

Electrical properties of PbTe doped with BaF₂

U. A. Mengui, E. Abramof,^{a)} P. H. O. Rappl, B. Díaz, H. Closs, J. R. Senna, and A. Y. Ueta

Laboratório Associado de Sensores e Materiais (LAS), Instituto Nacional de Pesquisas Espaciais (INPE), CP 515, 12245-970 São José dos Campos, SP, Brazil

(Received 11 November 2008; accepted 9 January 2009; published online 26 February 2009)

We study here the *p*-type doping of PbTe with BaF₂. For the investigation, PbTe layers were grown on (111) BaF₂ substrates by molecular beam epitaxy. The beam flux ratio between BaF₂ and PbTe, defined as the nominal doping level, was varied from 0.02% to 1%. The hole density increases from 5×10^{17} to 1×10^{19} cm⁻³ as the doping level rises from 0.02% to 0.4% and saturates at $p \sim 10^{19}$ cm⁻³ for higher levels. The saturation effect was attributed to self-compensation. The carrier concentration of all samples remained almost constant as the temperature was varied from 10 to 350 K, indicating that no thermal activation is present in the whole doping range. It suggests that the impurity level in PbTe doped with BaF₂ remains resonant with the valence band, similar to the native defects behavior. The low-temperature mobility showed a pronounced reduction from 50 000 to 2 000 cm²/V s as the doping level rises from 0.02% to 1%, mainly due to the substantial increase in the hole concentration. For temperatures higher than 80 K, the mobility was essentially limited by phonon scattering. Our results demonstrate that a controlled *p*-type doping of PbTe with BaF₂ can be obtained up to 10^{19} cm⁻³. © 2009 American Institute of Physics. [DOI: 10.1063/1.3082043]

I. INTRODUCTION

Lead telluride is a narrow gap semiconductor that finds applications in thermoelectric devices¹⁻³ and in infrared lasers^{4,5} and detectors.^{6,7} The molecular beam epitaxial (MBE) technique has been successfully applied to grow high-quality thin films and heterostructures of PbTe-based alloys.⁸⁻¹⁰ Highly doped layers ($> 10^{19}$ cm⁻³) are required to increase the impedance-temperature (ZT) figure of merit in thermoelectric devices³ and to minimize electrical losses in lasers.⁴ In addition, the doping control to produce a wide range of free carrier densities is very interesting for optoelectronic devices. Doping is also very important to obtain high-quality samples to study quantum confinement effects. Fine control of the electron density in PbTe/PbEuTe quantum wells made possible the observation of the integer quantum Hall effect^{11,12} and of the conductance quantization in constricted samples.¹³ The effects of localization and antilocalization were investigated in *n*-type¹⁴ and *p*-type¹⁵ doped Pb_{1-x}Eu_xTe layers and an enhancement of the thermoelectric power was observed in PbTe/PbEuTe multiquantum wells.¹

In principle, the lead salts can be easily doped by controlling the stoichiometric deviation, i.e., *p*-type (*n*-type) material is obtained from a chalcogen-rich (metal-rich) growth regime. However, the doping levels of lead salt layers are rather limited under off-stoichiometric MBE growth conditions. For this reason, extrinsic doping is preferred in order to obtain carrier densities higher than 10^{18} cm⁻³. Using Bi impurity, *n*-type doping of PbTe is obtained in a controlled manner up to 10^{20} cm⁻³. To facilitate the complete incorporation of Bi on substitutional Pb lattice sites, the element Bi is usually offered under chalcogen-rich conditions from a

Bi₂Te₃ effusion cell in the MBE system.^{16,17} The best results for *p*-doping of PbTe have been achieved with Tl impurity, using a Tl₂Te solid source in the MBE effusion cell,¹⁸ which has given *p*-type layers with hole concentrations from 10^{18} to 10^{20} cm⁻³. BaF₂ is mentioned as an alternative *p*-type dopant in the study of thermoelectric figure of merit ZT in PbTe-based superlattices.³

