THE MATERIALS RESEARCH LABORATORY

THE PENNSYLVANIA STATE UNIVERSITY

SIXTH SEMIANNUAL REPORT

on

Research on The Mechanism and Kinetics of Oxidation of Silicon in Air

For the period

1 December 1967 to 31 May 1968

Grant Number NASA Grant NGR-39-009-042

National Aeronautics and Space Administration
Washington, D. C. 20546

June 17, 1968

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ABSTRACT

From a series of ellipsometric measurements it is now possible to obtain uniquely all the optical parameters of the system: absorbing substrate + non-absorbing surface film. The method utilizes the fact that the reflectivity of such a system remains essentially constant for a small but finite range of surface film thicknesses. Furthermore it hinges on the fact that the ellipsometric parameters Δ and ψ measured on different film thicknesses grown on the same sample, are compatible with only one unique choice of the parameters n_2, k_2, and n_1. Measurements on chemically etched samples of silicon yield the values of the optical parameters as $n_2 = 4.052$ and $k_2 = 0.029$ in agreement with the results of earlier workers. The results on the cleaved samples of silicon, on the other hand, reveal that the true values are $n_2 = 4.14_0$ and $k_2 = 0.03_4$ for $\lambda 5461$Å.

GENERAL INTRODUCTION

The period covered by this report has been extremely fruitful and productive in that a new and powerful method has been developed by which the fundamental optical parameters of any absorbing material can now be determined by an ellipsometric technique. It is not necessary to make any assumptions regarding the refractive index of the contaminating film on the material since this value is also one of the final results of this method of analysis of the experimental data. This new method is in many ways different from that described in the last report and further can be employed successfully even with materials which are highly absorbing. This report describes this method in detail along with some of the results obtained on chemically etched as well as cleaved samples of high purity silicon. Such measurements are absolutely essential before any investigations on the kinetics of oxidation or the effect of radiation damage on the optical parameters of the silicon solar cells are undertaken.

A paper on "The ellipsometric method for the unique determination of all the optical parameters of the system: isotropic absorbing substrate + isotropic non absorbing surface film" has been accepted for presentation at the conference on "Recent developments in Ellipsometry" being held at Lincoln, Nebraska during August 7-9, 1968.

The following paper was also published during this report period: "Simultaneous Independent Determination of the refractive index and the thickness of thin films by Ellipsometry." by K. Vedam, R. Rai, F. Lukes and R. Srinivasan, Jour. Opt. Soc. Amer. <u>58</u>, 526-532, 1968.

The Ellipsometric method for the unique determination of all the optical parameters of the system: Isotropic absorbing substrate + isotropic non absorbing surface film.

I. Introduction

It is well known that the ellipsometric method which is most often used for the determination of the index of refraction n_1 and the thickness d_1 of a nonabsorbing film on an absorbing substrate (see e.g. [1], [2]) can be used only in the case when the true values of the complex refractive index $n_2 + i k_2$ of the substrate are known precisely. Conversely it has also been shown by many authors, (e.g. Archer [1], Burge and Bennett [3] etc.) that the optical constants of the substrate can be determined only if the values of n_1 and d_1 of the film are known, even though the thickness of the film may be as small as 10 - 50 Å. Burge and Bennett [3] demonstrate this fact in detail for the special case of silicon. Since Δ and ψ, the ellipticity parameters determined experimentally depend on all the values of n_1, d_1, n_2, and k_2, which characterize the system: absorbing substrate + nonabsorbing film, we have to know at least two of these parameters when we wish to use the standard ellipsometric method for the determination of the other two parameters.

As is well known there is a certain surface film on all surfaces exposed to the normal atmosphere. The direct determination of the optical constants of the substrate from the measured values Δ and ψ without any assumption about the nature of the surface film, has in the past been rather unsuccessful. Hence attempts were usually made to apply suitable corrections and extrapolations to the measured values to yield the optical constants of the substrate (See Archer [4] for Ge, Zaininger and Revesz [5] for GaAs), but the problem is very complicated and in each case we have to know at least one of the optical constants of the substrate rather precisely from another type of measurement. Further the refractive index of the surface film n_1 had to be assumed. But the value of n_1 is usually either not known precisely or the validity of using the refractive index of the bulk material for thin films is questionable. For example, in the case of germanium the refractive index of the surface film was assumed[4] to have a value 1.9±0.2, thus introducing a fairly large margin of error. Even in the case of silicon where the refractive index of the silicon dioxide film is quite accurately known, the recent measurements of Vedam et al[6] on very thin films of SiO_2 on silicon yielded values quite different from that of the vitreous silica, 1.460.

The problem of the measurement of the optical constants of the homogeneous solids can be solved by measurements on clean surfaces in ultra-high cacuum of the order 10^{-10} mm Hg. In this case it is possible to preserve the clean surface obtained either by cleaving or special treatment for several hours without essential contamination [2]. This method is far from being used in practice, since there are other difficulties which complicate the measurement such as the problem of cleavage of the sample in a vacuum or the treatment of the surface leading to the removal of the surface film or damaged surface layer. Another major difficulty is the presence of the glass or silica windows in the high-vacuum system and their unavoidable strain birefringence in the optical path.

In this article we shall describe an ellipsometric method which may be used for the unique determination of all the four parameters characterizing the above mentioned system without making any assumptions about the nature of the substrate or the film. Since the present day computers can handle the ellipsometric equations in their exact form, recourse to various approximate linear relations was not required, and all the calculations and computations described below were carried out using the exact ellipsometric equations.

II. Description of the method

Let us consider the following system: an ideally perfect homogeneous and optically isotropic substrate with the optical constants n_2 and k_2 and a homogeneous, optically isotropic nonabsorbing film on the substrate with an index of refraction n_1, thickness d_1. Both the boundaries, i.e. that between the ambient (with index of refraction n_o) and the film, as well as that between the film and the substrate are assumed to be flat, and the film thickness is assumed to be constant. Any departure from the above specification of the system, for example absorption in the film, anisotropic optical constants of the substrate, or an inhomogeneous film etc., would bring additional optical parameters into consideration and the problem cannot be solved in the way described in this article.

It may be remarked that the ellipsometric parameters Δ and ψ depend on the values of n_2, k_2, n_1, d_1 and also on the angle of incidence ϕ, the wavelength λ and on the initial state of the polarization of the incident light. We shall not repeat here all the equations characterizing the given case since they are well known and may be found e.g. in [7].

The procedure used for the unique determination of n_2, k_2, n_1 and d_1 is as follows:

(i). We measure Δ and ψ for the real surface (generally the substrate with a surface film) at some convenient angle of incidence ϕ, such that the accuracy of measurement is high for both Δ and ψ. Angle of incidence of 70° is usually found to be satisfactory for most substances.

