Prediction that Uniaxial Tension along ⟨111⟩ Produces a Direct Band Gap in Germanium

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We predict a new way to achieve a direct band gap in germanium, and hence optical emission in this technologically important group-IV element: tensile strain along the ⟨111⟩ direction in Ge nanowires. Although a symmetry-breaking band splitting lowers the conduction band at the corner of the Brillouin zone (at the L point), a direct gap of 0.34 eV in the center of the Brillouin zone (at Γ) can still be achieved at 4.2% longitudinal strain, through an unexpectedly strong nonlinear drop in the conduction band edge at Γ for strain along this axis. These strains are well within the experimentally demonstrated mechanical limits of single-crystal Ge (or Ge_xSi_{1-x}) nanowires, thereby opening a new material system for fundamental optical studies and applications.

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Under normal conditions, both silicon and germanium are indirect-gap semiconductors, meaning that a transition from the lowest electronic excited state (i.e., the bottom of the conduction band) to the top of the valence band requires a change in electron momentum. Light emission from Si and Ge is thus inefficient since the relevant photons carry negligible momentum and so cannot span this transition without assistance from a phonon or a lattice defect. Bulk silicon and germanium do not lase. A direct band gap can in principle be achieved by alloying Ge with ~10% Sn, but defects arising from lattice mismatch between the alloy and an Si substrate frustrate attempts to produce photoluminescence [1]. Pure Ge could in theory be driven direct gap by epitaxial growth on a substrate with a larger lattice constant, but the biaxial strains so far achieved are well below those required for a direct gap [2]. Alternating layers of Si/Ge [3] or Si/SiO_2 [4] can be forced direct gap by zone folding and quantum confinement, but folded optical transitions are typically very weak. These manifold challenges have motivated exotic alternative approaches to optical activity in group-IV materials, such as spatial confinement to dislocation loops [5] or lasers based on stimulated Raman scattering [6]. However, recent advances in the synthesis and manipulation of single-crystal Si and Ge nanowires now open up a new route towards engineering direct gaps in group-IV materials: large uniaxial strains along the nanowire axis. Here, we predict that germanium stretched along the ⟨111⟩ axis goes direct gap at strains well below those already obtained in Ge nanowires [7].

To obtain a direct gap in Ge, the lowest point in the conduction band must be shifted to the zone center (Γ), since the valence band maximum remains at Γ under strain. Uniform (hydrostatic) lattice expansion does cause the Ge conduction band edge at Γ to fall rapidly in energy, but practical applications of tension occur along specific axes. Stress along ⟨111⟩ decomposes into a transverse strain ϵ_t along $\langle 1\bar{1}0\rangle$ and $\langle 11\bar{2}\rangle$ plus a longitudinal strain ϵ_l along ⟨111⟩. These can be reexpressed in terms of hydrostatic and asymmetric components:

$$\epsilon_h = \epsilon_l + 2\epsilon_t \tag{1}$$

$$\epsilon_a = \epsilon_l - \epsilon_t. \tag{2}$$

Previous work on epitaxial Ge films generally avoided strain along the ⟨111⟩ axis since it splits the conduction band at L into a singlet (L_s) along ⟨111⟩ and triplet (L_t) along $\langle\bar{1}11\rangle$ $\langle 1\bar{1}1\rangle$ and $\langle 11\bar{1}\rangle$: the lower of these then more easily undercuts the Γ-point conduction edge (see Fig. 1). In addition, the lower component of the split L point drops linearly with ϵ_a, whereas the Γ-point conduction band is insensitive to ϵ_a at first order. Therefore, it appears unlikely for Γ to drop below L at moderate (i.e., realizable) strains. However, we demonstrate here that an unexpectedly strong nonlinearity in the response to ϵ_a pulls germanium direct at a surprisingly low strain. Tension along ⟨111⟩ (i.e., $\epsilon_a > 0$) is particularly favorable since it lowers the L triplet and raises the singlet: the triplet moves more

