

FILMES DE COMPOSTOS SEMICONDUTORES IV-VI CRESCIDOS PELA TÉCNICA HWBE

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RESUMO: Os detectores de infravermelho são transdutores que convertem a energia da radiação em energia elétrica e geralmente trabalham sob refrigeração na temperatura de 77 K. Uma ferramenta que vem se mostrando suficientemente útil é a pesquisa termográfica que é a tecnologia da aquisição das imagens geradas pela captação da radiação infravermelha. Detectar estas emissões é de extrema importância para as indústrias aeroespaciais e bélicas. Análises geradas por Microscopia Eletrônica de Varredura (SEM) e Difração de raios-X (DRX) são usadas a fim de comparar as camadas epitaxiais do semicondutor com gap estreito telureto de chumbo (PbTe), crescidas com elevada qualidade cristalina pelas técnicas *Hot Wall Beam Epitaxy* (HWBE ou somente HWE) e *Flash Evaporation* (FE), diretamente sobre lâminas monocristalinas de silício (Si), tipo-p. Estas heterojunções são usadas como detectores do infravermelho termal, que trabalham na temperatura ambiente (GUIMARÃES, ZASSAVITSKII, BANDEIRA, 2000).

Palavras-chave: crescimento epitaxial, telureto de chumbo, Si.

SEMICONDUCTORS COMPOUNDS IV-VI FILMS BY HWBE GROWTH TECHNIQUE

ABSTRACT: Infrared detectors are radiant energy transducers, which convert this energy in electric energy, and usually have to be cooled and kept at 77 K to work property. A tool that comes if shown sufficiently useful of research is the thermographic that is the technology of acquisition of images generated from the capitation of the thermal infrared radiation, to detect these emissions of is extreme importance for aeronautical and warlike industries. Analyzes generates by Scanning Electronic Microscopy (SEM) and X-Ray Diffraction were used in order to compare epitaxial layers of the semiconductor with narrow gap lead telluride (PbTe), grown of high quality by Hot Wall Beam Epitaxy technique (HWBE or only HWE) and Flash Evaporation (FE), directly over single crystal silicon (Si) wafers, p-type. These heterojunctions are used as thermal infrared detectors, which work at room temperature (Guimarães, Zassavitskii, Bandeira, 2000).

Keywords: *epitaxial growth, lead telluride, Si.*

1. INTRODUCTION

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.

Scott, Mercer and Helms (1991) predicted the heterojunctions n-PbTe/p-Si as an ideal detector similar to a Schottky diode, because the n-type doping of PbTe (NaCl structure) is sufficient for any band bending to be negligible. The photo response threshold is the energy difference between the valence band maximum of the Si and conduction band minimum of PbTe. This structure will minimize the inelastic processes. The band gap of PbTe is less than the threshold, which can maximize absorption in the over layer. In the absorption step, the narrow gap semiconductor will produce more detectable carriers than a metal or silicide. Consequently the density of states will make the absorption length in a semiconductor larger than that in a metal, therefore a thicker PbTe layer can be used to absorb more photons. In the transport step, there are few holes near the valence band maximum on n-PbTe, so hole-hole scattering can be neglected. In the transmission step the K_{\parallel} matching is better than for a Schottky barrier, reducing reflections near the threshold. The above factors can result in a substantial increase in quantum efficiency of a n-PbTe/p-Si heterostructure over other Si-based infrared detectors. In PbTe the type of the carriers are not defined by doping, but by stoichiometric equilibrium in the crystalline structure. The layers grown with atomic imperfections for interstitial metal (Frenkel type) produce donor's levels (N type), those associates to the excess of the calcogen (Schottky type) produce acceptors levels (P type), and combination of both.

The HWBE 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. Flash evaporation used in this work consisted of modified vacuum equipment with three basic steps: a) solid phase source transition to gas phase, using the heat of a resistor, which contains the material to be evaporated; b) vapor transportation to the substrate surface, c) vapor condensation on the substrate surface. The modification performed in the evaporator was to provide a sample heater system, which enable us to heat, and control the Si substrates temperature till about 230°C.