In this work, we study the *p*-type doping of PbTe with BaF₂. The electrical properties of PbTe epitaxial layers doped with BaF₂ are investigated as a function of doping level and temperature. For this purpose, PbTe:BaF₂ epilayers were grown by MBE on (111) BaF₂ substrates. In order to control the doping level, the flux ratio between BaF₂ and PbTe was varied from 0.02% to 1%. The electrical properties were determined by Hall effect and resistivity measurements at temperatures from 10 to 350 K. X-ray rocking curves around the (222) PbTe Bragg peak were measured to evaluate the structural characteristics.

II. EXPERIMENTAL

The samples were grown on (111) BaF₂ substrates by MBE in a Riber 32P MBE system equipped with effusion cells containing solid sources of PbTe, Te, and BaF₂. A 12 keV reflection high energy electron diffraction (RHEED) system was used to evaluate *in situ* the growth evolution. The beam equivalent pressure (BEP) of each cell was measured separately with a Bayer-Alpert ion-gauge flux monitor near the substrate position. The (111) BaF₂ substrates were cleaved, just before loading in the load-lock chamber, and fixed with gallium-indium alloy to a molybdenum sample holder. They were then transferred to the preparation chamber and preheated at 200 °C for 10 min to degas. In the main chamber, the substrates are heated to 500 °C for 15 min to clean the surface before growth. During this experiment, the

^{a)}Author to whom correspondence should be addressed. Electronic mail: abramof@las.inpe.br.

TABLE I. Data of the PbTe layers doped with BaF₂: BEP of the PbTe cell (BEP^{PbTe}=5.8×10⁻⁷ Torr), substrate temperature $T^{\text{sub}}=300$ °C, growth time =2.5 h, BaF₂ effusion cell temperature (T^{BaF_2}) and flux (BEP^{BaF₂}), nominal doping level (BEP^{BaF₂}/BEP^{PbTe}), layer thickness (t), FWHM of the (222) PbTe Bragg peak, electrical resistivity (ρ), hole concentration (p), and Hall mobility (μ) at 300 and 10 K.

Sample	T^{BaF_2} (°C)	BEP ^{BaF₂} (Torr)	Doping Level (%)	t (μm)	FWHM (arcsec)	$\rho^{300\text{ K}}$ ($\Omega\text{ cm}$)	$p^{300\text{ K}}$ (cm^{-3})	$\mu^{300\text{ K}}$ ($\text{cm}^2/\text{V s}$)	$\rho^{10\text{ K}}$ ($\Omega\text{ cm}$)	$p^{10\text{ K}}$ (cm^{-3})	$\mu^{10\text{ K}}$ ($\text{cm}^2/\text{V s}$)
8037	850	1.0×10 ⁻¹⁰	0.02	3.36	122	2.54×10 ⁻²	4.76×10 ¹⁷	5.17×10 ²	2.53×10 ⁻⁴	4.69×10 ¹⁷	5.26×10 ⁴
8038	890	2.0×10 ⁻¹⁰	0.04	3.24	124	1.05×10 ⁻²	1.12×10 ¹⁸	5.29×10 ²	1.73×10 ⁻⁴	1.26×10 ¹⁸	2.86×10 ⁴
8039	930	4.0×10 ⁻¹⁰	0.06	3.40	172	5.18×10 ⁻³	2.44×10 ¹⁸	4.94×10 ²	1.05×10 ⁻⁴	2.86×10 ¹⁸	2.07×10 ⁴
8040	940	5.0×10 ⁻¹⁰	0.08	3.36	248	3.96×10 ⁻³	3.16×10 ¹⁸	4.99×10 ²	8.46×10 ⁻⁵	4.00×10 ¹⁸	1.84×10 ⁴
8041	945	7.0×10 ⁻¹⁰	0.10	3.34	172	4.32×10 ⁻³	2.72×10 ¹⁸	5.31×10 ²	1.11×10 ⁻⁴	3.49×10 ¹⁸	1.61×10 ⁴
8042	970	1.2×10 ⁻⁹	0.21	3.29	180	2.16×10 ⁻³	6.73×10 ¹⁸	4.29×10 ²	1.07×10 ⁻⁴	8.89×10 ¹⁸	6.57×10 ³
8043	1003	2.3×10 ⁻⁹	0.40	3.47	283	1.63×10 ⁻³	7.99×10 ¹⁸	4.81×10 ²	1.42×10 ⁻⁴	1.06×10 ¹⁹	4.16×10 ³
8044	1016	3.5×10 ⁻⁹	0.60	3.30	213	2.19×10 ⁻³	6.95×10 ¹⁸	4.11×10 ²	2.13×10 ⁻⁴	8.64×10 ¹⁸	3.40×10 ³
8045	1027	4.7×10 ⁻⁹	0.80	3.42	231	1.81×10 ⁻³	8.24×10 ¹⁸	4.19×10 ²	2.10×10 ⁻⁴	1.05×10 ¹⁹	2.83×10 ³
8047	1041	5.8×10 ⁻⁹	1.00	3.44	335	2.09×10 ⁻³	7.57×10 ¹⁸	3.94×10 ²	3.03×10 ⁻⁴	9.31×10 ¹⁸	2.21×10 ³