(ii). We use the measured values Δ and ψ for the evaluation of the pseudo-optical constants $\bar{n}_2$, $\bar{k}_2$ by means of the equations valid for clean surfaces, i.e.,

$$\bar{n}_2^2 - \bar{k}_2^2 = n_0^2 \sin^2\phi + n_0^2 \sin^2\phi \tan^2\phi \; \frac{\cos^2 2\psi - \sin^2 2\psi \sin^2\Delta}{(1 + \sin^2\psi \cos\Delta)^2} \qquad (1)$$

$$2\bar{n}_2\bar{k}_2 = \sin^2\phi \tan^2\phi \frac{\sin 4\psi \sin\Delta}{(1 + \sin 2\psi \cos\Delta)^2} \qquad (2)$$

$\bar{n}_2$, $\bar{k}_2$ would be identical with the true optical constants of the substrate under consideration only in the case that Δ and ψ correspond to measurements made on a truly clean surface.

(iii). Then we calculate the reflectivity R from $\bar{n}_2$, $\bar{k}_2$ for all angles of incidence ϕ, with the help of the relation,

$$R = \frac{(\bar{n}_2 - n_o)^2 + \bar{k}_2^2}{(\bar{n}_2 + n_o)^2 + \bar{k}_2^2} \qquad (3)$$

As Burge and Bennett [3] have shown, the value of $\bar{n}_2$ and $\bar{k}_2$ and hence R derived from their values do not depend on the angle of incidence ϕ. Hence one can carry out the measurement of Δ and ψ for a number of angles of incidence and evaluate the value of R therefrom, in order to obtain a more reliable value of R. However this may not be feasible in every case. For example as will be shown in (v) below, in the case of freshly cleaved samples where the film thickness will be varying rapidly, this is impractical.

(iv). The very important feature of the next step is that the reflectivity calculated by means of Eq. 3 is very close to the reflectivity of the clean surface even though the surface is covered with a film of appreciable thickness as shown in Table I for silicon. Table I illustrates this very slow variation in R with increasing d_1. Thus it is seen that an ellipsometric measurement on a silicon substrate covered by a surface film of SiO_2 anywhere up to 200Å thick yield a reflectivity which is the same as that of a clean surface to within ±0.1%.

It should be noted, however, that even though the reflectivity R remains fairly constant the measured values of Δ and ψ would show considerable variation with increasing values of d_1 or δ. In fact if the influence of the film thickness is neglected, the computed values of $\bar{n}_2$ and $\bar{k}_2$ from such measured values of Δ and ψ would be disproportionally in error, though the computed values of R from such values of $\bar{n}_2$ and $\bar{k}_2$ still correspond to the true value. This is illustrated in Fig. 1.

It is possible to prove generally that with increasing index of absorption k_2, or rather with an increasing ratio k_2/n_2 the above limits of the film thickness d_1 decreases considerably e.g. ($d_1 \leq$ 50Å for an oxide film on GaAs and $\leq$ 15Å for a GeO_2 film on Ge). In other words, the above mentioned statement may be used only for materials with a low index of absorption. Since it is rather well known that the typical thickness for surface films

Table I

Calculated values of Δ and ψ for various thicknesses of film of refractive index 1.460 on a substrate of refractive index n_2 = 4.050 and k_2 = 0.028. The value $\bar{n}$, $\bar{k}$ and $\bar{R}$ computed from these Δ and ψ are also given in the table.

d_1(Å)	δ(°)	Δ(°)	ψ(°)	$\bar{n}$	$\bar{k}$	$\bar{R}$
0.0	0.0	179.038	11.763	4.05000	0.02800	0.36479
1.00	0.074	178.728	11.764	4.04984	0.03703	0.36479
2.00	0.147	178.418	11.765	4.04964	0.04606	0.36479
5.00	0.368	177.488	11.769	4.04877	0.07313	0.36478
10.00	0.737	175.941	11.781	4.04647	0.11819	0.36478
15.00	1.105	174.396	11.798	4.04311	0.16315	0.36478
20.00	1.473	172.857	11.821	4.03869	0.20798	0.36478
25.00	1.842	171.323	11.850	4.03322	0.25264	0.36478
35.00	2.578	168.279	11.923	4.01917	0.34131	0.36477
50.00	3.683	163.788	12.073	3.99048	0.47214	0.36477
75.00	5.525	156.569	12.424	3.92346	0.68230	0.36478
100.00	7.366	149.763	12.889	3.83471	0.87954	0.36480
125.00	9.208	143.427	13.453	3.72738	1.06106	0.36485
150.00	11.049	137.578	14.099	3.60498	1.22495	0.36494
200.00	14.732	127.295	15.580	3.32920	1.49648	0.36531
250.00	18.415	118.690	17.226	3.03364	1.69457	0.36607
300.00	22.098	111.466	18.961	2.73850	1.82797	0.36747
400.00	29.464	100.173	22.516	2.19513	1.95168	0.37362
500.00	36.831	91.992	26.063	1.73662	1.96530	0.38806
1000.00	73.661	85.118	52.853	0.70231	2.10519	0.61673