Besides PbTe, cadmium telluride (CdTe) flash evaporated layers are also attractive materials for fabrication of semiconductor devices, such as solar cells, α and IR detectors and field effect transistors (Rusu, Nicolaescu, Rusu, 2000; Bangava, 1996). Rusu and Rusu (2000) studied the electrical conductivity of CdTe thin films evaporated onto unheated glass substrates, and obtained <111> and amorphous structures. Domadara and Selvaraj (1998) studied the time dependent electrical resistance of $\text{Bi}_2(\text{Te}_{0.4}\text{Se}_{0.6})_3$ flash evaporated thin films, related with the effects of oxygen adsorption. These thin films find many applications, such as in small thermoelectric power generators, thermoelectric refrigerators, thermopile detectors, etc. Boustani et al. (1997) studied the influence of the substrate temperature during CuInTe_2 flash evaporation thin films, on its properties. These films have been extensively studied because of the potential applications in multijunction thin-film solar cells (Massé, Djessas, 1993)

2. MATERIALS AND METHODS

Si wafers <100> crystal oriented, $1 - 10 \mu\text{m}$ as resistivity, chemically and thermally treated before the epilayers growth, were used, in order to define the best conditions to obtain the higher specific detectivity values (D^*). High purity (99.9999%) tellurium and lead, $\text{Pb}_x\text{Te}_{1-x}$ ($x = 0.502$), was used. The evaporation was performed on modified JEOL vacuum equipment, model JEE4B (Fig. 1), working with vacuum pressure around 10^{-4} torr, using diffusion pump. HWE system is self-built equipment (Figs. 2 and 3), consisting of a vacuum chamber (10^{-10} torr) gotten for serial system: molecular trap, mechanics, turbo molecular and ionic pumps, where two HWE reactors, each one consisting of a main zone for the PbTe salt and a second zone for tellurium, were used. It is described by Boschetti et al. (1993).

Thickness was measured with an Alfa Step 500 Surface Profiler. X-ray diffraction spectrum of the samples was taken, with a High Resolution X-Ray Diffraction Spectrometer Philips X'Pert (PW3710), equipped with Copper anodic tube, Nickel filter, 40kV as voltage value, and 20 mA as current, $2\theta = 0.02^\circ$ step, each step taking 1 sec. Powder Diffraction Files had identified the diffraction lines, from International Center for Diffraction Data (ICDD). The SEM used to analyze the thin films surfaces under low vacuum pressure (10^{-5} torr) was a LEO 435 Vpi type; no coating was used over the samples.

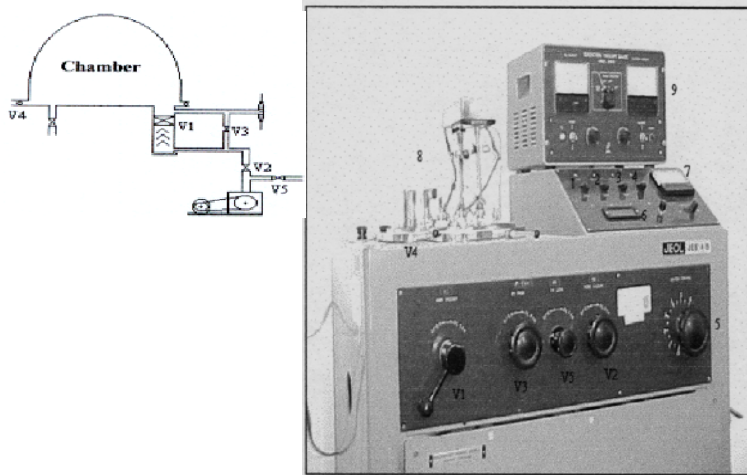


Figure 1a and 1b - Flash Evaporation System: V1 – high vacuum valve, V2 – fore vacuum valve, V3 – by pass valve, V4 – chamber valve, V5 – *R.P.* leak valve

The PbTe/p-Si heterostructures were electrically analyzed by making electrical contacts between PbTe layers and Si substrate, in order to make the current (*I*) *versus* voltage (*V*) measurements, and obtain the junction characterization, *I*x*V* plot. The junctions that presented better electrical characterization had their detectivity signal measured by irradiating infrared beams at the back of the Si substrate. This IR radiation coming from a black body at 700K ($\lambda_{max} = 4.3 \mu m$), 908 Hz as modulator frequency (Lock-in) PAR 124A, and pre-amplification bandwidth frequency $\Delta f = 14Hz$.

