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To cite this version:
I. Melngailis. LASER ACTION AND PHOTODETECTION IN LEAD-TIN CHALCOGENIDES. Journal de Physique Colloques, 1968, 29 (C4), pp.C4-84-C4-94. <10.1051/jphyscol:1968412>. <jpa-00213616>

HAL Id: jpa-00213616
https://hal.archives-ouvertes.fr/jpa-00213616
Submitted on 1 Jan 1968

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LASER ACTION AND PHOTODETECTION IN LEAD-TIN CHALCOGENIDES

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Résumé. — Par suite du croisement des niveaux $L_d^-$ et $L_6^-$ qui a été proposé pour expliquer la variation de la bande interdite en fonction de la composition et de la température dans Pb$_{1-x}$Sn$_x$Te et Pb$_{1-x}$Sn$_x$Se, on peut obtenir des semi conducteurs de bande interdite arbitrairement petite en choisissant convenablement la composition de l’un ou l’autre de ces alliages. Comme on peut produire des cristaux d’excellente homogénéité et de bonne qualité, ou bien par la méthode de Bridgman, ou par la préparation en phase gazeuse, avec des recuits ultérieurs, ces alliages sont très utiles pour les sources et les détecteurs infrarouges.

On a observé l’émission laser dans les deux systèmes d’alliages à 12 °K et 77 °K. Des diodes laser ayant des longueurs d’onde d’émission jusqu’à 28 μ à 12 °K et 15 μ à 77 °K ont été préparées en utilisant Pb$_{1-x}$Sn$_x$Te où x va jusqu’à 0.27. On a mesuré les propriétés des lasers pour de nombreuses compositions dans l’intervalle 0,15 ≤ x ≤ 0,27. Il a été possible d’obtenir une puissance crête de sortie d’environ 0,1 watt à 13 μ, de lasers à 12 °K. Les mesures du déplacement sous champ magnétique de la longueur d’onde du laser pour un champ orienté selon [100] donnent une masse effective de 0,010 et un facteur g de 75 pour Pb$_{0,83}$Sn$_{0,17}$Te à 12 °K.

A l’heure actuelle, les détecteurs photovoltaïques ont des limites de 20 μ à 77 °K et 30 μ à 12 °K du côté des grandes longueurs d’onde. Les rendements quantiques externes sont proches de 0,5, qui est la limite imposée par la réflectivité, et les détectivités à 77 °K vont de 10$^6$ à 10$^{10}$ cm/W cm$^{-2}$/s pour des diodes dont le front de détection est dans la fenêtre atmosphérique de 8 à 14 μ. Les temps de réponse sont de l’ordre de 10$^{-5}$ s. On a étudié la photoconductivité dans des cristaux de Pb$_{1-x}$Sn$_x$Te obtenus par la méthode de Bridgman et recuits. La concentration de porteurs est comprise entre 2 × 10$^{15}$ et 8 × 10$^{15}$ cm$^{-3}$ et les mobilités sont de l’ordre de 3 × 10$^{4}$ cm$^2$ V$^{-1}$ s$^{-1}$ à 77 °K. Dans les échantillons réduits par attaque chimique jusqu’à une épaisseur de 20 à 50 μ, les détectivités à 77 °K vont de 10$^6$ à 10$^{10}$ cm/W cm$^{-2}$/s à des longueurs d’onde jusqu’à 15 μ. Des durées de vie d’environ 10$^{-5}$ s à 77 °K et 10$^{-6}$ s et 4,2 °K ont été mesurées par observation directe de la décroissance de la photoconductivité.

Abstract. — Due to the crossover of the $L_d^-$ and $L_6^-$ states which has been proposed to explain the variation of the energy gap with composition and with temperature in Pb$_{1-x}$Sn$_x$Te and Pb$_{1-x}$Sn$_x$Se, semiconductors with an arbitrarily small energy gap can be obtained by suitably choosing the composition of either alloy. Since crystals with excellent homogeneity and good quality can be produced by either Bridgman- or vapor-growing and subsequent annealing, these alloys are very useful for longwavelength infrared sources as well as detectors.

Laser emission has been observed in both alloy systems at 12 °K and 77 °K. Diode lasers with emission wavelengths as long as 28 μ at 12 °K and 15 μ at 77 °K have been fabricated using Pb$_{1-x}$Sn$_x$Te with x up to 0.27. Laser properties have been measured for a number of compositions in the range 0.15 ≤ x ≤ 0.27. A peak output power of about 0.1 watt has been obtained at 13 μ from diode lasers at 12 °K. Measurements of the magnetic shift of the laser wavelength for a (100) oriented magnetic field give an effective mass of 0.010 and a g-factor of 75 for Pb$_{0.83}$Sn$_{0.17}$Te at 12 °K.

