

Above-room-temperature continuous-wave mid-infrared photoluminescence from PbSe/PbSrSe quantum wells

P. J. McCann,^{a)} K. Namjou, and X. M. Fang^{b)}

School of Electrical and Computer Engineering, Laboratory for Electronic Properties of Materials, University of Oklahoma, Norman, Oklahoma 73019-1023

(Received 24 August 1999; accepted for publication 11 October 1999)

Strong photoluminescence between 3 and 4 μm was observed at temperatures as high as 55 °C from PbSe/PbSrSe multiple-quantum-well structures grown on BaF₂ (111) substrates by molecular-beam epitaxy. Fabry–Perot interference fringes dominated the spectra, indicating that the luminescence was primarily due to stimulated emission processes. Peak emission energies were determined by fitting Gaussian functions to the spectra, and they showed that emission energies at 25 °C decreased from 402 to 312 meV as quantum-well thickness increased from 40 to 200 Å. The temperature tuning coefficient was also observed to decrease from 0.400 meV/K for a 200 Å multiple-quantum-well sample to 0.313 meV/K for a 40 Å multiple-quantum-well sample. © 1999 American Institute of Physics. [S0003-6951(99)02149-X]

With many potential applications in molecular spectroscopy there is increasing interest in the development of tunable mid-infrared lasers. Much progress has recently been made with III–V semiconductor quantum cascade laser structures in achieving high power emission and pulsed room temperature operation at various wavelengths between 5 and 17 μm .^{1–3} In addition, type II quantum-well structures made using narrow gap III–V antimonide semiconductor materials have shown promise in fabricating lasers covering the 2 to 5 μm spectral range; however, continuous-wave (cw) room temperature operation is still limited to wavelengths shorter than 2.3 μm .^{4–6} Even with these recent advances in developing mid-infrared lasers using mature III–V semiconductor materials technology, there remains a gap in the development of high performance lasers covering the 2.3–5 μm spectral range. Although much less developed than III–V semiconductors, IV–VI semiconductors still hold much promise for fabricating high operating temperature mid-infrared lasers. As evidence of such promise this letter reports on the observation of above-room-temperature continuous-wave photoluminescence between 3 and 4 μm from PbSe/PbSrSe multiple-quantum-well (MQW) structures grown by molecular-beam epitaxy (MBE).

IV–VI semiconductors have several unique properties that make them attractive for mid-infrared laser fabrication. Perhaps the main difference between IV–VI materials and narrow gap III–V materials is the symmetric band structure and the absence of a heavy hole band. Holes in IV–VI materials such as PbSe have effective masses just as small as electrons as evidenced by similar carrier mobilities in *n*-type and *p*-type materials.⁷ The corresponding lower combined density of states and stronger interband matrix elements allows the appearance of stimulated emission at relatively low generation rates. Auger recombination rates are also much smaller in IV–VI materials than in III–V materials. Recent pump probe measurements show that bulk PbSe has a room

temperature Auger coefficient of about $0.8 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1}$,⁸ one to two orders of magnitude lower than bulk narrow gap III–V and II–VI materials, and about four times lower than type II InAs/Ga_{1–*x*}In_{*x*}Sb quantum wells.⁹ In addition, IV–VI semiconductor materials can be grown on substrates with BaF₂ buffer layers, and this allows removal of the growth substrate by dissolving the BaF₂ buffer with water.¹⁰ This technique can be used to fabricate lasers with much improved active region heat dissipation possibly enabling cw operation at room temperature.¹¹

