bteen the phases is not strongly T-dependent in this temperature range.

Our analysis has focused on phase coexistence, where surface free energy plays the role of the chemical potential ($\beta\mu$). One could achieve the same advantages in heteroepitaxial structures, such as quantum dots, by having them in equilibrium with a reservoir of controlled chemical potential $\mu_{\text{res}}$, e.g., an ambient vapor at a specified partial pressure. For two-dimensional structures, elastic relaxation lowers the free energy relative to that of a uniform film for some range of island sizes. The chemical potential $\mu_0$ of the uniform film plays the role of $T^*$ here. For $\mu_{\text{res}} < \mu_0$, individual islands of a particular size are stable and do not grow. (The stable island size diverges as $\mu_{\text{res}}$ approaches $\mu_0$.) As $\mu_{\text{res}}$ is decreased, the island size shrinks, until below some critical value $\mu_{\text{min}}$, the islands become unstable and disappear. This point defines the minimum stable island size, analogous to $L^{\ast}$.

Thus, growth from a reservoir allows reversible configuration shown in Fig. 4 (with minimum stable island size, analogous to unstable and disappear. This point defines the metastable and conversion to the “$1 \times 1$” phase is still energetically favorable, although kinetically hindered. The domain size must be very large—greater than about 550 nm—in order for elastic relaxation effects to offset the energy cost associated with the (unfavorable) $7 \times 7$ phase. Our analytical theory shows that the nucleation, formation energy, and size selection of isolated domains can be described in terms of a small number of measurable parameters. Knowledge of these parameters in strain-mediated self-assembly systems will be required for a detailed understanding and control of size selection at surfaces.

References and Notes

Continuous Wave Operation of a Mid-Infrared Semiconductor Laser at Room Temperature

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Continuous wave operation of quantum cascade lasers is reported up to a temperature of 312 kelvin. The devices were fabricated as buried heterostructure lasers with high-reflection coatings on both laser facets, resulting in continuous wave operation with optical output power ranging from 17 milliwatts at 292 kelvin to 3 milliwatts at 312 kelvin, at an emission wavelength of 9.1 micrometers. The results demonstrate the potential of quantum cascade lasers as continuous wave mid-infrared light sources for high-resolution spectroscopy, chemical sensing applications, and free-space optical communication systems.

The mid-infrared portion of the spectrum, covering approximately the wavelength range from 3 to 12 μm, is sometimes referred to as “underdeveloped” because of its lack of convenient coherent optical sources. Especially when compared to the visible or near-infrared spectral range, where interband semiconductor lasers are now produced very economically, with continuous wave (CW) output power of tens of milliwatts, this assertion holds true.

In the mid-infrared, a new class of semiconductor lasers—intersubband quantum cascade (QC) lasers (1)—has become a promising alternative to interband diode lasers (2, 3) in the past 7 years. In these devices, photon emission is obtained by electrons making optical transitions between confined energy lev-
els. As such, QC lasers can be fabricated from wide-bandgap technologically mature semiconductors, and their emission wavelength can be tailored over a wide range by changing only the layer thicknesses. In addition, because their main nonradiative mechanism is optical phonon emission and because of the atomic-like joint density of states of intersubband transitions, QC lasers exhibit a gain that is weakly temperature dependent. As a result, QC lasers have demonstrated high mid-infrared output powers in pulsed operation up to temperatures above 400 K (4). However, CW operation of QC lasers based on standard designs has remained limited to cryogenic temperatures below 175 K (5). A recent active region design enabled CW operation up to 243 K (6), which is barely high enough to be maintained by a thermoelectric cooler.

Because the main nonradiative mechanism in mid-infrared interband lasers is Auger recombination, these devices exhibit a much stronger temperature dependence of the threshold current density, and CW operation is limited to temperatures below 225 K (2).

Although chemical absorption based on optical absorption has been successfully demonstrated with pulsed QC lasers (7), these systems are typically limited by the fairly wide emission linewidth of the QC laser (>500 MHz); high sensitivity can only be achieved with the narrow linewidth of a CW-operated device (8). Mid-infrared atmospheric optical communication systems (9, 10), using QC lasers for data transmission through the two transparent atmospheric windows, will potentially benefit from light sources operating in CW mode at noncryogenic temperatures.

