

Monoclinic textured HfO₂ films on GeO_xN_y/Ge(100) stacks using interface reconstruction by controlled thermal processing

Karen Paz Bastos,^{a)} Leonardo Miotti, and Gerald Lucovsky

Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202

Kwun-Bum Chung

Department of Physics, Dankook University, Dongnamgu Anseodong 29, Cheonan 330-714, Republic of Korea

Dennis Nordlund

Stanford Synchrotron Radiation Lightsource, Menlo Park, California 94025

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The authors used x-ray absorption spectroscopy of the O *K* edge to investigate the nanocrystalline structure of thin HfO₂ films deposited by remote plasma enhanced chemical vapor deposition on Ge(100). Postdeposition thermal process induced the interfacial reconstruction and the crystallization of the HfO₂ in the monoclinic structure driven by the Ge(100) substrate. The substrate templating of the HfO₂ crystallization is an evidence that the processing used here removes the undesired the interfacial layer and has the potential to yield interfaces with low density of defects. © 2010 American Vacuum Society. [DOI: 10.1116/1.3430563]

I. INTRODUCTION

The high carrier mobility of germanium as compared to that of silicon has elected it as an important candidate to replace Si as the semiconductor of the next generations of high performance metal-oxide-semiconductor field effect transistors that will use high dielectric constant oxides (high-*k*).¹⁻⁴ The most important high-*k* dielectric so far is HfO₂ and it is expected that it will remain as the gate dielectric of choice for some device generations. However, the interface HfO₂/Ge presents some physicochemical instabilities that must be overcome before its use. One of the critical issues impeding the application of Ge as the channel material is the poor quality of the interface between the dielectric and the Ge substrate, which is the source of high densities of negative charge during device operation.¹⁻⁴ This is possibly caused by the reaction of Ge with the high-*k* dielectric forming GeO₂ which is water soluble and thermally unstable, desorbing as volatile GeO at temperatures above 450 °C.⁵ In this work we propose a process to obtain HfO₂/Ge stacks with minimal interfacial GeO_x by passivation of the Ge(100) substrates before high-*k* deposition followed by a two-step postdeposition thermal annealing as described below. We used x-ray absorption spectroscopy of the O *K* edge to investigate the local structure of the HfO₂ layer on Ge and on Si for comparison. The O *K* edge spectra of the HfO₂ is interpreted here using a symmetry adapted molecular orbital description of its electronic structure revealing information on the nanocrystalline structure of the material.^{6,7}

II. EXPERIMENTAL PROCEDURES

Ge(100) substrates were wet chemically cleaned using sequential rinse with de-ionized water, hydrogen peroxide

(6%), methanol, and ammonium hydroxide (15%) bearing a clean Ge surface with controlled GeO_x passivation layer on top.^{7,8} Immediately after this step the Ge substrates were inserted into a remote plasma enhanced chemical vapor deposition (RPECVD) system where a GeO_xN_y layer was obtained by remote plasma assisted nitridation of the GeO_x/Ge(100) substrates. The thickness of the nitrated layer is estimated to be around 1 nm thick. Following this step, HfO₂ films 2, 4, and 6 nm thick were deposited by RPECVD at 300 °C using Hf *t*-butoxide and O₂ as precursors. The resulting HfO₂/GeO_xN_y/Ge(100) structures were submitted to a two-step rapid thermal annealing (two-step RTA) in Ar atmosphere, which consist of annealing at 550 °C during 30 s followed by annealing at 800 °C during 60 s. The two-step RTA processing aims to remove the interfacial transition region by controlled desorption of Ge–O and Ge–N species sequentially resulting in a thermally regrown interface between HfO₂ and Ge(100).⁹ Figure 1 depicts the process used to obtain these structures. Complementary 2, 3, and 4 nm thick HfO₂ films were deposited on Si (100) substrates after remote plasma assisted oxidation/nitridation steps yielding an amorphous SiO_xN_y interfacial layer. X-ray absorption spectroscopy measurements were performed on beam line 10-1 at the Stanford Synchrotron Radiation Laboratory (SSRL).