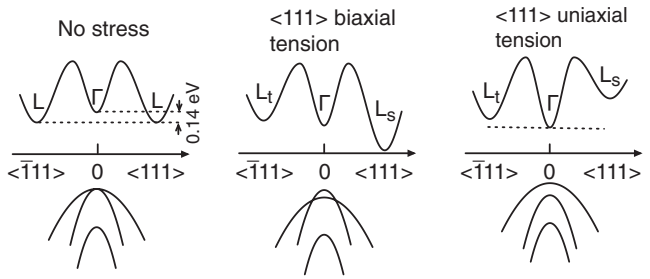

FIG. 1. Schematic band structure of Ge for tensile stresses along (uniaxial) and transverse to (biaxial) ⟨111⟩.

slowly than the singlet; hence, it provides weaker competition to the nonlinear fall of the Γ point.

Since the vanishing band gap for Ge in conventional density functional theory produces incorrect electron occupancies for bands around the Fermi level under strain and thus prevents reliable predictions for the shifts of conduction band edges under pressure, we carry out quasiparticle calculations within the GW approximation [8] to fix the band gap problem. Scalar relativistic effects [9] are included via the Ge pseudopotential, and spin-orbit coupling is incorporated following Pollak and Cardona [10]. At zero pressure, the calculation underestimates the direct and indirect band gaps by 0.22 and 0.12 eV, respectively [11]. However, the strain dependence of the conduction and valence bands is well described since the calculated deformation potentials for linear shifts of conduction and valence bands under strain [13] compare favorably with the experimental data of Table I (one significant discrepancy, between the two measurements of $\Xi_d^L + \frac{1}{3}\Xi_u^L - a_v$, actually reinforces our conclusions, since a downward revision of this parameter would decrease the predicted indirect-to-direct transition strains given below). Thus, we account for the discrepancies at zero pressure by predicting an indirect-to-direct transition when the conduction band at Γ shifts down by the experimental value of 0.14 eV [22] relative to the conduction band edge at L.

For strains with rhombohedral symmetry, the conduction band at L splits into a triplet L_t and a singlet L_s: these define the band edge at L for positive and negative ϵ_a, respectively. Referencing band shifts to the weighted average of the split states, $E_{\langle L\rangle} = \frac{1}{4}(E_{Ls} + 3E_{Lt})$, the singlet moves 3 times as fast as the triplet

$$\delta E_{(L-\langle L\rangle)} = \begin{cases} -\frac{2}{9}\Xi_u^L \epsilon_a & (\epsilon_a \geq 0) \\ -\frac{2}{3}\Xi_u^L |\epsilon_a| & (\epsilon_a < 0). \end{cases} \quad (3)$$

For simplicity, and to isolate the effect of ϵ_a, we first consider only volume conserving strains ($\epsilon_h = 0$). The linear dependence of Eq. (3) extends to fairly large (5%) strains. The shift of the conduction band edge at Γ (also relative to $E_{\langle L\rangle}$) is not so simple:

$$\delta E_{(\Gamma-\langle L\rangle)} = \left[a_c - \left(\Xi_d^L + \frac{1}{3}\Xi_u^L\right)\right]\epsilon_h + f(\epsilon_h, \epsilon_a). \quad (4)$$

Since this band edge is nondegenerate, it has no linear dependence on ϵ_a [13]. However, the higher-order terms $f(\epsilon_h, \epsilon_a)$ shown in Fig. 2(b) are very strong: $\delta E_{(\Gamma-\langle L\rangle)}$ undergoes a marked supra-linear decrease as the absolute value of ϵ_a increases.

