

Tensilely Strained Germanium Nanomembranes as Infrared Optical Gain Media

C. Boztug, J. R. Sánchez-Pérez, F. F. Sudradjat, RB Jacobson, D. M. Paskiewicz, M. G. Lagally,* and R. Paiella*

The use of tensilely strained Ge nanomembranes as mid-infrared optical gain media is investigated. Biaxial tensile strain in Ge has the effect of lowering the direct energy bandgap relative to the fundamental indirect one, thereby increasing the internal quantum efficiency for light emission and allowing for the formation of population inversion, until at a strain of about 1.9% Ge is even converted into a direct-bandgap material. Gain calculations are presented showing that, already at strain levels of about 1.4% and above, Ge films can provide optical gain in the technologically important 2.1–2.5 μm spectral region, with transparency carrier densities that can be readily achieved under realistic pumping conditions. Mechanically stressed Ge nanomembranes capable of accommodating the required strain levels are developed and used to demonstrate strong strain-enhanced photoluminescence. A detailed analysis of the high-strain emission spectra also demonstrates that the nanomembranes can be pumped above transparency, and confirms the prediction that biaxial-strain levels in excess of only 1.4% are required to obtain significant population inversion.

1. Introduction

The development of group-IV semiconductor lasers that can be fabricated on Si chips in a CMOS-compatible fashion has long been a major goal of research in optoelectronics, as these devices could enable the monolithic integration of electronics and photonics on an unprecedented scale. The main challenge is to obtain efficient light emission from group-IV materials such as Si, Ge, and related alloys, because these materials have indirect energy bandgaps, resulting in exceedingly low radiative recombination rates. Germanium is

particularly promising in this context, because the relatively small energy difference (141 meV) between its direct (Γ) and indirect (L) conduction-band minima can be further reduced through the application of biaxial tensile strain, until, at a strain level of about 1.9%, Ge is converted into a direct-bandgap material.^[1–7] As a result, in the presence of optical or electrical pumping, a large population of conduction band electrons can be established in the Γ valley, where they can efficiently recombine via interband light emission. For the same reason, population inversion and therefore optical gain across the direct energy bandgap also become achievable in Ge at sufficiently high tensile-strain levels.

Under such strain conditions, the bandgap energy of Ge also red-shifts into the mid-infrared (IR) spectral range (e.g., to a wavelength of about 2.6 μm at 1.9% tensile strain).^[5] Therefore tensilely strained Ge is a promising candidate for the development of efficient mid-IR light sources that can be monolithically integrated with CMOS electronics. In turn, a wide range of important applications exists for these devices, particularly in the area of biological and chemical sensing (e.g., for trace-gas detection, environmental monitoring, medical diagnostics, and industrial process control), as well as

C. Boztug, Dr. F. F. Sudradjat, Prof. R. Paiella
Boston University
Boston, MA 02215, USA
E-mail: rpaiella@bu.edu

J. R. Sánchez-Pérez, RB Jacobson, D. M. Paskiewicz,
Prof. M. G. Lagally
University of Wisconsin-Madison
Madison WI 53706, USA
E-mail: lagally@engr.wisc.edu



DOI: 10.1002/sml.201201090

spectroscopy and secure free-space optical communications.^[8] For example, group-IV mid-IR lasers may enable the development of highly integrated optical sensors comprising the required light sources, optics, and detectors, as well as read-out and data-processing electronics all on the same materials platform. Such systems could provide unparalleled miniaturization compared to existing hybrid solutions, and therefore be employed in presently inaccessible environments. It should also be noted that the emission band of tensilely strained Ge active layers (around the 2.1–2.5 μm atmospheric transmission window) lies at the boundaries between what is currently covered by high-performance interband diode lasers on the short-wavelength side and intersubband quantum cascade lasers at longer wavelengths.^[9] Besides their inherent CMOS compatibility, these materials are therefore attractive for the purpose of extending the overall spectral reach of mid-IR optoelectronics.

Motivated by these considerations, researchers have investigated several approaches in recent years to introduce the required levels of tensile strain in Ge films of high crystalline quality. Unfortunately, pseudomorphic growth of Ge on SiGe templates produces epilayers under compressive rather than tensile strain, because the in-plane lattice constant of Ge is larger than that of SiGe. Alternative growth template materials such as SiGeSn^[3,10] or InGaAs^[11,12] can be employed, at the expense, however, of increased complexity of the epitaxial process and (in the case of InGaAs) limited prospects for CMOS compatibility. A small amount of tensile strain (0.25%) can also be introduced in plastically relaxed (i.e., containing many dislocations) Ge films grown on Si, by using an annealing process to take advantage of the difference in thermal expansion coefficients between Si and Ge.^[4,13] Such low strain levels are insufficient to enable population inversion, but can be complemented with the use of highly degenerate *n*-type doping to raise the electronic quasi-Fermi level. With this approach, a Ge laser has, in fact, been demonstrated recently,^[13] although the need for heavy doping is undesirable as it necessarily results in high optical losses due to free-carrier absorption and limited radiative efficiency due to Auger processes (i.e., recombination via carrier-carrier scattering).

An alternative method to introduce strain in crystalline Ge is the application of external mechanical stress. In the case of bulk samples, this approach can only produce relatively low tensile-strain levels (e.g., about 0.6% in the work of Ref. [14]) before the onset of significant extended-defect formation. In contrast, single-crystal free-standing nanomembranes (NMs) can provide substantially larger strain thresholds for plastic deformation and cracking, by virtue of their nanoscale thicknesses and therefore proportionally small strain energy under stress.^[15] These nanostructures can be produced in a variety of materials systems, based on a fabrication process that has been developed in the past few years for a wide range of applications.^[16–23] Recently, we have reported a strong increase in photoluminescence (PL) efficiency and a large red shift in emission wavelength with increasing tensile strain using Ge NMs mechanically stretched with high-pressure gas.^[24] A maximum tensile strain of over 2% in a 24-nm-thick NM was also demonstrated, above the accepted threshold^[1–7] for the formation of direct-bandgap Ge. These Ge NMs are highly

luminescent already at room temperature, can be strained to a level where degenerate doping is no longer required to achieve population inversion, and are directly compatible with light emission via electrical injection (e.g., with a lateral *p-i-n* junction geometry). Their integration with CMOS electronics can in principle be realized using suspended-beam structures based on MEMS technology (as described in a recent theoretical study),^[5] or through the subsequent deposition of suitable stressor layers (an approach that has recently been pursued with micron-scale-thickness Ge wires^[25] and films^[26]).

