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Thomas R. Harris
Air Force Institute of Technology

Yung Kee Yeo
Air Force Institute of Technology

Mee-Yi Ryu
Kangwon National University

Richard T. Beeler
Arizona State University

John Kouvetakis
Arizona State University

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Observation of heavy- and light-hole split direct bandgap photoluminescence from tensile-strained GeSn (0.03% Sn)

Thomas R. Harris,[1] Yung Kee Yeo,[1,a)] Mee-Yi Ryu,[2,a)] Richard T. Beeler,[3] and John Kouvetakis[3]
[1]*Department of Engineering Physics, Air Force Institute of Technology, Wright-Patterson AFB, Ohio 45433, USA*
[2]*Department of Physics, Kangwon National University, Chuncheon 200-701, Korea*
[3]*Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, USA*

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Temperature- (T-) and laser power-dependent photoluminescence (PL) measurements have been made for the tensile-strained, undoped GeSn (0.03% Sn) film grown on Si substrate. The PL results show not only clear strain-split direct bandgap transitions to the light-hole (LH) and heavy-hole (HH) bands at energies of 0.827 and 0.851 eV at 10 K, respectively, but also clearly show both strong direct and indirect bandgap related PL emissions at almost all temperatures, which are rarely observed. This split of PL emissions can be directly observed only at low T and moderate laser power, and the two PL peaks merge into one broad PL peak at room temperature, which is mainly due to the HH PL emission rather than LH transition. The evolution of T-dependent PL results also clearly show the competitive nature between the direct and indirect bandgap related PL transitions as T changes. The PL analysis also indicates that the energy gap reduction in Γ valley could be larger, whereas the bandgap reduction in L valley could be smaller than the theory predicted. As a result, the separation energy between Γ and L valleys (~86 meV at 300 K) is smaller than theory predicted (125 meV) for this Ge-like sample, which is mainly due to the tensile strain. This finding strongly suggests that the indirect-to-direct bandgap transition of $Ge_{1-y}Sn_y$ could be achieved at much lower Sn concentration than originally anticipated if one utilizes the tensile strain properly. Thus, $Ge_{1-y}Sn_y$ alloys could be attractive materials for the fabrication of direct bandgap Si-based light emitting devices. *© 2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4894870]

I. INTRODUCTION

Intensive research efforts have been made in recent decade in developing Si- and Ge-based direct bandgap materials such as Ge, $Ge_{1-y}Sn_y$, and $Ge_{1-x-y}Si_xSn_y$ epitaxial layers grown on Si or Ge substrates[1–9] because of its possibility of optoelectronic device applications.[10–15] As a result, significantly enhanced direct bandgap optical transition was indeed achieved through the incorporation of Sn in Ge and strain.[16–21] Furthermore, many research groups have reported the observation of direct bandgap photoluminescence (PL) emission at room temperature (RT) from tensile-strained Ge and $Ge_{1-y}Sn_y$ alloys.[10,16,21–25] Also, direct bandgap electroluminescence was observed from the Ge and GeSn diodes,[9] n^+/p-Ge diode,[10] and $Ge_{0.93}Sn_{0.07}$ p-n junction devices[11] at RT. Recently, several groups have demonstrated Ge/Si homojunction p-n light emitting diode,[10] $Ge_{1-y}Sn_y$/Si p-i-n diodes,[9] $Ge_{1-y}Sn_y$/Ge p-n diodes,[11] Ge/Si p-n-n laser diodes,[12] and $Ge_{1-y}Sn_y$/Si photodetectors.[13–15]

The indirect to direct bandgap transition of strain-free $Ge_{1-y}Sn_y$ was more recently predicted to occur at a Sn composition of 6.5%[17] or less than 11%.[26] It is also well known that the tensile strain in Ge or $Ge_{1-y}Sn_y$ epitaxial layers grown on Si significantly affects the band structure of these materials.[17,21,27,28] That is, the tensile strain causes a significant change in the reduction of L and Γ conduction valleys of Ge or $Ge_{1-y}Sn_y$ epitaxial layers, and also causes the splitting of light-hole (LH) and heavy-hole (HH) valence bands.[22,23,27,28] It has been indeed shown through the temperature-(T-)dependent PL study of tensile-strained Ge and $Ge_{1-y}Sn_y$ grown on Si substrate[21] that the indirect to direct bandgap crossover might occur at lower Sn content than previously thought when tensile strain is incorporated into the sample. The direct bandgap energies of Ge grown on Si between Γ conduction band and LH band, ($E_{\Gamma,LH}$), and HH band, ($E_{\Gamma,HH}$), have been calculated as a function of in-plane strain. Their photoreflectance (PR) measurements made at RT showed that the separation between LH and HH was 12–15 meV[22,27] for the 0.18%–0.20% tensile-strained Ge compared to the theoretical value of 13 meV (Ref. 29) for 0.20% tensile-strained Ge. Although several papers reported on the splitting of HH and LH valence bands measured by PR for Ge (Refs. 22 and 27) and $Ge_{1-y}Sn_y$ (Ref. 30) grown on Si, there have been no reports on a direct PL observation of the splitting of HH and LH valence bands either for Ge or $Ge_{1-y}Sn_y$ layers, to the best of our knowledge. Most, if not all, previously reported direct bandgap PL spectra show mainly a single broad PL peak at RT which could be the sum of the contribution from LH and HH direct bandgap transitions. Furthermore, most of them did not specify whether their observed direct bandgap PL peak is either due to LH or HH band transition or a combination of both. Therefore, in order to further investigate these facts, to show the

