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Crystal Growth of GeSn-related Group-IV Thin Films for Integrating on Si Nanoelectronics Platform

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Abstract

$Ge_{1-x}Sn_x$ and related group-IV semiconductor thin films have a great potential for not only electronic but also optoelectronic applications fusing on Si nanoelectronics platform. The crystal growth of epitaxial and polycrystal $Ge_{1-x}Sn_x$-related thin films is an important key technology for realizing high performance, low power consumption, and high reliability of $Ge_{1-x}Sn_x$ device applications. In this presentation, we review recent achievements in our study for crystal growth and electronic properties of $Ge_{1-x}Sn_x$ and related thin film materials.

1. Introduction

$Ge_{1-x}Sn_x$ and related group-IV semiconductor alloys are attractive materials for electronic and optoelectronic applications [1-3]. These materials promise engineering of the energy band, strain structure, and carrier properties for group-IV semiconductor applications fusing on the Si nanoelectronics platform.

For practical applications of $Ge_{1-x}Sn_x$ and related thin films, there are still challenges in engineering of (1) strain and dislocation structure, (2) Sn precipitation, (3) distribution of Sn and other elements, (4) point defects such as vacancy, and (5) interface and surface property. Especially, a Ge-Sn binary alloy is eutectic type and the thermal equilibrium solid solubility of Sn in Ge and Si is too small to use for various applications. Hence, we need to develop the non-equilibrium crystal growth with the strain control, the low-process temperature, and the third element incorporation such as surfactant atoms, etc.

Engineering the energy band structure is also attractive and necessary to realize the application of $Ge_{1-x}Sn_x$ and related materials. Indirect-direct cross over can be realized by $Ge_{1-x}Sn_x$ with a Sn content higher than about 10% or tensile strained Ge with a strain value over about 1%, which extends the possibility for optoelectronic applications [4]. In addition, $Si_{1-x}Sn_x$ alloy with a very high Sn content of about 25% is promising a direct transition semiconductor with group-IV materials [5].

We need to clarify the relationship between the crystalline and energy band structures of $Ge_{1-x}Sn_x$ and related group-IV semiconductors in detail. In this report, we presented our recent achievements of the crystal growth of various $Ge_{1-x}Sn_x$-related thin films, and discuss the electronic properties of them for Si electronic applications.

2. Crystal growth and electronic properties

Epitaxial growth by MBE and CVD

We have developed the molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) technologies for epitaxial growth of $Ge_{1-x}Sn_x$ thin film. A key point for the epitaxial growth of high Sn content $Ge_{1-x}Sn_x$ is a low deposition temperature below 300 °C, typically at 100-150 °C for MBE. The strain engineering is another critical key point to increase in the substitutional Sn content and to suppress the dislocation generation. We demonstrated that the substitutional Sn content in $Ge_{1-x}Sn_x$ epitaxial layer can be increased over 27% by designing the lattice constant of substrate or the thickness of pseudomorphic $Ge_{1-x}Sn_x$ epitaxial layer [6-8].

However, a low temperature growth causes the introduction of many point defects and leads to degrading the crystallinity of epitaxial layer, that can be observed as increasing in the defuse scattering in the x-ray diffraction (XRD) profile. We recently demonstrated that a hydrogen surfactant epitaxy is effective to improve the crystalline structure of $Ge_{1-x}Sn_x$ epitaxial layer (**Fig. 1**) [9]. It is considered that point defects of vacancies, which are introduced during the low temperature growth of $Ge_{1-x}Sn_x$, leads to unintentional hole generation from electrically active defect states. The epitaxial growth with hydrogen effectively improves in the electronic properties, which can be seen as decreasing in the density of unintentional holes (**Fig. 2**) [9]. The $Ge_{1-x}Sn_x$ epitaxy with hydrogen also improves in the photoluminescence intensity.

We are recently developing MOCVD method with Ge and Sn precursors appreciable for low temperature growth. MOCVD growth including hydrogen in precursors promises the epitaxy of a high crystalline quality $Ge_{1-x}Sn_x$ layer [10].

Crystalline and electronic properties of ternary alloy

Ternary alloying such as $Ge_{1-x-y}Si_xSn_y$ promises the useful energy band engineering in which the energy band structure can be control independently on the lattice constant [11]. The energy band structures of $Ge_{1-x}Sn_x$ and related group-IV ternary alloys were investigated. We can control the energy bandgap of group-IV alloy semiconductors widely with controlling the content of Sn and other elements of Si or C **(Fig. 3)** [12,13]. In addition, we found the $Ge_{1-x-y}Si_xSn_y$/Ge heterostructure promises type-I energy band alignment with strain-free system **(Fig. 4)** [14].