In this article, we first present a detailed theoretical study of the optical gain properties of tensilely strained Ge NMs. As expected from the strain dependence of the Ge band structure, the transparency carrier density N_t (defined as the carrier concentration needed to reach population inversion) is found to decrease rapidly with increasing biaxial tensile strain. At the same time, relatively large peak gain coefficients of several 100 cm^{-1} become accessible with reasonably low densities of injected carriers, on the order of a few 10^{18} cm^{-3} . Next, we present strain-enhanced PL measurement results obtained with a 57-nm-thick Ge NM under external biaxial mechanical stress. The experimental emission photon energies are mapped as a function of strain, and found to be in excellent agreement with theoretical expectations. A quantitative analysis of the emission spectrum at the highest strain measured in this NM (about 1.4%) is also carried out, which allows inferring the quasi-equilibrium carrier density N produced by the PL pump pulses in the NM. The resulting estimate suggests that in this experiment the NM is already pumped above transparency (i.e., $N > N_t$), albeit with a relatively small population inversion corresponding to a calculated peak gain coefficient of less than 10 cm^{-1} . This tensile strain level of 1.4% can therefore be identified as a lower bound for what is required to obtain optical gain in Ge NMs under realistic pumping conditions, even though it is substantially smaller than the threshold for direct-bandgap behavior (1.9%). Higher strain levels can be introduced in even thinner NMs because they have a higher threshold for plastic deformation. To illustrate, we present PL data previously measured with a 40-nm-thick NM at near 1.8% tensile strain,^[24] and show that a large population inversion (corresponding to a peak gain of about 250 cm^{-1}) can be inferred from these data. If placed in a suitable cavity for optical feedback, such tensilely strained Ge NMs can therefore be expected to provide adequate gain for the development of CMOS-compatible lasers in the technologically important 2.1–2.5 μm atmospheric transmission window.

2. Results and Discussion

The optical-gain spectrum of tensilely strained Ge due to electronic transitions between the conduction-band Γ minimum and either the heavy-hole (HH) or the light-hole (LH) valence band is calculated as follows:^[27]

$$g(h\nu_0) = \frac{C}{h\nu_0} \int \left| M_{TE}^*(E_{21}) \right|^2 \rho_r(E_{21}) [f_2 - f_1] \xi(h\nu_0 - E_{21}) dE_{21} \quad (1)$$

In this equation, ν_0 is the optical frequency, $M_{TE}^{TE}(E_{21})$ is the polarization-dependent momentum matrix element, $\rho_r(E_{21})$ is the reduced density of states, f_1 and f_2 are the occupation probabilities of, respectively, the valence-band and conduction-band states of equal momentum and energy difference E_{21} , and $\xi(h\nu_0 - E_{21})$ is the lineshape function that describes gain broadening. Finally, the constant C is given by $C = \frac{q^2 h}{2n\epsilon_0 c m_0^2}$, where n is the refractive index of Ge, q the electron charge, h Planck's constant, ϵ_0 the permittivity of free space, c the speed of light in vacuum, and m_0 the electron charge. The momentum matrix element is different for transverse electric (TE) and transverse magnetic (TM) polarizations, which are defined, respectively, as linear in the directions parallel and perpendicular to the plane of the NM. The total gain spectrum for either polarization is computed by evaluating Equation (1) for both direct conduction-to-light-hole band (c Γ -LH) and direct conduction-to-heavy-hole band (c Γ -HH) transitions and then adding the results.

In the following we assume parabolic energy bands, so that the expression in Equation (1) only depends on a few well established materials parameters, namely the bandgap energies, the effective masses, and the momentum matrix elements. These parameters vary as a function of biaxial strain ϵ (defined as the fractional change of the in-plane lattice constant from its equilibrium value), and their strain dependence can be determined using data from the literature. In particular, the bandgap energies are calculated from standard formulas^[27,28] in terms of the deformation potentials a_v , a_c , $\Xi_d + \Xi_u/3$, and b (which describe, respectively, the strain-induced shift of the average valence-band maximum, the conduction band minimum at Γ , the conduction band minima at L, and the splitting of the valence bands at Γ). The specific values of the deformation potentials used in the simulations were chosen in accordance with available theoretical and experimental data^[2,3,29–32] and are listed in **Table 1**, together with the values of the unstrained direct and indirect bandgap energies ($E_{g\Gamma}$ and E_{gL}), spin-orbit splitting (Δ), and elastic moduli (C_{11} and C_{12}).

In **Figure 1a** we plot the calculated bandgap energies between the Γ or L conduction-band minima and the HH or LH valence-band maxima versus strain ϵ . The application of tensile strain (i.e., $\epsilon > 0$) is found to decrease all four bandgap energies, but at different rates, while at the same time lifting the degeneracy of the valence bands at Γ (with the LH band

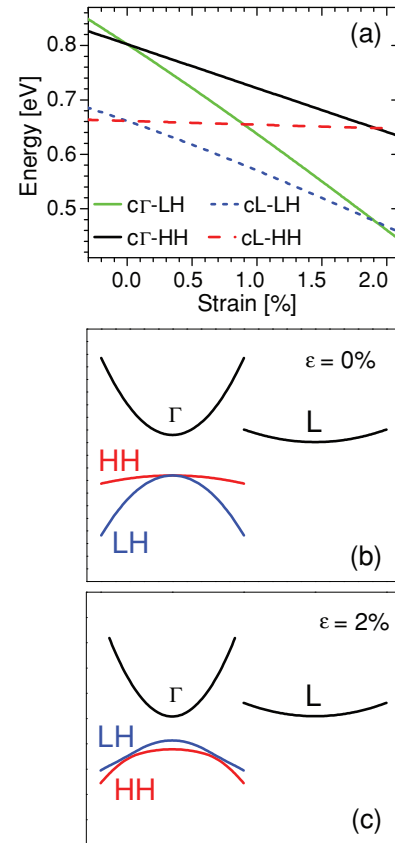


Figure 1. (a) Calculated bandgap energies between the Γ or L conduction-band minima and the HH or LH valence-band maxima, plotted as a function of strain. (b) Schematic band structure of unstrained Ge. (c) Schematic band structure of Ge under 2% biaxial tensile strain. In (b) and (c), the relative positions of all band edges correspond to their calculated values.