a)Authors to whom correspondence should be addressed. Electronic addresses: Yung.Yeo@afit.edu and myryu@kangwon.ac.kr

separation energy between $E_{\Gamma,LH}$ and $E_{\Gamma,HH}$, and to better understand the unique nature of the direct bandgap emission in the indirect bandgap semiconducting material, excitation-laser power- and T-dependent PL studies were carried out for tensile-strained $Ge_{1-y}Sn_y$ (0.03% Sn) film grown on Si substrate.

II. EXPERIMENTAL DETAILS

The Ge-like material of 800 nm thick $Ge_{1-y}Sn_y$ (y = 0.03%) film was grown directly on a high resistivity *n*-type Si(100) substrate using ultra-high vacuum chemical vapor deposition, and was produced by means of the reaction of Ge_2H_6 and SnD_4 at a temperature of 385 °C and a pressure of 0.30 Torr.[16,31] The sample composition, layer thickness, and strain state were characterized using the procedures described by Refs. 13 and 32. The strain in the epitaxial layer was initially slightly compressive, became fully relaxed after annealing at a temperature of 825 °C for 30 min, and then changed to slightly tensile strain upon cooling to RT due to the large difference in thermal expansion coefficients between GeSn and Si, with a final residual value of 0.19% according to high-resolution x-ray diffraction measurements. PL measurements were performed using a tunable Ti-Sapphire laser set to 830 nm and pumped by an Ar-ion laser at 514.5 nm. The laser beam was focused to a spot size of around 200 μm with laser power ranging from 150 to 650 mW. The emitted light was dispersed with a ½-m monochromator using a 1.6 μm blazed grating, and was analyzed by a TE-cooled, wavelength-extended InGaAs detector and an SR850 lock-in amplifier. PL was measured at temperatures (Ts) ranging from 10 to 300 K.

III. RESULTS AND DISCUSSION

The results of excitation-laser power-dependent PL measurements taken at 10 K are shown in Fig. 1 for the undoped $Ge_{0.9997}Sn_{0.0003}$ film grown on *n*-Si substrate. The PL results show clear PL peaks related to both direct and indirect bandgap optical transitions from both the direct (Γ) and indirect (L) valleys in the conduction band to the strain-split LH and HH valence bands. As shown in Fig. 1, at a laser power of 450 mW, three clear direct bandgap related PL peaks were observed at 0.851, 0.827, and 0.807 eV. These values were slightly corrected from the apparent measured PL peak positions after careful curve fitting analysis. The smaller apparent energy separation value is due to the overlap of two closely spaced peaks with nearly comparable intensities. The PL peak centered at 0.851 eV is attributed to the direct bandgap optical transition from the Γ valley to the HH valence band, ($E_{D,HH}$), and the peak at 0.827 eV is attributed to the direct bandgap transition from the Γ valley to the LH band ($E_{D,LH}$). The splitting of the HH and LH bands in this sample could also be observed through polarization-dependent PL measurements[33,34] if the proper experimental conditions are met, and this could further aid in the assignment of the HH and LH peaks. For example, Nam *et al.*[34] very recently observed two separated LH and HH PL peaks through polarization-dependent PL measurements of highly (≥0.59%) uniaxial strained Ge micro-bridges. The