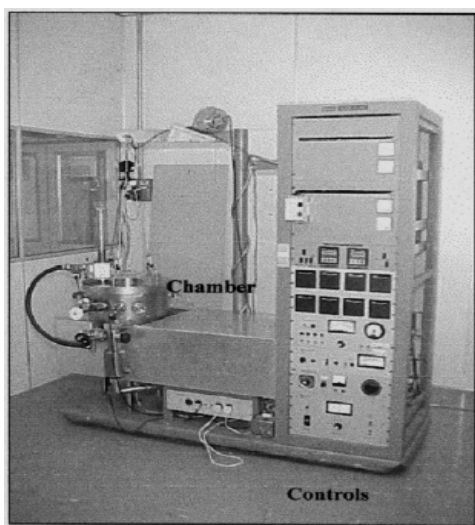


Figure 2 – Hot Wall Beam Epitaxy System

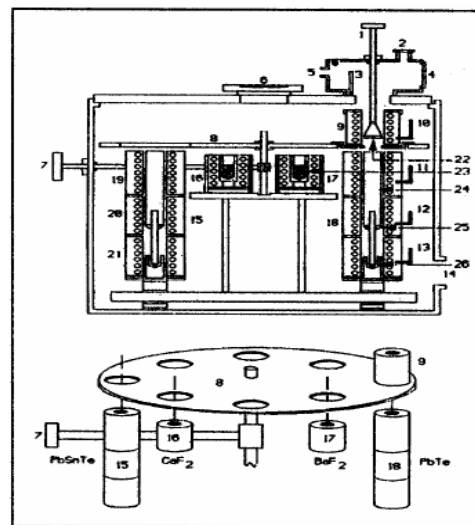


Fig. 3 – Hot Wall Epitaxy Chamber: 8 – substrate disc, 9 – substrate oven, 18 – PbTe oven, 22, substrate holder, 24 – quartz tube, 25 – PbTe source, 26 – Te compensation

3. RESULTS

The thin films grown in various operational conditions have been characterized by XRD, SP, D^* and SEM. For optimal operational conditions: source temperature 790 K, wall temperature 870 K, substrate temperature 695 K, distance between source and substrate 25 cm, and time of deposition: 150 min (HWE05) and 30min (HWE170).

Table 1 summarizes the results. Analyze made with X - Ray Diffraction confirmed that the epilayers obtained with both techniques are all single crystal as can be seen in Fig. 4, which represents the X - Ray results of both

methods. The SEM images of them showed some surface defects, like cracks as can be seen in Figs 5, 6 and 8, and, in some cases, they are not very flat, Fig. 5. However, sample FE15, HWE1170 and 172, did not show majors defects, as shown in Fig 6.

Table 1 – Epilayer thickness and optoelectrical characteristics of the studied samples: ρ – substrate resistivity, d – epilayer thickness, D^* - specific detectivity

Samples	ρ (Ω .cm)	d (μ m)	$D^* \cdot 10^5$ ($\text{cm.Hz}^{1/2}.\text{W}^{-1}$)
FE05	3-8	4.9	4.7
FE12	1-10	0.9	4.8
FE04	3-8	1.2	2.2
FE15	1-10	0.6	1.8
HWE172	1-10	0.5	4.8
HWE170	3-8	0.2	3.2
HWE142	1-10	0.9	3.2
HWE153	1-10	1.0	2.8

