PbTe EPITAXIAL LAYERS GROWTH BY THE HOT WALL TECHNIQUE

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Abstract

The Hot Wall Epitaxy (HWE) technique can be defined as an evaporation process in which the main characteristic is the growth of epitaxial layers under conditions as near as possible to the thermodynamic equilibrium, with a minimum loss of material. The process differs from a normal evaporation method by the use of a heated collimator whose function is to confine and direct the vapor from the source to the substrate. In this way it is possible to avoid loss of material, to keep the vapor pressure high and to reduce to a minimum the temperature difference between source and substrate. In the PbTe samples grown in this work, the carrier concentration varied from 7 x 10^{16} to 5 x 10^{18} cm^{-3} for p- and n-type layers. The highest mobility at 77 K was 3.14 x 10^4 cm^2/V.s, but values from 2.1 x 10^4 to 2.8 x 10^4 cm^2/V.s were obtained very often for n-type layers. The highest mobility for p-type was 1.2 x 10^4 cm^2/V.s. The best mobility for n-type layers reached the value of 8 x 10^5 cm^2/V.s at 12 K.

Introduction

The Hot Wall Epitaxy technique has become a recognized approach to prepare thin films of PbTe [1] and $Pb_{1-x}Sn_xTe$ [2,3] for infrared device applications. The HWE method combines two characteristics, growth under near-equilibrium conditions and versatility. The first serves to provide crystals with the required crystalline perfection; the second is necessary for the preparation of different types of materials with different characteristics and for the production of modern solid state devices. The technique is capable of producing nearly stoichiometric epitaxial films of high crystalline quality at comparatively low growth temperatures and in relatively short growth periods. Furthermore, p-n junction layers can either be grown by controlling the stoichiometry through the controlled vapor pressure of one of the constituent substances or by heterojunction layer techniques [4].

Narrow gap semiconductors are among the most suitable materials for infrared detectors due to their high quantum efficiency, low noise level at given operating temperatures and their band gap that can be tailored to achieve the desired cut-off wavelengths.

Generally, IV-VI narrow gap semiconductor devices are based on epitaxial films grown on cleaved BaF_2 <111> substrates, due to the close match of the lattice constants and the thermal expansion coefficients.

In this work n- and p-type lead telluride epilayers were grown on cleaved BaF_2 substrates by HWE in order to construct infrared sensors for wavelengths around 6 μm at 77 K. Several growths were carried out and optimal conditions for good quality layers and reproduction of results was determined. The better charge composition used was $Pb_{0.502}$ $Te_{0.498}$. Also the substrate-source approximation to near 2 mm improved the layer quality. The former distance between then was 15 mm, causing material loss and difficulty to obtain p-type layers. The reason of this difficulty may be the higher loss of tellurium since it is more volatile, and without Te it is not possible to have p-type material.

Experimental Procedure and Results

The whole growth process was carried out in a self-built HWE system constructed at LAS/INPE and now being used at AMR/IAE/CTA described elsewhere [5,6]. It consists of an oil-free high-vacuum chamber at a pressure of 10^{-7} torr, where a three-zone HWE reactor made of a stainless steel and with molybdenium heaters is used. Independent temperature controllers drive each zone (compensation, source, and wall). Tellurium was used at the compensation zone so that its temperature could control the electron or hole concentration. The source temperature determines the growth rate, and the substrate furnace, which stays on top of the reactor, determines the growth temperature. The growth conditions, for most of the samples, was 5 - 10 x 10^{-7} torr as base vacuum pressure, 350 °C as substrate temperature, and 460 - 480 °C as PbTe source temperatures. The Te compensation temperature was varied to obtain n - (200 - 260°C) or p - (270 °C) type. The epitaxial layer thickness varied from 3 to 7 µm, with 1 to 2.3µm/h as the growth rate. The BaF_2 substrates were cleaved along the ‹111› direction immediately before the growth and preheated at 500° C for 15 min, which has showed to be crucial for the crystalline quality and perfection of IV-VI films grown [7].

The chamber where the epitaxial growth takes place is connected with an ionic pump, which is responsible for the vacuum pressure stability, which is very important for the crystal growth quality. Photoluminescence measurements using Nd-YAG laser (λ ≅ 1.06 µm) showed that the crystal grown is very good as can be seen in Fig. 1.

