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PbTe Flash Evaporation on Si <100> Substrates for Heterojunction Infrared Detectors

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ABSTRACT

This work is to present results of flash evaporation of PbTe directly over single crystals p-type Si substrates, in order to produce heterojunction infrared detectors (HIRD), working at 4.3 μm IR wavelength. The evaporation was performed on modified JEOL vacuum equipment, model JEE4B(a), working with vacuum pressure around 10^{-5} torr, using diffusion pump. The HIRDs produced with this method presented the same detectivity (D^*) values of HIRDs made with Hot Wall Epitaxial System (HWE)(b), in which PbTe epitaxial layers were grown directly over the same Si substrates, where an ionic pump reached about 10^{-7} torr as vacuum pressure. The best results, were obtained with PbTe layers grown with Molecular Beam Epitaxial (MBE) method(c) directly over Si substrates, where the vacuum pressure is around 10^{-9} torr, also using an ionic pump. The advantage of growing PbTe directly over Si wafers is that the HIRDs perform at room temperature. The detectivity values of HIRDs obtained with methods (a) and (b), were $D^* \approx 4,8 \times 10^5 \text{ cm.Hz}^{1/2} \text{ W}^{-1}$ and with method (c), $D^* \approx 6,7 \times 10^6 \text{ cm.Hz}^{1/2} \text{ W}^{-1}$. Different technologies: (a) very low costs, (c) high technology; not very different results.

INTRODUCTION

Single crystal semiconductor thin layers can be processed through several growth techniques. However, when it is grown for devices application, epitaxial techniques are the most used. Among the epitaxial growth methods: Hot Wall Epitaxy (HWE) [1,2], Molecular Beam Epitaxy (MBE) [3] and Flash Evaporation (FE) [4,5], are some of them.

Flash evaporation used in this work consisted of a 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, γ and IR detectors and field effect transistors [5,6]. Rusu and Rusu [6] studied the electrical conductivity of CdTe thin films evaporated onto unheated glass substrates, and obtained <111> and amorphous structures. Domadara Das and Selvaraj [7] 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.* [8] 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 [9].

In this paper metal rich alloy ($\text{Pb}_{0.502}\text{Te}_{0.498}$) with 6N pure materials (99,9999% purity), melted in tungsten boat, was flash evaporated over $\langle 100 \rangle$ and $\langle 111 \rangle$ crystal orientated, 1-10 Ω .cm resistivity Si substrate surfaces, chemically cleaned and heated at 200 and 230 °C, before and during the evaporation. The thin layers resulted of this procedure were characterized. X-ray diffraction spectrum of these thin films showed that some are single crystals, some are poli, and some are poli with strong tendency to single crystal on $\langle 100 \rangle$ orientation. Scanning Electronic Microscopy (SEM) of them showed some surface defects, like cracks, and, in some cases, they are not very flat. The experimental procedures of this work have been made in order to reach these improvements.

EXPERIMENTAL PROCEDURE

The Si wafers cleaning procedure which showed better results in layer adherence and crystal quality, was based in a chemical treatment [10-12] that first degreased the surface substrate with boiled trichloroethylene and methanol, then ammonia hydroxide, hydrogen peroxide and deionized water solution (1 NH_4OH : 1 H_2O_2 : 4 H_2O). The oxide layer was removed with HF : NH_4F (BOE - Buffered Oxide Etchant) or diluted fluoridric acid (1 HF : 10 H_2O). Afterwards, the substrate surface was passivated with boiled cloridric acid, hydrogen peroxide and deionized water (3 HCl : 1 H_2O_2 : 1 H_2O or 1 HCl : 1 H_2O_2 : 4 H_2O). Finally deoxidized by HF : NH_4F (BOE - Buffered Oxide Etchant) or diluted fluoridric acid (1 HF : 10 H_2O), once more, and put in the evaporator chamber. Inside the evaporator chamber, Si substrates distant about 3 cm from the PbTe source, were pre-heated (200 - 230 °C), during different periods of time (2 - 4.5 h), then evaporation took place, with the same pre-heating substrate temperature.