Photovoltaic detectors at present have long wavelength limits of 20 μ at 77 °K and 30 μ at 12 °K. External quantum efficiencies are close to the reflection-limited maximum of 0.5 and detectivities at 77 °K range from 10$^6$ to 10$^{10}$ cm/W cm$^{-2}$/s for diodes with cutoff wavelengths in the 8 to 14 μ atmospheric window. Response speeds are of the order of 10$^{-5}$ s. Photoconductivity has been studied in Bridgman-grown and subsequently annealed Pb$_{1-x}$Sn$_x$Te crystals with carrier concentrations between 2 × 10$^{15}$ and 8 × 10$^{15}$ cm$^{-3}$ and mobilities of about 3 × 10$^{4}$ cm$^2$ V$^{-1}$ s$^{-1}$ at 77 °K. In samples etched down to a thickness of 20 to 50 μ detectivities at 77 °K range from 10$^6$ to 10$^{10}$ cm/W cm$^{-2}$/s at wavelengths up to 15 μ. Lifetimes of approximately 10$^{-5}$ s at 77 °K and 10$^{-6}$ s at 4.2 °K have been measured by direct observation of the photoconductivity decay.

(*) Operated with support from the U. S. Air Force.
1. Band Structure. — The model for the energy bands in Pb$_{1-x}$Sn$_x$Te and Pb$_{1-x}$Sn$_x$Se was originally proposed [1] to explain the variation of the energy gap with composition and with temperature in Pb$_{1-x}$Sn$_x$Te which was inferred from laser emission at low temperatures [1, 2], from optical absorption data at room temperature [3, 4] and from the results of tunneling experiments [5]. According to the model, which to date appears to be consistent with all experimental results, the energy gap first decreases with increased Sn content as the conduction and valence band states (L$_5^c$ and L$_6^c$ respectively [6]) approach each other, goes to zero at an intermediate composition and then increases as the states cross over and separate. Since the L$_5^c$ and L$_6^c$ states each have only a twofold spin degeneracy the alloy can be a semiconductor on both sides of the crossover. This variation of the energy gap with composition can be explained on the basis of the difference in the relativistic effects [7] in Pb and Sn. Figure 1 shows the variation of the energy gap with composition in Pb$_{1-x}$Sn$_x$Te at 120° and 77°K as determined from laser wavelengths [1, 2, 8, 9], photovoltaic cutoffs [10] and from tunneling data for SnTe [5].

On the basis of the difference between the relativistic shifts in Pb and Sn, similar variations in band structure with composition could be expected in the Pb$_{1-x}$Sn$_x$Se and Pb$_{1-x}$Sn$_x$S alloys with rocksalt structure. In Pb$_{1-x}$Sn$_x$Se, which can be grown with the rocksalt structure in the range 0 < x < 0.4 [13], this variation has been demonstrated by means of laser emission [8, 11] and photovoltaic effect [12], as shown in figure 2, as well as by optical absorption in thin films [13]. The observation of laser emission out to a wavelength of 28 μ in Pb$_{1-x}$Sn$_x$Te and to 19 μ in Pb$_{1-x}$Sn$_x$Se provides evidence that the energy gap remains direct at least down to 0.046 eV and 0.065 eV in the two alloys respectively.

2. Preparation of Materials. — Crystals of both Pb$_{1-x}$Sn$_x$Te and Pb$_{1-x}$Sn$_x$Se grown by the Bridgman method are found to be very homogeneous in their Pb-Sn ratio [14]. Within the experimental accuracy of the electron microprobe of ± 0.005, no variation can be detected in the Pb-Sn ratio across the surface of crystal slices (typically 1.5 cm diameter) cut perpendicular to the growth direction. The as-grown crystals are p-type with a hole concentration of about 10$^{19}$ cm$^{-3}$, which is attributed to a deviation from stoichiometry due to an excess of Te and Se in Pb$_{1-x}$Sn$_x$Te and Pb$_{1-x}$Sn$_x$Se respectively. To reduce the carrier concentration, slices of the crystal are annealed under controlled conditions of temperature and vapor pressure [14]. Pb$_{1-x}$Sn$_x$Te crystals are annealed isothermally in an evacuated ampoule using a crushed Pb-Sn rich ingot as a vapor source to anneal out the excess Te by diffusion. By using this technique carrier concentrations as low as 2 x 10$^{15}$ cm$^{-3}$ with mobilities of 3 x 10$^4$ cm$^2$/Vs at 77°K have been obtained in Pb$_{1-x}$Sn$_x$Te crystals in the 0 < x < 0.2 composition range. A two-zone annealing technique is used in the case of Pb$_{1-x}$Sn$_x$Se, where the crystal slice and a Se pellet are located at opposite ends of a closed evacuated tube. The temperature of the Se, which determines the vapor pressure, can thus be adjusted independently of the sample temperature. The crystal growth and the annealing procedures for both alloys are described in detail elsewhere [14].

![Figure 1. Energy gap of Pb$_{1-x}$Sn$_x$Te as a function of x, the mole fraction of SnTe. The data points have been obtained from laser wavelengths [1, 2, 8, 9] photovoltaic cutoffs [10] and from tunneling experiments in SnTe [5].](image)

![Figure 2. Energy gap of Pb$_{1-x}$Sn$_x$Se as a function of x, the mole fraction of SnSe. The data points have been obtained from laser wavelengths [8, 11] and photovoltaic cutoffs [12].](image)
Crystals of both alloys have also been grown from a vapor in a closed ampoule containing a crushed alloy ingot. These crystals measure from a fraction of a millimeter to several millimeters, and are usually annealed in their as-grown form.