In this work, IV–VI quantum-well structures were grown on BaF₂ (111) substrates by MBE. Growth was carried out in an Intevac GEN II Modular MBE system. Before transfer to the growth chamber, freshly cleaved 1 cm×1 cm BaF₂ substrates were outgassed in the preparation chamber at 200 °C for 1 h. A 100-nm-thick BaF₂ buffer layer was first grown on the substrate at 500 °C. X-ray diffraction data have shown that growth of such a BaF₂ buffer layer improves the crystalline quality of subsequently grown PbSe and PbSrSe layers. A 3- μm -thick PbSrSe layer with a 3% Sr-to-PbSe flux ratio was grown at 360 °C on top of the BaF₂ layer by evaporating PbSe and elemental Sr from low-temperature effusion cells with an additional 10% Se flux ratio provided by a valved cracker effusion cell to keep the growth surface under Se rich conditions. PbSe/PbSrSe multiple quantum well structures with 40 periods were then grown at 360 °C on top of the PbSrSe buffer layer. PbSe quantum-well and PbSrSe barrier layer thicknesses were in the range of 40–200 Å and 400–500 Å, respectively. Thicknesses were determined using calculated growth rates of 180 and 250 Å/min, respectively, obtained from previously grown single layer thickness measurements. The same 3% strontium flux ratio was used for barrier layer growth, and, based on the work of Lambrecht *et al.*,¹² this resulted in material with 7.8% Sr and a room temperature absorption edge of about 0.5 eV. Finally, a 10-nm-thick PbSe cap layer was grown on top of the MQW structure to prevent oxidation of the Sr in the barrier layer material.

Photoluminescence measurements were performed using

^{a)}Electronic mail: pmccann@ou.edu

^{b)}Present address: Quantum Epitaxial Designs, Inc., Bethlehem, PA.

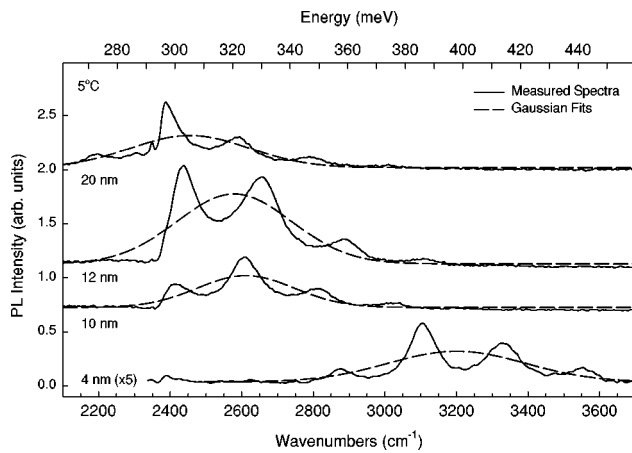


FIG. 1. Photoluminescence spectra at 5 °C from 40-period PbSe/PbSrSe multiple-quantum-well samples grown by MBE on BaF₂ (111).

a modular Fourier transform infrared (FTIR) spectrometer (Oriel, MIR8000). MBE samples were mounted on a single stage thermoelectric (TE) cooler and illuminated with an InGaAs laser having a peak emission wavelength of 972 nm. Sample temperature was monitored with a thermistor mounted adjacent to the sample. The injection current for the InGaAs pump laser was 500 mA, and according to the manufacture's test data, this produced about 250 mW of power. The unfocused laser, located about 10 mm from the sample at about a 45 degree angle, produced a spot size of about 2 mm×7 mm on the sample surface. An average power density of about 1.8 W/cm² is thus estimated. Luminescence from the sample was collected by a 2 in. diam gold-coated off-axis parabolic mirror (OAPM) and passed through the FTIR scanner. Light from the FTIR scanner was collected by a second OAPM and focused through a ZnSe lens onto a TE-cooled HgCdZnTe detector (Boston Electronics, PDI-2TE-6) with a 6 μm cutoff wavelength and a detectivity in the 3–4 μm range of about 2×10¹⁰ cm Hz^{1/2}/W. Spectra were collected with an 8 cm⁻¹ (1 meV) resolution, co-added at least 50 times, and corrected by subtracting the background radiation.