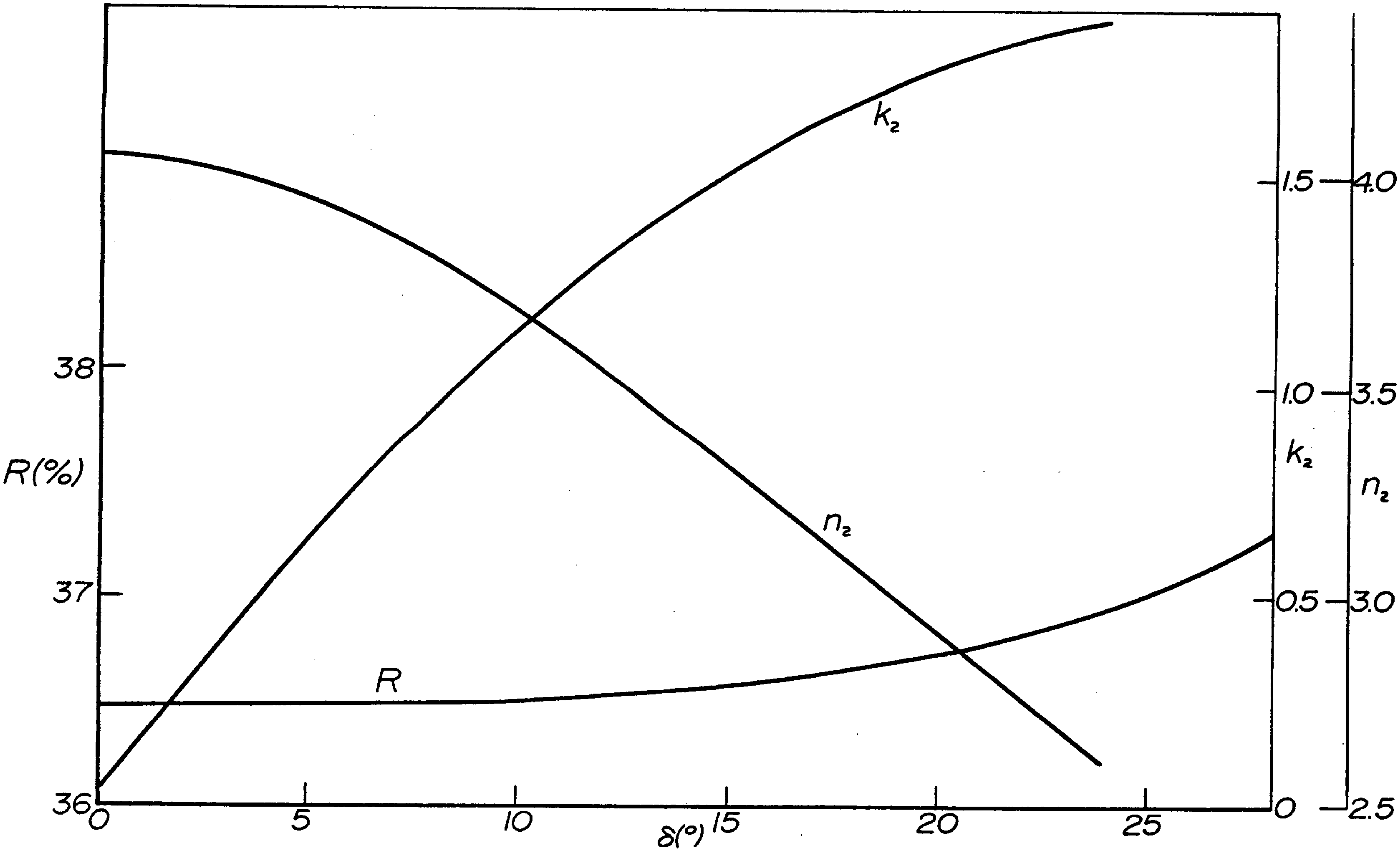

Fig. 1 The variation of $\bar{n}_2$, $\bar{k}_2$ and R as a function of film thickness δ

on freshly cleaved or freshly etched semiconductors is about 20-50Å, we expect that this assumption can be used for many semiconductors in a suitable spectral region.

(v). Starting from as clean a surface as possible, the determination of R with increasing film thickness up to a maximum of about 100Å should be carried out. For materials with fairly low values of the absorption coefficient k_2 (like silicon), the value of R so determined for a number of thicknesses will essentially be constant. On the other hand for materials with large values of k, R will show a slight tendency to decrease initially and then increase with d_1. However, it may be noted that the variation of R with δ (or d_1) at the early stages is rather slight ($\lesssim 1\%$ even for $d_1 \sim 100$Å on a fairly highly absorbing material like Ge). Thus from a plot of these values with d_1, by extrapolating asymptotically to zero film thickness, it is possible to arrive at a value of $\bar{R}$ representing the true value of the reflectivity of the film-free substrate. It is estimated that the error in the value of $\bar{R}$ thus determined will not exceed 0.1% in materials with low absorption coefficient like silicon and will be better than 1% in materials with larger absorption coefficient.

It may be pointed out, that for this extrapolation procedure it is necessary to know only approximate values of d_1. For example one can carry out the measurements on Δ and Ψ and thus R, as soon as a sample is either cleaved or freshly polished and etched - and follow the variation of R with increasing time. If necessary the measurements can be extended to samples heated in air at moderate temperatures for varying periods of time.

(vi). From this value of the true reflectivity $\bar{R}$, the various possible combinations of the values of (n_2', k_2') are then evaluated with the help of the relation

$$k_2' = [2(\frac{1 + \bar{R}}{1 - \bar{R}})\, n_2'\, n_o - [(n_2')^2 + n_o^2\,]]^{1/2} \quad (4)$$

The results of these calculations are shown by the solid line in Fig. 2. It is easy to see from the facts mentioned above that the true values of the optical constants n_2 and k_2 must lie on the curve given in Fig. 2. On the same figure are shown two other curves corresponding to the reflectivity values $\bar{R} + \Delta\bar{R}$ and $\bar{R} - \Delta\bar{R}$, where $\Delta\bar{R} = 0.001$ to demonstrate the influence of error in the measurement on the optical constants.

(vii). At this stage it may be pointed out that if either of the parameters n_2 or k_2 can be determined from an independent experiment (as for example k_2 from absorption measurements) then the other parameter can be evaluated from $\bar{R}$ with the help of Equation (4). If such a procedure is not feasible, then the ellipsometric method described below can be followed.

(viii). Now we may calculate the values of Δ and Ψ as functions of δ $(\delta = 2\pi n_1 d_1/\lambda)(n_1^2 - n_o^2 \sin^2\phi)^{1/2})$for several sets of the optical constants n_2', k_2' chosen from the curve in Fig. 2 in the region of the expected true values of n_2, k_2. The calculations are also performed for several different values of the index of refraction of the film.

