

Liquid-Solid Coexisting Annealing of a-GeSn/Si(100) Structure for Low Temperature Epitaxial Growth of SiGe

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INTRODUCTION

To achieve further improvement of LSI performance, functional materials of Si based mixed crystals become essential. We have developed the SiGe mixing-triggered rapid melting growth technique and realized defect-free single crystal Ge, SiGe, and GeSn layers [1-3]. However, high temperature annealing above melting point of Ge (938°C) was necessary for this technique. Recently, Nakatsuka et al. reported low-temperature (~400°C) formation of SiGe(Sn) by annealing of a-GeSn/Si stacked structures, which was attributed to solid-phase atomic mixing [4]. It is noted that the liquid-solid coexisting (L+S) region exists in the phase diagram of GeSn. Since the solidification point of GeSn is 231°C, we can expect that low-temperature (<300°C) liquid-phase growth should propagate through partially-melted channel running across the liquid-solid coexisting region. In the present study, we investigate the Sn-doping effects on the growth characteristics of a-GeSn/Si(100) stacked structures. This enables epitaxial-growth of SiGe at much lower temperatures (~300°C).

EXPERIMENTS

Amorphous $\text{Ge}_{1-x}\text{Sn}_x$ ($x = 0, 0.26$) layers (100 nm thickness) deposited on Si(100) substrates were patterned into a dot shape (20 $\mu\text{m}\phi$). After capping SiO_2 layers (1 μm thickness) by sputtering, they were annealed (300 – 1000°C, 1sec – 48h) in N_2 . The sample structure is shown in Fig.1(a).

RESULTS AND DISCUSSION

After etching off the capping layers, micro-probe Raman spectroscopy measurements were carried out. The results for Ge and $\text{Ge}_{0.9}\text{Sn}_{0.1}$ samples after annealing at 650-950°C (1 sec) are summarized in Fig.1(b). In all spectra, Raman peaks due to Ge-Ge bonding in crystal are observed. Moreover, Raman peaks due to Si-Ge bonding are clearly observed for annealing temperatures above 950 and 800°C for Ge and $\text{Ge}_{0.9}\text{Sn}_{0.1}$ samples, respectively. It is noted that the SiGe mixing temperature (800°C) for $\text{Ge}_{0.9}\text{Sn}_{0.1}$ samples is lower than the melting point of $\text{Ge}_{0.9}\text{Sn}_{0.1}$ (~890°C).

Crystal orientation of the grown layers was investigated with electron backscattering diffraction (EBSD). The EBSD images are shown in Fig.1(c). For samples without Sn doping, a (100)-oriented layer is obtained after annealing at 950°C (1 sec), which indicates SiGe mixing-triggered melting growth from the Si(100) substrate. This result agrees with our previous study [1-3]. On the other hand, for $\text{Ge}_{0.9}\text{Sn}_{0.1}$ samples, a (100)-oriented layer is obtained after annealing at temperatures above 800°C (1 sec), where the temperature (800°C) is identical to that for SiGe mixing as shown in Fig. 1(b). The Auger electron spectroscopy measurements revealed that Sn concentration in the grown samples was very small (1-2%), probably due to segregation during growth. From these results, it is found that SiGe epitaxial growth, as well as SiGe mixing, is generated at a temperature in the liquid-solid coexisting region of the phase diagram for Sn-doped samples.

To explain this Sn-induced crystallization, we consider partial melting of GeSn layers during liquid-solid coexisting annealing. We speculate that SiGe mixing starts to occur at the interface between the liquid GeSn regions and Si substrates. Such SiGe mixing should generate one-directional growth from Si substrates [1]. Here, the fraction of the liquid regions becomes large for higher Sn concentration at the same annealing temperature.

Based on this consideration, we expect that epitaxial growth temperature can be further decreased by increasing Sn concentration and annealing time. To examine this, growth features of GeSn samples with various Sn concentrations (0 ~ 26%) and annealing time (1sec ~ 48hour) were investigated. The crystallization temperatures are summarized in Fig.2. This evidences that the epitaxial growth temperature significantly decreased to 300°C by increasing Sn concentration and annealing time. This well supports our model based on partial melting of GeSn.

In summary, growth features in the liquid-solid coexisting region have been investigated. As a result, low-temperature (~300°C) epitaxial growth of SiGe becomes possible. This technique is useful to realize next-generation LSIs, where various multi-functional devices are integrated.

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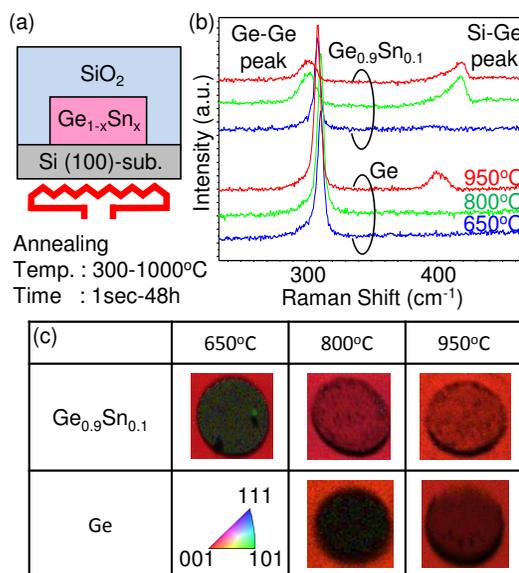


Fig.1. Schematic sample structure (a), Raman spectra obtained from Ge and $\text{Ge}_{0.9}\text{Sn}_{0.1}$ samples after annealing (650, 800, 950°C, 1sec) (b) and EBSD images of Ge and $\text{Ge}_{0.9}\text{Sn}_{0.1}$ samples (c).

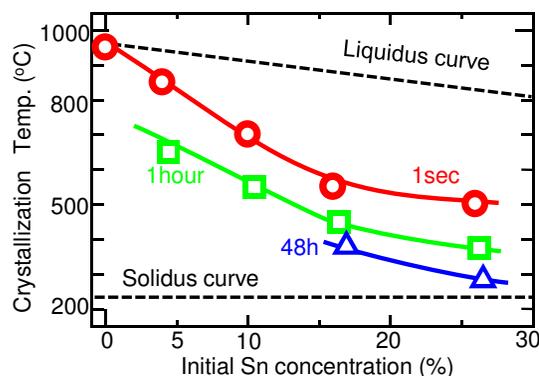


Fig.2. Crystallization temperature as a function of initial Sn concentration.