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Pulsed laser deposition and characterization of Hf-based high-*k* dielectric thin films

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Abstract

The continuous downward scaling of the complementary metal oxide semiconductor (CMOS) devices has enabled the Si-based semiconductor industry to meet the technological requirements such as high performance and low power consumption. However, the ever-shrinking dimensions of the active device, metal-oxide-semiconductor-field-effect-transistor (MOSFET), in the circuit create other physical challenges. The industry standard SiO_2 for the gate region is reaching to its physical limits. New materials with higher dielectric constant are needed to replace the silicon dioxide in these gate regions. One of the candidates for this replacement is Hf-based oxides. In this project, we have used pulsed laser deposition (PLD) to synthesize Hf-based high-*k* dielectric films on Si single crystal substrates with varying deposition parameters and mixtures of HfO_2 and ZrO_2 then used X-ray absorption fine-structure spectroscopy (XAFS) in order to probe the local structure around the Hf metal. The local structural information extracted through XAFS has been correlated with the deposition parameters such as the substrate temperature and the HfO_2, to ZrO_2 ratio in the mixtures.

Keywords: Hafnium dioxide; Pulsed laser deposition; XAFS; High-*k* dielectric

1. Introduction

The continuous downward scaling of the complementary metal oxide semiconductor (CMOS) devices brings important materials challenges in transistor design. One crucial challenge is in the transistor gate region. The unique characteristics, such as superior electrical isolation, low defect density, thermal stability, and better lattice match with silicon have made thermally grown silicon dioxide the best choice for the gate region for years. Unfortunately, with the increased need for higher capacitance (inversely proportional to gate thickness), while maintaining low leakage current (proportional to gate thickness), the semiconductor industry is reaching to the physical limits of SiO_2. In choosing the replacement high-*k* materials for SiO_2 for the transistor gate region several challenging factors should be taken into account such as: a) the dielectric-silicon interface quality and stability b) the relation between the dielectric constant and the energy level configurations (energy band gap) c) energy band offsets, which could lead to an increase in the leakage current d) defect density at the interface. Although the high-*k* dielectric oxides seem to be the most promising candidates for the gate region of the future semiconductor devices, none of the challenges discussed above have been solved successfully so far.

Hf-based oxides are one of the promising candidates for the replacement of SiO_2 [1,2] and have been studied extensively. Previously, HfO_2/Si interface has been shown to be stable with respect to silicide formation [2]. In order to reduce the defect density at the interface, SiO_xN_y has been added between HfO_2 and Si and valence band offsets have been investigated using X-ray photoelectron spectroscopy (XPS) [3]. In recent years, not only HfO_2 films on Si but also combinations of HfO_2, ZrO_2, and Y_2O_3 have been deposited and using pulsed laser deposition (PLD) [4]. Since the amorphous film structure would be more effective in reducing the leakage current [5], pseudobinary systems like $(HfO_2)_x(SiO_2)_{1-x}$ ($x<0.2$), which remains amorphous

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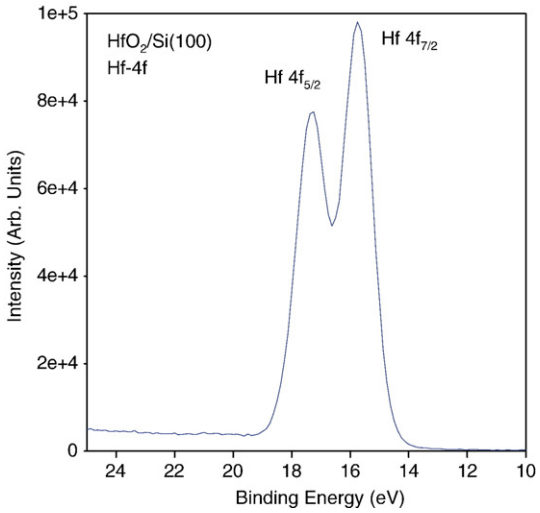

Fig. 1. Hf-4f XPS spectra for the PLD synthesized HfO_2/Si (100) films. The 4f spin-orbit splitting and intensity ratio of $4f_{7/2}$ and $4f_{5/2}$ are in agreement with theoretical expectations.

