SAND--90-0256C

DE90 009727

Tin doping of InSb Grown by MOCVD Using Tetraethyltin*

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Tetraethyltin was investigated as an n-type dopant for InSb. Carrier concentrations between 6 x 10^{15} and 4 x 10^{18} cm^{-3} with 77 K mobilities ranging from 75,000 to 10,000 cm^2/Vs were achieved for Sn doped InSb. SIMS measurements indicate a diffusion coefficient for Sn in InSb at 470 C that is approximately $1x10^{-15}$ cm^2/s. Both Hall and SIMS measurements on Sn doped samples indicate that Sn is incorporated as an n-type dopant with no memory effect and no self compensation, making Sn a much better doping source than Te or Se.

INTRODUCTION

$InAs_{1-x}Sb_x$/InSb strained-layer superlattices (SLS's) have been proposed for use as long wavelength detectors in the 8-15 micron range. The preparation of high quality materials was achieved by the minimization of cracks and dislocations in these $InAs_{1-x}Sb_x$/InSb SLS's by using 2-3 μm thick, compositionally graded $InAs_{1-x}Sb_x$ buffer layers [1]. Infrared absorption and photoluminescence were determined for these high quality SLS's in the 8-12 μm region for As content less than 20% [2]. Recently, infrared response has been demonstrated for these SLS's out to 16 μm [3]. An $InAs_{1-x}Sb_x$/InSb photodiode with a broad spectral response and a high detectivity has been prepared by MOCVD using dimethyltellurium as an n-type dopant [4]. This extended infrared activity is due to the type II heterojunction band offset in these SLS's.

Fabrication of a photodiode is an important step in the development of a new infrared material. The preparation of the first MOCVD grown p-n junction diode was achieved by using dimethyltellurium as an n-type dopant [4]. The structure of the SLS used in this photodiode consisted of $InAs_{0.18}Sb_{0.82}$/InSb layers with equal layer thicknesses, 13.0 nm. Several factors, such as background doping and dopant profiles, are believed to affect the performance of this device. Recently, a high detectivity, > $1x10^{10}$ cm $Hz^{1/2}/W$ at 10 μm, InAsSb SLS photodiode was prepared by MBE [5]. The MBE InSb has a lower background carrier concentration than the MOCVD InSb and Se was the n-type dopant. This paper discusses the use of tetratethyltin as an n-type dopant. The results of SIMS profiles are presented and compared to the previously reported results for Te. Both Se and Te have been found to have memory effects in doping experiments with InSb. These measurements indicate that Sn is the preferred n-type dopant for InSb.

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The results of the use of lower growth temperatures in an effort to reduce the p-type background are also presented.

EXPERIMENTAL

Studies investigating the use of tetraethyltin (TESn) and diethylselenium (DESe) were carried out in a previously described horizontal, atmospheric pressure system [3]. The sources of In, Sb and As were trimethylindium (TMIn), trimethylantimony (TMSb) or triethylantimony (TESb) and arsine (AsH_3). Tetraethyltin (TESn) was used in its pure state in a bubbler at a variety of different flow rates and temperatures. Dilution of the TESn was obtained by two different techniques. Some samples were grown by the standard technique of using all of the hydrogen which passed through the TESn bubbler in the reaction chamber flow. The temperature of the bubbler was varied between -16 and -82 C and the flow was varied between 20 and 0.2 sccm. In the other samples, the TESn flow was diluted with hydrogen after passing through the bubbler. The scheme for achieving dilution of TESn is illustrated in Fig. 1. The flow through the bubbler was 0-20 sccm and 0-20 sccm for the inlet to the reaction chamber. The dilution flow can be varied from 0-4000 sccm. The flow to the vent is controlled by an automatic pressure regulation system consisting of a pressure transducer and a proportioning valve with the associated controlling circuitry. Dilution flows of 2800 to 333 sccm were used with bubbler flows of 20 to 2 sccm in a temperature range of -22 to -26 C and diluted TESn flows into the reactor of 20 to 2 sccm. Using this dilution technique, doping levels of 1×10^{16} cm^{-3} could be reproducibly obtained. Diethylselenium was used as a mixture in hydrogen at a concentration of 26 ppm. Purified hydrogen was used as the carrier gas. The layers were grown at 410-470 C on (100) InSb substrates. The optimum growth conditions at 470 C have been previously described [3,6]. At 470 C a 5/3 ratio of 2.4 and a growth rate of 0.5 μm/h were used. At 410 C a 5/3 ratio of 3.0 and a growth rate of 0.1 μm/h were necessary to obtain the same surface morphology. The InSb substrates were cleaned by degreasing in hot solvents and deionized water. They were then etched for two minutes in a 10 to 1 mixture of lactic acid and nitric acid, rinsed with deionized water and blown dry with filtered nitrogen.

