Application of non-linear optical second harmonic generation and X-ray absorption and spectroscopies to defect related properties of Hf silicate and Hf Si oxynitride gate dielectrics

K. Gundogdu [a], G. Lucovsky [a,*], K.-B. Chung [a], J.-W. Kim [a], D. Nordlund [b]

[a] Dept of Physics, NC State University, 4201 Stinson Dr, Raleigh, NC 27695-8202, USA
[b] Stanford Synchrotron Radiation Laboratory, Meno Park, CA, USA

ARTICLE INFO

ABSTRACT

Three different Hf oxide based dielectrics have emerged as *viable candidates* for applications in advanced ULSI devices. This article focuses on two of these: (i) phase separated Hf silicates with (i) 70–85% nano-crystalline HfO_2 with a nano-grain size <2 nm, and 15–30% $\sim$2 nm non-crystalline SiO_2 inclusions, and (ii) Hf Si oxynitride alloys, the most promising of which has a composition, $(HfO_2)_{0.3}(SiO_2)_{0.3}(Si_3N_4)_{0.4}$ designated as 3/3/4 Hf SiON. X-ray absorption spectroscopy has been applied to identification of defect associated with vacancy structures in phase separated silicates, and network disruption defects in the Hf Si oxynitrides. Optical second harmonic generation is introduced in this article for the first time as a non-invasive approach for detecting macroscopic strain, that is shown to be absent in these low defect density dielectrics, the phase separated Hf silicates, and Hf Si oxynitrides, but present in HfO_2 films, and Hf silicates with lower HfO_2 content, e.g., the 40% HfO_2 film of this article.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Electrical studies of (i) a 1000 °C stable Hf Si oxynitride composition, $(HfO_2)_{0.3}(SiO_2)_{0.3}(Si_3N_4)_{0.4}$, hereafter 3/3/4 HfSiON, and (ii) a chemically phase separated $(HfO_2)_x(SiO_2)_{1-x}$, with $x \sim 0.2$; each have yielded defect densities acceptable for applications as dielectrics in MOS gate stacks. These films have defect densities comparable to defect densities in ultra-thin HfO_2 with a physical thickness of less than 2 nm [1,2]. Additionally, X-ray and γ-ray induced defect densities in 3/3/4 HfSiON are comparable to those of SiO_2 [3]. This paper has identified microscopic aspects of these nano-structure dielectrics that help to explain the low defect state densities. No detectable macroscopic strain determined by nonlinear optical Second Harmonic Generation spectroscopy, SHG, has been detected in the phase separated Hf silicates, and Hf Si oxynitride alloys. The XAS studies, also reported in these INFOS 2009 issue [4], also for the first time have been able to distinguish between mobile and immobile vacancy defects in these and other Hf-based dielectrics with low defect densities.

References [1,2] have narrowed the field of Hf-based dielectrics to three qualitatively different Hf oxide based compositions/structures that have sufficiently low defect densities for applications in scaled Si microelectronic devices. The are (i) ultra thin <2 nm thick nanocrystalline HfO_2, in which the nano-grains are too small to support cooperative Jahn–Teller, J–T, distortions, (ii) optimized non-crystalline 3/3/4 Hf Si oxynitride (HfSiON), as well as other compositions, e.g., 4/4/2 with low defect densities as well, and (iii) phase separated $(HfO_2)_x(SiO_2)_{1-x}$, with $x \sim 0.2$–0.3 [1,2]. Spectroscopic studies have underpinned the qualitative distinguishing properties of these three dielectrics, and spectra have been included in Refs. [1,2], with new results reported in Ref. [4]. This paper extends these studies to one additional spectroscopic approach, non-linear optical SHG [5], that has identified an important and expected correlation between the low defect densities determined by electrical studies, and the low levels of local and macroscopic strain determined optically.

