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Qualitative and quantitative assessments of the growth of (Al,Ga) As-GaAs heterostructures by *in situ* ellipsometry

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Résumé. — Le développement d'ellipsomètres automatiques a permis la caractérisation en temps réel de la croissance d'hétérostructures, dans l'environnement haute température et haute pression des réacteurs d'épitaixie en phase vapeur. On décrit la mise en œuvre et l'utilisation d'un ellipsomètre automatique associé à un système d'épitaixie aux organométalliques. L'application de l'ellipsométrie *in situ* au contrôle en temps réel de la croissance d'hétérostructures est ensuite décrite. Enfin, on montre qu'une analyse *a posteriori* des mesures *in situ* permet une caractérisation détaillée du profil de composition et en particulier des interfaces entre films de compositions différentes.

Abstract. — Fast ellipsometers have made feasible real-time assessment of heterostructure growth in a vapour phase ambient. A fast ellipsometer/MO-VPE experimental system is described and the possibilities of *in situ* ellipsometry are investigated in the case of GaAs-(Al, Ga)As structure growth : qualitative assessment in real-time and quantitative assessment (growth rate, composition determination and transition width) by experimental data processing after growth.

Introduction. — The growth of GaAs-(Al, Ga)As heterostructures is of particular interest for the fabrication of many devices, such as lasers [1], photocathodes [2], microwave FETs [3].

The control of the epitaxial growth of single or multiple heterostructures requires well-defined growth conditions and a careful assessment of the deposited layers. Such a characterization, usually performed *a posteriori*, is a time consuming step in the fabrication process of the device. The possibility of *in situ* assessment, which operates during the epitaxial growth, is then very attractive as it can save time and provide results for the selection of the wafers. *In situ* ellipsometry appears in this respect as a well-adapted tool, provided that the growth technology is compatible with the use of optical measurements.

The necessary conditions are met in the VPE process, in MBE as well but not in LPE. Previous work [4] has already demonstrated the feasibility of *in situ* ellipsometry during the growth of GaAs by the AsCl₃/Ga/H₂ process and early results on the growth of GaAs-(Al, Ga)As heterostructures by MO-VPE have also been reported [5]. The present paper deals with a description of the ellipsometric technique applied to the monitoring of the growth of GaAs-

(Al, Ga)As heterostructures by MO-VPE. The results of : i) real-time measurements and ii) *a posteriori* experimental data processing treatment designed to assess the composition profile at a GaAs/(Al, Ga)As interface quantitatively, are described and correlated to the growth conditions.

1. Experimental. — A desktop computer-assisted ellipsometer and a suitable MO-VPE reactor have been designed and developed to provide reliable, real-time ellipsometry measurements during the growth of device-type (Ga, Al)As/GaAs epitaxial layers in a MO-VPE system.

1.1 GROWTH SYSTEM DESCRIPTION. — The metal-organic VPE (MO-VPE) is based on the co-pyrolysis of one or more organometallic compounds of group III elements (e.g. trimethylgallium TMG, trimethylaluminium TMA) with a group V hydride (e.g. arsine AsH₃) in a gaseous environment (H₂ carrier gas). A detailed review of the MO-VPE process is given in reference [6].

The growth system is based on a cold wall horizontal reactor (Fig. 1), the main features of which are similar to a design previously described [7]. However

Fig. 1. — Reactor for the MO-VPE growth of (Ga, Al)As compounds : 1. Gas inlet; 2. Front liner; 3. Graphite susceptor; 4. Substrate heater; 5. Heater feedthrough; 6. Gas outlet; 7. Ellipsometry windows.

in order to meet the requirements imposed by quick and accurate *in situ* ellipsometry measurements :

- the susceptor, tilted with respect to reactor axis, has to be maintained in an horizontal plane, which requires accurate positioning of both the reactor and the susceptor jig ;

- 15 mm diameter optical windows have been added to the quartz reactor, with their axis parallel to the ellipsometry light beam. The heating of these windows eliminates possible deposits during a complete run ; and makes possible ellipsometry measurements during a complete run ;

- special care has been taken to ensure a good mechanical stability of the substrate during a growth procedure ;

- direct Joule heating has been used, by means of a Pt-Rh alloy winding enclosed in a quartz ampoule nested in a hollow graphite susceptor. A graphite front liner was attached to the susceptor to get a good hydrodynamic flow and to improve the homogeneity of the deposits.

1.2 ELLIPSOMETER. — Real-time ellipsometry during film growth implies the use of a fast automatic ellipsometer [8, 9] which can be described as a system composed of three parts : the basic ellipsometer (optical and mechanical components), the signal processing circuit and finally the computer which drives the system and analyses the processed electrical signals.