The limiting factor for CW operation of semiconductor lasers is the large heat dissipation. At high duty cycles, the temperature of the active region \( T_{\text{act}} \) is much higher than the heat sink temperature \( T_{\text{sink}} \). In a simple model (11), the heat transport between active region and heat sink is characterized by the thermal conductance \( G_{\text{th}} \) per unit of area of the active region; that is, \( T_{\text{act}} = T_{\text{sink}} + U \times J_0 / G_{\text{th}} \) at threshold. Assuming a constant threshold voltage \( U \) and that the temperature dependence of the threshold current density \( J_0 \) can be described by the phenomenological relation \( J_0 = J_0 \exp(T_{\text{act}}/T_0) \), the maximum CW operating temperature \( T_{\text{sink max}} \) of a QC laser is given by \( T_{\text{sink max}} = T_0 \times \ln(T_{\text{sink}}/J_0/J_0) - 1 \). A high value of the characteristic temperature \( T_0 \) is therefore an absolute necessity to achieve room-temperature CW operation. The large value of \( T_0 \) achieved in recent QC laser structures (\( T_0 > 170 \text{ K} \)) results in a low temperature sensitivity of \( J_0 \), and shows the potential of these devices for CW operation. However, the devices used in the early attempts to reach high-temperature CW operation (12, 5) had a \( J_0/U \) product of about 10 kW/cm². This value, corresponding to a threshold current density of \( 5 \text{ kA/cm}^2 \) at 300 K, is just too large to be evacuated from the active region when the laser is operated at high duty cycles, even assuming an idealized device geometry.

In addition, the actual core temperature is equal to \( T_{\text{core}} = T_{\text{sink}} + \ln(T_{\text{sink}}/G_{\text{th}}/J_0/U) \) when the laser is operated at \( T_{\text{sink max}} \) (13), resulting in a temperature difference between the active region and the heat sink of \( T_0 \). For large \( T_0 \) values, the device might fail by thermal stress before reaching the temperature \( T_{\text{sink max}} \). For this reason, it is essential to (i) minimize the threshold current density and (ii) use a device geometry that minimizes thermal stress. To reduce the room-temperature threshold current density, active region designs based on a double-phonon resonance (6) and a bound-to-continuum transition (14) were recently developed. In these structures, the injection and extraction efficiency to and from the active region were significantly improved by means of wave function engineering. Additionally, growth conditions and the doping concentration of the active region were optimized. As a consequence, the pulsed threshold current density at 300 K dropped to a value as low as 3 kA/cm² (6).

We present QC lasers with an active region based on a double-phonon resonance and designed for a lasing transition at an energy of 135 meV (corresponding to a wavelength of 9.18 \( \mu \text{m} \)) between the upper and lower lasing states (levels 4 and 3 in Fig. 1A). The active region is composed of four quantum wells (QWs), which results in three coupled lower energy states (levels 1, 2, and 3) separated from each other by one phonon energy (15). The active region used a narrow QW-barrier pair just after the injection barrier [similar to the classical three-QW design (16)] that enhances the injection efficiency into the upper lasing level by increasing locally the magnitude of the upper state wave function (12). The observation of a clear resonant tunneling effect in structures with a three-QW active region demonstrated the effectiveness of this approach (17).

The fast intersubband scattering between the lowest subbands separated by an optical phonon energy should lead to a high population inversion in a three-QW active region.
device, even at room temperature. However, the relatively slow measured tunneling time from the active region of about 2 ps (18, 19) introduces an effective bottleneck to the electron transport, enhancing the lower laser state population. A model of the room-temperature electron kinetics in the active region (20), which included optical phonon emission and absorption from all points in $k$-space of the active region subbands, demonstrated that this bottleneck effect resulted in an effective lower state lifetime as long as 0.8 ps for a typical three-QW structure. The same computation also shows that the presence of an additional state in the active region (that is, level 1) allowing the emission of two optical phonons from the lower laser level decreases the lifetime of that level down to 0.5 ps. As a result, the computed ratio between the upper and lower state population increased from 1.9 for the three-QW structure to 2.8 in the double-phonon resonance structure, simultaneously decreasing the threshold current density and increasing the slope efficiency and maximum power, as was indeed observed (6).