3. Laser Characteristics. — 3.1 Optical Pumping. — Laser action was first observed in Pb_{1-x}Sn_xTe at 12 K by optically pumping small vapor-grown crystals with 0.84 μ radiation from a GaAs diode laser [1]. Both the sample and GaAs diode were mounted on a liquid helium cooled copper heatsink in such a way that the laser cavity of the sample was formed by two parallel faces which were perpendicular to the surface irradiated by the GaAs laser beam.

The vapor-grown n-type crystals (n ≈ 2 × 10^{17} cm^{-3} at 77 K) had the as-grown shape of a rectangular parallelepiped, typically ½ mm long in the direction of laser emission. The laser thresholds were typically at 1 to 2 W of the 0.84 μ pump power. Coherent emission was obtained at several wavelengths between 10 and 16 μ by optically pumping alloys with compositions up to x = 0.2.

3.2 Diode Lasers. — P-n junction lasers have been made from both Pb_{1-x}Sn_xTe [8, 9] and Pb_{1-x}Sn_xSe [8, 11] using both Bridgman-grown and vapor-grown crystals. The p-n junctions are generally prepared by altering the stoichiometry of a layer near the surface by means of diffusion. The diffusion technique [14] is very similar to that used in isothermal annealing. Whereas in annealing the entire crystal is allowed to come to equilibrium, in junction fabrication the time and temperature are chosen so as to convert the type of a thin layer.

As the Sn content of Pb_{1-x}Sn_xTe is increased beyond x = 0.25 it becomes increasingly more difficult to convert the crystals to n-type by annealing. Thus, in fabricating diodes from some of the higher composition Pb_{1-x}Sn_xTe crystals, bismuth doping was used to aid in producing an n-type layer on a p-type substrate.

A method of vapor-growth, annealing, and junction formation by diffusion all performed in a combined operation has proven to be particularly successful in the fabrication of diode lasers. A schematic diagram of the growth and diffusion-annealing ampoule is shown in figure 3a. The evacuated (10^{-7} torr) ampoule is suspended in a vertical tubular furnace, which has the temperature profile shown in figure 3b. The temperature difference between the source material and vapor-grown crystals was about 1°C. The vapor source, which is a two-phased coarse powder obtained from a quenched ingot of composition

\[(\text{Pb-Sn})_{0.51}\text{Te}_{0.49},\]

is contained in the inner quartz tube. The crystals usually grow on the walls of the ampoule in the conical tip region. After a growing time of approximately 20 hrs., the tube is air-cooled. Crystals with (100) surfaces 1 mm² or larger in area have been obtained by this method. The rapidly cooled, as-grown crystals are p-type with bulk interior carrier concentrations of the order of 10^{19} cm^{-3}. N-type layers of thickness > 25 μ were diffused by isothermally annealing the crystals in a horizontal furnace in the unopened growth ampoule and thus in the presence of the remaining source ingot. This method of preparing junctions utilizes the property [14] that, at least for values of x up to x = 0.27, metal-saturated crystals change from p-type to n-type conductivity as the temperature is decreased. From isothermal metal-saturation experiments, type conversion temperatures of 580 °C, 525 °C, and 425 °C are estimated for x = 0.17, 0.20, and 0.27 respectively. For x < 0.27 annealing parameters for junction formation are given in Table I. For x = 0.27, the annealing schedule for preparing junctions was 4 hrs. at 700 °C, 6 days at 650 °C, 7 days at 450 °C and 21 days at 400 °C, giving an n-region approximately 30 μ deep. Annealing studies indicate the surface electron concentration of annealed undoped Pb_{0.37}Sn_{0.27}Te to be < 10^{16} cm^{-3}.
After annealing, laser structures in the shape of rectangular parallelepipeds were obtained by cleaving perpendicular and parallel to natural (100) faces. To reduce planarity and reflectivity of the longer pair of sides perpendicular to the p–n junction plane, these were subjected to a chemical etch consisting of equal volumes of a saturated water solution of Na₂S₂O₈ and a 15 wt. % water solution of NaOH. This leaves the smaller end faces to define the Fabry-Perot cavity. Linear dimensions of the lasers were typically a few hundred microns. Electrical contacts to the entire top and bottom surfaces were made with electroplated gold followed by electroplated indium. The laser structures were mounted in low-inductance packages and leads were attached by room-temperature bonding with indium.

It has been consistently found that a final fabrication step consisting of the removal by an electrolytic etch (20 g KOH, 45 ml H₂O, 35 ml glycerin, and 20 ml ethanol [15]) of approximately 10 μ of material from the four exposed laser sides reduces the threshold currents by at least 50%. This may be due to the removal of a damaged layer at the cleaved faces which exhibits a high rate of nonradiative recombination. Etching studies have shown that such damage exists to a depth of at least several microns [16]. The volt-ampere characteristics of the diode lasers exhibit a marked increase in zero-bias impedance after the electrolytic etch, which is evidence of the removal of a region with a high recombination rate.