III. RESULTS

Figure 2(a) shows the O *K* edge spectra for HfO₂ films on Si after RTA at 900 °C. The energy regions corresponding to transitions to the bottom of the HfO₂ valence band, namely, the *E_g* and *T_{2g}* molecular orbital states, are indicated in the figure. These states are derived mainly from the Hf 5*d* states and are split by the crystal field. Transitions to other higher energy molecular orbital states are also indicated. The comparison of the spectra clearly reveals that a transition in the

^{a)}Electronic mail: kpazbas@ncsu.edu

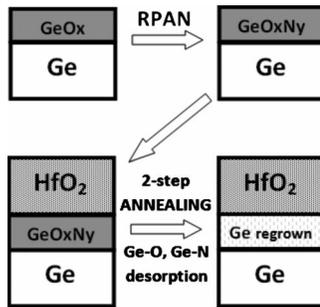


FIG. 1. Description of sample preparation by remote plasma assisted nitridation of native GeO_x followed by remote plasma assisted chemical vapor deposition of HfO₂ and subsequent two-step annealing processing.

electronic structure around 3 nm thick HfO₂ films exists. As previously reported,^{10,11} this is the minimum length scale of nanograins necessary to cooperative Jahn–Teller distortion take place in HfO₂ films. This distortion breaks the degeneracy of the E_g states as opposed to the structureless feature of the 2 nm thick HfO₂. Also, a smaller number of local configurations are expected, yielding sharper features in the spectra. These spectra are benchmarks for the investigation of HfO₂ on Ge substrates.

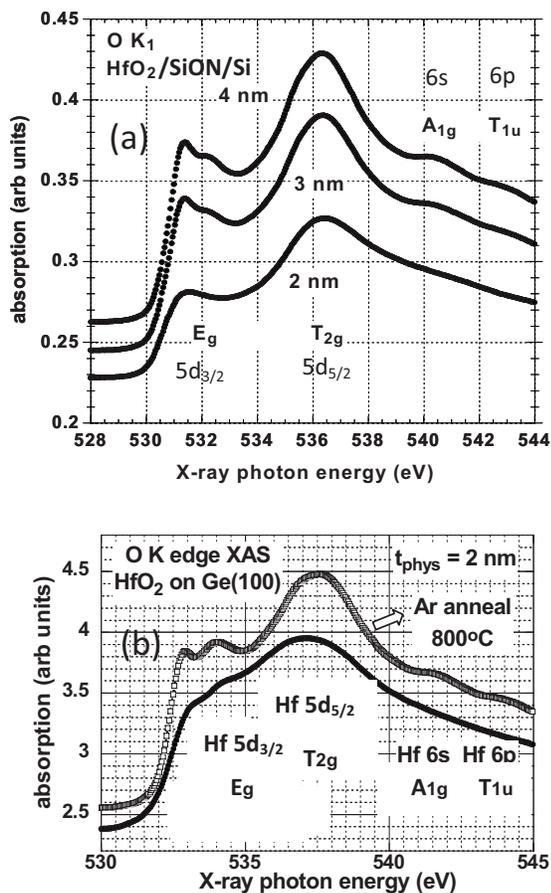


FIG. 2. (a) O K edge spectra of HfO₂ with 2, 3, and 4 nm thick deposited on SiO_xN_y/Si and annealed at 900 °C. (b) O K edge spectra of 2 nm thick HfO₂ deposited on GeO_xN_y/Ge as deposited (bottom curve) and after two-step annealing processing.

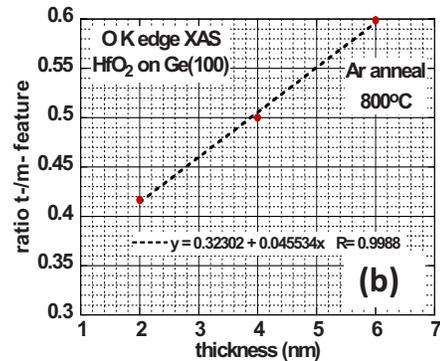
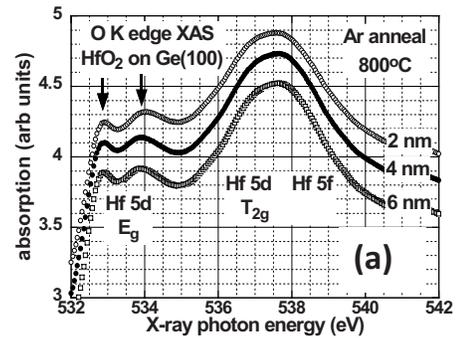


FIG. 3. (Color online) (a) O K edge spectra of HfO₂ for physical thickness of 2, 4, and 6 nm after the two-step annealing processing. (b) Plot of the ratio of intensities of distinct E_g Hf 5d features corresponding to tetragonal/monoclinic phases vs HfO₂ film thickness.