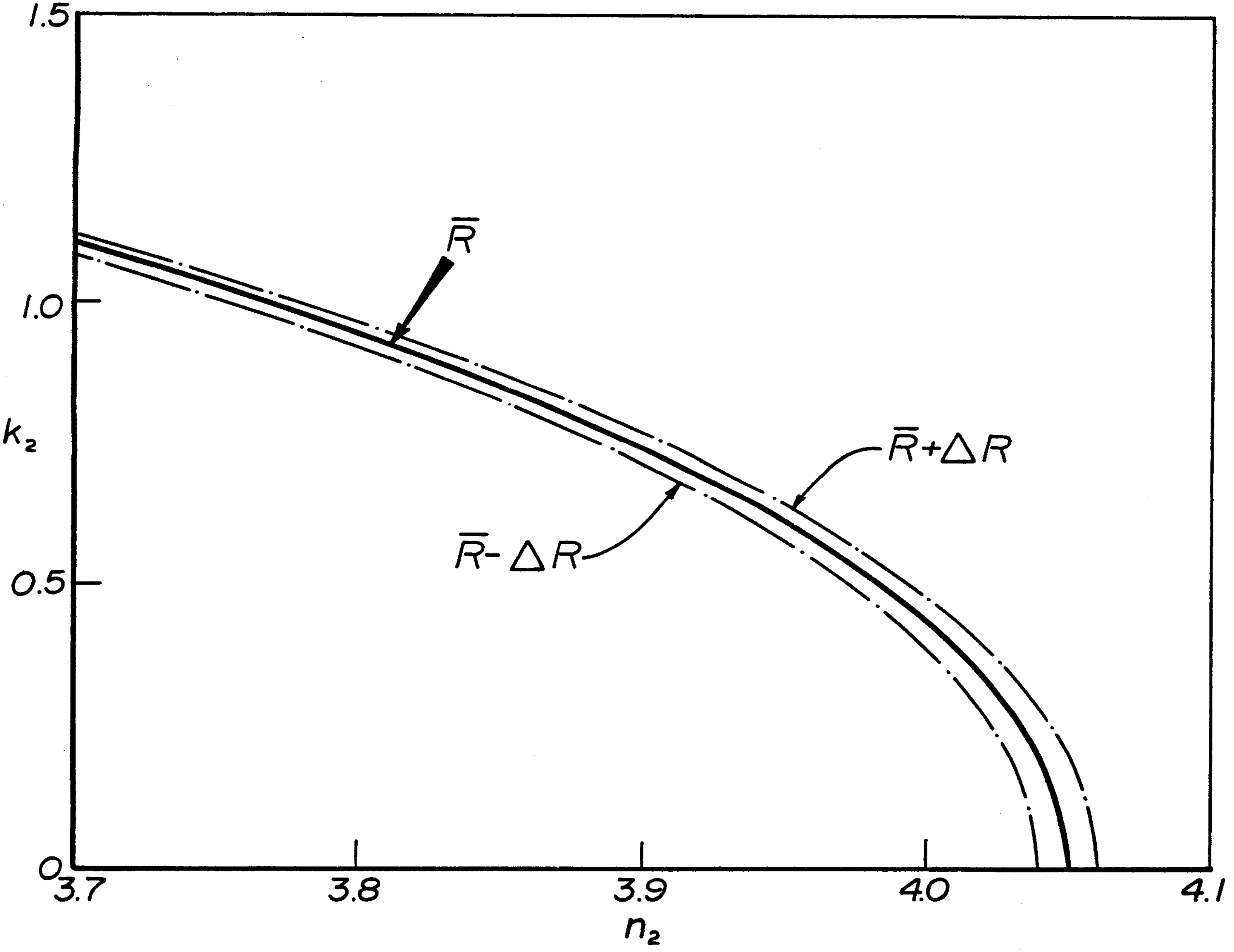

Fig. 2 The permissible sets of (n_2, k_2) for the given reflectivity R = 36.495% (solid line). The hatched lines indicate the permissible range of (n_2, k_2) sets for a possible error in determination of R of ±0.1%.

(ix). It is possible to show that if the angle of incidence ϕ is fixed, the observed values of Δ and ψ on a number of samples with different film thicknesses (or δ) can correspond to only one possible combination of n_2, k_2 and n_1. In other words if the values of n_1 evaluated (as shown below) from measurements on different film thicknesses on the same substrate, are plotted as a function of n_2 (and hence k_2 as well), since it is fixed mutually related to $\bar{R}$ by Eqn. (5) for which the calculated values of Δ and ψ correspond to the experimentally observed values, then all the curves should cross at one point which defines n_2, k_2 and n_1 —as illustrated in Fig. 3. In this case the values of n_2, k_2, n_1 and ϕ were initially assumed as 4.0517, 0.028, 1.460 and 70° respectively. This choice of the values of n_2 and k_2 automatically fixes the value of $\bar{R}$ as 36.495%. Using these parameters the values of Δ and ψ were then computed for several different values of $\delta(\delta_1, \delta_2, \ldots)$ and these sets of values of Δ and ψ were now treated as experimentally observed values $[\Delta_{obs}, \psi_{obs}]\delta_1$ $[\Delta_{obs}, \psi_{obs}]\delta_2$ ... By such a procedure the possible complications introduced by the experimental errors are avoided and thus we can consider this as an example under ideal conditions to test our method.

Even at the cost of slight redundency it will be worthwhile to mention in brief the essential steps adopted to arrive at Fig. 3 from these sets of data $[\Delta_{obs}, \psi_{obs}]\ \delta \ldots$

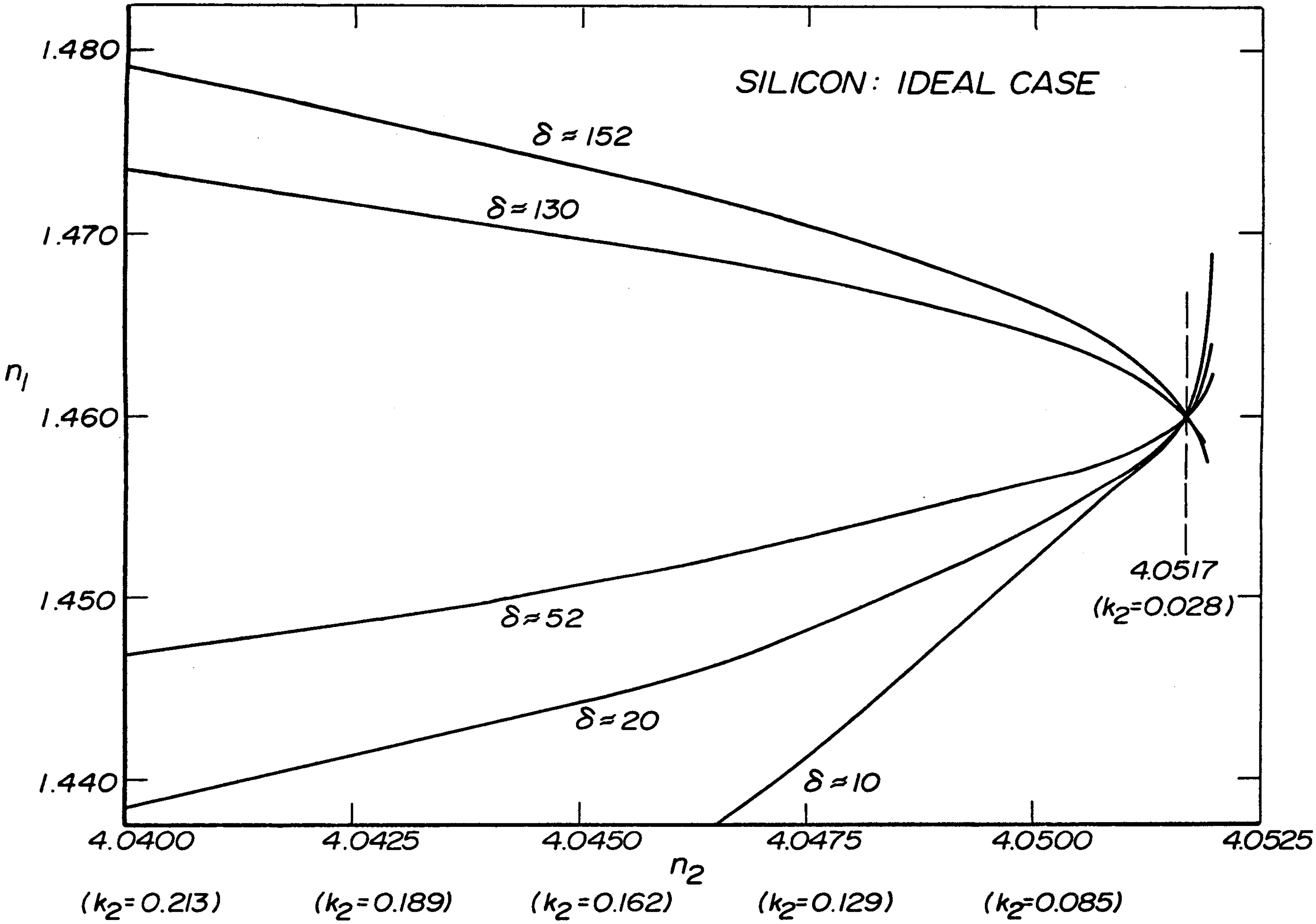

Fig. 3 Calculated values of n_1 vs. n_2 for various values of film thickness δ for the silicon ideal case. $n_2 = 4.0517$ and $k_2 = 0.028$ were assumed in the calculation of n_1 vs. n_2.

