

Thermal stability and Sn diffusion in GeSn heterostructures

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Abstract

In this work, we address the thermal stability of GeSn alloys regarding strain relaxation and Sn diffusion. The two competing processes, i.e. dislocation formation and Sn diffusion, are investigated in different heterostructures to deduce the influence of the Ge buffer quality and annealing temperature. Detailed characterization including Rutherford Backscattering Spectrometry (RBS), Secondary Ion Mass Spectrometry (SIMS) and High Resolution X-Ray Diffraction (HR-XRD) are employed for characterization. From this, we conclude that thermal annealing is not the method of choice for strain relaxation of Sn based alloys. Thick and highly strained relaxed GeSn layers can rather be obtained by in-situ growth.

1. Introduction

Thermal stability of GeSn has been the subject of a few papers on GeSn alloys grown by different deposition methods, like Molecular beam epitaxy (MBE) [1] or Chemical Vapor Deposition (CVD) [2]. Since GeSn is a group IV alloy, the experiments were performed in a similar fashion as for SiGe alloys, where strain relaxation theory via dislocation dynamics is well studied. Its viability was considered a priori valid for all group IV alloys. Literature reports are, however, contradictory. Some indicate that GeSn layers pseudomorphically grown on Ge buffers plastically relax by thermal treatment above 420°C. The formation of a strain relieving misfit dislocation network at the GeSn/Ge interface and threading dislocations in the GeSn layers were observed by Transmission Electron Microscopy (TEM) and the degree of strain relaxation was mostly quantified by XRD [3]. The change of the surface topology and Sn diffusion following the annealing of pseudomorphic Ge_{0.9}Sn_{0.1} layers has also been reported, but strain relaxation based on dislocation formation has not been observed. The reduced thermal stability of GeSn alloys is a consequence of the low solid solubility of Sn in Ge [4]. Our experiments indicate that Sn incorporation and layer thermal stability depend on multiple factors but especially on growth conditions and Ge buffer quality.

2. Experimental

For strain relaxation and diffusion experiments, heterostructures consisting of 20 nm Ge_{0.92}Sn_{0.08} capped by 50 nm Ge were grown pseudomorphically on different buffers: i) Ge buffers grown using a not-optimized process with high threading dislocation densities (TDD); ii) on high quality Ge

buffer layers with a TDD of $\sim 10^7 \text{ cm}^{-2}$. In the defective Ge buffer case, where dislocations are already present in large numbers in the layer, de-channeling (i.e. the enhanced backscattering of accelerated ions entering the crystal in a channeling direction) is observed at the GeSn/Ge interface after annealing at 500°C for 10 min. (Fig. 1a). This indicates the existence of a dense misfit dislocation network typically formed during strain relaxation. De-channeling is neither observed in the Ge signal nor in the Sn signal for the GeSn layer grown on high quality Ge buffer after 10 min annealing at 550°C (Fig. 1b). This data, together with reciprocal space map-XRD (RSM-XRD) analyses (not shown here), show that high quality GeSn layers do not relax via dislocation formation movement but via Sn diffusion into the substrate and the Ge-capping layer.

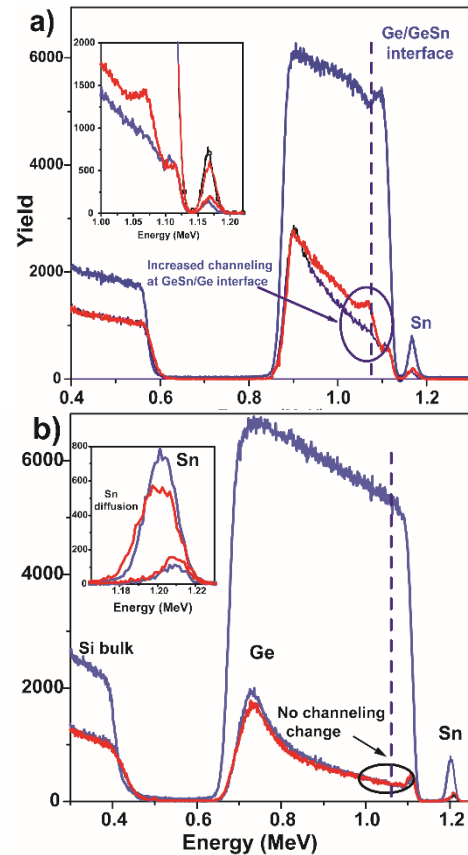


Fig. 1: RBS random and channeling spectra of as-grown and annealed GeSn layers grown on (a) a non-optimized Ge Buffer and (b) high quality Ge buffer.

The evolution of layer thickness and concentration with annealing temperature and time of a thin GeSn layer with 8% of Sn grown pseudomorphically on Ge is shown in Fig 2. Thin GeSn layers embedded in Ge layers are used to study diffusion parameters like activation energies and diffusion coefficients, based on RBS and SIMS analyses. Sn diffusion depends strongly on temperature and less on the annealing time.