The spectra shown in Fig. 2(b) were obtained from a 2 nm thick HfO₂ film deposited on GeO_xN_y/Ge(100), before and after a two-step RTA. The broad features in the spectrum of the as-deposited sample are consequences of a small local order due to the relatively low deposition temperature. On the other hand, the splitting of the E_g states and the relatively sharp T_{2g} , A_{1g} , and T_{1u} features observed after the two-step RTA are clear evidences of the crystallization of the HfO₂ film in a monoclinic structure during the thermal processing. This is in direct contrast with the findings described above that revealed that a minimum 3 nm length scale is necessary for the HfO₂ nanograins develop cooperative Jahn–Teller distortion (here, the splitting of the E_g states) and sharp spectral features. In a 2 nm thick film, this cannot take place unless the coherent growth on the nanograins is driven by an external medium. In this case the crystalline Ge(100) substrate must have induced the HfO₂ crystallization. This suggests that the GeO_xN_y decomposition during the two-step RTA resulted in the direct contact of the 2 nm HfO₂ film with the regrown Ge(100). The nanograins of the HfO₂ are possibly oriented with respect to dimer rows of the Ge(100) which have acted as a template for the crystallization.

To investigate the extent of the Ge(100) substrate guided crystallization of HfO₂ as a function of thickness, we measured the O K edge spectra of 2, 4, and 6 nm thick HfO₂ films deposited on GeO_xN_y/Ge(100) after a two-step RTA and the results are shown in Fig. 3(a). As previously discussed, the nanocrystallinity in these HfO₂ is especially re-

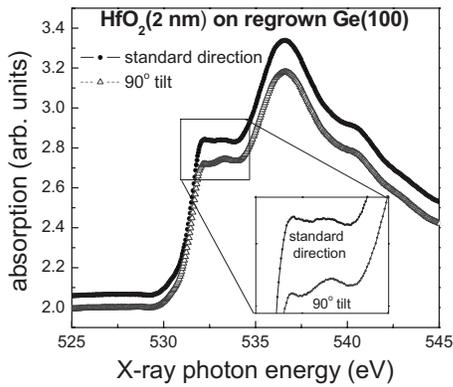


FIG. 4. O *K* edge spectra from annealed HfO₂ (2 nm)/Ge (100) stack measured at two different experimental configurations. The inset shows the *E_g* state region in detail.

flected in the splitting of the *E_g* states. The two peaks in the *E_g* feature are related to the tetragonal and monoclinic structures of HfO₂. Furthermore, the intensity of these peaks is associated with the extent of the two crystalline structures in the film. The *E_g* feature at the edge dominates in *t*-HfO₂ while both feature are expected in *m*-HfO₂.^{10,11} Figure 3(a) shows that as the thickness of the HfO₂ film is increased, there is a change in the intensity ratio of these *E_g* peaks. A plot of the intensity ratio of the two features as a function of the film thickness is shown in Fig. 3(b). We found that increasing the film thickness the tetragonal phase becomes dominant in these structures and increases linearly with thickness in the range investigated.

Figure 4 further shows that the crystallization of the HfO₂ in these structures is driven by the Ge(100) substrate. It plots the O *K* edge spectra for two HfO₂ films on Ge(100) deposited and measured with the $\langle 110 \rangle$ direction of the Ge substrate rotated by 90° in respect to each other. In both cases the x-ray polarization axis was on the plane of the substrate surface. In a homogeneous film, two perpendicular directions on the plane of the film are equivalent, and thus rotations around the normal of the surface should yield no difference in the absorption spectra. However, this is not the case as it is clearly shown by the difference in the *E_g* state intensity ratio of the samples measured here. Since the *E_g* states are related to the symmetry of the main axis of the crystal structure, the

difference observed in Fig. 4 can only be caused by the presence of a preferential growth direction of the main axis of the nanograins, in particular, with respect to the dimer rows of the substrate.

IV. SUMMARY

We have shown in this article a process to prepare nanocrystalline HfO₂ films textured by the Ge(100) substrates with minimal interfacial layer. The comparative investigation by x-ray absorption spectroscopy of HfO₂/Ge structures and HfO₂ films deposited on SiO_xN_y/Si(100) revealed the crystallization of HfO₂ films on Ge (100) with thickness below the length scale required for nanograin formation. In this case, it is required that the nanograin growth be externally driven by the Ge(100) substrate that must be in close contact with the dielectric after the two-step RTA. This finding is corroborated by the dependence on the monoclinic to tetragonal concentration ratio with the film thickness and the anisotropy of the nanograin growth direction with the Ge(100) dimer rows.

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