Cooperative J–T effects dominate the properties of many of the elemental and complex oxides that have been addressed for extending Moore's Law scaling and also for introducing increased functionality in Si integrated circuits and systems. This paper applies a new approach to the identification of macroscopic strain. Finally, the identification of mobile and immobile vacancies, and the

microscopic basis for J–T cooperative distortions is based on the concept of symmetry adapted linear combinations of atomic orbitals as a basis for analyzing O K edge spectra [6].

2. Experimental approach and results

Fig. 1 indicates qualitative changes in the O K edge XAS spectra of HfO_2 as a function of film thickness for films annealed at 900 °C. The features in the 2 nm thick film are broad, and differentiation indicates no detectable J–T splittings in either the Hf 5d E_g or T_{2g} features. In contrast physically thicker films indicate J–T degeneracy removal in the band edge Hf 5d E_g state. Defect densities are ~10× lower in the thinner films [1,2]. Fig. 2 compares O K edge XAS spectra for the 2 nm film of Fig. 1, and a 2 nm thick film for a chemically phase separated Hf silicate with ~80% HfO_2 content. Each of these films display no Hf 5d Eg state degeneracy removal and low densities of defects. Fig. 3 contains 2nd derivative O K edge XAS spectra in the pre-edge regime, which indicate quantitatively different spectral features assigned, respectively to fixed or immobile divacancy defects in the 4 nm thick film that displays a Jahn–
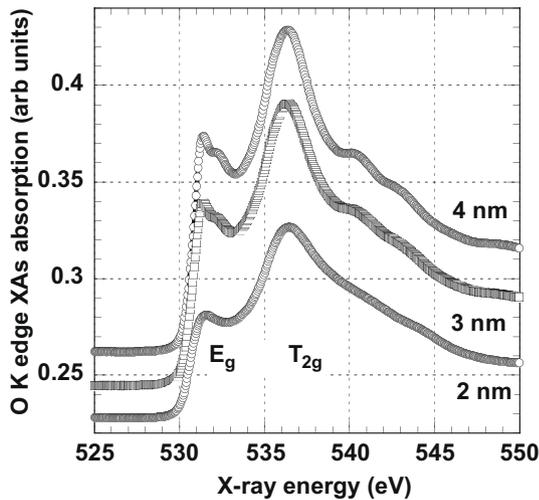
Fig. 3. Highest transitions for divacancy defects in the pre-edge 2nd derivative XAS O K edge spectra for 4 nm thick and 2 nm thick HfO_2 thin films.

