

**TERAHERTZ EMISSION FROM *p*-TYPE GERMANIUM LASERS
DOPED WITH NOVEL ACCEPTORS**

O. D. Dubon,^{1,2} D. R. Chamberlin,^{1,2} W. L. Hansen¹ and E. E. Haller,^{1,2}

Lawrence Berkeley National Laboratory¹

Department of Materials Science and Mineral Engineering²

University of California, Berkeley, CA 94720, USA

and

L. A. Reichertz, G. Sirmain, E. Bründermann, A. M. Linhart and H. P. Röser

DLR, Institute for Space Sensor Technology, Rudower Chaussee 5, D-12489

Berlin, Germany

Abstract

We have studied the stimulated emission from Ge single crystals doped with the multivalent acceptors Be, Zn, and Cu. Unlike those containing shallow acceptors, lasers doped with the double acceptors Be and Zn exhibit stimulated emission over the full frequency range of 1 to 4 THz. First results on Ge doped with the Cu triple acceptor show that emission between 1.5 and 4 THz can be achieved. By using crystals that contain these novel dopants, we have increased the duty cycle up to the 10^{-2} range which is one order of magnitude higher than the maximum duty cycle reported for shallow acceptor doped lasers.

I. Introduction

The interest in a compact, tunable local oscillator for the heterodyne detection of THz radiation has led to considerable interest in the *p*-type Ge hot-hole laser as a potential continuous wave (cw) source in the 1 to 4 THz range. This laser operates in crossed electric (E) and magnetic (B) fields at liquid helium temperatures. Stimulated emission arises from a) intervalence band (IVB) transitions from the light- to the heavy-hole subbands and b) cyclotron resonance (CR) transitions between Landau levels of the light-hole subband. Thus far these lasers have been shown to operate only in a pulsed mode achieving an output power as high as a few Watt and duty cycles in the 10^{-3} range.¹ The operating principles of these lasers are explained in detail elsewhere.²

The emission spectrum of lasers operating in the IVB mode has previously been shown to consist of two regions, the "low frequency" (1.0-1.8 THz) and the "high frequency" (2.4-4 THz) region. It has been recently demonstrated that internal absorption of the radiation by neutral acceptors suppresses the emission between the low and high frequency region.³ Until recently, all previous spectral investigations have been performed with crystals doped with shallow hydrogenic acceptors (mostly Ga), all of which exhibit internal hole transitions that partially overlap in energy with IVB transitions. There has therefore been a strong interest in producing lasers from Ge crystals that are doped with deeper acceptors.

Here we present spectral measurements of the stimulated emission from Be-, Zn- and Cu-doped Ge crystals. Neutral Be, Zn, and Cu have ionization energies of 25, 33, and 43 meV, respectively, and therefore should not lead to self-absorption. Laser action from multivalent-acceptor-doped Ge crystals was recently demonstrated.^{4,5} We show that stimulated emission from these materials can be achieved over the full range of 1 to 4 THz.

II. Sample preparation and measurement

For this study we used samples from two Czochralski-grown crystals, one doped with Be and the other with Zn. Wafers were lapped sequentially in 600 and 1200 mesh SiC powder/water slurries and polish-etched in a 4:1 HNO₃:HF mixture. Ohmic contacts were formed on the wafer surfaces by boron ion implantation with doses of 1×10^{14} and 2×10^{14} cm⁻² at 33 and 50 keV, respectively. 200 Å of Pd and 4000 Å of Au were then rf sputtered onto the implanted surfaces. Annealing for 1 hour at 300 °C in a N₂ ambient was performed to remove implantation damage and activate the boron acceptors in the implanted layer. The wafers were crystallographically oriented and cut into parallelepipeds. The freshly exposed surfaces were re-lapped, and the bar-shaped samples were re-etched in the 4:1 HNO₃:HF mixture.

The crystals were characterized by variable temperature Hall-effect measurements and photothermal ionization spectroscopy (PTIS) in order to determine the type and the concentration of the different impurities present in the crystals. For both crystals we determined a majority dopant concentration of 1.5×10^{14} cm⁻³ and a residual net shallow acceptor (mostly B and Al) concentration of 1.0 to 2.0×10^{12} cm⁻³.