pushed to higher energy relative to the HH one). The formation of direct-bandgap Ge is observed in this figure as the crossing of the direct- and indirect-bandgap energy curves at a strain of about 1.9%. To illustrate these results further, the schematic band structures of unstrained Ge and Ge under 2% tensile strain are plotted in Figures 1b and c, respectively, where the relative positions of the band edges correspond to their computed values. For 2% tensile strain, the Γ valley lies below the L valleys, so that under optical or electrical pumping a large fraction of the injected electrons can thermalize near the Γ minimum and therefore contribute to the optical gain. In the expression of Equation (1), this behavior is included through the conduction-band occupation probability f_2 , which is computed (for any given density of injected electrons N) by populating all the available states in both Γ and L valleys according to a single quasi-Fermi distribution. Throughout this work we consider undoped Ge at room temperature.

Of the remaining materials parameters needed to evaluate Equation (1), the electron and hole effective masses of Ge are obtained as a function of strain based on a linear interpolation of the values reported in Refs. [2] and [6]. The momentum matrix elements of the c Γ -HH and c Γ -LH

Table 1. Materials parameters used to compute the strain-dependent bandgap energies of Ge.

b [eV]	$-2.16^{[2]}$
a_v [eV]	$1.24^{[3,29,31]}$
a_c [eV]	$-8.24^{[3,29,31]}$
$\Xi_d + \Xi_u/3$ [eV]	$-2.34^{[3,30]}$
$E_{g\Gamma}$ [eV]	$0.802^{[32]}$
E_{gL} [eV]	$0.661^{[32]}$
Δ [eV]	$0.290^{[32]}$
C_{11} [GPa]	$128.53^{[2]}$
C_{12} [GPa]	$48.26^{[2]}$

transitions for TM- and TE-polarized light are calculated as follows:^[33]

$$\begin{aligned} |M_{TM,c\Gamma-HH}|^2 &= 0 \\ |M_{TE,c\Gamma-HH}|^2 &= \frac{3}{2} M_b^2 \\ |M_{TM,c\Gamma-LH}|^2 &= 3 f_z M_b^2 \\ |M_{TE,c\Gamma-LH}|^2 &= \frac{3}{2} (1 - f_z) M_b^2 \end{aligned} \quad (2)$$

where the bulk momentum matrix element M_b is evaluated as described in Ref. [28] and

$$f_z = \frac{1}{2} \left(1 + \frac{\Delta/3 - 6b\varepsilon}{\sqrt{\Delta^2 - 4b\varepsilon\Delta + 36b^2\varepsilon^2}} \right) \quad (3)$$

It follows from these equations that c Γ -HH transitions can only emit and amplify TE-polarized light, whereas c Γ -LH transitions generally couple to both states of polarization. Furthermore, because f_z is a monotonically increasing function of ε (given that $b < 0$), the latter transitions become increasingly TM polarized as more and more tensile strain is introduced in the NM. This behavior is particularly important, because at high tensile strain the valence-band splitting illustrated in Figure 1c (with the HH band pushed to lower electron energy compared to the LH one) causes most of the injected holes to thermalize into the LH band. As a result, the overall emission and gain of Ge NMs under high tensile strain is predominantly TM polarized.

Exemplary gain spectra for both polarizations and both c Γ -HH and c Γ -LH transitions are shown in Figure 2. The tensile strain ε and the carrier density N used in these calculations are 1.78% and $3.9 \times 10^{18} \text{ cm}^{-3}$, respectively, which correspond to actual values measured with a mechanically strained, optically pumped Ge NM (as described in the following). Inhomogeneous broadening is also included through a Gaussian lineshape function $\xi(h\nu_0 - E_{21})$, whose spectral width is determined from the standard deviation of the measured NM strain. Consistent with the discussion of the previous paragraph, the largest gain contribution in Figure 2 is

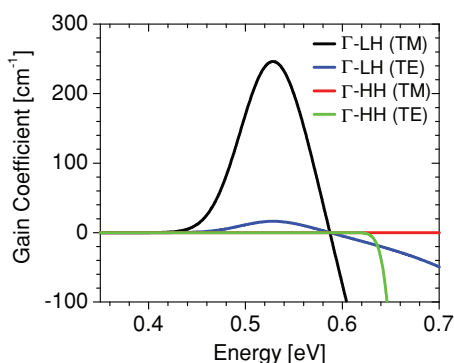


Figure 2. Calculated TE and TM optical-gain spectra due to c Γ -LH and c Γ -HH transitions in Ge under 1.78% biaxial tensile strain, in the presence of a density of injected carriers of $3.9 \times 10^{18} \text{ cm}^{-3}$.

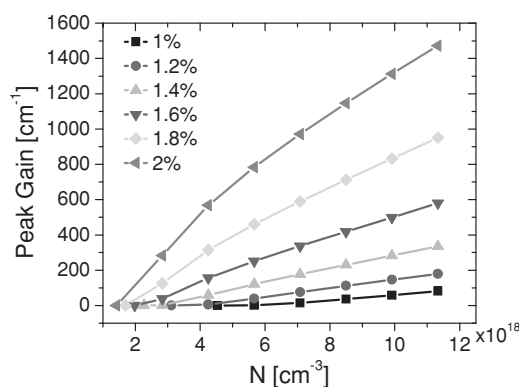


Figure 3. Peak TM gain coefficient due to c Γ -LH transitions in tensilely strained Ge, calculated as a function of carrier density for different strain values.

provided by the c Γ -LH transitions for TM-polarized light. TE-polarized photons can also be amplified via the same electronic transitions, but with an order-of-magnitude lower gain coefficient (due to the proportionally lower TE momentum matrix element). In contrast, the carrier concentration used in these calculations is not enough to obtain gain from the c Γ -HH transitions, because the HH band has a much lower energy (and hence smaller hole population) than the LH band at 1.78% tensile strain.

