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High Quality GeSn Layer Formation Due to Well-controlled Sn Migration at High Temperature

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Abstract

In order to form a high quality GeSn layer, Sn migration control during epitaxial growth at high temperature(400°C) was tried based on a proposed model. The experiments and calculations changing deposition speed (v_d) clarified that high v_d growth provides an epitaxial GeSn layer with good crystallinity and optical properties reducing Sn migration.

Introduction

Sn-related group IV semiconductors are attractive material for monolithically integrated electrical and optical devices on a circuit because of controllability of the energy band structure and process suitability for Si-based circuits. For realizing the Sn-related devices, formation of device quality crystal with high Sn content (C_{Sn}) is mandatory. Control of Sn migration is a most important issue for the formation, because high C_{Sn} induces Sn precipitation due to low eutectic temperature of ~ T_e=230°C and low solid solubility limit(1-2%) of Sn in Ge. In order to reduce the Sn precipitation, low temperature growths have been used[1,2]. Although a relationship between crystalline quality and growth temperature for Sn-related alloys has not yet been fully understood, low temperature growth of a GeSn layer could induce high defect density like in the GeSi system and electrical active defects in GeSn/Ge diodes[3,4]. An appropriate high temperature could lead Ge and Sn atoms to stable states in a lattice potential, which gives us high crystalline quality if Sn precipitation and segregation can be controlled. However, the Sn controllability higher than T_e during epitaxial growth has not been fully understood yet.

In this study, in order to form a GeSn layer avoiding Sn precipitation at high temperature, Sn migration was systematically investigated changing deposition speed(v_d) of GeSn layers through comparison with calculated results using a proposed model[5].

Experimental procedure

After chemical cleaning with a diluted HF solution and thermal cleaning at 830°C of a p-Si (001) substrate in an H_2 ambient condition of 1×10^{-2}Pa, a 100(or 200)-nm-thick Ge buffer layer was formed on the Si substrate at 300°C in the H_2 ambient with RF plasma to reduce surface roughening. Subsequently, the sample was annealed at 700°C in the H_2 ambient condition to elongate misfit dislocations located at the Ge/Si interface. After that, an Sb-doped GeSn layer with Sn content ($C_{Sn\text{-}XRD}$) of 1-2 or 3-4% was formed at 400°C in the H_2 ambient condition changing v_d. Here, $C_{Sn\text{-}XRD}$ was estimated by 2 dimensional x-ray reciprocal space map (2DRSM) assuming that lattice deformation and lattice parameters obey Poisson ratio and Vegard's law, respectively. Sb concentration of 10^{19}cm^{-3} was aimed. The GeSn layers were characterized by XPS, TEM, XRD and photo-luminescence method (PL).

Results and discussion

Recently, we established a model describing the Sn migration in epitaxial growth of a GeSnSi layer[5], which is composed of small slabs(Fig.1). Taking into account exponential decay of Sb migration flux drawn by green lines, Sn migration flux at each slab can be calculated. Integrating the Sn flux at each slab, a Sn depth distribution reflecting the Sn migration can be obtained. According to the model, amount of Sn content changes (ΔC_{Sn}) were calculated for 200°C(Fig. 2(a)) and 400°C(Fig. 2(b)) for the various v_d/v_m values as a function of the layer thickness. In Fig.2(a), ΔC_{Sn} at more than v_d/v_m of 0.680 hardly depend on the layer thickness, which means a Sn-related material layer with uniform C_{Sn} can be formed. On the other hand, in Fig. 2(b), less than v_d/v_m of 0.690, uniform C_{Sn} could not be obtained. These results indicate that high v_d is required for forming uniform Sn distributions at high growth temperature(T_d). To compare these calculations and experimental data, ΔC_{Sn} in the GeSn layers were evaluated by XPS with sputtering for v_d=4 and 13 nm/min (Fig. 3). For v_d=4 nm/min, the experimental ΔC_{Sn} increases toward to the surface, while for v_d=13 nm/min, the experimental ΔC_{Sn} hardly changes. Also, the calculated results are in good agreement with the experimental results, indicating the model can well describe the Sn migration in the GeSn/Ge buffer system. On the other hand, the model was not able to describe C_{Sn} at the surfaces, which could be owing to discontinuity of the Sn migration at the surface. C_{Sn} at the surfaces for $C_{Sn\text{-}XRD}$ of 3-4% decreases with increasing v_d, although C_{Sn} at the surfaces for $C_{Sn\text{-}XRD}$ of 1-2% hardly depend on v_d(Fig. 4). These results mean that high v_d is effective for forming a GeSn layer with high C_{Sn}.