Structures for Hall measurements were grown on compensated, Cd doped InSb with measured hole densities at 77 K of 10^{12}-10^{13} cm^{-3}. The general structure which was used for the Hall measurements consisted of a single layer of InSb 2 to 4 μm thick grown directly on the substrate. Hall measurements were made by standard van der Pauw techniques with a magnetic field which could be varied between 0.1 to 6 kG. The epitaxial layers were uniformly doped. The samples were examined by optical microscopy and a lapping technique to determine layer thicknesses.

Secondary ion mass spectroscopy (SIMS) profiles were obtained by using Cs^+ ion bombardment and negative sputtered ion mass spectrometry. The conversion of sputtering time to depth was based on the measurements of the analytical craters by a profilometer. This procedure is nominally accurate to within seven percent.

RESULTS AND DISCUSSION

Results of the doping experiments which used TESn and DESe are illustrated in Figs. 2 and 3. Fig. 2 shows the resulting carrier concentration as a function of the concentration of TESn in the reaction chamber. The solid circles represent the results for samples in which the hydrogen flow was passed directly through the TESn bubbler. The open circles represent the results for Sn doping in which the TESn flow was diluted with hydrogen after passing through the bubbler. For dilution flows greater than 1 SLM the samples were always p-type even for dilution flows which should have resulted in a sufficient concentration of TESn being introduced into the reactor to form n-type InSb. This is possibly due to poor mixing in the experimental apparatus which resulted in very little if any of the TESn being transported to the reactor. For certain combinations of low flow into the reaction chamber, the doping results were not reproducible. Under the conditions of high dilution flow or low reaction chamber flow, the samples would be n- or p-type depending on the history of the reaction chamber. When concentrations of TESn were less than 1.2×10^{-9} M/l, the samples were always p-type. The carrier concentrations at 77 K for this concentration of TESn varied from 6×10^{15} to 1.7×10^{16} cm^{-3}. This is evidence for the residual p-type impurity or defect having a concentration of about 1×10^{16} cm^{-3}. Using this dilution technique, doping levels of 2×10^{16} cm^{-3} could be reproducibly obtained and doping concentrations as low as 6×10^{15} cm^{-3} were obtained on some occasions. The lowest n-type dopant levels were obtained when only a few growths had been done in the system. As the reaction chamber experienced more growths, the samples became p-type for the same concentration of TESn that originally produced n-type material. This indicates that the p-type impurity or defect increased as the amount of material on the inside of the reaction chamber increased. When the chamber was cleaned and more samples were grown, the lower n-type doping could be obtained again for several runs before converting back to p-type. As shown in Fig. 2, the measured carrier concentration is directly proportional to the TESn concentration in the reactor over three orders of magnitude. This indicates that the Sn is incorporated entirely as an n-type dopant and that it does not self-compensate.

Fig. 3 shows the 77 K Hall mobilities for TESn and DESe doped InSb as a function of carrier concentration. Also illustrated in Fig. 3 are the mobilities for four undoped samples of InSb grown from TESb and TMIn at 410 C. The solid line represents typical literature values for the mobilities of bulk n-type InSb [7]. Carrier concentrations of 6×10^{15} to 4×10^{18} cm^{-3} and mobilities of 6.7×10^4 to 1.1×10^4 cm^2/Vs have been measured at 77 K for TESn doped samples. Results for DESe samples are shown for comparison. The mobilities for the Sn and Se doped samples are similar for similar carrier concentrations. These mobilities are also similar to the typical literature values. This is further support for the lack of self-compensation of Sn. The fall off in mobilities of the Sn doped samples compared to the literature values can be explained by the residual p-type background of the undoped InSb grown at 470 C. The mobilities for the undoped samples grown at 410 C also fall below the line and indicate that some form of compensation is present at about 1×10^{16} cm^{-3}. SIMS measurements of the carbon levels in InSb grown at, 410 and 470 C, and using triethylantimony instead of trimethylantimony, indicate a reduction in the amount of carbon that is incorporated during the growth of InSb at 410C.

