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Th. Jakobus, W. Rothmund, A. Hurrle, J. Baars. Pb_{0.8}Sn_{0.2}Te Infrared photodiodes by indium implantation. *Revue de Physique Appliquée*, 1978, 13 (12), pp.753-756. 10.1051/rphysap:019780013012075300 . jpa-00244540

HAL Id: jpa-00244540

<https://hal.science/jpa-00244540>

Submitted on 1 Jan 1978

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Pb_{0.8}Sn_{0.2}Te INFRARED PHOTODIODES BY INDIUM IMPLANTATION

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Résumé. — Des ions d'indium ont été implantés dans des films de Pb_{0.8}Sn_{0.2}Te de type p pour produire des photodétecteurs à jonction p-n à niveau peu profond. Les films ont été obtenus par épitaxie sur des plans de clivage (111) de BaF₂ et ont montré des concentrations de trous de l'ordre de 10¹⁷ cm⁻³. L'implantation d'indium a été obtenue en utilisant des quantités comprises entre 2 × 10¹³ et 1 × 10¹⁵ cm⁻² et une énergie de 700 keV, les films étant, soit à température ambiante, soit à 450 K. Les profils de concentration d'indium ont été déterminés par SIMS avant et après recuit, des films implantés, à des températures atteignant 670 K. Les films implantés étaient recouverts d'une couche de nitrure de silicium pour éviter l'évaporation pendant le recuit. Les propriétés électriques résultant de l'implantation d'indium ont été étudiées par des mesures de réflectivité en infrarouge lointain dans la région de résonance du plasma. Le type de porteur des couches implantées a été déterminé par la méthode thermoelectrique usuelle.

Pour changer les couches implantées en type n, les films ont dû être recuits à une température d'au moins 570 K pendant 30 min. indépendamment de la quantité d'indium implantée.

Des diodes méso ont été fabriquées par des procédés photolithographiques habituels. On a obtenu des résistances surfaciques atteignant 0,4 Ω cm².

Abstract. — Indium ions were implanted in p-type Pb_{0.8}Sn_{0.2}Te films to produce shallow p-n junction infrared photodetectors. The films were grown epitaxially on BaF₂ (111) cleavage planes and showed hole concentrations of the order of 10¹⁷ cm⁻³. The indium implantation was carried out using doses between 2 × 10¹³ and 1 × 10¹⁵ cm⁻² and an energy of 700 keV with the films either at room temperature or 450 K. The indium concentration profiles were determined by SIMS before and after annealing of the implanted films at temperatures up to 670 K. The implanted films were covered with silicon nitride layers to avoid evaporation during the subsequent annealing. The electrical properties caused by the indium implantation were examined by far infrared reflectivity measurements in the plasma resonance region. The carrier type of the implanted layers was determined by a conventional thermoelectric method.

To convert the implanted layers into n-type the films had to be annealed at a temperature of at least 570 K for 30 min. regardless of the implanted indium dose.

Mesa diode were fabricated by standard photolithographic procedures. Zero bias resistance area products as high as 0.4 Ω cm² were obtained.

1. Introduction. — Implantation of In⁺⁺ ions has successfully been used to fabricate p-n junction photodiodes in PbTe. The results have been reported at the ESSDERC last year. In this study the effect of In implantation in thin films of p-type Pb_{0.8}Sn_{0.2}Te was investigated. The use of In⁺⁺ ion implantation to convert layers of p-type Pb_{0.8}Sn_{0.2}Te into n-type material will be discussed and some results on infrared photovoltaic detectors for the 8 to 12 μm region fabricated by this technique will be presented.

