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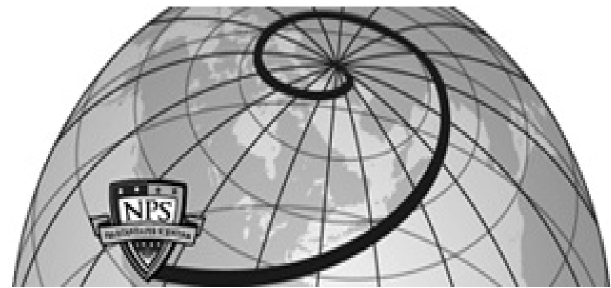

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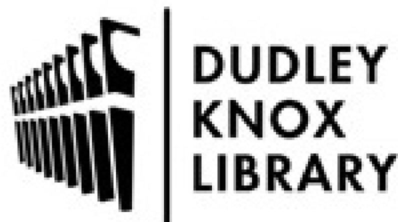

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Effect of Proton Bombardment on $Pb_{0.76}Sn_{0.24}Te$ †

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Effects of 200–450-keV proton bombardment on the electrical properties of $Pb_{0.76}Sn_{0.24}Te$ were studied. p-type samples of initial hole concentration in the low $10^{17}/cm^3$ range were converted to n type after a proton dose of 5×10^{13} p/cm^2. For samples of higher initial hole concentration, the conversion was less consistent. The change in mobility due to bombardment was found to be moderate. The mobilities of some p-type samples were doubled after type conversion.

It was recently reported that the proton bombardment can change the surface layer of several p-type semiconductors to n-type semiconductor. Using this effect, n-p junctions of InSb, [1] $Hg_{1-x}Cd_xTe$, [2] PbTe, [3] and $Pb_{0.88}Sn_{0.12}Te$ [4] have been made. Used as photovoltaic detectors, they were reported to have high-zero-bias resistance, fast response, and high sensitivity. However, the properties of the bombarded layer have not been well studied. This letter reports the results of our study of the effects of proton bombardment on the electrical properties of p-type $Pb_{0.76}Sn_{0.24}Te$. The composition of 24% tin was studied because its energy gap in the temperature range from 80 to 100 °K meets the requirement of 8–14-μ infrared detection. The proton energy ranged from 200 to 450 keV. We found that the proton bombardment generally reduces the carrier concentration. The change of carrier type depends on the initial carrier concentration. For p-type $Pb_{0.76}Sn_{0.24}Te$ samples starting with low 10^{17} hole/cm^3, a proton dose of approximately 5×10^{13} p/cm^2 converted them into n type. However, if the initial hole concentration was above the high $10^{17}/cm^3$ range, the type conversion was not consistent. The mobility was changed by the bombardment as expected. However, both increase and decrease of mobility have been found. For total dose up to 1×10^{15} p/cm^2, the changes were all within a factor of 2.

$Pb_{0.76}Sn_{0.24}Te$ thin-film samples were used for this study. By properly choosing the film thickness and the proton energy, protons can be made to penetrate through the film. The formation of an n-p junction in the sample can be avoided. The presence of such a junction would have made the analysis of the bombarded layer difficult. We calculated[5] that, in this energy range, 100 keV of proton energy is needed to penetrate every micron of film thickness. Thin films used in this study were deposited on either CaF_2 or BaF_2 substrate by a one-boat evaporation method.[6–8] The samples were in the conventional Hall shape. The as-deposited films were p type with carrier concentrations typically in the low $10^{18}/cm^3$ range. Both the carrier type and the carrier concentration can be controlled by isothermal annealing.[9] Electrical contacts were made by depositing gold pads onto the side arms of the Hall sample after annealing. Hall coefficient and conductivity were measured before and after each bombardment in the temperature range from 300 to 87 °K, which was the lowest temperature at the cold finger of our liquid-nitrogen

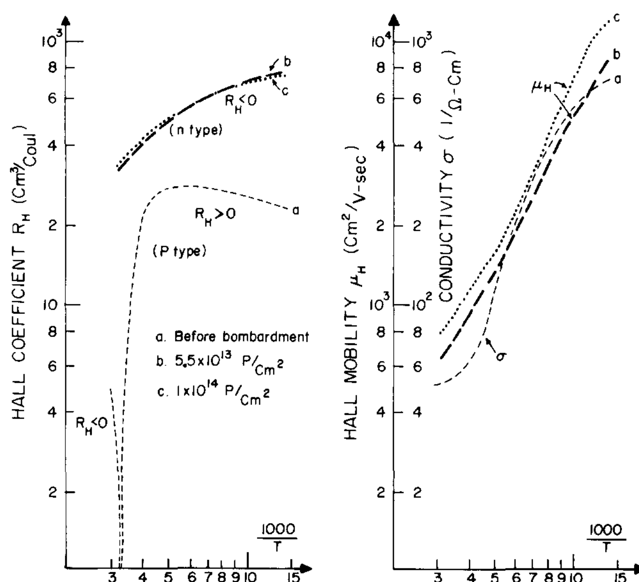

FIG. 1. Effect of 200-keV proton bombardment on a p-type $Pb_{0.76}Sn_{0.24}Te$.