Several lasers were fabricated at each of a number of compositions and were evaluated at 77 °K and 12 °K. Spectral measurements were made with a prism spectrometer using either a KBr or a CsI prism and liquid He cooled Cu-activated Ge detector. The diodes were mounted on a copper heat sink in contact with the liquid refrigerant in a dewar equipped with KRS-5 windows. The spectrum of a Pb₀.₇₃Sn₀.₂₇Te laser, which at 28 μ is the longest wavelength semiconductor laser to date, is shown in figure 4. Modes of the Fabry-Perot cavity, pointed out by arrows in the figure, are well resolved and evenly spaced. Emission wavelengths and minimum threshold current densities for a number of compositions are listed in Table I. In every case

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![Graph of emission spectrum](image)

**Figure 4.** Emission spectrum of a Pb₀.₇₃Sn₀.₂₇Te diode laser at 12 °K.

**Table I**

<table>
<thead>
<tr>
<th>x</th>
<th>Annealing Time (Days)</th>
<th>Annealing Temp. °C</th>
<th>Emission 12 °K</th>
<th>Wavelength (μ) 77 °K</th>
<th>Minimum Threshold Current Density (A/cm²)</th>
<th>12 °K</th>
<th>77 °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>None</td>
<td></td>
<td>11.7</td>
<td>9.5</td>
<td>250</td>
<td>3,000</td>
<td></td>
</tr>
<tr>
<td>0.17</td>
<td>2</td>
<td>450</td>
<td>13.0</td>
<td>9.9</td>
<td>55</td>
<td>10,000</td>
<td></td>
</tr>
<tr>
<td>0.19</td>
<td>3</td>
<td>450</td>
<td>14.5</td>
<td>11.0</td>
<td>130</td>
<td>9,000</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>3</td>
<td>450</td>
<td>15.1</td>
<td>11.2</td>
<td>275</td>
<td>12,500</td>
<td></td>
</tr>
<tr>
<td>0.21</td>
<td>2</td>
<td>450</td>
<td>16.8</td>
<td>12.0</td>
<td>175</td>
<td>7,000</td>
<td></td>
</tr>
<tr>
<td>0.22</td>
<td>7</td>
<td>450</td>
<td>17.2</td>
<td>—</td>
<td>175</td>
<td>&gt; 30,000</td>
<td></td>
</tr>
<tr>
<td>0.24</td>
<td>14</td>
<td>400</td>
<td>20.0</td>
<td>—</td>
<td>230</td>
<td>&gt; 30,000</td>
<td></td>
</tr>
<tr>
<td>0.25 (a)</td>
<td>3</td>
<td>450</td>
<td>22.4</td>
<td>14.9</td>
<td>75</td>
<td>5,000</td>
<td></td>
</tr>
<tr>
<td>0.27</td>
<td>see text</td>
<td>see text</td>
<td>28.0</td>
<td>—</td>
<td>125</td>
<td>&gt; 30,000</td>
<td></td>
</tr>
</tbody>
</table>

(a) The quenched ingot used for the vapor growth source was doped with 4 × 10¹⁹ Bi atoms/cm³.
laser action was evidenced by a spectrum with a well-defined mode structure exhibiting the mode spacing expected for the Fabry-Perot cavity.

Power measurements were performed on a

$$\text{Pb}_{0.88}\text{Sn}_{0.20}\text{Te}$$

laser using a calibrated thermopile positioned so as to intercept nearly all of the radiation emitted from one laser end face. With pulse bias, a peak power output of 0.1 watts at 15 amps corresponding to an external quantum efficiency \( \eta_x \) of 0.08, was observed at 12 °K and a peak power of 0.03 watts at 25 amps, giving \( \eta_x = 0.01 \), was measured at 77 °K. With CW operation at 12 °K, \( 5 \times 10^{-3} \) watts at 2 amps, corresponding to \( \eta_x = 0.03 \), was observed.

Similar results have been obtained with \( \text{Pb}_{1-x}\text{Sn}_x\text{Se} \) diode lasers. Figure 5 shows the peak 13 μ wavelength infrared power output of a \( \text{Pb}_{0.945}\text{Sn}_{0.055}\text{Se} \) diode laser at 12 °K as a function of pulsed current density.

![Figure 5](image)

**Fig. 5.** Peak 13 μ wavelength infrared power output of a \( \text{Pb}_{0.945}\text{Sn}_{0.055}\text{Se} \) diode laser at 12 °K as a function of pulsed current density.

The duty cycle was about 10⁻⁴. The maximum power of 80 milliwatts corresponds to an external quantum efficiency of about 0.05. The output power continues to rise superlinearly even at the highest measured levels, indicating that the internal quantum efficiency has not attained its limiting value. This implies that power output for this diode is probably still limited by some competing recombination process. The nature of the competing process is not presently known. However, earlier studies of photoluminescence in PbTe and PbSe indicate that there may be important non-radiative recombination centers associated with lattice defects [17]. This is consistent with measurements of photoconductive lifetime described below.

Preliminary measurements of the spatial distribution of the emission were made on a \( \text{Pb}_{0.945}\text{Sn}_{0.055}\text{Se} \) diode which at 12 °K emitted in a single mode near 13 μ. The beam angle in the plane of the junction was about 1.5°, indicating that nearly the entire 500 μ wide face of the diode was emitting. In the plane perpendicular to the junction the angle was limited by the diode package but was at least 30°, corresponding to a maximum 25 μ width for the emitting region in this direction.

A number of factors may act to limit the longest wavelength one may hope to achieve with these lasers. In the vicinity of 90 microns, for example, interaction with LO phonon modes is expected [18]. This will probably quench laser action, but may produce other interesting effects associated with phonon generation. We feel, however, that diode laser action between 50 and 100 microns is not an unrealistic goal.

