ROBL-CRG	**Experiment title:** **Materials Characterization for DRAM-Trench-Technology**	**Experiment Number:** **20_02_643**
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Report:

The continuous size reduction in the DRAM technology requires the replacement of traditional materials, e.g. the classical gate SiO_2 films has to be substituted by insulators with significant higher dielectric constant κ, the so-called high-κ dielectrics. Doped HfO_2 layers are candidates for the application as dielectric in next generation trench capacitors [1]. The formation of different crystalline phases plays a crucial role for the dielectric properties. The equilibrium phase diagram of HfO_2 shows at ambient conditions a stable monoclinic phase. Tetragonal and cubic (CaF_2-type) or orthorhombic phases exist at high temperatures (T > 1600°C) or high pressures, respectively. Doping with e.g. Si can be used to stabilize the cubic/tetragonal/orthorhombic phase of HfO_2 in thin films [2]. Theoretical calculations showed that the dielectric constants of the cubic/tetragonal phases can possess significantly higher k values in comparison to the monoclinic phase [3]. The experimental data support these results for the correlation of structural and electrical properties [2, 4].

In the experiment mixed $Hf_{0.92}Si_{0.08}O_2$ and nanolaminates (HfO_2-SiO_2 layer stacks) grown by atomic layer deposition (ALD) on Si(001) substrates have been analyzed by X-ray diffraction (XRD) at 8.045 keV. All layers (thickness = 10...15 nm) were annealed in an RTP process for 30 s in a N_2 atmosphere after the deposition process for variable temperatures in the range between 600 and 1000°C. Grazing incidence geometry (α = 0.5°) was performed to collect the diffraction pattern in a wide range of scattering angles (2θ = 15° – 92°).

The as-deposited $Hf_{0.92}Si_{0.08}O_2$ films are in the amorphous state. After annealing at temperatures > 600°C all mixed Hf-oxide films crystallize preferably into the cubic phase (fig. 1a). It is interesting to note that the monoclinic phase is suppressed very efficient for an annealing treatment up to 1000°C. In addition to the cubic phase small traces of the orthorhombic phase may be present in the films. The polycrystalline films contain randomly oriented grains as proved by intensity ratio of the reflexes (see comparison with powder diffraction pattern in fig. 1b).

In contrast, the GIXRD data of the nanolaminate (fig. 2) point to a texture of the film. The (111) pole figure reveals a fibre texture with components at chi=15° and chi=56° ... 58°. The component at chi=15° may result from grains with {221} || Si substrate (001). In CaF_2-type crystals this orientation is typically observed as a result of a twin formation by a rotation of 180° around the <111> axis of grains with {100} || (001) Si substrate. Furthermore, these {100} oriented grains would explain the 2nd component of the (111) pole figure at chi = 56 … 58°. However, further measurements are needed to support this discussion.

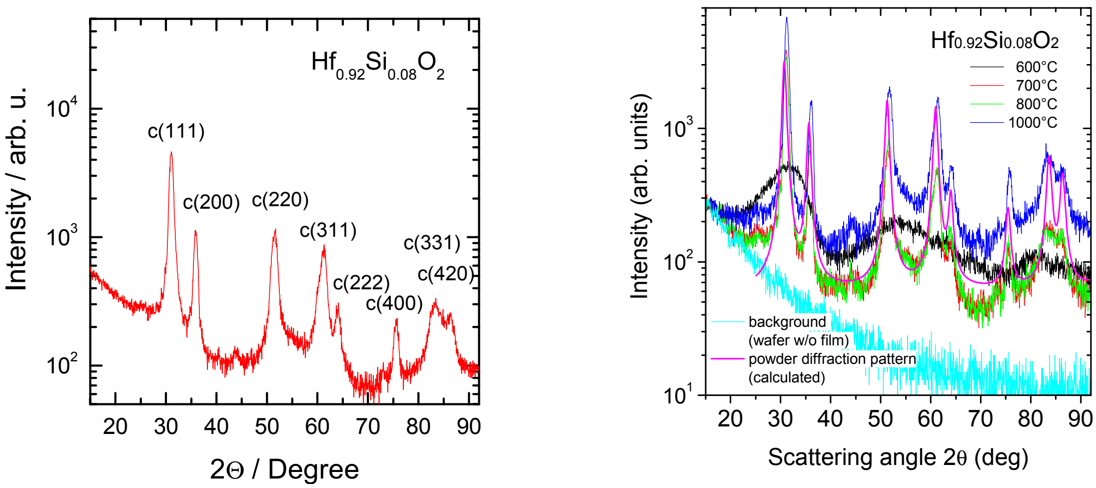
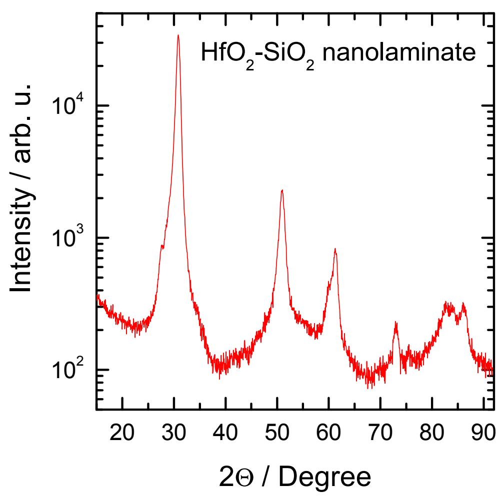


Fig 1: Examplary GIXRD scans for a mixed $Hf_{0.92}Si_{0.08}O_2$ film after annealing at 1000°C in N_2 (a) or in a sequence after different annealing treatments (b). Reflexes are indexed for the cubic phase of HfO_2.



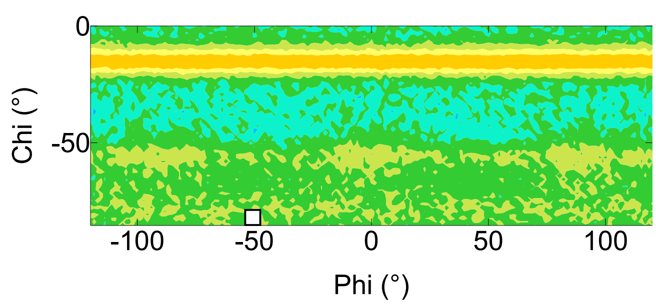


Fig 3: Pole figure for 2θ=30.9° near to the cubic HfO_2(111). Fibre Texture: 1st component at chi=15°, 2nd component at chi=56..58° with a partially preferential azimuthal orientation to the Si lattice.

Fig 2: GIXRD scan for a HfO_2-SiO_2 nanolaminate film after annealing at 1000°C in N_2.

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