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TABLE I. Effect of proton bombardment on p-type $Pb_{0.76}Sn_{0.24}Te$.

Sample	Thickness (μ)	Proton energy (keV)	Accumulated dose (p/cm^2)	Carrier concentration at 87 °K (per cm^3)	Mobility at 87 °K (cm^2/V sec)
1	1.8	200	before	2.7×10^{17} (p)	6200
			5.5×10^{13}	8.4×10^{16} (n)	8000
			1×10^{14}	8.7×10^{16} (n)	10 500
			2.2×10^{14}	8.4×10^{16} (n)	12 000
2	1.8	200	before	2.4×10^{17} (p)	2100
			5×10^{13}	1.8×10^{17} (n)	3800
			1×10^{14}	1.7×10^{17} (n)	4100
3	1	200	before	1.1×10^{18} (p)	1900
			1×10^{14}	1.7×10^{17} (n)	2000
4	4.2	450	before	8.8×10^{17} (p)	8200
			5×10^{13}	7×10^{17} (p)	6700
			2.7×10^{14}	6.7×10^{17} (p)	6700

Dewar. The proton bombardment was carried out using a defocused low-energy beam from a 2 MV Van de Graff accelerator. The total proton dose was measured in a Faraday-cup arrangement.

The results of our study are presented in two ways. First, the temperature variations of both the Hall coefficient and the mobility from 300 to 87 °K of a p-type $Pb_{0.76}Sn_{0.24}Te$ sample are shown in Fig. 1 for several bombardment steps. Before bombardment, the Hall coefficient was negative at 300 °K but became positive at low temperature, which indicated that it was a p-type sample. Its thickness was 1.8 μ, and 200-keV protons were used. The sample was converted to n type after a proton dose of 5×10^{13} p/cm^2 as indicated by its negative Hall coefficient throughout the temperature range. Subsequent bombardments up to a total dose of 2.2×10^{14} p/cm^2 produced little additional change. Results of other p-type samples are presented in Table I using carrier concentration and mobility values at 87 °K to describe the effects of proton bombardment. The following observations are of interest.

(i) The carrier concentration was generally reduced by proton bombardment up to a dose of 1×10^{14} p/cm^2. Beyond this dose the change of carrier concentration became very small.

(ii) For p-type $Pb_{0.76}Sn_{0.24}Te$ with initial hole concentrations of 2.7 and $2.4\times10^{17}/cm^3$, the carrier type was changed to n type after a dose of approximately 5×10^{13} p/cm^2. The same dose was able to convert a thin (1-μ) p-type sample of higher hole concentration of $1.1\times10^{18}/cm^3$ to n type. However, another sample of initial hole concentration of $8.8\times10^{17}/cm^3$ remained p type even after a total dose of 2.7×10^{14} p/cm^2. It should be pointed out that this film was 4.2 μ thick and that a higher proton energy of 450 keV was used.

(iii) Mobilities were changed by the bombardment. For p-type samples which were converted to n type, the mobilities were increased. For the p sample which remained p type, a small decrease was found. In both cases, the change due to the bombardment of total dose up to 2.7×10^{14} p/cm^3 was moderate and within a factor of 2.

(iv) It is well known that the electrical properties of PbSn chalcogenide alloy semiconductors are affected by nonstoichiometry.[9] Pb/Sn vacancies and chalcogenide interstitials behave as acceptors. Chalcogenide vacancies and Pb/Sn interstitials behave as donors. The fact that proton bombardment can convert p-type $Pb_{0.76}Sn_{0.24}Te$ to n type suggested that the crystal defects created by the bombardment behaved as donors such as Te vacancies. Similar to the effect of electron bombardment on InAs,[10] one would expect that the carrier concentration of n-type sample would be increased by the bombardment. However, we found that the carrier concentration of an n-type $Pb_{0.76}Sn_{0.24}Te$ sample was reduced. This sample, 3.7 μ thick, was exposed to 450-keV protons. The changes of its electrical properties are shown in Fig. 2 for three bombardment steps. The carrier concentration was initially $1.3\times10^{18}/cm^3$ and was reduced to $1.5\times10^{17}/cm^3$ after a total dose of 1×10^{15} p/cm^2. Its mobility, on the other hand, was doubled. It indicated that the defects caused by the proton bombardment in this n-type sample behave like acceptors.