(a) We determine various possible sets of (n_2, k_2) to correspond to the fixed value of $\bar{R}$.

(b) We then choose a range of reasonable values of n_1.

(c) We compute the values of Δ and ψ for each of the sets (n_2, k_2) for all the values of n_1 chosen and δ in the range 0 to 180°.

(d) We compare these calculated values of Δ and ψ with $[\Delta_{obs}, \psi_{obs}]_\delta$. A reasonable match will be obtained for only one value of n_1 for each set of (n_2, k_2).

(e) We plot the values of n_1 so obtained against the corresponding values of n_2 (or k_2).

(f) We repeat the above steps for each of the sets of data $[\Delta_{obs}, \psi_{obs}]_\delta$,..., to yield a number of curves relating n_1 and (n_2, k_2) corresponding to each of the initially assumed values of δ.

(g) Since the value of the refractive index n_1 is an intrinsic property of the film, it should not be a function of δ or the film thickness, provided the film is not too thin [6] (i.e., say less than about 300Å). Hence all the curves obtained in (f) above, should cross at one point corresponding to the true value of the refractive index of the film. At the same time the true values of the optical parameters of the substrate are also obtained from this crossing point in the figure.

Here it may be worthwhile to mention that the steps (c) and (d) mentioned above can be considerably simplified by a suitable programming of a digital computer, such that the computer prints out only those computed values of (Δ and ψ) which are within some narrow limits of $\Delta_{obs.}$ and $\psi_{obs.}$.

Such a procedure would obviate the necessity of scanning through voluminous computer print out. Further the computer can also be used to automatically interpolate in between the two calculated values of (Δ,ψ) which lie on either side of $(\Delta,\psi)_{obs.}$, to yield the final appropriate value of n_1 corresponding to each (n_2, k_2) set. Such programs have been written and are included in this report as an appendix.

The method described above can be applied equally well to materials which are highly absorbing. For example Figs. 4, 5, and 6 represent respectively the cases of GaAs, Ge and Tungsten under ideal circumstances. In these cases the assumed values of n_2 and k_2 for $\lambda 5461\text{Å}$ were,
GaAs: $n_2 = 3.923$ and $k_2 = 0.304$, $n_1 = 1.93$; Ge: $n_2 = 5.30$, $k_2 = 1.983$, $n_1 = 1.90$ and Tungsten: $n_2 = 3.46$, $k_2 = 3.25$, $n_1 = 2.50$. It is seen that in all cases the final values obtained are in excellent agreement with the assumed values.

III. Optical Constants of Silicon

(a) Chemically etched samples

The method described above in the previous section in a general form for the ideal case will now be used for the characterization of real systems. Single crystal of silicon covered with an oxide layer is an obvious first choice for such a study, since the optical parameters of this system are known with reasonable accuracy. However a reference to the literature reveals that all such previous determinations of the optical parameters of silicon were carried out on samples which were mechanically polished and later chemically etched. Even though it is well known that the film on such chemically etched samples are not quite homogeneous [8] , it was felt desirable to carry out the initial studies on such chemically etched samples in order to test the capabilities and limitations of the above method.

