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Electroluminescence from GeSn heterostructure *pin* diodes at the indirect to direct transition

J. D. Gallagher,¹ C. L. Senaratne,² P. Sims,² T. Aoki,³ J. Menéndez,¹ and J. Kouvetakis²

¹Department of Physics, Arizona State University, Tempe, Arizona 85287-1504, USA

²Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, USA

³LeRoy Eyring Center for Solid State Science, Arizona State University, Tempe, Arizona 85287-1704, USA

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The emission properties of GeSn heterostructure *pin* diodes have been investigated. The devices contain thick (400–600 nm) Ge_{1-y}Sn_y *i*-layers spanning a broad compositional range below and above the crossover Sn concentration y_c where the Ge_{1-y}Sn_y alloy becomes a direct-gap material. These results are made possible by an optimized device architecture containing a single defected interface thereby mitigating the deleterious effects of mismatch-induced defects. The observed emission intensities as a function of composition show the contributions from two separate trends: an increase in direct gap emission as the Sn concentration is increased, as expected from the reduction and eventual reversal of the separation between the direct and indirect edges, and a parallel increase in non-radiative recombination when the mismatch strains between the structure components is partially relaxed by the generation of misfit dislocations. An estimation of recombination times based on the observed electroluminescence intensities is found to be strongly correlated with the reverse-bias dark current measured in the same devices. © 2015 AIP Publishing LLC.

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Recent experimental studies of Ge_{1-y}Sn_y alloys point to an indirect-to direct-gap transition at $y = y_c = 0.09$, making this system an intriguing alternative to Ge for purely group-IV interband lasers that can be easily integrated onto Si-platforms.^{1,2} The required Sn concentration to achieve direct gap conditions is much less than originally predicted by theory,^{3,4} which should facilitate the fabrication of appropriate *pn* junction devices as the first step towards electrically injected GeSn lasers, following the recent demonstration of optically pumped devices.⁵ However, systematic studies of light-emitting diodes at and beyond the indirect-to-direct threshold are still lacking. After the initial report of electroluminescence (EL) from Ge_{0.98}Sn_{0.02} diodes by Roucka *et al.*, (Ref. 6) several groups have observed EL from GeSn materials,^{7–12} but the highest reported Sn concentration in those devices is $y = 0.08$, still below y_c . A significant issue to be reckoned with in reaching high concentrations is the strong compositional dependence of the lattice parameter. Even at the modest $y_c = 0.09$ value, the lattice mismatch with pure Ge is 1.2%, a very substantial amount. Fully strained GeSn films on relaxed Ge buffer layers cannot exceed the critical thickness for strain relaxation. For $y_c = 0.09$, this critical thickness is less than 10 nm, and even the metastable critical thickness at typical GeSn growth temperatures is estimated to be less than 100 nm.¹³ In addition, the compressive nature of the mismatch strain makes the material more indirect, which is undesirable for light emission. Strain-relaxed films can be grown much thicker and have a band line-up more favorable to light emission, but at the price of generating misfit dislocations that increase the non-radiative recombination rate.

In this letter, we report the observation of direct-gap EL from Ge_{1-y}Sn_y *pin* diodes over the concentration range of $0 \leq y \leq 0.11$. The intrinsic layers in the samples are largely

strain-relaxed, and the effect of dislocations is minimized by growing the devices on Ge-buffered Si, following the observation that the emission properties of relaxed GeSn on Ge-buffered Si are much better than those from relaxed GeSn grown directly on Si.¹³ Moreover, the structure is designed so that misfit dislocations can appear at only one interface, namely that between the intrinsic GeSn layer and the Ge buffer. All other interfaces are lattice-matched or fully strained. To maximize the external quantum efficiency of the samples with the highest Sn concentration, a heterostructure approach is followed in which the top *p*-layer has a lower Sn concentration than the intrinsic layer from which most of the emission originates.

