CSiGeSn Epitaxy: Future Isovalent Isomorphism in Group-IV Materials

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1. Introduction

Group-IV materials constitute the foundational platform for advancing silicon-based photonics, spintronic, and energy technologies.[1] Recent breakthrough in the field includes the demonstration of continues-wave electrically pumped lasing based on advanced (Si)GeSn/GeSn MQWs.[2] Theoretical calculations predicts that the C substitution into Ge lattice even enhance the directness of band gap leading to laser performance improvement.[3] Hence, successful incorporation of C into these alloys and understanding on growth mechanism is beneficial for the Si-based alloys applications. However, thermodynamic, low solubility and large lattice mismatch limits the C and Sn substitutional incorporation in Ge diamond lattice. Apart from epitaxial challenges, T. Yamaha *et al.* reported that C could enhance the Sn alloying in Ge due to strain compensation via C-Sn pair formation in $C_yGe_{1-x-y}Sn_x$ films.[4] This effect aligns with A. Chroneos's theory, which suggests that Sn promotes the formation of isovalent C-Sn-V complexes (V = vacancy), thereby reducing vacancy formation energy with minimum lattice distortions.[5]

In this study, we address the growth aspects of ternary and quaternary Group-IV alloys, in comparison with GeSn epitaxy, which serve as benchmark. Additionally, an unconventional carbon precursor - CBr_4 is introduced and its chemical influence on onset Sn alloying for CGeSn alloys is presented. Later, the Si induce defect engineering to compensate the effect of C alloying on strain relaxation in diamond cubic lattice during (Si)GeSn epitaxy is studied.

2. Materials and Methods

The epitaxial growth is performed on 200 mm Si (001) wafers under reduced-pressure chemical vapor deposition (RP-CVD) conditions (45 Torr). To avoid the large lattice mismatch between C, Sn and Si, a ~300 nm Ge buffer layer is deposited prior to the growth of these alloys. Detailed experimental growth parameters for GeSn thin films can be found elsewhere. [6] The obtained alloys are synthesized using multi-source chemical precursors such as Si_2H_6, Ge_2H_6, $SnCl_4$, and CBr_4. The compositions and layer thicknesses of the samples are extracted by Rutherford backscattering spectrometry (RBS), while crystallinity and the defect formation are investigated by high resolution- transmission electron microscope (HR-TEM).

3. Results and Discussion

As already previously known and discussed in literature, for GeSn alloys the growth rate increases with the temperature, here from 10.2 nm/min at the growth temperature T_g = 330°C to 25 nm/min at 380°C, associated with a reduction in the Sn content in the film. Interestingly, the introduction of CBr_4 changed the GeSn growth kinetics, where the activation energy for the formation of CGeSn alloys is reduced by ~4 kcal/mol (Fig. 1a). Simultaneously, at all growth temperatures, the increase on the growth rate is associated with increase Sn concentration into Ge lattice. At a growth temperature of 330°C the Sn content reaches 18 at.% and C content of 0.2 at.%. Additionally, onset coaxial ligands exchange

(-H, -Br, -Cl) at the growth surface can also influence the overall adatoms diffusivity, which then can alters the chemisorption process of individual atoms during the film growth.

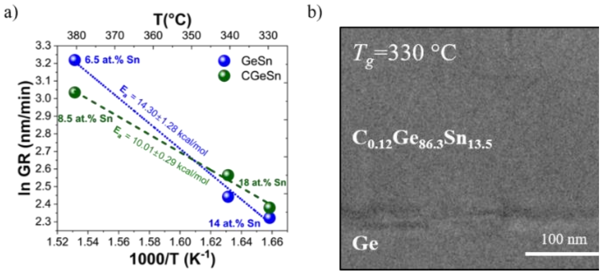

Fig. 1. a) Arrhenius plots of CGeSn growth in comparison with GeSn alloys grown under similar growth conditions in nitrogen ambient. b) HR-TEM micrograph showing high quality CGeSn films with carbon about 0.12 at.%..

However, C in GeSn alloys restricts the lateral motion of atomic displacement by pinning the dislocation glide along the <110> crystal direction. The crystalline quality of CGeSn alloy is mentioned high up to C contents of 0.12 at.% as shown in Fig. 1b and it strongly degrade at high C incorporation as shown in Fig. 2a. This effect has already been reported for CSiGe alloys.[7] Therefore, to overcome such dislocation nucleation pile-up at the CGeSn/Ge interface, further Si was incorporated into the CGeSn alloy which then could compensate the accumulated strain, while retaining the crystal quality by forming 90° Lomer dislocations at the interface, as shown in inset of Fig. 2b.[6]

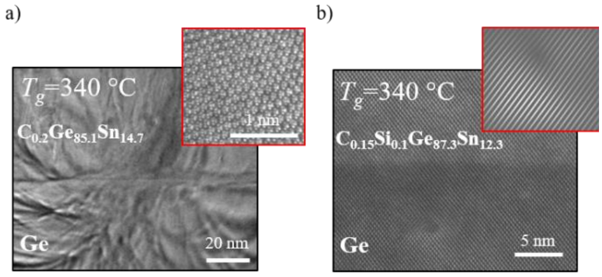

Fig. 2. a) HR-TEM micrograph showing presence of strain-field in CGeSn films with carbon about 0.2 at.%. Inset: zoomed-in image showing distorted crystal lattice. b) HR-TEM of CSiGeSn alloys indicating showing sharp Ge/CSiGeSn interface. Inset: inverse fast Fourier transform (FFT) of Lomer dislocation along (001) plane.

Apart from stain compensation effect, density functional theory (DFT) calculations by E. Kamiyama *et al.* shown that C (Ge) and Sn atoms would be stable and preferentially occupy 1NN (nearest neighbor), while Si and Sn atoms only stable at 1NNN (next-nearest neighbor) in a Ge diamond cubic lattice. [8]

4. Conclusions

In this work, we present growth studies of ternary- CGeSn and quaternary CSiGeSn alloys. The use of CBr_4 precursors lead to C incorporation up to 0.2 at.% that simultaneously induces Sn content increase by about 20%. The increase in Sn content build-up lattice strain which relaxation is hindered by the C dislocation pinning. The lattice strain engineering via Si incorporation stabilized the diamond cubic lattice, while forming quaternary CSiGeSn alloys. This prefer covalent bonding over entropy gain, stabilizes the isovalent group IV alloys in addition to the effects of strain compensation. Further investigations on the influence of chemical short-range-order (SRO) on formation of these alloys is under investigations. The resulting material exhibits both structural uniformity and tunable compositions, opening new avenues for covalent group-IV semiconductors and quantum technologies.

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