After evaporation, 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. The PbTe/p-Si hetero structure was 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 ($\lambda_{\text{max}} = 4.3 \mu\text{m}$), 908 Hz as modulator frequency (Lock-in) PAR 124A, and pre-amplification bandwidth frequency $\Delta f = 14\text{Hz}$.

RESULTS AND DISCUSSION

Table I shows that the cleaning treatment with (3 HCl : 1 H_2O_2 : 1 H_2O) presents better detectivity results than the cleaning treatment with (1 HCl : 1 H_2O_2 : 4 H_2O), when (1 HF : 10 H_2O) solution is used to perform the deoxidization. The opposite happens when BOE is used as deoxidizer, samples F21, F24 and F25. On the other hand, sample F19, deoxidized with HF, demonstrates that these two cleaning treatment did not make difference. Sample F23 showed that

BOE deoxidization decrease detectivity values. The first solution is more concentrated, consequently produces a thicker passivation layer than the second, consequently HF solution is probably stronger than BOE solution.

Table I – Influence of crystallographic orientation $\langle \rangle$, cleaning and thermal treatment of Si, on the detectivity values.

Samples	$\langle \rangle$	Cleaning Treatment	T_p (°C)	τ_p (hours)	$D^* \times 10^{-5}$ (cm.Hz ^{1/2} .W ⁻¹)
F12a	100	3HCl and HF	200	3	4,8
F05b	100	3HCl and HF	200	3,8	4,7
F05c	111	3HCl and HF	200	3,8	0,4
F04a	100	3HCl and HF	200	3,5	2,2
F07b	100	1HCl and HF	200	3,5	0,5
F07c	111	3HCl and HF	200	3,5	0,4
F02b	100	3HCl and HF	200	3,5	1,5
F06b	100	1HCl and HF	200	3,6	0,8
F13a	100	1HCl and HF	200	3	0,5
F20b	100	1HCl and BOE	230	2	0,7
F20a	111	1HCl and BOE	230	2	0,2
F21a	111	1HCl and BOE	230	2	0,7
F21b	100	1HCl and BOE	230	2	0,7
F25a	111	1HCl and BOE	200	2	0,4
F25c	100	1HCl and BOE	200	2	0,4
F24a	100	3HCl and BOE	200	2	0,3
F24c	111	3HCl and BOE	200	2	0,3
F19b	100	1HCl and HF	230	2	0,5
F19c	111	3HCl and HF	230	2	0,5
F23c	100	1HCl and HF	230	2	0,4
F23b	111	1HCl and BOE	230	2	0,3

T_p = pre-heating and evaporation substrate temperature, τ_p = pre-heating time
 D^* = specific detectivity.

The detectivity values also decreased when the crystal orientation changed from $\langle 100 \rangle$ to $\langle 111 \rangle$, independently of cleaning treatment, compare samples F05b and c, or F07b and c. This behavior was not observed when epitaxial layers were grown using HWE technique [13,14]. An explanation may be the substrate temperature during the evaporation. In the case of HWE [14], the substrate temperature is 300 °C, and no difference on the detectivity values was noticed, related with crystal orientation. However, samples F21, F24 and F25, where the solution used to perform the deoxidization was BOE, presented same detectivity values, independently of Si crystal orientation. The only exception is sample F20.

Results with Scanning Electronic Microscopy and X-ray Diffraction Spectrometry

Flash evaporated surface layers showed different aspects, being mirror like most of the time. The following SEM micrographs showed some surface defect, as Figure 1 cracks, caused probably due the very different crystal lattice parameters ($\text{Si} = 5,431$ and $\text{PbTe} = 6,459$, at 300K) and linear coefficient of thermal expansion ($\text{Si} = 2,6$ and $\text{PbTe} = 19,8$, at $300\text{K}(10^{-6} \text{K}^{-1})$), between substrate and evaporated layer. The same defects have been noticed when the PbTe layer was grown with HWE [14] and MBE [15] techniques.

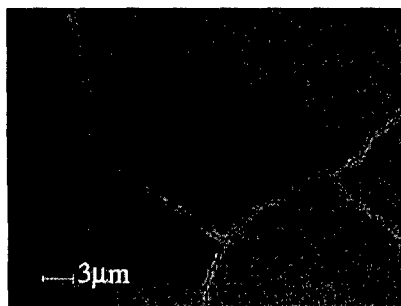


Figure 1 – SEM micrograph of sample F02b, with a $0.45 \mu\text{m}$ epilayer.