Copper doping can be readily obtained in Ge crystals by thermal diffusion. This makes Cu-doped Ge an attractive material for producing these hot-hole lasers.⁶ In this study a wafer 6 mm thick was cut from a Czochralski-grown, *p*-type Ge ingot with a residual shallow acceptor concentration of $2 \times 10^{11} \text{ cm}^{-3}$. It was lapped and etched in the manner described above. A 1000 Å layer of Cu was rf sputtered onto the wafer as a diffusion source. The wafer was crystallographically cut to produce sample geometries with dimensions slightly larger than the final device. Each laser crystal was cleaned and annealed separately in an ampoule sealed under vacuum. In-diffusion of Cu was performed for 40 hours at a fixed temperature of 700 °C. The ampoules were quenched rapidly in ethylene-glycol to reach the desired substitutional Cu concentration of $1 \times 10^{15} \text{ cm}^{-3}$.

Reference samples 1 mm thick were cut at each end of the laser crystals to check the Cu concentration, the homogeneity of Cu along the length of each laser crystal and the concentration of residual shallow impurities (acceptor and donor contaminants). Hall effect measurements performed on these samples show the homogeneity of the Cu acceptors to be better than 20%. These measurements reveal a residual shallow acceptor net concentration in the low 10^{12} cm^{-3} range which is approximately five times higher than the concentration measured for unannealed samples. We relate this shallow acceptor concentration increase, at least in part, to the dissociation of hydrogen-acceptor complexes.⁷ The residual acceptors are Al and Ga impurities in a 1:1 concentration ratio according to PTIS measurements. The concentration of compensating shallow donors lies in the low 10^{11} cm^{-3} range and is attributed to phosphorus impurities.

Upon completion of Cu in-diffusion and characterization of the annealed crystals, the laser crystal surfaces were lapped and polish-etched to their final dimensions. Ohmic contacts were formed on two opposite surfaces in the same manner described previously.

The laser samples were mounted between two copper electrodes and placed inside a superconducting magnet in a liquid helium cryostat. Electric field pulses with lengths of 1 to 2 μs were applied. The high refractive index of germanium enables laser operation without external resonators, the laser surfaces forming an internal cavity. The radiation was detected in the Faraday configuration with the outcoupling direction parallel to the magnetic

