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ELLIPSOMETRIC INVESTIGATIONS OF OXIDE FILMS ON Ga As

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Résumé. — Les constantes optiques de support en GaAs ont été déterminées par ellipsométrie pour $\lambda = 5\,461$ Å. Leurs valeurs sont : 3,923 pour n et 0,304 pour k. L'équation fondamentale de l'ellipsométrie a été résolue pour le cas de films transparents déposés sur GaAs. Les recherches effectuées sur GaAs oxydé thermiquement ont montré que le film obtenu a une structure complexe, avec une accumulation d'arsenic sur la face du film côté GaAs.

Abstract. — The optical constants of GaAs substrates have been determined by ellipsometry for $\lambda = 5\,461$ Å. They are $n = 3.923$ and $k = 0.304$. The fundamental equation of ellipsometry was solved for the case of transparent films on GaAs. Investigations on thermally oxidized GaAs revealed that the resulting film has a complex structure, with an accumulation of arsenic at the GaAs-film interface.

I. **Introduction.** — The thermal oxidation of III-V compounds has recently been investigated [1] and the detailed kinetics for InSb established on the basis of oxygen absorption. However. no measurements of the thickness and optical properties of the resulting oxide films have been reported. The purpose of this investigation is to study the thermal oxidation of GaAs and to examine the optical properties of the oxide films by ellipsometry. In order to apply this method the optical constants of the GaAs substrate had first to be determined since considerable differences exist in the reported values.

II. **Technique.** — Ellipsometry is a method which allows the determination of the phase difference, Δ, and amplitude ratio, $\tan \psi$, of the components of a reflected wave parallel and perpendicular to the plane of incidence. The fundamental equation of ellipsometry is [2]

$$\tan \psi \, e^{i\Delta} = \left[\frac{r_{1p} + r_{2p}\, e^{-2i\delta}}{1 + r_{1p}\, r_{2p}\, e^{-2i\delta}}\right] \left[\frac{1 + r_{1s}\, r_{2s}\, e^{-2i\delta}}{r_{1s} + r_{2s}\, e^{-2i\delta}}\right]. \quad (1)$$

Here $r_{\alpha s}$ and $r_{\alpha p}$ are the Fresnel reflection coefficients for the interfaces involved ($\alpha = 1$ or 2), φ is the angle of incidence in the immersion medium, and δ is the phase change (in degrees) caused by the presence of a film of thickness t and index of refraction n_1 :

$$\delta = (360\, t/\lambda_0) \sqrt{n_1^2 - \sin^2 \varphi}. \quad (2)$$

The ellipsometer used is a spectrometer with analyzer, polarizer and quarter wave plate all mounted in divided circles and a monochromatic light source of 5461 Å wavelength. A photomultiplier microphotometer was used as a detector. The angle of incidence was kept constant at 70.00°. Extinction settings were obtained by employing a method of successive approximations.

III. **Optical constants of GaAs at $\lambda_0 = 5\,461$ Å.** — In order to evaluate eq. (1) for the case of transparent films on GaAs an accurate value of the complex index of refraction ($\bar{n} = n - ik$) of this compound must be known. The following values have been reported for $\lambda_0 = 5461$ Å at nearly normal incidence :

n	k	AUTHOR
3.46	1.51	Morrison [3]
4.11	0.6	Philip and Ehrenreich [4]
—	0.276	Sturge [5]

Because of the large discrepancy and the insufficient accuracy of these values, the complex index of refraction of GaAs was re-determined by ellipsometry. The optical constants of a material are related to the ellipsometric parameters of eq. (1) by the following relationships [6],

$$n^2 = k^2 + \sin^2 \varphi + \frac{\sin^2 \varphi \tan^2 \varphi \, (\cos^2 2\bar{\psi} - \sin^2 2\bar{\psi} \sin^2 \bar{\Delta})}{(1 + \sin 2\bar{\psi} \cos \bar{\Delta})^2} \qquad (3)$$

$$k = \frac{\sin^2 \varphi \tan^2 \varphi \sin 4\bar{\psi} \sin \bar{\Delta}}{2n(1 + \sin 2\bar{\psi} \cos \bar{\Delta})^2} \qquad (4)$$

where the bars on ψ and Δ indicate a film free surface.

