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GeSn nanodots crystal nuclei for solid phase crystallization of poly-SiGeSn

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Abstract

Solid phase crystallization of polycrystalline $Si_{1-x-y}Ge_xSn_y$ using $Ge_{1-x}Sn_x$ nanodots ($Ge_{1-x}Sn_x$-ND) as crystal nuclei was examined. The effects of the substrate temperature and the initial Ge/Sn composition on the dot size, coverage, and substitutional Sn composition in the $Ge_{1-x}Sn_x$-ND were investigated. Lowering deposition temperature increased the substitutional Sn composition in $Ge_{1-x}Sn_x$-ND. Crystallization of Si deposited on the $Ge_{1-x}Sn_x$-ND was confirmed at the deposition temperature of 150 °C. The Si and Sn composition in the poly-$Si_{1-x-y}Ge_xSn_y$ layer was 36.3% and 4.2% after annealing at 225 °C.

1. Introduction

Poly-$Si_{1-x-y}Ge_xSn_y$ is effective in improving thermoelectric conversion efficiency because lattice heat conduction is suppressed by alloying [1]. However, there are some issues: the crystallization temperature of Si is very high compared to that of Ge and Sn, and the solid solubilities of Sn in Si and Ge are very low [2]. It has been found in previous studies that Ge and Si can be crystallized at low temperatures by using Sn nanodots (Sn-ND) as crystal nuclei [3].

In this study, we demonstrated the poly-$Si_{1-x-y}Ge_xSn_y$ formation by using $Ge_{1-x}Sn_x$-ND as crystal nuclei. First, the effects of formation conditions, such as the deposition temperature on physical properties and Sn composition in $Ge_{1-x}Sn_x$-ND were investigated. Besides, it was confirmed that the crystalline $Ge_{1-x}Sn_x$-ND can act as the crystal nuclei for the formation of poly-$Si_{1-x-y}Ge_xSn_y$.

2. Experimental

$Ge_{1-x}Sn_x$-ND and poly-$Si_{1-x-y}Ge_xSn_y$ were prepared on SiO_2/Si substrates using an MBE system. $Ge_{1-x}Sn_x$-ND were prepared by co-depositing Ge and Sn with changing their ratio. The substrate temperature during the deposition was RT or 150 °C to 250 °C. Some $Ge_{1-x}Sn_x$-ND were in-situ annealed after the deposition. The coverage and average dot radius were estimated using SEM, and the Sn composition was estimated using X-ray diffraction (XRD) and Raman spectroscopy.

2. Result and Discussion

$Ge_{1-x}Sn_x$-ND prepared by depositing 4 nm-thick Ge and 1 nm-thick Sn at RT followed by annealing at 275 °C for 30 min had an average dot radius of 20.4 nm and a coverage of 43.3%. The $Ge_{1-x}Sn_x$-ND formed by co-depositing 8 nm Ge and 2 nm Sn at a substrate temperature of 200 °C had an average dot radius of 18.0 nm and a coverage of 52.0%. The average dot radius and coverage of Sn-ND formed by annealing at 275 °C for 30 minutes after the deposition of 10 nm Sn-ND at RT was 43.7% and the dot radius of 21.8 nm. These results indicate the $Ge_{1-x}Sn_x$-ND can be smaller than Sn-ND and the $Ge_{1-x}Sn_x$-ND formed using the heated substrate had higher coverage and smaller dot size than the ND deposited at RT followed by annealing.

