Extended Abstracts of the 2007 International Conference on Solid State Devices and Materials, Tsukuba, 2007, pp. 776-777

F-5-2

Plasma Deposition of HfO_2 and TiO_2 onto Plasma-Nitrided Ge Surfaces

Sanghyun Lee[1], Gerald Lucovsky[1], Joseph P. Long[1] and Jan. Lüning[2]

[1] Department of Physics, North Carolina State University, Raleigh, NC 27695-8202, USA
email: lucovsky@ncsu.edu, phone: +01 (9190 515 3301, fax: +01 (919) 859 3191
[2] Stanford Synchrotron Radiation Laboratory (SSRL), Stanford, CA 94025, USA

1. Introduction

A significant problem in the development of CMOS devices on Ge substrates has beeen formation of *defective* interfacial transition regions with Ge-O bonds between Ge substrates and gate dielectrics [1]. One solution is to deposit a thin Si layer on the Ge, and then form a passivating/protective SiON interfacial layer. This will increase channel mobilities with respect to Si, but add ~0.3 nm to the equivalent oxide thickness [2]. This paper presents an alternative approach in which a sacrificial interfacial GeN layer protects the Ge surface from oxidation during deposition. This layer is then removed by a post deposition anneal in Ar at 800°C leaving the high-κ HfO_2 dielectric in direct bonding-contact with the Ge substrate with no detectable nitride transition region.

2. Experimental Methods

HfO_2 thin films ~2 to 6 mn thick were plasma deposited onto plasma-nitrided Ge substrates and compared with HfO_2 films deposited onto Si substrates with ~0.6-0.8 nm thick SiON interfacial layers. The O K_1 and N K_1 edge gate stack spectra were studied by near edge X-ray absorption (NEXAS) spectroscopy. These spectra were obtained at beam-line 10-1 at SSRL. The combination of resonant atom-specific O K_1 and N K_1 spectra are a good way to study buried interfaces, and relationships between bonding in oxide dielectrics, and nitrided interface regions.

3. Experimental Results

Fig. 1(a) is the N K_1 spectrum for remote plasma assisted nitridation (RPAN) of a Ge (100) substrate used for deposition of HfO_2 films. Based on on-line Auger electron spectroscopy (AES), the thickness of the GeN layers is 0.8±0.1 nm. Films of HfO_2 ~2 and 6 nm thick were then deposited onto the plasma-nitrided Ge(100) substrates at 300°C, and then subjected to a one minute 800°C anneal in Ar. Fig 1(b) is the N K_1 spectra for the buried interface on a 2 nm thick HfO_2 film annealed at 800°C. This plot indicates significantly reduced inter-facial Ge-N bonding after the 800°C anneal. The O K_1 spectrum for the as-deposited 2 nm HfO_2 film in Fig. 2(a) on a GeN interface shows broad spectral features that are different than those of the 800°C annealed 2 nm film. There are similar differences between 6 mn films: as-deposited and annealed at 800°C. The features in Fig. 2 between 532 and 535 eV are assigned to Hf E_g anti-bonding π-states, and the peak between 536 and 540 eV to Hf T_{2g} anti-bonding σ states [3,4].

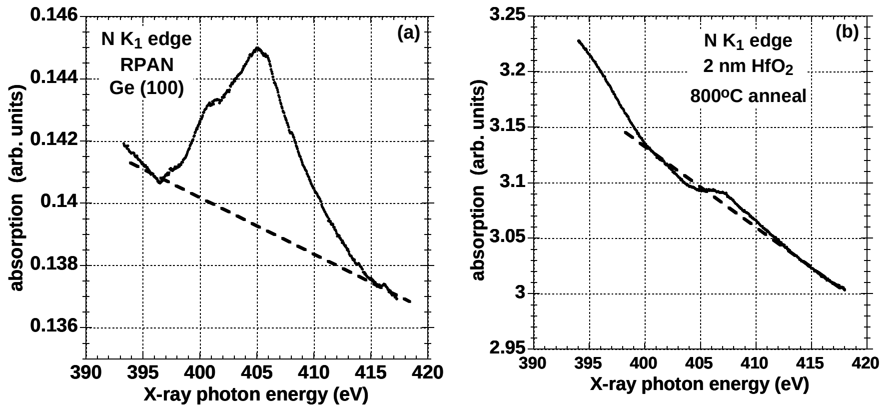

Fig. 1. N K_1 Spectra: (a) Ge interface nitridation RPAN process: (b) HfO_2 2nm film after 800°C anneal.