Figure 1 shows measured spectra along with Gaussian fits to the data for four MQW samples at 5 °C with different quantum-well thicknesses. Each measured spectrum exhibits multiple peaks separated by about 200 cm⁻¹. These are Fabry-Perot interference fringes due to resonance in the optical cavity formed by the layer. Using the equation $n = (2t\Delta\nu)^{-1}$, where n is the index of refraction, t is the measured total film thickness including the 3-μm-thick PbSrSe buffer layer, and $\Delta\nu$ is the fringe spacing, the average value for the index of refraction for the layers is 4.79. This index of refraction is smaller than the 4.9 value for the index of refraction of PbSe near its band gap, which is consistent with the fact that most of the optical cavity consists of larger band gap (and thus smaller index) PbSrSe. The appearance of Fabry-Perot interference fringes in the PL spectra shows that there is significant internal reflection inside the layer and indicates that sample luminescence is dominated by stimulated emission processes.¹³

Figure 2 is a plot of the peak energies obtained from Gaussian fits to the measured 25 °C PL spectra for each sample as a function of quantum-well thickness. A shift in

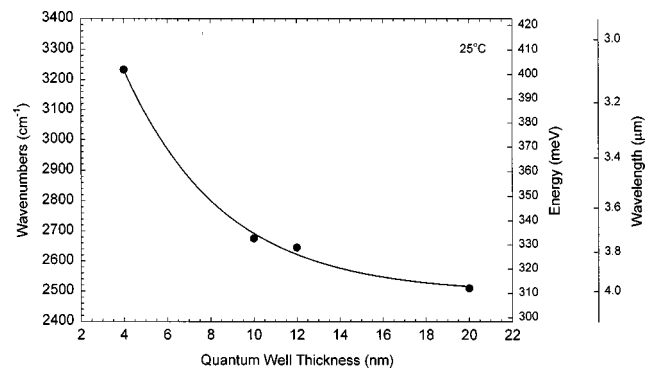


FIG. 2. Photoluminescence peak energies, obtained from fitted Gaussian functions to the 25 °C spectra, as a function of quantum-well thickness.

the PL emission energy from 312 to 402 meV is observed as the quantum-well thickness is decreased from 200 to 40 Å. With PL energies significantly above the 275 meV room temperature band gap value of bulk PbSe and a strong blue-shift with decreasing well width it is clear that this photoluminescence is due solely to recombination of quantum confined electron-hole pairs. Full width half maxima (FWHM) values obtained from the Gaussian fits were 36.3 and 41.3 meV for two samples with 500 Å barriers and 45.6 and 51.0 meV for two samples with 400 Å barriers, respectively. There is no correlation between FWHM and the quantum-well thickness. Larger peak widths for samples with thinner barriers suggests that the confined states form a miniband and that the amplitudes of the electron and/or hole wave functions are not zero after penetrating a 400-Å-thick barrier.

Figure 3 shows PL spectra from 5 to 55 °C in 10° increments for a sample with 200-Å-thick quantum wells. Each spectrum exhibits three Fabry-Perot interference peaks in the vicinity of 2400, 2600, and 2800 cm⁻¹. Note that the shape of the low energy side of the peak near 2400 cm⁻¹ at temperatures below 35 °C is somewhat distorted due to absorption by atmospheric CO₂ in the open path PL test setup. The intensity of this lower energy peak also decreases while the intensity of the peak near 2600 cm⁻¹ increases somewhat as the temperature increases. Gaussian fits to the spectra reflect this shift in energy distribution. A similar dependence on temperature is also seen from samples with 120-, 100-, and 40-Å-thick quantum wells. The PL intensity from all

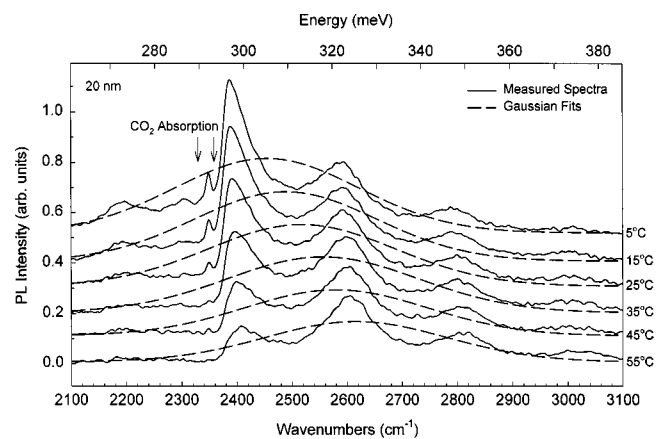


FIG. 3. Photoluminescence spectra from 5 to 55 °C from a 40-period MQW sample with 200 Å thick quantum wells. Note the absorption due the P and R branches of CO₂ marked by the arrows.

