Nucleation of atomic-layer-deposited HfO_2 films, and evolution of their microstructure, studied by grazing incidence small angle x-ray scattering using synchrotron radiation

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We report the results of grazing incidence small angle x-ray scattering experiments on the nucleation and growth of atomic layer deposited HfO_2 films. The scattering features are internal (porosity) and external (roughness) surfaces. Films grown on H-terminated Si exhibit greater scattering than films grown on chemically oxidized Si. The films grown on H-terminated Si may be as much as 50% porous. Characteristic scattering feature sizes are those of the film nuclei, about 2 nm, which then coalesce and become inherited features of the films. Films grown on chemically oxidized Si are observed to coalesce at about 25 growth cycles. *© 2006 American Institute of Physics*.
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Atomic layer deposition (ALD) is a commercially important film growth technique that enables highly accurate growth of ultrathin layers.[1,2] It is the technique of choice for high-κ gate dielectrics,[3,4] and has been used for other Si microelectronics applications as well.[5–7]

In this letter we report the use of grazing incidence small angle x-ray scattering (GISAXS) to study the nucleation and growth of ALD HfO_2 films. GISAXS is an ideal technique to determine the size and shape of nanostructures in thin films,[8] and has been used to advantage to study phase decomposition of thin Hf–Si–O films.[9] In this work, HfO_2 was chosen due to its importance as an alternate gate dielectric to SiO_2; further, our earlier research[3] has shown that two distinct ALD growth modes may be observed, depending upon the pretreatment of the Si substrate on which the films are grown. Growth on chemically oxidized (Chemox) Si, characterized by a high density of Si–OH groups, resulted in linear growth (with number of cycles) and smooth, relatively planar films. Growth on hydrogen terminated (H-term) Si, characterized by few Si–OH groups, resulted in parabolic growth behavior, islanded growth and rough films. Linear growth is important for microelectronic applications, such as gate dielectric and barrier layer films, because it results in a continuous, coalesced film of minimum thickness. On the other hand, films of sufficient roughness are of interest as catalysts, where surface area is all important.

The goal of this work was to use GISAXS to understand nucleation and growth in films grown by either mode. Two sets of ALD HfO_2 films (Table I) were grown, on Chemox or H-term Si, at 300 °C using $HfCl_4$ and H_2O, on 200 mm Si (100) wafers. After growth, the HfO_2 coverage was measured by Rutherford backscattering (RBS). Then, x-ray scattering measurements were made at sector 1-BM at the Advanced Photon Source at Argonne National Laboratory. Both GISAXS and reflectivity measurements were carried out in grazing-incidence reflection geometry using an incident x-ray wavelength, λ, of 0.132 nm. Each measurement interrogates structure in the direction of the scattering vector, $\mathbf{q}$, which bisects the incident and scattered (or reflected) beam. GISAXS was measured with a two-dimensional charge coupled detector for incidence angles between 0.1° and 0.6°, in 0.05° increments. Thus, with a sample to detector distance of 1515 mm, GISAXS data were obtained in the $\mathbf{q}$ range of 0.3–5 nm^{-1}. GISAXS, measured with $\mathbf{q}$ perpendicular to the substrate, yields information on the HfO_2 through-thickness microstructure, and measuring with different glancing angles reveals changes in microstructure with depth into the film. Intensity measured along other azimuthal directions yields

TABLE I. HfO_2 films used in this study.

Substrate preparation	ALD cycles	Coverage (10^{14} HfO_2/cm^2)	Monolayers of HfO_2[a]	Scattering feature size, nm (±0.1 nm)
Chemically oxidized (Chemox) Si	1	4.19	0.5	1.9
	3	6.74	0.7	2.1
	5	9.39	1.0	2.0
	9	14.7	1.6	2.2
	15	23.0	2.5	2.3
	25	35.9	3.9	2.3
	60	78.1	8.5	2.4,4.9
Hydrogen terminated (H-term) Si	5	1.09	0.1	1.8
	20	7.00	0.8	2.2
	30	14.8	1.6	2.5
	40	26.8	2.9	2.8
	50	41.4	4.5	2.4,3.9
	80	87.7	9.6	2.5,5.1
	140	No data	No data	2.5,4.9,7.7

[a]Equivalent monolayers of HfO_2; a monolayer of HfO_2 contains 9.15×10^{14} Hf/cm^2.