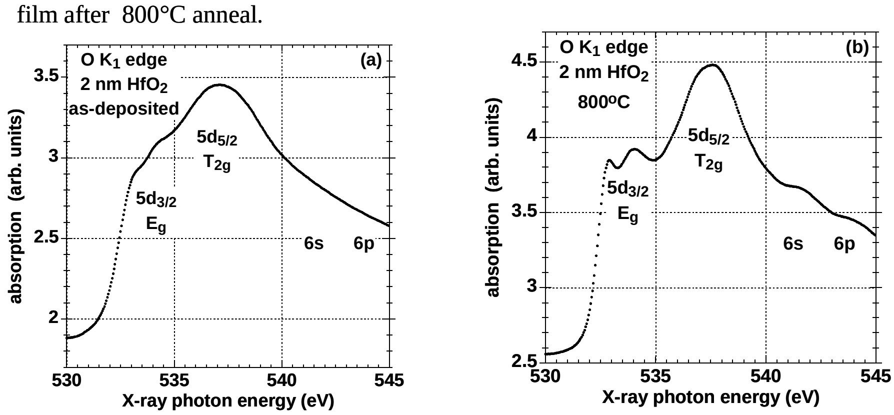

Fig. 2. O K_1 Spectra: 2 nm O_2 on Ge (100) (a) as-deposited and (b) after 800°C anneal.

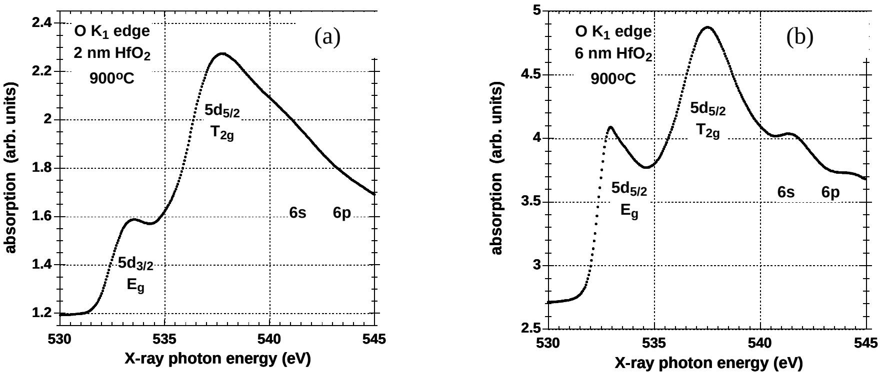

Fig. 3. SiON-Si substrates HfO2 (a) 2 nm and (b) 6 nm after 900°C anneals in Ar.

The OK $_1$ spectra in Fig. 2 will be compared with the spectra in Fig. 3 for HfO_2 deposited on SiON interfaces. The broader spectral features for the as-deposited films in Fig. 2(a) are attributed to < 2 nm nano-crystallite grains, and the sharper features in 800°C annealed films in Fig. 2(b) to nano-crystallite grains larger than about 4 nm. In particular, the splitting of the band edge E_g state into a doublet in Fig. 2b is due to a collective Jahn-Teller distortion that removes the degeneracy [4].

