# PROBLEM OF IMPURITY STATES IN NARROW-GAP IV-VI SEMICONDUCTORS

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Starting from mid-70th, a great deal of both experimental and theoretical efforts has been attracted to the unexplained puzzle of impurity states arising in the IV-VI narrow-gap cubic semiconductors doped with some of the group III elements, and to the unusual effects observed in these materials. We review the experimental results obtained in the field: the electrical activity of impurity centers, persistent photoconductivity and related effects, unusual optical, dielectric and magnetic phenomena. Some of the features of these semiconductors, such as possibility of realization of the semiinsulating state with the persistent photoresponse, possibility of fast quenching of persistent photoconductivity, microwave stimulation of the quantum efficiency up to 100, and some others, have made it possible to construct the far-infrared photodetector with extremely high characteristics. The theoretical models proposed so far to account for the physical picture of the processes involved are discussed in view of the recent advances in the field.

Many of the sensitive photodetecting systems operating in the far infrared wavelength range (20-200) μm are based on germanium or silicon doped with shallow impurities [1]. The highest cutoff wavelength reported $\lambda_{co} \approx 220$ μm corresponds to the uniaxially stressed Ge(Ga) [2].

An alternative possibility for construction of sensitive far-infrared photodetectors is provided by unique features of a narrow-gap semiconductor - indium-doped $Pb_{1-x}Sn_xTe$. Exciting results of fundamental research on the group III - doped lead telluride - based alloys [3] provided possibilities for construction of far-infrared photodetectors based on new physical principles [4].

Doping of the lead telluride with indium in amount exceeding concentration of other impurities and defects results in the Fermi level pinning effect [5]. A consequence of this effect is homogenization of electrical properties of the semiconductor. This feature results in almost absolute reproducibility of sample parameters independent of the growth technology. High sample homogeneity gives rise to enhanced carrier mobility reaching $10^5$-$10^6$ cm$^2$/V·s at low temperatures.

Position of the pinned Fermi level $E_0$ may be tuned by alloying [6]. It crosses the gap in the tin content range ($0.22 < x < 0.28$) providing the semiinsulating state of the semiconductor for this range of alloy compositions. Conductivity of material in the semiinsulating state ($0.22 < x < 0.28$) is defined by activation from the impurity local level $E_0$, and therefore the free carrier concentration is very low $n,p < 10^8$ cm$^{-3}$ at temperatures $T < 10$ K. So we have a very unusual situation, when a heavily doped narrow-gap semiconductor with high number of growth defects acts as an almost ideal semiconductor with practically zero background free carrier concentration and very high electrical homogeneity. This makes very attractive the idea to use this material as an infrared photodetector.

External infrared illumination leads to the substantial increment of material conductivity at the temperatures $T < 25$ K reaching several orders of magnitude [7]. High amplitude of photoresponse at the low temperatures is a consequence of the persistent photoconductivity effect: the photoresponse increases linearly in time providing a kind of «internal integration» of the incident radiation flux. When the radiation is switched off, the conductivity relaxes very slowly. The characteristic relaxation time $\tau > 10^4$ s at 4.2 K < T < 10 K. The effect is defined by the specifics of impurity states that form DX-like centers [8].

If sample temperature is so that $\tau$ is higher that the operation time required, then a photoresistor may operate only if there exists a possibility to return to the initial "darkness" state, i.e. to quench quickly the persistent photoconductivity. The most efficient way of quenching of the persistent photoconductivity in $Pb_{1-x}Sn_xTe(In)$ is application of strong microwave pulses to sample contacts [4]. Using this technique the long-living photoexcited free electrons may be localized for 10 μs. Therefore it is possible to operate in the regime of periodical accumulation and successive fast quenching of photoresponse. Moreover, application of microwave pulses in some special regime results in giant increment of the quantum efficiency up to ~ 100 [4].

A laboratory model of the IR-radiometer based on $Pb_{1-x}Sn_xTe(In)$ operating in the regime of periodical accumulation and successive fast quenching of the persistent photoconductivity, has been demonstrated in [4]. Despite low sensitivity of the measuring electronics used, the photon flux with $\lambda = 18$ μm detected in [4] was as low as $N \approx 2\cdot10^4$ $s^{-1}$ that corresponds to NEP $\approx 2\cdot10^{-16}$ W for the detector area of 0.3·0.2 $mm^2$ and the operating rate 3 Hz.

Direct comparison of the $Pb_{0.75}Sn_{0.25}Te(In)$ photodetector, the Si(Sb) BIB structure and the Ge(Ga) photodetector using the same cryogenic equipment and measuring electronics has been performed in [9].The responsivity $S_I$ of the $Pb_{0.75}Sn_{0.25}Te(In)$ photodetector at 116 μm was of the order of $10^3$ A/W at 40 mV bias, that is by 2-3 orders of magnitude higher than the $S_I$ value obtained for a state of the art Ge(Ga) photodetector in the same measuring conditions.

