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# High-performance 8–14 μm $Pb_{0.80}Sn_{0.20}Te$ Schottky barrier photodiodes

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Planar $Pb_{0.80}Sn_{0.20}Te$ photodiodes sensitive in the 8–14 μm spectral region with high-performance characteristics have been fabricated by using indium Schottky barriers. The vacuum-deposited $BaF_2$ films as an insulator and the standard photolithographic techniques were used to achieve planar detector arrays. These photodiodes exhibited resistance–area products of (1.0 1.3) $10^{-4}\,\Omega m^2$, quantum efficiency of ~30% and detectivity limited by background at $(10.3 \pm 0.1)$ μm and 77 K.

## 1. Introduction

The energy gap of $Pb_{1-x}Sn_xTe$ can be continuously varied from 0 to 0.22 eV as $x$ ranges from 0.4 to 0 [1]. A considerable attention has been given to the composition range $0.20 \leqslant x \leqslant 0.22$ for infrared detectors [2] and lasers [3] operating in the 8–14 μm spectral region. Such devices, operating at 77 K can find applications in reconnaissance, guidance, surveillance and communication systems.

Metal-lead/tin chalcogenide contact barrier structures provide convenient conditions for relatively inexpensive fabrication of high-quality infrared detectors for application in the 8–14 μm region [2]. The effective barrier energies were observed mainly for lead and indium [4], [5]. Up to now only one paper has been published on the subject of $Pb_{1-x}Sn_xTe$ Schottky barrier photodiodes [5].

In the present paper a fabrication process of planar $Pb_{0.80}Sn_{0.20}Te$ Schottky barrier photodiodes is presented. High-quality photodiodes were fabricated by using indium barriers. The vacuum-deposited $BaF_2$ films were used instead of photoresist as an insulator. Standard photolithographic technique was used to achieve planar detector arrays.

## 2. Experimental

The planar Schottky photodiodes were fabricated from crystals prepared by unseeded vapour growth of $Pb_{0.80}Sn_{0.20}Te$ [6]. After a week lasting growth at approximately 810°C the crystals ranging in size from a few millimeters to approximately 1 cm with smooth and shiny facets (usually (100)-oriented) were obtained. Single crystals of $Pb_{0.80}Sn_{0.20}Te$ were strongly of $p$-type, with typical acceptor concentrations of approximately $10^{25}\,m^{-3}$ due to native point defects which occur because the crystals grew slightly rich in Te. In order to reduce high $p$-type carrier concentrations, wafers cut from the crystals were annealed for about three weeks at 560°C under isothermal conditions in the presence of metal-rich powder [7]. Typical temperature dependences of Hall coefficient, hole mobility and resistivity of the annealed crystals are shown in Fig. 1. The hole concentrations and mobilities at 77 K were ranged within $(1-2)\,10^{23}\,m^{-3}$ and (1.0–2.0) $m^2/Vs$, respectively. The crystals show the expected $T^{-5/2}$ temperature dependence of the mobility [7].