PbTe cell temperature was kept at 645 °C, leading to a BEP of 5.8×10⁻⁷ Torr, and the layers were deposited at a substrate temperature of 300 °C. In these conditions the growth rate was ~1.3 $\mu\text{m}/\text{h}$. All layers were grown during 2.5 h resulting in thicknesses from 3.0 to 3.5 μm .

The growth of all PbTe layers doped with BaF₂ starts with a three-dimensional nucleation, evidenced by the spotty RHEED pattern. After 2–4 min (40–80 nm), the initial islands coalesce and the RHEED pattern changes to a streaky one. When the layer thickness reaches approximately 0.5 μm , the RHEED pattern already shows elongated spots lying on a semicircle, characteristic of an atomically flat surface. This RHEED pattern persists until the end of growth. No surface reconstruction is observed during the growth.

For the electrical characterization, Van der Pauw geometry samples were prepared by soldering Au wires with In pellets. An automated Hall Effect system was used to measure the resistivity, carrier concentration, and Hall mobility of the samples at temperatures ranging from 10 to 350 K. A magnetic field of 0.7 T was applied for the Hall measurements. The structural quality of the doped layers was evaluated from the full width at half maximum (FWHM) of the x-ray rocking curves measured around the (222) PbTe Bragg peak in a Philips X'Pert high resolution diffractometer.

III. RESULTS AND DISCUSSION

The electrical characteristics of undoped lead telluride are controlled by native defects created by the deviation from stoichiometry, i.e., Pb or Te vacancy acts as acceptors or donors, respectively. In vacancy doped PbTe, the carrier concentration is almost independent of temperature, which means that no carrier freeze-out is present.^{19,20} In order to control the electrical character of PbTe by deviation from stoichiometry during the MBE growth, we normally use a Te-rich solid source (Pb_{0.49}Te_{0.51}) and an additional Te flux to compensate the preferential evaporation of tellurium. At a growth temperature of 300 °C and without additional Te flux, the PbTe layers grow *n*-type with an electron concentration of ~1×10¹⁷ cm⁻³.

Before growing the BaF₂ doped PbTe sample series, we first determined the additional Te flux necessary to obtain a *p*-type PbTe layer controlled only by Pb vacancies. The tran-

sition from *n*- to *p*-type was found to occur at a Te flux of 8.3×10⁻⁹ Torr, originated from the Te cell at a temperature of 285 °C. The sample with this additional Te flux, which exhibited a hole concentration of 1×10¹⁷ cm⁻³, was set as a reference to start doping with BaF₂.

