Structural Differences in Doped HfO_2: Root Causes for Varying Ferroelectric Properties Across Different Dopants

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Recently, the ferroelectric (FE) behavior of thin doped hafnium oxide films or hafnium zirconium mixed oxide layers caused by a non-centrosymmetric orthorhombic phase was reported [1]. In the following years, novel devices ranging from FE RAM (random access memory) to FE FET (field effect transistor) and negative capacitance devices using these dielectrics were proposed. For all devices a detailed understanding of the structural properties is necessary to improve the electrical performance of the material stack. Ferroelectric doped HfO_2 films were processed by pulsing a certain amount of dopant oxide sub-cycles during HfO_2 deposition on a TiN/Si substrate followed by a TiN top electrode deposition and crystallization anneal.

On this material stack the ferroelectric properties and crystal structure of doped HfO_2 thin films were investigated. Piezo-response force microscopy (PFM) in conjunction with transmission electron microscopy (TEM) measurements revealed a domain size in the order of single grains with a diameter of ~20-30 nm for 10 nm thick films. TOF-SIMS depth profiling together with TEM imaging suggest different dopant diffusion behaviors within a HfO_2 dielectric during anneal (see figure 1 and 2). Al and Gd dopants resulted in an almost uniform distribution of dopants whereas a heterogeneous distribution of Si is still visible in HfO_2 after a 1000 °C, 1 s anneal. One possible explanation would be the different valence of the dopants. Si is tetravalent resulting in minimal oxygen vacancy generation in the HfO_2 lattice. Al and Gd are trivalent dopants and thus have increased potential for generating oxygen vacancies in HfO_2. Higher oxygen vacancy amounts in the layer are expected to enhance the diffusion of the dopants like Al and Gd. Local changes in the dopant concentration are also visible in TEM as lattice constant variations within the HfO_2 lattice in areas of high dopant concentration. After implementation of HfO_2 in ferroelectric capacitors for non-volatile memory applications, important parameters for data storage were characterized and related to structural changes: e.g. remanent polarization, wake-up performance, endurance, and fatigue together with typical dielectric properties like leakage current and dielectric constant.

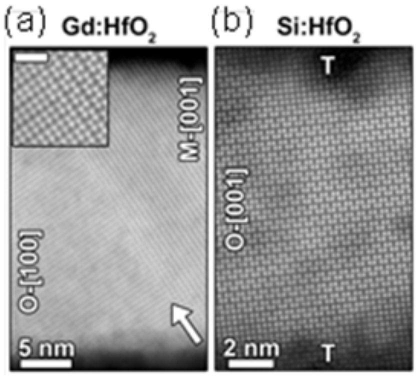

Figure 1. Scanning transmission electron microscopy images of (a) Gd-doped HfO_2 and (b) Si-doped HfO_2 thin films. Darker regions in (b) are related to higher Si dopant concentrations.

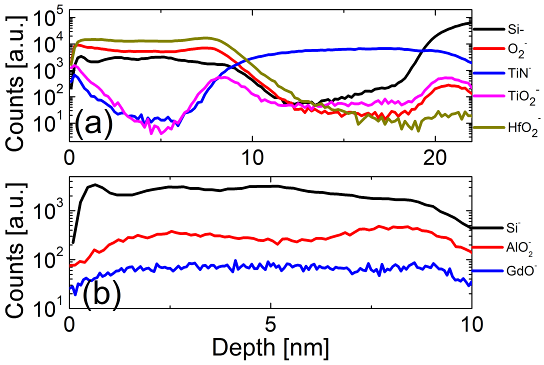

Figure 2. (a) Time of flight secondary ion mass spectra of 10 nm-thick Si-doped HfO_2, (b) detailed view on Si, Al, and Gd dopant profile in HfO_2 films.

[1] T. Boescke et al. *Appl. Phys. Lett.* 99 (2011)