Growth studies and physical characterizations of Pb-Se-Te epilayers grown by H.W.E.

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Abstract - The deposition process of IV-VI semiconductors is studied in order to determine optimal conditions of evaporation. A thermodynamical model of the growth is proposed and its use explained in HWE applications. Using these results, epitaxial thin films have been achieved on BaF₂ and Si substrates in all the composition range from PbSe to PbTe. The epilayers obtained were then characterized by Xray diffraction, Auger spectroscopy, SEM observations and electrical measurements. An optical study from 4.2 to 300K is finally presented and the energy band gap dependence versus composition and temperature has been established.

Introduction

The evaporation of IV-VI compounds and particularly lead chalcogenides has been the subject of considerable attention [1, 2, 3] for many years because of their technological applications in the infrared field: laser emission and detection. It is very important to note that their narrow energy band gap can be easily adjust by the substitution of IV or/and VI element in ternary or quaternary alloys [4].

In this paper, we present a general study of the substitution of selenium by tellurium in PbSe which have an important interest in the accordance between the lattice constants of substrate and layer in the case of epitaxial elaborating methods. In this particular case, the change of energy band gap is very slight and does not present great interest.

We choose to elaborate epilayers using the Hot Wall Epitaxy (HWE) technique even if MBE is generally described to be most suitable for the applications [5]; HWE present the great advantage of permitting a good modelisation of the evaporating process [6].

The study presented begin with thermodynamic considerations allowing the determination of the experimental parameters before any manipulation. A general presentation of elaboration and use of these calculations is given in order to permit its utilisation in other cases.

A quick revue of the manipulations performed is then given with some physical characterizations of samples obtained.

In the third part, we develop infrared investigations of epilayers in order to study the energy band gap evolution; a variation law as a function of composition and temperature is finally proposed.

Thermodynamic study of the deposition process

The Hot Wall Epitaxy method permits the growth of thin layers under conditions close to thermodynamic equilibrium. In our deposition case of PbSe_{1-x}Te_x, we use two materials sources, one hold with PbSe and the other with PbTe; this use of two sources rather than one allows us to have an easy control of the layer's composition.

In the apparatus used [7], we can adjust three parameters to control the deposition process: the PbSe and PbTe source temperatures and the substrate temperature.

In order to determine these parameters prior to undertaking the experiments, we build a theoretical model of crystal growth, applied to our case of epitaxy. HWE being a vapor phase deposition technique, we begin to define the gaseous phase by calculating the partial pressures of all species present as a function of the source temperatures. These parameters are then linked to the substrate temperature through the deposition rate which stays the only experimental factor chosen by the user.

According to previous investigations on crystal growth by HWE[8], two basic hypotheses can be considered

- classical thermodynamic laws can be applied to the growth interface,
- deposition process is related to a closed tube cristallogenesis.

We know that the vapor phase is mainly composed of non dissociated molecules even though the molecular dissociation of PbSe and PbTe is partially dissociative; according to Brebrick and Strauss[9], there is 80% of PbX molecules in the vapor phase. However, we could consider two other types of sublimation: congruent and total dissociative one; the choice of the kind of evaporation is in fact not very important, previous works showing that the results obtained in the three cases are very similar [10].

So, we can describe the evaporation by the equation:

The equilibrium constant can be expressed versus partial pressure: $K_p = P_{\text{PbX}}^{0.8} \cdot P_{\text{Pb}}^{0.2} \cdot P_{\text{X}_2}^{0.1}$.

The flux of different species can be expressed from the relation given by Luscher and al [11], as a function of pressure and temperature (P in atm):

$$J = 2.67 \cdot 10^{25} P_{\text{PbX}} (M_{\text{PbX}} T)^{-1/2} = 4[2.67 \cdot 10^{25} P_{\text{Pb}} (M_{\text{Pb}} T)^{-1/2}] = 8[2.67 \cdot 10^{25} P_{\text{X}_2} (M_{\text{X}_2} T)^{-1/2}]$$

These relations allow to express P_{Pb} and P_{X_2} and consequently K_p in function of P_{PbX} .

In other part, K_p can be calculated from thermodynamic data: $\ln K_p = -\Delta G^\circ / RT$

From these two expressions of K_p , it is possible to obtain the values of partial pressures as a function of temperature for each species. These values allow to calculate the deposition rate previously expressed by Lopez-Otero [8] and given by the expression:

$$V_d = J_{\text{inc}} - J_{\text{evap}} = 2.67 \cdot 10^{25} \left[(M_{\text{PbX}} T^{\text{So}})^{-1/2} P_{\text{PbX}}^{\text{So}} (M_{\text{PbX}} T^{\text{Su}})^{-1/2} P_{\text{PbX}}^{\text{Su}} \right] = \beta \left[2.67 \cdot 10^{25} (M_{\text{PbX}} T^{\text{So}})^{-1/2} P_{\text{PbX}}^{\text{So}} \right]$$

in which β represents a sticking coefficient [12].

As we considered independently the compounds PbSe and PbTe, V_d is calculated for these two species.