It is possible that each defect can act either as an acceptor or as a donor depending on the position of the

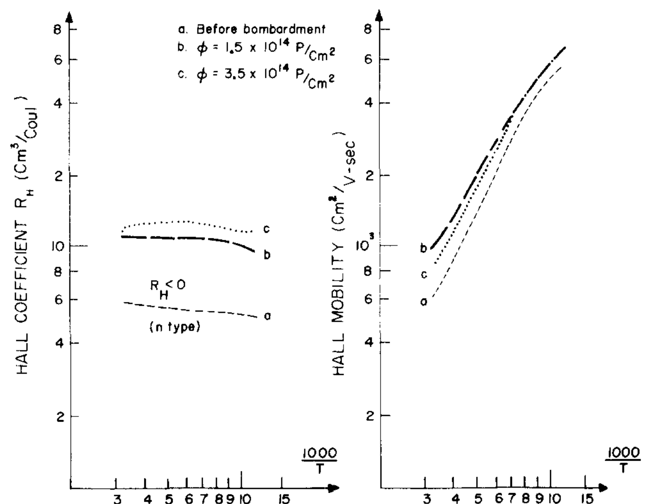

FIG. 2. Effect of 450-keV proton bombardment on an n-type $Pb_{0.76}Sn_{0.24}Te$.

Fermi level.[11] On the other hand, both acceptors and donors could have been introduced by 450-keV proton bombardment. It is interesting to note that in InSb, 1-MeV electron bombardment was found to create net acceptors, but 4.5-MeV electrons were believed to create both acceptors and donors.[12] Detailed mechanisms in $Pb_{0.76}Sn_{0.24}Te$ are not yet known. Further efforts are being pursued.

In conclusion, we have shown that protons of moderately high energies can be used to control the carrier type of $Pb_{0.76}Sn_{0.24}Te$. The effects of proton bombardment depend on the initial carrier concentration and carrier type. The electrical properties of the bombarded layer were not degraded for total dose up to 1×10^{15} p/cm^3. Some increase of mobility was even found.

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Beam Effects in the Analysis of As-Doped Silicon by Channeling Measurements*

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Channeling-effect measurements with MeV He ions have been used to study the lattice location of As in silicon. Over the concentration range studied (5×10^{19}–$1.2\times10^{21}/\text{cm}^3$) As was found to be 90–95% on substitutional sites. However, it was found that bombardment with the analysis beam caused 20–40% of the As to move off lattice sites. This effect may be responsible for the relatively low As substitutional fraction found in previous investigations. No bombardment-induced off-lattice movement was found in Sb-doped Si indicating that this movement is species dependent.

Arsenic, because of its high solubility ($\gtrsim 1.5\times10^{21}/\text{cm}^3$) in silicon, is an ideal candidate for channeling-effect investigation of the lattice location of dopant species. Previous studies of As, diffused and implanted in Si, have shown[1–4] that As was only 50 – 70% substitutional over a range of dopant concentrations from ≈ 0.2 to $2\times10^{21}/\text{cm}^3$. Channeling-effect measurements taken in the course of this work indicate instead a 90 – 95% As substitutional fraction. Recently, Ziegler and Schwenker have found large substitutional fractions in As-diffused and -implanted Si.[5] However, we found that the interaction of the analysis beam of MeV He ions with the As-doped Si caused 20 – 40% of the As to move off substitutional lattice sites. This effect may have played a large role in previous analyses of As in Si because an integrated flux of MeV He ions comparable to that required to align a crystal for channeling studies results in a marked decrease in the substitutional fraction. Although beam-induced motion of dopant atoms off lattice sites has been found previously for Group-III elements, notably B[6] and Tl[7] in Si, this is the first observation of such an effect for a Group-V dopant.

Diffused and grown As-doped samples were obtained with dopant concentrations of 5×10^{19} (diffused), 6×10^{19} (grown), 2×10^{20} (diffused), and 1.2×10^{21} (diffused) per cm^3. The crystals were etch polished and ⟨100⟩ or ⟨111⟩ oriented. The location of As atoms has been determined by channeling-effect measurements with backscattered 1.8-MeV He^+ ions.[8] In these measurements the samples were first aligned so that a major crystallographic axis was parallel to the incident beam. A typical alignment dose is about 10^3 $\mu\text{C}/\text{cm}^2$ for a beam spot of 1.7 mm^2. To avoid influence of the alignment dose, the beam is displaced 2 beam diameters to an unbombarded region before an aligned spectrum is taken. To investigate bombardment effects, the sample is tilted 5° to 7° so that the beam is incident in a "random" direction.

Figure 1 shows random and ⟨110⟩ aligned spectra for an as-grown sample with a concentration of 6×10^{19} As atom/cm^3. In the aligned spectra before bombardment (virgin spot), the backscattering yield from As was 8% of the random yield. A similar reduction in the ⟨111⟩ aligned yield was found, thus confirming the high substitutional fraction of As atoms. This same substitutional fraction (90 – 95%) was found in all samples, diffused or grown, for As concentrations between 5×10^{19} and $1.2\times10^{21}/\text{cm}^3$. The diffused samples were either quenched or rapidly cooled following diffusion. For samples that