

Photoresponse of Metal-PbTe Structures to CO₂ Laser Excitation

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We report on the investigation of photoresponse signal arising across metal-PbTe structures exposed to CO₂ laser radiation. Three different metals, Al, Au, and Bi, have been used for Schottky diode-like structure fabrication. The experimental investigations of the photoresponse have been performed in temperature range from 240 K down to 92 K. The dependencies of the detected signal on the applied bias voltage and the signal decay transients were explored as well. Hot carrier effect as well as electron-hole pair generation are considered to be responsible for the photoresponse.

Keywords: Schottky contact, narrow band gap semiconductor, lead telluride, CO₂ laser, detection.

1. INTRODUCTION

Lead telluride (PbTe) and a wide range of its solid solutions represent a group of materials that are extensively used in different fields of optoelectronics and microelectronics, thermoelectricity, and even as gas sensors [1]. It is a narrow band gap semiconductor material with an energy gap $E_g = 190$ meV at $T = 0$ K temperature. Since the room temperature band gap of PbTe corresponds to the infrared spectral region of (3–5) μm , PbTe devices are often considered as promising middle IR range detectors [2].

PbTe compound, which crystallizes in the cubic rock salt structure, exhibits a number of electronic properties quite different from the tetrahedrally bonded cubic semiconductors, such as Si and Ge, or III-V compounds, such as GaAs, or II-VI compounds such as CdTe. In lead telluride, both the valence band maximum and the conduction band minimum occur at the L point of the Brillouin zone [1]. The band gap of PbTe has a positive temperature coefficient, i. e. in contrast to the energy gap of most classic semiconductors its value increases with temperature [3]. In addition, the Coulomb interaction in PbTe is reduced drastically due to extremely high value of the static dielectric constant (its value reaches almost 1000 at liquid nitrogen temperature [4]), what, along with low carrier effective mass, leads to a very small value of the ionization energy for shallow impurities ($\sim 10^{-5}$ eV– 10^{-6} eV). Thus, shallow states are not observed, and carrier concentration in the material is practically independent of temperature. These peculiar features of lead telluride make it attractive for optoelectronic applications in various infrared spectral regions.

On the other hand, Schottky barrier based diodes are well-known as first-rate detectors of radiation. Such attributes as: monolithic construction, possibility to tailor

cutoff wavelength by picking appropriate metal to a semiconductor, uniformity in responsivity and signal to noise, absence of noticeable $1/f$ noise; make Schottky barrier devices a challenging competitor to the mainstream infrared systems and applications [5].

Detection of CO₂ laser radiation of 10.6 μm wavelength (photon energy 117 meV) on PbTe structures has been already declared. The investigations were performed on Ni-PbTe ohmic and Schottky contacts [6, 7] at room and liquid nitrogen temperatures as well as on p - n -PbTe diodes in a 90 K–140 K temperature range [8]. The principal mechanism of photoresponse electrical signal formation in narrow band gap semiconductor structures exposed to CO₂ laser radiation was stated to be free carrier absorption of IR light and the consequent energy transfer to crystal lattice. Moreover, it was observed [6] but not emphasized [8] that in some cases the photoresponse signal rises also due to carrier generation resulting from two-photon absorption. Investigation of photosignal across potential barriers of different height can educe knowledge about its formation mechanisms.

In this paper we report a photoresponse signal across Schottky barrier (Al, Au, Bi)-PbTe structures under CO₂ single-pulse laser excitation in a 90 K–220 K temperature range.

2. EXPERIMENTAL DETAILS

For sample preparation, p -type PbTe single crystals were grown by Czochralski technique. The temperature gradient at the crystallization front and the crystal pull rate were of the order of (20–25) K/cm and (5–10) mm/h, respectively. Thus the crystals were grown with excess of tellurium (up to 1 at. %). Hall effect measurements of hole concentration which is equal to the concentration of lattice point defects, i.e. to the excess of Te, revealed it to be of the order of $(0.5–1) \times 10^{19}$ cm⁻³. Rectangular wafers have been cut from the single crystal ingots. One side of the

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wafer has been polished mechanically and electrochemically. In the electrochemical bath the wafer was used as anode and Pt plate served as cathode. 180 ml of Norr solution electrolyte (30 ml of ethanol, 30 g KOH, 52.5 ml glycerol and 67.5 ml H₂O) has been used in the process. The electrochemical treatment consisted of two competing processes: oxidation and dissolution of oxide.

