Extended Abstracts of the 2018 International Conference on Solid State Devices and Materials, Tokyo, 2018, pp817-818

Development of GeSn-related group-IV thin films for designing energy band

O. Nakatsuka[1,2], M. Kurosawa[1,3], W. Takeuchi[1,4], M. Sakashita[1], and S. Zaima[5]

[1]Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603 Japan
Phone: +81-52-789-5963 E-mail: nakatuka@alice.xtal.nagoya-u.ac.jp
[2]Institute of Materials and Systems for Sustainability, Nagoya University
[3]Institute for Advanced Research, Nagoya University, Japan
[4]Aichi Institute of Technology, Yakusa-cho,Toyata 470-0392, Japan
[5]Institute of Innovation for Future Society, Nagoya University, Japan

Abstract

We have developed the crystal growth technology of $Ge_{1-x}Sn_x$ and related group-IV semiconductor thin films for electronic and optoelectronic applications. We will report our recent research progress of the crystal growth and characterization of electronic properties of these semiconductor thin films.

1. Introduction

The development and research of $Ge_{1-x}Sn_x$ and related group-IV semiconductors have been actively progressed for electronic and optoelectronic applications in the world during recent 10 years [1-4]. $Ge_{1-x}Sn_x$ has unique properties; indirect-to-direct transition with increasing the Sn content approximately above 8%, theoretically expected higher mobilities of both electron and holes than Ge and Si, appropriate optoelectronic properties with a higher efficiency, good compatibility for Si large-scale integrated circuit (LSI) platform, a lower crystallization temperature with a higher Sn content, and a low thermal conductivity suitable for thermoelectronic device. Recently, there are various applications of $Ge_{1-x}Sn_x$ for CMOS transistors, photodiode light emitting diode, laser diode, and thermoelectornic generator.

The crystal growth technology of $Ge_{1-x}Sn_x$ and related thin films is essential for integrating of these materials on the state-of-the-art Si LSI devices. Also, we have to develop the engineering technology of not only crystalline properties related to defects, dislocations, and doping but also electronic properties of energy band, mobility, and band-to-band interactions. In addition, the interface engineering technology at heterostructures of group-IV semiconductors, metal/$Ge_{1-x}Sn_x$, and insulator/$Ge_{1-x}Sn_x$ should be developed deeply for realizing nanoelectronics applications.

We have been developing the crystal growth of $Ge_{1-x}Sn_x$ and various group-IV thin films including $Si_{1-x}Sn_x$, $Si_xGe_{1-x-y}Sn_y$, $Ge_{1-x-y}Sn_xC_y$, and $Si_{1-x-y}Sn_xC_y$. We have also investigated the electronic properties of the interface with those semiconductor thin films for devise applications. In our presentation, we will introduce our recent research progress and demonstrate the impact of group-IV alloy semiconductors for electronic and optoelectronic applications.

2. Crystal growth of $Ge_{1-x}Sn_x$ and related thin films

Epitaxy of high Sn content $Ge_{1-x}Sn_x$ and related layers

We have developed the crystal growth technologies including molecular beam epitaxy [5,6], chemical vapor deposition [7], and solid-phase crystallization (SPC) of $Ge_{1-x}Sn_x$ [8,9] and related semiconductors [10]. One of serious issues of these alloys are how to realize a high substitutional Sn content with avoiding the precipitation and segregation of Sn in matrix elements since the thermal-equilibrium solid-solubility limits of Sn in Ge and Si are very low below 1%.

Our research have revealed that the low-temperature growth and strain engineering are key factors for enhancing the substitutional Sn content in Ge and Si. The formation of a $Ge_{1-x}Sn_x$ epitaxial layer with a Sn content as high as 27% was achieved with using InP substrate having a large lattice constant corresponding with that of a 25%-Sn content $Ge_{1-x}Sn_x$ [11]. In addition, the reduction of the strain energy with thinning the epitaxial layer thickness is effective to suppress the Sn precipitation, and we demonstrated the epitaxial growth of $Ge_{1-x}Sn_x$ epitaxial layer with a Sn content as high as 46% [12].

The concept of engineering the lattice constant of substrate is effective also for the growth of $Si_{1-x}Sn_x$ epitaxial layer. Recently, we reported the self-organized lattice matched epitaxy of $Si_{1-x}Sn_x$ layer on Ge and InP substrates with annealing an amorphous $Si_{1-x}Sn_x$ layer at a low temperature of 150 °C [9]. The crystal growth of a high-Sn-content $Si_{1-x}Sn_x$ layer occurs with the self-organized redistribution of Sn atoms to realize the lattice matching to the substrate.