The deposition rate of PbSe versus source temperature T_{so} is presented in figure 1; it was calculated considering the ideal case where no re-evaporation takes place at the surface of the substrate. In this case: $\beta=1$ and $J_{\text{inc}} \gg J_{\text{evap}}$.

For one selected value of deposition rate, we can deduce the source temperature. Then, it is possible to determine a value of substrate temperature T_{su} corresponding to this T_{so} from figure 2 which represents deposition rate V_d as a function of source and substrate temperatures. In fact, T_{su} can take several values because, in the flat zone, the deposition rate is independent of the substrate temperature. The value selected must be inferior to a limit given by the onset of the steep part of the curve.

The same calculations can be made in the PbTe case and so, source and substrate temperature determined. Like that, we know the minor temperature limit in the both cases: PbSe and PbTe; consequently the value of the substrate temperature must be chosen in the recovering zone and $T_{\text{su}} < \text{lowest value of the two limit temperatures}$.

The zone of interest allowing definition of optimal conditions for deposition is the flat one. Nevertheless, if the material obtained has a p type conductivity (excess of Se or Te) in order to change the conductivity (type n), we have to increase T_{su} so that Se or Te evaporate from the surface of the film; in this case the region of interest is the steep part.

Fig. 1: Deposition rate versus the source in the PbSe case.

Fig. 2: Deposition rate as a function of source and substrate temperature in the PbSe case

Realisation of deposits and characterization

Using the results of the thermodynamical study, we have optimised the experimental temperatures in order to realise the deposition of all the ternary alloys $\text{PbSe}_{1-x}\text{Te}_x$ ($0 \leq x \leq 1$). In these conditions, we carried out numerous layers of different compositions on $\text{BaF}_2(111)$ and $\text{Si}(111)$.

The epilayers obtained have been characterized using X-ray diffraction, SEM observations and Auger spectroscopy [5, 10, 13]. The results are summarised in figure 3 and compared both to a theoretical Vegard's law and to bulk literature data [14, 15, 16].

Fig.3: Lattice parameters of $\text{PbSe}_{1-x}\text{Te}_x$ versus the Te composition.

* Experimental results ☆ Bibliographic data

Some transport properties have also been measured on the BaF₂ epitaxial layers; the result obtained at 300K for two samples of PbSe and PbTe are given as an example.

	Type	Thickness (μm)	E _g (meV)	ϵ	ρ ($\Omega.\text{cm}$)	μ ($\text{cm}^2/\text{V.s}$)	Population (cm^{-3})
PbSe	p	0.1	285	24	$2.84 \cdot 10^{-2}$	113	$1.95 \cdot 10^{18}$
PbTe	n	4.4	330	32	$1.18 \cdot 10^{-3}$	1150	$4.60 \cdot 10^{18}$

The energy band gap variation law as a function of composition and temperature.

With aid of a Fourier Transform IFS 113 Spectrometer, optical characterizations was performed on a number of PbSe_{1-x}Te_x samples. The band gap values were determined by the measurements of the absorption coefficient α , as a function of energy.

The non linear band gap dependence as a function of the composition of PbSe_{1-x}Te_x alloys was previously established at 300 K [10,13]. The results are compared of those of the bulk in order to control the role of, for example, the alloying effect in a system with small thickness [17]. This behaviour confirmed other results obtained by different methods: photoluminescence and photovoltaic effect [18, 19]. This nonlinearity has been explained by an inversion between the L_2' and L_3' level in the PbSe and PbTe band structure, respectively [19].

The aim of this paper is to illustrate two different laws:

- the band gap variation as a function of temperature for a define composition,
- the band gap dependence versus the composition and the temperature.

The evolution of the PbSe_{1-x}Te_x alloys'band gap with the temperature is shown on figure 4. The expression established by Varshini [20] for the change in temperature, differs only by a change in sign [21]:

$$(1) \quad E_g(T) = E_g(0) + \beta T^2/(T+\gamma)$$

where $E_g(T)$ is the energy band gap at the temperature T , $E_g(0)$ the band gap at 0 K for the given material, β and γ two constants, in particular γ complies to the size of the Debye temperature.

Fig. 4: Temperature dependence of the band gap for a given composition: a) $x=0$, b) $x=1$, c) $x=0.6$. The continuous line represents the expression $E_g(T)$ where $E_g(0)$, β and γ are adjustable parameters. Symbols are experimental results.

This temperature dependence band gap is due to two different mechanisms:

- the shift of the conduction and valence bands due to the temperature dependence of the electron-lattice interactions;
- the temperature dependence of the lattice dilatation which also brings a shift in the relative position of the valence and conduction bands.

The former of these effects is more dominant.

Fig. 5: Dependence of the band gap as a function of the composition for different temperatures. Symbols are experimental results, solids lines are calculated from the expression (2).