2. Experimental. — The Pb_{0.8}Sn_{0.2}Te films used for this investigation were grown on cleaved BaF₂ substrates by evaporation in vacuo [1]. The crystallographic orientation of the films was checked by X-ray diffraction and was found to be in agreement with the (111) cleavage planes of the BaF₂ substrate. The as-grown films are typically 5 μm thick and exhibit hole concentrations of approximately 5 × 10¹⁷ cm⁻³ with mobilities of the order of 10⁴ cm² V⁻¹ s⁻¹ at the temperature of liquid nitrogen. The indium was doubly ionized and implanted with an energy of 700 keV. The implantation dose was varied between

2 × 10¹³ and 1 × 10¹⁵ cm⁻². During the implantation the film temperature was kept constant either at 300 K or 450 K. In the previous studies of In⁺⁺ implantation in p-type PbTe films, where the implantations were carried out with the films either at liquid nitrogen or room temperature, we have found a much larger radiation damage after implantation at 77 K than after implantation at 300 K. This result indicates a considerable self-annealing of the radiation damage in PbTe even at room temperature. In order to keep the radiation damage as small as possible in the Pb_{0.8}Sn_{0.2}Te films implantations at 450 K were also performed this time. As will be seen later, the high temperature implantation turned out to be of no advantage. In any case a subsequent annealing at much higher temperatures was necessary to restore the damaged film regions effectively and to convert the implanted layers into n-type material.

To avoid evaporation during the annealing the film surfaces had to be protected. The first annealing experiment was performed with films which were coated with pyrolytic SiO₂ at a temperature of 630 K for 5 min. Using growth rates of about 300 Å min.⁻¹

we produced SiO₂ coatings typically 1 500 Å thick. For the protection of PbTe surfaces this procedure proved to be sufficient. The Pb_{0.8}Sn_{0.2}Te surfaces, however, became strongly p-type after coating with pyrolytic SiO₂. Hole concentrations as high as 10¹⁹ cm⁻³ were determined from plasma resonance measurements at these surfaces. This finding can be explained by the formation of Sn-oxide in the beginning of the pyrolytic SiO₂ coating in agreement with surface examinations of SnTe by ESCA. Further on, RF-sputtered Si₃N₄ therefore was used as protective coating for Pb_{0.8}Sn_{0.2}Te. The results presented here refer to samples which were coated with approximately 1 800 Å of Si₃N₄ by sputtering at room temperature before the heat treatments. The annealing was performed at various temperatures between 420 K and 670 K.

Subsequently in some of the implanted and annealed samples the In concentration profile was determined by SIMS. To examine how implantation and annealing affects the electrical properties of Pb_{0.8}Sn_{0.2}Te the carrier concentration and the type of conductivity were analysed by far infrared reflectivity measurements and thermoelectric probing.

3. Results and discussion. — We shall discuss first the concentration and the distribution of the implanted indium which were determined by SIMS measurements. A typical In implantation profile in Pb_{0.8}Sn_{0.2}Te is shown in figure 1. The In concentration was determined by measuring the ion current ratio of In⁺ and Te⁺. For calibration In doped PbTe standards were used. In the table of figure 1 the measured In doses as determined by integration of the concentration profiles are given for some samples which were implanted and annealed at various temperatures. The integrated values of these samples which were implanted with 2 × 10¹⁴ In⁺⁺ ions cm⁻² agree well with each other regardless of the implantation and annealing temperatures. From these results we can conclude that losses of In during the annealing up to temperatures of 620 K are negligible. The measured doses, however, are smaller by a factor

FIG. 1. — Indium concentration analysis by SIMS in In⁺⁺ implanted Pb_{0.8}Sn_{0.2}Te films (dose 2 × 10¹⁴ cm⁻², 700 keV). Integrated values of the concentration profiles of films which were implanted and annealed at various temperatures are given in the table.

of 2.7 on the average than the nominal implantation doses. So far we have no explanation for this discrepancy which also was found in the implantation studies of PbTe.

In figure 2 the maximum indium concentration determined from the measured concentration profiles of some PbTe and Pb_{0.8}Sn_{0.2}Te samples is plotted versus the implantation dose. The In concentration of both the PbTe and the Pb_{0.8}Sn_{0.2}Te samples show the same linear dependence over the entire dose range.