The carrier concentration and mobility were determined from Hall measurements. The thickness measurements were obtained from a Fourier Transformed Infrared Spectrophotometry (FTIR), with reflection accessories. The best results are showed in Table I, the sample HW022 was on of the earlier growth, so the PbTe source was still a stoichiometric one. At that time the distance between sample and source was 15mm, but despite it, the carrier mobility is very good, and crystalline quality is also good.

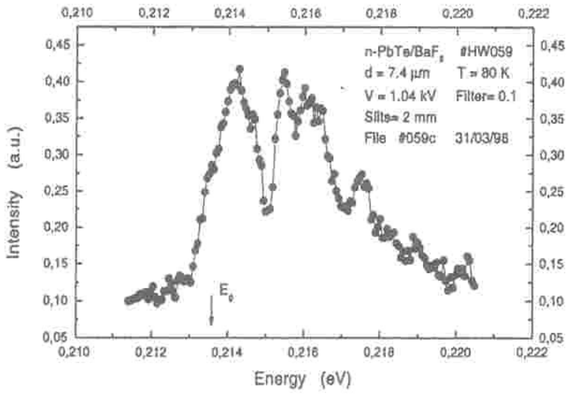

Fig. 1 - Photoluminescence spectra of a PbTe layer grown during 3 h at 9 x 10^{-7} torr. Temperature data was 200°C, 480°C, 550°C and 375°C for Te, source, wall, and substrate, respectively.

Table I - Properties of as-grown $Pb_{0.502}Te_{0.498}$ on cleaved preheated BaF_2 substrates.

Samples	Growth t (° C)				px10 ^{7}	d	Hall a 77 K		
	substrate	source	wall	Te	(torr)	(µm)	type	n x 10^{-17} (cm^{-3})	µ x 10^{-4} (cm^2/V.s)
HW022*	375	540	590	200	10	18.9	n	1.31	2.7
HW059	375	480	550	200	9⇒10	7.4	n	4.4	3.1
HW060	375	450	520	200	9.5⇒9	2.5	n	2.7	2.6
HW067	350	470	520	220	9	3.2	n	2.2	2.8
HW069	350	470	520	255	8⇒9.5	3.2	n	1.8	2.8
HW094	375	480	550	270	5.9⇒9	7	p	3.3	1.1

p = Hot Wall vacuum pressure chamber during the growth;
d = epilayer thickness; n = carrier concentration;
µ = Hall carrier mobility
(*) PbTe of this sample is stoichiometric.

Another way of analyze the crystal quality of the as-grown layers is by measuring the carrier mobility at very low temperature [4,8,9]. Figures 2 and 3 show that as grown epitaxial films on cleaved ‹111› oriented BaF_2 substrates have essentially the characteristics of bulk materials.

For temperatures between 50 and 300 K, the mobility of n-type films follows a $T^{-5/2}$ law, indicating scattering by acoustical phonons. Impurity scattering causes the mobility saturation bellow 50 K.

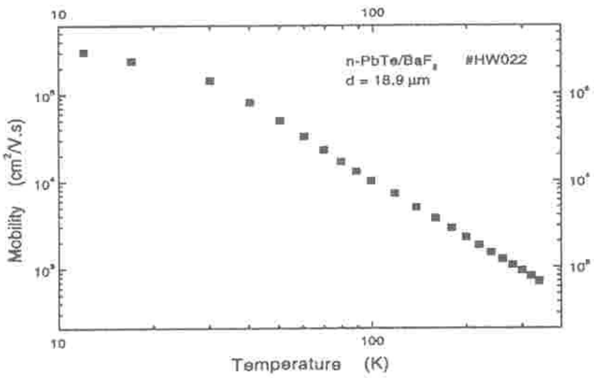

Fig. 2 - Temperature dependence of the Hall mobility, of as-grown layer at 200°C for Te, 540°C for a stoichiometric source, 590 °C for wall and 375 °C for substrates temperature, during 3h, with 10^{-6} torr as vacuum pressure.