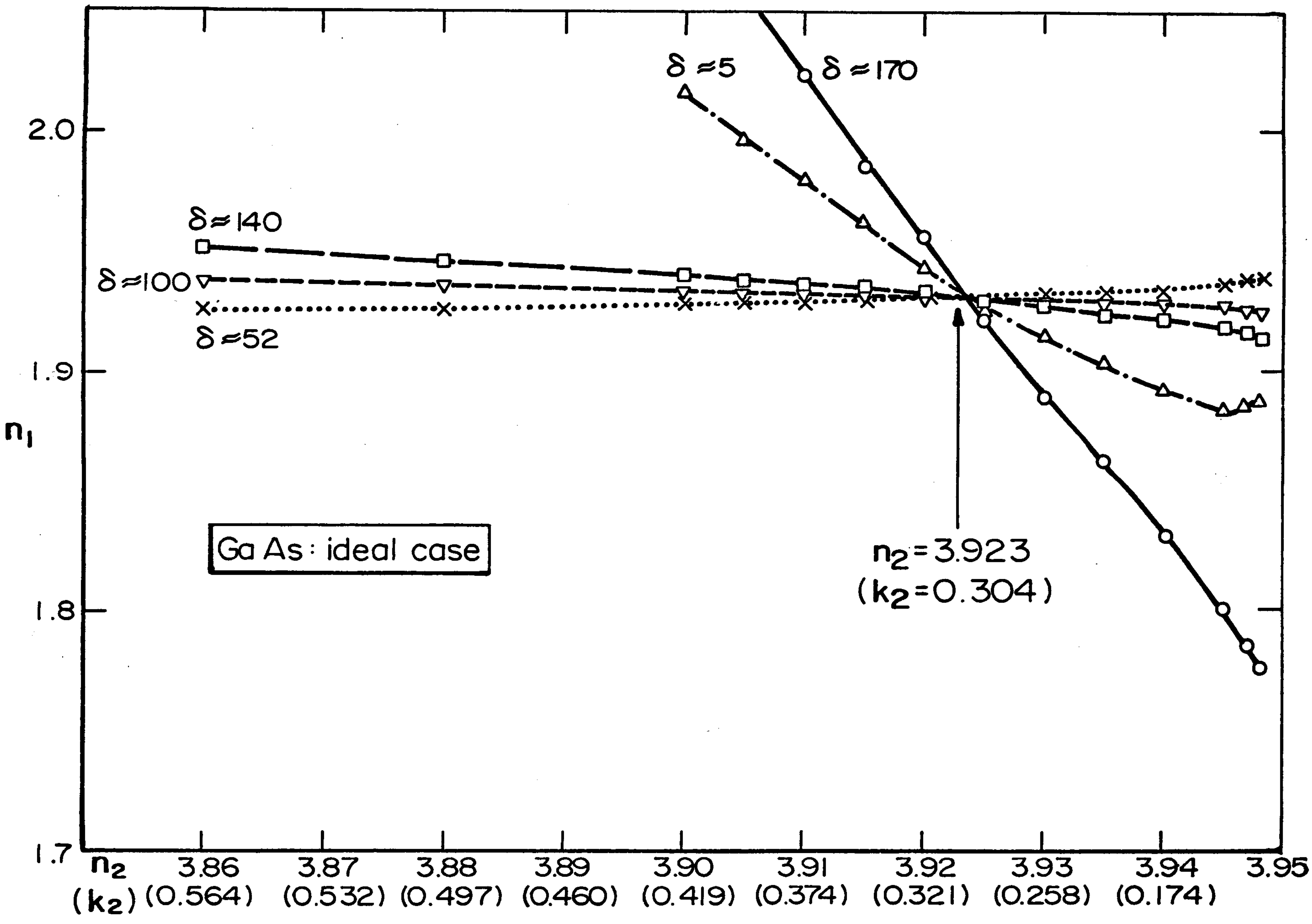

Fig. 4 Calculated values of n_1 vs. n_2 for various values of film thickness δ for the Gallium Arsenide ideal case. $n_2 = 3.923$ and $k_2 = 0.304$ were assumed in the calculation of n_1 vs. n_2.

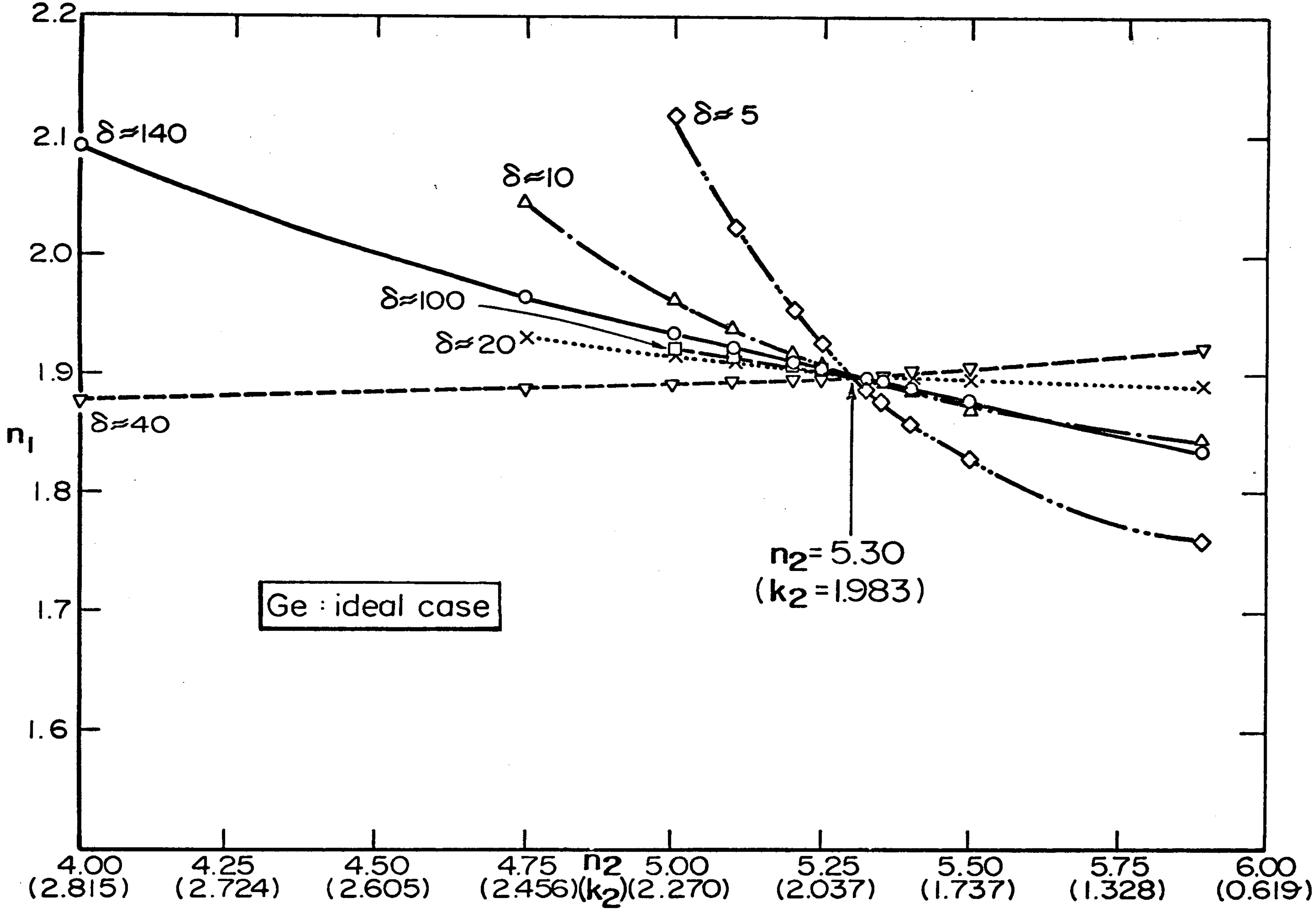

Fig. 5 Calculated values of n_1 vs. n_2 for various values of film thickness δ for the Germanium ideal case. $n_2 = 5.30$ and $k_2 = 1.983$ were assumed in the calculation of n_1 vs. n_2.