1.2.1 Basic ellipsometer. — A schematic representation of the basic ellipsometer is given in figure 2. The light source is a 2.5 mW He-Ne laser which provides a 6328 Å radiation with yet sufficient intensity when the reactor windows are coated with a deposit inherent to a one-hour growth run. A polarized laser is used to avoid intensity variations due to switching between polarization modes. Then a quarter-wave plate is used to get a circularly polarized light beam which in turn is linearly polarized by a stepping-motor-driven polarizer, the azimuthal angle of which, with reference to the incidence plane, is P . After reflection from the sample, the light beam passes through a second quarter-wave plate (compensator) of azimuthal angle C . The state of polarization is then analysed by a rotating analyser (azimuthal angle A).

Fig. 2. — Optical and mechanical components of the ellipsometer : 1. He-Ne laser; 2. Quarter-wave plate; 3. Polarizer; 4. Stepping motor; 5. Diaphragm; 6. Reactor window; 7. Wafer; 8. Quarter-wave plate; 9. Mechanical shutter; 10. Rotating analyser; 11. Optical encoder; 12. Photomultiplier tube.

This analyser is fixed on a hollow-shaft motor which also holds an optical encoder for the position sensing of the analyser. The encoder has two output signals : one which gives a single « start » pulse per rotation of the analyser and is used to synchronize the system, and another which gives 128 equally spaced pulses per rotation. The light coming from the rotating analyser is measured by a photomultiplier tube (PMT) with a 6328 Å interference filter and a limiting aperture (typically 1 mm in diameter) mounted on the entrance window. In the case of a laser light source, the ellipsometer configuration fixed polarizer-rotating analyser is preferred because, after passing through the first quarter-wave plate, the light beam is not perfectly circularly polarized.

The components of the optical system are mounted on arms set for a 72° fixed angle of incidence (for optimum sensitivity, this angle must be in the vicinity of the Brewster angle, typically 76° for GaAs at 6328 Å). However the actual angle of incidence θ is slightly dependent on the final positioning of the reactor and its graphite susceptor.

1.2.2 Principle of the data processing. — Ellipsometry measurements are based on the analysis of the intensity $I(A)$ reaching the photomultiplier tube, which can be written on the form :

$$I(A) = I_0(\alpha \cos 2A + \beta \sin 2A + 1) \quad (1)$$

where I_0 is the average intensity for a full rotation of the analyser and A is the azimuth of the transmitting axis of the analyser, measured counterclockwise from the plane of incidence looking towards the source.

The α and β coefficients, which represent the light polarization information, are usually determined by Fourier analysis of the PMT intensity data. However such a procedure requires a fast computer system. To overcome the data acquisition speed limitation of desktop computers, a signal processing circuit has recently been developed [10] to determine the Fourier coefficients of a periodical signal.

If N denotes the number of data points taken by optical cycle, (1) can be expressed in the form :

$$I(i) = a \cos \left(\frac{2\pi}{N} i + \frac{\pi}{N} \right) + b \sin \left(\frac{2\pi}{N} i + \frac{\pi}{N} \right) + c.$$

Defining an auxiliary parameter F by

$$F = \sum_{i=0}^{N/4-1} \cos\left(\frac{2\pi}{N}i + \frac{\pi}{N}\right) \\ = \sum_{i=0}^{N/4-1} \sin\left(\frac{2\pi}{N}i + \frac{\pi}{N}\right),$$

the following relations hold :

$$\sum_{i=0}^{N/4-1} y(i) = aF + bF + c \cdot \frac{N}{4} = S_1, \\ \sum_{i=N/4-1}^{2N/4-1} y(i) = -aF + bF + c \cdot \frac{N}{4} = S_2, \\ \sum_{i=2N/4-1}^{3N/4-1} y(i) = -aF - bF + c \cdot \frac{N}{4} = S_3, \\ \sum_{i=(3N-1)/4}^N y(i) = aF - bF + c \cdot \frac{N}{4} = S_4.$$

The a , b , and c coefficients are directly related to the Hadamard transforms of the four S_j sums, the determination of which *prior* to the calculation of the Fourier coefficients, leads to speed up the data acquisition phase by a factor greater than 10 and thus, to use a desktop computer for real-time ellipsometry.

A schematic representation of the complete ellipsometric set-up used in this study is given in figure 3 with the main features of the data acquisition and data processing parts.

1.2.3 Alignment calibration procedures. — The final accuracy of the ellipsometer depends on the system alignment : a misaligned sample yields error in both the angle of incidence and the plane of incidence. The system alignment is checked by monitoring the relative symmetry of successive optical cycles and the difference between the peak values of successive maxima of the signal.