The peak gain coefficient provided by the c Γ -LH transitions for TM-polarized light is plotted in Figure 3 as a function of injected-carrier density, for several different values of the applied tensile strain. At the lowest strain considered in this figure (1%), no appreciable gain is obtained even under extremely high pumping conditions (i.e., for $N > 10^{19} \text{ cm}^{-3}$). As the strain is increased, peak gain values of several 100 cm^{-1} are obtained with lower and lower densities of injected carriers.

In the same strain regime, transparency carrier densities N_t on the order of a few 10^{18} cm^{-3} are computed, as illustrated in Figure 4a, where N_t is plotted as a function of ε . It should be noted that these values of peak gain coefficient and transparency carrier density are comparable to those of traditional optical gain media based on III-V semiconductors,^[27,28] indicating that tensilely strained Ge NMs are similarly suited to the development of diode lasers. In Figure 4b we plot the calculated wavelength of maximum gain (at a fixed carrier density of $5 \times 10^{18} \text{ cm}^{-3}$) versus strain. A strong red shift with increasing tensile strain is observed, consistent with the strain dependence of the bandgap energies shown in Figure 1a. It follows from this plot that stimulated emission across the entire 2.1–2.5 μm atmospheric transmission window can be obtained in the low-transparency strain regime.

We have also experimentally investigated the use of biaxial tensile strain in mechanically stressed Ge NMs to increase light emission efficiency and enable optical gain. The samples used in these measurements are fabricated by first releasing the top Ge layer of a (001) Ge-on-insulator (GOI) substrate via etching of the underlying oxide layer. The resulting free-standing NMs are then transferred and bonded onto flexible polyimide (PI) films using liquid PI as a glue

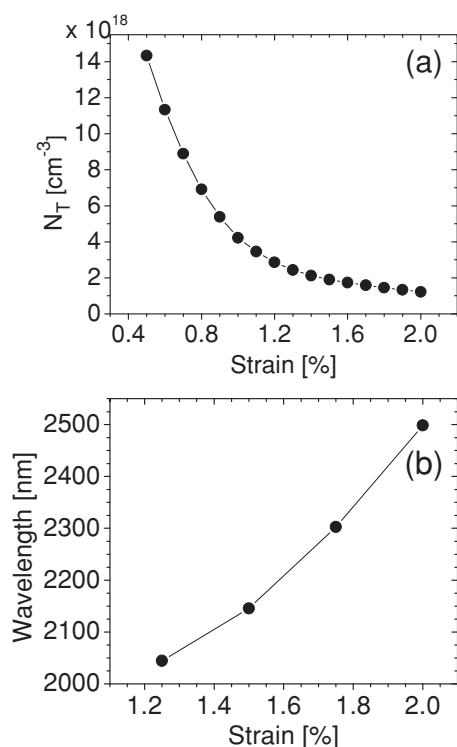


Figure 4. Transparency carrier density (a) and wavelength of maximum TM gain (b) of tensilely strained Ge, calculated as a function of tensile strain. In (b) a density of injected carriers of $5 \times 10^{18} \text{ cm}^{-3}$ is assumed.

layer, followed by a wet etch to reduce the NM thickness to the desired value. An optical micrograph of a Ge NM bonded on a PI film is shown in the inset of **Figure 5**. In the strain-resolved optical measurements described below, the NM-on-PI film is used to seal an otherwise rigid cavity, which is then filled with high-pressure gas. As a result, the PI film and the attached NM are mechanically stretched in a highly controllable fashion, producing a state of biaxial strain that depends on the gas pressure in the cell.

The amount of strain introduced in the NM with this arrangement is determined as a function of gas pressure via Raman spectroscopy. A representative strain-stress curve measured with a 60-nm-thick NM is shown in **Figure 5**. The small amount of compressive strain observed near zero pressure is due to PI-substrate curing effects. As the sample mount is pressurized, the average tensile strain is found to increase linearly with the applied stress (as expected in the elastic region of the stress-strain curve in the absence of delamination), up to the maximum measured value of 1.42%. Similar measurements with other NMs indicate that, as the gas pressure is further increased, the average strain eventually saturates, due to the formation of cracks in the NM that produce strain relaxation via plastic deformation in their immediate vicinity.^[24] The maximum achievable average strain tends to increase with decreasing NM thickness. Specifically, because the amount of strain energy stored in the NM is directly proportional to its thickness, when very thin compared to the substrate, the NM contains insufficient strain energy to drive defect formation.^[15] These

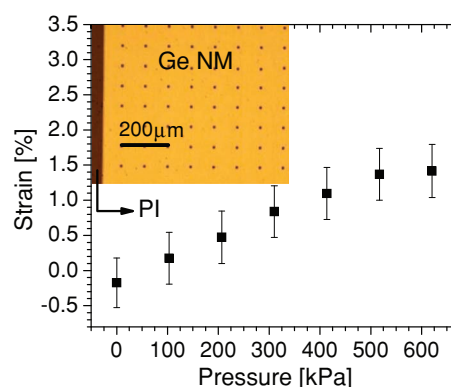


Figure 5. Strain versus stress curve for a 60-nm-thick Ge NM, as determined via Raman measurements. The inset shows an optical microscopy image of a similar NM bonded on a PI film. The array of etchant access holes used in the NM release process is clearly visible.

considerations underscore the importance of nanoscale thicknesses in the present context.

