Project Results - Stage III:
01.01.2018 – 29.12.2018

Stage III: Multilayer structures based on GeSn nanocrystals for optoelectronic demonstrators

Objectives, activities and estimated results of the third stage of the project were fully achieved by optimization of the deposition and annealing processes for obtaining nanocrystallized films of $(Ge_{1-x}Sn_x)_{1-y}(SiO_2)_y$ and multilayers $Ge_{1-x}Sn_x/SiO_2$, to be used for the fabrication of demonstrator DM1. For that, advanced studies on the structure, morphology and composition of the layers, together with undestanding and modeling of the GeSn nanocrystals (NCs) formation were emploied.

GeSn NCs formation in $(Ge_{1-x}Sn_x)_{1-y}(SiO_2)_y$ films was studied for Sn concentration in the range of 9% - 22%, while SiO_2 concentration was between 11% and 15%. Samples with low content of SiO_2 of about 2% have been also investigated for the proof of the role played by SiO_2 matrix in diminishing Sn diffusion, as well as in pasivation of the NCs boundary defects. The SiO_2 component delays the nanocrystalization of GeSn but also decreases the β-Sn segregation. The results are also confirmed on multilayer structures. Based on these results, a model for the formation and evolution of GeSn NCs was elaborated. Thus, due to a faster difusion of Sn into GeSn clusters, the NCs that are formed will have in the first stage of crystalization a higher Sn concentration that the mean value in the layer. At higher temperatures, or for more extended annealing, Sn segregats from GeSn nanocrystals, too. Thus, the concentration of Sn in NCs may become smaller than the mean value in the layer. The segragated Sn can form β-Sn NCs or/and difuse toward surface. As an example, from a layer with a mean concentration of 22% Sn, NCs with a concentration of 25% Sn are formed. By further annealing at 300 ^oC and 400 ^oC, Sn concentration in GeSn NCs is reduced to 21% and 18%, respectively. At 400 ^oC, β-Sn is segregated, as evidenced by XRD measurements. In another example, in a layer with 9% Sn GeSn NCs with 14% Sn are formed by annealing at 400^oC.

The composition and distribution of the elements in the film were also investigated by atomic probe topography (APT) and Rutherford Backscattering Spectrometry (RBS), in collaboration with FZ-Juelich_PGI-9, Germany and IFIN-HH, Romania. An uniform distribution of atoms in the as-grown amorphous layers was found. We also found that annealing at moderate temperatures of 400 ^oC leaves the mean concentration of Sn in the films unchanged. That is a proof that by rapid thermal annealing (RTA) there is no evaporation of Sn or difusion of Ge toward the surface. The oxidation due to exposure to air of Ge and Sn difused toward the surface is however reveled by X-ray Photoelectron Spectroscopy (XPS).

The multilayer samples were produced by 20 depositions of the bilayer pair GeSn/SiO_2, with a variable composition of GeSn and thicknesses of ~10 nm GeSn and 1.4 nm SiO_2, as measured by TEM. The growth and annealing parameters were taken from the results of monolayer investigations. HRTEM has revealed that nanocrystalization of GeSn takes place in the upper part of the multilayer stack, while the layers close to the intyerface with the Si substrate remain almost amorphous. This is another effect of SiO_2 that act as isolating interlayers for the crystalization proces. The effect of SiO_2 on nanocrystalization is even more pronounced in multilayer films in which GeSn is replaced by $GeSnSiO_2$ alloys, i.e. films of 20x($GeSnSiO_2$/SiO_2) have shown nanocristalization at higher temperatures.

The photosensitivity in SWIR was measured on heterojunctions of $GeSnSiO_2$ layer with p-Si substrate, in a photovoltaic regime, i.e. with zero external bias. The spectral photocurrent correlates very well with the growth and annealing conditions, confirming the model of nanocrystals formation and Sn diffusion. It is demonstrated that the photosensitivity of photodiodes can be extended in SWIR beyond Ge range, up to 2.4 µm for layers containing GeSn NCs of 14-15% Sn. The multilayer structures show higher photoresponce than that of monolayers, keeping however the extendended IR sensitivity range. Using a setup with light emitting diodes with emission at different wavelengths in the range 1.2 – 2.35 µm, first testing of the demonstrator structures were performed showing the linear dependence of the photoresponse in the whole sensitivity range. The results of this stage were reported in 5 published papers and 6 conference presentations. The next stage will have as main objective the optimization of demonstrator structure and its validation.

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