The calibration procedure refers to the determination of the azimuth references of the polarizer and of the compensator, respectively, with respect to the plane of incidence. For fast automatic calibration, both polarizer and compensator plates have been mounted on computer driven rotation stages. A convenient way to get the reference azimuth P_0 of the polarizer is, for a polarizer-surface-analyser configuration, to determine the local minima of the residual function [11] $R(P)$ defined by

$$R(P) = 1 - \alpha^2 - \beta^2$$

α and β being the coefficients appearing in equation (1).

The variations of $R(P)$ for two ideal surfaces, of refractive indexes $n = 2$ and $n = 3.5$, respectively, are given in the figure 4. $R(P)$ variations show a sharp minimum, which occurs for the transmission axis of the polarizer being in the plane of incidence. Moreover, the sharpness of this minimum depends on the refractive index. P_0 may be obtained by fitting a set of experi-

Fig. 3. — Functional representation of the computer-assisted ellipsometer.

Fig. 4. — Variations of the residual function $R(P)$ calculated for $n = 2$ and $n = 3.5$ respectively ($\theta = 72^\circ$).

mental data $\{R_j, P_j\}$, centred about P_0 , to a calculated parabola by means of least-square fitting procedure. This procedure requires a set of data showing rather low background fluctuations, which may be crafty to get in a growth reactor for low-index materials. A practical $R(P)$ curve obtained for a GaAs substrate before a growth procedure is given in the figure 5. After determining P_0 , the compensator is inserted and a similar procedure is used to get C_0 , the azimuth of the fast axis of the compensator with respect to the plane of incidence.

1.2.4 Ellipsometry measurements. — The ellipsometric angles Δ and Ψ are defined by the ratio :

$$\rho = \frac{r_p}{r_s} = \tan \Psi \exp(i\Delta),$$

between the reflection coefficients of a light polarized

Fig. 5. — Variations of $R(P)$, measured for a GaAs substrate in the MO-VPE reactor.

in the plane (r_p) and perpendicularly (r_s) to the plane of incidence.

For the configuration previously described, with both the polarizer and the compensator having their reference azimuth set at 45° to the plane of incidence, the intensity of the light beam striking the photomultiplier can be written :

$$I \propto \frac{1}{2} (1 + \tan^2 \Psi) - \tan \Psi \sin \Delta \cos 2A + \tan \Psi \cos \Delta \sin 2A.$$

The Δ and Ψ angles are related to the α and β coefficients of (1) by :

$$\Delta = \tan^{-1} (-\alpha/\beta),$$

and

$$\Psi = \frac{1}{2} \sin^{-1} (\sqrt{\alpha^2 + \beta^2}).$$

For a film of thickness t and refractive index $\tilde{n}$ deposited on a substrate of refractive index $\tilde{n}_s$, the relationship of these parameters takes the form :

$$\rho = \tan \Psi \exp(i\Delta) = f(t, \tilde{n}, \tilde{n}_s, \theta)$$

where θ is the angle of incidence and f represents a complex transcendental function.

Because of the poor reproducibility of the positioning of the suscepter in a MO-VPE reactor, the angle of incidence has to be determined at the beginning of each growth cycle by measuring at room temperature the ellipsometric angles of a reference sample provided in this study by the GaAs substrate after the *in situ* cleaning procedure or after the growth of homo-epitaxial layer. Consequently, *in situ* ellipsometry measurements bear a degree of confidence higher in terms of precision (limited by random errors) than in terms of accuracy (limited by systematic errors).

The precision of the measurements at large depends on the number N_{acc} of cycles accumulated for each data point. N_{acc} also sets the ellipsometric data speed.

For time variation phenomena, a typical value of N_{acc} is 15, for which a (Δ, Ψ) point is measured every 3 seconds with a precision of 0.01° for Ψ and 0.05° for Δ .

2. *In situ* monitoring of heterostructure growth. —

Aspects of real-time ellipsometry applied to heterostructure growth monitoring have been pointed out in previous publications [4, 5]. The primary function of real-time ellipsometry is to control the way the experiments comply to the planned growth sequences. This task is useful but does not provide eventful information as long as growth operates correctly. However in the case of deviation, the analysis of the ellipsometric angle variations allows us to diagnose the cause of the failure. In this section, three applications are reviewed in order to illustrate the various types of events which can be detected during the experiments. First it is shown that ellipsometry is valuable for the examination of the substrate stability during the heat treatments performed *prior* to growth and consequently for determining the practical heat treatment conditions. Then a calibration curve

$$\delta\Psi = \Psi_{Al_xGa_{1-x}As} - \Psi_{GaAs} = f(x)$$

is presented, the aluminium concentration x being determined by double X-ray diffractometry. Finally a detailed study of *in situ* assessment of (Al, Ga) As-GaAs heterostructure growth is carried out with special emphasis on quantitative evaluation of the transition behaviour.