In **Figure 6** we show several room-temperature PL spectra of a NM of similar thickness (57 nm) at different strains, whose values were inferred from the applied gas pressure using the data of **Figure 5**. As the strain is increased, the emission peak is significantly red-shifted and develops a pronounced long-wavelength shoulder (as indicated by the two arrows in the figure). As explained in the following, the main peak and the shoulder are associated, respectively, with $c\Gamma$ -HH and $c\Gamma$ -LH emission, with the latter contribution extending into the 2.1–2.5 μm atmospheric transmission window at high strain. At the same time, the integrated PL intensity strongly increases with increasing strain, indicating enhanced light emission efficiency. This behavior is consistent with the aforementioned lowering of the Γ -point conduction band edge relative to the L-valley minima with increasing tensile strain, so that more and more of the photoexcited electrons relax near the Γ minimum, where efficient radiative

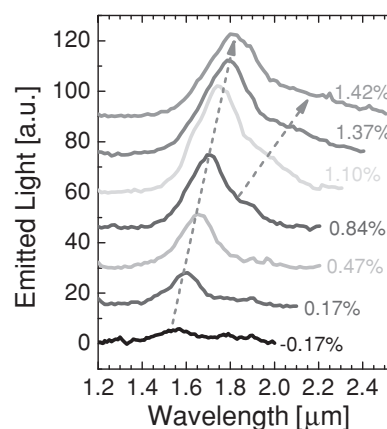


Figure 6. Measured room-temperature PL spectra of a 57-nm-thick Ge NM at different strains. The spectra are shifted vertically relative to one another for the sake of illustration clarity. The dashed arrows are drawn to illustrate the red-shift of the $c\Gamma$ -LH and $c\Gamma$ -HH PL peak positions with increasing strain.

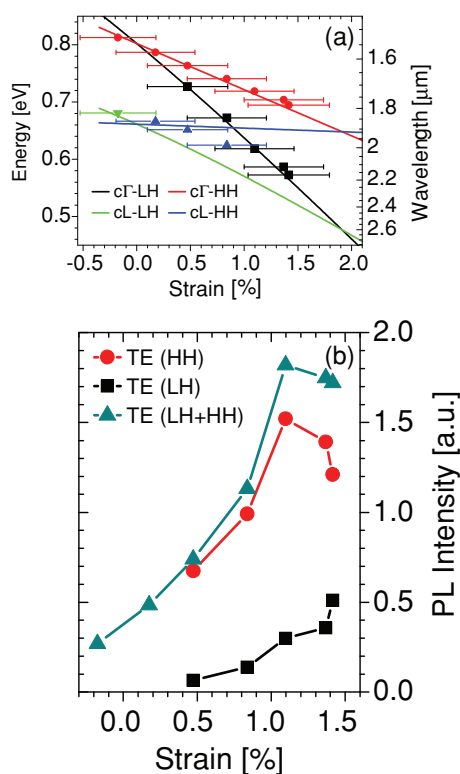


Figure 7. (a) Peak emission energies obtained by fitting the PL spectra of Figure 6 (symbols) and calculated bandgap energies (lines), plotted as a function of strain. (b) Measured PL intensities due to cΓ-LH and cΓ-HH transitions and their sum (obtained by fitting the PL spectra of Figure 6), plotted as a function of strain.

recombination can take place. Similar results were obtained using a thicker (84 nm) NM, with slightly smaller values of the maximum average strain and of the corresponding red shift in the PL spectrum. Vice versa, a larger amount of tensile strain could be introduced in thinner (40 nm) NMs, as discussed below.

In order to compare the PL data of Figure 6 with theoretical predictions, the measured spectra were normalized to the spectral response of the experimental setup, and then numerically fitted with multiple Gaussian peaks. The peak photon energies of the resulting fitting curves are plotted as a function of strain in **Figure 7a** (symbols) together with the calculated bandgap energies from Figure 1 (solid lines). In general, all four transitions shown in the figure (i.e., direct and indirect transitions involving HHs and LHs) contribute to the luminescence spectra. However, depending on their relative strengths and spectral positions, some of these contributions could not always be resolved in the data analysis, so that the measured spectra could only be fitted with two or three peaks. In any case, the agreement between the experimental peak emission energies and the theoretical bandgap energies in Figure 7a is quite good. These numerical-fit results demonstrate a very large strain-induced red shift of the cΓ-LH transition, from 1526 to 2166 nm as the strain is increased to 1.42%.

In Figure 7b we plot the strain dependence of the measured direct-bandgap PL intensity, together with its individual

cΓ-HH and cΓ-LH contributions where distinguishable, as obtained from the integrated areas under the corresponding fitting peaks. A small but non-negligible signal is already observed near zero strain, due to the relatively high-power pump pulses used in this experiment. As the NM is strained, the PL intensity increases as expected, with the cΓ-HH transitions providing the dominant contribution, despite the higher energy and therefore larger hole occupancy of the LH band under tensile strain. This behavior is a consequence of the aforementioned polarization selection rules: most photons emitted via cΓ-LH transitions under tensile strain are TM polarized, and therefore propagate on the plane of the NM and cannot be detected in our experimental setup (where the PL signals are collected along the sample surface normal). For example, calculations based on Equations (2) and (3) show that at 1.42% strain $|M_{TM,c\Gamma-LH}|^2$ is about 12 times larger than $|M_{TE,c\Gamma-LH}|^2$, implying that the TM PL intensity emitted via cΓ-LH transitions is stronger than the TE component by the same factor. Conversely, at zero strain all polarizations have equal emission probability in a cubic crystal and the luminescence is isotropic. We can therefore conclude that the overall strain-induced enhancement in total cΓ-LH PL intensity (including the TM component) is much larger than shown in Figure 7b (where only the TE component is plotted). In contrast, the light emitted via cΓ-HH transitions is entirely TE polarized but experiences a smaller enhancement with increasing strain, because the lowering of the HH band below the LH band decreases the population of HHs. In fact, eventually this trend more than compensates for the strain-induced increase in electron density at Γ , and the cΓ-HH PL intensity begins to decrease, as can be seen in Figure 7b.

