In situ TEM thermal study of MBE and CVD GeSn layers: cross-section and plan-view geometries

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Introduction

Direct band gap GeSn epilayers have great potential in high-performance Si-based electronics and optoelectronics. A transition to a direct band gap can be achieved in GeSn layers when the Sn concentration exceeds 6 at% [1], a value well above the solubility limit. Therefore, these non-equilibrium GeSn alloys with the desired materials concentrations are unstable at high temperatures, resulting in phase separation and decomposition processes [2]. Two main epitaxial methods used for the material synthesis are molecular beam epitaxy (MBE) and chemical vapor deposition (CVD). Depending on the method, the properties of the GeSn can vary strongly. For example, the CVD GeSn films exhibit better optical properties and, to the best of our knowledge, all GeSn-based lasers were grown via this technique. Thermal stability is another property that can vary. The excess of Sn and its possible segregation that, can occur during material growth, has a major influence on thermal stability. Understanding this is important for predicting the thermal budget that a Ge1-xSnx layer can be exposed to during device fabrication.

Methods

We use the powerful technique of in situ transmission electron microscopy (TEM) to study the dynamic process during thermal annealing experiments. We analyze how the Sn concentration and the presence of dislocations affect the thermal stability. In this regard, samples grown by CVD and MBE, 50 nm thick epilayers with 6-14 at% Sn on Ge substrate, were analyzed in cross-section and plan-view geometries. The cross-sectional lamellae were cut and installed on micro-electro-mechanical system (MEMS) heating chips with a Ga+ focused ion beam (FIB). In the case of the plan-view, first, the samples were prepared by wedge polishing technique, and then with FIB transferred to the MEMS chip and finally thinned [3]. The experiments were performed by heating-cooling-cycles with an increasing maximum temperature up to 750°C, investigating the sample via complementary HRTEM and STEM EDXS. In cross-section geometry, we can trace precipitation in relation to present interfaces and surfaces, while in plan-view geometry we can gain information about the morphological changes and particle size distribution on the surface of interest.

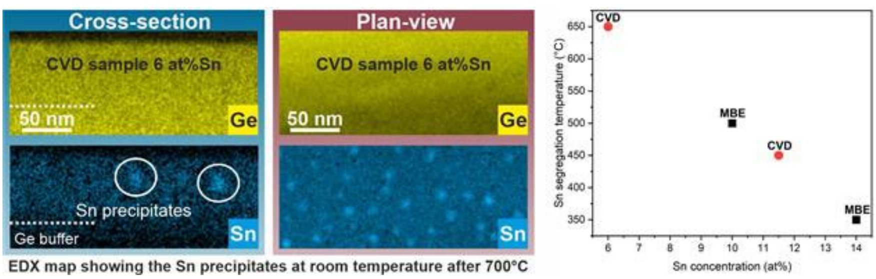
Results

For the MBE samples, two different concentrations of 10 and 14 at% Sn were investigated. The cross-section specimen with 10 at% Sn is stable up to 500°C. At 500°C, Sn-based precipitates are formed in the GeSn epilayer. HRTEM Fast Fourier transform (FFT) analysis of these inhomogeneities reveals a pattern well-fitted with the β-Sn crystal structure [4]. At the same temperature, we monitored the formation of Sn drops in the plan-view sample. In the case of a cross-section sample with 14 at% Sn, the start of the precipitation process is found at a lower temperature of 350°C. For a CVD GeSn layer with 11.5 at% Sn, the specimen shows stability up to 450°C where also β-Sn precipitates appeared. However, to achieve these results the cross-section specimen had to be prepared by the wedge polishing technique, reducing the FIB processing and Ga contamination. Without this measure, the CVD-grown sample decomposes already at 200°C under the influence of Ga impurities implanted during FIB-assisted specimen preparation. To better understand the present Ga contamination effects and the relation with defects, we analyzed CVD samples with different growth and buffer qualities, which influence the density of threading dislocations. However, all samples were highly susceptible to Ga contamination during the standard lamella preparation. Applying our optimized wedge polishing technique, we analyzed additionally a CVD sample with 6 at% Sn, which demonstrated stability up to 650°C during the in situ TEM experiment.

Conclusion

The measured Sn segregation temperature for cross-sectional and plan-view geometries correlate well, however, there are differences in the precipitate densities which are attributed to the free surface diffusion of Sn for the plan-view specimen compared to the suppressed one for the capped cross-section. Regarding the two MBE specimens, since no formation of liquid phases was observed, a solid-state diffusion and precipitation mechanism is believed to occur. Ga contamination during preparation can lead to the formation of a GaSn liquid phase during annealing [4], leading to a fast decomposition of the GeSn layer. CVD GeSn layers are more susceptible to this effect, which we believe is due to the presence of point defects induced by the CVD method. Nevertheless, using the wedge polishing approach it was possible to overcome this challenge. The obtained results show the highest stability for the sample with 6 at% Sn and the lowest for the sample with 14 at% Sn. The gained results indicate a strong dependence of the decomposition temperature on the Sn content, which is summarized in the figure presented.

Graphic:



Keywords:

In-situ TEM, GeSn, MBE, CVD

Reference:

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