\omega_{\rm LO}d\omega_{\rm LO}/d\rho = 2\omega_{\rm TO}d\omega_{\rm TO}/d\rho + 2\{Z^2/[\epsilon_{\infty}\epsilon_0(2m+M)]\}/m.$$
(3)

Assuming the initial values 1255 cm⁻¹ for $\omega_{\rm LO}$ and 1090 cm⁻¹ for $\omega_{\rm TO}$ (corrected for the forementioned effects of film thickness³), we can rewrite Eq. (3) in the form:

$$d\omega_{\rm LO}/d\rho = (\omega_{\rm TO}/\omega_{\rm LO})d\omega_{\rm TO}/d\rho + 70.3 \ {\rm cm}^2 {\rm g}^{-1}.$$
 (4)

Using the measured value for $d\omega_{\rm TO}/d\rho$ of $-93 \text{ cm}^2 \text{ g}^{-1}$ we conclude that $d\omega_{\rm LO}/d\rho \sim -10 \text{ cm}^2 \text{ g}^{-1}$, i.e., approximately 1/9 of the variation of the TO mode with density. From Figs.

FIG. 2. (o) variation of the (a) TO and (b) LO mode peak frequencies with oxide thickness obtained from calculations and fitting to the experimental data shown in Figs. 1(a) and 1(b). The solid lines indicate the actual spatial distribution of mode frequencies required to generate the observed peak shift variation resulting from convolution. The oxide thickness is measured from the Si/SiO₂ interface.

1(a) and 1(b) we see clearly that the measured variations near the *a*-SiO₂/Si interface are approximately equal so that they cannot, in fact, be attributed to changes in the density of the oxide structure. This further negates any argument that changes may be induced by interfacial strain since this would also induce density variations.

In order to proceed further with the analysis of the data of Figs. 1(a) and 1(b) must be deconvoluted to take account of the fact that the infrared absorption is occurring in an inhomogeneous medium. We assume that the absorbance (A) which is measured experimentally can be written in the form:

$$A = \log \left[\exp \left(\sum_{i} k \Delta x / \{ 1 + [2(\omega - \omega_{i}) / \Delta \omega]^{2} \} \right) \right].$$
 (5)

Here, the sample is divided into *i* slices of thickness Δx . A Lorentzian infrared absorption peak centered upon a frequency ω_i with a peak full width at half height of $\Delta \omega$ is associated with each of the *i* slices. Both the experimental absorption linewidths for the TO and LO modes and the absorption peak frequency shifts as a function of oxide thickness[Figs. 1(a) and 1(b)] are very much smaller than the peak

frequencies (ω_{LO} or ω_{TO}). On this basis we make the approximation that the peaks associated with each of the islices have the same extinction coefficients k, and the same widths $\Delta \omega$ (taken to be the thick oxide value of 75 cm⁻¹ throughout). We have used Eq. (5) to fit the data of Figs. 1(a)and 1(b) and thus deduced a profile of the peak frequency shifts, the fits are shown in Figs. 1(a) and 1(b) as the open circles. The spatial profiles of frequencies used to obtain the fits to the measured infrared peak shift as function of sample thickness are shown in Figs. 2(a) and 2(b) by the solid lines. One observes that although the "interfacial" region as determined by the infrared peak shift appears to extend over \sim 5 nm, the actual spatial distribution of frequencies generating this extends only over ~ 1.6 nm. We reiterate at this point that some uncertainty may arise because of the assumption of a fixed refractive index in estimating the thickness of the oxide film at each stage, given this limitation, the value of 1.6 nm must certainly be taken as an upper limit.

Finally, we discuss the physical origin of the spatial profile of infrared frequencies that gives rise to the experimentally observed curve shifts. For reasons discussed previously [Eq. (4)] comparison of the behavior of the TO and LO peaks eliminates the possibility that interfacial strain or density variations in the a-SiO₂ network are responsible. This leads us to conclude that stoichiometry/bonding variation must be relevant though we have no independent way to assess this in our samples. Infrared absorption associated with the TO mode in a-SiO_x have been made⁹ on deposited films as a function of x. The authors observed that for the TO mode, $d\omega_{\rm TO}/dx \sim 67.5$ cm⁻¹. Unfortunately, the LO mode variation was not measured. From Fig. 1(a) we see that the maximum variation (close to the Si substrate) is -37cm⁻¹ suggesting dx = 0.55. The stoichiometry of the oxide in the immediate vicinity of the Si substrate would then be $SiO_{1.45}$. Such a value is not surprising if one takes account of the fact that at the interface O's are bonded on the oxide side to $-SiO_3$ and on the Si side to $-SiSi_3$. On this basis a simplistic formula for the "oxide" in this region would be approximately SiO. A consequence of substoichiometry (equivalent to oxygen depletion) is that given the different polarisability of the Si–Si and Si–O bonds, the refractive index in the substoichiometric region would be larger than the value of 1.462 assumed when using ellipsometry to determine the oxide film thickness. The presence of regions with larger indices, however, leads us to conclude that we have probably overestimated the thickness associated with any given point (since we essentially measure the product refractive index times thickness). Consequently the "real" interfacial region would in fact be narrower than we have estimated (≤ 1.6 nm).

We have measured the oxide film thickness dependence of the LO and TO mode frequencies associated with the bridging oxygen asymmetric stretch and demonstrated that in the near-interfacial region the oxide is substoichiometric rather than simply denser than in the bulk of the film. Deconvolution of the infrared spectra suggests the region over which the stoichiometry varies is ≤ 1.6 nm, a value approximately 1/3 of the apparent distance which one estimates if spectral deconvolution is not performed. The exact nature of the substoichiometry and bonding in this region requires further investigation.

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