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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

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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% nanocrystalline HfO_2 with a nano-grain size <2 nm, and 15–30% ~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.

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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 ~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 non-linear 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 ~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

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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–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].

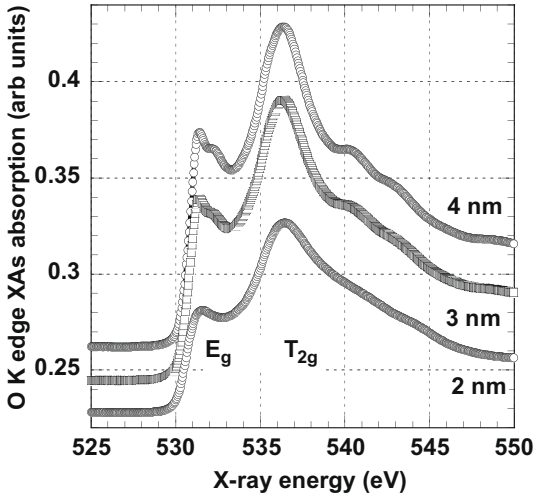

Fig. 1. O K edge XAS spectra for HfO_2 films annealed at temperatures in excess of 700 °C for three different physical film thicknesses: 2 nm, 3 nm and 4 nm.

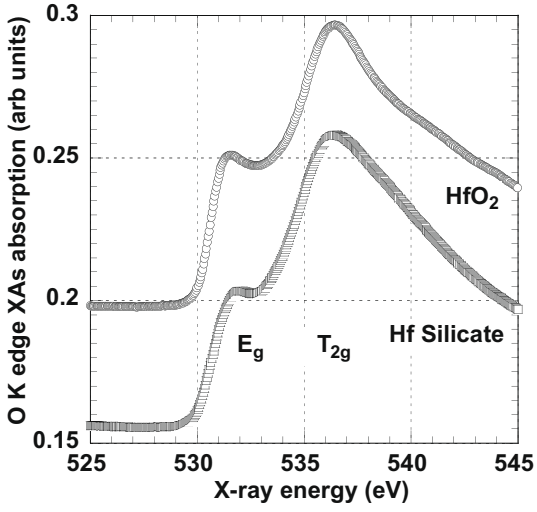

Fig. 2. Comparison between O K edge XAS spectra for 2 nm thick films: HfO_2 and a phase separated Hf silicate with 80% HfO_2 content.

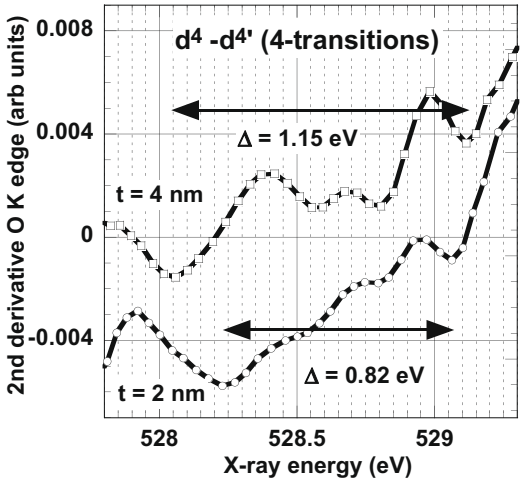

Fig. 3. Highest transitions for divacancy defects in the pre-edge 2nd derivative XAS O K edge spectra for 4 nm thick and 2 nm thick HfO_2 thin films.

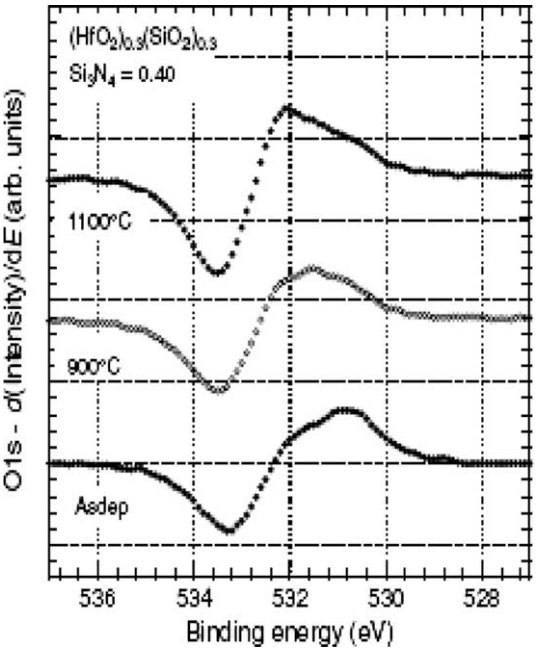

Fig. 4. The suppression of chemical phase separation in a 3/3/4 Hf Si oxynitride for annealing to temperatures in excess of 900 °C using O atom 1s XPS.

Fig. 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

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