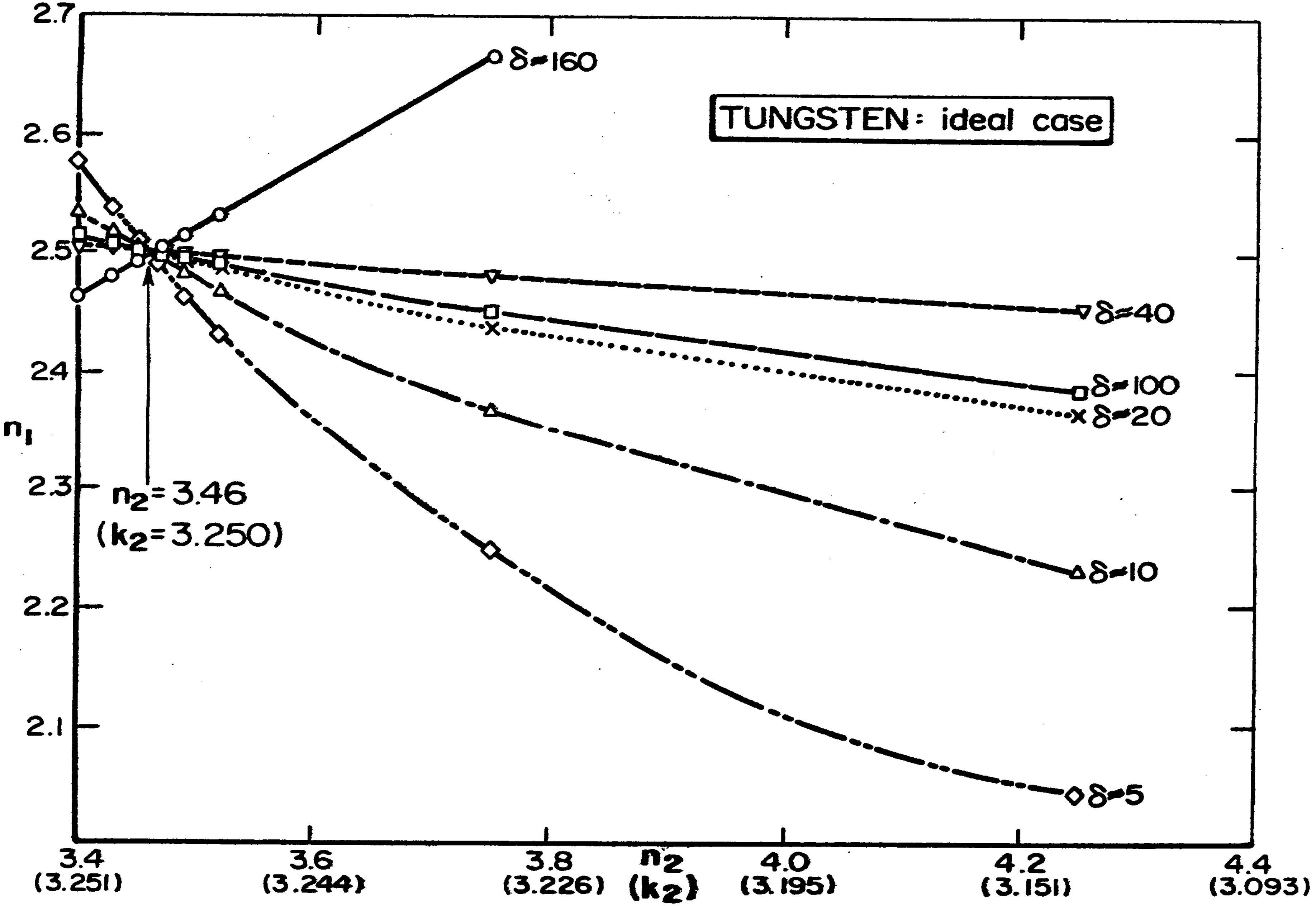

Fig. 6 Calculated values of n_1 vs. n_2 for various values of film thickness δ for the Tungsten ideal case. $n_2 = 3.46$ ~~and k_2~~ $= 3.250$ were assumed in the calculation of n_1 vs. n_2.

In real systems the departure from the ideal situation discussed in the previous section arises mainly from two causes: namely (i) the inhomogeneity of the film and the quality of perfection of the substrate and film surfaces and (ii) the influence of the experimental errors in the measurement of Δ and Ψ. While effect of the former can to some extent be minimized by carrying out measurements on a large number of samples, the latter poses a more fundamental problem and will be discussed in some detail in a later section. Broadly speaking the influence of these parameters would be to introduce a degree of uncertainty in the point of intersection of all the curves of Fig. 3. In other words the points of intersection of the curves instead of occurring at one well defined specific point corresponding to a particular combination of the parameters n_1, n_2, and k_2, will be distributed over a region in the n_1, n_2 (k_2) field. This is exactly what is noticed in the case of etched samples of silicon, as shown in Fig. 7.

The experimental arrangement and the method of the measurement we used were the same as that described in our previous paper [6]. We have measured both the ellipsometric parameters Δ and Ψ for both orientations of the $\lambda/4$ plate and for all possible combinations of the polarizer and the analyzer, which means that each Δ and Ψ value is the average of 16 measurements. All the measurements were carried out with Hg green radiation $\lambda = 5461\text{Å}$.

The samples used were cut from a single crystal, mechanically polished and then etched in a mixture of nitric acid, hydrofluoric acid and acetic acid mixed in the ratio 4:5:6, washed thoroughly successively in distilled water, acetone and ether. When necessary the samples were heated in air at 950°C for varying lengths of time as required.