Moreover, our devices were processed in a narrow-stripe, planarized, buried heterostructure geometry (21), in which the gain region was vertically and laterally buried within InP cladding layers, the geometry of which provides a number of advantages. The choice of a buried stripe greatly improves the heat transport by allowing heat flow from all sides of the active region. Additionally, the narrow-stripe geometry also decreases the total amount of strain that builds up in a material subjected to a very strong temperature gradient. Indeed, the results from a simulation, done with a commercial finite-elements differential equation solver (22), of both thermal transport and thermally induced stress lead to the same conclusions (Fig. 1, B and C). A thermal conductance of 820 W/Kcm$^2$ is predicted for a buried, 12-$\mu$m-wide, junction-down–mounted device, compared to the calculated value of 510 W/Kcm$^2$ for a 28-$\mu$m-wide, ridge, junction-down–mounted device (6). Similarly, the maximum thermally induced shear stress that builds up at the edges of the active region (Fig. 1C) decreases from 22 MPa in the ridge device to 3.6 MPa for the buried structure.

Fabrication of the laser structure relied on molecular beam epitaxy for the growth of the lattice-matched InGaAs/InAlAs laser core on an InP substrate. The laser core consists of 35 periods, each comprising a partially n-doped injector region and the undoped four-QW active region, embedded in an optical waveguide formed on one side by the substrate and a lower InGaAs waveguide layer and on the other side by an upper InGaAs waveguide layer and the InP top cladding, which was grown by metalorganic vapor-phase epitaxy (MOVPE).

The lasers were fabricated into 12-$\mu$m-wide buried stripes by wet etching and selective MOVPE regrowth of i-InP using a SiO$_2$ mask. The devices were then cleaved into 750-$\mu$m-long lasers, soldered junction-down onto a diamond platelet, and finally facet-coated by a ZnSe/PbTe high-reflectivity ($R = 0.7$) layer pair.

The CW optical output power emitted from one facet (Fig. 2) was measured with a calibrated thermopile detector, which was mounted directly in front of the laser facet. At room temperature (292 K), the laser exhibited a threshold current density of 510 mA/cm$^2$, a slope efficiency of 101 mW/A (where $P$ is optical power and $I$ is current). This device emitted 13 mW of optical power from a single facet at a driving current of 550 mA, resulting in a wall plug efficiency of 0.55% per facet. Continuous wave operation was observed up to 312 K (39°C). At this temperature, the threshold current increased to 520 mA ($J_{th} = 5.8$ kA/cm$^2$), while still more than 1 mW of output power was emitted at 550 mA. The electrical transport characteristics of the device (inset of Fig. 2) display the expected discontinuity of the differential resistance at threshold (390 mA).

A laser with the same cavity length but a slightly larger stripe width of 15 $\mu$m emitted 17 mW per facet at a drive current of 600 mA at room temperature. This device could be operated up to 311 K, with a maximum optical power of 3 mW and a threshold current of 540 mA ($J_{th} = 4.8$ kA/cm$^2$).

The performance of these buried heterostructure devices demonstrates the results of the thermoelastic predictions. Although the junction-down–mounted, 28-$\mu$m-wide, conventional ridge lasers failed systematically at 4.3 kA/cm$^2$ (compared to 4.3 kA/cm$^2$ in CW operation) for the 12-$\mu$m-wide device, corresponding to a threshold current $I_{th} = 280$ mA. The experimental pulsed threshold current densities (Fig. 4) can be fitted by the expression $J_{th} = J_0 \exp(T_{act}/T_0)$ with a $T_0 = 171$ K and $J_0 = 560$ A/cm$^2$.

The temperature dependence of the CW threshold current density can be computed from the data in pulsed operation, using a slightly modified model that takes into account the change in applied voltage with range, with a side mode suppression ratio better than 30 dB. This surprising fact can be explained by a small defect within the laser cavity, as indicated by an intensity modulation of the subthreshold Fabry-Perot fringes at twice the cavity mode spacing.

Assuming that the emission frequency $\nu$ is a function only of the temperature of the active region, we can deduce a thermal resistance $R_{th}$ of the device from the variation of the emission frequency ($\nu$) with $R_{th} = (\Delta \nu / \Delta T) = (\Delta I / \Delta P) \times (\Delta V / \Delta I)$.

Inserting the above tuning rates, we get a thermal resistance of 19.4 K/W in the range between 292 K and 313 K (corresponding to a thermal conductance $G_{th}$ of 574 W/Kcm$^2$). This $R_{th}$ value is higher than the calculated one (13.6 K/W), most likely because the thermal interface resistance was not included in our simulation.