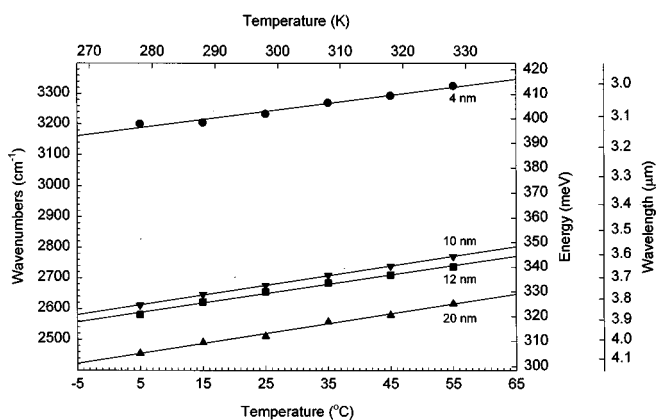


FIG. 4. Photoluminescence peak energies, obtained from fitted Gaussian functions to the spectra from 40, 100, 120, and 200 Å MQW samples, as a function of temperature.

samples is still quite strong even at 55 °C, a temperature limit imposed by the rated range of the temperature sensor used in the experimental setup.

In addition to the blue shift in the overall PL energy as shown by the Gaussian fits in Fig. 3 there is also a smaller blueshift with increasing temperature in the positions of the Fabry–Perot interference peaks. If these are cavity modes then this shift should be due solely to changes in cavity length and refractive index. Based on a measured room temperature thickness of 5.288 μm and a PbSe thermal expansion coefficient of $19.4 \times 10^{-6} \text{ K}^{-1}$ the cavity length will increase from 5.286 to 5.291 μm as the sample is heated from 5 to 55 °C. Assuming $6 \frac{1}{2}$ wavelengths in the cavity mode corresponding to the 2586 cm^{-1} peak in the 5 °C spectrum, a refractive index value of 4.755 is obtained. The same number of wavelengths in the cavity mode corresponding to the 2606 cm^{-1} peak in the 55 °C spectrum yields a refractive index value of 4.714. This rate of refractive index change with temperatures of $8.2 \times 10^{-4} \text{ K}^{-1}$ agrees exactly with the refractive index versus temperature data for PbSe reported in Ref. 14, thus, showing that this analysis accounts fully for the observed peak shift.

Figure 4 is a plot of PL peak energies, determined from Gaussian fits to the measured spectra, as a function of temperature for the four different quantum-well thicknesses. PL energies for samples with quantum-well thicknesses of 200, 120, and 100 Å increased with temperature at similar rates of 0.400, 0.388, and 0.398 meV/K, respectively. These rates are smaller than the 0.46 meV/K value obtained for the absorption edge change with temperature of a $\text{PbSe}_{0.78}\text{Te}_{0.22}$ layer on BaF_2 (100)¹⁵ and the 0.45 meV/K bandgap versus temperature value reported for bulk PbSe.¹⁴ The sample with 40 Å quantum wells exhibited an even smaller temperature coefficient of 0.313 meV/K. This is the first known observation of a temperature coefficient dependence on quantum-well thickness and is similar to what was recently observed for PbSe quantum dots.¹⁶ These results provide evidence that the energy states are becoming more atomic-like as quantum-well size decreases and are less subject to extended lattice properties such as thermal expansion and electron–phonon interaction.

In summary, above-room-temperature continuous-wave mid-infrared photoluminescence was observed from PbSe/

PbSrSe MQW samples by pumping with a near-infrared diode laser. Samples exhibited strong PL at temperatures as high as 55 °C. To the authors' knowledge, these are the only known mid-infrared PL spectra obtained under such testing conditions, i.e., above-room-temperature, continuous-wave diode laser pumping, and without any type of lock-in amplification or double modulation signal enhancing techniques. The luminescence was dominated by stimulated emission processes as evidenced by the existence of Fabry–Perot interference peaks in the spectra. PL energies behaved as expected, i.e., they increased as quantum-well thickness decreased and increased as temperature increased. The data presented here should provide useful information for the eventual design and fabrication of room temperature continuous-wave tunable mid-infrared lasers.

