Modulation of the Amorphous Structure of SiO_2/Si(001) – Part II

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Introduction

Amorphous silica (SiO_2) is a useful material in the electronics industry. Recently there has been an increased interest in replacing the SiO_2 gate dielectric, due to the necessity of thickness reduction faced by the semiconductor industry. An important concern, notwithstanding the advantageous functional properties of this oxide [1], is the high leakage current obtained upon film oxide thinning [2]. This SiO_2-Si system has been carefully studied with various experimental techniques [3-6] and by theoretical examinations [7-9], but as indicated in prior investigations [10], the amorphous structure factor of thin SiO_2 requires further attention. We are concerned about investigating, primarily, changes in the SiO_2 first sharp diffraction peak (FSDP) when it grows on Si(001) substrates, as well as other structural ordering that arises throughout thin SiO_2 films. Our findings show that the FSDP modulation adjacent to the interface is stronger in the nearby interface but statistically vanishes at the surface region, in a 500 Å SiO_2 film.

Methods and Materials

The thin-film samples investigated were prepared at North Carolina State University, with an RCA clean procedure that leaves a native oxide on the p-type Si(001)-oriented wafers from Okmetic. After being cleaned, the wafers were loaded into a tube furnace for thermal oxidation at 950°C for 66 minutes in order to produce a 500-Å film (as measured from ellipsometry). The samples were cleaned and placed inside a cryostat at 10K to suppress the thermal diffuse scattering (TDS) contribution. The cleaning procedure included an acetone bath, followed by rinses with ethanol and deionized water. Subsequently, flowing nitrogen dried the sample surface. This cleaning procedure attempted to remove possible contamination [4] observed in the 100-Å film. To study the depth-dependence of the film, a Braun position-sensitive detector (PSD) and a slit, oriented perpendicular to the sample surface in grazing incidence diffraction geometry, were used. The PSD resolution allowed us to record scattered photons between 0.176° below and 0.848° above the critical angle, α_c = 0.174° (at λ = 1.239 Å) for two different incident angles, 0.15° and 0.25°. The sample surface was rotated about its normal axis, and a series of radial scans were taken at intervals of 10° to collect scattered photons from the sample surface and entire-film regions of interest (ROIs) (surface-ROI and film-ROI, respectively) shown in Fig. 1, to investigate the FSDP azimuthal dependence.

Results

Figure 1 shows the contour plot of a PSD radial scan. The peak at $Q \cong 1.5$ Å^{-1} is the glass FSDP. At $Q \cong 3.27$ Å^{-1}, the narrow peak shows the Si(220) reflection (right side of Fig. 1). The plot in the lower half of Fig. 2 shows the intensity variations exhibited by the entire film contribution. As observed in the 100-Å SiO_2 film [14], there is a fourfold intensity modulation of the FSDP. Additionally, Q reaches a maximum of 1.485 Å^{-1} along the Si<110> (where the FSDP is maximum), gradually decreasing to Q = 1.455 Å^{-1} (where the FSDP is minimum, at $\phi \cong 65°$ and 155°). Thus, for the 500-Å film, the compression of the SiO_2 structural units is about 2%, when compared with the FSDP of standard vitreous silica. On the other hand, the surface region of the analogous profile (upper half of Fig. 2) shows considerably lower intensity (70% decrease) and has a statistically null FSDP fourfold modulation. The α_i = 0.15° data yielded qualitatively analogous results, but with lower counting statistics.

Truncation rod measurements along the (11L) crystal truncation rod (CTR) of Si disclose the presence of a crystalline peak at L = 1.455 reciprocal lattice units,

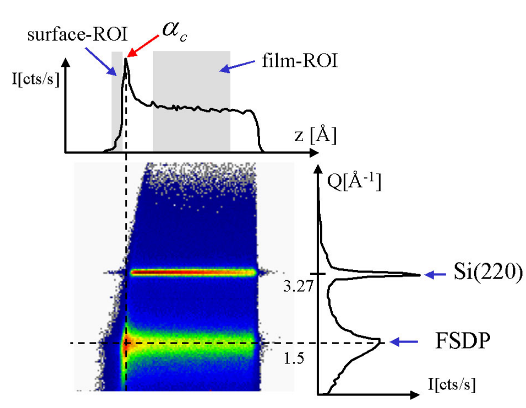

FIG. 1. Contour plot of a PSD data set (along Si[110]).

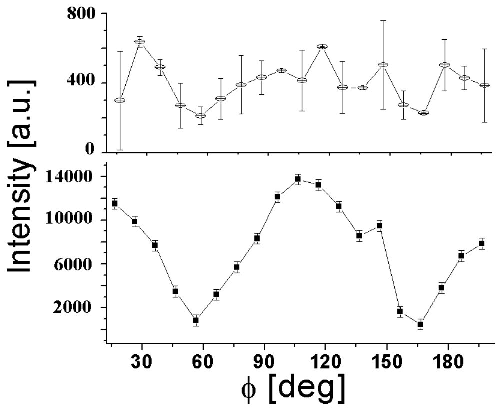

FIG. 2. FSDP intensities at their corresponding ϕ-positions, at α_i = 0.25. Upper: surface-ROI, Lower: entire film-ROI.

together with its Laue oscillations. Those oscillations match the 500-Å film thickness [12, 13].

Discussion

In comparison to the 8% compression observed in the 100-Å film [10], the 2% compression measured in the 500-Å film suggests a relaxation of the SiO_2 structural units. (Note that films grown at lower temperatures are thinner and expected to withstand higher compression.)

The measurements reported here may indicate that the structural correlations of the SiO_4 tetrahedral units [11], enhanced at the interface, can lead to further ordering in the glassy film. The ordering may start from a preferential alignment along the Si<110> through some crystal-like interfacial layer, matching to a great degree the Si<110> distance (therefore the FSDP modulation) and propagating (diminished) toward the film surface. This conclusion is based on a preliminary analysis of the CTR data, which require supplementary analysis and additional measurements.

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