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GISAXS study on the annealing behavior of sputtered HfO_2 thin films

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Abstract

Grazing Incidence Small-Angle X-ray Scattering (GISAXS) is a versatile technique for the analysis of nano and micro thin films surfaces. The scattering data depend strongly on the form and distribution of the scattering objects. In the present work GISAXS is used to study hafnium dioxide (HfO_2) thin films deposited by magnetron sputtering using different deposition processes and post-deposition annealing conditions. Two distinct types of 15 nm thick samples were produced using different sputtering targets and different gas mixtures. The GISAXS results show that the ellipsoids that compose the thin films present a reduction in their size for both samples sets. For the sputtered Hf metal target samples, the ellipsoid diameter value shifted from 9 nm (as-deposited) to 6 nm following a 800 ^oC thermal treatment. For the sputtered HfO_2 target samples the diameter value shifts from 19 nm (as-deposited) to 3 nm after a 800 ^oC anneal in oxygen. The size distribution, for both sets of samples, follows a Gaussian distribution function.

Introduction

In CMOS technology large numbers of MOSFET's are integrated onto a small chip. To continue scaling and increase performance, the number and density of transistors on each chip requires the reduction of the individual MOSFET device dimensions. This continuous scaling has driven the SiO_2 gate dielectric below 2 nm causing the exponentially increasing gate leakage current to become unmanageable [1-5]. Many materials have been studied to replace SiO_2 as the gate dielectric and hafnium dioxide (HfO_2) has been found to be one of the most promising. Hafnium dioxide have been found suitable to replace SiO_2 because their relatively high dielectric constant (~25), reasonable conduction band offsets (~1.5 eV), thermal stability and for the most part compatibility with CMOS technologies [6,7]. However, many of the physical and electrical properties of this material are not well understood. Differences in these characteristics are very dependent upon the deposition method and subsequent post-processing used. One of the greatest of implementing these films is the difficulty in achieving a good Si/high-κ interface along with a high quality thin film with few defects.

Many deposition methods have been used to deposit high-κ dielectric thin films and these include physical sputtering and atomic layer deposition (ALD) [8]. The advantages of ALD include good thickness control, high conformality and a low temperature deposition. However, ALD typically has a low deposition rate which is a direct consequence of the atomic layer by layer film growth. For most ALD processes only a fraction of a monolayer is deposited per cycle [9]. While ALD produces precise monolayer control, the process times tend to be longer which can add to production costs. On the other hand magnetron sputtering is a good and cheaper alternative for HfO_2 deposition in MOS structures. Sputtering is a low temperature technique that may allow a better understanding of oxidation process of these thin films. Reactive gases (such as oxygen) can be mixed with Ar in order to form a reactive plasma and hence reactive sputtering. Therefore, the thin film stoichiometry can be improved and properties such as resistivity and permittivity can be controlled [10].

Extensive characterization of such materials in thin film form is crucial, not only for the selection of the alternative gate dielectrics and processes, but also for the development of appropriate metrology for these high-κ films on silicon (and other) substrates. Precise control of growth parameters is critical to achieve a thin film with the desired characteristics and for good process reproducibility. The details of the processing can dictate different physical properties resulting from crystallites of different shape and distribution. Common examples of electronic and physical characteristics being controlled by size effects are found in quantum wires and quantum dots [11]. To investigate the processing dependence of the size, shape and distribution of crystallites within these films, Grazing Incident Small Angle X-ray Scattering (GISAXS) was used for morphological characterization. In the present work GISAXS was used to study the annealing behavior of sputtered hafnium dioxide (HfO_2) thin films deposited by magnetron sputtering using either HfO_2 target or an Hf target in an oxidizing ambient. These films then went through a series of post-deposition annealing.

Experimental Details

Two 15 nm thick samples were produced using different sputtering targets and different gas mixtures. The details of the two samples are given in Table I below.

Table I. Deposition conditions.

	Target	Ambient	Pressure	Power Density
Sample 1	Hf	$Ar:O_2$ (1:4)	12 mTorr	3.7 W/cm²
Sample 2	HfO_2	Ar	12 mTorr	3.7 W/cm²

Post-deposition rapid thermal annealing (RTA) was performed on separate sample pieces in O_2 at atmospheric pressure, for 90 s at 400 °C, 600 °C and 800 °C

The GISAXS measurements were carried out at the national synchrotron light laboratory (LNLS) at Campinas, Brazil. The samples were illuminated for 10 seconds by an 8 KeV ($\lambda \sim$ 1.55 Å) synchrotron X-ray beam with a grazing incidence angle $\theta_i = 0.35^o$. The distance between the detector and the sample was 617.5 mm. The GISXAS scattering data (images) were captured by a Pillatus detector with a resolution of 70 DPI.