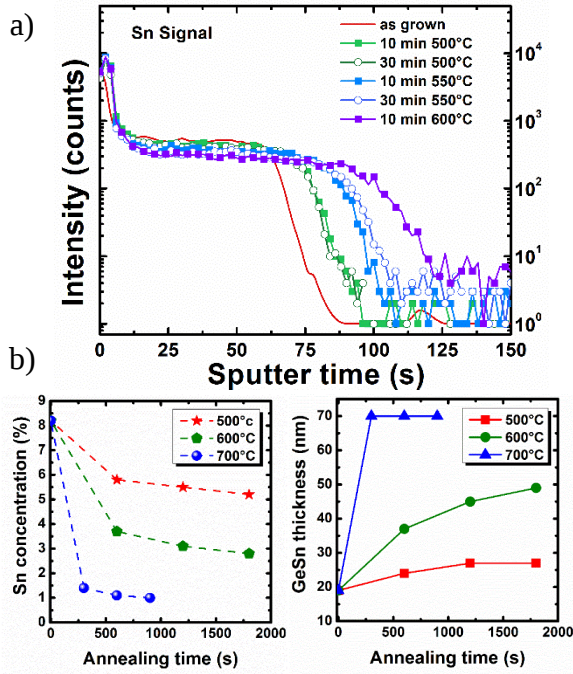


Fig.2: a) SIMS profiles showing time and temperature dependent diffusion behavior of Sn in a $\text{Ge}_{0.92}\text{Sn}_{0.08}$ layer for various thermal treatments. b) Layer thickness and Sn content extracted by RBS.

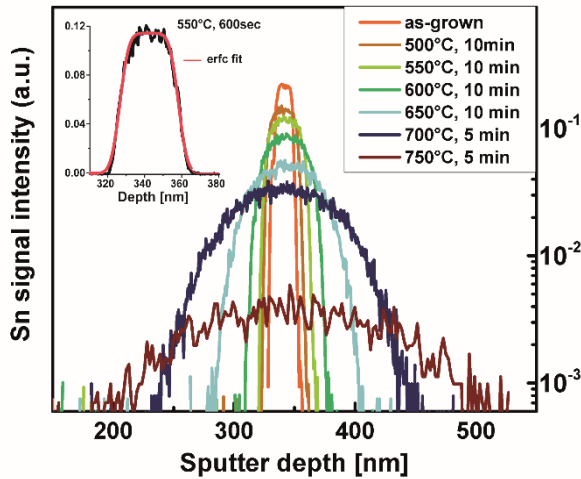


Fig.3: Sn signal from SIMS depth profiling of a 300 nm Ge/ 20 nm $\text{Ge}_{0.92}\text{Sn}_{0.08}$ /Ge-VS structure after various thermal treatments.

Due to fast Sn diffusion and segregation at the surface, a 50 nm Ge cap, as used in the above experiments, limits the temperature and time range for Sn diffusion characterization. Therefore, a 300 nm Ge capped heterostructure was grown. The activation energy and the diffusion coefficient were determined from SIMS profiles (Fig. 3) using the thick layer solution of Ficks' second Law.

In terms of carrier confinement, reduced dimensionality from 3D (bulk) over 2D (quantum well structures) to 0D (quantum dots) opens the path towards new possibilities concerning device performance and material tuning. In this context the stability of GeSn/Ge Multi Quantum Wells (MQWs) and of Single Quantum Wells (SQWs) were investigated.

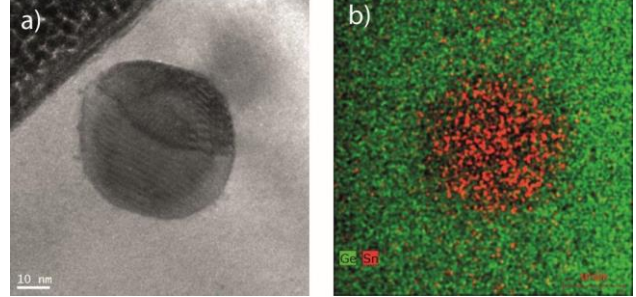


Fig. 4 a,b) XTEM micrograph of GeSn precipitate and corresponding EDX map for Ge and Sn atoms.

Rapid thermal annealing of GeSn/Ge SQWs at temperatures above the growth temperature clearly show a precipitation of dot-like structures (Fig. 4). Although these structures feature facets, their orientation seems to be random concerning the surrounding matrix. SIMS profiles resemble a simple diffusion of Sn into the surrounding Ge layers and towards the sample surface. Moreover, huge voids, which can be described as open volume defects, created by an aggregation of vacancies inside many dots, indicate that the precipitation is supported or initiated by defects.

3. Conclusions

This contribution investigates different processes that lead to strain relaxation of coherently grown GeSn layers under thermal treatment. The influence of diffusion, threading dislocations and point defects are depicted separately. Moreover, dot like structures have been observed, which seem to originate in the aggregation of vacancies.

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