Completely film-free surfaces are unattainable (except possibly in ultra-high vacuum). In order to measure Δ and ψ for essentially film free surfaces, mechanically polished GaAs samples of $(\bar{1}\bar{1}\bar{1})$, (110), and (100) orientations were successively etched and measured. The etch consisted of 1 part H_2O_2, eight parts H_2SO_4, and one part H_2O [7]. Both Δ and ψ asymptotically approached a value with increasing etching time, probably due to the removal of the work damaged layer. The asymptotic value of ψ was well defined while that of Δ showed some scatter, which is most probably a result of the variation in the thickness of the oxide formed during the interval between the removal of the sample from the etch and the measurement. It was also noticed that there is a slight difference in the asymptotic values of these quantities for the different crystallographic directions. This will have to be investigated in further detail. For the present we restrict ourselves only to the (110) orientation. For this case, the asymptotic values were $\Delta = 165°$ and $\psi = 11.2°$. These values differ from $\bar{\Delta}$ and $\bar{\psi}$ because of the presence of an unavoidable thin oxide film. However, from the Drude equations [2] it is obvious that this difference is very small for ψ and therefore, we take $\psi = 11.2°$ as $\bar{\psi}$. On the other hand, $\bar{\Delta}$ may differ from its experimentally determined lower limit of 165° by an amount of the order of degrees. In ordr to get a first approximation for n we use $\bar{\Delta} = 165.0°$, $\bar{\psi} = 11.2°$, and the value of k as given by Sturge, which has been corrected for room temperature [8] ($k = 0.307$). This procedure is justified because n does not strongly depend on $\bar{\Delta}$, as can be seen from eq. (3), and results in $n = 3.881$. Now eq. (4) can be solved for $\bar{\Delta}$ using $n = 3.881$, $\bar{\psi} = 11.2°$ and $k = 0.307$. This results in $\bar{\Delta} = 168.5°$. If this value is now used instead of 165.0° in eq. (3) we calculate $n = 3.923$. If we use now this value of n, as well as $\bar{\Delta} = 168.5°$ and $\bar{\psi} = 11.2°$ in eq. (4) we get a value of $k = 0.304$. This is in very good agreement with the value of k as determined by absorption experiments. By repeating this successive approximation, using this last value of n it was found that $\bar{\Delta} = 168.4°$. This small change in $\bar{\Delta}$ is insignificant as far as the optical constants of GaAs are concerned, and so our final values are $n = 3.923$ and $k = 0.307$. A schematic of this procedure if shown in figure 1. These values give

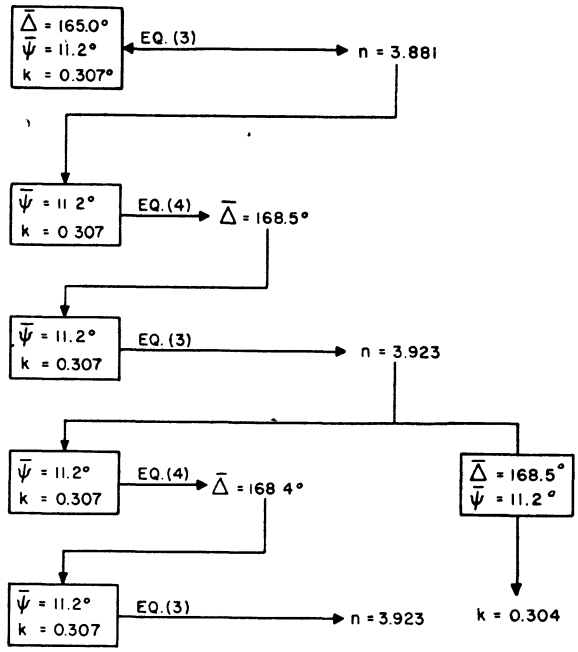

FIG. 1. — Successive approximation for the calculation of the real part of the index of refraction of Ga As.

a principal angle of incidence $\theta = 75.75°$, which can be used in the theoretical relationship between $\bar{\Delta}$ and the an gle of incidence, φ, as given in reference 9, to a pproximately determine $\bar{\Delta}$ for $\varphi = 70.00°$. From this graph we get $\bar{\Delta} = 14°$ which, in our experimental arrangement corresponds to $\bar{\Delta} = 180° - 14° = 166°$. This is in good agreement with our results.

It should be noted th at in the above calculations the final value $n = 3.923$ represents an upper limit because of the possibility that $\bar{\psi}$ is somewhat smaller than 11.2°.