The back contacts were prepared by physical vapor deposition of a thin (20 nm) layer of Cr followed by deposition of a 120 nm layer of Au onto the non-polished side of the wafer. The Cr layer ensures good adhesion of the golden layer to the PbTe and exhibits ohmic contact characteristics on *p*-type PbTe. Al, Au and Bi metallic ~20 nm-thick contacts were formed by physical vapour deposition through 1 mm-diameter holed metal matrix on the polished surface of PbTe wafer (see Fig. 1).

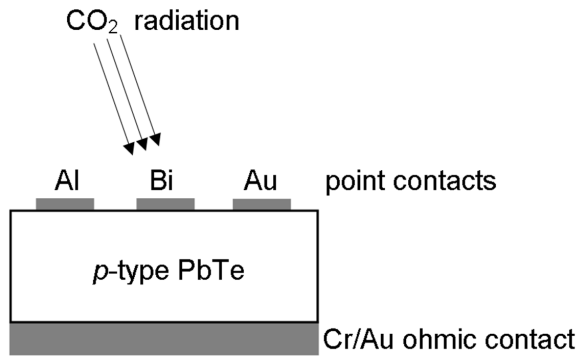


Fig. 1. Samples under investigation. CO₂ laser radiation is schematically shown falling separately on Bi-PbTe contact

Each point contact of a different metal was illuminated and investigated separately by a focused laser beam. CO₂ laser provided normally incident radiation at wavelength 10.6 μm and peak intensity reaching up to 1 MW/cm². The radiation was modulated in 200 ns-duration pulses at 40 Hz repetition rate. The laser pulse shape and peak intensity were controlled using liquid nitrogen cooled Ge<Au> photodetector.

3. RESULTS AND DISCUSSION

Current-voltage (*I-V*) characteristics of the fabricated structures revealed their Schottky diode-like asymmetric character almost in the whole tested temperature range from 50 K up to 230 K. The rectifying feature, of course, gets less pronounced with temperature (symbolic temperature limits could be set as 230 K, 200 K and 190 K for Al-, Au-, and Bi-PbTe, respectively).

Photoresponse signal (photoelectromotive force) is induced into the CO₂ laser illuminated point Schottky contact and the ohmic contact. Its polarity indicates the flow of holes away from the point contact. Low temperature (92 K) photoresponse as a function of bias voltage for all the investigated Schottky contacts is shown in Fig. 2. Disappearance of the signal at ~150 mV of the forward bias coincides well with the potential barrier height value of ~120 meV estimated from the *I-V* characteristics. However, this result is not in good agreement with the theoretical values of the barriers for different metals under investigation calculated as [9]:

$$\varphi_B = E_g - (\varphi_m - \chi), \quad (1)$$

where φ_B is Schottky barrier height, φ_m stands for a metal work function, and $\chi = (4.6 \pm 0.3)$ eV is electron affinity for PbTe [10]. Forbidden energy gap values for PbTe at 92 K temperature were calculated according ref. [3]. Comparison of the barrier heights evaluated from different sources is presented in Table 1. This obvious difference between experimental and calculated results can be explained by the existence of electronic states within the band gap in the interlayer between the metal and the semiconductor [9].

Table 1. Work functions for Al, Au, and Bi and their Schottky barrier heights for PbTe

	Al	Au	Bi	Source
φ_m , eV	4.2	4.8	4.4	[11]
φ_B , eV	0.12	0.10	0.12	<i>I-V</i>
φ_B , eV	0.63	0.03	0.43	eq. (1)

Low values of reverse bias voltage causes increase of the photoresponse signal, while at higher voltages (100 meV–150 meV) the signal saturates or even gets lower (see Fig. 2). Such decrease is most probably caused by the rise of saturation current of the diodes, what was supported by the analysis of the *I-V* characteristics. Its is worth noting that Bi-PbTe contact produces signally higher values of the photoresponse at the same radiation intensity of the CO₂ laser.