The dependence of the threshold current density $J_{th}$ on the actual core temperature $T_{act}$ of the laser is measured in pulsed mode at low duty cycles, where heating effects are negligible (that is, $T_{act} \sim T_{sink}$). At 292 K, we measured a pulsed $J_{th}$ as low as 3.1 kA/cm$^2$. Continuous wave operation was observed up to 311 K, with a maximum optical power of 3 mW and a threshold current of 540 mA ($J_{th} = 4.8$ kA/cm$^2$).

The CW optical power (mW/facet) can be tuned over a small range of a few cm$^{-1}$ by changing the current and temperature. The CW spectral properties were analyzed with a Fourier transform infrared spectrometer. The emission spectra (Fig. 3A) collected at a constant heat sink temperature of 292 K and various currents between 395 and 530 mA reveal frequency tuning from 1092.74 cm$^{-1}$ to 1094.54 cm$^{-1}$, linear with the electrical input power (inset of Fig. 3A). At a fixed current of 530 mA, the emission frequency of the laser shifts from 1094.54 cm$^{-1}$ at 292 K to 1092.90 cm$^{-1}$ at 313 K (Fig. 3B). The measured center frequencies are well fitted by a linear function (inset of Fig. 3B) with a tuning coefficient of $\Delta \nu / \Delta T = -0.078$ cm$^{-1}$/K. Single mode operation was observed for this particular device over the whole investigated current and temperature range.

![Fig. 2. CW optical power from a single laser facet as a function of drive current for various heat sink temperatures. The laser is 0.75 mm long and 12 $\mu$m wide. The power was measured with near-unity collection efficiency and a calibrated thermopile detector. (Inset) Electrical transport characteristics of the laser at 292 K: bias voltage as a function of injection current and differential resistance deduced from the V-I curve.](http://www.sciencemag.org/science/vol295/11jan2002/303/fig2.jpg)
injected current (23) and uses the thermal conductance $\Gamma_{\text{th}}$ obtained from the spectral measurements. The calculated $J_{\text{th}}$ curve fits well with the experimental CW $J_{\text{th}}$ values (solid symbols in Fig. 4). The data also show that, at 292 K, the temperature difference $\Delta T = T_{\text{act}} - T_{\text{sink}}$ between laser core and heat sink is 8 K at threshold and increases to 87 K at the maximum injected current. With this modified model, we calculate a maximum CW operating temperature $T_{\text{sink, max}} = 321$ K and a $\Delta T = 119$ K at that operating temperature.

The threshold currents of our buried heterostructure QC lasers scale accurately with the laser stripe width (inset of Fig. 4). It means that our device architecture does not introduce additional lateral waveguide losses or current leakage paths.

The far-field distributions in the two directions parallel and perpendicular to the grown layers exhibited a Gaussian profile with far-field angle of 40° full width at half maximum in the in-plane direction and 80° perpendicular to the layers, proving that the device oscillates in its fundamental lateral and transverse mode. Fundamental intersubband processes did not limit the device performance. Assuming the measured waveguide loss value of $10 \, \text{cm}^{-1}$ (24) and in the limiting case of unity injection efficiency, the threshold current density of our QC laser should be $2.1 \, \text{mA/cm}^2$ (25), which is significantly lower than the measured value ($3.1 \, \text{mA/cm}^2$). We believe that further improvements in active region design and growth conditions should bring us closer to this limiting case. In addition, a reduction of the stripe width to 5 to 6 $\mu$m should further improve $G_0$ (by about 20%) while still maintaining a large value of confinement factor. In that case, our model predicts a maximum CW operating temperature of $T > 370$ K.