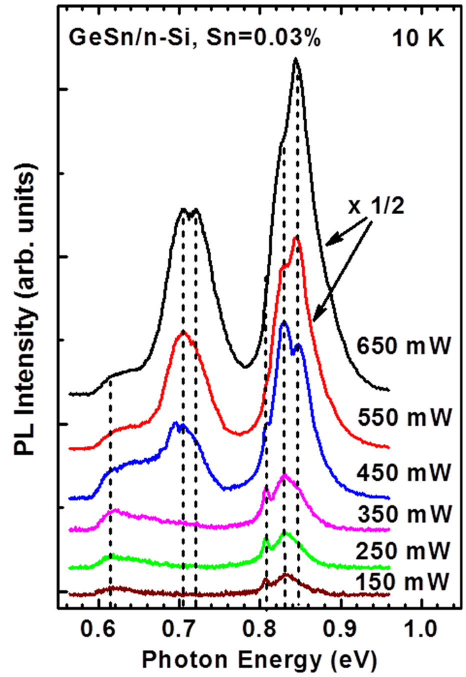

FIG. 1. Laser excitation power-dependent PL spectra of the undoped $Ge_{0.9997}Sn_{0.0003}$ grown on *n*-Si substrate.

third peak at 0.807 eV is very sensitive to the sample temperature and it disappears at 50 K as shown in Fig. 2. This PL peak could be attributed to either the phonon replica or free-to-bound (FB) peak, and at present, there do not appear to be any other better assignments. Although the 0.807 eV peak is only 20 meV smaller than the direct bandgap transition from the Γ valley to the LH band ($E_{D,LH}$), the peak was tentatively assigned to the Ge-like longitudinal acoustic (LA) phonon replica of the strong $E_{D,LH}$ PL peak at the Γ point. This assignment is the closest known LA phonon (27 meV) related to the L valley in bulk Ge.[35] Alternatively, the PL peak at 0.807 eV could be related to a FB transition involving a shallow acceptor with a binding energy of about 20 meV. This PL peak was not observed in other similar GeSn samples.

The measured energy separation, ($E_{D,HH}-E_{D,LH}$), between the HH and LH transitions at 10 K is about 24 meV compared to our calculated value of 26 meV using a deformation potential of −2.55 eV at 10 K. This observed separation energy is consistent with the value of about 22 meV (Ref. 30) estimated from the PR spectrum measured at 10 K for the 0.17%–0.19% tensile-strained $Ge_{0.98}Sn_{0.02}$/Si. It is also consistent with their theoretically calculated value of 21 meV, which was determined using the parameters found in Ref. 36. On the other hand, our observation is slightly different from the value of 16 meV (Ref. 22) (=0.787–0.771 eV) estimated from the PR measurement at RT for the 0.20% tensile-strained Ge/Si. However, it is also worth noting that a calculated value of about 20 meV (Ref. 28) (=0.78–0.76 eV) was reported for the 0.22% tensile-strained Ge-on-Si at RT. The separation energy ($E_{D,HH}-E_{D,LH}$) will be discussed in more detail later.

At laser powers above about 450 mW, the overall integrated PL intensity increases very rapidly with laser