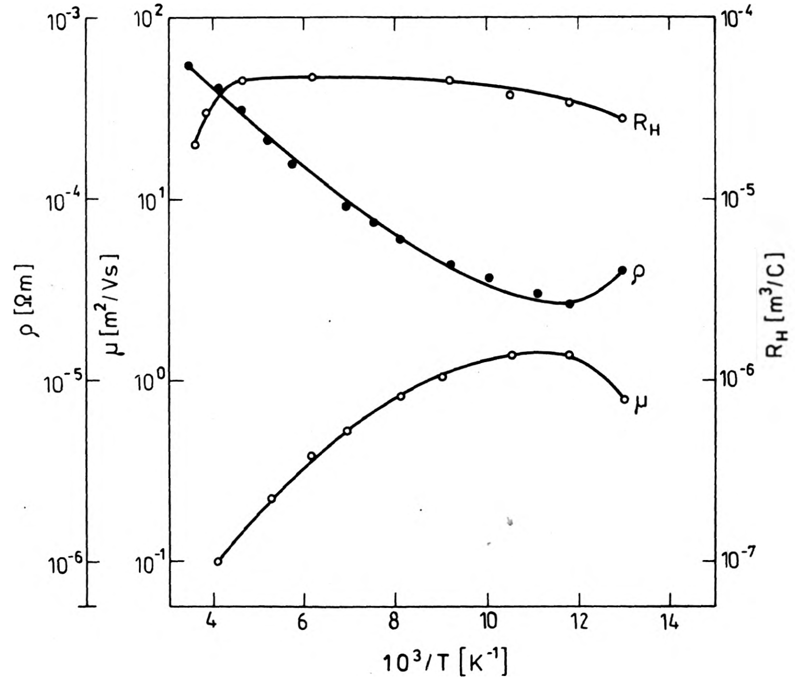


Fig. 1. Hall coefficient $R_H$, hole mobility $\mu$ and resistivity of the annealed $Pb_{0.80}Sn_{0.20}Te$ single crystal

Cross-sections illustrating the steps in fabricating discussed planar $Pb_{0.80}Sn_{0.80}Te$ Schottky barrier arrays are shown in Fig. 2. To reduce strains due to either thermal etching or handling, both surfaces of ~ 1 mm-thick annealed wafers were etched in the Norr solution [8] to a final thickness of approximately 0.7 mm. Immediately after etching, $BaF_2$ films of ~ 1 μm thickness were evaporated on the $Pb_{0.80}Sn_{0.20}Te$ surface in a vacuum chamber. During $BaF_2$ deposition the sample temperature was maintained at 200°C to minimize the re-evaporation of PbTe, SnTe and Te. $BaF_2$ provided a comparable lattice match and the best thermal expansion match to $Pb_{0.80}Sn_{0.20}Te$ [9]. The insulating $BaF_2$ films were found to adhere well, even after repeated heating and cooling cycles. The ohmic contact to the substrate side was made by chemical deposition of gold. Standard

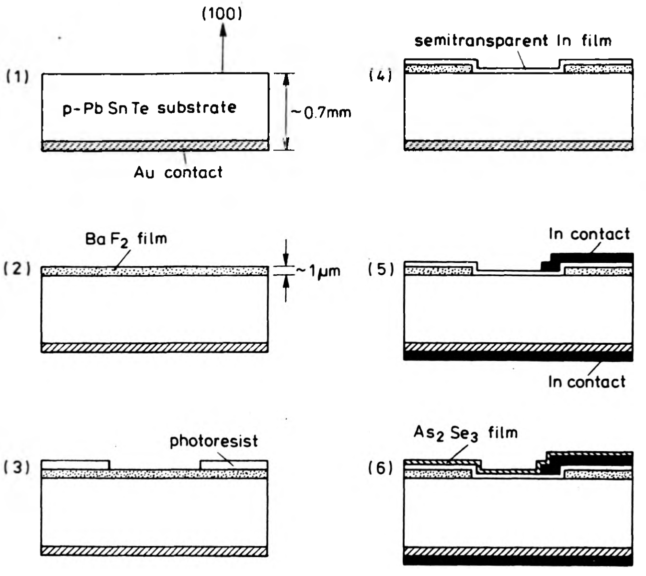


Fig. 2. Cross-sections showing steps (1–6) in Schottky barrier photodiode fabrication

photolithographic technique was used to delineate detector windows with square dimensions of 0.6 mm by 0.6 mm. Next, the Schottky barriers with semi-transparent In electrodes were fabricated. The In barriers were prepared by exposing the $Pb_{0.80}Sn_{0.20}Te$ surface to the atmosphere at room temperature prior to the In vacuum deposition. Surface preparation of single crystals was not made. The next preparation stage consisted in providing the structures with electrical contacts. Thick In layers were vapour deposited on the substrate side as well as on the top active regions. The delineation of the top ohmic contacts was made by using photolithographic technique. After wire bonding, an anti-reflection (A-R) coating was applied by vapour deposition of $As_2Se_3$ layer. The detector arrays consisted of 12 elements. These photodiodes were illuminated through semi-transparent In electrodes.

## 3. Schottky barrier characteristics

The resistance-area product $R_0 A$ of the photodiodes ranging from 1.0 to 1.3 $\times 10^{-4}\,\Omega m^2$ at 77 K has been obtained. The resistance $R_0$ decreases considerably with the increasing temperature.