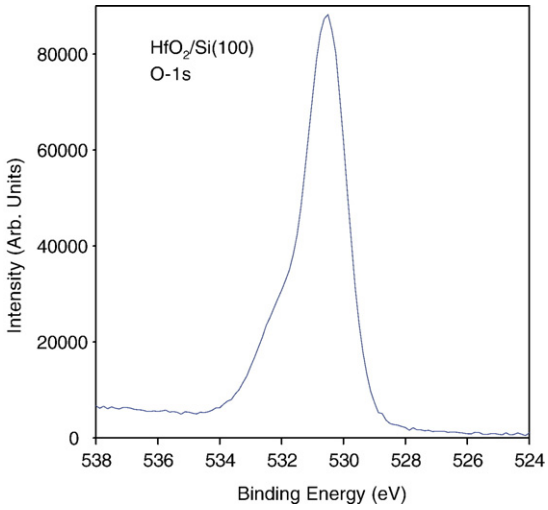

Fig. 2. O-1s XPS spectra for the PLD synthesized HfO_2/Si (100) films. The shoulder above 532 eV may indicate presence of hafnium silicates at the film substrate interface.

on Si and complexes like $(HfO_2)_x(SiO_2)_{1-x}$ which are also expected to be stable up to 1050 °C for $x<0.2$ were suggested [6].

In this study, we have used (PLD) technique to synthesize Hf-based oxide films on Si substrates. We have used X-ray absorption fine-structure spectroscopy (XAFS) in order to correlate the local structures around the Hf atom with deposition parameters and the stoichiometry. In one part of this work, we have prepared HfO_2/Si (100) films varying the substrate temperature and investigate the effects of the substrate temperature on the local structural order. In another part, we have prepared various mixtures of HfO_2 and ZrO_2 used PLD to form films of the mixture on Si (100) substrates. The ratio of HfO_2 to ZrO_2 in the mixtures has been correlated with the structural information from the XAFS data. The oxidation states and the composition of the HfO_2/Si (100) PLD films were investigated by XPS.

2. Experiment

We used the PLD technique to prepare oriented high-k thin films. The thin films of HfO_2, and $(HfO_2)_x(ZrO_2)_{1-x}$ ($x=0.50$, 0.75, 0.90, 1.00), were deposited on 2 in. p-type Si (100) and wafers using a KrF excimer laser with a wavelength of 248 nm. The PLD chamber was pumped to a base pressure of 5.3×10^{-4} Pa. In the depositions the laser energy density and laser frequency was set to 1.5 J/cm^2 and 15 Hz, respectively. The substrate temperature was varied between 200 °C and 400 °C for HfO_2/Si depositions. The target to substrate distance was set to 5 cm and the oxygen partial pressure was 13.3 Pa during the deposition. The films were annealed in nitrogen at 750 °C for 60 min after the deposition. The film thicknesses range between 50 nm–80 nm according to Auger depth profiles. The films were verified to be in the monoclinic phase by X-ray diffraction with using a two-circle diffractometer using Cu K_α radiation. Hf L_3-edge X-ray absorption fine-structure spectroscopy (XAFS) experiments were performed at the National Institute of Standards and Technology's (NIST) beamline (X23A2) at National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). XAFS data were acquired in the fluorescence detection mode and the X-ray angle of incidence was set to 5° during the measurements. XPS analyses were performed at the Evans Analytical Group using monochromated Al K_α source.

3. Results and discussion

The HfO_2/Si (100) film was analyzed by XPS in order to check stoichiometry. XPS results indicate all the films were fully oxidized (stoichiometric hafnium and oxygen content). Fig. 1 shows the high resolution XPS data for the Hf-4f levels. The 4f spin-orbit energy splitting for Hf was found to be ≈1.6 eV and the intensity ratio is ≈3:4 in agreement with the expected theoretical ratio. Fig. 2 shows the O-1s level. The shoulder just above 532 eV may be an indicator of the presence of hafnium silicate phases ($HfSi_xO_y$) at the interface [7]. Hf L_3