With these insights in hand, we now consider the experimentally realistic boundary condition of a semiconducting nanowire oriented along $\langle 111\rangle$ under uniaxial stress, with free transverse boundaries so that $\epsilon_t = -0.16\epsilon_l$, 0.16 being the $\langle 111\rangle$ Poisson ratio of Ge [23]. Thus, $\epsilon_h = 0.68\epsilon_l$ and $\epsilon_a = 1.16\epsilon_l$. Subtracting Eq. (3) from Eq. (4) and using the computed deformation potentials, we obtain the shift of the conduction edge at Γ relative to the lower of L_s, L_t under tension along $\langle 111\rangle$:

$$\delta E_{(\Gamma-L)} = -0.64 \text{ eV} \times \epsilon_l + f(0.68\epsilon_l, 1.16\epsilon_l). \quad (5)$$

A direct band gap occurs when $\delta E_{(\Gamma-L)} \leq -0.14$ eV. The standard linear term of Eq. (5) alone cannot do this within practical ϵ_l. However, the full nonlinear expression generates an indirect-to-direct transition at an experimentally accessible longitudinal strain of 4.2% (Fig. 3), with a gap of 0.34 eV at the transition [24]. The threshold tensile strength to access this transition is 6.5 GPa (for a Young's modulus of Ge along $\langle 111\rangle$ of 154 GPa), well below the ultimate strength of 15 GPa which has already been reported for Ge nanowires (albeit along $\langle 112\rangle$) [7]. In contrast, uniaxial stress along $\langle 100\rangle$, the direction that has been the focus of attention for biaxially strained epitaxial Ge films, is much less effective at inducing a direct gap. $E_{(\Gamma-L)}$ decreases only sublinearly with ϵ_l along $\langle 100\rangle$, achieving a direct gap at a (larger) 7.4% strain and a (smaller) gap of 0.21 eV [24], as compared to tension along $\langle 111\rangle$. In supplementary information [25], we provide more details on tension along $\langle 100\rangle$, as well as a generalization of the results by studying the full dependence of the indirect-to-direct transition on arbitrary strain conditions with rhombohedral or tetragonal symmetry.

Although experimental Ge nanowires can be 20 to 80 nm wide [7], well into the bulk limit as regards electronic properties, we also examine small-diameter nanowires, aligned along $\langle 111\rangle$, to explore the influence of quantum confinement on the indirect-to-direct transition. The wires have H-passivated surfaces and stress-free diameters of

TABLE I. Comparison of Ge deformation potentials obtained in the present calculation with experiment (in units of eV).

	This work	Experiment
$a_c - a_v$	−11.2	−8.0 [14], −8.97 [15], −9.0 ± 0.4 [10], −9.08 ± 0.15 [16], −10.3 ± 0.4 [17], −10.4 ± 0.8 [18], −11.5 ± 0.4 [19]
$\Xi_d^L + \frac{1}{3}\Xi_u^L - a_v$	−4.34	−2.0 ± 0.5 [18], −3.6 [20]
Ξ_u^L	15.6	16.2 ± 0.4 [18]
b_v	−2.59	−2.86 ± 0.15 [18]
d_v	−4.91	−5.28 ± 0.50 [21]

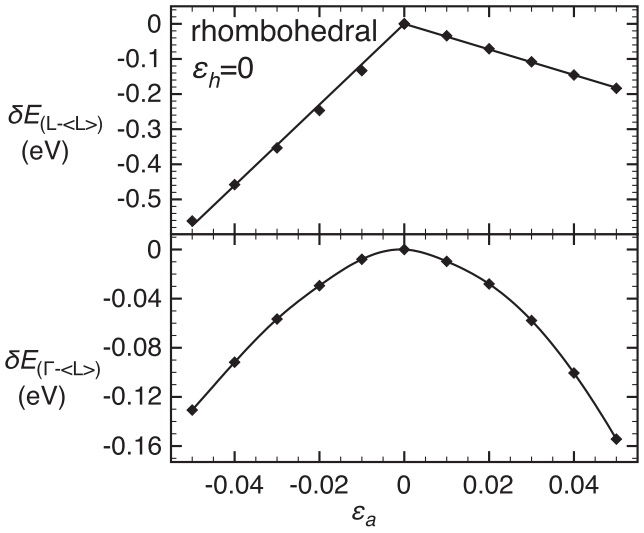

FIG. 2. Pressure dependence of the conduction band edges at L (a) and Γ (b), both measured with respect to the weighted average of L_s and L_t, as a function of ϵ_a for strains along $\langle 111 \rangle$ (i.e., with rhombohedral symmetry). For clarity in revealing the asymmetric contribution, the hydrostatic component ϵ_h is set to zero. Solid lines are guides for the eye. The strong nonlinear dependence of the Γ point is not reflected in the experimental linear deformation potential data of Table I.