The $I$–$V$ characteristic of the photodiode at 77 K together with the dependence of the differential resistance on the bias voltage are illustrated in Fig. 3. The curve in the $I$–$V$ characteristic was measured for 300 K background ($2\pi$ srd FOV). The influence of leakage effects (lack of saturated current) can be clearly seen in the reverse characteristic. The forward $I$–$V$ characteristics of these photodiodes at 77 K may be expressed in the form $I = I_0 \exp(qV/\beta kT)$, where the parameter $\beta$ was found to be between 1.8 and 2.0.

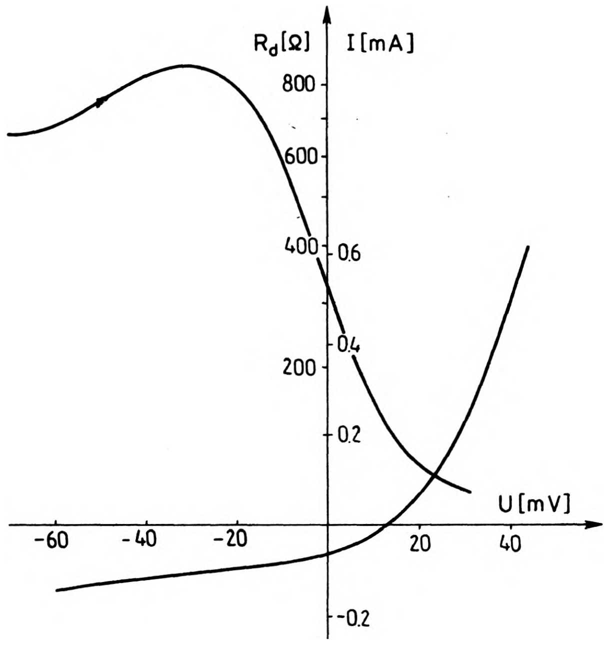


Fig. 3. *I–V* characteristic and the differential resistance of the indium barrier $Pb_{0.80}Sn_{0.20}Te$ photodiode at 77 K

Capacitance measurements were performed to determine the junction profiles. It was found that at 77 K there is a linear dependence of the reciprocal square capacitance on the junction bias. This means that the junctions were abrupt. The capacitance-voltage (*C V*) characteristic of the diode is shown in Fig. 4. The

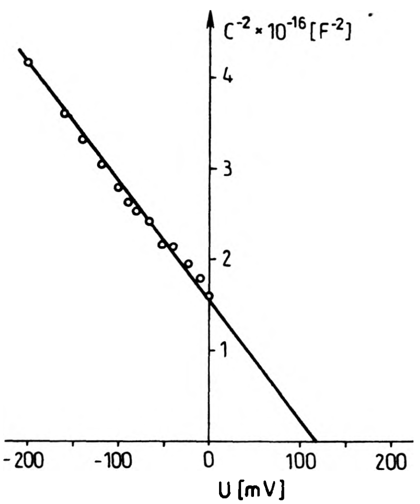


Fig. 4. *C–V* characteristic ($C^{-2}$ as a function of the bias voltage) for the indium barrier $Pb_{0.80}Sn_{0.20}Te$ photodiode at 77 K

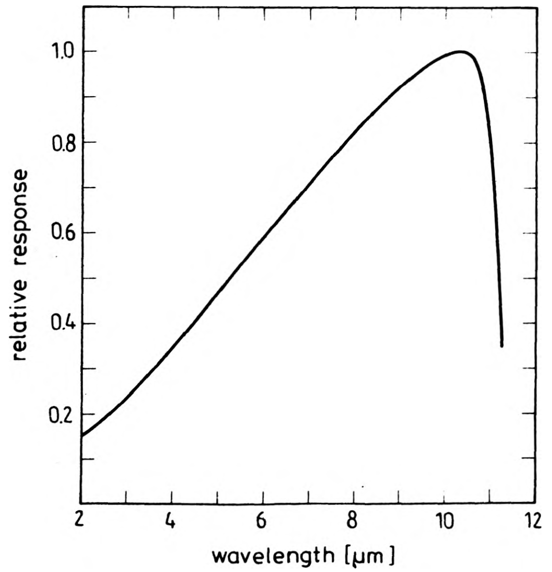


Fig. 5. Relative response of the indium barrier $Pb_{0.80}Sn_{0.20}Te$ photodiode at 77 K

intersection of the straight line with the horizontal axis gives a diffusion voltage of about 0.12 V, which corresponds to the band gap of $Pb_{0.8}Sn_{0.2}Te$.