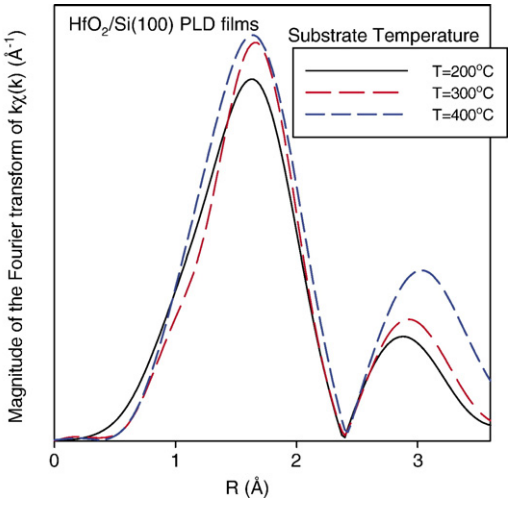

Fig. 3. The Fourier Transformed XAFS data for the PLD deposited HfO_2/Si (100) films at substrate temperatures of 200 °C, 300 °C, and 400 °C.

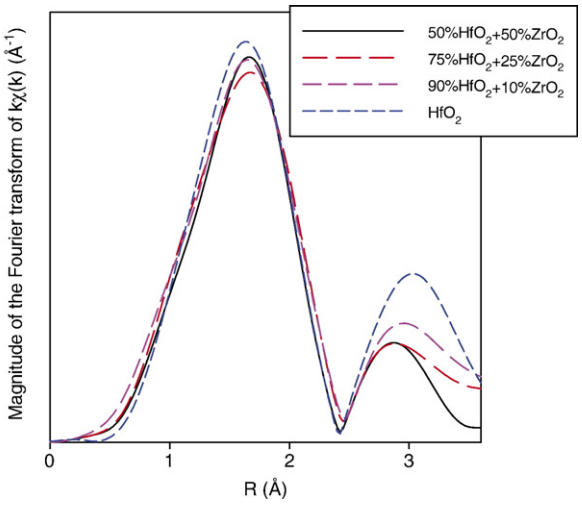

Fig. 4. The Fourier Transformed XAFS data for the PLD deposited $(HfO_2)_x(ZrO_2)_{1-x}$/Si (100) (x=0.50, 0.75, 0.90, 1.00).

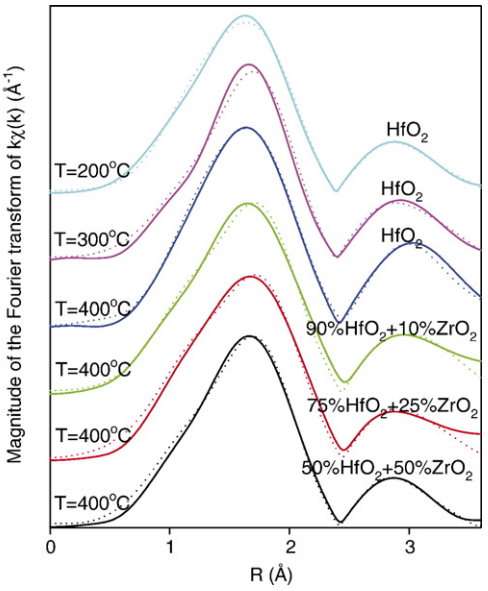

Fig. 5. Non-linear least-square fits to all of the Fourier Transformed XAFS data.