A Se-memory effect was observed for doping with DESe. Samples grown immediately after a Se-doped sample exhibited an n-type background. These results indicate that the use of DESe contaminated the reaction chamber with residual Se or DESe which caused a dopant memory effect. When the reaction chamber was cleaned, the InSb layers reverted to p-type. This behavior is similar to that previously reported for Te [4].

The results of SIMS measurements on a buried Sn-doped InSb structure are illustrated in Fig. 4. The grown structure consisted of an undoped InSb substrate, a 0.4 μm thick undoped InSb layer, a Sn-doped 1.1 μm layer and a final undoped, 0.7 μm layer. The sharp profiles as shown in Fig. 4 indicate that very little diffusion of the Sn is taking place. The level of Sn in this structure is estimated to be 2×10^{18} cm^{-3} from Hall measurements on similarly doped samples. This structure was grown over a period of 5 hours at 470 C. A diffusion coefficient for Sn at 470 C of 1×10^{15} cm^2/s was calculated from the SIMS profile by assuming a complimentary error function for the diffusion profile. This result is similar to the diffusion coefficients reported for Cd (1×10^{-15} cm^2/s [8]) and Mg (3×10^{-15} cm^2/s [8]) in InP at 650 C, but smaller than the diffusion coefficients for Zn (4×10^{-13} cm^2/s [8]) in InP at 650 C and Te (2×10^{-14} cm^2/s [4]) in InSb at 470. Both Hall and SIMS measurements on Sn doped samples indicate that Sn is incorporated as an n-type dopant with no memory effect and no self-compensation, making Sn a much better doping source than Te or Se.

The current-voltage characteristics of a diode made from InSb and using Sn doping were typical of a narrow bandgap semiconductor [9]. The preparation of SLS diodes using Sn will determine if the use of Sn improves the device parameters for infrared detection. The background carrier concentration for undoped InSb needs to be improved to enhance the infrared photodiode behavior.

ACKNOWLEDGMENTS

The author wishes to thank D. R. Moore for her technical support, and F. A. Greulich for the SIMS analysis. *This work was performed at Sandia National Laboratories supported by the US DOE under Contract No. DE-AC04-76DP00789.

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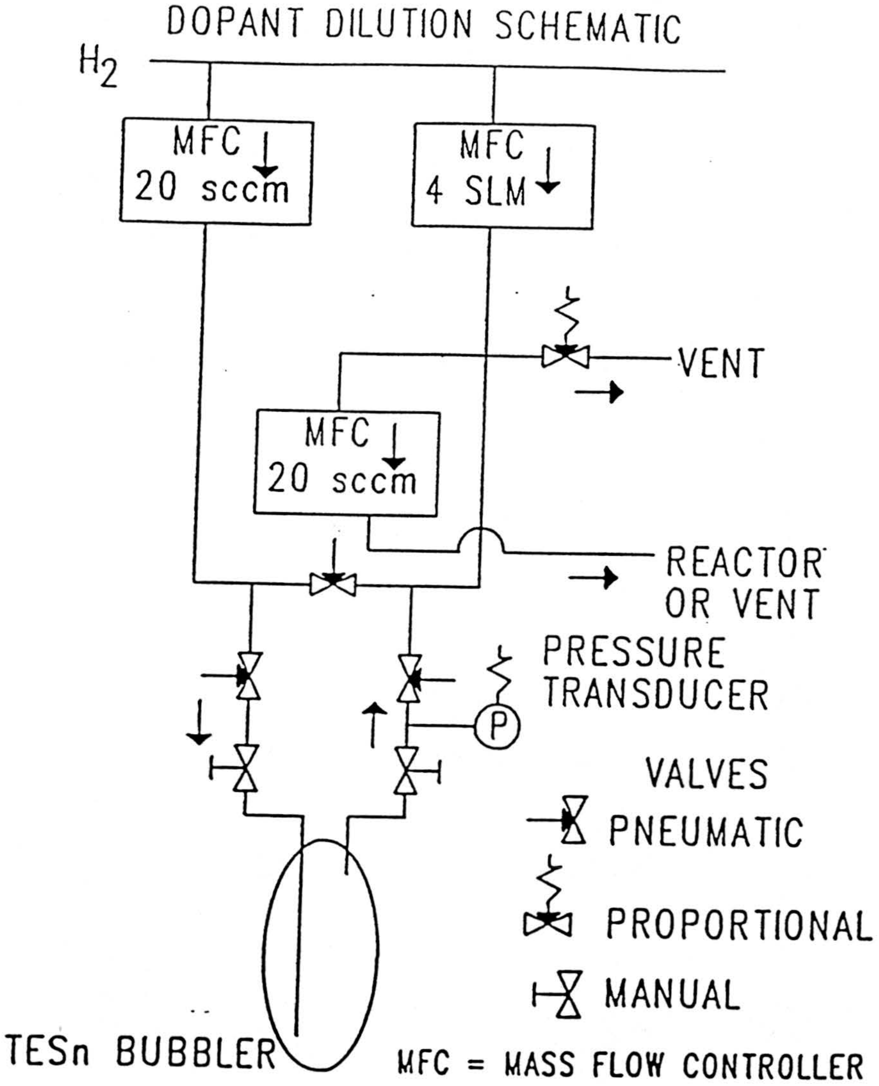