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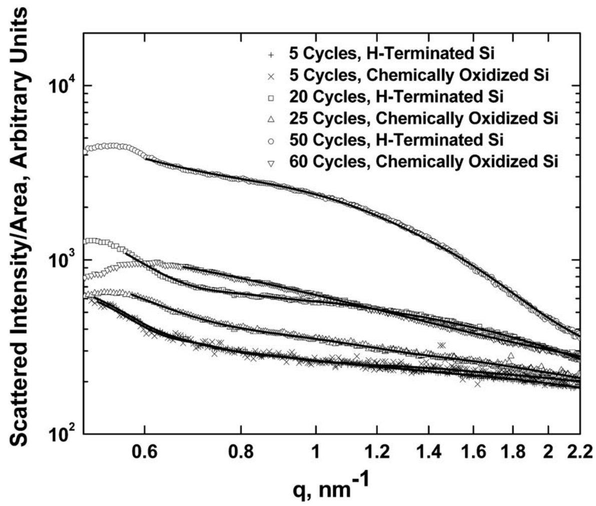

FIG. 1. Small angle scattering intensity curves, per unit area, for selected samples, showing enhanced scattering from HfO_2 grown on H-term Si. Azimuthal angle range is 45°–60°, and grazing incidence angle is 0.35°. Solid curves show excellent fits to the data.

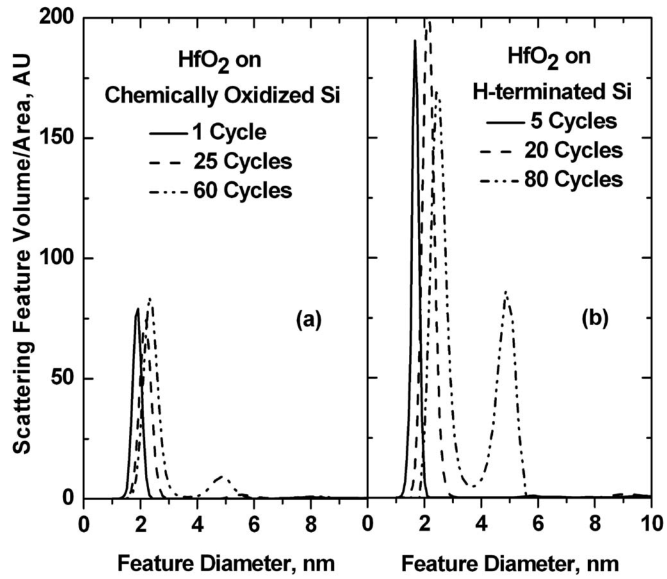

FIG. 2. Scattering feature size distributions, per unit area, for selected samples: (a) 1, 25, and 60 cycle samples grown on Chemox Si and (b) 5, 20, and 80 cycle samples grown on H-term Si.

information on the in-plane microstructure. The GISAXS data were sector averaged in 15° wide sectors around the unscattered beam direction. Complete experimental details of GISAXS studies may be found elsewhere.[10–12]

Specular reflected intensity was measured with the incident beam collimation and linear detector slits set to equal angles of grazing incidence and specular reflection. The intensity was measured as a function of angle over the range from 0° to 6°, corresponding to **q** values perpendicular to the substrate of $0-10\ \mathrm{nm}^{-1}$. The angular resolution was 0.015° with respect to the sample plane, and the critical grazing angle was determined to be $0.17° \pm 0.05°$. The reflectivity data were analyzed using the IMD[13] software package[14] to determine the mean parallel-sided HfO_2 layer thickness.