The same authors have directly observed persistent photoresponse in the $Pb_{0.75}Sn_{0.25}Te(In)$ photodetector at the wavelengths of 90 and 116 μm that are considerably longer than the wavelength corresponding to the thermal activation energy of the ground impurity state. Indications exist that the red cutoff wavelength for this photodetector may exceed 220 μm - the highest $\lambda_{co}$ observed so far. Later this conclusion was confirmed by a direct experiment: the persistent photoresponse has been detected at the wavelengths of 176 and 241 μm [10].

Specifics of impurity states may make very easy construction of a focal-plane array on $Pb_{1-x}Sn_xTe(In)$. Local infrared illumination leads to local generation of nonequilibrium free electrons, i.e. the persistent photoconductivity effect is observed only in the illuminated part of the sample, and the photoexcitation does not propagate into the darkened regions [11]. The characteristic time of the excitation propagation is at least more than $10^4$ s at T = 4.2 K. The spatial characteristic scale is ~ 10 μm.

Therefore the distribution of the radiation exposure over the sample surface reflects in a distribution of the concentration of long-living free electrons. In other words, it is possible to construct a focal plane "continuous" array, in which the signal is internally integrated in every effective element.

Readout technique is a special problem. The approach proposed in [4] seems to be the most promising. Let us consider a thin slice of $Pb_{1-x}Sn_xTe(In)$ with a semitransparent electrode deposited on one side (Figure 1). The investigated radiation flux illuminates the sample from the same left side in Figure 1. A buffer insulating fluoride layer is deposited on another side of the sample followed by a thin layer of silicon or some other semiconductor with a relatively wide gap, and a second semitransparent electrode. If the sample is illuminated by a shortwavelength laser from the right side, it is possible to generate a local highly conductive region in the wide-gap semiconductor. If then a bias between the electrodes is applied, the current is defined by the $Pb_{1-x}Sn_xTe(In)$ sample conductivity in the region of the laser spot, because the thickness of the semiinsulating wide-gap semiconductor layer is be much less in this point. Another advantage of such a readout technique is heavy damping of the dark current in such a structure. It is analogous to certain extent to the ideas involved in BIB structures. If the recombination rate in the wide-gap semiconductor is high enough, it is easy to reconstruct the conductivity distribution over the $Pb_{1-x}Sn_xTe(In)$ sample simply by scanning the laser beam over the structure surface and by measuring the respective current. Unfortunately this idea is not realized in practice so far.

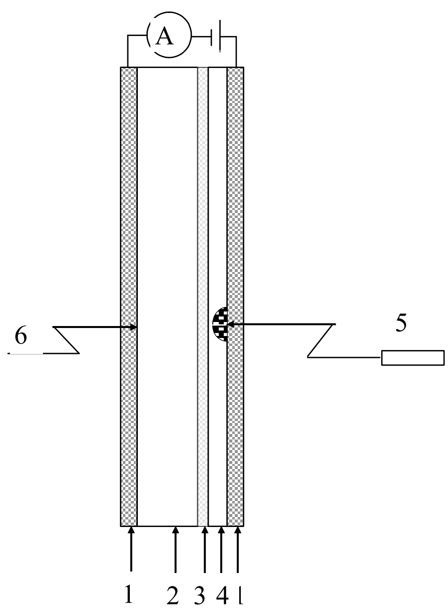


**Fig.1.** Device for readout of information from the "continuous" focal-plane array on $Pb_{1-x}Sn_xTe(In)$. 1 - semitransparent electrodes, 2 - active $Pb_{1-x}Sn_xTe(In)$ layer, 3 - fluoride buffer layer, 4 - layer of a silicon (or other semiconductor with a relatively wide gap), 5 - short-wavelength laser, 6 - incident infrared radiation flux [4].

High radiation hardness is one more advantage of the photodetectors based on $Pb_{1-x}Sn_xTe(In)$. This is a consequence of a very high density of impurity states (~ $10^{18}$ - $10^{19}$ $cm^{-3}$) that pin the Fermi level. The fast electron irradiation with fluencies up to $10^{17}$-$10^{18}$ $cm^{-2}$ does not affect the photoresponse [12]. This value is at least by 4 orders of magnitude higher than for $Hg_{1-x}Cd_xTe$, doped Ge and Si.

In summary, application of the lead-tin tellurides doped with the group III impurities as base elements for the infrared photodetectors gives a challenging opportunity to produce universal and sensitive systems. They have a number of advantageous features that allow them to compete successfully with the existing analogs: internal accumulation of the incident radiation flux, possibility of effective fast quenching of an accumulated signal, microwave stimulation of the quantum efficiency up to $10^2$, possibility of realization of a "continuous" focal-plane array, possibility of application of a new readout technique, high radiation hardness. In our opinion, these features make the $Pb_{1-x}Sn_xTe(In)$-based photodetectors ideal for the space-borne applications, for example, in the infrared astronomy.

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