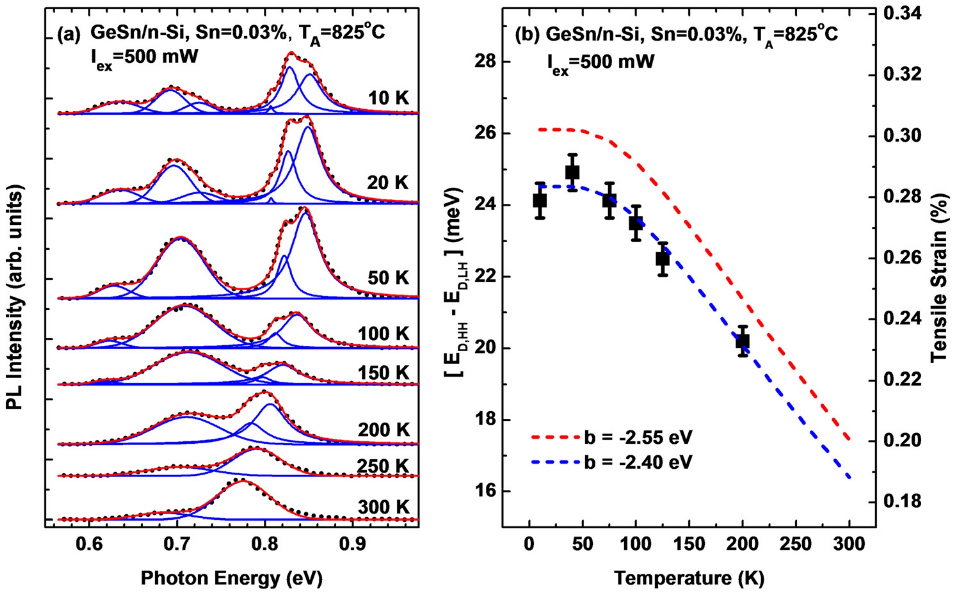

FIG. 2. (a) Temperature-dependent PL spectra of the tensile-strained undoped $Ge_{0.9997}Sn_{0.0003}$ grown on *n*-Si substrate. (b) Measured separation energies $[E_{D,HH} - E_{D,LH}]$ (black squares) between the direct bandgap PL transitions from the Γ conduction valley minimum to the HH and LH valence bands plotted as a function of temperature with error bars of ±0.5 meV. Predicted calculated values of $[E_{\Gamma,HH} - E_{\Gamma,LH}]$ (dashed red line) using the deformation potential b = −2.55 eV and best fit curve using b = −2.40 eV (dashed blue line) are also shown.

excitation power. Apparently, efficient optical pumping with the laser wavelength of 830 nm (1.49 eV) leads to increased photoexcited electron densities in the Γ and L valleys from the LH and HH bands and even possibly from split-off band. At about 550 mW, the $E_{D,HH}$ peak becomes dominant, and the direct $E_{D,LH}$ peak appears as a shoulder peak of the HH-PL peak and begins to merge into the strong HH-PL peak as the laser power increases further to 650 mW. Evidently, as the laser power increases, the population of photoexcited holes in the HH valence band increases more than that of LH valence band due to the greater joint density of states for the HH band and also due to the closer proximity of the hole quasi-Fermi level. Thus, the HH PL intensity increases more rapidly than the LH PL intensity. The merging into nearly one broad peak is also due to the small energy separation (∼24 meV) between the two peaks and due to the overlap of the somewhat broad two band-to-band HH and LH PL peaks. Thus, they are not easily resolvable at higher excitation laser power. Similar strong HH-PL peak and LH-shoulder peak were also seen from the PL spectrum of a 0.19% tensile-strained unintentionally doped *p*-Ge/Si sample[21] taken at 20 K with an excitation laser power of 400 mW. For the high laser powers, the phonon replica peak at 0.807 eV appears as a shoulder peak of the strong broad peak of HH- and LH-PL peaks.

On the other hand, as the laser power decreases below about 450 mW, the LH-PL peak now becomes dominant, and the HH-PL peak only appears as a shoulder peak of the LH-PL peak. Apparently, as the laser power decreases, the overall total population of photoexcited holes and electrons at Γ point decreases, and thus the PL intensities of the two HH and LH PL peaks become weak. Furthermore, the relative population of photoexcited holes in the up-shifted LH valence band becomes greater than that of the down-shifted HH band due to the reduced tail of the Fermi-Dirac distribution. The merging into one nearly unresolvable broad peak at lower excitation laser power is also due to the small energy separation of the two peaks as well as the overlap of the somewhat broad HH and LH peaks. Now, the LA phonon replica of the $E_{D,LH}$ PL peak appears as a clear sharp peak at lower excitation laser power. It turns out that the split of LH- and HH-PL peaks and the LA phonon replica of the $E_{D,LH}$ PL peak can only be observed at low temperatures and at moderate or lower laser powers.

As shown in Fig. 1, at a laser power of 650 mW, two clear indirect bandgap related PL emissions were observed at 0.732 and 0.702 eV, which were also slightly corrected from the apparent measured PL peak positions after careful curve fitting analysis. At this laser power, apparently, the population of photoexcited holes in HH and LH valence bands and accordingly that of photoexcited electrons in Γ and L valleys are very high, so that the overall direct and indirect bandgap related PL intensities are very strong at low temperatures. As the excitation laser power is reduced from 650 mW down to about 450 mW, both overall PL intensities decrease due to decreased number of photoexcited electrons and holes. The almost disappearance of the indirect bandgap related PL at or below 350 mW is believed to be due to decreased fraction of electron population in L valley than that in Γ valley. Also, since the radiative direct bandgap transition is much more efficient than the phonon-assisted radiative indirect bandgap transition, the direct bandgap PL peak can still be observed even for the small electron population in Γ valley which occurs at a lower laser power.