The lattice-matching growth of $Si_xGe_{1-x-y}Sn_y$ ternary alloy also enable the high crystalline quality and thermal robustness of the epitaxial layers [13, 14]. The epitaxial layers of $Si_xGe_{1-x-y}Sn_y$ with lattice-matching growth on Ge substrate shows a small broadening of its diffraction profile compared to that of $Ge_{1-x}Sn_x$ even with a high Sn content over 10% (**Fig. 1**). Also, it shows a high thermal robustness even after annealing at 500 °C.

Polycrystalline $Ge_{1-x}Sn_x$, $Si_{1-x}Sn_x$, and ternary alloy layers

$Ge_{1-x}Sn_x$ and related materials promises lowering the polycrystallization temperature due to a low melting point of Sn and a low eutectic temperature of Ge-Sn and Si-Sn systems. We examined the SPC of various group-IV alloys of $Ge_{1-x}Sn_x$, $Si_{1-x}Sn_x$, $Si_xGe_{1-x-y}Sn_y$, and related materials [8-10, 15]. Low-temperature SPC also enables to enhance the Sn content over the thermal-equilibrium limit of the substitutional Sn content in $Ge_{1-x}Sn_x$ and $Si_{1-x}Sn_x$. Practically, we reported a possibility of a Sn content as high as 20% in polycrystalline (poly-) $Si_{1-x}Sn_x$ layer grown on insulator after annealing at as low as 150 °C [9].

In addition, ternary alloying of group-IV elements promises increasing the substitutional contents of Sn and C in $Ge_{1-x-y}Sn_xC_y$ and $Si_{1-x-y}Sn_xC_y$, while the solid solubility of them in Ge and Si is very limited (**Fig. 2**) [16, 17]. We deduce that the compensation of a local strain between Sn and C in Ge or Si matrix would be effective to enhance the substitutional content of them.

3. Engineering of electronic properties

$Si_{1-x}Ge_x$ binary alloy has been developed long time for energy band engineering. Recently, $Ge_{1-x}Sn_x$ and related materials opens new possibility for not only extending the bandgap range but also designing energy band structure of thin films and heterostructures. Especially, ternary alloy semiconductor such as $Si_xGe_{1-x-y}Sn_y$ promises controlling the energy band structure independently on the lattice constant, that is similar to group III-V compound semiconductors.

In practice, we experimentally demonstrated that lattice-matching $Si_xGe_{1-x-y}Sn_y$/Ge heterostructure realizes the formation of type-I energy band alignment with enough large band offsets at both of conduction and valence band edges [18]. Recently, we successfully showed the impact of carrier confinement with this type-I band alignment in $Ge_{1-x}Sn_x$/$Si_xGe_{1-x-y}Sn_y$/$Ge_{1-x}Sn_x$ double-hetero structures (DHS) from the photoluminescence (PL) measurement (**Fig. 3**) [19].

4. Conclusions

We developed the crystal growth technology of epitaxial and polycrystalline $Ge_{1-x}Sn_x$ and related group-IV semiconductor thin films for integrating on Si LSI platform. Controlling the strain and growth condition enables to form a high Sn content $Ge_{1-x}Sn_x$ and related thin films with improving the crystalline quality. These materials promise extending the potentiality of group-IV semiconductors for designing energy band structures.

Acknowledgements

This work was partly supported by Grants-in-Aid for Scientific Research (Nos. 26220605, 26870261, 15H03565, and 17H04919) of JSPS, JSPS/DAAD Bilateral Program, Core-to-Core Program ICRC-ACP4ULSI of JSPS, and Strategic Young Researcher Overseas Visits Program for Accelerating Brain.