When the model of asymmetric abrupt junction is applied, the impurity concentration and the depletion width in the lightly doped region can be estimated [10]. If dielectric constant is assumed to amount 500, values of acceptor concentrations of $\sim 10^{23}$ $m^{-3}$ are obtained. These impurity carrier concentrations are in good agreement with the carrier concentrations which were obtained from the Hall measurements on the *p*-type single crystals. The width of the space-charge region was estimated as $\sim 0.2$ μm.

Typical spectral response of the Schottky barrier photodiodes is shown in Fig. 5. The detectors have a peak response at $(10.3 \pm 0.1)$ μm and a 50% cutoff at $\sim 11.0$ μm.

Quantum efficiency was determined from diode short circuit current $I_{sc}$ measurements using $I_{sc} = q\eta A\Phi_B$ (where $\Phi_B$ is the photon flux incident on the detector), and from blackbody (at temperature of 500 K) responsivity measurements. At 77 K the quantum efficiency was about 30%.

The normalized detectivity of the Schottky barrier detectors is limited by background ($D^* \approx 2 \times 10^{10}$ cmHz$^{1/2}$W$^{-1}$, $T = 77$ K, $\lambda_p = (10.3 \pm 0.1)$ μm, FOV $= 2\pi$ srd). The total noise of the photodiodes was measured over the frequency range to 100 kHz. In the range of frequency up to 1 kHz the detectivity was limited by $1/f$ noise. For frequencies higher than 1 kHz up to 50 kHz white noise was observed (the photon flux contributing to the detector noise was almost entirely from the background). The diode capacitances were high, approximately 3000 pF. Thus, the *RC* time constant became very long, about 1 μs. Effect of bias on noise current $I_n$ (corrected for the bandwidth) in photodiodes is shown in Fig. 6. The minimum of the total diode noise was found at zero bias voltage.

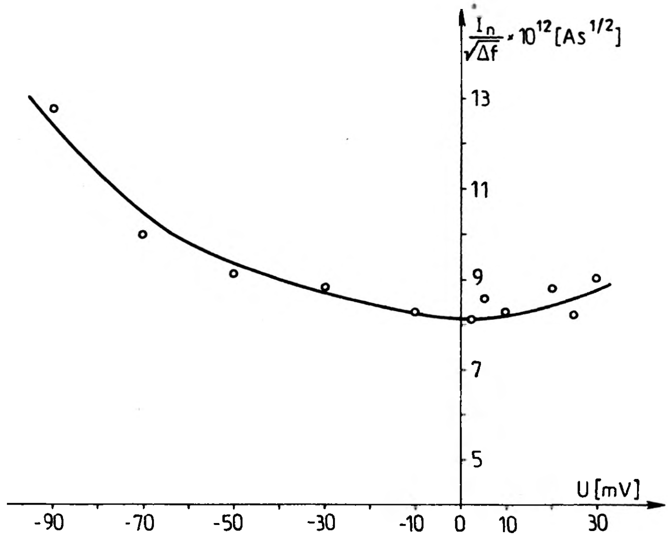


Fig. 6. Effect of bias on noise current in the indium barrier $Pb_{0.80}Sn_{0.20}Te$ photodiode at 77 K

## 4. Discussion

For fabricating the Schottky barrier photodiode from a *p*-type semiconductor, the work function of a metal $\Phi_m$ should be less than the electron affinity $\chi_S$ of the semiconductor. The barrier height in this case is given by $\Phi_B = \chi_S + E_g - \Phi_m$. If $\Phi_B > E_g$, a layer of the semiconductor adjacent to the surface is inverted in type and we have then a *p-n* junction within the material. But in practice it is difficult to obtain an ideal Schottky barrier and simple relationship like the above expression is not fulfilled. It depends either on surface states or on metal-induced gap states and it is due to interface chemical reactions between metal and semiconductor atoms.