To obtain the PbTe layers with different BaF₂ doping levels, a series of samples was produced with BaF₂ effusion cell temperature varying from 850 to 1040 °C, which gives a BaF₂ BEP ranging from 1.0×10⁻¹⁰ to 5.8×10⁻⁹ Torr. In this manner, the nominal doping level, defined as the BEP ratio between BaF₂ and PbTe, varied from 0.02% to 1%. Table I summarizes the MBE growth parameters and the electrical properties at 300 and 10 K of the PbTe layers doped with BaF₂.

Figure 1 shows the hole concentration at 10 and 300 K of the PbTe layers doped with BaF₂ as a function of the nominal doping level. It increases from 5×10¹⁷ to 1×10¹⁹ cm⁻³ as the BaF₂ doping level rises from 0.02% to 0.4% and saturates at $p\sim 10^{19}$ cm⁻³ for higher levels. These results demonstrate that PbTe MBE films can be effectively *p*-type doped with BaF₂ up to 10¹⁹ cm⁻³, and that the doping can be controlled by varying the BaF₂ beam flux in a specific range. For the lead salts, the saturation of the free carrier density on the impurity concentration within the solubility limit can be attributed to Fermi level pinning or self-compensation.²¹ Self-compensation means that the in-

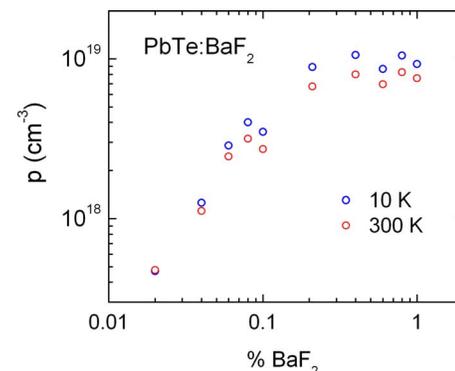


FIG. 1. (Color online) Hole concentration at 10 and 300 K as a function of BaF₂ doping level in PbTe layers. The carrier density saturates at $p\sim 10^{19}$ cm⁻³ for doping levels above 0.4%.

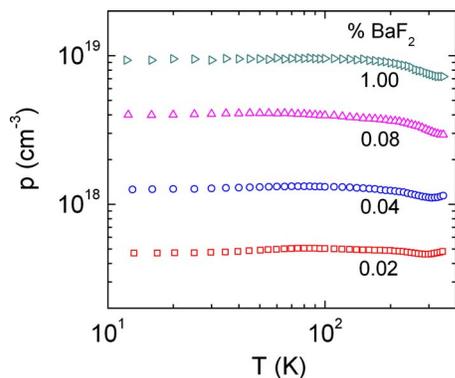


FIG. 2. (Color online) Temperature dependence of the hole density in PbTe layers doped with BaF₂ at different levels.

corporation of an impurity atom into the crystal lattice creates a native defect which neutralizes the impurity atom. This phenomenon has been observed for many dopants in PbTe films.²¹ We observed here that for BaF₂ doping levels higher than 1%, the electrical character of the PbTe layer is not well controlled anymore. Due to the high defect density produced at this doping range, both *p*- and *n*-type PbTe layers are obtained. This behavior indicates that self-compensation is probably responsible for the saturation effect.

The small difference between the carrier concentration at room temperature and at 10 K indicates that no thermal activation is present in the whole doping range investigated. This fact is illustrated in Fig. 2, where the hole concentration of some PbTe doped layers is plotted as a function of temperature from 10 to 350 K. The result observed here suggests that the impurity level in PbTe doped with BaF₂ remains resonant with the valence band and follows the same behavior as the native defects do.