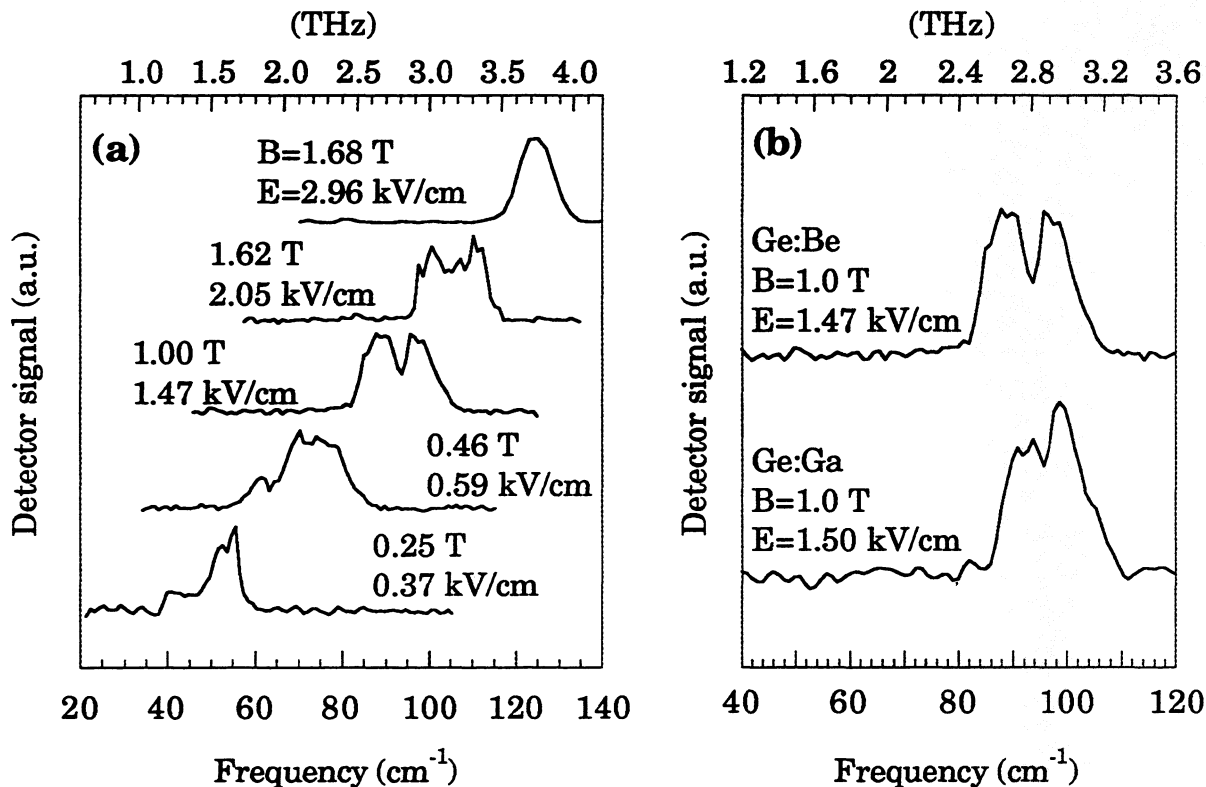


Figure 1. (a) Stimulated emission spectra from Ge:Be for various combinations of E and B fields. The spectral resolution is 1 cm⁻¹ (0.03 THz) except for the spectrum measured at 1.68 T which has a resolution of 2 cm⁻¹ (0.06 THz). (b) Stimulated emission from Ge:Ga (4x4x25 mm³, Ga concentration of 8x10¹³ cm⁻³) compared to Ge:Be tested under the same conditions, including crystallographic orientation with respect to the E and B fields.

field. We measured the emission spectra by Fourier transform spectroscopy using a Michelson interferometer and a broadband 4.2 K bolometer.

III. Results and discussion

Figure 1(a) shows the emission spectra of a 4x4x20 mm³ Ge:Be laser for different combinations of E and B fields. The magnetic field was oriented parallel to the long axis of the crystal which pointed along a [110] crystallographic direction. The E field was applied along a [001] direction.

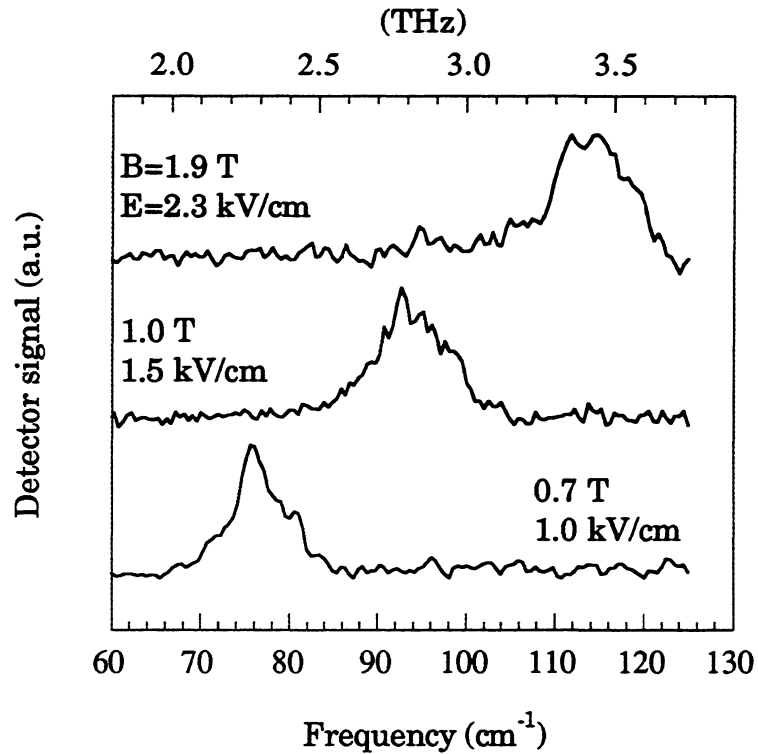


Figure 2. Stimulated emission spectra from Ge:Cu for various combinations of E and B fields. The spectral resolution is 0.5 cm^{-1} (0.015 THz).

By varying both fields we were able to achieve IVB stimulated emission throughout the range of 1 to 4 THz unlike the case for Ga-doped Ge lasers which exhibit an emission gap between 1.8 and 2.4 THz. The emission of Zn-doped germanium lasers possesses the same spectral characteristics displayed in Fig. 1(a). In addition, we find that outside the spectral region where dopant self-absorption occurs, double acceptor doping does not change the character of the emission spectrum [Figure 1(b)]. These results clearly demonstrate that the observed emission is related to the intrinsic properties of the Ge valence band and is not due to the nature of the dopant species.