The two observed PL peaks at 0.732 and 0.702 eV are attributed to Ge-like transverse acoustic (TA) (0.739 − 0.732 = 7 meV) and transverse optical (TO) (0.739 − 0.702 = 37 meV) phonon replicas associated with the LH band (and not the HH band), respectively, which are consistent with previously reported PL peak positions.[37] Here, we used the indirect bandgap energy of about 0.739 eV deduced from our PL measurements for this sample, which also agrees well with previous measurements of a Ge/Si sample taken at 20 K.[21] We must anticipate that our tensile-strained GeSn sample will have slightly different phonon values than bulk Ge. If, however, the theoretically predicted bandgap of 0.718 eV is used (see Fig. 3), then the PL peak observed at 0.732 eV at 10 K must be related to the absorption of a phonon with an energy of 14 meV, which does not make any physical sense at all at 10 K. In the meantime, as the laser power decreases below about 650 mW, the TA phonon peak becomes a shoulder peak of TO phonon peak up to about 450 mW, and then these two PL peaks almost disappear at about 350 mW laser power. There is also a broad weak PL peak at around 0.639 eV at 650 mW laser power, but the exact nature of the peak is not known at present. This peak could be shallow donor–deep acceptor pair (DAP) related transitions, FB to deep acceptor transitions, and/or defect (dislocations) related transitions.

The T-dependent PL spectra of undoped $Ge_{0.9997}Sn_{0.0003}$ taken with 500 mW are shown in Fig. 2(a). The PL spectra taken at 10 K are composed of three emission peaks at 0.851, 0.827, and 0.807 eV at the higher energy side, which are assigned to $E_{D,HH}$, $E_{D,LH}$, and 1LA phonon replica of the $E_{D,LH}$ PL peak as explained in Fig. 1. The observed PL spectra are drawn in dotted black color, the individual fitting curves are shown in blue color, and the sum of the fitting curves are in red color. The PL spectra show very strong direct PL emission at RT and both strong direct and indirect bandgap related emissions at all temperatures, which are rarely observed. Apparently, the photo-excitation of electrons out of the LH and HH valence bands directly into both Γ and L valleys is efficient at a laser power of 500 mW and a wavelength of 830 nm. Also, the T-dependent PL shows very interesting evolution of direct and indirect bandgap related emissions along with various phonon related optical transitions. The overall integrated PL intensity of the direct bandgap emission, $(E_{D,HH} + E_{D,LH})$, remains strong up to about 50 K, decreases gradually to a minimum intensity at around 150 K, and then starts to increase as T increases to RT. This increase could be due in part to the thermalization of electrons from the L valley to the Γ valley in the higher T range. In the meantime, the PL intensity of 1LA phonon replica of the $E_{D,LH}$ PL peak decreases rapidly as T increases, and it disappears at around 50 K. It can also be clearly seen in Fig. 2(a) that the relative intensity of HH PL peak compared to LH PL peak gradually increases as T increases. At around 200 K or above, the LH PL peak becomes a shoulder peak of HH PL peak, and then it disappears within the broad strong HH peak at higher Ts. Since the separation energy between the HH and LH valence bands becomes even smaller (16–18 meV) at higher temperatures and due to the overlap of the somewhat broad two band-to-band HH and LH PL transitions, the two peaks easily merge into one broad peak. The evolution of the T-dependent PL for this sample strongly shows that the direct bandgap related emission observed at room temperature is mainly due to the optical transition from the Γ conduction valley to the HH band rather than to the LH band.

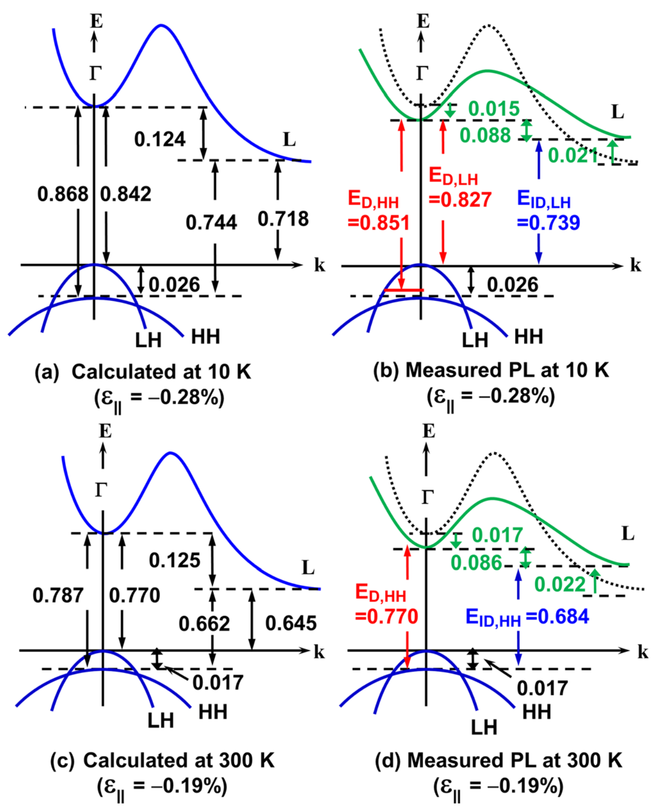

FIG. 3. (a) Calculated simple band diagrams (not scaled) and (b) experimentally determined band diagrams from PL measurements at 10 K along with the same theoretically predicted band diagrams (black dotted line) for 0.28% tensile-strained undoped $Ge_{0.9997}Sn_{0.0003}$ grown on *n*-Si substrate. (c) Calculated band diagrams and (d) experimentally determined band diagrams at 300 K for 0.19% tensile-strained undoped $Ge_{0.9997}Sn_{0.0003}$ grown on *n*-Si substrate. The measured PL peak energy positions (red color for direct and blue color for indirect transitions) are indicated in the figure. The green numbers indicate the difference between theoretical and experimental values.