This work was supported by Grants from the National Science Foundation (No. DMR-9802396) and the Oklahoma Center for the Advancement of Science and Technology (OCAS No. AR6-054).

- ¹D. Hofstetter, J. Faist, M. Beck, A. Müller, and U. Oesterle, *Appl. Phys. Lett.* **75**, 665 (1999).
- ²A. Tredicucci, C. Gmachl, F. Capasso, D. L. Sivco, A. L. Hutchinson, and A. Y. Cho, *Appl. Phys. Lett.* **74**, 638 (1999).
- ³J. Faist, A. Tredicucci, F. Capasso, C. Sitori, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, and A. Y. Cho, *IEEE J. Quantum Electron.* **34**, 336 (1998).
- ⁴W. W. Bewley, C. L. Felix, E. H. Aifer, I. Vurgaftman, L. J. Olafsen, J. R. Meyer, H. Lee, R. U. Martinelli, J. C. Connolly, A. R. Sugg, G. H. Olsen, M. J. Yang, B. R. Bennett, and B. V. Shanabrook, *Appl. Phys. Lett.* **73**, 3833 (1998).
- ⁵J. I. Malin, J. R. Meyer, C. L. Felix, J. R. Lindle, L. Goldberg, C. A. Hoffman, F. J. Bartoli, C. H. Lin, P. C. Chang, S. L. Murry, R. Q. Yang, and S. S. Pei, *Appl. Phys. Lett.* **68**, 2976 (1996).
- ⁶S. R. Kurtz, R. M. Biefeld, A. A. Allerman, A. J. Howard, M. H. Crawford, and M. W. Pelczynski, *Appl. Phys. Lett.* **68**, 1332 (1996).
- ⁷P. J. McCann, S. Aanegola, and J. E. Furneaux, *Appl. Phys. Lett.* **65**, 2185 (1994).
- ⁸P. C. Findlay, C. R. Pidgeon, R. Kotitschke, A. Hollingworth, B. N. Mordin, C. J. G. M. Langerak, A. F. G. van der Meer, C. M. Ciesla, J. Oswald, A. Homer, G. Springholtz, and G. Bauer, *Phys. Rev. B* **58**, 12908 (1998).
- ⁹J. R. Meyer, C. L. Felix, W. W. Bewley, I. Vurgaftman, E. H. Aifer, L. J. Olafsen, J. R. Lindle, C. A. Hoffman, M. J. Yang, B. R. Bennett, B. V. Shanabrook, H. Lee, C. H. Lin, S. S. Pei, and R. H. Miles, *Appl. Phys. Lett.* **73**, 2857 (1998).
- ¹⁰H. Z. Wu, X. M. Fang, D. McAlister, R. Salas, Jr., and P. J. McCann, *J. Vac. Sci. Technol. B* **17**, 1297 (1999).
- ¹¹K. R. Lewelling and P. J. McCann, *IEEE Photonics Technol. Lett.* **9**, 297 (1997).
- ¹²A. Lambrecht, N. Herres, B. Spanger, S. Kuhn, H. Bottner, M. Tacke, and J. Evers, *J. Cryst. Growth* **108**, 301 (1991).
- ¹³J. W. Tomm, K. H. Herrmann, and A. E. Yunovich, *Phys. Status Solidi A* **122**, 11 (1990).
- ¹⁴A. Katzir, R. Rosman, Y. Shani, K. K. Bachem, H. Bottner, and H. M. Preier, in *Handbook of Solid State Lasers*, edited by P. K. Cheo (Marcel Dekker, New York, 1989), p. 227.
- ¹⁵P. J. McCann, L. Li, J. Furneaux, and R. Wright, *Appl. Phys. Lett.* **66**, 1355 (1995).
- ¹⁶A. Olkovets, R. C. Hsu, A. Lipovskii, and F. W. Wise, *Phys. Rev. Lett.* **81**, 3539 (1998).