Self-organized lattice-matched epitaxy of $Si_{1-x}Sn_x$ alloys on (001)-oriented Si, Ge, and InP substrates

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The crystal growth of single-crystalline $Si_{1-x}Sn_x$ layers with various Sn contents and analytical comparisons of their fundamental physical properties are strongly desired for next-generation group-IV electronics. In the present study, $Si_{1-x}Sn_x$ layers with varying Sn contents (1%–40%) were grown on various substrates [(001)-oriented Si, Ge, or InP] by solid-phase epitaxy. Crystallographic and composition analyses indicated that the grown $Si_{1-x}Sn_x$ layers were nearly lattice-matched to the substrates. When grown on Si, Ge, and InP substrates, the substitutional Sn contents were ~1%, ~20%, and ~40%, respectively. Hard X-ray photoelectron spectroscopy revealed a valence-band offset resulting from the Sn substitution. The offset exhibited an upward-bowing tendency when plotted against the Sn content. The $Si_{0.78}Sn_{0.22}$/n-type Ge junction displayed rectifying diode characteristics with the ideality factor of 1.2. *Published by AIP Publishing.*
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To clarify the electrical, optical, and thermal properties of silicon tin ($Si_{1-x}Sn_x$) alloys and their relationships, we should vary the Sn contents in the alloys and perform comparison studies. Previous theoretical[1–10] and experimental[3,7,11–19] studies have identified $Si_{1-x}Sn_x$ alloys as strong candidate materials for near infrared light-emitting (and/or receiving) elements[1–6,9,10,13,14,17,19] and thermoelectric generators.[8,15] At a sufficiently high Sn content, $Si_{1-x}Sn_x$ theoretically possesses a direct bandgap in the optical communication band (typical wavelength range: $1.0-1.6\,\mu m$).[1,3–6] The Sn atoms incorporated in the Si matrix significantly influence phonon scattering related to thermal transport,[8] implying that $Si_{1-x}Sn_x$ enables high-performance thermoelectric generators. However, $Si_{1-x}Sn_x$ synthesis is impeded by the large (~20%) mismatch between the Si and Sn lattices and the extremely low thermal equilibrium solubility of Sn in Si (0.1% at 1066 °C[20]). Owing to these difficulties, experimental reports of strain-free $Si_{1-x}Sn_x$ alloys with a wide range of Sn contents and their comparisons with theoretical studies are much rarer than similar studies on $Ge_{1-x}Sn_x$ alloys. Therefore, discrepancies between experiments and calculations, such as Sn transitions from indirect to direct gaps and the energy band structure, remain unresolved.

$Si_{1-x}Sn_x$ alloys with various Sn contents can be fabricated by polycrystallization from amorphous $Si_{1-x}Sn_x$ (a-$Si_{1-x}Sn_x$) layers. Previously, we grew polycrystalline a-$Si_{1-x}Sn_x$ layers (poly-$Si_{1-x}Sn_x$) with Sn contents of 2%–30% on insulators.[17] The substitutional Sn content in poly-$Si_{1-x}Sn_x$ was uniquely determined from the annealing temperature regardless of the initial Sn content, and the solid-phase crystallization significantly suppressed the Sn precipitation during growth. In this Letter, we grow single crystalline $Si_{1-x}Sn_x$ layers with various Sn contents by solid-phase epitaxy (SPE), varying the Sn contents over a wide range (1%–40%). The $Si_{1-x}Sn_x$ layers were grown on (001)-oriented Si, Ge, or InP substrates. The substrate-dependent behaviors of the $Si_{1-x}Sn_x$ layers, which showed hetero-epitaxial growth in all samples, were systematically analyzed. In addition, a valence band offset resulting from Sn substitution was observed in hard X-ray photoelectron spectroscopy (HAXPES) measurements. The measured valence band offset was compared with the calculated value. These results might guide the design of future $Si_{1-x}Sn_x$ based optoelectronic devices and thermoelectric generators.

The substrates for the grown $Si_{1-x}Sn_x$ layers [Si, Ge, or InP wafer, each with (001) orientation] were cleaned by a wet-chemical process. The Si, Ge, and InP wafers were cleaned in 1% HF solution, sequential alkali ($NH_4OH:H_2O = 1:4$) and acid ($H_2SO_4:H_2O = 1:7$) solutions, and an acid ($H_2SO_4:H_2O_2:H_2O = 3:1:1$) solution. Next, the Ge and InP substrates were heat-treated at 400 – 430 °C in an ultra-high vacuum chamber with a base pressure of $10^{-7}-10^{-8}$ Pa. Prior to $Si_{1-x}Sn_x$ deposition, the substrate was cooled to below 100 °C. $Si_{1-x}Sn_x$ layers (20 or 50 nm thick) with different Sn contents (20%–44%) were deposited on the substrates using a molecular beam deposition system[17] or a multisource radio-frequency magnetron sputtering system in an Ar atmosphere at 1.0 Pa.[21] In the X-ray diffraction (XRD) measurements of the samples, no peaks were assignable to crystallized $Si_{1-x}Sn_x$ or to any of the substrate compounds. Consequently, we can judge that all the as-deposited $Si_{1-x}Sn_x$ layers were in the amorphous state. After re-cleaning the substrate surfaces in 1% HF solution, a capping layer—a 10 nm-thick SiO_2 layer stacked on a 5 nm-thick a-Si layer or the SiO_2 layer alone—was formed on the

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