The detailed T-dependent PL peak positions corresponding to $E_{D,HH}$ and $E_{D,LH}$ emission energies were estimated by fitting each set of $E_D(T)$ PL data mainly with two Lorentzian peaks of $E_{D,HH}$ and $E_{D,LH}$ up to 200 K and one Gaussian peak above 200 K. The PL peak positions of $E_{D,HH}(T)$ are well defined at all Ts, but the positions of the $E_{D,LH}(T)$ PL peaks cannot be determined reliably at 150 and 175 K due to weaker $E_{D,LH}$ PL intensities compared to the relatively strong indirect bandgap related PL transitions. The measured separation energies, $[E_{D,HH} - E_{D,LH}]$, (black squares) between the direct bandgap PL transitions from the Γ band to the HH and LH valence bands are plotted as a function of T in Fig. 2(b). The separation energies at 150 and 175 K were not included in this figure due to unreliable values. Error bars are also shown with a range of ±0.5 meV, which was determined by adjusting the peak position of the fitted curves and examining the change in the residuals. The theoretical separation (dashed red line), which was calculated using a deformation potential of $b = -2.55$ eV,[21] is also plotted as a function of temperature in Fig. 2(b). Although there is certainly a difference between the experimental and theoretical separation values, they do seem to follow the same trend over a wide temperature range. This observed offset can be partly explained by the choice of deformation potential, b, whose reported values vary from about −1.88 to −2.86 eV.[27] The predicted separation between the HH and LH bands is very sensitive to the deformation potential used, and even a slight change can result in a significant difference. For example, using a value of $b = -1.88$ eV gives a separation of only 19 meV at 10 K, much lower than the experimental value of 24 meV. Therefore, in order to better explain the difference, we searched for the deformation potential that would give the best overall fit to our measured values for all temperatures, and were able to determine that a value of $b = -2.40$ eV gave the best fit. Accordingly, an additional curve (dashed blue line) using a deformation potential of -2.40 eV is also plotted in Fig. 2(b). It can be seen that the value of -2.40 eV matches the experimental data very well; however, it was not derived from any particular theoretical model. On the other hand, the value of -2.55 eV was obtained from the theory described in Ref. 21, although it does not fit the data well for this sample. This result, along with the large variation of deformation potential values reported in the literature, indicates that further study of the deformation potential in tensile- and compressive-strained Ge/Si and GeSn/Si materials is needed. It is worth noting that the tensile strain, which has a value of 0.19% at RT, is estimated to be about 0.28% at 10 K due to the thermal expansion mismatch. Because of this, the energy separation between the HH and LH bands is expected to be a little larger at 10 K (~26 meV) compared to RT (~17 meV). Evidently, the separation energy increases as T decreases, which follows with the T-dependent behavior of the tensile strain.

As shown in Fig. 2(a), three indirect bandgap related PL emissions were observed at around 0.725, 0.692, and 0.635 eV at 10 K. It should be noted here that it is difficult to determine the exact peak positions from a broad peak composed of multiple peaks, which also depend slightly on laser power. The analysis of the T-dependent indirect bandgap related emissions is also difficult because of the involvement of various T-dependent phonons involved. Although these peak positions are, certainly, slightly different from the observed values of 0.732, 0.702, and 0.639 eV from the PL measured at 650 mW laser excitation, a similar assignment was made here. That is, the two peaks at 0.725 and 0.692 eV are attributed to the Ge-like TA ($E_{ID,LH} - 1TA$) and Ge-like TO ($E_{ID,LH} - 1TO$) phonon replicas, respectively, both of which are associated with the LH valence band. The ($E_{ID,LH} - 1TA$) emission either disappears or is absorbed into the much stronger ($E_{ID,LH} - 1TO$) related peak as T increases above around 50 K. A similar trend can be seen in the laser power dependent PL shown in Fig. 1. The dominant peak changes from ($E_{ID,LH} - 1TO$) to dominant 1LA phonon related emission to the LH band, ($E_{ID,LH} - 1LA$), at around 0.704 eV at temperatures ranging from around 50 to 100 K. As T increases further, the no-phonon (NP) related emission to the LH band, ($E_{ID,LH} - NP$), at around 0.712 eV now becomes dominant at temperatures ranging from around 100 to 200 K. For T above around 250 K including 300 K, the optical transition now becomes NP related emission to the HH band ($E_{ID,HH} - NP$) at around 0.684 eV. Here, one must note that the NP related PL peak will change with T due to the change in the T-dependent bandgap energy, and phonon energies themselves could also change slightly as the lattice constant changes. It is also very interesting to observe that the indirect PL intensities increase up to around 50 K (strongest), and then decrease gradually as T increases. Additionally, one can clearly observe the competitive nature between direct and indirect emission intensities as T varies. As mentioned previously, there is an additional weak, broad peak observed at about 0.635 eV at low Ts, which could be DAP, FB, and/or defect related peak.

