Tuning the dielectric response of HfO_2 nanoparticles by Si-doping

T. S. N. Sales[1*], A. Burimova[1], A. W. Carbonari[1], B. Bosch-Santos[1], L.F. D. Pereira[1]

[1]Nuclear and Energy Research Institute (IPEN-CNEN/SP), São Paulo, Brazil

* tatianenas@yahoo.com.br

Abstract

The properties of bulk materials and corresponding nanostructures may differ significantly which leads to distinct scopes of their applications. As the miniaturization continues, nanostructures show great potential in microelectronics. Among others, nanostructured hafnium (IV) oxide (hafnia, HfO_2) has attracted considerable attention due to its chemical stability and physical characteristics[1]. It has high dielectric constant (~25) and is relatively thermally stable (melting point at 3085 K)[2]. These qualities have made hafnia an alternative to SiO_2 for gate oxide layers in field-effect transistors, since the leakage current issue and consequent thickness limitations of silica were hindering miniaturization. Clearly, the features of HfO_2 can be further tuned by doping[3]. Understanding the relation between the macro-properties of such complex systems and their architecture at atomic scale should help select doping parameters adequate for particular applications.

In this work 0at%, 5at% and 10at% Si-doped HfO_2 nanoparticles (NPs) were synthesized via sol-gel method. Basic characterization included scanning/transmission electron microscopy, electron backscattering and X-ray diffraction. NPs were demonstrated to have spherical shape, sizes in the range of 10─40nm and monoclinic structure (m-HfO_2).

Local structure and electronic environment of the samples was probed with perturbed angular correlation (PAC) spectroscopy. Sample irradiation resulted in the formation of ^{181}Hf isotopes (PAC probes[4]) at several sites whose decay to ^{181}Ta is preferentially through an intermediate (metastable) state with lifetime depending strongly on local extra-nuclear fields. Thus, time distribution of decay probability provided information on the ambient of the probe.

For undoped sample PAC data has revealed two distinct Hf sites, one of those possessing well-defined quadrupole frequency $\nu_Q \approx 750$ MHz and electric field distribution asymmetry $\eta \approx 0.36$. Site occupation raised with temperature from 16% at T = 473K to 75% at T = 1073K, which agrees with the results found in the literature for the quadrupole interactions of ^{181}Ta in m-HfO_2[4]. For the doped samples (both Si 5at% and 10at%) additional site was observed. Symmetrical electric field distribution ($\eta = 0$) and a greater site fraction at T = 673─873K allowed to attribute it to a tetragonal phase of hafnia. First principles analysis has shown that doping m-HfO_2 with certain cations can induce the formation of tetragonal phase[5]. We emphasize that this phase is desirable for transistor applications since it is associated with the highest dielectric constant.

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