FIG. 2. — Maximum indium concentration determined from SIMS measurements versus In⁺⁺ implantation dose for various PbTe and Pb_{0.8}Sn_{0.2}Te films.

The influence of annealing on the In concentration profiles is presented in figure 3. In spite of the marked scattering there are clear tendencies. At temperatures above 500 K a pronounced shift of the peak position towards the surface is accompanied by a decrease of the half width. At low temperatures the average of the measured peak positions corresponds to that which was calculated for a 700 keV In implantation. In the high temperature region the measured peak positions equal approximately the calculated position of maximum damage. Thus a diffusion of In into the damaged surface region is likely to occur during the annealing at temperatures above 500 K.

Next the doping effect of the implanted indium shall be discussed. To determine the charge carrier concentration the infrared reflectivity in the plasma resonance region of the Pb_{0.8}Sn_{0.2}Te films at room temperature was analysed. This is a handy and reliable method to measure the charge carrier concentration of implanted layers. The conduction type of the implanted layers was checked by the common thermoelectric hot point method with the films at liquid nitrogen temperature.

The results obtained for a In⁺⁺ dose of 2 × 10¹⁴ cm⁻² after the samples had been annealed

FIG. 3. — Peak position (upper half) and half width (lower half) of indium concentration profiles in Pb_{0.8}Sn_{0.2}Te films versus annealing temperature.

at various temperatures are presented in figure 4. For implantations at room temperature and subsequent annealing for 30 min. at temperatures up to 520 K the implanted layers of the Pb_{0.8}Sn_{0.2}Te films remained p-type and exhibited almost the same carrier concentrations as before implantation.

FIG. 4. — Carrier concentration of various Pb_{0.8}Sn_{0.2}Te films after In⁺ implantation ($2 \times 10^{14} \text{ cm}^{-2}$, 700 keV) and annealing for 30 min versus annealing temperature.

Somewhat higher hole concentrations were obtained in films which were implanted at 450 K. This finding can be explained by vacuum annealing during

the implantation at 450 K which results in a depletion of metal atoms in the surface region.

When the implanted films were annealed at 570 K or even at higher temperatures for 30 min. the implanted layers were converted into n-type material with electron concentrations of the order of 10^{18} cm^{-3} . For two of the films implanted at 450 K lower electron concentrations have been found which is probably due to the vacuum annealing effect just mentioned.

From these results we can conclude that the implanted In atoms are immobile and electrically inactive as long as the annealing temperature does not exceed 520 K. At higher annealing temperatures the indium moves into the region of the radiation damage and becomes electrically active as a donor.

In this connection the dependence of the electron concentration on the In⁺ dose is of interest. This is shown in figure 5. A large number of p-type Pb_{0.8}Sn_{0.2}Te films were implanted with various In⁺ doses between 10^{13} and 10^{15} cm^{-2} . Subsequently they were annealed for 30 min at temperatures equal to or above 570 K. Irrespective of the experimental scattering the electron concentration in the implanted layers seems to follow the average In concentration up to an implantation dose of about 10^{14} cm^{-2} where the implanted layers exhibit electron concentrations of about $3 \times 10^{18} \text{ cm}^{-3}$. Higher doses apparently do not produce higher electron concentrations. This saturation effect has also been found in PbTe. The saturation level in PbTe, however, is lower by a factor of 5.

FIG. 5. — Variation of the electron concentration in Pb_{0.8}Sn_{0.2}Te films with In⁺ implantation dose after annealing for 30 min. at $T \geq 570 \text{ K}$.