Fig. 1. The experimental arrangement for the dilution flow of TESn. The mass flow controllers, MFC, are 0-20 sccm for the inlet to the bubbler and 0-20 sccm for the inlet to the reaction chamber. The dilution flow can be varied from 0-4000 sccm. The flow to the vent is controlled by an automatic pressure regulation system consisting of a pressure transducer and a proportioning valve with the associated controlling circuitry.

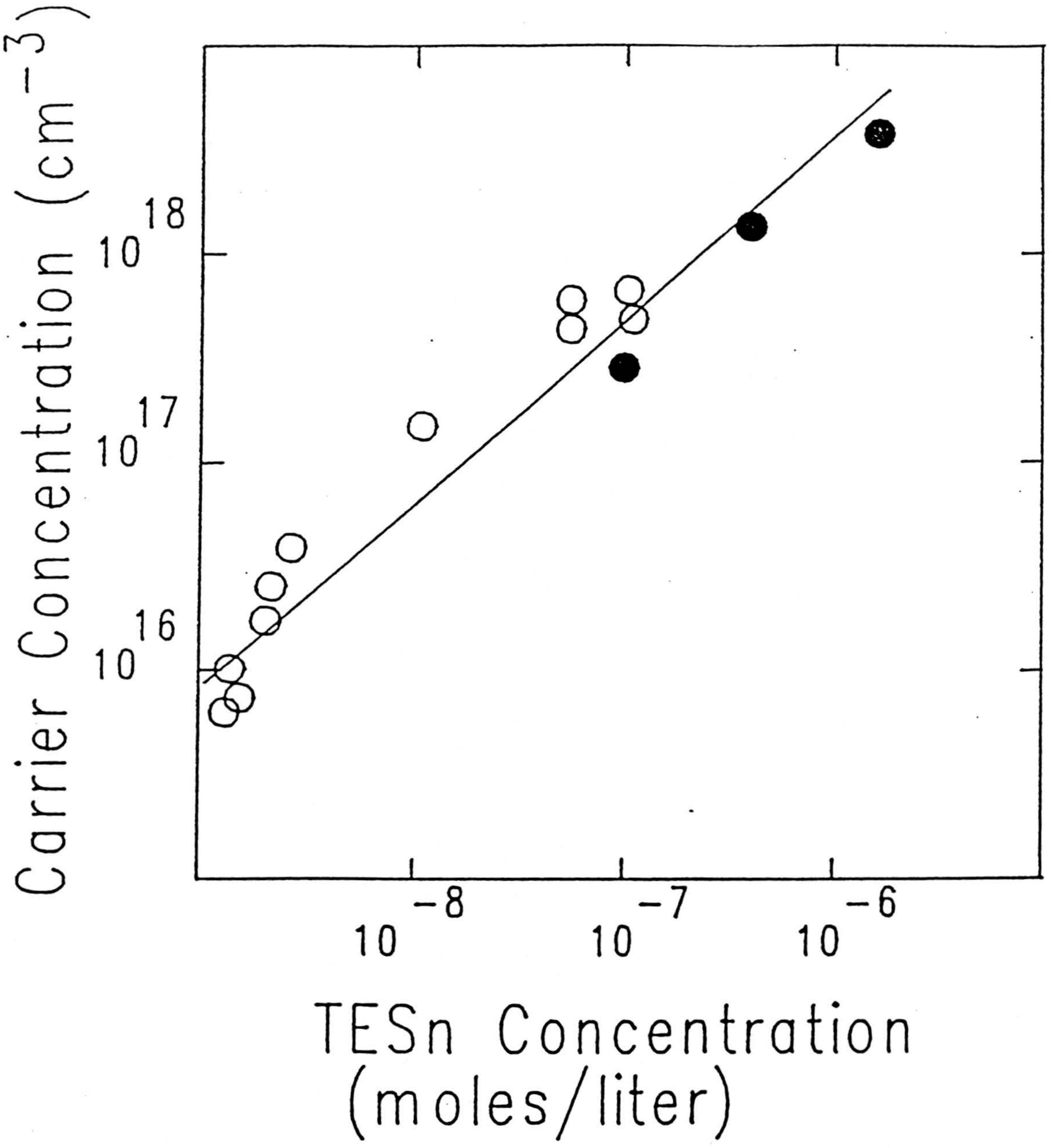

