Phase separation in metastable $Ge_{1-x}Sn_x$ epilayers induced by free running Sn precipitates

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Recently, optical gain was demonstrated in $Ge_{1-x}Sn_x$ alloys [1], which are the only known group-IV materials that assume a direct band gap for compositions x > 10%. However, Ge and Sn are immiscible over >98% of the composition range, which renders direct-gap $Ge_{1-x}Sn_x$ epilayers inherently metastable.

Here, we address the temperature stability of pseudomorphic $Ge_{0.9}Sn_{0.1}$ films grown by MBE on Ge(001) substrates [2]. In particular, we studied by in-vivo scanning electron microscopy (SEM) the influence of post-growth annealing steps. Decomposition of the metastable epilayers was found to set in above ≈ 230°C, the melting point of Sn.

Video sequences taken during the annealing experiments reveal the crucial role of liquid Sn precipitates in the phase separation process (Fig. 1). Driven by a gradient of the chemical potential, the Sn droplets move on the surface along <110> or <100> directions, thereby taking up Sn and Ge from the intact $Ge_{1-x}Sn_x$ layer. Whereas Sn-uptake increases the volume of the melt, dissolved Ge becomes re-deposited as a single-crystalline Ge trail by liquid-phase epitaxy (LPE). Secondary droplets launched from the Ge trails into adjacent GeSn regions lead to an avalanche-like transformation front between the GeSn film and re-deposited Ge (Fig. 1(c)).

This peculiar decomposition process was confirmed by cross sectional TEM and EDX analyses along the trajectories of Sn droplets. In front of the moving Sn droplet the GeSn film remains in the as-deposited strain and composition state, whereas the trail consists of almost pure, single crystalline Ge which exposes low energy surface facets (Fig. 1(b)). The Sn droplets extend all the way down to the Ge substrate and were found to take up a supersaturated Ge concentration of about 10%.

Overall, each of the free-running Sn droplets behaves like a microscopic LPE reactor: The strained and metastable GeSn film on the one side acts as a feeding medium, whereas the opposite side leads to epitaxial deposition of the Ge trail. This process propels the droplets making phase separation in these metastable GeSn alloys particularly efficient already at rather low temperatures.

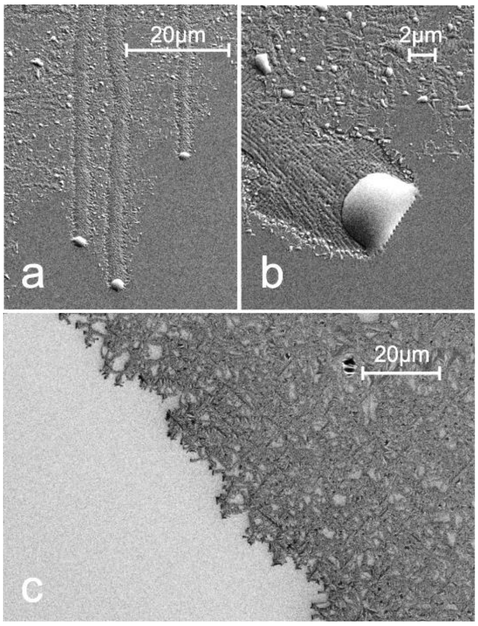

Fig. 1: SEM images taken from real-time video sequences of the precipitate-induced phase separation process in GeSn epifilms. The Sn droplets in (a) and (b) appear bright, the corrugate trails consist of single-crystalline Ge. (a) and (b) were recorded in-vivo at 250°C, (c) at 350°C.

[1] S. Wirths et al., Nature Photonics **9**, 88 (2015)
[2] H. Groiss et al., arXiv 1705.05156

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