2.1 SURFACE STABILITY DURING INITIAL HEAT-TREATMENTS. — The standard growth procedure implies first to heat the GaAs substrate up to the working temperature in hydrogen flow. Using the direct Joule heater it takes several minutes before reaching the required temperature at the surface of the sample, as controlled by an infrared pyrometer. During that period there is some risk to decompose the GaAs or to produce a degraded surface layer. It has been shown that this can be avoided by adding AsH_3 to the main hydrogen flow [12]. Variations of Δ and Ψ can be examined to describe the experiments. However Ψ not being sensitive to tiny changes in the composition of the dense adsorption layer, reliable evaluation of the material optical properties can be assessed *via* Ψ variations, rather than *via* Δ variations which are very sensitive to such changes.

Figure 6 shows the evolution of Ψ *versus* time for a heating procedure under pure hydrogen (curve a) and a heating procedure under arsine hydrogen mixture with arsine partial pressure of 10^{-2} (curve b). Independently of any surface modification, raising the temperature changes the refractive index of the substrate and consequently increases the value of Ψ . This can be seen in the figure 6, for the first few minutes of heating. At about $600^\circ C$, an anomalous behaviour of the Ψ variations is observed, which could

Fig. 6. — Variations of Ψ (arbitrary units) with time during a heating procedure in hydrogen (curve a) and in a hydrogen-arsine atmosphere (curve b).

be attributed to desorption of physisorbed molecules such as H_2O , CO , oxygen... [18]. As the temperature reaches a plateau at about 730°C , it becomes clear that only the hydrogen-arsine mixture allows a stabilization of Ψ . For pure hydrogen carrier (curve a) gas, Ψ shows oscillations of more than 1 degree in amplitude : it might be assumed in this case arsenic losses induce surface roughness phenomena [20]. It is also worth noticing that it takes rather a long time for the hydrogen-arsine experiments before reaching a stable Ψ value, that is to say an equilibrated arsenic coverage of the surface.

From all this, it is concluded that for initiating the growth on a stable surface, one needs to perform the heating cycle under hydrogen-arsine mixture and to allow sufficient time for surface equilibration.

2.2 COMPOSITION DETERMINATION BY ELLIPSOMETRIC MEASUREMENTS. — The variations of

$$\delta\Psi = \Psi_{\text{Al}_x\text{Ga}_{1-x}\text{As}} - \Psi_{\text{GaAs}}$$

as a function of the aluminium concentration x have been plotted in the figure 7 for a number of thick homogeneous layers for $x < 0.70$. The Al concentrations have been measured by double X-ray diffrac-

Fig. 7. — Variations of $\delta\Psi = \Psi_{\text{Al}_x\text{Ga}_{1-x}\text{As}} - \Psi_{\text{GaAs}}$ as a function of the aluminium concentration x .

tometry [13], and the Ψ angle selected because it is more accurately measured than the Δ angle. Moreover only relative ellipsometric angle variations have been considered because of the slight alignment alterations likely to occur from run to run. Finally, as the ellipsometric measurements have been carried out *in situ*, and at growth temperature, they refer to oxide free surfaces. The $\Psi = f(x)$ curve which exhibits a linear variation for $x < 0.5$, can be used to determine the Al content of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers. These results are in good agreement with a previous study by Kuphal [14] who treated in detail the composition determination of LPE grown (Al, Ga)As by ellipsometry, with emphasis on the natural oxide layer contribution.

Another ellipsometric determination of the Al content worth considering, may be gained by spectroscopic ellipsometry measurements performed *a posteriori* in this work used to determine the imaginary part ε_2 of the epitaxial layer dielectric function. The variations of ε_2 as a function of energy (in the range 2.5-3.5 eV) have been plotted in the figure 8 for a GaAs

Fig. 8. — The measured imaginary part ε_2 of the dielectric function for GaAs (curve a) and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (curve b).

sample and a $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$ sample respectively. For these two wafers, the E_1 structure [9, 15] respectively lies at 2.95 eV and 3.10 eV. The variations of E_1 as a function of the aluminium content are given in the figure 9. The one to one relationship between E_1 and x previously reported by Lande *et al.* [16] from reflectivity measurements, allows the determination by spectroscopic ellipsometry of the Al content of an uncalibrated (Al, Ga)As sample with an accuracy similar to the one encountered for X-ray diffractometry measurements.

Fig. 9. — Variations of the E_1 transition as a function of the aluminium concentration x .