Figure 1 shows typical GISAXS data for similar cycle HfO_2 layers grown on Chemox and H-term Si. In principle, these data must be corrected for refraction and reflection effects related to the experimental geometry.[10–12] However, for the present case, corrections for refraction and incident beam normalization vary negligibly across the **q** range of interest. Also, with an incidence angle of 0.35°, the entire ALD film thickness is sampled, and the correction for the sampling volume is calculated to vary by less than 6%. Thus, the corrections can be omitted provided that, when comparing results from different films, the scattered intensity is attributed to a given area of film coverage, rather than film volume. In Fig. 1, the scattered intensity clearly increases with increasing ALD cycles, and except for relatively thin, discontinuous films (five cycles), is more intense from the films grown on H-term Si. The scattering is not simply due to the amount of material present, but rather to the way in which it coalesces in the film. The scattering contrast is dominated by the HfO_2/air interfaces, due to the high electron number density of HfO_2.[15] For example (Fig. 1, Table I), the 50 cycle H-term film has about half the HfO_2 coverage ($4.14 \times 10^{15}\ \mathrm{Hf/cm^2}$) of the 60 cycle Chemox film ($7.81 \times 10^{15}\ \mathrm{Hf/cm^2}$), but scatters about four times more intensely. The actual scattering features are internal surfaces (porosity) present in the layers, which result from coalescence of the HfO_2 nuclei, as well as external surfaces associated with film surface roughness. The size distribution of features in the film that give rise to the GISAXS data may be determined using the entropy-maximization, size-distribution algorithm, MaxEnt,[16] which has been applied directly to the GISAXS data. Figure 2 shows scattering feature size distributions for typical films deposited on Chemox and H-term Si (see also Table I). The mean feature size should relate closely to the HfO_2 coalesced nuclei size, whereas the GISAXS intensity is related to the internal and external surface area of the film. For either substrate preparation, the size of the predominant scattering feature does not change appreciably with number of cycles, and is approximately the same for either case. For small cycle films that have not coalesced, the features are clearly the film nuclei, and are about 2 nm in size. This compares well with observations in the literature.[17,18] A coarser scattering feature appears after large numbers of ALD cycles but before that, the films maintain a scattering feature size of roughly the HfO_2 nuclei size, which must correspond to the nuclei that coalesced into the film; ALD HfO_2 films cannot grow in a layer-by-layer fashion, since less than 1 ML is deposited per growth cycle.[19] Note in Fig. 2 that the apparent fraction of the scattering features is larger for the H-terminated films, indicative of a greater internal and external HfO_2/air surface area.

In Fig. 3, the volume of the scattering features per unit film area, normalized to that for the 25-cycle film grown on Chemox Si, is plotted as a function of HfO_2 layer thickness (calculated from the RBS data). Chemox Si films show relatively little change with film thickness, although once the film has coalesced (after about 1 nm),[3] there is a modest linear increase in the scattering with film thickness. Since the scattering is attributed to the internal and external surface area, one may argue that the Chemox Si films grow with little porosity and minimal external roughness. Earlier work has found that as-grown HfO_2 films grown on Chemox Si are about 90% dense,[3] while more recent work suggests that such films are almost 100% dense.[20] The films grown on H-term Si show a very different behavior. Initially, films grown on either substrate preparation show little scattering, but with increased coverage the scattering increases dramati-