Discussion

The data analysis was made using FitGISAXS software [12] within the framework of the distorted-wave Born approximation (DWBA) [13]. The thin film was modeled as ellipsoid islands supported on a semi-infinite Si substrate. This structure has been chosen based on AFM images (Figure 1). It was assumed that there was no correlation between the type, size and shape of the scattering object and its position (This is referred to as the “decoupling approximation”) [13]. The organization of the scatterers was assumed to be random due to the nature of the

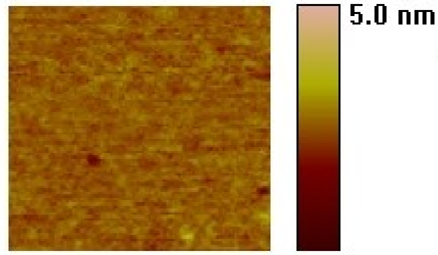

Figure 1 AFM image of sample surface

sputtering deposition process. The size distribution was assumed to have a Gaussian distribution function. The Gaussian distribution was the simplest distribution function that fitted the experimental data.

In Figure 2 the GISAXS scattering data is shown which illustrates the change in the intensity at $q_z = 3\ nm^{-1}$ as a function of the annealing temperature. These films were fabricated using Hf metal in an oxygen ambient. The changes in the GISAXS data are due to the changes in the ellipsoid dimensions.

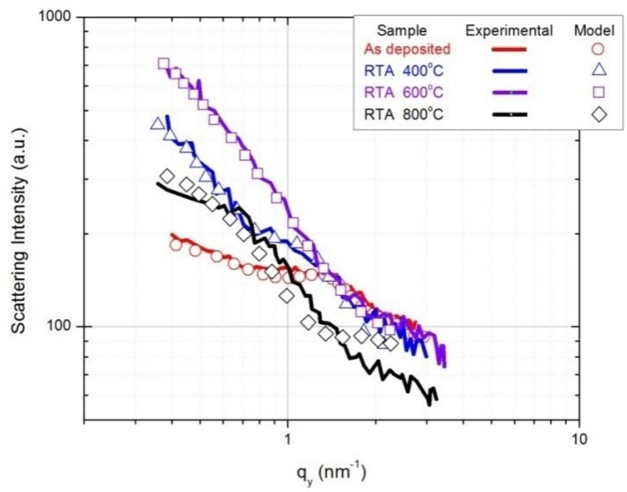

Figure 2. GISAXS evolution for sputtered Hf metal target for as-deposited, 400 °C, 600 °C and 800 °C post deposition annealing.

In Figure 3a) the evolution of the diameter (length along the y axis) is shown as a function of the annealing temperature. The extracted diameter value shifts from 9 nm (as-deposited) to 6 nm for 800 °C. The size correlation as a function of the temperature is shown in Figure 3b). The ellipsoid dimensions are shown to decrease as the temperature increases. At 600 °C the crystallization process has started [14] and the GISAXS data suggest that the scatterers are beginning to coalesce. At 800 °C the volume reaches a minimum and the scatterers dimension are more uniform as shown by the narrow diameter distribution. The dimension of the scatterers and their geometry for the RTA at 800 °C can be compared to HfO_2 thin films deposited by ALD [15, 16].

In Figure 4 the GISAXS data (at $q_z = 3\ nm^{-1)}$ is shown for the sample set sputtered from the HfO_2 target. In Figure 4a) the change in the diameter (length along the y axis) is shown as a function of the annealing temperature. The diameter, extracted from this data, shifts from 19 nm in the as-deposited film to 3 nm for the 800 °C annealed film. As the RTA temperature increases, the diameter of the scatterers (ellipsoids) decreases. It should be noted that the change in the ellipsoid dimension with anneal temperature is distinctly for the two sample sets.

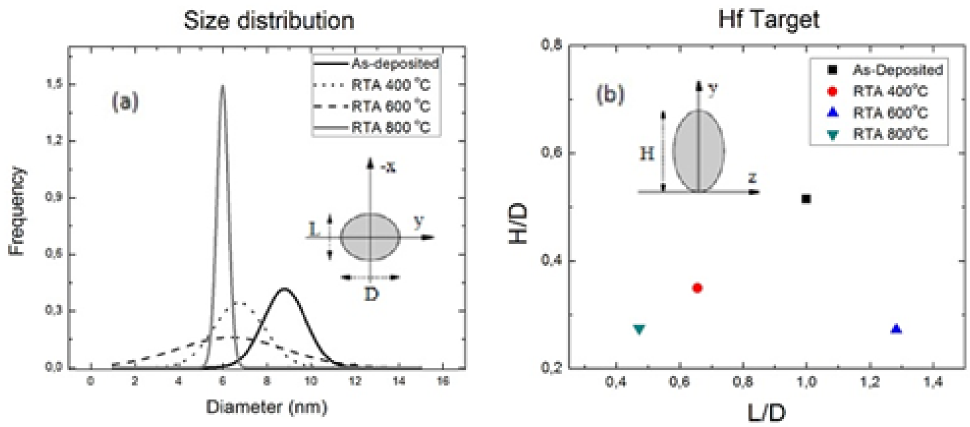

Figure 3. (a) Diameter size distribution and (b) size correlation as a function of the RTA.