1.21, 1.65, and 2.13 nm. Unlike bulk Ge, these nanowires have finite band gaps within DFT-LDA [26,27]. Hence, GW calculations are not required; (DFT and GW usually agree on pressure-induced band-edge shifts [28]). The gap of the unstrained 1.21 nm wire is indirect, with the conduction band at the zone edge 0.05 eV lower than that at zone center [26]. Also, the optical transition from ψ_v to ψ_c across the gap at Γ has a vanishingly small matrix element $M_{vc} = \langle \psi_v | \hat{e} \cdot \mathbf{p} | \psi_c \rangle$ ($\hat{e}$ is the polarization and $\mathbf{p}$ the momentum). The weakness of this optical transition indicates that the conduction band edge at zone center does not derive from the bulk Γ point state, which generates a much larger longitudinal matrix element M^l_{vc}.

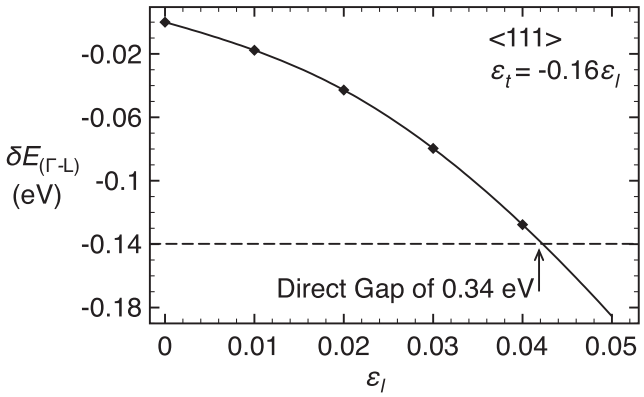

FIG. 3. Shift of the conduction band edge at Γ relative to L for uniaxial stress along $\langle 111 \rangle$. A transition from indirect-to-direct gap occurs at $\epsilon_l = 4.2\%$.

Under uniaxial tension, this bulk-derived Γ-point state drops in energy and becomes the conduction minimum above $\epsilon_l \approx 3.5\%$, causing the sudden jump in M^l_{vc} shown in Fig. 4. Since the directness of the band gap is ultimately determined by the energy difference between this optically coupled state and the conduction band at the zone edge, we call it $E_{(\Gamma-L)}$ to be consistent with the previous notation. At zero pressure, $E_{(\Gamma-L)} = 0.39$ eV, much larger than the bulk value of 0.14 eV, due to quantum confinement and the contribution of the terminating hydrogens to the zone-edge state [27]. However, a rapid downshift of $E_{(\Gamma-L)}$ (faster than in the bulk: compare Figs. 3 and 4) induces an indirect-to-direct transition at $\epsilon_l = 5.3\%$. Figure 5 shows the required strains both for the zone-center gap to become optically active (i.e., the bulk-derived Γ point state becomes the lowest conduction band) and for the overall gap to become direct, in three $\langle 111 \rangle$ Ge nanowires. The strain at which the zone-center transition becomes optically active decreases as the diameter increases, as quantum confinement weakens. The nonmonotonic dependence of the indirect-to-direct transition strain on wire diameter may arise from the variable effects of surface termination, or the narrow range of diameters considered. In contrast, a $\langle 110 \rangle$ Ge nanowire of similar diameter already has a direct band gap from zone-folding at zero pressure, but the longitudinal matrix element M^l_{vc} is an order-of-magnitude weaker than for the $\langle 111 \rangle$ nanowire at the transition ϵ_l. The gap for a $\langle 100 \rangle$ nanowire with a similar diameter remains indirect, and no indirect-to-direct transition is observed for $\epsilon_l < 10\%$.