Finally, the theoretical framework presented in this work is used to fit the experimental PL spectra in order to infer the quasi-equilibrium carrier density N produced by the pump pulses in the NM. In particular, we apply this procedure to the spectrum measured at the highest strain tested (1.42%), where the cΓ-LH and cΓ-HH emission peaks can be clearly resolved. As a result, N can be uniquely determined based on the relative strength of these two contributions, which are calculated using the following general expression for the TE-polarized spontaneous emission spectrum:^[27]

$$R_{sp}(h\nu_0) = Kh\nu_0 \int |M_{TE}(E_{21})|^2 \rho_r(E_{21}) f_2 [1 - f_1] \xi(h\nu_0 - E_{21}) dE_{21} \quad (4)$$

In this equation, K is a constant that in practice depends on the collection efficiency of the PL measurement setup, among other factors, and all other symbols are as defined in Equation (1). Once again, parabolic energy bands are assumed, and the relevant materials parameters are calculated as discussed previously. For a more realistic description of the actual experimental sample, the spectrum of Equation (4) is initially computed [with a Lorentzian lineshape function $\xi(h\nu_0 - E_{21})$ accounting for lifetime broadening] as a function of strain, and then convoluted with a Gaussian strain distribution with mean value and standard deviation based on the Raman spectroscopy results. The only fitting parameters used

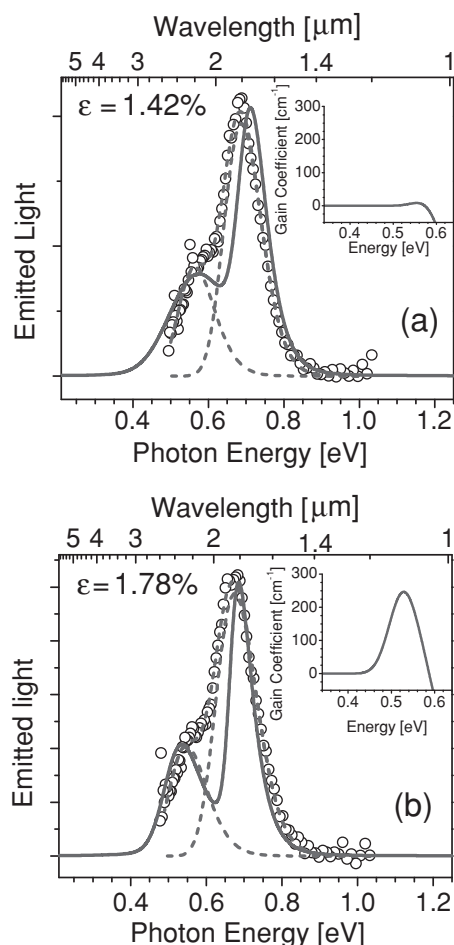


Figure 8. (a) Normalized PL spectrum of the NM of Figure 6 at a strain of 1.42% (symbols) and calculated TE-polarized spontaneous emission spectrum (solid line). (b) Normalized PL spectrum of a 40-nm-thick Ge NM at a strain of 1.78% (symbols) and calculated TE-polarized spontaneous emission spectrum (solid line).^[24] The dashed lines are the Gaussian fits to the experimental data. The insets show the calculated TM gain spectra of Ge at the corresponding strain levels and carrier concentrations inferred from the fits.

in these simulations are the prefactor K and the carrier density N .

The calculated room temperature emission spectrum including both c Γ -LH and c Γ -HH contributions is plotted in **Figure 8a** (solid line) together with the normalized PL data at 1.42%-strain (symbols) and the double-Gaussian fit used in Figure 7 (dashed lines). The agreement with the data is reasonably good, except for the dip between the two peaks in the theoretical spectrum, which can be attributed to the assumption of parabolic valence bands. In reality, as we move down in energy from the top of the LH band towards the top of the HH band, the LH band becomes increasingly nonparabolic^[6] as illustrated in the schematic band diagram of Figure 1c; as a result, its curvature decreases, leading to an increased joint density of states ρ_r and therefore increased light emission. Furthermore, a small discrepancy in the peak positions of the calculated and measured spectra is also observed in Figure 8a, which can be due to small heating of the NM by

the strong PL pump pulses, leading to lattice thermal expansion (equivalent to more tensile strain) and therefore reduced bandgap energies. The specific value of N inferred from the fit of Figure 8a is $3.0 \times 10^{18} \text{ cm}^{-3}$, which is above the calculated transparency carrier density of Ge under 1.42% biaxial tensile strain ($2.1 \times 10^{18} \text{ cm}^{-3}$ as shown in Figure 4a).

Therefore, the same NM under the same strain and pumping conditions used in this measurement already features a population inversion. At the same time, however, using the theoretical model of Equation (1), a relatively small peak gain coefficient of less than 10 cm^{-1} is predicted for this estimated carrier density of $3.0 \times 10^{18} \text{ cm}^{-3}$ at 1.42% strain, as shown in the inset of Figure 8a. We therefore conclude that this strain level can be regarded as a lower bound to what is needed to obtain significant optical gain in Ge under high but realistic pumping conditions (as in our measurements). It should also be noted that this conclusion is fully consistent with the simulation results of Figure 4a, where the calculated transparency carrier density can be seen to approach experimentally accessible values of a few 10^{18} cm^{-3} for tensile strain levels in excess of about 1.4%. As the strain is further increased, substantially larger population inversions and therefore higher peak gain coefficients can be obtained, as illustrated in Figure 3.