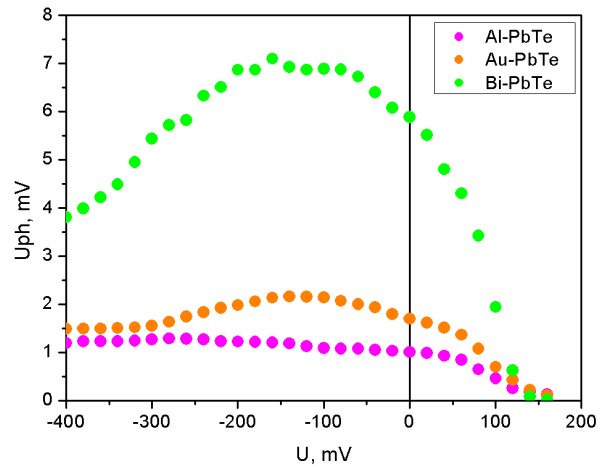


Fig. 2. Photoresponse signal across Al-, Au-, and Bi-PbTe Schottky contacts exposed to CO₂ laser radiation vs applied bias voltage at 92 K temperature

The dependencies of the photoresponse signal across the investigated Schottky contacts on temperature is presented in Fig. 3. Temperature decrease inspires growth of the signal value. And again, Bi-PbTe contact exhibits different characteristics: in contrast to the other two contacts, its photoresponse increases sharper with lower temperatures.

Typical photoresponse signal pulse shapes for different sample temperatures are presented in Fig. 4. Note that the pulse maximum increases with temperature decrease but also shifts slightly to the right side.

The model that could account for the effect of photoresponse generation involves the following:

- emission of laser-excited holes over the metal-PbTe barrier into the semiconductor and their subsequent drift in the built-in internal electric field of the junction;
- absorption of the radiation by free carriers on the semiconductor surface due to semi-transparent thin metal layer;
- heat transfer from the hot holes to the lattice within a characteristic picosecond carrier energy relaxation time;
- localized temperature rise and consequent inducement of thermo emf (Seebeck effect) as well as thermal generation of nonequilibrium electron-hole pairs that are separated by the internal electric field;
- two-photon absorption induced generation of the electron-hole pairs and separation by the internal electric field;
- recombination of the carriers after the end of the laser pulse.

All these effects are possible to arise under certain conditions.

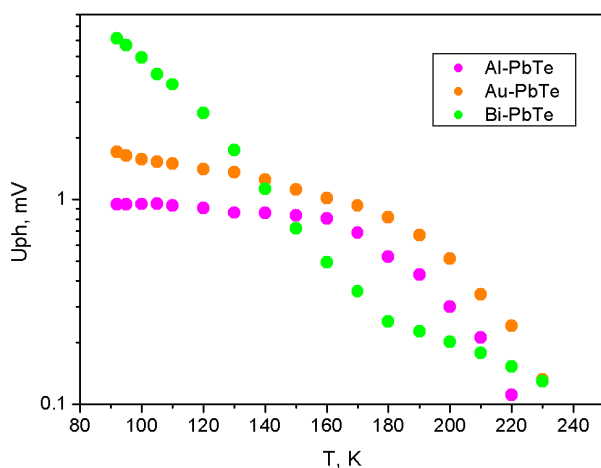


Fig. 3. Photoresponse signal across Al-, Au-, and Bi-PbTe Schottky contacts exposed to CO₂ laser radiation as a function of temperature

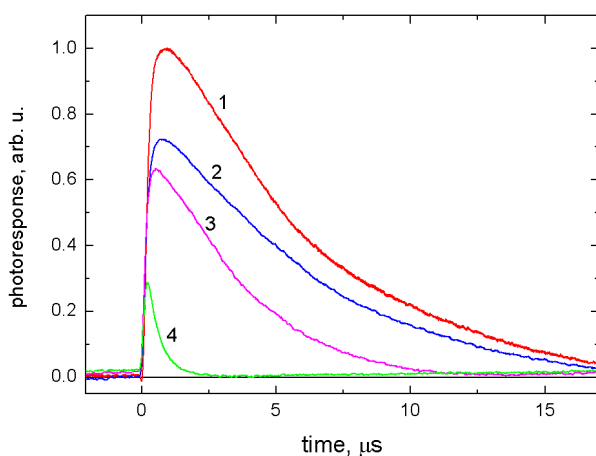


Fig. 4. Photoresponse signal pulses across Au-PbTe point contact exposed to CO₂ laser radiation at 92 K (1), 110 K (2), 140 K (3) and 200 K (4) temperature