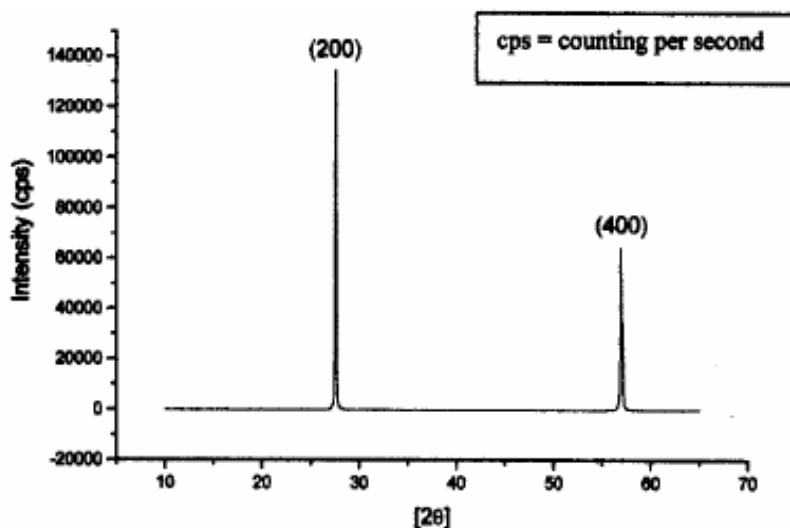


Figure 4 – X-Ray Diffraction of sample FE05

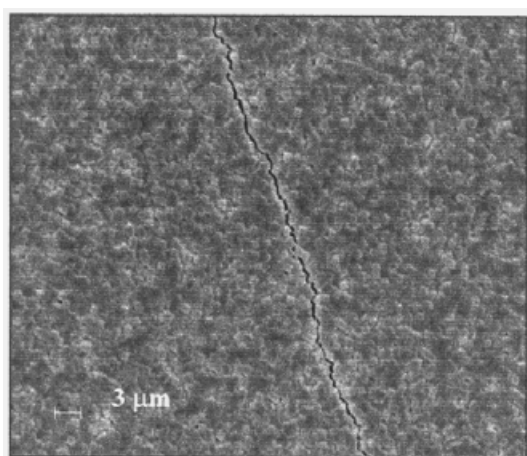


Figure 5 – SEM micrograph of sample FE05

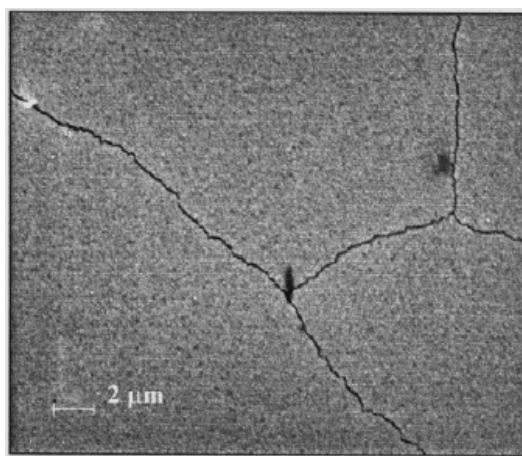


Figure 6 – SEM micrograph of sample FE12

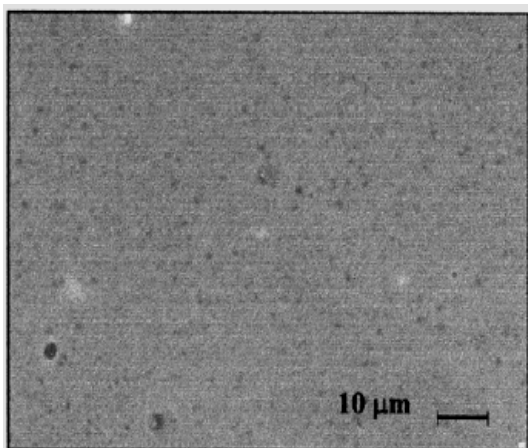


Figure 7 – SEM micrograph of sample HWE170

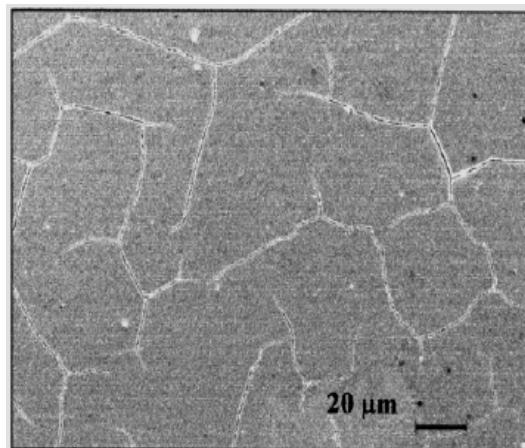


Figure 8 – SEM micrograph of sample HWE153

4. DISCUSSIONS

With crystal lattice parameters: Si= 5.431 and PbTe= 6.459, at 300K, consequently a lattice mismatch around 17%. Moreover, the linear coefficient of thermal expansion: Si 2.6 and PbTe= 19.8, at 300 K (10^6 K^{-1}), near 10 times. These differences may be the cause of cracks in the layer surface. The same defects have been noticed even when the PbTe layer was grown with MBE (Boschetti et al. 1993) techniques. In the case of HWE samples and published (Guimarães, Silva, 2002), the layer quality improves when the layer is thinner.

The cracking originates from an inefficient strain relaxation mechanism in this orientation. Whereas, in PbTe (111) films the strain is relieved by a dislocation glide in the main {001} <110> glide system, since in this case the {001} planes are inclined to the interface. A thin buffer layer of fluorides (CaF_2 or BaF_2) already it was used for overcoming the high lattice and thermal expansion mismatches between Si and PbTe films applied on it, however it generated samples with D^* little (Damodara, Selvaraj, 1998). Epitaxial layers thinner than 0.9 μm follow the Fran-Van der Merwe epitaxial growth mechanism, described by a layer-by-layer growth. On the other hand, for thicker epilayers, the growth mechanism is dictated by Stranski-Krastanov (Herman, Sitter 1996), which is described by layers plus island. Meaning, after forming the first monolayer, or a few of them, the following one growth is unfavorable, and islands are formed. This second mechanism can be more evident in Fig. 5, where the layer thickness is more than 4μm. However, in the case of FE samples they are very sensible with the cleaning procedure, pre-heating and growth temperature, and crystal lattice orientation (Guimarães, Silva, Assis 2002).

5. CONCLUSIONS

The crystal layer quality seems not interfere in the device detectivity, as can be seen for samples FE05 and HWBE 153.

Despite the epilayers have been grown for so different equipments (HWE sophisticated, FE low cost) the results are not different, even the surface defects are very similar, as well as the detectivity values of the devices.

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