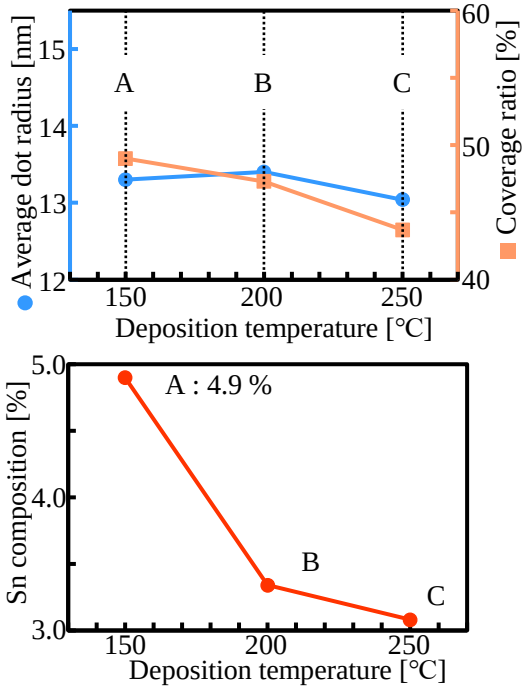

Fig. 1 (a) Average dot radius and (b) substitutional Sn composition of $Ge_{1-x}Sn_x$-ND coverage as a function of deposition substrate temperature. The ratio of deposited Ge and Sn was 9 nm and 1 nm.

The coverage ratio, the average dot radius, and the substitutional Sn composition as a function of the deposition temperature are summarized in Fig.1. The increase in substrate temperature during deposition causes agglomeration more easily, resulting in a decrease in coverage. Despite the agglomeration, the average dot radius for the sample prepared at 250 °C was smaller than that prepared at lower temperature. It is considered due to too high substrate temperature causing Sn desorption (Fig.1a). The Sn composition of $Ge_{1-x}Sn_x$-ND formed at a deposition substrate temperature of 150 °C, was higher than that deposited at 200 °C and 250 °C (Fig.1b). This

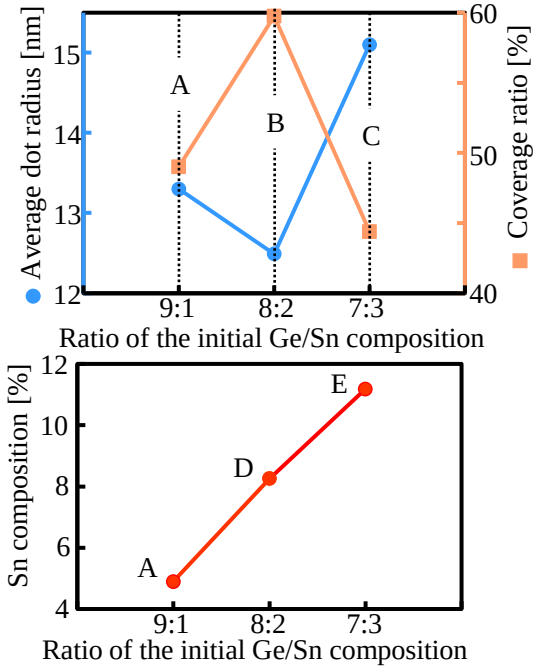

Fig.2 (a) Average dot radius and coverage and (b) substitutional Sn composition of $Ge_{1-x}Sn_x$-ND as a function of deposition the initial Ge/Sn composition. The deposited temperature was 150 °C.

result can be explained by that the high amount of Sn can remain to in Ge at the lower substrate temperature. The Sn composition of sample A was estimated as high as 4.9% which is higher than the solid solubility of Sn in Ge.

Next, the effect of the ratio of initial Ge/Sn composition on the $Ge_{1-x}Sn_x$-ND was investigated at a substrate temperature of 150 °C. $Ge_{1-x}Sn_x$-ND formed by depositing 7 nm-thick Ge and 3 nm-thick Sn had a large dot radius and low coverage (Fig.2a) due to higher amount of Sn which tends to cause agglomeration. The Sn composition in $Ge_{1-x}Sn_x$ increased with the amount of Sn deposited (Fig.2b). In sample E, the Sn composition was calculated to be 11.2% which is exceeded well the solid solution limit of Sn into Ge.