The model of Schottky barrier photodiodes with inversion layer has been proposed by Walpole and Nill for Pb and Sn contacts on (100)-oriented surfaces of *p*-type PbTe crystals [11]. The scheme of energy bands for such a junction is shown in Fig. 7, where three regions may be distinguished: inverted, depleted, and

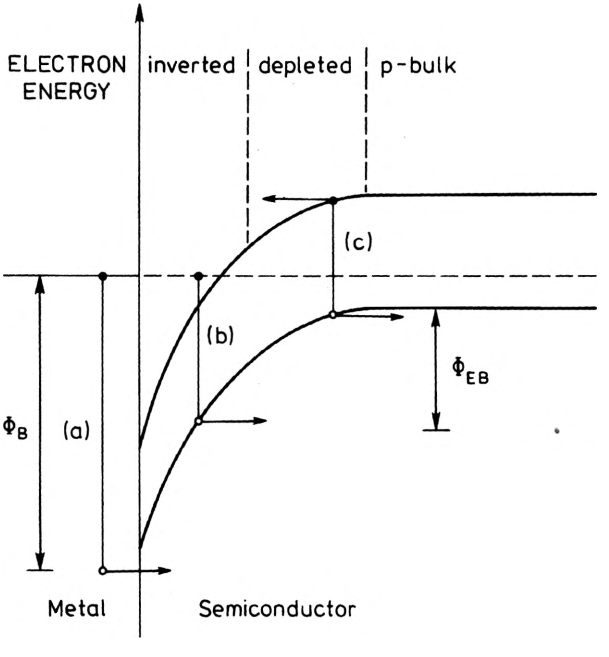


Fig. 7. Schematic energy band diagram for Schottky barrier with a narrow-gap *p*-type semiconductor

bulk ones. In the ideal junction model only processes (a), i.e., the hole emission from the Fermi level in metal to the valence band for $h\nu = \Phi_B$ are considered. No account is taken of the excitation of electron-hole pairs in the inverted region (processes (b)) and of band-to-band excitation of hole-electron pairs in the depleted region (processes (c)). According to the authors of paper [11] the barrier height $\Phi_B$ for holes is lowered considerably to assume the value $\Phi_{EB}$ slightly exceeding the energy gap $E_g$. Since for the hole with kinetic energy slightly exceeding $E_g$ the narrow top of the barrier is transparent due to tunneling effects, the effective barrier $\Phi_{EB}$ is for majority of metals independent of the work function of the metal [12].

In indium barrier $Pb_{0.80}Sn_{0.20}Te$ photodiodes the above described excitations of hole-electron pairs in the depleted region are of particular importance because the depleted region is wide due to high dielectric constant. As indicated previously, the value of the coefficient $\beta$ is close to 2, which indicates the domination of the depleted layer current. These results were confirmed by measuring the zero-bias resistance as a function of temperature. Figure 8 presents the measured $R_0$ as a