### 3.3 Effects of Pressure and Magnetic Field

The tuning of laser wavelength by means of hydrostatic pressure has been previously observed in PbSe diode lasers [19]. By applying a pressure of 14 kilobars to a PbSe diode laser at 77 °K the wavelength has been changed from 7.5 μ to 22 μ corresponding to a decrease of energy gap from 0.165 eV to 0.056 eV. Applying a pressure of this magnitude to small-energy gap lead-tin alloys on the Pb-rich side of the zero-energy gap composition should bring about crossing of the \( L_d \) and \( L_g \) states, and a tuning of the energy gap through the zero point. A study of laser emission during this process may aid in determining the long-wavelength limit of the lasers and provide information about the band-structure in the near-zero gap region.

Laser emission corresponding to transitions between magnetic levels of the conduction and valence bands has previously been studied in PbTe and PbSe [5]. Similar results are observed in the Pb-Sn alloys. Figure 6 shows the photon energy of the emission of an optically pumped \( \text{Pb}_{0.88}\text{Sn}_{0.17}\text{Te} \) laser as a function of magnetic field. The two branches correspond to transitions between sublevels of spin-split, zero-order Landau levels. The magnetic field here is oriented in a [100] crystallographic direction. The two branches have been previously observed in PbTe and PbSe lasers. By means of polarization measurements the upper line has been identified with the nearly degenerate pair of spin-reversing transitions between \( l = 0 \) Landau
levels (b and c in the inset in figure 8) and the lower line with the lowest energy spin conserving transition (a). If the effective masses and the g-factors for the valence and conduction bands are assumed equal [5] the upper line gives the reduced effective mass as \( m^* = 0.010 \), and the energy difference between the two lines gives a g-factor of 75. The reduced mass for PbTe which has an energy gap of 0.18 eV is 0.022, i.e. the effective mass in the alloys appears to be very nearly directly proportional to the gap energy, as expected, at least down to a gap of 0.08 eV.

4. Photovoltaic Effect. — Sensitive photovoltaic detectors have been fabricated from both Pb\(_{1-x}\)Sn\(_x\)Te [10] and Pb\(_{1-x}\)Sn\(_x\)Se [12]. A typical structure of a photovoltaic diode is shown in figure 7. The infrared radiation is absorbed within approximately one micron of the surface and the photogenerated carriers diffuse to the junction. The p-n junctions are prepared in a way very similar to that used in lasers. Both Bridgman and vapor grown crystals have been used as starting materials. The stoichiometry of a thin layer of 5 to 10 \( \mu \) is altered by means of diffusion. In some cases the diffusion was made through a circular opening in a Si\(_2\)O\(_2\) diffusion mask, show in figure 7, which was prepared by using photo-resist techniques. The diode is mounted on a copper heat sink after making electrical contacts by electroplating gold and indium. In the case of vapor grown crystals the combined operation of vapor-growth, annealing, and diffusion described in connection with lasers has been successfully applied to photovoltaic diodes as well. A number of etches have been used to reduce the surface recombination in the active area, to reduce the junction depth, and to improve the current voltage characteristics of diodes. For Pb\(_{1-x}\)Sn\(_x\)Te diodes the electrolytic etch [15] mentioned earlier in connection with diode lasers has been found most successful. A chemical etch consisting of a concentrated solution of KOH, H\(_2\)O\(_2\) and ethylene glycol [20] has also been used with some success. For Pb\(_{1-x}\)Sn\(_x\)Te the volume ratio of the ingredients was 10 : 1 : 10, respectively and for Pb\(_{1-x}\)Sn\(_x\)Se 10 : 2 : 10.

Response spectra were measured with the diodes in the unbiased open-circuit condition using a globar source and a prism spectrometer. To determine the values of responsivity and efficiency a calibrated blackbody source, chopped at 900 cps was used. Noise measurements were made using a Princeton Applied Research type B low-noise preamplifier with a 1 : 100 or a 1 : 350 step-up transformer. With this arrangement it was possible to measure thermal noise of resistors of several ohms at 77 °K.

The responsivity spectra of a Pb\(_{0.93}\)Sn\(_{0.06}\)Se diode at three temperatures are shown in figure 8. At 77 °K the responsivity peaks at 11 \( \mu \) and hence this diode is particularly useful for detecting the 10.6 \( \mu \) CO\(_2\) laser radiation. The peak in response just prior to cutoff is attributed to an increase in the number of
photo-excited carriers at the junction as the radiation begins to penetrate the n-type layer in the vicinity of the band-gap absorption edge of the crystal. When the surface recombination velocity and the junction depth are reduced by etching, the overall efficiency can be greatly enhanced and the peaking prior to cutoff eliminated. The response spectrum of a Pb_{0.936}Sn_{0.064}Se diode at 77 °K shown in figure 9 resembles more closely that of an ideal quantum detector. Photovoltaic cutoff wavelengths as long as 20 µ at 77 °K and 30 µ at 12 °K have been observed in Pb_{1-x}Sn_xTe diodes with a higher Sn content.