The sample D with 8.3% Sn content, which has the highest coverage and the smallest average dot radius, was used as a crystal nucleus for Poly-$Si_{1-x-y}Ge_xSn_y$. 8 nm-thick Si was deposited on the prepared $Ge_{1-x}Sn_x$-ND at 150 °C and annealed in-situ at 275 °C for 30 min. As shown in Fig. 3, Si is crystallized without the in-situ annealing using $Ge_{1-x}Sn_x$-ND as the crystal nuclei because the peak position was shifted from near the ideal peak position of Ge111 (27.28 deg.) to that of Si111 (28.44 deg.). However, exhibiting strong peaks of β-Sn200 (30.64 deg.) and 101 (32.02 deg.) means that the deposition of Si also caused the precipitation of Sn. The lower solubility limit of Sn in Si compared to that in Ge is supposed to be the reason of the Sn precipitation.

An increase in the peak intensity of Si-Ge vibration mode around 400 cm^{-1} was observed in the annealed sample (Fig. 4). This indicates that Si is bound not only to Sn but also to Ge, suggesting that heat treatment after Si deposition is effective for crystallization of $Si_{1-x-y}Ge_xSn_y$ further.

Using both XRD peak position and Raman peak position, the compositions of Si, Ge, and Sn were calculated to be 36.3 %, 59.5 %, and 4.2 %, respectively.

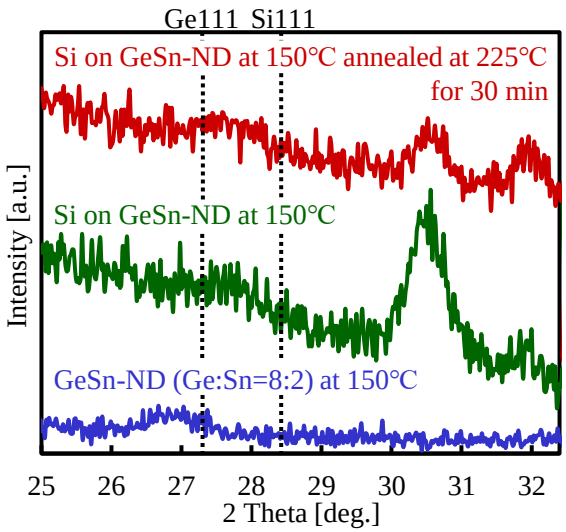

Fig.3 XRD measurement results of $Ge_{1-x}Sn_x$-ND used as crystal nuclei and poly-$Si_{1-x-y}Ge_xSn_y$ grown on the $Ge_{1-x}Sn_x$-ND.

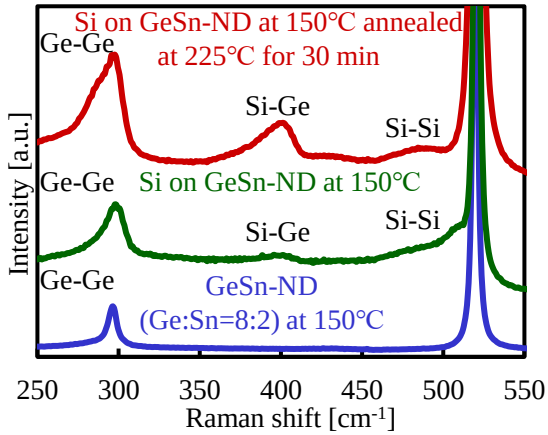

Fig.4 Raman spectra of $Ge_{1-x}Sn_x$-ND used as crystal nuclei and poly-$Si_{1-x-y}Ge_xSn_y$ grown on the $Ge_{1-x}Sn_x$-ND.

3. Conclusions

By co-depositing Ge and Sn on SiO_2/Si at a substrate temperature of 150 °C, $Ge_{1-x}Sn_x$-ND with a high coverage and small average dot radius were prepared. Its Sn content greatly exceeded the solid solution limit of Sn to Ge. Increasing the amount of deposited Sn increases the Sn content, but also has a risk of agglomeration reducing the coverage. It has been confirmed that $Ge_{1-x}Sn_x$-ND is effective as a crystal nucleus for poly-$Si_{1-x-y}Ge_xSn_y$ formation at low temperature as low as 150 °C.

Acknowledgements

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