Schematic diagrams (not scaled) showing calculated band structures of the undoped $Ge_{0.9997}Sn_{0.0003}$ film having tensile strain values of 0.28% and 0.19% at 10 and 300 K, respectively, are shown in Figs. 3(a) and 3(c). The details of the bandgap calculation are explained in Ref. 21. The larger strain value at LT is due to the thermal expansion mismatch described earlier. The observed PL peak positions from the Γ and L valleys to the heavy-hole and light-hole bands at 10 and 300 K, which were seen in Figs. 1 and 2, are also shown in Figs. 3(b) and 3(d), respectively. For this sample, theory predicts that the $E_{\Gamma,LH}(10)$ is reduced to 0.842 eV from the value of 0.890 eV of bulk Ge at 0 K due to 0.28% tensile strain as shown in Fig. 3(a). However, the observed value of $E_{D,LH}(10)$ (=0.827 eV) as shown in Fig. 3(b) is slightly smaller by about 15 meV than the predicted value, which implies that the actual $E_{\Gamma}(10)$ [$=E_{D,LH}(10)$] reduction in Γ valley minimum might be a little larger than the theory predicted, which agrees with the observations reported in Ref. 21. On the other hand, the indirect bandgap at 10 K, $E_{L,LH}(10)$ [$=E_g(10)$], is expected to be reduced to 0.718 eV for this sample, compared to the value of 0.742 eV in bulk Ge. However, the PL peak energy of the NP peak at 10 K [$E_{ID,LH}(10) \approx E_{L,LH}(10) = E_g(10)$] is estimated to be 0.739 eV for this sample, which is slightly higher (by about 21 meV) than the predicted value as shown in Fig. 3(b). This indicates that the $E_{L,LH}(10)$ could be as high as 0.739 eV. This also implies that the actual reduction in the L conduction valley might be smaller than the theory predicted. Thus, for this sample, the estimated energy separation between the Γ and L valleys at 10 K, [$E_{\Gamma,LH}(10) - E_{L,LH}(10)$], could be about 88 meV (=0.827 − 0.739 eV) compared to the theoretically predicted value of 124 meV (=0.842 − 0.718 eV) as can be seen in Figs. 3(a) and 3(b), which is smaller by about 36 meV. This is a very significant difference.

Similarly, the direct bandgap, $E_{\Gamma,LH}(300)$, at RT shown in Fig. 3(c) is expected to be reduced to 0.770 eV for this 0.19% tensile strain and 0.03% Sn content sample compared to the value of 0.800 eV in bulk Ge. However, the observed HH PL peak energy, $E_{D,HH}(300)$, is 0.770 eV for this thin film sample as shown in Fig. 3(d). If the theoretical LH and HH splitting of about 17 meV is taken into account, the LH PL peak energy, $E_{D,LH}(300)$ ($\approx E_{\Gamma,LH}(300)$), could be about 0.753 eV, which is smaller (by about 17 meV) than the predicted value of 0.770 eV. On the other hand, the indirect bandgap at 300 K, $E_{L,LH}(300)$ [$=E_g(300)$], is expected to be reduced to 0.645 eV for this sample compared to the value of 0.661 eV in bulk Ge. However, the observed PL peak energy of the NP peak at 300 K to the HH band [$\approx E_{ID,HH}(300)$] is 0.684 eV for this sample as shown in Fig. 3(d). Then this value is higher (by about 22 meV) than the predicted value of 0.662 eV, indicating that the LH PL peak energy, $E_L(300)$ [$\approx E_{ID,LH}(300)$], could be as high as 0.667 eV (=0.684 − 0.017 eV). This implies that the reduction in the indirect bandgap might be smaller (by 22 meV) than the theory predicted. Therefore, for this sample, the estimated energy separation between the Γ and L valleys at 300 K,