The device structures were produced in three stages using separate reactors. Heavily *n*-doped Ge buffer layers with carrier densities of $\sim 2 \times 10^{19}/\text{cm}^3$ and thicknesses of 1–1.5 μm were used as the bottom contact. These were grown on 4 in. Si (100) wafers in a single wafer Gas-Source Molecular Epitaxy reactor using Ge₄H₁₀ and P(GeH₃)₃ and annealed *in situ* at 650 °C for 3 min. The wafers were then cleaved into quadrants and cleaned using an aqueous HF solution prior to being loaded into an Ultra High Vacuum Chemical Vapor Deposition (UHV-CVD) reactor where they were further cleaned by flowing 5% Ge₂H₆ at 30 mTorr for 5 min. Nominally intrinsic Ge_{1-y}Sn_y layers with $0.02 \leq y \leq 0.11$ and thicknesses 400–600 nm were grown on these surfaces at temperatures ranging from 335 °C to 285 °C using appropriate mixtures of Ge₃H₈ (Ge₂H₆ for ≤ 0.02) and SnD₄, as described in detail in Refs. 13 and 14. For samples with $y > 0.08$, it was found that an additional Ge “spacer” layer grown using Ge₃H₈ prior to the alloy growth improved the structural quality of the stack. Thereafter, these layers were chemically cleaned and loaded into a separate UHV-CVD chamber dedicated to *p*-type doping. Again, in this case, a Ge₂H₆ clean was applied

to prepare an epi-ready surface. Reaction mixtures combining Ge_2H_6 and SnD_4 were used, while the B_2H_6 p -dopant was introduced separately into the reaction zone. For devices with i -layer compositions $0.02 \leq y \leq 0.05$, the top electrode composition was chosen to match that of the intrinsic counterpart, creating a lattice matched i - p structure. For devices with $0.07 \leq y \leq 0.11$, the external quantum efficiency was further maximized by choosing a smaller Sn concentration for the p -layers, which reduced reabsorption of the i -layer emission. This allowed an increase in growth temperature to 330–320 °C from 300–285 °C, so that this step would also act as an annealing treatment for the i -layer. At all stages of growth of the device stack, the samples were subjected to High Resolution X-Ray Diffraction (XRD) and ellipsometry characterizations to determine doping, crystallinity, composition, and thickness.

Figure 1(a) shows a diffraction-contrast Cross-Sectional Transmission Electron micrograph (XTEM) of a device stack comprising n -Ge, i -Ge, i - $\text{Ge}_{0.895}\text{Sn}_{0.105}$, and p - $\text{Ge}_{0.95}\text{Sn}_{0.05}$ layers. The results show that the free surface is flat and the upper interface is defect-free, but the bottom interface is highly defected, as evidenced by the high density of dislocations confined to the plane of growth. Figure 1(b) shows 224 Reciprocal Space Map (RSM) plots of the same device. The XRD peaks of the n -buffer and Ge “spacer” are in perfect

overlap, while the peaks of the i - and p - $\text{Ge}_{1-y}\text{Sn}_y$ are widely separated due to the difference in Sn contents between the two materials. However, the two GeSn layers are coherently strained to each other, as shown by the vertical alignment of the peak maxima along the pseudomorphic line in the figure. The i -layer exhibits a residual compressive strain of $\sim 0.30\%$ as grown, corresponding to 75% strain relaxation, while the p -type is tensile-strained by 0.5%. By contrast, Figure 1(c) corresponds to a device stack comprising a n -Ge buffer, i - $\text{Ge}_{0.98}\text{Sn}_{0.02}$ active layer, and a p - $\text{Ge}_{0.98}\text{Sn}_{0.02}$ top contact. The plot demonstrates that the GeSn layers are almost perfectly relaxed and lattice-matched to the Ge buffer layers. This is because the Ge buffer possesses a biaxial tensile strain of 0.15% induced by the *in situ* annealing step. For this strain, the basal parameters of Ge are close to the cubic value of $\text{Ge}_{0.98}\text{Sn}_{0.02}$ ($a_0 = 5.670 \pm 0.001$ Å), allowing perfect lattice matching between the materials.

The defected interface between the i -GeSn layer and the Ge layers was further characterized by scanning transmission electron microscopy (STEM). Representative data for devices with $\text{Ge}_{0.895}\text{Sn}_{0.105}$ and $\text{Ge}_{0.915}\text{Sn}_{0.085}$ i -layers are shown in Figures 2(a) and 2(b) as STEM bright field (BF) images, respectively. Fig. 2(a) shows a pair of short stacking faults appearing as dark contrast areas extending from the interface down into the Ge buffer along the [111] direction. These defects are randomly distributed and tend to penetrate a short distance into the Ge buffer. A similar behavior has been observed previously not only in GeSn films on Ge^{5,13,14} but also in the case of SiGe growth on Si or Ge substrates.^{15,16} The same type of defect appears on the left side of panel (b) for the 8.5% Sn device. In this case, a 60° dislocation appears on the right side. The latter along with the stacking faults represent the commonly observed defect types that predominately relax the misfit strain. Higher defectivities at the interface are expected to lead to undesirable non-radiative recombination. Nevertheless, the propensity of