Fig. 1. O K edge XAS spectra for HfO_2 films annealed at temperatures in excess of 700 °C for three different physical film thicknesses: 2 nm, 3 nm and 4 nm.
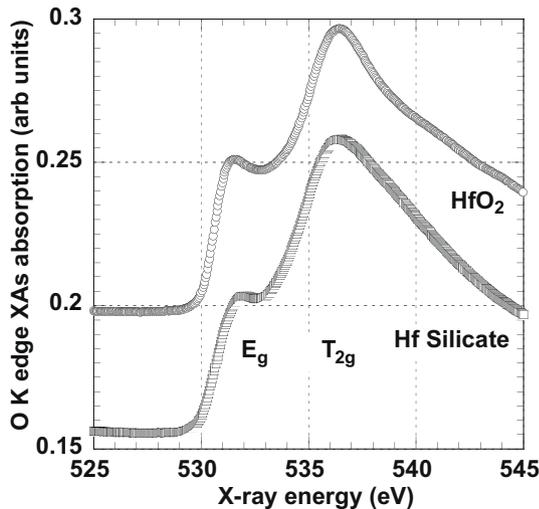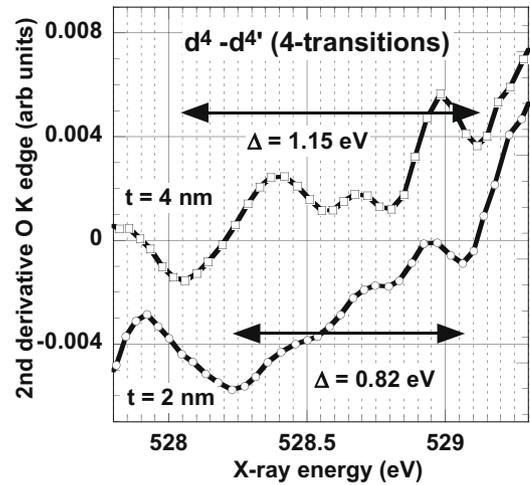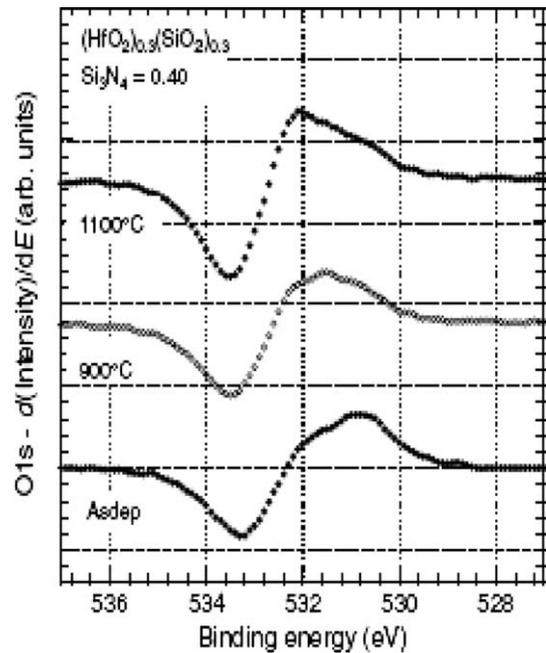
Fig. 4. The suppression of chemical phase separation in a 3/3/4 Hf Si oxynitride for annealing to temperatures in excess of 900 °C using O atom 1s XPS.

Fig. 2. Comparison between O K edge XAS spectra for 2 nm thick films: HfO_2 and a phase separated Hf silicate with 80% HfO_2 content.

Teller distortion, and mobile divacancy defects in the 2 nm thick film that does not. Fig. 4 presents spectroscopic evidence in the form of O 1s XPS spectra that establish the stability with respect to chemical phase separation (CPS) in a 3/3/4 HfSiON film. This stability correlates with optimized electrical performance, i.e., low defect state densities [1].

Fig. 5 is schematic of the experimental set-up for the non-linear optical SHG measurements. A similar experimental set-up was employed in Ref. [7]. These experiments are performed in the reflection geometry by using p-polarized 100 fs pulses with 808 nm (or 1.53 eV photon energy) central frequency out of a Ti:Sapphire oscillator as ω_1, the frequency to be doubled. The pulses are focused onto the sample with 45 degrees of incidence angle. A colored glass filter, which eliminates the fundamental beam, is followed by a polarizer for analyzing the p-polarized component of the SHG signal radiated from the sample. A photo multiplier
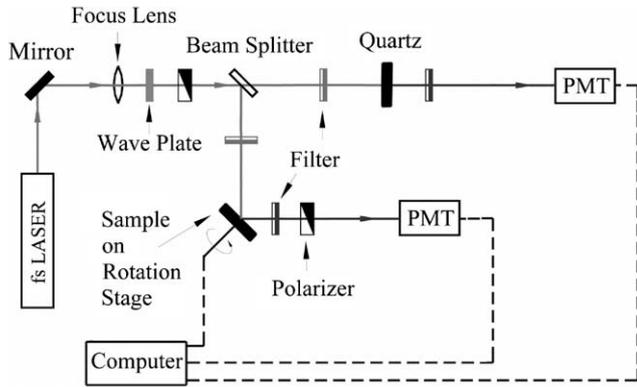
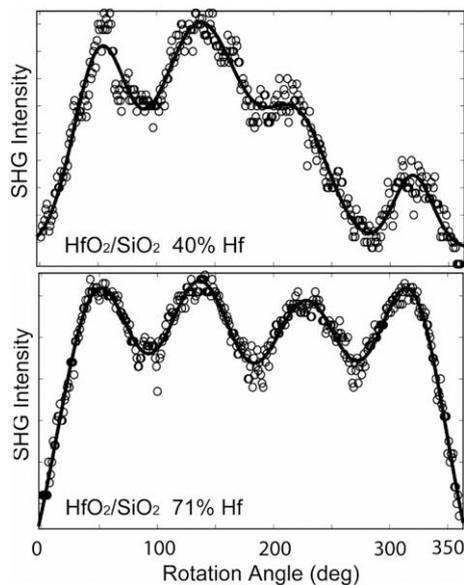**Fig. 5.** Schematic diagram of experimental set-up for non-linear optical SHG in the reflection geometry mode.