Fig. 2. The variation of net carrier concentration as a function of TESn in the reaction chamber during the growth of InSb. The filled circles are grown with a standard bubbler arrangement and the open circles were grown with a dilution flow of hydrogen added to the output of the TESn bubbler.

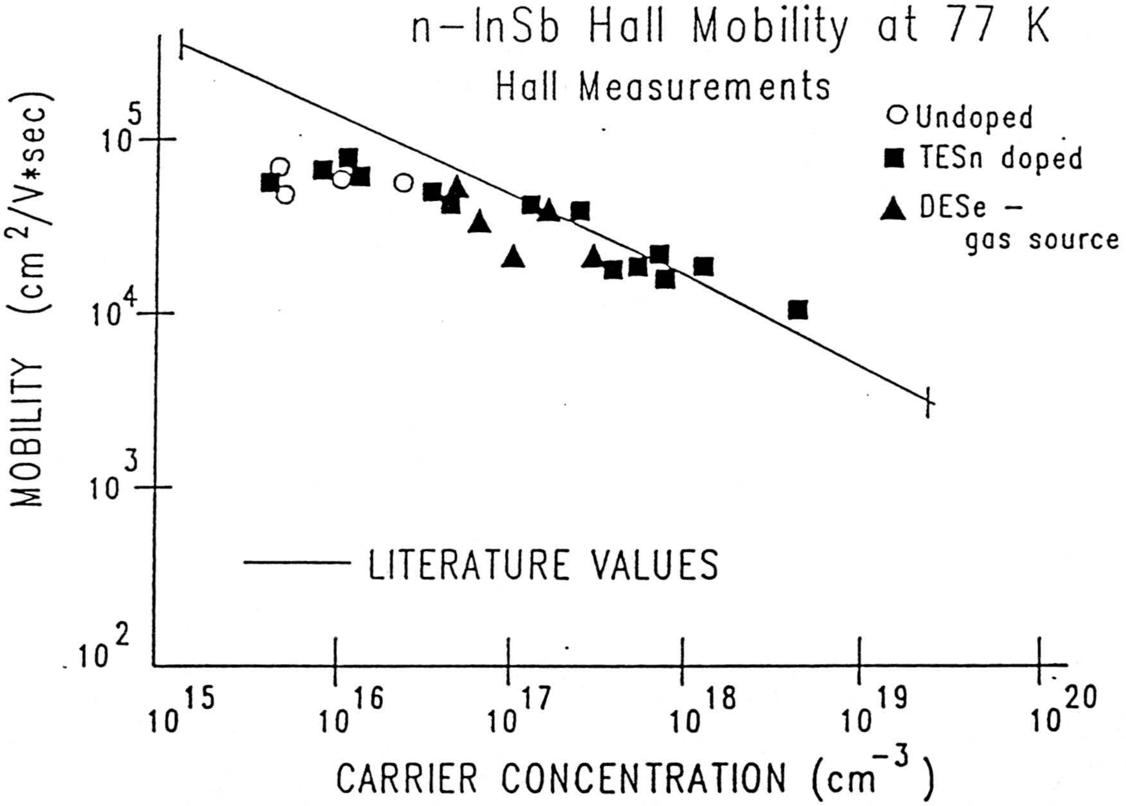

Fig. 3. Mobility versus net carrier concentration at 77 K for uniformly doped epitaxial layers InSb. The undoped samples, open circles, were grown using TESb and TMIn at 410 C. The Sn-doped, filled squares, and Se-doped, filled triangles, layers were grown at 470 C using TMSb and TMIn.