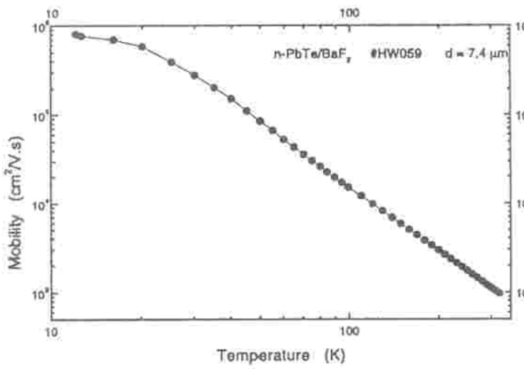

Fig. 3 - Temperature dependence of the Hall mobility of as-grown layer at 200°C for Te, 480 °C for $Pb_{0.502}Te_{0.498}$ source, 550 °C for wall and 375 °C for substrates temperature, during 3 h, with 10^{-6} torr for vacuum pressure.

Table II - Comparing properties of as-grown PbTe obtained in similar HWE systems.

Samples	Growth t (° C)				d	Hall a 77 K		
	substrate	source	wall	Te	(μm)	type	$nx10^{-17}$ (cm^{-3})	$\mu x10^{-4}$ ($cm^2/V.s$)
Clemens [10]	300⇒450	550	565	--	2	n	2.1	4.1
Clemens [10]	300⇒450	550	565	300⇒450	3.7	p	2.8	1.6
Kasai [4]	370	--	490	220	9.8	n	1.2	3.3
Kasai [4]	370	--	490	280	11.6	p	6.7	1.4
Lopez-Otero[1]	280	500⇒600	500⇒600	300	1⇒10	n	32	2.4
This work	375	480	550	200	7.4	n	4.4	3.1
This work	375	480	550	270	7	p	3.3	1.1

p = Hot Wall vacuum pressure chamber during the growth;
d = epilayer thickness; n = carrier number;
μ = carrier mobility

Results obtained in others laboratories are summarized in Table II. Clemens [10], achieved his values, showed on this table, growing PbTe over ‹111› oriented BaF_2 substrate, using a similar semi-closed HWE system to make superlattices. Kasai et all [4] have grown their film with a HWE system similar to this works also over cleaved BaF_2. However, neither Clemens nor Kasai preheated their substrates. Lopez-Otero and Haas [1] worked with a similar closed HWE system, but they have grown over cleaved NaCl instead of BaF_2.

Discussion

The E_g indicated in Fig. 1 corresponds to the measured value of the energy gap of the PbTe; the theoretical value is about 0,18 eV, which means that the measurements are very near of what was expected.

Fig. 2 and 3 shows that for temperatures between 50 and 300 K, the mobility of n-type films follow a $T^{-5/2}$ law indicating scattering by acoustical phonons. The mobility saturation below 50 K is caused by impurity scattering [4].

The large low temperature mobilities reported on Fig. 2 and 3 should correspond, according to Logothetis and Holloway [8], to relatively low levels of compensation, which is to be expected for the growth temperature used here if the deposition indeed occurs near equilibrium conditions.

Another mechanism influencing the carrier mobility, particularly at low temperatures, is scattering at the grain boundaries that form the film. Preliminary studies carried out [9] on PbTe films grown on BaF_2 substrates by HWE have shown a good correlation between the low temperature mobilities and the size of these grains.

The HWE technique has been used to produce high-quality PbTe films on cleaved BaF_2 substrate. Their electrical properties have indicated that the qualities of the as-grown films are comparable to those of similar systems in laboratories with good scientific production. Using the n- and p-type layers will make possible to produced p-n junctions to make infrared sensors.

Lopez-Otero [9] studies have indicated, in agreement with the conclusion reached by Zemel et all. [11], that it is impossible to obtain carrier mean free paths larger than the dimensions of the grains. Lopez-Otero concluded that they obtained mobilities in PbTe thin films as large as 4×10^6 cm^2 V/s at 4,2 K [9] because with the method of HWE they are able to establish the appropriate growth conditions for obtaining films with large grains. In this work we got $8 \times 10^5 cm^2$ V/s as carrier mobilities at 12 K.

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