Detector parameters of a few representative diodes are summarized in table II. The efficiency defined as the number of carriers reaching the p-n junction per incident photon is limited by a loss of about 0.5 due to reflection at the surface and by losses due to recombination at the surface and in the bulk of the n-type layer. To optimize the efficiency the junction depth has been made smaller than the carrier diffusion length, the surface recombination velocity has been reduced by etching, and for some detectors the reflection has been reduced over a relatively broad wavelength range by antireflection coating with Se (see last detector in table II). The efficiencies of 0.37 and 0.4 for the uncoated detectors are reduced to 0.13 and 0.15, respectively, after antireflection coating with Se.

**Table II**

Properties of photovoltaic detectors

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Area (mm²)</th>
<th>Temperature (°K)</th>
<th>Cutoff Wavelength (µ)</th>
<th>Incremental Resistance (Ohm)</th>
<th>Efficiency</th>
<th>Peak Respons. (V/W)</th>
<th>Peak Detectivity (cm/Ws²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb_{0.936}Sn_{0.064}Se</td>
<td>0.78</td>
<td>77</td>
<td>11.5</td>
<td>2.5</td>
<td>0.15</td>
<td>3.5</td>
<td>3 × 10⁹</td>
</tr>
<tr>
<td></td>
<td>195</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb_{0.8}Sn_{0.2}Te</td>
<td>1.7</td>
<td>12</td>
<td>17</td>
<td>18</td>
<td>0.4</td>
<td>110</td>
<td>4 × 10¹⁰</td>
</tr>
<tr>
<td></td>
<td></td>
<td>77</td>
<td>13</td>
<td>1.3</td>
<td>0.01</td>
<td>0.15</td>
<td>3 × 10⁸</td>
</tr>
<tr>
<td>Pb_{0.86}Sn_{0.14}Te</td>
<td>0.1</td>
<td>77</td>
<td>9.5</td>
<td>180</td>
<td>0.14</td>
<td>190</td>
<td>5.3 × 10⁹</td>
</tr>
<tr>
<td>Pb_{0.81}Sn_{0.15}Te</td>
<td>0.1</td>
<td>77</td>
<td>12</td>
<td>16</td>
<td>0.37</td>
<td>70</td>
<td>7.5 × 10⁹</td>
</tr>
<tr>
<td>Pb_{0.85}Sn_{0.15}Te</td>
<td>0.17</td>
<td>77</td>
<td>10</td>
<td>25</td>
<td>0.32</td>
<td>64</td>
<td>8 × 10⁹</td>
</tr>
<tr>
<td>Pb_{0.89}Sn_{0.11}Te</td>
<td>0.18</td>
<td>77</td>
<td>12</td>
<td>10</td>
<td>0.19</td>
<td>18</td>
<td>3.7 × 10⁹</td>
</tr>
<tr>
<td>Pb_{0.84}Sn_{0.16}Te</td>
<td>0.4</td>
<td>77</td>
<td>9.5</td>
<td>8</td>
<td>0.43</td>
<td>32</td>
<td>6.8 × 10⁹ (*)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.60</td>
<td>45</td>
<td>1.1 × 10¹⁰ (*)</td>
</tr>
</tbody>
</table>

(*) After antireflection coating with Se.
ted diodes are close to the theoretical limit of 0.5. The measured values of noise voltage were between $10^{-10}$ and $10^{-9}$ volts in a 1 cps bandwidth and agreed in every case very closely with the Johnson noise calculated for the incremental diode resistance at zero bias.

For a Johnson-noise limited detector we can readily calculate the maximum achievable detectivity for a specified peak wavelength and operating temperature. The responsivity of a photovoltaic detector in volts per watt can be written as $R = \frac{q\eta R}{E_x}$ where $R$ is the incremental diode resistance at zero bias, and $E_x$ is the photon energy; $\eta$ is the quantum efficiency, which for a detector structure of the type shown in figure 7 can be expressed as

$$\eta = \frac{1 - r}{\cosh \frac{d}{L_h} + \frac{s\tau_s}{L_h} \sinh \frac{d}{L_h}}.$$  

(1)

Here $r$ is the reflectivity of the detector surface, $s$ the surface recombination velocity, $\tau_s$ the hole lifetime in the $n$ region and $L_h$ the hole diffusion length. For the case of Johnson-noise limited operation the noise voltage is given by $V_n = (4kTR\Delta f)^{1/2}$ and the detectivity (for a 1 cps bandwidth) is

$$D_\lambda^* = \frac{\mathcal{R}_s A^{1/2}}{V_n} = \frac{q\eta (RA)^{1/2}}{2E_x(kT)^{1/2}}.$$  

(2)

Thus the detectivity is proportional to the efficiency and to the square root of the incremental diode resistance. If the diode resistance scales with the junction area, the detectivity is area independent.