For these results, a polynomial dependence law can be assumed:

$$(2) \quad E_g(x, T) = A_1(T) + A_2(T)x + A_3(T)x^2 \quad \text{with the coefficients } A_i(T) \text{ defined by the relation:}$$

$$(3) \quad A_i(T) = E_{gi}(0) + \beta_i T^2 / (T + \gamma_i) \quad \text{in which } E_{gi}(0), \beta_i \text{ and } \gamma_i \text{ are different constants for the coefficients } A_i(T).$$

The continuous lines in figure 5 represent the dependence relation defined by the expression (2) where the parameters are given in Table 1; as illustrated, this expression is in very good agreement with the experimental values, and with results obtained on bulk samples; probably due to the fact that the epilayers studied are completely relaxed [22].

Table 1: β , γ and $E_g(0)$ parameters for $A_i(T)$

	$A_1(T)$ (meV)	$A_2(T)$ (meV)	$A_3(T)$ (meV)
$E_g(0)$ (meV)	151	130	-91.5
β (meV/K)	0.049	0.08	-0.22
γ (K)	41	35	511

Conclusion

Using the case of HWE epitaxial technique, we performed a large serie of $\text{PbSe}_{1-x}\text{Te}_x$ thin films samples on BaF_2 and Si substrates.

In order to determine experimental conditions before any experiment, we proposed a thermodynamic study of the deposition process. This model, presented here with the basic hypothesis and the main stages of reasoning, can be extended to any IV-VI semiconductor system but also to others, with minor modifications. The particular case of PbSe is developed to illustrate how to use these results.

All the elaborated layers were characterized by various methods: Xray, Auger, SEM and IR analysis particularly. This last technique has been chosen to obtain a good approach of the energy gap measurement.

This study allowed us to established, for the first time, an energy band gap variation law as a function of temperature (15 to 300K) and composition of $\text{PbSe}_{1-x}\text{Te}_x$ ($0 \leq x \leq 1$) thin films. This law is in very good agreement with experimental measurements and our results correctly agree with these obtained on bulk samples.

All these results can be considered as previous investigations for future works on new materials. The substitution of selenide by tellurium will be used to ajust of lattice parameter and the change of band gap realised in a larger range by substitution of lead by tin or europium.

References

- [1] MASEK J., MAISSEN C., ZOGG H., BLUNIER S., WIBEL H., LAMBRECHT A., SPANGER B., BOTTNER M. and TACKE M., *Journal de Physique*, **49**(9), (1988), C4-587
- [2] MEINGAILIS I., *Lecture Notes in Physics, Narrow Gap Semiconductors-Physics and Applications Proceeding*, **133**, (1979), 558
- [3] KASAI I., HORNUNG J. and BAARS J., *J. Electroph. Mat.*, **4**, (1975), 299
- [4] PREIER H., *Semicond. Sci. Technol.*, **5**, (1990), S12-S20
- [5] CLENMENS H., KRENN H., WEILGUNI P.C., STROMBERGER U. and BAUER G., *Surface Sciences*, **228**, (1990), 236
- [6] BAUER G. and JANTSCH W., *Journal de Physique*, **48**, (1987), C5-293
- [7] MULLER M., LIAUTARD B., ASTIER R., BRUN G. et TEDENAC J.C., *Journal de Physique*, **50**(5), (1989), C5-549
- [8] LOPEZ-OTERO A., *Thin Solid Films*, **49** (1978), 3
- [9] BREBRICK R.F. and STRAUSS A.J., *The Journal of Chemical Physics*, **40**(11) (1964), 3230
- [10] LIAUTARD B., DAL CORSO S., BRUN G., TEDENAC J.C., OBADI A., FAU C., CHARAR S., GISBERT F. and AVEROUS M., *Physic.Stat.Sol.(a)*, **133** (1992), 411
- [11] LUSCHER P.E. and COLLINS D.M., *Design considerations for MBE systems*, Varian Associates Inc.C.A.94303 USA (1978)
- [12] ROSENBLATT G.M., *Treatise on solid state.Chap.3*.Plenum N.Y. (1976)
- [13] TEDENAC J.C., DAL CORSO S., LIAUTARD B., BRUN G., CHARAR S., OBADI A., FAU C. and EL Kholdi M., *Electrochemical Society*, accepted for publication
- [14] STEININGER J., *Metallurg. Trans.*, **1**, (1970), 2939
- [15] YAMAMOTO S., *Sci. Rep. Tohoku Univ.*, **40**, (1956), 11

- [16] ELAGINA I. and ABRIKOSOV N.K., Doklady Akad. Nauk SSSR, **111**, (1956), 353
- [17] DALVEN R., Infrared Phys., **9** (1969), 149
- [18] VALEIKO M., ZASAVITSKII I.I., KUZNETSOV V.L., KURGANSKII A.V. and MATSONASHVILI B.N., Soviet Phys. Semicon., **19** (1985), 388
- [19] JEDRZEJCZAK A., GUILLOT D. and MARTINEZ G., Phys.Rev.**B17** (1978), 829
- [20] VARSHNI Y.P., Physica, **34** (1967), 149
- [21] RAVINDRA N.M., SUSHIL AULUCK and SRIVASTAVA V.K., Phys.Stat.Sol.(a), **52** (1979), K151
- [22] MULLER M., LIAUTARD B., BRUN G. et TEDENAC J.C., C.R. Acad. Sci. Paris, **t316-sérieII**, (1993), 13-18