$[E_{\Gamma,LH}(300) - E_{L,LH}(300)]$, could be about 86 meV (=0.753 − 0.667 eV) instead of the theoretically predicted value of 125 meV (=0.770 − 0.645 eV) as can be seen in Figs. 3(c) and 3(d), which is smaller by about 39 meV. This result is very consistent with the results obtained from the PL analysis at 10 K for this sample and with the results reported in Ref. 21. It is believed that these discrepancies are mainly due to uncertainties in the parameters used in the theoretical calculation, some of which are not well known. These include the bowing parameter and the deformation potential, which determine the change in the direct and indirect bandgap energies due to Sn content and strain amount, respectively. The values of these parameters reported in the literature vary significantly as indicated above. The values that were chosen for these calculations are believed to be the best available, however, there is still some inherent uncertainty. Given the low Sn content of this sample, the effect of the bowing parameter should be very small, so the majority of the discrepancy should be due to the inaccurate values of deformation potential and tensile strain used.

In general, the laser power- and T-dependent PL measurements consistently indicate that the E_Γ [$\approx E_D$] reduction in Γ valley could be larger, whereas the E_L reduction in L valley could be smaller than the theory predicted. Therefore, the estimated separation of $(E_\Gamma - E_L)$ could be much smaller than the predicted value mainly due to the tensile strain. This finding strongly suggests that the indirect-to-direct bandgap transition of $Ge_{1-y}Sn_y$ could be achieved at much lower Sn concentration than originally anticipated if one utilizes the tensile strain properly. Furthermore, these studies could indicate that the single PL peak observed at RT could be mainly due to the HH transition rather than LH transition. Therefore, care must be taken in estimating the direct bandgap of tensile-strained GeSn layer from the PL peak position because the direct bandgap, $E_{\Gamma,LH}(300) \approx E_{D,LH}(300)$, must be determined by the energy difference from the bottom of the Γ valley to the top of the LH band at the same wave vector $\boldsymbol{k}$ value. Otherwise, the error in estimating $E_{D,LH}(300)$ could be as large as the separation energy between the LH and HH valence bands, which could be 17–26 meV depending on the tensile strain.

IV. CONCLUSION

The laser power- and T-dependent PL has been investigated for 0.19% and 0.28% (at 300 and 10 K, respectively) tensile-strained undoped $Ge_{0.9997}Sn_{0.0003}$ film grown on *n*-Si substrate. This sample shows not only both direct ($E_{D,LH}$ and/or $E_{D,HH}$) and indirect bandgap ($E_{ID,LH}$ and/or $E_{ID,HH}$) related optical transitions but also clearly shows the optical emission from the Γ valley to the strain split light hole and heavy hole valence bands. At a moderate laser power (450 mW) and at low T, three direct bandgap related PL peaks were observed at energies of 0.851, 0.827, and 0.807 eV, which are attributed to heavy hole, ($E_{D,HH}$), and light hole, ($E_{D,LH}$), transitions and 1LA phonon replica of ($E_{D,LH}$ − 1LA), respectively. The relative intensities between HH and LH transitions depend on the excitation laser power, showing a strong HH transition at higher laser power and strong LH transition at lower laser power. The T-dependent PL also shows how the relative PL intensities between HH and LH transitions change as a function of T. At low T, LH transition is stronger or comparable to HH transition. As T increases, LH emission decreases faster than the HH, and at higher T including 300 K, the PL shows almost entirely HH emission. The intensity of E_D(T) PL reaches a minimum at about 150 K, and then increases up to 300 K. These T-dependent PL results also clearly show the competitive nature between the direct and indirect bandgap related PL transitions as T changes. Strong E_D emissions were observed at low T along with slightly weaker E_{ID} transitions. At RT, a strong dominant E_D transition and a very weak E_{ID} PL emission were observed. The observed PL results for this sample show that the estimated energy separation between the Γ and L valleys at 10 K, $[E_{\Gamma,LH}(10) - E_{L,LH}(10)]$, could be about 88 meV instead of the theoretically predicted value of 124 meV, and the separation at RT, $[E_{\Gamma,LH}(300) - E_{L,LH}(300)]$, could be about 86 meV compared to the theoretically predicted value of 125 meV. These observations obviously show that strong direct bandgap optical transitions at RT could be obtained from $Ge_{1-y}Sn_y$ alloys with proper tensile strain. Thus, $Ge_{1-y}Sn_y$ alloys could be attractive materials for the fabrication of direct bandgap Si-based light emitting devices.

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