Fig. 6. SHG signals for 71% Hf silicate and 40% Hf silicate phase separated alloys as a function of the rotation angle.
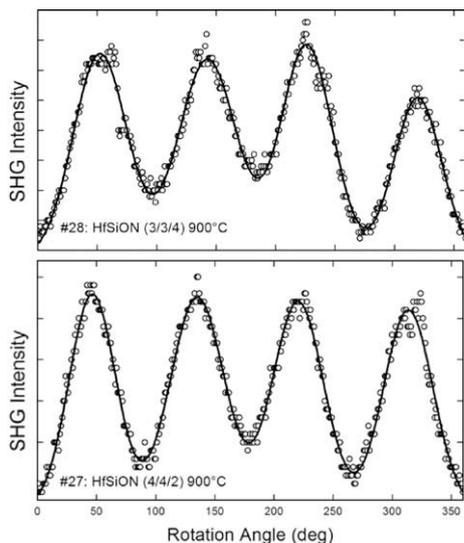

Fig. 7. SHG signals for 3/3/4 and 4/4/2 Hf Si oxynitride alloys as a function of the rotation angle.

tube in the photon counting mode detects the SHG signal intensity as the sample is rotated azimuthally 360° with 1° increments. In order to normalize the SHG signal and reduce the effect of long term laser intensity fluctuations, a beam splitter is used to direct a weaker beam to a quartz substrate and use the SHG generated in the quartz as a reference. The doubled frequency, ω_2, is 404 nm, or 3.06 eV.

Figs. 6 and 7 summarize the SHG results. The four peaks in the data clearly indicate a four-fold rotational symmetry which is fit to four Gaussians. The peak widths and intensities are more evenly distributed in 71% Hf silicate than in the 40% Hf silicate. In the 40% Hf silicate there is more scattering, and three of the four peaks are merged leaving only one of the peaks as a distinct feature. Both Hf Si oxynitride films in Fig. 7 indicate four-fold rotational symmetry with well-separated and distinct features, except of a modest amount of *sagging* for the 3/3/4 sample.

3. Analysis of optical SHG results

The Si(100) surface exhibits four-fold symmetry, and the films in Figs. 6 and 7 are transparent at the photon energies of ω_1(1.53 eV) and the doubled response at ω_2(3.06 eV). The strong four-fold modulation in the oxidized Si(100) is due to Si–O bonds at the interface between Si(100) and Si [8] This means that the azimuthal dependence of the SHG signal for the high-k Hf silicates and the Hf Si oxynitride alloys due to Si-O bonds at the interface between Si(100) which would then predict a four-fold rotational symmetry it this bonding symmetry remained in tact. The peaks in the SHG pattern are directly related to the interface bonds. Therefore the changes in the intensity of the peaks and their widths directly indicate how the bonds are organized. The high HfO_2 content phase separated Hf Silicates, and the Hf Si oxynitride alloys display relatively low defect densities, correlating with dielectric layers that are relatively free of macroscopic strain. This is not the case for the 40% phase separated Hf Silicate alloys.