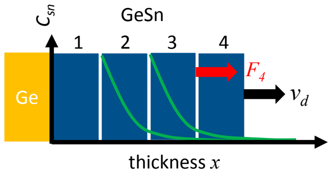
Crystallinity of the GeSn layers formed at different v_d at 400°C was evaluated by XRD. Although broadening of $\bar{2}\bar{2}4$ omega scan profiles for v_d=2 and 4 nm/min are almost identical, the broadening for v_d=13 nm/min is much sharper than those for the others(Fig. 5). Indeed, an isolated $\bar{2}\bar{2}4$ peak from the Ge peak was observed in 2DRSM(Fig. 6). Also, it was found that the GeSn layer was pseudomorphically grown on the Ge buffer layer. In order to make it clear the impact of v_d on full-width at half maximum (FWHM) of the $\bar{2}\bar{2}4$ peaks for the omega scans, the FWHM values were plotted as a function of v_d (Fig. 7). It is found that high v_d leads to small FWHM values for the GeSn layers, and that the value for v_d=13 nm/min is comparable to the value of the Ge layer formed at 700°C. Furthermore, no significant Sn precipitation was observed at the high v_d growth (Fig. 8) even at much higher temperature than T_e. These results mean that high v_d results in good crystallinity of the GeSn layer.

C_{Sn} and v_d dependences of optical properties of the GeSn layers were investigated to confirm the energy band engineering due to Sn introduction and impact of v_d on optical properties. For the Ge layer formed at 400°C, no obvious peak was observed, while the clear peaks were observed in the Ge layer formed at 700°C and the GeSn layers formed at 400°C(Fig. 9). It is found that the peak energies depend on the Sn contents. These results indicate that Sn introduction induces changes on the energy band structures in the GeSn layer, and is effective for improving the optical property. Furthermore, it is found that high v_d leads to sharper PL spectra and higher intensity(Fig. 10). Consequently, high v_d growth avoiding Sn migration is effective for formation of a high quality GeSn layer, although further systematic study for T_d should be done.

Conclusions

The experimental and calculated v_d dependences of the crystalline and optical properties clarified that high v_d growth makes it possible to form a high quality GeSn layer with C_{Sn} higher than solid solubility limit of Sn at T_d higher than T_e. Consequently, a high quality GeSn layer was successfully formed at v_d=13 nm/min and 400°C. These results could help forming Sn-related crystal with device quality.

References: [1] Y. Shimura, *et al*, Thin Solid Films **518**, S2 (2010). [2] M. Bauer, *et al*, Appl. Phys. Lett.,**81**,2992 (2002). [3] Knights et al., J. Appl. Phys., **89**, 76 (2001). [4] N. Taoka, *et al*, Ext. abst. of SSDM 2014, p.8. [5] N. Taoka, *et al*, Appl. Phys. Lett., **106,** 061107 (2015).



$$F_{n+1} = F_{mi} \left\{ \frac{1}{2} + \sum_{n=0}^{n} 2^{n-1} \exp\left(-\frac{n v_d}{v_m} \right) \right\}$$

F_{n+1}: Sn flux migrated from 1st to nth slabs, F_{mi}: Temperature dependent Sn migration flux, n: Slab number, v_d: Deposition speed, l: Decay length of Sn migration, Δt: Time determined by $\Delta x/v_d$, Δx: Slab width, v_m: Sn migration speed determined by l /Δt.

Fig. 1: Schematic diagram and equation of Sn migration model[5]. F_{mi} is expressed by an Arrhenius type function with temperature independence pre-factor (P_f) and activation energy (E_{am}).

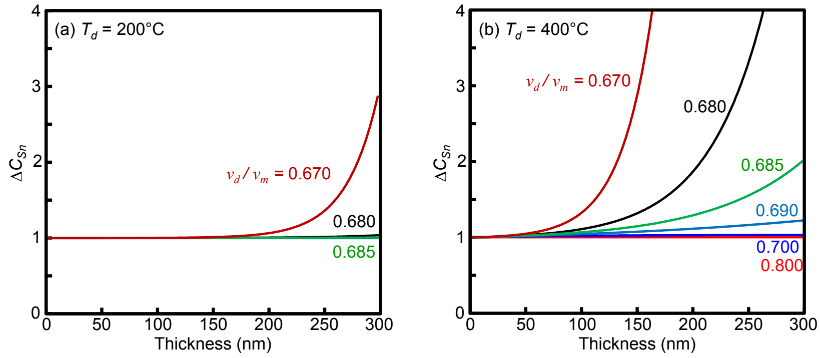


Fig. 2: ΔC_{Sn} for (a) T_d = 200°C and (b) 400°C for the various v_d/v_m values. Here, 0.7eV and 5×10^{14}cm^{-2}sec^{-1} were used for E_{am} and P_f, respectively, referenced the values for the GeSiSn layer. T_d means deposition temperature.