To substantiate the latter prediction, in Figure 8b we show the results of a similar analysis performed on the PL spectrum from a more highly strained (1.78%) thinner (40 nm) NM.^[24] The larger average tensile strain that could be introduced in this sample is a direct consequence of its smaller thickness, which allows for a proportionally higher stress to be applied before the onset of extended-defect formation. The carrier density N inferred from this analysis ($3.9 \times 10^{18} \text{ cm}^{-3}$) is over twice as large as the calculated transparency value at 1.78% strain ($1.5 \times 10^{18} \text{ cm}^{-3}$ in Figure 4a). The data of Figure 8b therefore suggest a much stronger population inversion compared to the NM of Figure 8a, consistent with the continuous decrease of the Γ minimum relative to the L valleys with increasing strain. The corresponding theoretical gain spectrum, computed with the model presented in this work, is shown in the inset, where a large peak value of 250 cm^{-1} (at a wavelength of about 2.3 μm) is observed. It should be emphasized that, in the present experimental geometry, no indications of stimulated emission and optical amplification can be observed, because of the ultrasmall propagation length ($\leq 40 \text{ nm}$) of the detected light in the NM. At the same time, however, the analysis of Figure 8b indicates that if the same NM were placed in an optical cavity for in-plane propagating light with reasonably low losses and high optical confinement, lasing action would be feasible.

3. Conclusion

We have shown that tensilely strained Ge NMs can be used as optical gain media in the 2.1–2.5 μm mid-IR atmospheric transmission window. Our numerical simulations indicate that Ge under $>1.4\%$ biaxial tensile strain can provide peak gain coefficients of several 100 cm^{-1} in this wavelength region, with low transparency carrier densities of less than

about $3 \times 10^{18} \text{ cm}^{-3}$. These favorable gain properties are the results of the large decrease in the direct energy bandgap relative to the indirect one with increasing tensile strain in Ge. Because of their nanoscale thicknesses, NMs feature high thresholds for plastic deformation, and therefore can accommodate the required tensile strain levels for optical gain while maintaining good crystalline quality. To substantiate this idea experimentally, Ge NMs fabricated from GOI substrates are mechanically stressed with high-pressure gas, and used to demonstrate strain-enhanced PL. A quantitative analysis of the high-strain emission spectra is also carried out to estimate the carrier density produced by the PL pump pulses in the NM, and used to demonstrate pumping above optical transparency. The results of this analysis with a 57-nm-thick NM confirm the prediction that at a biaxial tensile strain level of about 1.4% transparency can already be reached, albeit with a rather low population inversion. Similar results obtained with a 40-nm-thick sample further suggest that large gain coefficients can indeed be achieved at higher strains. Similar strained NMs can be integrated on Si microelectronics chips, where mechanical stress can be introduced using MEMS-based cantilevers or subsequently deposited stressor layers. Furthermore they can be pumped via electrical injection, e.g., using a lateral p-i-n junction geometry, as already demonstrated in a recent report of flexible Ge photodetectors.^[20] We conclude that tensilely strained Ge NMs are promising candidates for the development of CMOS-compatible mid-infrared diode lasers, which may find a wide range of applications in sensing, spectroscopy, and free-space optical communications.

4. Experimental Section

Sample Fabrication: The free-standing Ge NMs used in this work are fabricated by releasing the Ge layers of commercial (001) GOI substrates. Specifically, the substrates are first patterned with UV lithography to define the membrane boundaries and small etchant access holes. Reactive ion etching is then employed to etch the Ge template layer along these boundaries, followed by a wet etch in a mixture of 49% hydrofluoric-acid and water solution (1/10) to dissolve the underlying SiO_2 layer. The resulting Ge NMs settle onto and weakly bond to the original Si host wafer. The NMs are subsequently transferred and bonded onto 125- μm thick, flexible PI films (Kapton, DuPont), by using spin-on liquid PI as a glue layer and pressing the membrane onto the PI film. After transfer, the spin-on PI is cured at 350 °C and the Ge NM is thinned from its original thickness ($84 \pm 2 \text{ nm}$) to the desired thickness using a wet etch with dilute hydrogen peroxide (H_2O_2) in water at 80 °C. The final NM thickness can be determined using X-ray diffraction and ellipsometry, and these measurements have been used to calibrate the etch rate (0.9 nm/s). X-ray diffraction data also indicate that the NMs are single-crystalline with excellent structural quality. Additional characterization studies include AFM measurements, where a small degree of surface roughness (less than 1 nm rms) is observed, which is not expected to affect the strain and luminescence properties investigated in this work.

Raman Measurements: The amount of biaxial strain introduced in the NMs is measured as a function of applied stress (i.e.,

gas pressure) via Raman spectroscopy, using a LabRAM ARAMIS (HORIBA Scientific) Raman microscope. In these measurements, a laser beam with 633 nm wavelength and ~1 mW power is focused onto the NM with a 50 $\times$ objective lens, producing a spot size of about 2 μm . The resulting power density is sufficiently low to avoid heating the NM, which would otherwise affect the Raman shifts and therefore the inferred strain values. Ten random sites on each NM are measured for each value of the applied stress. The biaxial strain values are calculated from the Raman shifts using experimental phonon deformation potentials from the literature.^[34]

Photoluminescence Measurements: A tunable optical parametric oscillator is used as the pump light source in the PL measurements. Its output consists of a train of pulses with 5 ns width, 20 Hz repetition rate, 960-nm wavelength, and 3 mW average power (0.15 mJ pulse energy). The pump light is focused onto the NM with a spot size of about 1 mm. Due to the pulsed laser excitation used in these measurements, thermal effects are not expected to play any significant role. The emitted light is collected along the direction perpendicular to the plane of the NM, dispersed through a monochromator, and finally measured with an InGaAs detector with 1.2 to 2.6 μm spectral response and 45 MHz bandwidth. To increase the measurement sensitivity, gated detection is performed using a box-car integrator.

Acknowledgements

This work was primarily supported by the National Science Foundation under Grant #DMR-0907296. Nanomembrane fabrication, straining, and Raman facilities and measurements (J.R.S.-P., D.M.P., R.B.J., and M.G.L.) were supported by DOE (Grant #DE-FG02-03ER46028). D.M.P. acknowledges support from the NSF and NDSEG Graduate Research Fellowship Programs.