Epitaxial layers thinner than $0.9 \mu\text{m}$ probably follow the Fran-Van der Merwe epitaxial growth mechanism [16], described by a layer-by-layer growth. On the other hand, for thicker epilayers, the growth mechanism is probably dictated by Stranski-Krastanov [16], 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 noticed in Figure 2, where the layer thickness is about $4 \mu\text{m}$.

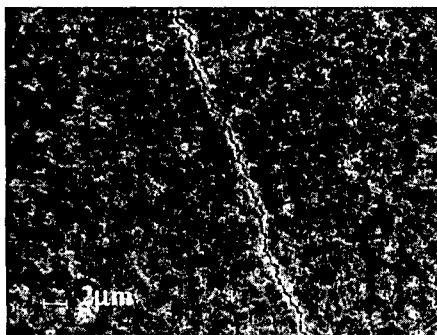
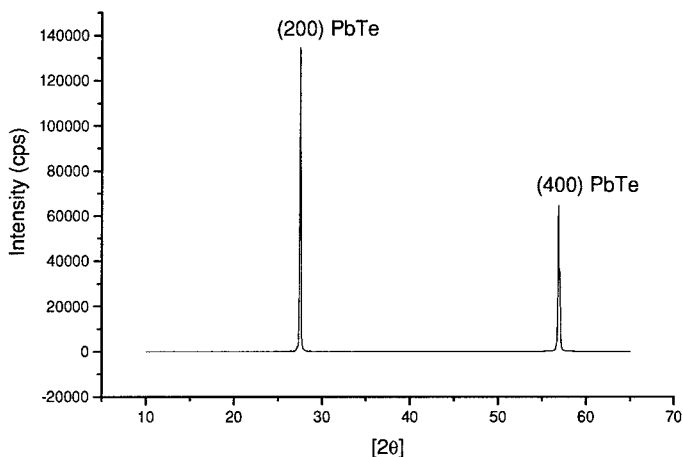


Figure 2 – SEM micrograph of sample F05c, with a $4 \mu\text{m}$ epilayer.

The thin films with single crystal characteristics, revealed X-ray diffraction spectrum as showed in Figure 3, which represents a layer evaporated over a $\langle 111 \rangle$ substrate (sample F05c),

where the Full Width at Half Maximum (FWHM) of peak (200) is 731 sec of degree. However, samples that have <100> crystal oriented substrates, present similar spectrum.



cps = counting per second.

Figure 3 - X-ray diffraction spectrum of sample F05c.

CONCLUSIONS

Concluding, the pre-heating temperature apparently influenced only the flash evaporation over <111> Si substrate, since in these cases thermal treatments at 200°C, resulted in cracks and surface defects, even in thin layers (0.2-0.4 μm). On the other hand, due to thermal treatments at 230 °C, epilayers did not present any surface defect. In both cases, the thin film resulted <100> crystal oriented, despite the Si wafer is <111>.

The reason of flash evaporating PbTe over <111> Si wafers was that first it was very studied to growth PbTe over <111> BaF₂ [1-3]. According with the epitaxy definition it is epitaxial film only in case of the same orientation, substrate and layer. In the experiment you can get any orientation depending on the concrete conditions. PbTe thin layers growth with HWE techniques over <111> Si substrate, are <100> crystal orientated either [17].

Chemical oxidization, or passivation made to protect the substrate surface is a very important step, and also, its complete elimination before the flash evaporation. HF solution demonstrated to be better than BOE to remove thicker passivation layers.

Apparently all the improvements tried on this work resulted no good at all, the former devices were better than the last ones. On the other hand, it was discovered the influence of having a thicker passivation instead a thinner one when HF or BOE solution are used to deoxidize the Si surface. The substrate temperature is very important on the device performance. However, most of these results are very similar as the ones obtained with HWE and MBE

techniques. Consequently this work was able to show that a very simple technique can obtain the same results as others much more sophisticated.

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