FIG. 1. (a) XTEM of a device with a $\text{Ge}_{0.895}\text{Sn}_{0.105}$ i -layer and a $\text{Ge}_{0.95}\text{Sn}_{0.05}$ top p -layer obtained with a JEOL 4000 EX microscope operated at 400 kV. The top interface is defect free, whereas mismatch defects appear at the interface with the Ge buffer layer. (b) 224 XRD RSM of the same device show that the p - and i -layers are fully coherent, but partially relaxed relative to the Ge buffer. (c) 224 XRD RSM for a $\text{Ge}_{0.98}\text{Sn}_{0.02}$ device showing that in this case all layers are fully coherent.

FIG. 2. High resolution STEM BF images of defected $\text{Ge}/i\text{-Ge}_{0.895}\text{Sn}_{0.105}$ and $\text{Ge}/i\text{-Ge}_{0.915}\text{Sn}_{0.085}$ interfaces are shown in panels (a) and (b), respectively. The images were acquired in an aberration-corrected JEOL ARM 200F microscope. The common defects in both cases are short stacking faults and 60° dislocations (dashed white circle) compensating the misfit strain between the bottom contact and the intrinsic layer of the devices. (c) STEM HAADF image shows no defects at the top i - p interface.

these defects to propagate through to the Ge buffer mitigate these adverse effects and represent a significant design advantage.¹⁷ In contrast to the *i*-Ge/*i*-GeSn, the *i*-GeSn/*p*-GeSn interfaces are defect-free as shown in the STEM high angle annular dark field (HAADF) image of Fig. 2(c). This is because the thinner *p*-type top layer can be grown fully strained to the intrinsic counterpart. This is manifested as a dark band along the interface in the aberration corrected image taken under strain contrast conditions. The microstructure presented in Figure 2 is common to all samples with four layer architectures containing 8%–11% Sn active layers.

The devices in this study were fabricated using protocols similar to those employed for $\text{Ge}_{1-y}\text{Sn}_y/\text{Si}$ prototypes in prior work.¹⁵ Figure 3 compares *I*-*V* curves for a series of representative samples. The diode ideality factors range from 1.10 to 1.55. The reverse-bias dark currents measured for the 5.5%–8.5% Sn devices are similar to those reported for similar samples within this composition range.¹³ However, in forward bias, our currents are 10 times higher, indicating that our fabrication approach leads to better ideality factors and/or lower parasitic series resistances. The dark currents in Fig. 3 increase rapidly as a function of Sn concentration. To understand this behavior, we studied the temperature dependence of the dark current. The inset in Fig. 3 shows the activation energies determined from such measurements. We see that that for low Sn concentrations, the activation energies clearly exceed $E_g/2$, where E_g is the fundamental band gap. This indicates a significant diffusion contribution to the dark current, which can only be observed in devices with low defect concentrations. For higher Sn concentrations, on the other hand, the activation energies approach $E_g/2$, as expected from a Shockley-Read-Hall generation mechanism via defects.

EL measurements were performed at room temperature using a Keithley 2602A source, pulsed to 50 Hz. The light emitted from the device surface was passed through a grating spectrometer ($f=320$ mm), and detected using either an extended liquid nitrogen-cooled InGaAs detector (1300–2300 nm) or a PbS detector (1500–2700 nm).

Fig. 4 shows normalized EL results for selected diodes. For low Sn concentrations, we see clear evidence of direct

FIG. 3. (Top) *I*-*V* characteristics of 300 μm diameter diodes with Sn compositions up to 11%. The inset compares the activation energies of the dark currents at -0.2 V with the fundamental band gap and half its value. While the low Sn-concentration diodes show evidence for a diffusion component of the current, at high Sn-concentrations, Shockley-Read-Hall recombination at defects seems to be dominant contribution.