- [1] R. A. Soref, L. Friedman, *Superlattices Microstruct.* **1993**, *14*, 189.
- [2] M. V. Fischetti, S. E. Laux, *J. Appl. Phys.* **1996**, *80*, 2234.
- [3] J. Menéndez, J. Kouvetakis, *Appl. Phys. Lett.* **2004**, *85*, 1175.
- [4] J. Liu, X. Sun, D. Pan, X. Wang, L. C. Kimerling, T. L. Koch, J. Michel, *Opt. Express* **2007**, *15*, 11272.
- [5] P. H. Lim, S. Park, Y. Ishikawa, K. Wada, *Opt. Express* **2009**, *17*, 16358.
- [6] M. El Kurdi, G. Fishman, S. Sauvage, P. Boucaud, *J. Appl. Phys.* **2010**, *107*, 013710.
- [7] G. Pizzi, M. Virgilio, G. Grosso, *Nanotechnology* **2010**, *21*, 055202.
- [8] R. Soref, *Nature Photon.* **2010**, *4*, 495.
- [9] R. Paiella in *Comprehensive Semiconductor Science & Technology*, Vol. 5 (Eds: P. Bhattacharya, R. Fornari, H. Kamimura), Elsevier, Saint Louis, MO **2011**, pp. 683–723.
- [10] Y. Y. Fang, J. Tolle, R. Roucka, A. V. G. Chizmeshya, J. Kouvetakis, V. R. D'Costa, J. Menendez, *Appl. Phys. Lett.* **2007**, *90*, 061915.
- [11] Y. Huo, H. Lin, R. Chen, M. Makarova, Y. Rong, M. Li, T. I. Kamins, J. Vuckovic, J. S. Harris, *Appl. Phys. Lett.* **2011**, *98*, 011111.
- [12] R. Jakomin, M. de Kersauson, M. El Kurdi, L. Largeau, O. Mauguin, G. Beaudoin, S. Sauvage, R. Ossikovski, G. Ndong, M. Chaigneau, I. Sagnes, P. Boucaud, *Appl. Phys. Lett.* **2011**, *98*, 091901.

- [13] R. E. Camacho-Aguilera, Y. Cai, N. Patel, J. T. Bessette, M. Romagnoli, L. C. Kimerling, J. Michel, *Opt. Express* **2012**, *20*, 11316.
- [14] M. El Kurdi, H. Bertin, E. Martincic, M. de Kersauson, G. Fishman, S. Sauvage, A. Bosseboeuf, P. Boucaud, *Appl. Phys. Lett.* **2010**, *96*, 041909.
- [15] L. B. Freund, S. Suresh, *Thin Film Materials: Stress, Defect Formation and Surface Evolution*, Cambridge University Press, Cambridge, UK **2003**.
- [16] M. M. Roberts, L. J. Klein, D. E. Savage, K. A. Slinker, M. Friesen, G. Celler, M. A. Eriksson, M. G. Lagally, *Nat. Mater.* **2006**, *5*, 388.
- [17] D. H. Kim, J. H. Ahn, W. M. Choi, H. S. Kim, T. H. Kim, J. Z. Song, Y. G. Y. Huang, Z. J. Liu, C. Lu, J. A. Rogers, *Science* **2008**, *320*, 507.
- [18] Z. X. Qiang, H. J. Yang, L. Chen, H. Q. Pang, Z. Q. Ma, W. D. Zhou, *Appl. Phys. Lett.* **2008**, *93*, 061106.
- [19] H. C. Ko, G. Shin, S. D. Wang, M. P. Stoykovich, J. W. Lee, D. H. Kim, J. S. Ha, Y. G. Huang, K. C. Hwang, J. A. Rogers, *Small* **2009**, *5*, 2703.
- [20] H. C. Yuan, J. H. Shin, G. X. Qin, L. Sun, P. Bhattacharya, M. G. Lagally, G. K. Celler, Z. Ma, *Appl. Phys. Lett.* **2009**, *94*, 013102.
- [21] L. Sun, G. X. Qin, J. H. Seo, G. K. Celler, W. D. Zhou, Z. Q. Ma, *Small* **2010**, *6*, 2553.
- [22] P. Feng, I. Moench, G. S. Huang, S. Harazim, E. J. Smith, Y. F. Mei, O. G. Schmidt, *Adv. Mater.* **2010**, *22*, 3667.
- [23] J. A. Rogers, M. G. Lagally, R. G. Nuzzo, *Nature* **2011**, *477*, 45.
- [24] J. R. Sánchez-Pérez, C. Boztug, F. Chen, F. F. Sudradjat, D. M. Paskiewicz, R. B. Jacobson, M. G. Lagally, R. Paiella, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 18893.
- [25] M. de Kersauson, M. El Kurdi, S. David, X. Checoury, G. Fishman, S. Sauvage, R. Jakomin, G. Beaudoin, I. Sagnes, P. Boucaud, *Opt. Express* **2011**, *19*, 17925.
- [26] D. Nam, D. Sukhdeo, A. Roy, K. Balram, S. Cheng, K. Huang, Z. Yuan, M. Brongersma, Y. Nishi, D. Miller, K. Saraswat, *Opt. Express* **2011**, *19*, 25866.
- [27] L. A. Coldren, S. W. Corzine, *Diode Lasers and Photonic Integrated Circuits*, John Wiley & Sons, New York **1995**.
- [28] S. L. Chuang, *Physics of Photonic Devices*, John Wiley & Sons, Hoboken, NJ **2009**.
- [29] C. G. Van de Walle, *Phys. Rev. B* **1989**, *39*, 1871.
- [30] C. N. Ahmad, A. R. Adams, *Phys. Rev. B* **1986**, *34*, 2319.
- [31] A. R. Goñi, K. Syassen, M. Cardona, *Phys. Rev. B* **1989**, *39*, 12921.
- [32] NSM Archive - Physical Properties of Semiconductors: www.ioffe.rssi.ru/SVA/NSM/Semicond/, accessed: May, 2012.
- [33] G. Jones, E. P. O'Reilly, *IEEE J. Quantum Electron.* **1993**, *29*, 1344.
- [34] F. Cerdeira, C. J. Buchenauer, M. Cardona, F. H. Pollak, *Phys. Rev. B* **1972**, *5*, 580.

Received: May 18, 2012

Revised: August 30, 2012

Published online: November 2, 2012