2.3 REAL-TIME STUDY OF THE GaAs $\rightarrow$ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ AND $\text{Al}_x\text{Ga}_{1-x}\text{As} \rightarrow$ GaAs TRANSITIONS. — The experimental data are plotted and recorded in the (Δ, Ψ) plane, see for instance figures 10 to 12. The starting point, labelled A in the figure 10, corresponds to the stabilized state of the initial GaAs substrate or to the stable state of growth of a GaAs layer using AsH_3 and $(\text{CH}_3)_3\text{Ga}$. When $(\text{CH}_3)_3\text{Al}$ is added to the gas phase, the experimental (Δ, Ψ) point starts moving along a spiral shape locus: $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is only weakly absorbant at 6328 Å, an interference regime establishes in the layer, inducing damped oscillations on Δ and Ψ which are seen as a spiral in the (Δ, Ψ) plane. When the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layer is thick enough, the (Δ, Ψ) point stabilizes at a place which is representative of the (Al, Ga)As layer. The same phenomena occur when going from $\text{Al}_x\text{Ga}_{1-x}\text{As}$ to GaAs as shown in the figure 11.

Two aspects can be considered in the analysis of the GaAs to $\text{Al}_x\text{Ga}_{1-x}\text{As}$ or $\text{Al}_x\text{Ga}_{1-x}\text{As}$ to GaAs transitions :

- i) a qualitative examination of the experimental curves during the growth of the layers,
- ii) a quantitative analysis of the results, which is performed *a posteriori*. This second aspect which enlarges the use of ellipsometry to complete assessment technique, makes use of the real-time measurements but is rather time-consuming. It will be discussed in the next section.

Typical experimental curves are given in the figures 10, 11 and 12. In all cases the theoretical calculated spirals have been drawn in the same figure using the experimental starting and final (Δ, Ψ) points and assuming either abrupt transitions (Figs. 10 and 11) or transition layers exhibiting a linear composition profile (Fig. 12). In the case of the GaAs $\rightarrow$ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ growth given in the figure 10, it is obvious that the experimental spiral deviates from the calculated one. This occurs for graded transitions for which the rapidly converging spiral is due to a damping in the interference regime in the graded layer. This shape is easily recognized by the user and can be correlated with poor growth conditions. On the contrary, figure 12

Fig. 10. — Real-time examination of GaAs $\rightarrow$ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ heteroepitaxy with poor growth conditions (light solid line). Point (A) is the stable state for GaAs epitaxy. The heavy solid line is the (Δ, Ψ) locus calculated for an abrupt transition between GaAs and AlGaAs layers. The dashed line is the calculated (Δ, Ψ) locus assuming a 500 Å linear transition.

Fig. 11. — Real-time examination of a $\text{Al}_x\text{Ga}_{1-x}\text{As} \rightarrow$ GaAs heteroepitaxy (light solid line). Point (B) is the stable state for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epitaxy. The heavy solid line is the (Δ, Ψ) locus calculated for an abrupt transition between AlGaAs and GaAs layers.

Fig. 12. — Real-time examination of a GaAs $\rightarrow$ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ heteroepitaxy with good growth conditions (heavy solid line). The (Δ, Ψ) loci respectively calculated for 100 Å (light solid line), 200 Å (---) and 300 Å (----) transition widths are also given.

shows a qualitative agreement between the experimental curve and the calculated one, assuming an abrupt interface. Calculated curves for 100 Å, 200 Å

and 300 Å transition widths are also shown. The $\text{Al}_x\text{Ga}_{1-x}\text{As}$ growth was deliberately stopped at a thickness of 400 Å.

The $\text{Al}_x\text{Ga}_{1-x}\text{As} \rightarrow \text{GaAs}$ transition given in the figure 11 exhibits an experimental (Δ, Ψ) locus which is in qualitative agreement with the calculated one, assuming an abrupt interface.

The real-time observation of the (Δ, Ψ) variations does not allow any further accurate determination of the transition width, but it provides a qualitative assessment of the growth interface. Furthermore, it allows the determination of the thickness of the growing layer, provided that its refractive index is known (this can be roughly estimated from the $\text{Al}/(\text{Al} + \text{Ga})$ ratio in the gas phase). The thickness d corresponding to one pseudo-period is readily determined [9]. For instance, assuming that the real part of the refractive index is 4.20 for GaAs and 3.9 for $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ at 720 °C, leads to about 900 Å for each pseudo-period of the spirals of figure 11. Thus, the knowledge of the growth time required to get a pseudo-period allows the calculation of the growth rate.

3. Non destructive and quantitative assessment of the composition profiles by ellipsometry. — In this section, we intend to give a detailed description of the treatment of the real-time *in situ* ellipsometry data leading to a composition profile determination of a complex heterostructure. Firstly, the formalism used for this quantitative assessment is outlined. Then it is applied to determine the profiles of layers studied in the former section with special emphasis on the study of the transition sharpness between two successive layers of uniform compositions.