IV. **Solution of ellipsometry equation for films on GaAs.** — The case of films on a reflecting substrate is governed by equation (1). For very thin films this expression can be approximated by the Drude relation [2] :

$$\Delta = \bar{\Delta} - \alpha t \quad (5)$$

where

$$\alpha = \left(\frac{4\pi}{\lambda_0}\right)\left(1 - \frac{1}{n_1^2}\right)\frac{\cos\varphi \sin^2\varphi\,(\cos^2\varphi - a)}{(\cos^2\varphi - a)^2 + a_1^2} \quad (6)$$

$$a = (n^2 - k^2)/(n^2 + k^2)^2$$

$$a_1 = 2nk/(n^2 + k^2)^2$$

and where n and k are the optical constants of the substrate, and n_1 is the real part of index of refraction of the film. Assuming that the film is basically Ga_2O_3 and can be characterized by $n_1 = 1.93$ [10] one can calculate α from eq. (6) by using the optical constants of GaAs as determined in the previous section and an angle of incidence $\varphi = 70.00°$. This yields $\alpha = 0.504$ degrees/Å. This value can now be used in conjunction with $\Delta = 168{,}4°$ in eq. (5) for the determination of the thickness of very thin films on GaAs (e.g. the thickness of the film present immediately after etching was determined to be approximately 7 Å).

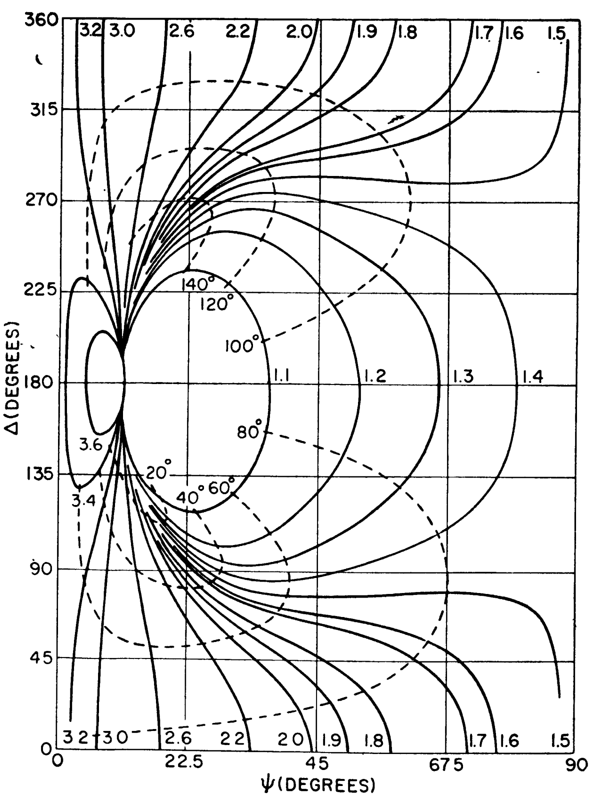

FIG. 2. — Δ and ψ as a function of the index of refraction and thickness of transparent film on Ga As. Full lines are loci of constant index of refraction, dashed lines are loci of constant δ.

It is important to realize, however, that the concept of the index of refraction, as defined for bulk material, cannot be applied without reservations to very thin films. Therefore, the value of α cannot be used with great confidence for the exact evaluation of the thickness of thin films. Moreover, as will be shown in the next section, the properties of the GaAs-film interface depend upon the thickness of the film and the arguments outlined above represent only a first approximation to this complex problem.

For the evaluation of thicker films eq. (1) was solved by computer methods using the complex index of refraction of GaAs as given in Sec. 3. The graphical representation of this solution is shown is shown in figure 2. The curves are loci of constant n ; values of δ are indicated on them. The thickness of the film is determined by using the proper δ and n-values in eq. (2).

V. **Thermal oxidation of GaAs.** — Mechanically polished wafers having (110), (111), and $(\overline{111})$ orientations were oxidized in dry oxygen at 660°C for various times (4-400 min). The (111) and $(\overline{111})$ surfaces became very pitted, whereas the (110) surface remained quite smooth. For this reason this study is restricted to the (110) orientation. After the oxidation bright interference colors could be observed. The oxidized samples were investigated by phase contrast microscopy and it was found that the films had granular structure. (The average size of the granules is about 0.5 μ). This observation is in accord with the reported fact [11] that thermal oxidation of GaAs results in polycrystalline β-Ga_2O_3. Chemical analysis revealed that the films are essentially free of arsenic.