References

[1] R. Soref, IEEE J. Sel. Top. Quantum Electron. **12**, 1678, (2006). [2] J. Kouvetakis *et al*. Annu. Rev. Mater. Res. **36**, 497 (2006). [3] S. Zaima *et al*., Sci. Technol. Adv. Mater. **16**, 043502 (2015). [4] S. Wirths et al., Prog. Crystal Growth Character. Mater. **62**, 1 (2016). [5] S. Takeuchi *et al*., Semicond. Sci. Tech. **22**, S231 (2007). [6] Y. Shimura *et al*. Thin Solid Films **518**, S2 (2010). [7] Y. Inuzuka *et al*., ECS Solid State Lett. **4**, P1 (2015). [8] W. Takeuchi *et al*., APL **107**, 022103 (2015). [9] M. Kurosawa *et al*., APL **104**, 061901 (2014). [10] M. Kurosawa *et al*., APL **106**, 171908 (2015). [11] M. Nakamura *et al*., Thin Solid Films **520**, 3201 (2012). [12] A. Suzuki *et al*., JJAP **55**, 04EB12 (2016). [13] T. Asano *et al*., Solid State Electron. **110**, 49 (2015). [14] O. Nakatsuka *et al*., *Abstra of IEEE Summer Topicals Meeting*, Newport Beach, USA, July, 2016. [15] T. Ohmura *et al*., Trans. MRS-J **40**, 351 (2015). [16] T. Yamaha *et al*., JJAP **54**, 04DH08 (2015). [17] S. Yano *et al*., JJAP **56**, 01AB02 (2017). [18] T. Yamaha *et al*., Appl. Phys. Lett. **108**, 061909 (2016). [19] M. Fukuda *et al*., Semicond. Sci. Technol. *submitted*.

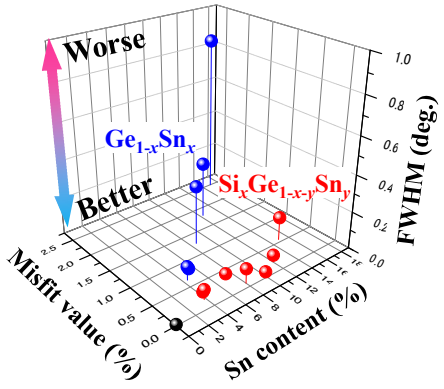

Fig. 1 The full-width half maximum (FWHM) of the diffraction peak as functions of the Sn content and misfit value of $Si_xGe_{1-x-y}Sn_y$ and $Ge_{1-x}Sn_x$ epitaxial layers grown on Ge substrate [14]. The FWHM value was estimated with the X-ray diffraction measurement. The $Si_xGe_{1-x-y}Sn_y$ layers lattice-matching to Ge shows smaller FWHM values than $Ge_{1-x}Sn_x$ even though the Sn content is as high as 15%.

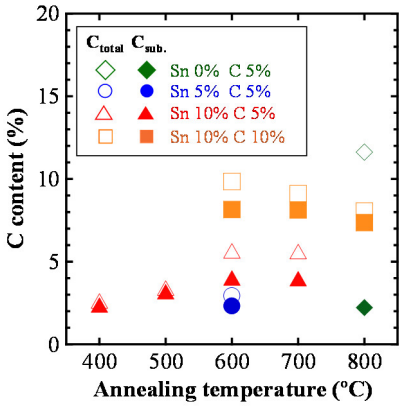

Fig. 2 The annealing temperature dependence of the total (chemical) and substitutional C contents of poly-$Si_{1-x-y}Sn_xC_y$ layers with various Sn and C contents [17]. An amorphous $Si_{1-x-y}Sn_xC_y$ layer was deposited on quartz substrate and annealed for SPC. These contents were evaluated using X-ray photoelectron spectroscopy. A higher substitutional C content with lower-temperature SPC can be achieved by incorporating Sn atoms with a higher content.

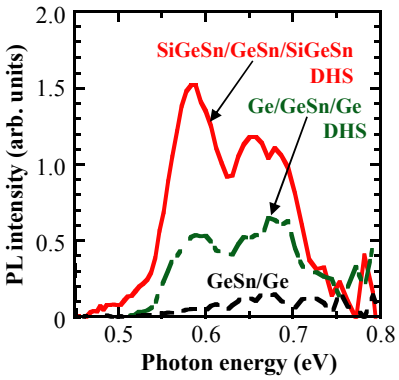

Fig. 3 The PL spectrum of $Si_{0.23}Ge_{0.66}Sn_{0.11}$/$Ge_{0.91}Sn_{0.09}$/$Si_{0.23}Ge_{0.66}Sn_{0.11}$/Ge DHS sample at room temperature [19]. Those of Ge/$Ge_{0.91}Sn_{0.09}$/Ge DHS and $Ge_{0.91}Sn_{0.09}$/Ge single-layer structure samples were also shown for comparison. The $Si_xGe_{1-x-y}Sn_y$/$Ge_{1-x}Sn_x$/$Si_xGe_{1-x-y}Sn_y$ DHS effectively improves the PL intensity.