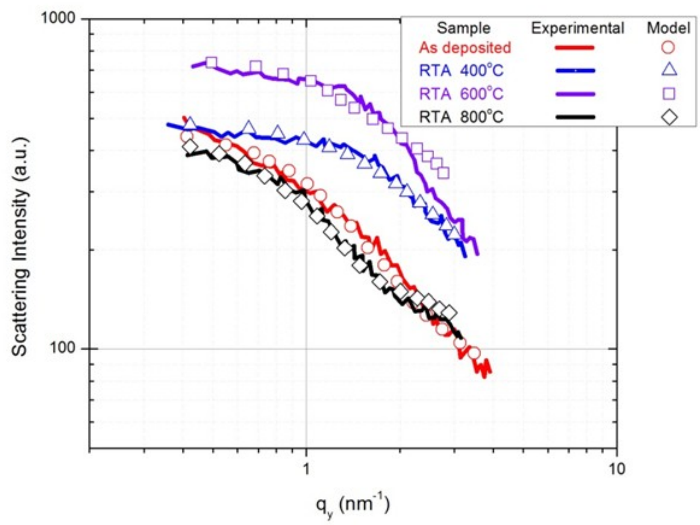

Figure 4. GISAXS evolution for sputtered HfO_2 target for as-deposited, 400 °C, 600 °C and 800 °C post deposition annealing.

For the HfO_2 target films, the diameter of the ellipsoids decreases in contrast to the Hf target films. The diameter of the ellipsoids decrease but also to increase the thin film crystallinity. The uniformity increases with increasing temperature as shown by the distribution width (Figure 5a). However, the distribution at 800 °C is wider than that of the films from the Hf target. In Figure 5b), the size correlation (dependence of the other dimensions on the ellipsoid diameter) is shown as a function of the temperature. The volume of the ellipsoids increase at 400 °C and decreases at 600 °C and 800 °C.

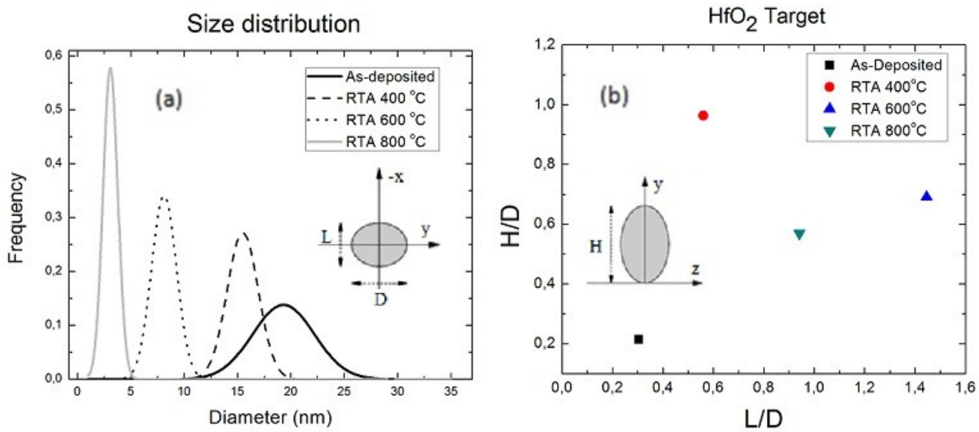

Figure5. (a) Diameter size distribution and (b) size correlation as a function of the RTA.

Conclusions

Grazing Incident Small Angle X-ray Scattering was used to study the behavior of the morphology of the thin HfO_2 films that arise as a function of the deposition conditions and temperature of rapid thermal annealing. The GISAXS data suggest that the HfO_2, thin film nanostructure, for both deposition conditions, maybe be modeled as ellipsoids whose dimensions follow a Gaussian size distribution. As the temperature increases the ellipsoid volume tends to decrease and the uniformity of the size increases.

The GISAXS data for the sputtered Hf target suggests that the ellipsoids coalesce in order to find the best crystal organization minimizing the volume. The data for the HfO_2 target thin films show that the ellipsoid volume are greater than those from the Hf target. At 400 ^{o}C the ellipsoid volume reaches its maximum and decreases for increasing temperatures.

The GISAXS results show that the ellipsoids that compose the thin films present a reduction in their size for both samples sets. Perhaps somewhat counter-intuitively, these results suggest a decrease in the density of films with increasing RTA temperature. However, these results are consistent with other published results on ALD, HfO_2 films.

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