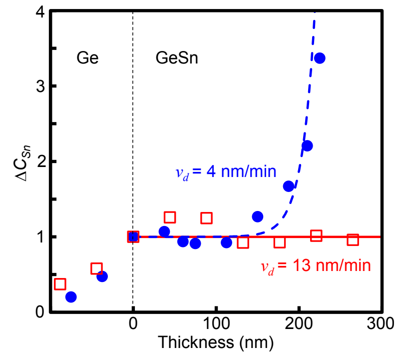


Fig. 3: Experimental changes of C_{Sn} in the GeSn layers formed at 4 and 13 nm/min. Solid and dashed line were calculated using the model with v_m= 6 nm/min.

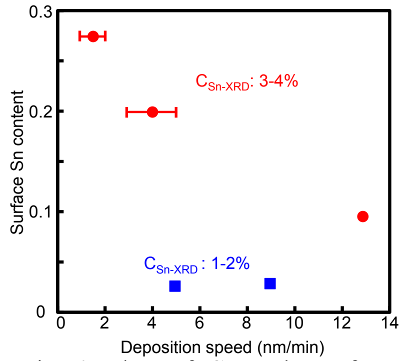


Fig. 4: Plots of C_{Sn} at the surface evaluated from XPS as a function of v_d.

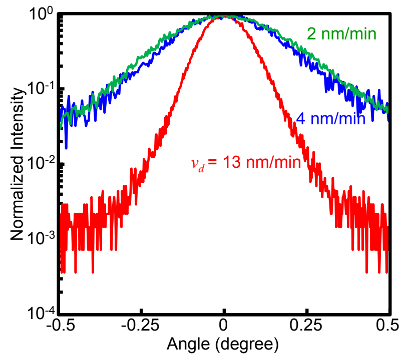


Fig. 5: XRD profiles of $\bar{2}\bar{2}4$ omega scan for the GeSn layers formed at different v_d. Here, the profiles were normalized by the peak intensities and the peak angles were set to zero.

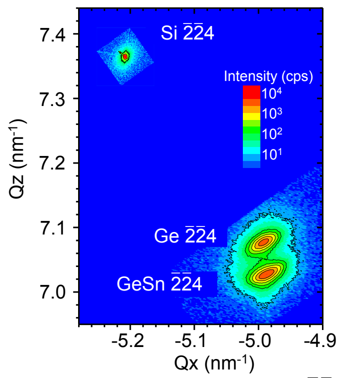


Fig. 6: 2DRSM for the $\bar{2}\bar{2}4$ diffractions for Si, Ge and GeSn layer formed at v_d = 13 nm/min and T_d=400°C.

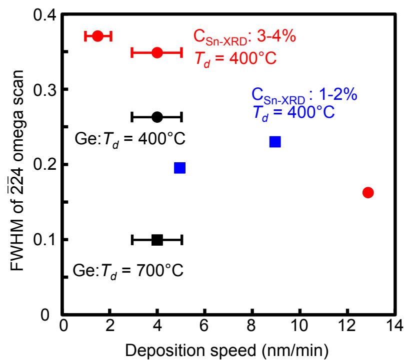


Fig. 7: Plots of FWHM of the $\bar{2}\bar{2}4$ omega scans for the GeSn and Ge layers as a function of v_d. The values for homoepitaxial Ge layers formed at 400°C and 700°C are also plotted as benchmarks.

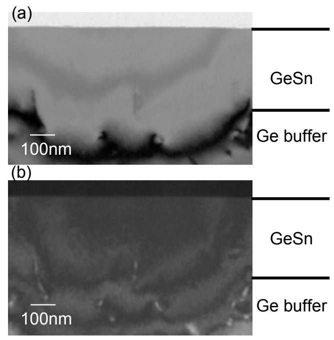


Fig.8: Cross-sectional TEM images for the GeSn layer formed at 400°C with v_d = 13 nm/min taken at (a) bright field and (b) weak beam condition using the 220 diffraction vector.

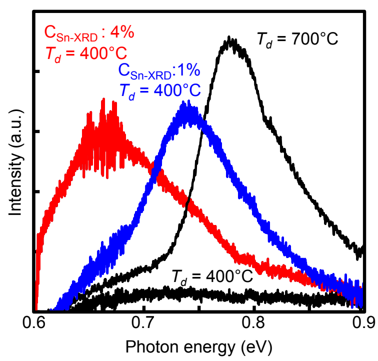


Fig. 9: PL spectra for the Ge and GeSn layers formed at v_d ~ 4nm/min. Here, the spectra were measured at room temperature. Black lines mean the Ge samples.

Fig. 10: PL spectra for the GeSn layers formed at 400°C with three kinds of v_d. Here, the spectra were also measured at room temperature.