Presence and influence of the built-in electric field of the junction is obvious from the photoresponse dependence

on bias voltage (see Fig. 2). Shift and relatively longer trailing edges of the photoresponse pulses at lower temperatures (compare traces 1–3 with 4 in Fig. 4) both evidence increase of carrier lifetime with temperature reduction; also, both of them can be influenced by the boost of free carrier absorption at lower temperatures and consequent intensification of processes (c) and (d). Specific features of Bi-PbTe contacts, i.e. higher magnitude of the photoresponse signal and sharper dependence on low temperature, could be explained not only by thinner Bi layer compared to Al and Au but by the presence of two-photon absorption inspired carrier pair generation [process (e)]. This assumption is strongly supported by observed superlinear dependence of the detected signal on power at high laser intensities observed only on Bi-PbTe contact.

4. CONCLUSIONS

We observed the photoresponse signal in the narrow band gap PbTe semiconductor-metal (Al, Au, Bi) junctions under far infrared CO₂-laser irradiation of 10.6 μm wavelength, i.e. in the case when the semiconductor band gap is wider than the incident photon energy. The signal rise is caused by a complex superposition of carrier excitation and generation effects and their separation by the internal built-in electric field of the junction exhibiting itself at low temperatures.

REFERENCES

- Lead Chalcogenides. Physics and Applications. Ed. **D. Khokhlov**. Taylor & Francis, New York, 2003.
- Rogalski, A.** Infrared Detectors: Status and Trends *Progress in Quantum Electronics* 27 2003: pp. 59–210. [http://dx.doi.org/10.1016/S0079-6727\(02\)00024-1](http://dx.doi.org/10.1016/S0079-6727(02)00024-1)
- Tauber, R. N., Machonis, A. A., Cadoff, I. B.** Thermal and Optical Energy Gaps in PbTe *Journal of Applied Physics* 37 (13) 1966: pp. 4855–4860. <http://dx.doi.org/10.1063/1.1708150>
- Sandomirsky, V., Schlesinger, Y., Dashevsky, Z.** Pyroelectric Effect of a P–N Junction in a Nonpolar Solid *Applied Physics Letters* 86 2005: pp. 133501-1–133501-3.
- Kosonocky, W. F.** State-of-the-Art in Schottky-Barrier IR Image Sensors *Proceedings of SPIE* 1682 1992: pp. 2–19.
- Ašmontas, S., Dashevsky, Z. M., Gradauskas, J., Seliuta, D., Sužiedėlis, A., Širmulis, E.** Electromotivity in PbTe-Metal Contacts under CO₂ Laser Illumination *Lithuanian Journal of Physics* 41(4–6) 2001: pp. 289–293.
- Ašmontas, S., Dashevsky, Z., Dariel, M. P., Gradauskas, J., Jarashneli, A., Shusterman, S., Sužiedėlis, A., Valušis, G.** Photo-Thermovoltaic Effects Induced by CO₂ Laser Illumination of PbTe-Metal Junctions *Proceedings of SPIE* 4318 2001: pp. 230–234. <http://dx.doi.org/10.1117/12.417602>
- Dashevsky, Z., Kasiyan, V., Asmontas, S., Gradauskas, J., Širmulis, E., Flitsiyan, E., Chernyak, L.** Photothermal Effect in Narrow Band Gap PbTe Semiconductor *Journal of Applied Physics* 106 2009: pp. 076105-1–076105-3.
- Sze, S. M.** Physics of Semiconductor Devices. Wiley & Sons, New York, 1981.
- Spicer, W. E., Lapeyre, G. J.** Photoemission Investigation of the Band Structure of PbTe *Physical Review* 139 1965: pp. A565–A569. <http://dx.doi.org/10.1103/PhysRev.139.A565>
- <http://www.goodfellow.com/e/a.html>