In summary, we demonstrate that germanium can be converted into a direct band gap material by uniaxial tensile stress along $\langle 111 \rangle$ with the assistance of a supralinear decrease of the conduction band edge at Γ under rhombohedral strains. The required longitudinal strain of

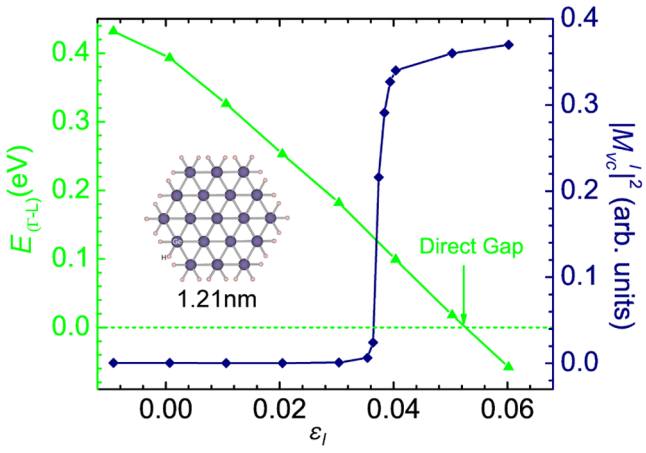

FIG. 4 (color online). $E_{(\Gamma-L)}$ (light, green line) and $M^l_{vc}(0)$ (dark, blue line) as functions of ϵ_l for the 1.21 nm diameter Ge nanowire. The bottom of the conduction band at Γ becomes optically active first (around $\epsilon_l \approx 3.5\%$, due to a band crossing at Γ), then the actual indirect-to-direct transition occurs at $\epsilon_l = 5.3\%$. The inset gives a top view of the nanowire.

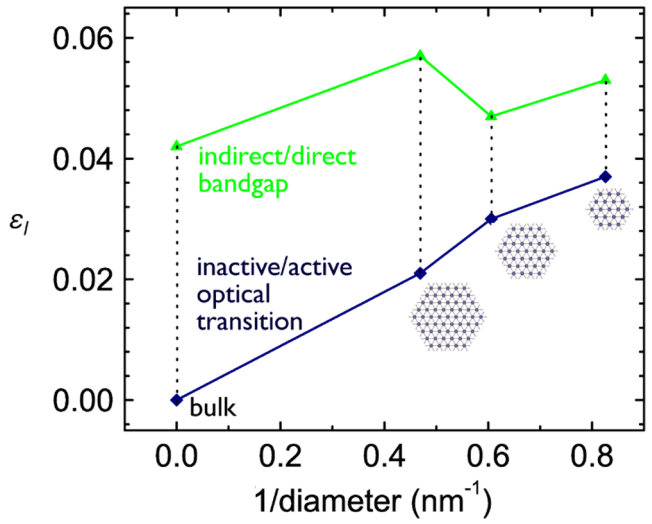

FIG. 5 (color online). Strains for transitions between optically inactive and active vertical transitions at Γ (bottom line) and also between indirect and direct band gaps (top line) for Ge nanowires of diameters 1.21, 1.65, and 2.13 nm, compared to bulk germanium.

4.2% is well achievable for Ge nanowires since the tensile strength of materials increases dramatically at the nanoscale. The magnitude of the direct band gap at the transition is significant, 0.34 eV. The bandstructures of other group-IV semiconductors such as zinc-blende GeSi experience a similar nonlinear response to ⟨111⟩ tensile stress. Thus, stretching along ⟨111⟩ could be a generic approach to converting Ge_xSi_{1-x} alloys (with high enough x) into direct-gap materials.

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