Laser processing of heteroepitaxial GeSn and SiGeSn alloys

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GeSn and SiGeSn alloys are attractive group IV semiconductor materials with superior carrier mobility, tunable band gaps in the midinfrared with indirect to direct transition above certain composition ranges [1–3]. The interesting properties of those alloys for independent adjustment of lattice parameters and band gap over a wide range stimulated the research dedicated to CMOS compatible novel device concepts including the combination of Si based with III/V based technologies [4–6]. Considerable efforts have been recently devoted on growing Ge-rich GeSn and SiGeSn alloys on Si, Ge and InP via MBE and CVD techniques [7–10]. The major problem for incorporating Sn into the Ge is the large lattice mismatch of 4.2% and 19.6% between Si (a_0=0.5431 nm) and Ge (a_0=0.5658 nm) or a-Sn (a_0=0.6493 nm), respectively, the instability of the diamond-cubic structure of α-Sn and the low thermodynamic solubility of Sn in Ge (<1%)[11].

Because of these constrains conventional CVD and MBE growth is done at out of equilibrium conditions and low processing temperature that lead to Sn segregation[7]. To counteract theses effects and improve the intermixing of the elements in order to obtain binary and ternary Si/Ge/Sn alloys with acceptable crystal quality we propose an alternative, out of equilibrium growth, based on ultra fast (several ns) laser melting/intermixing/epitaxial recrystallization cycles. This technique features low optical absorption depth and well controlled temperature gradient for ultra-rapid heating/cooling cycles, induced by pulses of about 25 ns, which provoke controlled changes in composition and structure of the material. These changes are directly related to the laser processing parameters energy density and number of pulses, thus determine the properties of the final product. An effective control of the experimental parameters is achieved simulating numerically the 1-D spatial thermal depth profile using finite element methods[12–15]. Laser processing of Ge/Sn layers was one of the first routes to metastable GeSn[16] with a strong lack of epitaxy. Pulsed Laser Induced Epitaxy (PLIE) is a technique that improves the epitaxial growth and has already proven to be effective for GeSn and SiGeSn alloys with Sn content bellow the solubility limits[14,15,17].

Virtual Germanium (v-Ge) with different thickness on top of Si has been used for the GeSn and SiGeSn alloys. Sn concentration is controlled varying both processing parameters and the thickness of the top Sn layer deposited on the Ge. This layer was realized either after the v-Ge MBE deposition from Sn effusion cell. GeSn is obtained by intermixing of the Ge and Sn layers, whereas SiGeSn alloying results after intermixing of the Ge and Sn layers with the Si substrate. Samples were irradiated in Ar atmosphere, using 193 nm Excimer Laser (Lambda Physik LPX 220i). The laser beam was spatially homogenized using a fly-eye system (EX-HS-700D) and its energy was "in situ" controlled (Ophir PE50-DIF). Time Resolved Reflectivity (TRR) at 633 nm was used to monitor the phase change duration on the sample surface in real time. Experimental variables were energy density and number of laser shots. Analysis of the samples was performed by Raman spectroscopy (HJY LabRam HR800), TOF-SIMS (IonTOF TOF-SIMS-IV) and RBS.

We started with a comparison of the melt duration extracted from the TRR signal and the one derived from the numerical solution of the heat conduction differential equation. The sample structure used for the numerical simulation was 4 nm Sn on top of 100 nm v-Ge on Si substrate. Melt depth and laser energy density, respectively, were adjusted depending if only the Sn and Ge layers melt (bellow 104 nm) is wished and GeSn is formed, or if also the Si substrate is included so that the resulting layer forms SiGeSn alloy. The estimated values were 200 mJ/cm^2 for GeSn and 500 mJ/cm^2 for SiGeSn (Fig. 1). However, the expected alloys were not obtained with one laser shot of these energy densities. We saw that the level of intermixing of the corresponding layers (alloy components resp.) was strongly dependent on the number of laser shots (Fig. 2) and therefore samples irradiated with 100 pulses were further studied. Sn substitutional content from RBS yields 1% in GeSn and 0.6% in SiGeSn. We suggest that higher Sn content might be obtained varying Sn and Ge layer thickness that would reflect on the amount of incorporated Sn in both Ge and SiGe.

In summary, we report on an alternative technique to synthesize epitaxial GeSn and SiGeSn alloys and point out a route to reach Sn content above the solubility limit. Also, an improvement of the scalability of the applied technique for GeSn and SiGeSn alloys ranging from micrometer structures to large area substrates is included in this route.

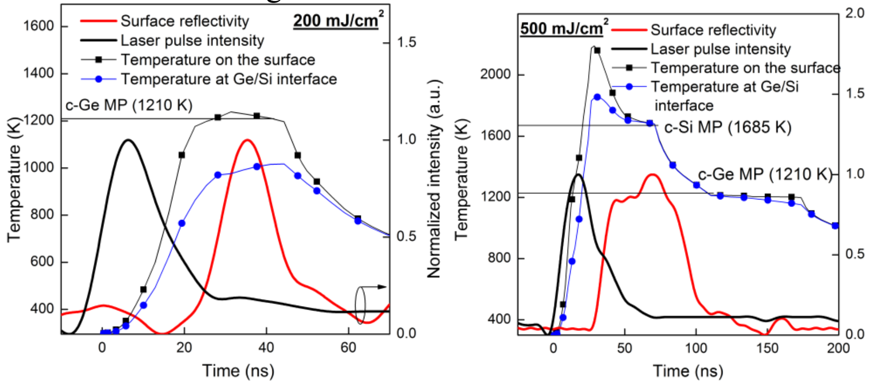

Fig. 1 Comparison of calculated and experimentally obtained melt duration for the first puls of 200 (left panel) and 500 (right panel) mJ/cm^2.

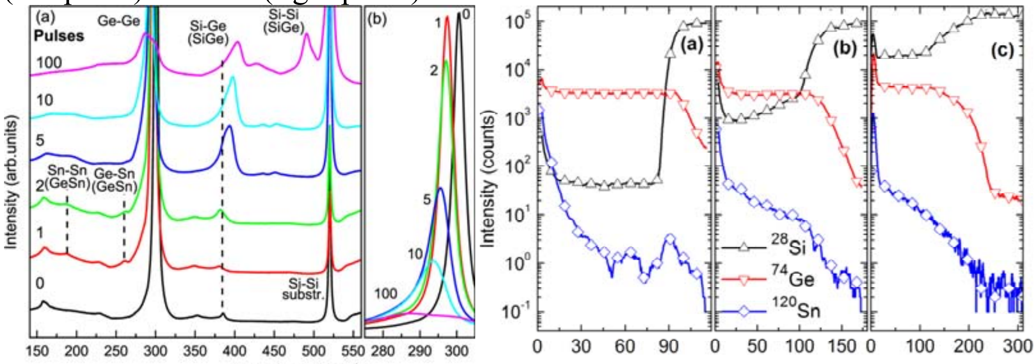

Fig. 2 Evolution of the level of intermixing with increasing number of pulses[15]. The left panel (a) shows the transition of the Raman modes from GeSn to SiGeSn for 0 to 100 pulses of 500 mJ/cm^2, (b) represents the intensity of the Ge-Ge Raman mode that decreases with increasing intermixing of the three components. The right panel shows TOF-SIMS depth profile of the as received (a) irradiated with 5 shots (b) and 100 shots (c) of 500 mJ/cm^2 samples.

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