Plasma Deposition of HfO₂ and TiO₂ onto Plasma-Nitrided Ge Surfaces

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1. Introduction
A significant problem in the development of CMOS devices on Ge substrates has been 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-k HfO₂ dielectric in direct bonding-contact with the Ge substrate with no detectable nitride transition region.

Fig. 1. N K₁ Spectra: (a) Ge interface nitridation RPAN process: (b) HfO₂ 2nm film after 800°C anneal.

Fig. 2. O K₁ Spectra: 2 nm O₂ on Ge (100) (a) as-deposited and (b) after 800°C anneal.

2. Experimental Methods

HfO₂ thin films ~2 to 6 nm thick were plasma deposited onto plasma-nitrided Ge substrates and compared with HfO₂ films deposited onto Si substrates with ~0.6-0.8 nm thick SiON interfacial layers. The O K₁ and N K₁ 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 K₁ and N K₁ 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 K₁ spectrum for remote plasma assisted nitridation (RPAN) of a Ge (100) substrate used for deposition of HfO₂ films. Based on on-line Auger electron spectroscopy (AES), the thickness of the GeN layers is 0.8±0.1 nm. Films of HfO₂ ~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 K₁ spectra for the buried interface on a 2 nm thick HfO₂ film annealed at 800°C. This plot indicates significantly reduced interfacial Ge-N bonding after the 800°C anneal. The O K₁ spectrum for the as-deposited 2 nm HfO₂ 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 nm films: as-deposited and annealed at 800°C. The features in Fig. 2 between 532 and 535 eV are assigned to Hf E₂ anti-bonding π-states, and the peak between 536 and 540 eV to Hf T₂g anti-bonding σ states [3,4].
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 $K_1$ spectra for the Si-SiON-HfO$_2$ hetero-stacks that indicate $E_g\pi$ and $T_{2g}\sigma$ Hf d-state bonding [3].

4. Summary

The combination of resonant O and N $K_\epsilon$ 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 $\sim$4 nm, and thus promotes observable J-T spittings in O $K_\epsilon$ 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 $\pi$-bonding is film thickness determined.

This paper has presented 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