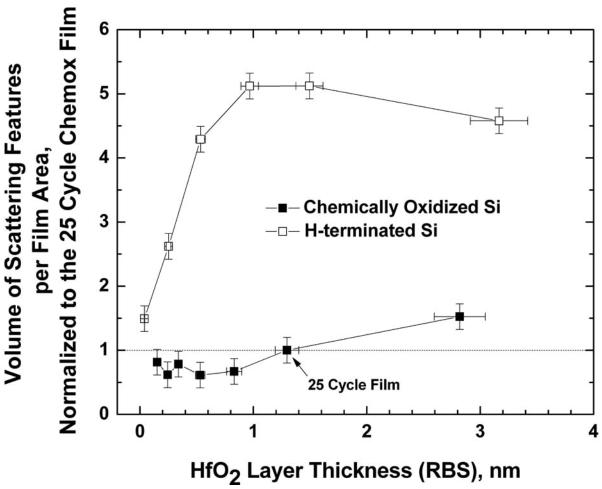

FIG. 3. Volume of scattering features per film area, normalized to the 25 cycle film grown on Chemox Si, as a function of layer thickness.

cally for films grown on H-term Si. However, the scattering from films grown on H-term Si does not continue to increase with film thickness above 1 nm (Fig. 3), even though such a film is only about 30% coalesced.[3] This suggests that the film surface roughness does not further change as it thickens and coalesces, and that the films grown on H-term Si may be as much as 50% porous.

Turning to the reflectivity data, in Fig. 4 we have plotted film thickness, measured by reflectivity, as well as calculated from the RBS coverage measurements, as a function of ALD cycles for both sets of samples. Reflectivity is only sensitive to those portions of the film whose surfaces are parallel to the interface, as it is the interference of the reflected beams from the top surface and the film/substrate interface that gives rise to the oscillations from which one calculates the thickness. Thus, the measured reflectivity thickness is likely to be thicker than the average RBS thickness, until the film is sufficiently thick (coalesced and two-dimensionally continuous). This is in fact observed in Fig. 4(a), where coalescence

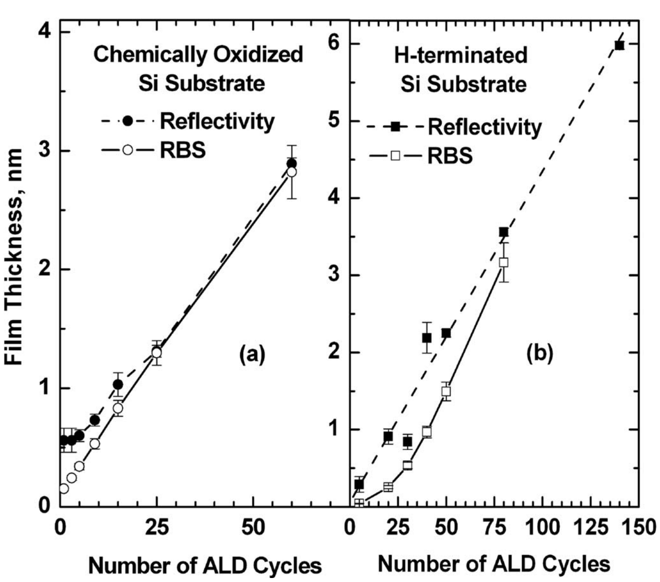

FIG. 4. Comparison of HfO_2 layer thickness determined from reflectivity curves and RBS measurements, for layers grown on (a) Chemox Si and (b) H-term Si. The curves are guides for the eye.

may be observed to occur for Chemox Si films at 25 cycles, corresponding to about 1.3 nm film thickness. That two-dimensionally continuous films grown on chemically oxidized Si exist after 25 cycles, is consistent with earlier time-of-flight secondary ion mass spectrometry data.[3] H-terminated films do not coalesce until many more deposition cycles, as shown in Fig. 4(b), where the two thickness measurements do not coincide until >75 cycles, due to their internal porosity and roughness.

In conclusion, we report GISAXS results on the nucleation and growth of ALD HfO_2 films. The scattering features can be attributed both to porosity in the films, resulting from film coalescence, and to the external surface area, or roughness. The H-term films have greater total surface area, exhibit greater scattering, and may be as much as 50% porous. Characteristic scattering feature sizes are those of the film nuclei, which then coalesce and become inherited features of the films. The nuclei size is about 2 nm. Films grown on Chemox Si are seen to coalesce at about 25 cycles consistent with literature data.

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