3.1 PRINCIPLE OF THE INVERSION PROCEDURE. — Consider an epitaxial deposit on a substrate of refractive index $\tilde{n}_s$, for which a set of ellipsometric data points (Δ_i, Ψ_i) with $i = 0, 1, \dots, n$ has been obtained at regular time intervals during growth. Let assume that the time elapsed between two successive measurements is small enough for the corresponding variation of the refractive index of the deposited layer be small. The principle of the inversion procedure relies on the fact that knowing $\tilde{n}_s$, deduced from the substrate ellipsometric angles Δ_s and Ψ_s , it is possible to calculate the variations of (Δ, Ψ) corresponding to the growth of a layer of index $\tilde{n}_i$ (Fig. 13).

The principle is illustrated in the figure 13 with simulated ellipsometric data (curve A) corresponding to a calculated $\text{Ga}_{0.5}\text{Al}_{0.5}\text{As}/\text{GaAs}$ transition with a linear 100 Å width transition profile. Let (Δ_s, Ψ_s) be the ellipsometric angles of the bare substrate, (Δ_1, Ψ_1) and (Δ_2, Ψ_2) the first two sets of experimental ellipsometric angles. The (Δ_s, Ψ_s) and (Δ_2, Ψ_2) points define a film stratum noted I.

Assuming a constant refractive index value $\tilde{n}_{\text{guess}} = \tilde{n}_{\text{Ga}_{0.5}\text{Al}_{0.5}\text{As}}$ (which would correspond to an abrupt transition) for the stratum I, the (Δ, Ψ) locus associated to $\tilde{n}_{\text{guess}}$ is calculated *via* a two phase model (curve B).

Fig. 13. — Principle of the inversion procedure intended to deduce the refractive index variations as a function of the layer thickness from the (Δ, Ψ) experimental data (see the text).

To an experimental (Δ_i, Ψ_i) point, a moving point $(\Delta(t_i), \Psi(t_i))$ corresponding to a dummy thickness t_i is associated on the calculated locus. According to Azzam and Bashara [9], an error function can be defined as :

$$N = \sum_{i=1}^2 [(\Delta(t_i) - \Delta_i)^2 + (\Psi(t_i) - \Psi_i)^2].$$

For a given value of $\tilde{n}_{\text{guess}}$, the minimum $N_{\min}$ of this expression in respect of t_1 and t_2 is an estimation of the divergence between the experimental points and the calculated locus. $N_{\min}$ can be expressed as

$$\begin{aligned} N_{\min} &= \sum_{i=1}^2 [(\Delta(t_i^*) - \Delta_i)^2 + (\Psi(t_i^*) - \Psi_i)^2] \\ &= f(\tilde{n}_{\text{guess}}), \end{aligned}$$

where $(\Delta(t_i^*), \Psi(t_i^*))$, $(i = 1, 2)$ are the calculated (Δ, Ψ) points which are nearer the experimental points (Δ_i, Ψ_i) , $(i = 1, 2)$.

The minimization of $N_{\min}$ in respect of $\tilde{n}_{\text{guess}}$ (which is obtained through the linear relationship binding $\tilde{n}_{\text{Ga}_{1-x}\text{Al}_x\text{As}}$ to the composition x) allows the determination of the unique refractive index $\tilde{n}_1$ [14, 19] so that the calculated (Δ, Ψ) evolution fits the first two experimental points. The $d_2 = t_2$ value for which $N_{\min} = f(\tilde{n}_1)$ is minimal gives the thickness of the stratum I.

The inversion procedure is then pursued in the following way :

— The reflectivity coefficients of the stratum I-substrate system is calculated following a well-established procedure ;

— the above calculation is repeated with the experimental points (Δ_3, Ψ_3) and (Δ_4, Ψ_4) , which leads to the refractive index $n_{II}^{(0)}$ and the thickness $d_{II}^{(0)}$ for the layer II defined by the (Δ_2, Ψ_2) and (Δ_4, Ψ_4) points. This scheme is then repeated up to the final couple of ellipsometric data points. Eventually, the deposit is described in terms of stratified structure which consists of parallel homogeneous layers, the indexes and thicknesses of which are successively determined.

3.2 ASSESSMENT OF THE INVERSION PROCEDURE. —

In order to assess the validity of the inversion procedure, the method is tested on three different computer simulated profiles. The structures consist of a substrate, an interface layer, a thick homogeneous deposited layer and only the nature of the interface layer is varied. The three cases of interest corresponds to :

- i) an abrupt interface,
- ii) a 50 Å thick oxide layer,
- iii) a 300 Å thick graded layer.