FIG. 4. Room temperature EL spectra of GeSn heterostructure diodes at a current density of 490 A/cm^2 ($I = 0.5 \text{ A}$), normalized to the intrinsic layer thickness. The samples are labeled by the Sn concentration in their intrinsic layers. The noisier data for the 10.5% Sn are due to the use of a PbS detector, as opposed to the InGaAs detector used for the other diodes. For this sample, the solid black line is the EMG fit of the emission profile. The inset shows the current dependence of the EL for the 7% Sn diode and the PL spectrum for the same sample, normalized to the intensity of the EL emission for the highest current.

and indirect gap emission, whereas at high values of y , a single peak is observed. A strong signal is seen from a diode with a $\text{Ge}_{0.915}\text{Sn}_{0.085}$ intrinsic layer, very close to y_c , and from a diode with a $\text{Ge}_{0.895}\text{Sn}_{0.105}$ intrinsic layer, which is a direct gap material according to the known compositional dependence of the band gaps.¹ The inset shows the experimental EL spectra as a function of the injection current for a diode with a $\text{Ge}_{0.93}\text{Sn}_{0.07}$ *i*-layer, together with a photoluminescence (PL) spectrum for the same sample. The main peak in the EL spectra is assigned to direct gap emission from the intrinsic layers in the device. The PL signal also shows contributions from the top *p*-layer (which has a lower Sn concentration for the sample in the inset) and even from the *n*-Ge buffer layer. The spectral lineshapes as well as the peak energies are in excellent agreement with previous detailed studies of the compositional dependence of the PL signal from $\text{Ge}_{1-y}\text{Sn}_y$.^{1,2} As in the PL case, the data are well described using an Exponentially Modified Gaussian (EMG) for the direct gap emission and a simple Gaussian for the indirect gap emission. An example of an EMG fit is shown in Fig. 4 for the case of a diode with a $y=0.105$ intrinsic layer.

The compositional dependence of the EL signal strength is quite remarkable. At room temperature, we expect a monotonic increase as the direct gap approaches the indirect gap, without any observable discontinuity at y_c . Instead, the EL intensity decreases between $y=0.02$ and $y=0.055$, and reverts to the expected trend for $y > 0.055$. To understand these results, we take advantage of our ability to model the direct gap emission in these systems very accurately, as discussed in Ref. 6 and more recently in Ref. 2. The emission spectrum can be expressed as a generalized van Roosbroeck-Shockley expression that depends on the non-equilibrium

FIG. 5. Recombination lifetimes obtained from the relative intensity of the EL spectra compared with the inverse dark currents from the I - V characteristic of the diodes. The recombination lifetime is normalized to the value $\tau(0)$ for a pure Ge diode ($y = 0$).

carrier concentration n and the energies of the direct and indirect gap, as explained in detail in previous work.² Since the non-equilibrium carrier concentration is related to the diode current by¹⁸ $n = J\tau/(ed)$ (where J is the current density, e —the elemental charge, d —the i -layer thickness, and τ —the total recombination time), we can adjust the relative values of τ to match the spectra in Fig. 4. The results are shown in Fig. 5, and we see that the recombination time decreases sharply until it reaches at minimum near $y = 0.05$. Beyond this concentration, the recombination time is roughly constant. We also show in Fig. 5, the inverse of the dark currents at -1 V, which are also proportional to the carrier lifetime, and we see a similar trend. We attribute this behavior to the onset of strain relaxation in the intrinsic layer. Whereas the 2% Sn device is fully strained, the 5.5% Sn device, with an intrinsic layer thickness of 440 nm that exceeds the metastable critical thickness,¹³ is found to be 70% relaxed. The associated misfit dislocations shorten the non-radiative recombination time, overwhelming the increase in EL intensity predicted from the reduction of the direct-indirect separation relative to pure Ge. For the $y > 0.055$ samples, on the other hand, the level of strain relaxation is comparable,¹³ and therefore, we expect the non-radiative recombination time to saturate, so that the compositional dependence of the EL intensity follows the theoretical prediction again, increasing as the separation between direct and indirect gaps decreases and eventually reverses.

In summary, we have observed direct gap emission from GeSn *pin* heterostructure diodes for a broad compositional range than extends beyond the critical concentration y_c at which the alloy becomes a direct gap material. These results were made possible by a sample design that only allows for

a single defected interface. The observation of EL over such a broad range suggests that the presence of Sn in the lattice does not have any deleterious effect on the emission properties. Instead, the increase in non-radiative recombination as a function of composition is attributed to the lattice mismatch at the defected interface. Accordingly, reducing this mismatch with further buffer-layer engineering, for example, using GeSn or GeSiSn buffer layers with larger lattice constants than Ge, should make it possible to fabricate highly efficient GeSn laser diodes.

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