Raman scattering from fully strained $Ge_{1-x}Sn_x$ ($x \leqslant 0.22$) alloys grown on Ge(001)2×1 by low-temperature molecular beam epitaxy

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Fully strained single-crystal $Ge_{1-x}Sn_x$ alloys ($x \leqslant 0.22$) deposited on Ge(001)2×1 by low-temperature molecular beam epitaxy have been studied by Raman scattering. The results are characterized by a Ge–Ge longitudinal optical (LO) phonon line, which shifts to lower frequencies with increasing x. Samples capped with a 200-Å-thick Ge layer exhibit a second Ge–Ge LO phonon line whose position remains close to that expected from bulk Ge. For all samples, capped and uncapped, the frequency shift $\Delta\omega_{GeSn}$ of the Ge–Ge LO phonon line from the $Ge_{1-x}Sn_x$ layer, with respect to the position for bulk Ge, is linear with the Sn fraction x ($\Delta\omega_{GeSn} = -76.8x$ cm^{-1}) over the entire composition range. Using the elastic constants, the Grüneisen parameter, and the shear phonon deformation parameter for Ge, we calculate the contribution of compressive strain to the total frequency shift to be $\Delta\omega_{strain} = 63.8x$ cm^{-1}. Thus, the LO phonon shift in $Ge_{1-x}Sn_x$ due to substitutional-Sn-induced bond stretching in fully relaxed alloys is estimated to be $\Delta\omega_{bond} = -140.6x$ cm^{-1}. © *1998 American Institute of Physics.* [S0021-8979(98)09816-8]

I. INTRODUCTION

$Ge_{1-x}Sn_x$ and related alloys are of interest due to the potential they offer for developing totally group-IV-based optoelectronic materials systems. $Ge_{1-x}Sn_x$ is predicted to exhibit a direct band gap in unstrained alloys, tunable from ≈0.55 to 0 eV with x ranging from 0.20 to 0.65 as the Γ-point conduction-band minimum decreases more rapidly than the L-point valleys.[1–4] Moreover, the presence of compressive strain is expected to decrease the Sn concentration at which the indirect $L_6^+ \rightarrow \Gamma_8^+$ to direct $L_7^- \rightarrow \Gamma_8^+$ band-gap crossover is observed.[5] The growth of these alloys, however, presents severe challenges. The equilibrium solid solubility of Sn in Ge is less than 1 at. % (Ref. 6) and Sn has a very strong tendency to surface segregate,[7,8] both of these effects arguing for deposition at low temperatures. An additional obstacle to be overcome in the epitaxial growth of $Ge_{1-x}Sn_x$ on Ge is that the lattice constant mismatch between α-Sn ($a_{\alpha\text{-Sn}} = 6.4892$ Å) and Ge ($a_{Ge} = 5.6579$ Å) is 14.7%.

We have recently demonstrated low-temperature molecular beam epitaxy (MBE) of $Ge_{1-x}Sn_x$ alloys[9] and $Ge/Ge_{1-x}Sn_x$ superlattices[10] with x up to 0.26. Film growth temperatures T_s were limited to a very narrow range around 100 °C by the combination of increased kinetic roughening at lower growth temperatures and Sn surface segregation at higher temperatures. Growth at such low temperatures, however, introduces a limit to the thickness of epitaxial material that can be grown prior to epitaxial breakdown. Based upon reflection high-energy electron diffraction (RHEED) and cross-sectional transmission electron microscopy (XTEM) analyses, critical epitaxial thicknesses t_{epi}, defined as the onset of amorphous growth, were found to decrease from 1080 Å for pure Ge to 330 Å for $Ge_{0.91}Sn_{0.09}$ to 35 Å for $Ge_{0.74}Sn_{0.26}$.

Very little is known about the optical properties of Ge-rich $Ge_{1-x}Sn_x$ alloys. He and Atwater[11] recently used optical absorption spectroscopy to probe the room-temperature band-gap E_g of relaxed $Ge_{1-x}Sn_x$ layers grown on Ge buffer layers on Si(001). They found that E_g remains indirect (although the difference between the direct and indirect gaps was within experimental uncertainty) for alloys with $x = 0.06$ and 0.11 while the band gap of $Ge_{0.85}Sn_{0.15}$ was direct with $E_g = 0.35$ eV. Raman scattering experiments performed on Sn-rich alloys ($x \geqslant 0.92$) revealed Sn–Sn and Ge–Sn longitudinal optical (LO) phonon peaks near 190–200 and 215–225 cm^{-1}, respectively.[12] The frequency of the Ge–Sn peak decreases with increasing Sn fraction in the alloy. A splitting in the Ge LO mode was reported for strained Ge-rich $Ge_{1-x}Sn_x$ ($0.03 < x < 0.10$) layers grown on Ge(001).[13] The Raman spectra from Sn/Ge short-period superlattices are primarily characterized by zone-folded longitudinal acoustic phonons whose frequencies depend upon the superlattice period. However, due to significant intermixing between the Sn and Ge layers, Sn–Sn, Ge–Sn, and Ge–Ge LO phonon peaks were also detected near 180, 230–260, and 300 cm^{-1}, respectively.[8,14,15]

In this article, we present the results of Raman scattering measurements carried out on fully strained Ge-rich $Ge_{1-x}Sn_x$ alloys grown on Ge(001)2×1 by MBE at $T_s = 60-100$ °C. Single-layer alloy samples exhibit a Ge–Ge LO phonon peak at a frequency ω_{GeSn}, which decreases with

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