From the starting structure, the (Δ, Ψ) values are calculated every 5 Å and then used as input values for the inversion procedure which calculates the real part n and imaginary part k of the refractive index of the film as a function of thickness.

i) The (Δ, Ψ) values corresponding to an abrupt profile between a substrate of index $\tilde{n}_s = 4.5-0.5 i$ and a deposited layer of index $\tilde{n}_1 = 4.0-0.1 i$ have been plotted in the figure 14a and fed to the inversion procedure programme, which in turn delivered the calculated n and k values plotted in the figure 14b. The calculated n and k points fit to the starting index values with a superimposed noise which depends on the convergence criterium used. However, experimental (Δ, Ψ) measurements bear random errors which must be considered. The refractive index values calculated by taking into account typical random errors ($\delta\Psi = 0.02^\circ$ and $\delta\Delta = 0.05^\circ$), have also been plotted (crosses) in the figure 14b, for the same convergence criterium as in the previous case. The noise has largely increased. Finally, the parameter error in n and k mainly depends on the parameter error in Δ and Ψ , and on the incremental thickness between two (Δ, Ψ) points.

ii) The presence of an oxide at the growth interface is simulated in the following system :

- substrate of refractive index $\tilde{n}_s = 4.5-0.5 i$;
- 50 Å thick oxide film, $\tilde{n}_{ox} = 2.0-0. i$;
- deposited layer, $\tilde{n}_1 = 4.1-0.1 i$.

The corresponding variations of (Δ, Ψ) are given in the figure 15a and the n and k profiles calculated with the inversion procedure profiles are shown in the figure 15b.

iii) The last test refers to the inversion of the (Δ, Ψ) variations corresponding to a gradual transition (in terms of composition) between two homogeneous

Fig. 14. — Assessment of the inversion procedure for an abrupt interface. (a) (Δ, Ψ) calculated locus; (b) refractive index profile.

Fig. 15. — Assessment of the inversion procedure for an abrupt transition with a 50 Å thick oxide layer at the substrate-epitaxial layer interface. (a) (Δ, Ψ) calculated locus; (b) refractive index profile.

materials, namely a substrate ($\tilde{n}_s = 4.5-0.5 i$) and a layer ($\tilde{n}_1 = 4.1-0.1 i$). The 300 Å thick transition layer is simulated by a stack of 1 Å thick virtual strata, the

refractive indexes of which linearly vary from $\tilde{n}_s$ to $\tilde{n}_1$ by increment. The (Δ, Ψ) and refractive index variations have been respectively plotted in the figures 16a and 16b. The inversion procedure renders an account of the initial specifications of the system, especially the linear index variation from the substrate to the layer and the thickness of this transition layer.

Fig. 16. — Assessment of the inversion procedure for a 300 Å thick graded layer interface layer. (a) (Δ, Ψ) calculated locus; (b) refractive index profile.

The three test cases, which have just been discussed, evidence that the inversion procedure is quite a powerful tool to determine the composition profile of deposited layers, the growth of which has previously been monitored by *in situ* ellipsometry. The limitations of this procedure arises from the accuracy and the data rate of the ellipsometric measurements. For standard experimental conditions met with a practical growth reactor plus ellipsometer system, a resolution of 50 Å for the thickness determination is typically achieved. For more drastic experimental conditions, and a (Δ, Ψ) point being measured every 2 Å, a final resolution of 10 Å could be achieved in the analysis of a composition profile.

3.3 PROFILE ANALYSIS OF MO-VPE GROWN (Al, Ga)As-GaAs HETEROSTRUCTURE BY MEANS OF THE INVERSION PROCEDURE. — The inversion procedure has been performed to analyse the transition profiles of two practical heterostructures described in 2.3, a GaAs $\rightarrow$ (Al, Ga)As transition and the reverse (Al, Ga)As $\rightarrow$ GaAs transition. The GaAs-(Al, Ga)As

system is well suited to an inversion procedure type analysis which assumes that :