In ideal diodes in which the current is due to minority carrier injection, the detectivity is limited by the reverse saturation current $I_0$, since in such diodes $R = kT/qI_0$. If the diode current is predominantly due to electron injection then

$$RA = (kT\tau_e)^{1/2}/q^{3/2} n_p \mu_e^{1/2},$$

where $n_p$ is the equilibrium density of electrons in the $p$-region, $\mu_e$ is the electron mobility, and $\tau_e$ is the electron lifetime. For an alloy whose energy gap at 77 °K is 0.1 eV (peak photoresponse at about 12 μ), the calculated intrinsic carrier concentration

$$n_i = 2.2 \times 10^{13} \text{ cm}^{-3}.$$  

Assuming a majority carrier density of $5 \times 10^{16} \text{ cm}^{-3}$ adjacent to the junction, $n_p$ is about $10^{19} \text{ cm}^{-3}$. For a typical mobility of $2 \times 10^4 \text{ cm}^2/Vs$ and a lifetime of $10^{-8}$ s, estimated from photoconductivity measurements, $RA = 40 \Omega \text{ cm}^2$. This gives an estimate of $10^{12} \text{ cm/Ws}^{1/2}$ for the maximum achievable detector-noise limited $D_\lambda^*$, if the quantum efficiency is assumed to be unity. (The detectivity limited by noise due to the photon flux of a room temperature background for a $2\pi$ steradian aperture is about $5 \times 10^{10} \text{ cm/Ws}^{1/2}$ in this wavelength range.)

Since the measured efficiency values in present devices are already close to the theoretical limit, the largest improvement can be expected from increasing the diode resistance. The highest resistance diode in table II has an RA of 0.18 Ω cm². Although the conduction mechanisms responsible for the reverse current are not certain at present, there is evidence that at least in some cases a shunt conductance is created by metallic inclusions in the crystal [16]. The highest value of incremental resistance corresponding to an RA of about 2 has been observed in a Pb₀.₈₅Sn₀.₁₅Te laser diode, for which the current-voltage characteristic is shown in figure 10. Although

![Fig. 10. — Current-voltage characteristic of a 0.2 mm² Pb₀.₈₅Sn₀.₁₅Te diode at 77 °K.](image)

the structure of this diode was not suitable for photodetection, the relatively low reverse current indicates that large improvements in the detectivity of photovoltaic detectors should indeed be possible.

The speed of response of detectors was measured by observing the photovoltage due to a light pulse from a GaAs diode laser. The photovoltage pulse shown in figure 11 has a rise (and fall) time of about 15 nsec.

![Fig. 11. — Response of a Pb₀.₉₃₆Sn₀.₀₆₄Se diode at 77 °K to a GaAs laser pulse.](image)
which in this case corresponds to the effective carrier lifetime. Since we expect that the effective lifetime can be reduced by decreasing the junction depth and hence the carrier storage time, the speed will ultimately be limited by the junction capacitance. Based on the diode RC time constant, a response time of 1 nsec with a detectivity of about $10^{10} \text{cm/W}^{1/2}$ should be possible for the lead-tin alloy diodes.

5. Photoconductivity. — Photoconductivity at wavelengths up to 15 μ at 77 °K has been observed in Bridgman-grown and subsequently annealed crystals of Pb$_{1-x}$Sn$_x$Te [21]. The annealing parameters and the resulting carrier concentrations and mobilities of the crystals used for photoconductors are shown in Table III. The two compositions, $x = 0.17$ and 0.20 are

<table>
<thead>
<tr>
<th>Crystal No.</th>
<th>$x$</th>
<th>Sample Temperature (°C)</th>
<th>Annealing Time (days)</th>
<th>Sample Thickness (mm)</th>
<th>Hall Carrier Concentration at 77 °K (cm$^{-3}$)</th>
<th>Hall Carrier Mobility at 77 °K (cm$^2$/V·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>66-16A</td>
<td>0.17</td>
<td>500</td>
<td>22</td>
<td>0.29</td>
<td>$2.3 \times 10^{15}$ P</td>
<td>$3.1 \times 10^4$</td>
</tr>
<tr>
<td>66-16B</td>
<td>0.17</td>
<td>450</td>
<td>38</td>
<td>0.27</td>
<td>$5.8 \times 10^{15}$ P</td>
<td>$2.6 \times 10^4$</td>
</tr>
<tr>
<td>67-41</td>
<td>0.20</td>
<td>600</td>
<td>8</td>
<td>0.25</td>
<td>$7.5 \times 10^{15}$ N</td>
<td>$3.2 \times 10^4$</td>
</tr>
<tr>
<td>67-3R</td>
<td>0.17</td>
<td>450</td>
<td>14</td>
<td>0.06</td>
<td>$2.6 \times 10^{16}$ N</td>
<td>$2.9 \times 10^4$</td>
</tr>
</tbody>
</table>

of particular interest for detectors because for the 0.17 alloy the photoconductivity at 77 °K peaks very close to the 10.6 μ CO$_2$ laser wavelength, whereas for the 0.20 alloy the peak is at 14 μ, i.e., detectors of this composition cover the 8-14 μ atmospheric window.

After annealing, the samples were chemically etched (10 KOH, 1 H$_2$O$_2$, 10 ethylene glycol) both to reduce their thickness and to lower the surface recombination velocity. Contacts were made by electroplating gold. In order to insure uniform cooling and to avoid the danger of thermal stresses the samples were immersed directly in the liquid coolant in preference to mounting them on a heat sink. Figure 12 shows the response spectra of two photoconductors at 77 °K, one for a 0.17 and one for a 0.20 alloy. The response peaks are at 10 and 14 μ respectively. Prior to the cutoff there is a small peak as the radiation begins to penetrate into the bulk where the lifetime of carriers is longer than near the surface. The fact that the peak is small indicates that the surface recombination velocity is not very high, and that the effective photoconductive lifetime provides an approximate measure of the bulk lifetime.