Figure 2 shows the emission spectra of a $4.5 \times 39.2 \times 6.0 \text{ mm}^3$ Ge:Cu laser. As in the case of the Be- and Zn-doped samples, the magnetic field was oriented parallel to the long axis of the crystal along a [110] direction. However, the Ohmic contacts were made on the $6.0 \times 39.2 \text{ mm}^2$, [110]-oriented surfaces. With this configuration we have observed stimulated emission in

the range of 2.1 to 3.6 THz. In addition, we have measured the spectrum for the same laser crystal but with the contacts (and hence the electric field) oriented in a [001] direction similarly to the Be-doped Ge lasers. We find that the spectral range of the emission broadens and we have observed lasing between 1.5 and 4 THz. Changing the direction of E redistributes the hole population within the valence subbands, and lasing conditions are achieved between different levels as reflected by the differing ranges in the emission spectra.

The onset of stimulated emission at a higher photon energy for the case of Ge:Cu compared to Ge:Be is related to the deeper ground state of the copper acceptors. The stronger localization of the Cu-acceptor ground state requires that higher electric fields be applied in order to impact ionize the neutral Cu centers.⁸ In the range of small E fields (and small B fields) where lasers normally operate, stimulated emission is not achieved due to the low density of holes in the valence band. Because of the partial ionization of Cu acceptors throughout the operating E - B conditions, Cu-doped Ge lasers can operate with acceptor densities that are significantly higher than for lasers containing either single or double acceptors.

By removing the effect of dopant self-absorption and improving the power dissipation of the laser during operation, we have reached record duty cycles as high as 2.5%. Also, we have observed additional features in the emission spectra of these materials.⁹ Studies on the nature of this new emission are under way.

IV. Conclusion

We have shown stimulated emission from Be-, Zn- and Cu-doped Ge single crystals. By doping with these acceptors and significantly reducing the shallow impurity background during crystal growth, we have been able to produce lasers that are continuously tunable from 1 to 4 THz. Understanding the dynamics of terahertz emission in these new materials systems will be crucial to the development of a cw p-Ge laser.

Acknowledgments

The authors are grateful to J.W. Beeman (LBNL), K. Roderick (LBNL), and W. Esch (MPIfR Bonn) for their technical support. This work was performed

with facilities at the Lawrence Berkeley National Laboratory operated under U.S. DOE Contract No. DE-AC03-765F00098.

- 1 E. Bründermann, A.M. Linhart, H.P. Röser, O.D. Dubon, W.L. Hansen and E.E. Haller, Proc. of 7th Int'l. Symp. on Space Terahertz Technol., Charlottesville, VA, USA, p. 187 (1996).
- 2 For a comprehensive review see: E. Gornik and A.A. Andronov (Eds.), *Optical and Quantum Elec.*, Special issue **23** (2), S111-S310 (1991). Also see: E. Bründermann, H.P. Röser, W. Heiss, E. Gornik and E.E. Haller, *Appl. Phys. Lett.* **67**, 3543 (1995); and E. Bründermann, A.M. Linhart, H.P. Röser, O.D. Dubon, W.L. Hansen and E.E. Haller, *Appl. Phys. Lett.* **68**, 1359 (1996).
- 3 W. Heiss, K. Unterrainer, E. Gornik, W.L. Hansen and E.E. Haller, *Semicond. Sci. Technol.* **9**, 638 (1994).
- 4 E. Bründermann, A.M. Linhart, L. Reichertz, H.P. Röser, O.D. Dubon, G. Sirmain, W.L. Hansen and E.E. Haller, *Appl. Phys. Lett.* **68**, 3075 (1996).
- 5 G. Sirmain, L.A. Reichertz, O.D. Dubon, E.E. Haller, W.L. Hansen, E. Bründermann, A.M. Linhart and H.P. Röser, *Appl. Phys. Lett.* **70**, 1659 (1997).
- 6 H.H. Woodbury and W.W. Tyler, *Phys. Rev.* **105**, 84 (1957); and R. N. Hall and J. H. Racette, *J. Appl. Phys.* **35**, 379 (1964).
- 7 N.M. Haegel and E.E. Haller, *SPIE* **659**, 188 (1986).
- 8 P.R. Bratt, "Impurity germanium and silicon infrared detectors" in *Semiconductors and Semimetals*, edited by R.K. Willardson and A.C. Beer (Academic Press, New York, 1977), Vol. 12, p. 39.
- 9 L. A. Reichertz, O.D. Dubon, G. Sirmain, E. Bründermann, W.L. Hansen, D.R. Chamberlin, A.M. Linhart, H.P. Röser and E.E. Haller, submitted for publication (1997).