References and Notes

13. This follows from the derivation of the equation $T_{\text{sink}} = T_{\text{act}} - U \times J_0 \exp(T_{\text{act}}/T_{\text{sink}}) G_0$.  
15. The layer sequence of one period, in nanometers, from left to right in Fig. 1A and starting with the injection barrier, is as follows: $0.1/0.9/0.7/5.8/0.9/5.7/0.9/5/0.2/2/3.4/1.3/3.3/1.3/1.5/1.9/3.0/2.9/2.9/2.9/2.9$, where InAlAs barrier layers are in bold, InGaAs well layers are in roman, and n-doped layers ($2 \times 10^{17}$ cm$^{-3}$) are underlined.
16. The three-QW active region design has widely been used in QC devices. Its schematic band structure roughly corresponds to the first three QWs, counting from the injection barrier, of the active region in Fig. 1A. The corresponding energy spectrum is similar to the double-photon resonance device but without the $n = 1$ state.
20. The electron kinetic computation assumed that the electrons interacted with a thermal distribution of bulk optical phonons at 300 K. The emission (e) and absorption (a) lifetimes from the active region states ($t_{\text{esc}}$) are (in ps): $t_{\text{esc}} = 1.88$, $t_{\text{esc}} = 9.3$, $t_{\text{esc}} = 1.92$, $t_{\text{esc}} = 8.5$, $t_{\text{esc}} = 2.51$, $t_{\text{esc}} = 11.5$, $t_{\text{esc}} = 0.73$, $t_{\text{esc}} = 3.8$, $t_{\text{esc}} = 0.23$, $t_{\text{esc}} = 2.3$, $t_{\text{esc}} = 0.28$, $t_{\text{esc}} = 2.7$ ($n = 4$ is the upper laser level). The lifetime for intrasubband processes is $t_{\text{esc}} = 0.14$ ps for emission and $t_{\text{esc}} = 0.53$ ps for absorption of optical phonons. The escape time $t_{\text{esc}} = 2$ ps was the same for all the lower ($n = 1$) states.
22. The simulation of the thermoelastic behavior of the device was done with a commercial finite-elements software package (PDEase2D). Room-temperature thermal conductivities were used. The elastic properties of the semiconductor were approximated by...
Carbon-carbon bonds are the molecular “bricks and mortar” from which diverse architectures in living organisms and man-made materials are constructed. As the field of organic chemistry has evolved, numerous methods for carbon-carbon bond construction have been developed, ranging from classic examples, like the Diels-Alder reaction, to more recent metal-catalyzed processes, such as olefin polymerizations and metatheses.

Biaryl subunits and their heteroaromatic analogs are abundant in natural and synthetic materials, and controlled methods for linking aromatic rings via C–C sigma bonds have long been pursued by organic chemists. Activity in this regard intensified in the late 1970s, during which Pd-catalyzed methods for C–C bond construction emerged (1). First disclosed by Miyaura and Suzuki, the Pd-catalyzed coupling of aromatic rings via C–C sigma bonds have long been studied. This reaction has been extended to include Pd-mediated cross-couplings of organoboron compounds and organohalides.

Arylboron compounds have intriguing properties and are important building blocks for chemical synthesis. A family of Ir catalysts now enables the direct synthesis of aryloboron compounds from aromatic hydrocarbons and boranes under “solventless” conditions. The Ir catalysts are highly selective for C–H activation and do not interfere with subsequent in situ transformations, including Pd-mediated cross-couplings with aryl halides. By virtue of their favorable activities and exceptional selectivities, these Ir catalysts impart the synthetic versatility of aryloboron reagents to C–H bonds in aromatic and heteroaromatic hydrocarbons.

A comparison of precatalysts 1 and 2 in borylations of various substituted arenes revealed that the Ir system was more selective toward arene C–H activation (15). Given the importance of selectivity in chemical synthesis, these findings spurred a detailed investigation of the original Ir system.

Compound 1 was stable in benzene solutions after prolonged thermolysis, which eliminates several mechanistic possibilities, including PMe₃ dissociation to generate Cp*Ir(H)(HBPin), an analog of proposed intermediates in the Rh system. However, added PMe₃ strongly inhibited catalysis where HBPin was present. This finding raised the possibility that small quantities of phosphine-free IrV species could be active. Because Cp*IrH₄(BPin) species (where x = 1, 2) form in the thermolysis of Cp*IrH₄ and HBPin (16), anisole borylations with identical loadings of Cp*IrH₄ and 1 were compared. From this experiment, Cp*IrH₄(BPin)ₖ intermediates could be eliminated because these species are not kinetically competent for catalysis and because the borylation regioselectivities for Cp*IrH₄ and 1 differed substantially (17).

Exclusion of a simple phosphine dissociative pathway narrows the plausible catalysts to two choices: (i) Ir phosphine species arising from Cp* loss or (ii) species where both Cp* and PMe₃ have been lost. The latter possibility is