- i) the growth interface remains smooth at an atomic scale and,
- ii) there is no redistribution of metallic species during growth inside the layer (in other words, the composition only depends on the respective concentrations of TMA and TMG in the vapour phase). The first condition is usually fulfilled as to the epitaxial layers are deposited on thin buffer layers with no microroughness. The second condition is always verified for growth temperatures less than 650 °C, for which solid state diffusion is negligible. Calculations given in this section assume, for the refractive index of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ as a function of x at 650 °C, the following relation :

$$n_{\text{Al}_x\text{Ga}_{1-x}} = 4.20 - 0.45i - 2(0.45 - 0.35i)x.$$

— GaAs $\rightarrow$ (Al, Ga)As transition

The analysis of the GaAs $\rightarrow$ $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$ heterostructure described in the section 2 leads to the refractive index profiles plotted in the figure 17. The variations of the real and imaginary parts of the refractive index as a function of the layer thickness show that the Al content reaches about half its steady state value after ~ 100 Å and its steady state value after a thickness of ~ 500 Å. Such a smooth profile is typical of a first GaAs $\rightarrow$ (Al, Ga)As transition when growing a stack of such layers. This behaviour has to be related to the strong reactivity of $(\text{CH}_3)_3\text{Al}$ which combines with oxygen adsorbed on the walls of the reactor until complete saturation. Thus depending on the residual oxygen and/or H_2O amount present before the growth cycle and the growth conditions, a more or less smooth composition profile is observed for the GaAs $\rightarrow$ (Al, Ga)As transitions. In fact, specific reactor designs and/or growth procedures may lead to a large reduction of the transition width. This is illustrated in the figure 18 which gives the refractive index variations of a GaAs $\rightarrow$ (Al, Ga)As transition obtained with

Fig. 17. — Refractive index profile corresponding to the experimental (Δ, Ψ) locus shown in the figure 10.

Fig. 18. — Refractive index profile corresponding to the experimental (Δ, Ψ) locus shown in the figure 12.

appropriate growth conditions. The transition width is then reduced to ~ 100 Å, which is considered to be typical for an MO-VPE growth.

— (Al, Ga)As $\rightarrow$ GaAs transition

The result data of the inversion procedure applied to the $\text{Al}_{0.30}\text{Ga}_{0.70}\text{As} \rightarrow \text{GaAs}$ heterostructure described in the section 2 have been plotted in the figure 19. They evidence a rather sharp composition profile and the transition width is estimated to ~ 100 Å, which is a typical value for a standard growth system.

3.4 DISCUSSION. — The profile assessment of the dummy transitions on the one hand, and of the practical (Al, Ga)As $\rightarrow$ GaAs and GaAs $\rightarrow$ (Al, Ga)As transitions on the other hand, have unambiguously demonstrated the interest of the inversion procedure applied to real-time ellipsometry measurements. Moreover, it allowed us to evidence the role of the oxygen and/or water vapour gettered on the reactor walls in the transition width of the GaAs $\rightarrow$ (Al, Ga)As heterostructures, which depends mainly on the growth procedure.

Fig. 19. — Refractive index profile corresponding to the experimental (Δ, Ψ) locus shown in the figure 11.

The present study, restricted to the growth and the analysis of standard heterostructures, intended to show the possibilities of original applications of ellipsometry. It has previously been shown, using *in situ* ellipsometry, that transition widths of ~ 40 Å and ~ 25 Å could be respectively achieved for GaAs-(Al, Ga)As and GaAs-AlAs superlattices grown by MO-VPE [17]. These figures were estimated by a fitting procedure between experimental and calculated curves corroborated by SIMS measurements [17]. The inversion procedure appears to be a more systematic approach for the thickness and composition assessment of such multilayer structures.

4. Summary. — A fast automatic ellipsometer designed for *in situ* measurements during vapour-phase growth has been described as well as the MO-VPE reactor used in the study. A simple and quick calibration procedure for the optical components is also reported. Operator skill is only required for the mechanical alignment of the ellipsometer-reactor system. Fast data acquisition and treatment has been achieved by developing a specific data processing unit which virtually feeds the Fourier coefficients of the ellipsometric signal to a microcomputer. Thus a (Δ, Ψ) point can be obtained in three seconds with a typical precision of 0.01° for Ψ and 0.05° for Δ .

It has been shown that *in situ* monitoring could be useful to assess the growth conditions which is valuable for investigation of new growth procedures or new epitaxial structures. The deposition of a layer A of refractive index $\tilde{n}_A$ on a substrate S of index $\tilde{n}_S$ ($n_A \neq n_S$) can be *in situ* monitored in terms of growth rate, thickness and composition profile provided that the growth interface remains smooth at the atomic scale during the growth cycle, condition satisfied in case of the GaAs-(Al, Ga)As system. Real-time observation of the (Δ, Ψ) variations provides a real-time qualitative assessment of the growth and the final (Δ, Ψ) measurement of a thick homogeneous $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layer yields the Al concentration determination within $\pm 5\%$ (for $x < 0.5$), as checked by X-ray diffraction or *a posteriori* ellipsometric measurements. The processing of the (Δ, Ψ) real-time data by an inversion procedure has been developed and proved to be a powerful, precise and non destructive tool to determine the concentration profile and the transition width at a GaAs-(Al, Ga)As interface.

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