Fig. 3 displays OK_1 spectra for the Si-SiON-HfO_2 hetero-stacks that indicate E_g π and T_{2g} σ Hf d-state features for the 2 and 6 nm thick 900°C annealed films on Si substrates. Fig. 3(a) displays broad spectral features similar to those for the as-deposited 2 nm thick HfO_2 films in Fig. 2(a). The absence of J-T degeneracy splitting for the band-edge Hg E_g features indicates of a suppression of *coherent* π-bonding [3,4]. This *incoherent* π-bonding in 2 nm thick HfO_2 as-deposited and 900°C annealed films on SiON is associated with homogenous nucleation of ~2 nm nano-grains with a length scale below the threshold level for *coherent* π-bonding [3]. *Coherent* π-bonding with a J-T distortion is observed in annealed 6 nm thick films: nano-grains are > 3.5-4 nm and their size is not constrained by the thickness of the film.

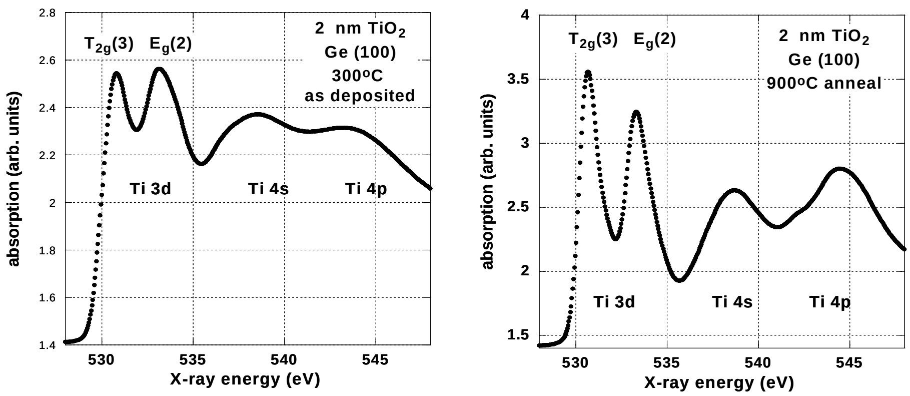

Fig. 4. O K1 TiO2: (a) on a GeN interfacial layer, (b) after anneal in *bonding contact* with Ge.

Figure 4 shows O K_1 spectra for nano-crystalline TiO_2: (a) as-deposited on a GeN interfacial layer, and (b) after an 800°C anneal and in *bonding contact* with the Ge. The half-width half-maximum (hwhm) for the annealed film is 0.5 eV and 1.0 eV in the as-deposited film. The hwhm in the 800°C anneal film correlates with a J-T term splitting, is 0.5 eV and ~35% less than the ~0.67 eV hwhm for 900°C annealed TiO_2 films deposited onto SiON-Si(100) substrates. This result for TiO_2 parallels results in Fig. 2 for HfO_2 on Ge substrates.

4. Summary

The combination of resonant O and N K_1 edge spectra is an ideal way to study buried interfaces. The results in Figs. 1-4 demonstrate the removal of interfacial GeN transition regions for annealed stacks allows the Ge surface to act as a *template for mosaic* HfO_2 and TiO_2 grain growth to >4 nm, and thus promotes observable J-T spittings in O K_1 edge spectra. The spectral weighting factors for these splittings are different than those for annealed HfO_2 on SiON terminated Si substrates supporting a Ge *template mosaic controlled* grain growth morphology. This model is supported by the results in Fig 2(b) that indicate J-T splitting can not be suppressed by out of the plane film thickness, and is different than in HfO_2 films on SiON interfaces where coherent π-bonding is film thickness determined.

This paper has presented is a new and novel application for NEXAS based on the resonant character of absorption 1s state absorptions for the respective O K and N K edges. Their X-ray energy difference, and the transparent spectral windows of oxides to both X-ray absorption and electron emission, is critical for this technologically important application [1].

References

[1] M. Houssa and M.M. Hyens, in *High-K gate dielectrics*, ed. M. Houssa (IOP, Bristol, 2004) Chap 1.1.
[2] H. Niimi and G. Lucovsky, J. Vac. Sci. Technol. B **17**, (1999) 2610.
[3] G. Lucovsky *et al.*, Jap. J. Appl. Phy. 46 (2007) in press.
[4] R.A. Wheeler *et al.*, J. Am. Chem. Soc. **108** (1986) 2222.