Effect of Low-Temperature Diffusion Annealing on the Properties of PbSnTe(In) Epilayers

L. F. Vasil’eva, A. E. Klimov, N. I. Petikov, and V. N. Shumskii

Institute of Semiconductor Physics, Siberian Division, Russian Academy of Sciences, pr. akademika Lavrent’eva 13, Novosibirsk, 630090 Russia

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Abstract—A procedure was proposed for low-temperature vapor-phase In doping of Pb$_{1-x}$Sn$_x$Te films grown by molecular-beam epitaxy on BaF$_2$ substrates. Diffusion annealing was carried out in a hydrogen atmosphere in the presence of a vapor source identical in composition to the film and a dopant source at temperatures which were, in most cases, no higher than the growth temperature (300–460°C). The effect of diffusion annealing on the composition, transport properties, and homogeneity of both undoped and In-doped films was examined. The results suggest that indium is transported in the vapor phase in the form of indium tellurides resulting from the reaction between Te vapor and liquid In.

INTRODUCTION

Indium-doped Pb$_{1-x}$Sn$_x$Te (PbSnTe) solid solutions are among the most attractive materials for photodetectors sensitive in the far-IR spectral region.

Earlier work [1] showed that, below 20 K, PbSnTe(In) materials are in a so-called dielectric state in which the carrier concentration is close to the intrinsic one, and both the photoresponse and the photocurrent decay time attain their highest levels. Thin PbSnTe films [2, 3] (including Pb$_{0.74}$Sn$_{0.26}$Te(In) [4]) produced by molecular-beam epitaxy (MBE) on BaF$_2$ can be used to fabricate linear and two-dimensional array photodetectors for the spectral range 25–30 μm. The performance parameters of array photodetectors depend strongly on the uniformity of element detectors and, hence, the homogeneity of the films.

A major technical problem in the thin-film growth of In-doped multicomponent solid solutions is to ensure both reproducibility and uniformity of film composition. In this context, precise control over the temperatures of the major, additional Te, and dopant sources and the uniformity of the film temperature is critical. Such control is however difficult to exercise in MBE growth. Moreover, doping with indium during growth gives rise to surface roughness, which degrades the quality of photolithographic patterning [5].

The purpose of this work is to assess the effect of diffusion annealing on the composition, transport properties, and homogeneity of undoped and In-doped MBE PbSnTe films. The results are used to optimize the annealing conditions.

EXPERIMENTAL AND RESULTS

Undoped and In-doped Pb$_{1-x}$Sn$_x$Te ($x = 0.18–0.30$) films, ranging in thickness from 1.5 to 2 μm, were produced by MBE on BaF$_2$ at substrate temperatures from 400 to 420°C. The films were then annealed between 300 and 450°C in a sealed reactor under a hydrogen atmosphere in the presence of a dopant source. Indium is fairly difficult to transport to the film in the vapor phase, because its vapor pressure is extremely low in the temperature range of interest. To obviate this difficulty, use can be made of volatile In compounds, in particular tellurides, presynthesized or forming in the process of annealing.

The carrier concentration and mobility in the as-grown and annealed films were evaluated from Hall and conductivity data. We also measured the current through the sample as a function of temperature in the dark ($I_d$) and under the action of a 300-K background radiation ($I_b$).

Diffusion anneals were performed using various film–vapor source systems:

1. Films with $x = 0.2$, both of $n$- and $p$-type, with a carrier concentration of $10^{17}$ to $10^{18}$ cm$^{-3}$, were annealed in the presence of a Pb$_{0.8}$Sn$_{0.2}$Te source (ground crystals) with $p = 3 \times 10^{19}$ cm$^{-3}$, without In. After annealing at 350°C for 180 min, all of the films were $p$-type, with a carrier concentration $p \geq 10^{19}$ cm$^{-3}$ and mobility $\mu = 2000–3000$ cm$^2$/V s.

2. Annealing was carried out in the presence of the same Pb$_{0.8}$Sn$_{0.2}$Te source material and a metallic In source. The films and sources, out of contact with each other, were heated to identical temperatures—300, 350, or 400°C. The influence of the annealing temperature and duration on the carrier concentration and mobility...
in the annealed films is illustrated in Fig. 1. It can be seen that, regardless of the annealing temperature, the hole concentration decreases with time, to the point of type conversion. Then, the electron concentration decreases to a minimum value, which depends on the annealing temperature, and finally levels off. Carrier mobility increases upon conversion from p- to n-type and continues to rise with decreasing electron concentration.

(3) Films with a nominal composition of Pb\textsubscript{0.74}Sn\textsubscript{0.26}Te doped with 2–3 at. % In, which underwent no transition to an insulating state, were annealed at 430–440°C in the presence of a [(Pb\textsubscript{0.74}Sn\textsubscript{0.26})\textsubscript{1-x}In\textsubscript{x}]\textsubscript{-1}Te\textsubscript{y} (x = 0.03, y = 0.5) source. Figure 2 displays the Arrhenius plots of \(I_d\) and \(I_b\) for the films annealed under different conditions. These data demonstrate that annealing reduces \(I_d\), eventually transferring the material to an insulating state. The conditions under which this occurs vary from sample to sample. At the same time, the effect of annealing is virtually independent on the In content of the source material in the range \(x = 0.005–0.03\).

(4) Undoped Pb\textsubscript{0.74}Sn\textsubscript{0.26}Te films were annealed in the presence of a [(Pb\textsubscript{0.74}Sn\textsubscript{0.26})\textsubscript{1-x}In\textsubscript{x}]\textsubscript{-1}Te\textsubscript{y} (x = 0.03, y = 0.5) source at 460°C for 6 h. The anneal caused no changes in the transport properties of the films. Four anneals at 460°C, each for 3 h, in the presence of the same source material as above and In metal produced changes in \(I_d\) and \(I_b\) similar to those described above (Fig. 3). Characteristically, these films had a smooth, lustrous surface, both before and after annealing, which is a favorable condition for high-quality photolithographic patterning.

(5) To establish the applicability limits of our approach, undoped Pb\textsubscript{0.74}Sn\textsubscript{0.26}Te films, undergoing no transition to an insulating state, were annealed in the presence of a [(Pb\textsubscript{0.74}Sn\textsubscript{0.26})\textsubscript{1-x}In\textsubscript{x}]\textsubscript{-1}Te\textsubscript{y} (x = 0.03, y = 0.5) source and In metal at 440–460°C. Figure 4 illustrates the variation of the 77-K carrier concentration in the course of annealing, and Fig. 4b displays the Arrhenius plots of \(I_d\) and \(I_b\) for films annealed for different lengths of time. In this system, annealing for a few hours also reduces \(I_d\), as in system 4.

The presence of indium in the surface layer of the annealed films was ascertained by Auger electron and x-ray photoelectron spectroscopy techniques (NANOSCAN-50 instrument). The observed In peaks in the Auger spectrum corresponded to PbSnTe(In) (401.7 and 403 eV) and In\textsubscript{2}Te\textsubscript{3} (408.3 and 411.7 eV). The amount of In on the film surface was found to rise with annealing time. If the film and vapor source differed in composition (system 5), the Pb/Sn ratio also depended on the annealing time. Neither Auger nor x-ray photoelectron spectra showed the presence of In in the initially undoped films. The surface layer of the films doped with In during MBE growth contained up to 10% In.