Solid phase epitaxy and polycrystallization on insulators

For the epitaxial growth of high Sn content alloy of group-IV semiconductors, solid phase epitaxy (SPE) is an attractive technique to suppress the migration and segregation of Sn atoms. Recently, we can achieve the formation of a $Si_{1-x}Sn_x$ epitaxial layer lattice-matching to Ge substrate by using SPE method [15]. We also demonstrated that SPE effectively enhances the introduction of substitutional C atoms in $Ge_{1-x-y}Sn_xC_y$ epitaxial layer with suppressing the segregation of C atoms **(Fig. 5)** [16]. The low temperature polycrystallization of $Ge_{1-x}Sn_x$, $Si_{1-x}Sn_x$, and $Ge_{1-x-y}Si_xSn_y$ layers on insulator also promises the improvement in the substitutional Sn content, the grain size, and the mobility [12,17,18].

3. Conclusions

We comprehensively studied the crystal growth and electronic properties of $Ge_{1-x}Sn_x$ and related group-IV semiconductor thin films. The energy band engineering based on the crystal growth technology of epitaxial and/or polycrystal thin films with high crystalline quality promises novel future applications of group-IV semiconductor materials integrating on Si nanoelectronics platform.

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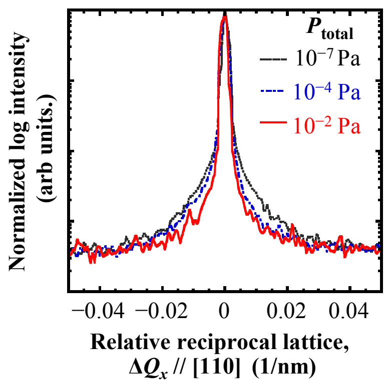

Fig. 1. XRD profiles of the $Ge_{1-x}Sn_x$ 224 Bragg reflection for $Ge_{1-x}Sn_x$/Ge samples grown with and without H_2 gas introduction [9]. The total pressure, P_{total} during the $Ge_{1-x}Sn_x$ growth was controlled with H_2 gas introduction into MBE chamber.

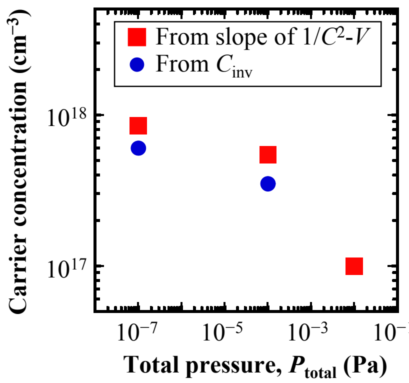

Fig. 2. The dependence of the carrier density measured from C-V characteristics of $Ge_{1-x}Sn_x$ MOS capacitors at 300 K [9].

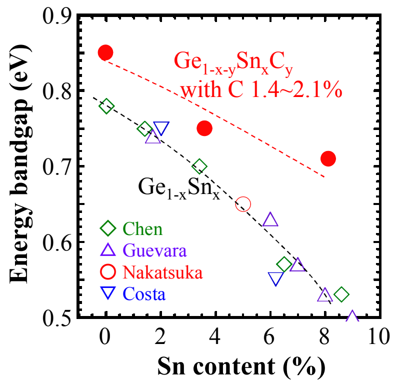

Fig. 3. The Sn content dependence of the energy bandgap of $Ge_{1-x-y}Sn_xC_y$ ternary alloys [13]. That of $Ge_{1-x}Sn_x$ is also shown for comparison [2, 19-21].

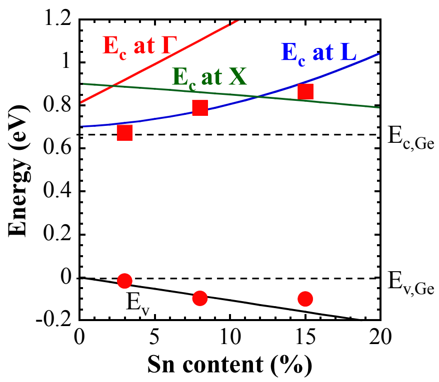

Fig. 4. The energy band alignment of $Ge_{1-x-y}Si_xSn_y$ epitaxial layer as a function of Sn content. $Ge_{1-x-y}Si_xSn_y$ epitaxial layer was grown for lattice matching condition on Ge(001) substrate [14].

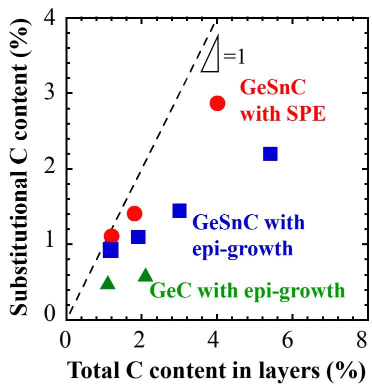

Fig. 5. The substiutional C content as a function of total C content introduced in $Ge_{1-x-y}Sn_xC_y$ layers prepared with SPE and MBE method [16]. The result of $Ge_{1-x}C_x$ is also shown [22].