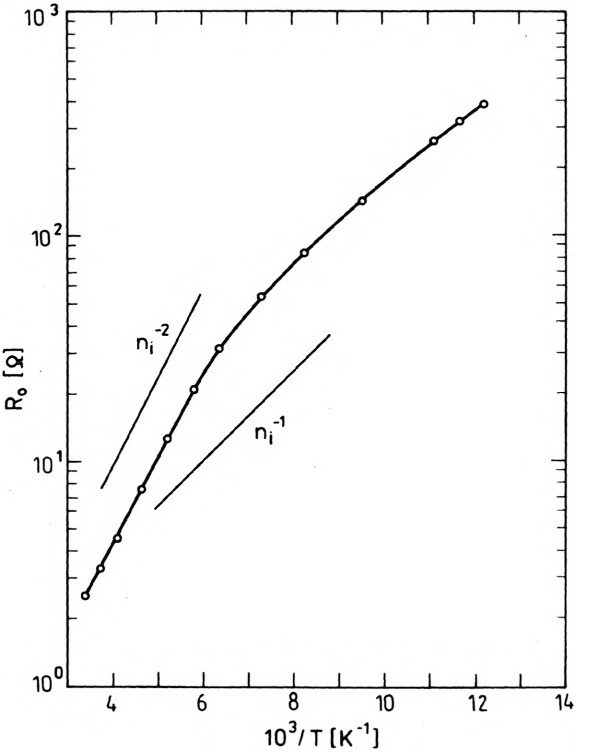


Fig. 8. Dependence of the zero-bias resistance $R_0$ on the temperature for indium barrier $Pb_{0.80}Sn_{0.20}Te$ photodiode

function of the reciprocal temperature for one of the junctions. When the resistance follows the temperature dependence of $n_i^{-1}$ this implies that the resistance is dominated by generation-recombination processes within the depletion region of the junction. When $R_0 \propto n_i^{-2}$ then the resistance is dominated by the diffusion current. It can be seen that the zero-bias resistance of indium Schottky barriers with p-type $Pb_{0.8}Sn_{0.2}Te$ at 77 K is dominated by the depletion layer current, although the minority diffusion current dominates $R_0$ at higher temperatures. The transition from the diffusion current to the depletion layer one occurs at $T \approx 150$ K.

Polishing and chemical etching of the semiconductor surface invariably produce a thin oxide layer. The exact nature and the thickness depend on the method of preparation [13]. BUCHNER et al. [14] have shown that Schottky barrier of Pb on $Pb_{0.8}Sn_{0.2}Te$ are formed only when the semiconductor surface is exposed to oxygen prior to the deposition of Pb. According to Schoolar and Jensen, however, the $Pb_{1-x}Sn_xSe$ surface must be annealed at 170°C for 30 min and cooled down to room temperature prior to the metal deposition, in order to desorb an oxide layer from the material [15]. It has been recently found that the presence of chloride in the interface vastly improves *I–V* characteristics of Schottky junctions [16].

Long-term *I–V* characteristic measurements of the indium barrier $Pb_{0.8}Sn_{0.2}Te$ photodiodes have been carried out. These measurements indicate a slow degradation of rectifying properties of the Schottky barriers. It may be due to the chemistry of the interface, such as the presence of oxygen or migration of Sn across the interface. Attempts to "sensitize" the crystals with oxygen by baking them in the presence of oxygen, vacuum annealing at 200°C prior to the metal deposition, and introducing chloride to the surface in the manner described in paper [16], did not produce consistent yields.

## 5. Conclusions

It has been shown that high-performance planar $Pb_{0.80}Sn_{0.20}Te$ Schottky photodiodes can be fabricated by using indium barriers and $BaF_2$ films as an insulator. The performance of these photodiodes is similar to that reported previously [5]. It should be noticed that the bias voltage has a small influence on the noise current in our planar photodiodes. However, long-term measurements indicate a slow degradation of rectifying properties of these Schottky barriers. The precise nature of the chemistry of interface between indium and $Pb_{0.80}Sn_{0.20}Te$ surface is not known. It is necessary to elaborate a special surface preparation of the crystals to prevent degradation of the barrier properties. Further studies of $Pb_{0.80}Sn_{0.20}Te$ surfaces and interfaces are necessary to enable resolving of some of the present controversial issues concerning Schottky barrier formation.

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## Фотодиоды $Pb_{0,80}Sn_{0,20}$Te высокой мощности с барьерами Шоттки в пределе 8–14 мк

Изготовлены планарные фотодиоды $Pb_{0.80}Sn_{0.20}$Te высокой производительности, чувствительные в спектральной области 8–14 мк, при применении индиевых барьеров Шоттки. Запариваемые в вакууме слои $BaF_2$ применялись в качестве изолятора. Для изготовления маски планарных детекторов использована стандартная фотолитографская техника. Эти фотодиоды показали произведение активное сопротивление — поле со значением (1,0–1,3) $10^{-4}$ $\Omega м^2$, квантовый вывод около 30%, а также детективность, ограниченную фоном при $(10.3 \pm 0.1)$ мк и 77 К.