absorption edge has been used in XAFS data acquisition. XAFS functions, $\chi(k)$'s, are extracted by subtracting atomic absorption background using the AUTOBK code [8]. The $\chi(k)$'s are then Fourier Transformed (FT) using a Gaussian window for 2.0–10 $Å^{-1}$ k-range. Fig. 3 shows the FT data for HfO_2/Si (100) PLD films deposited at different substrate temperatures. The analysis of the FT data provides information on the near-neighbor coordination, distance, and the local disorder around the main absorbing atom. The additional phase shifts due the backscattering from the near-neighbor atoms shifts the FT data peaks from the actual near-neighbor distances. Using the University of Washington's multiple scattering XAFS calculation code FEFF8.2 [9], we have calculated the theoretical reference XAFS functions for HfO_2 monoclinic structure. In this way, we have identified the scattering paths contributing to FT data. The first shell peak around 1.9 Å corresponds to seven nearest O atoms in the monoclinic structure. The second shell peak around 3.0 Å is dominated by Hf–Hf backscattering. The multiple scattering contributions from Hf–O–O scattering paths are negligible. As shown in Fig. 3, the intensity of the first and second shell FT peaks with respect to temperature increases indicating a trend towards higher crystallinity with higher deposition temperature as the coordination numbers increase. It is promising that XAFS is very sensitive to subtle changes in the local structure caused by modest variations in the deposition temperature. Fig. 4 is an overlay of the $(HfO_2)_x(ZrO_2)_{1-x}$ (x=0.50, 0.75, 0.90, 1.00) PLD films deposited on Si (100) substrates at 400 °C. Here the sensitivity of the second shell peak, which is a signature of the Hf–Hf coordination to ZrO_2 content in the film, is well exhibited in the FT data. Hf coordination decreases and local disorder increases when more ZrO_2 is introduced to the PLD films.

Fig. 5 shows FT data and the non-linear least squares fits for all of the PLD films used in this study. The fits were performed using FEFF8.2 generated theoretical scattering amplitudes and phases for and using WINXAS, XAFS analysis and fitting program. In the first shell, Hf–O scattering amplitude and phases were used. In the second shell, multiple scattering contributions from Hf–O–O paths were negligible compared to Hf–Hf scattering contribution. The results from the XAFS fits for the near-neighbor distances, coordination numbers for the first two shells were summarized in Table 1. The uncertainties in the near-neighbor distances and the coordination numbers are ±0.01 Å and ±0.05, respectively. The coordination numbers for the Hf–O in the first shell decrease upon increasing substrate temperature. This behavior is more robust in the Hf–Hf coordination numbers in the second shell indicating the sensitivity to Hf coordination to substrate temperature during the deposition. In this way, XAFS can be used as a very sensitive probe to correlate the local structural modifications to subtle changes in the deposition parameters. When fits results for $(HfO_2)_x(ZrO_2)_{1-x}$/Si (100) (x=0.50, 0.75, 0.90, 1.00) samples were compared, even though the both Hf–O and Hf–Hf coordination numbers both exhibit a decrease with decreasing x value, the change in Hf–Hf coordination numbers is much greater with increasing ZrO_2 content.

Table 1
Fourier Transformed XAFS data and the non-linear least square fits for all the Hf-based pulsed laser deposited films deposited on Si (100) in this work

PLD film	1st shell		2nd shell	
	N_{Hf-O}	R (Å)	N_{Hf-Hf}	R (Å)
HfO_2/Si (100) T=200 °C	5.52	2.02	4.59	3.47
HfO_2/Si (100) T=300 °C	5.64	1.98	5.55	3.47
HfO_2/Si (100) T=400 °C	6.39	2.02	8.28	3.46
$(HfO_2)_x(ZrO_2)_{1-x}$/Si (100) (x=0.90) T=400 °C	6.09	2.09	6.23	3.47
$(HfO_2)_x(ZrO_2)_{1-x}$/Si (100) (x=0.75) T=400 °C	6.00	2.01	5.02	3.47
$(HfO_2)_x(ZrO_2)_{1-x}$/Si (100) (x=0.50) T=400 °C	5.91	1.99	4.19	3.48

4. Conclusions

HfO_2 and $(HfO_2)_x(ZrO_2)_{1-x}$ based thin films were synthesized using pulsed laser deposition technique. The local structures of the films were probed by X-ray absorption spectroscopy. The effect of the substrate temperature during deposition and the ZrO_2 content were correlated with the local order around Hf. XAFS results clearly show that an increase in substrate temperature (in 200 °C–400 °C range) increases the Hf–Hf coordination numbers leading to better crystallinity. Hf–Hf coordination numbers obtained form XAFS, are also very sensitive to compositional variations caused by the inclusion of more ZrO_2 to the PLD films.

Acknowledgments

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