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Formation and thermal stability of $Ge_xHf_{1-x}O_2$ solid solutions

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As twin-oxides, hafnia and zirconia are usually considered to demonstrate similar reaction on their doping with group IV elements including a stable tetragonal "high-k" phase. However, this statement was needed direct experimental confirmation. Recently, we have proved the role of Ge in the stability of tetragonal ZrO_2 "high-k" phase for Ge-doped ZrO_2 thin films (with Ge content up to 50 at.%) prepared by magnetron co-sputtering [1,2]. Here, we present the results obtained for Ge-doped HfO_2 thin films grown with the same deposition approach. The Ge content was varied from 0 up to 50 at%. The effect of thermal treatment on structural transformation in the films was studied by Auger spectroscopy, Raman scattering, FTIR and XRD methods.

As-deposited HfO_2 films were found to be crystalline. Their doping with [Ge]5at% reduces the degree of film crystallinity towards amorphous structure that demonstrates its stability for T_A<600C. At higher T_A, the formation of Ge-ncs and tetragonal HfO_2 was detected. This latter formed at T_C=600-670C, while the Ge-ncs crystallized at T_C=700-800C. The comparison of these results with those reported earlier for Ge-doped ZrO_2 films [1,2] shows that the smaller Ge-ncs formed in Ge-HfO_2 films than that in Ge-ZrO_2 ones at the same thermal treatment. Our results support the theoretical consideration about stability of tetragonal "high-k" phases in Ge-doped films. However, they show also the difference in the reaction of Ge-doped HfO_2 and ZrO_2 materials on thermal treatment followed by phase separation. Its mechanism will be discussed in details.

1. D. Lehninger, et al. ECS Transactions, 2015, 68, 203.
2. L. Khomenkova, et al. Nanoscale Res. Lett., 2017, 12, 967.