In order to study the influence of the oxidation upon the properties of the GaAs-film iterface the oxide of two samples (oxidation times 4 and 16 minutes, respectively) was stepwise removed by etching in boiling HCl. After each etching the sample was measured in the ellipsometer. During these experiments it was found that Δ and ψ asymptotically approached the following values : $\Delta = 130°$ and $\psi = 11.2°$. Although ψ approached the value characteristic of a nearly film free surface, Δ did not. It is quite obvious, therefore, that the film has a composite nature and cannot be completely removed by the boiling HCl. In analogy with the thermal oxidation of InSb [1] it was suspected that during the oxidation arsenic accumulated at the interface and that this was responsible for the above observations. From this it is quite clear that the solution of the ellipsometry equation as evaluated for transparent films on GaAs is not applicable, without further consideration, to oxide films produced by thermal oxidation. For the ellipsometric evaluation of these oxide films it is necessary to use the optical constants of this interface. These constants were determined by the same method of successive approximations as outlined above using $\bar{\psi} = 11.2°$, $\bar{\Delta} = 130.0°$, and the real part of the index of refraction of arsenic $n = 3.17$ [12]. In this way it was found that $n = 3.231$ and $k = 0.959$. It is of interest to note that this n-value is somewhat larger than that of arsenic but significantly lower than that of GaAs. This strengthens our previous assumption that even for short oxidation times arsenic accumulates at the interface during the oxidation. Electron diffraction experiments showed the presence of As_2O_3. This oxide might be due to the oxidation of the arsenic film during the time that elapsed between the ellipsometric measurement and the electron diffraction experiment. It is also possible that some of the arsenic was already oxidized, and this could be the reason why the calculated k-value is smaller than that characteristic of bulk arsenic (2.48 [12]).

Eq. (1) was solved again for these new optical constants and the results presented in the same graphical form, as described earlier. Points representing oxidized samples were then plotted on both graphs, i.e. the graphical solutions of the ideal case and that of GaAs covered with an arsenic film (see *fig.* 3). In neither of the two cases do the points fall on a line of constant index of refraction, but the spread for case (*a*) is smaller than that for case (*b*). *A priori*, there is no assurance that the refractive index should be independent of the thickness of the film. However, it seems unlikely that this could be responsible for the large variations indicated in figure 3. This is especially true for the points representing the two thinnest oxide films. For thicknesses larger than about 500 Å the n-values in both cases approach that reported for bulk Ga_2O_3 (1.93[10]). The fact that essentially the same value is approached in both cases is due to the diminishing influence of the optical properties of the interface on the position of the constant n curves with increasing film thickness. Therefore, the evaluation of the index of refraction and thickness could be performed with more confidence for points falling in this area of the Δ vs. ψ graph.

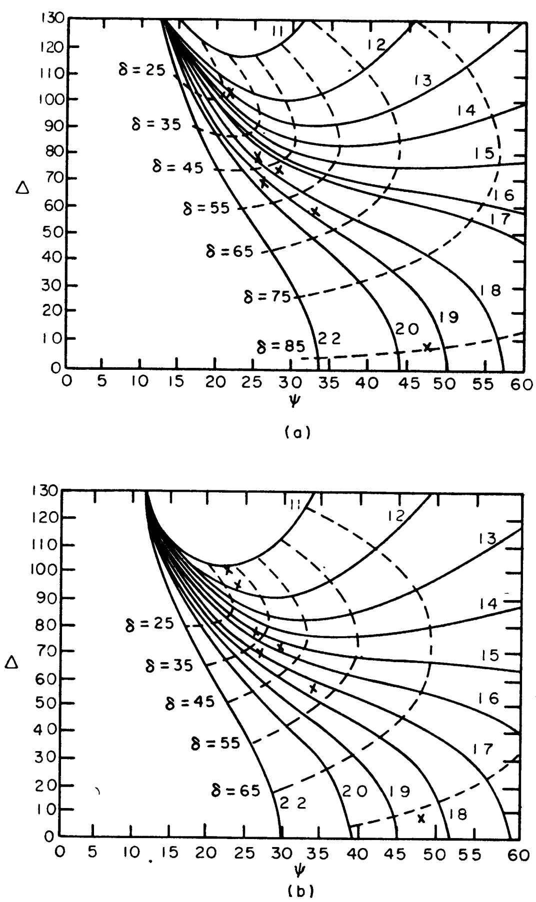

FIG. 3. — Section of the Δ vs. ψ plane with experimental points representing oxidized specimens. Evaluated for (a) ideal Gas As-film interface (b) arsenic film at the interface.

From these considerations it is clear that neither of the above solutions can be used for the ellipsometric study of films produced by thermal oxidation of GaAs before the exact nature of the resulting complex structure has been more accurately determined.

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