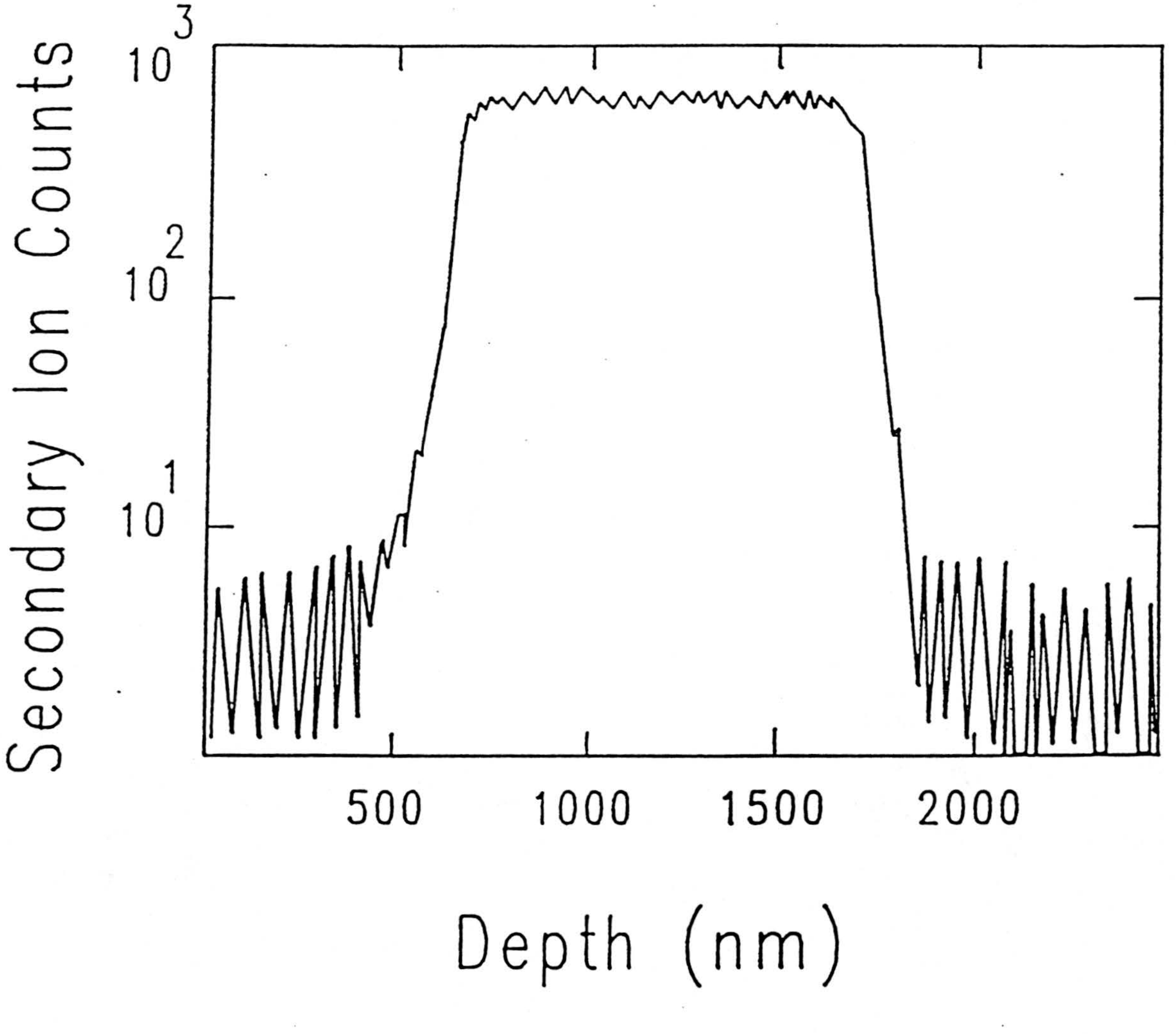

Fig. 4. SIMS profile of a buried, Sn-doped InSb epitaxial layer grown on an undoped InSb substrate. The profile indicates that very little Sn diffusion is taking place during growth at 470 C.