Properties of a number of photoconductors are shown in Table IV. At 77 °K the noise measured at 900 Hz at the bias current used was generally less than twice the Johnson noise calculated for the sample resistance. The excess portion of the noise increased with the bias current and decreased with frequency. In case of the first sample in Table IV the measured noise at 900 Hz was about 50 % higher than the Johnson noise for the 42 Ω resistance at 77 °K. At frequencies higher than 4 kHz the noise was thermal and the peak detectivity increased to $4.5 \times 10^8 \text{cm/W}^{1/2}$.

![Fig. 12. — Responsivity spectra of Pb$_{1-x}$Sn$_x$Te photoconductors at 77 °K.](image-url)
At 4.2 °K the sensitivity is greatly improved because the lifetime at 4.2 °K is longer by about two orders of magnitude than at 77 °K. Lifetime measurements obtained by observing directly the decay of the photoconductivity current following a GaAs diode laser pulse are shown in table IV for a number of temperatures. For the crystals for which both responsivity and lifetime measurements were available the lifetime calculated from the responsivity was in good agreement with the measured lifetime.

The radiative recombination lifetime at 77 °K estimated following a treatment outlined by Smith [22] is about $10^{-5}$ s in Pb$_{1-x}$Sn$_x$Te with an energy gap of 0.1 eV and with a carrier concentration of $5 \times 10^{13}$ cm$^{-3}$.

<table>
<thead>
<tr>
<th>Crystal No.</th>
<th>Dimensions (mm)</th>
<th>Temperature (°K)</th>
<th>Resistance (Ohms)</th>
<th>Bias Current (ma)</th>
<th>Respons. (V/W)</th>
<th>Cutoff Wavelength (µ)</th>
<th>Peak Detectivity cm/Ws$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>66-16B</td>
<td>Length Width</td>
<td>77</td>
<td>42</td>
<td>10</td>
<td>0.7</td>
<td>11</td>
<td>$3 \times 10^8$</td>
</tr>
<tr>
<td></td>
<td>Thickness</td>
<td>4.0</td>
<td>2.0</td>
<td>0.05</td>
<td>2.0</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>67-41</td>
<td>1.5</td>
<td>77</td>
<td>13</td>
<td>30</td>
<td>0.6</td>
<td>15</td>
<td>$1 \times 10^8$</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.0</td>
<td>0.05</td>
<td>1.0</td>
<td>0.01</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

Since Auger recombination has previously been found to be insignificant in PbTe [17], the lifetime in the Pb$_{1-x}$Sn$_x$Te photoconductors at 77 °K and higher temperatures is probably associated with dislocations or other crystalline imperfections. At temperatures below 77 °K radiative recombination may begin to play a major role because at 4.2 °K the calculated radiative lifetime agrees within an order of magnitude with the measured lifetime. This is also consistent with the higher efficiency and lower threshold in diode lasers at lower temperatures.

At 77 °K improvements by at least two orders of magnitude in the detectivity of photoconductors can be expected from an increase of lifetime with decreased imperfection density, a further decrease in the carrier concentration and a further reduction of sample thickness.

**References**

[21] MELNGAILIS (I.) and HARMAN (T. C.), to be published.

DISCUSSION

omez, J. N. — A) In the case of the Pb salt photoconductive detectors, the surface recombination velocity, s, is very small, virtually zero as best as can be told. Is the s in these alloys due to a surface process on a damaged layer in the neighborhood of the surface?

B) You have used the term «relativistic» shifts in describing the band crossing in Pb1−xSnxSe Te. In Pb1−xCdx chalcogenides, the band gap increases with x. Is it really appropriate to ascribe the band crossing exclusively to «relativistic» contributions to the band structure?

MELNGAILIS, I. — A) Our experiments cannot distinguish between surface recombination and recombination in a thin (≤ 2 µ) short-lifetime layer adjacent to the surface. However, the photoconductivity work of Coates, Lawson and Prior seems to contradict your statement. They quote a minimum surface recombination velocity of 80 cm sec⁻¹ for PbSe.

B) Although the difference in the relativistic effects in Pb and Sn can account for the shift of the Lσ and Lπ states necessary to produce the crossing of the bands, we do not rule out the simultaneous presence of other effects on the band structure, such as the ones associated with changes in atomic spacing with alloy composition, as pointed out by Professor F. Herman. In any case, the variation of the energy gap in Pb1−xCd chalcogenides has no relevance to the gap variation in Pb1−xSn chalcogenides.

Paul, W. — You discussed the possibility of extending laser action to between 50 and 100 microns with a possible limit at 90 microns corresponding to LO phonon emission. Other intrinsic limiting processes are Auger recombination and recombination with multiphonon emission which conserves total momentum. Have you considered the possibility that the second of these processes may eventually limit the radiative recombination, and also incidentally provide new and interesting physical effects?

MELNGAILIS, I. — Auger recombination has been shown to be insignificant in PbTe by Cuff. We expect that it will still be weak compared to radiative recombination in Pb-Sn chalcogenides up to 100 µ. We do not know the strength of the multiphonon processes.

WOLFF, P. A. — What is radiative lifetime during laser action?

MELNGAILIS. — τ < 50 ns.