Based on studies of Si(100) surfaces, the dependence of the SHG signal on azimuthal angle for a strain-free surface, plotted as a function of the rotation angle displays four peaks separated by 90°. Significant deviations from this pattern, both in relative amplitude and in the angular dependence are indicative of either a chemically or physically strained Si surface, or a transparent over-layer that is strained. Proceeding in this way, the distorted pattern for the 40% silicate indicates an over-layer with strain-induced birefringence, whist the pattern for the 71% silicate indicates a strain-free over-layer. The traces in Fig. 7 for 3/3/4 and 4/4/2 Hf Si oxynitride layers also display four-fold peaks separated by 90°, indicating these films are essentially free of macroscopic strain as well.

4. Summary and conclusions

The results presented in Figs. 1 and 2, respectively establish (i) changes in the character of the band edge E_g state in O K edge XAS spectra as a function of film thickness for HfO_2 thin films annealed at 900 °C in Ar; the two thicker films display this spitting, whereas the 2 nm film does not, and (ii) similarities between the OK edge spectra for the 2 nm thick film in Fig. 1 and a phase separated Hf Silicate films with 80% HfO_2 in nano-grains <2 nm thick, and 20% SiO_2 in 2 nm SiO_2 clusters [1,2]. The results reported in Refs. [1,2], correlate the XAS spectral data with electrical measurements. The 3 and 4 nm thick films exhibit tunneling into conduction band edge traps, and a temperature dependent current-voltage characteristic, whereas the 2 nm thick films exhibit a very weak temperature dependence similar to 2 nm thick SiO_2. Similar temperature independent tunneling is also found in MOSCAPs with 2 nm thick,

phase separated 80% HfO_2 silicates. Spectroscopic studies reported in Ref. [4], and displayed in Fig. 3 indicate differences in the band edge defect spectral features. The defects in the 4 nm thick HfO_2 film have a 10 fold higher density, $\sim 10^{12} \, cm^{-2}$, and a larger crystal field separation, consistent with fully coordinated divacancy bonding, whereas the defect density is reduced in the 2 nm thick HfO_2 film, and defects exhibit a smaller crystal field splitting assigned to an incompletely coordinated divacancy that is mobile.

The differences in the rotation angle dependence of the optical SHG response between the 2 nm phase separated Hf silicate with 80% HfO_2 content, and a 40% HfO_2 phase separated silicate with a grain size comparable to that in a 4 nm thick HfO_2 film have been displayed in Fig. 6. As noted above azimuthal dependencies of the SHG response for the 71% Hf Silicate film, and the two Hf Si oxynitride films establish that these films are relative free of macroscopic bond strain. This confirms a relationship between macroscopic strain, and defects which limit performance, and defect precursors which have an impact on device reliability.

The compliant behavior for the 3/3/4 HfSiON is for a non-crystalline film in which Hf and its nearest neighbor O-atoms are in a distorted and compliant tetrahedral environment meeting the 16% volume percolation criterion of Scher and Zallen [8]. Analysis of O K edge spectra for the 4/4/2 Hf Si oxynitride alloy indicates a similar compliant bonding environment for the Hf atoms, which is this instance occupy about 35% of the Si sites, corresponding to a 35% volume fraction, also above the precolation limit for macroscopic strain relief.

References

[1] D.K. Chen et al., IEEE Trans. Nucl. Sci. 54 (2007) 1931.
[2] G. Lucovsky et al., Jap J. Appl. Phys. 46 (2007) 1899.
[3] G. Lucovsky, J. Mol. Struct. 838 (2007) 187.
[4] G. Lucovsky et al., these proceedings.
[5] U. Emmerichs et al., J. Vac. Sci. Technol. B 12 (1994) 2489.
[6] F.A. Cotton, Chemical Applications of Group Theory, second ed., Wiley Interscience, New York, 1963. Chapter 8.
[7] G.D. Powell et al., Phys. Rev. B 65 (2002) 205320.
[8] H. Scher, R. Zallen, J. Chem. Phys. 53 (1970) 3579.