To gain a deeper insight into the doping mechanism additional experiments were performed with n-type Pb_{0.8}Sn_{0.2}Te. The results are given in table I. The electron concentration of various n-type samples was measured before and after implantation and anneal. For comparison two samples are included

TABLE I

Electron concentration of n-Pb_{0.8}Sn_{0.2}Te before and after In⁺⁺ implantation and anneal

Sample No.	Before n $10^{18} \text{ (cm}^{-3}\text{)}$	Implantation dose $10^{14} \text{ (cm}^{-2}\text{)}$	Anneal T_A (K) 30 min.	After n $10^{18} \text{ (cm}^{-3}\text{)}$
687/4	0.3	1	620	2
600/1	0.2	2	620	3
598/3	0.3	2	620	5
702/1	0.3	2	620	4
687/1	0.4	10	620	1
728/4	0.4	—	670	0.4
732/3	0.4	—	620	0.3

which were not implanted but annealed for 30 min. As can be seen from the data the carrier concentrations of these two samples did not change significantly. The other samples, however, which were implanted with doses ranging from 10^{14} to 10^{15} cm^{-2} exhibited electron concentrations one order of magnitude higher than before the implantation and the anneal. The average equals $3 \times 10^{18} \text{ cm}^{-3}$ and agrees with the saturation value found in the p-type samples after implantation.

This saturation effect is well known from numerous studies of the solid solution of InTe in PbTe and there are many speculations to explain this behaviour. Rosenberg and Wald [3] for example suggest an internal charge compensation by a vacancy-interstitial mechanism. Recently Averkin [4] and Borovikova [5] proposed a model of so called deep levels produced by replacement of Pb in In.

The results of the present investigations suggest that the implanted In combines with some charge compensating defect and annealing at temperatures above 520 K only offers a chance for In to replace metal atoms of the lattice and to become active as a donor. The cause of the saturation effect is still obscured.

Finally, diodes were defined by a photolithographic mesa etch technique which was originally developed for testing implanted PbTe diodes, where on the n-type mesa surfaces of the diodes thick In pads were evaporated and 15 μm gold wires were attached by pressure bonding. Gold was evaporated on the p-type PbTe forming a framelike back-contact to the diodes. The same procedure was applied to implanted Pb_{0.8}Sn_{0.2}Te except for the bonding technique. By bonding the Pb_{0.8}Sn_{0.2}Te mesas directly on top of

the In pads the diodes were destroyed presumably by mechanical damage.

However, the current-voltage characteristics of the diodes could be measured at liquid nitrogen temperature by probing. An example of these measurements is presented in figure 6. The BaF₂ substrate was mounted on a cold finger made of copper. Therefore the measurements correspond to 0° FOV. The resistance area product of the diode as determined from the I - V curve at zero voltage amounts to approximately $0.4 \Omega \text{ cm}^2$. This value corresponds to a calculated detectivity of $4 \times 10^{10} \text{ cm W}^{-1} \text{ s}^{-1/2}$ at a wavelength of 10 μm .

FIG. 6. — Current-voltage characteristic of an In⁺⁺ implanted Pb_{0.8}Sn_{0.2}Te diode No. 775/4-34 at $T = 77 \text{ K}$ and 0° FOV. Diode area $A = 4 \times 10^{-4} \text{ cm}^2$. Vertical scale 100 $\mu\text{A}/\text{div.}$, horizontal scale 100 mV/div.

4. Conclusion. — In conclusion, the present work demonstrates that In ion implantation in Pb_{0.8}Sn_{0.2}Te can be used to produce p-n junctions. The implanted layers, however, have to be annealed at temperatures of at least 570 K for 30 min. to convert the initially p-type material into n-type. The electron concentration caused by In implantation and annealing was found to saturate at a value of $3 \times 10^{18} \text{ cm}^{-3}$ for doses larger than $1 \times 10^{14} \text{ cm}^{-2}$. This result is in agreement with investigations of solid solutions of InTe in PbTe. Finally, mesa diodes have been fabricated by standard lithographic procedures. Zero bias resistance area products as high as $0.4 \Omega \text{ cm}^2$ have been obtained.

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