Since the carrier concentration almost does not change with temperature, the mobility in the lead salts is, in general, determined by phonon scattering at temperatures higher than 80 K. At low temperatures, the carrier scattering due to ionized impurities, which is normally observed for the most common semiconductor materials, is not present in the IV-VI compounds. The huge static dielectric constant, which screens the Coulomb potential of the impurities, and the relatively small effective masses are responsible for the high mobilities observed in PbTe at low temperatures. If well-controlled additional Te flux and elevated growth temperatures are used, low-temperature saturation mobility above 10⁶ cm²/V s is obtained in *n*-PbTe.⁸ Usually, the saturation mobilities of the *p*-type PbTe samples are one order of magnitude smaller. The mobility saturation at low temperatures is related to carrier scattering due to defects, mainly dislocations.

Figure 3 shows the Hall mobility as a function of temperature for the *p*-PbTe layers with increasing BaF₂ doping level. At room temperature, where phonons dominate over other scattering mechanisms, the mobility shows a small decrease from 500 to 400 cm²/V s, as the doping level increases from 0.02% to 1%. At 80 K, this reduction becomes more evident (10 000–2000 cm²/V s), indicating that additional carrier scattering processes start to limit the mobility at

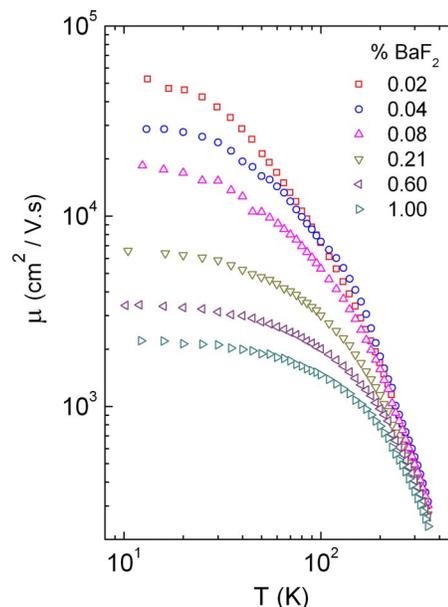


FIG. 3. (Color online) Hall mobility as a function of temperature for PbTe layers with increasing BaF₂ doping level.

this intermediate temperature as the carrier concentration increases. The low-temperature saturation mobility has the most pronounced reduction with BaF₂ doping concentration, as expected. It decreases from 50 000 to 2000 cm²/V s as the doping level rises from 0.02% to 1%.

In order to test the influence of the doping process on the crystalline quality of the layers, x-ray rocking curves were measured around the (222) PbTe Bragg diffraction peak of all samples. The FWHM of the PbTe rocking curves, which is a direct measure of the dislocation density, varied from 120'' to 330'' as the BaF₂ doping level is raised from 0.02% to 1% (see Table I). It indicates that PbTe layers remain with a relatively good crystalline quality even for the highest doping level produced here. Therefore, the pronounced reduction in the mobility at 10 K as a function of increasing doping level can be explained mainly by the substantial increase in the hole concentration and, to a less extent, by the increase in the dislocation density.

IV. CONCLUSIONS

We demonstrated that PbTe layers can be effectively doped with BaF₂ up to a hole concentration $p \sim 10^{19}$ cm⁻³, which proves that BaF₂ is an alternative *p*-type dopant for PbTe. Hole densities from 10¹⁷ to 10¹⁹ cm⁻³ were obtained as the doping level varied from 0.02% to 0.4% and saturated for higher levels due to self-compensation effect. No carrier freeze out was observed in the whole doping range, similar to the behavior of vacancy doped PbTe. The increase in carrier concentration and dislocation density is responsible for the reduction in the low-temperature mobility as the doping level rises. The Hall mobility at temperatures higher than 80 K is essentially limited by phonon scattering mechanisms.

ACKNOWLEDGMENTS

The authors are very grateful to FAPESP (Grant No. 2007/50968-0) and CNPq (Grant No. 141223/2005-7).

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