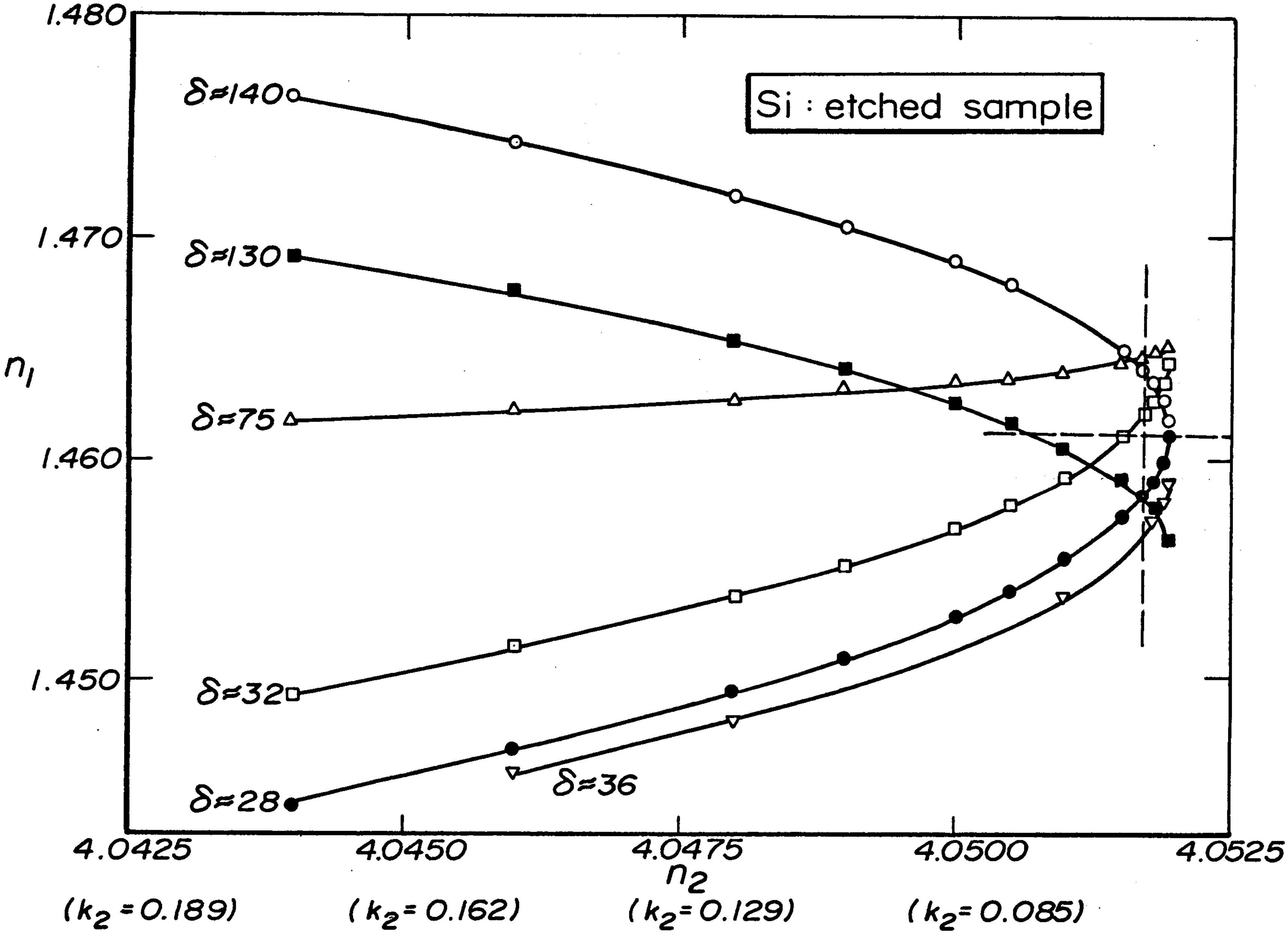

Fig. 7 Calculated values of n_1 vs. n_2 for various values of film thickness δ for the case of chemically etched Silicon. Experimental data were used and no value of the optical parameters was assumed.

The value of the reflectivity $\bar{R}$ evaluated by the method described above on five different samples was found to be $36.49_5\%$. Using this value of $\bar{R}$, the curves shown in Fig. 7 were obtained by the computational procedure described above. Here it may be mentioned that while the value of $\bar{R}$ was obtained on samples which were freshly prepared and aged in air, the data for Fig. 7 were obtained on the same samples after various heating treatments.

In Fig. 7, it is seen that all the curves are terminated at the value of n_2 at 4.0519. The reason for this will become obvious from Table II which gives the various possible values of n_2 and k_2 when the reflectivity $\bar{R}$ is fixed on $36.49_5\%$. Any further increase of n_2 beyond 4.0519 would imply an imaginary value for k_2.

It is seen that the mean value of the different intersections occur at $n_2 = 4.051_7$ and $n_1 = 1.461$. Since the value of reflectivity $\bar{R}$ is taken as $36.49_5\%$ for these samples, the above value of n_2 automatically fixes the value of k_2 as 0.029. These values compare very well with the accepted values $n_2 = 4.050$ and $k_2 = 0.028$ as determined by Archer [1] on chemically etched samples with the assumption that $n_1 = 1.460$.

Thus it may be concluded that the method described above can be used successfully to determine the values of n_1 and n_2 (and thus k_2 as well) i.e., the refractive index of the film as well as the optical constants of the optically absorbing substrate.

(b) Cleaved silicon samples

As Fainshtein and Fistul [8] have experimentally demonstrated, a considerable portion of the etchant is usually trapped in the oxide film which is invariably present on an etched surface. In other words an etched surface is not in general uniquely characterized since its structure

TABLE II

Silicon: Chemically Polished Sample

$R = 36.49_5\%$

n_2	k_2
3.50	1.340
4.00	0.441
4.02	0.347
4.03	0.288
4.04	0.213
4.045	0.162
4.050	0.085
4.051	0.059
4.0515	0.040
4.0516	0.035
4.0517	0.029
4.0518	0.022
4.0519	0.009
4.05192	0.0004
4.05195	$i\sqrt{0.0001}$

and hence its properties depend on its preperative history [9] . On the other hand a crystal cleaved and aged in air does not suffer from this disadvantage and measurements on such surfaces would be truly representative of the intrinsic material. Hence we have carried out ellipsometric measurements on samples of silicon cleaved and aged in air, analyzed the data along the lines described above and determined the optical parameters of silicon and the contaminating film on its surfaces. These results are given below.

The experimental specimens were cleaved from low dislocation density silicon ingots grown by the Czochralski method. All the specimens were N-type with resistivities ranging from 25 to 200 Ω-cm . By suitably orienting and shaping the specimens in the form of an L and cleaving by the method described by Gobeli and Allen [10], we could get cleavage-tear-line free, nearly optically flat regions of about 3-4 mm^2 area on which the ellipsometric measurements could be carried out quite easily.

As soon as each of these specimens were cleaved, it was quickly centered and aligned on the ellipsometer and then measurements of the ellipsometric parameters Δ and Ψ were begun. The time after cleavage before the first measurements was made, was generally not more than 3 to 5 minutes. The variations in Δ and Ψ were followed continuously at room temperature for a period of about 2 days. Such measurements yielded the value of the true reflectivity $\bar{R}$ as 37.30%. Then the specimen was slowly heated to 900°C in a furnace, kept at this temperature for a few minutes such that the film grew to a thickness of about 400Å, and then it was cooled slowly to room temperature. Then the new values of Δ and Ψ were determined before returning the sample to the furnace in order to increase the film thickness and repeat the process. In this way a set of $(\Delta_i, \Psi_i)_{i = 5-10}$ values were obtained on each specimen. Following the computational procedure described earlier, the data necessary for the curves similar to Figs. 3-7 could be obtained.

However at this stage it will be useful to consider in some detail the effects of the experimental errors in the measurement of Δ and ψ and how this can be minimized. Since the value of $\bar{R}$ is determined from the measurement on Δ and ψ, any errors in the latter will be reflected in $\bar{R}$ as well, and since further computations are all based on the unique value of $\bar{R}$, any error in $\bar{R}$ can influence the graphical solution method described above to be impractical. In order to find out the degree of influence or the sensitivity of an error in $\bar{R}$ on this method of solution as well as on the final optical parameters, recourse was taken to the ideal situation described in Fig. 3. It may be recalled in this case $\bar{R}$ was found to be 36.495%. Assuming a reasonable value of the error as ±0.1%, similar computations were performed with $\bar{R}$ as 36.395%, 36.495%, and 36.595% using the same input "experimental" data $[\Delta_{obs}, \psi_{obs}]_{\delta_1}, [\Delta_{obs}, \psi_{obs}]_{\delta_2} \ldots$ as described in section II (ix) above. The data obtained on all these three values of $\bar{R}$, are then plotted on the same graph as in Fig. 8. This is possible in the case of silicon since $k_2 \approx 0$ and hence for each value of $\bar{R}$, n_2 can have values only up to a certain maximum as explained earlier. When the value of $\bar{R}$ is increased slightly, the maximum value of n_2 is also correspondingly increased and thus we can draw the curves for R-ΔR, R, and R + ΔR on the same figure without much overlap.

From Fig. 8, it is seen the curves meet at one unique point only for $\bar{R}$ = 36.495% and that the curves intersect one another over a finite region for both R-ΔR and R + ΔR. However if one were to follow the trend of the

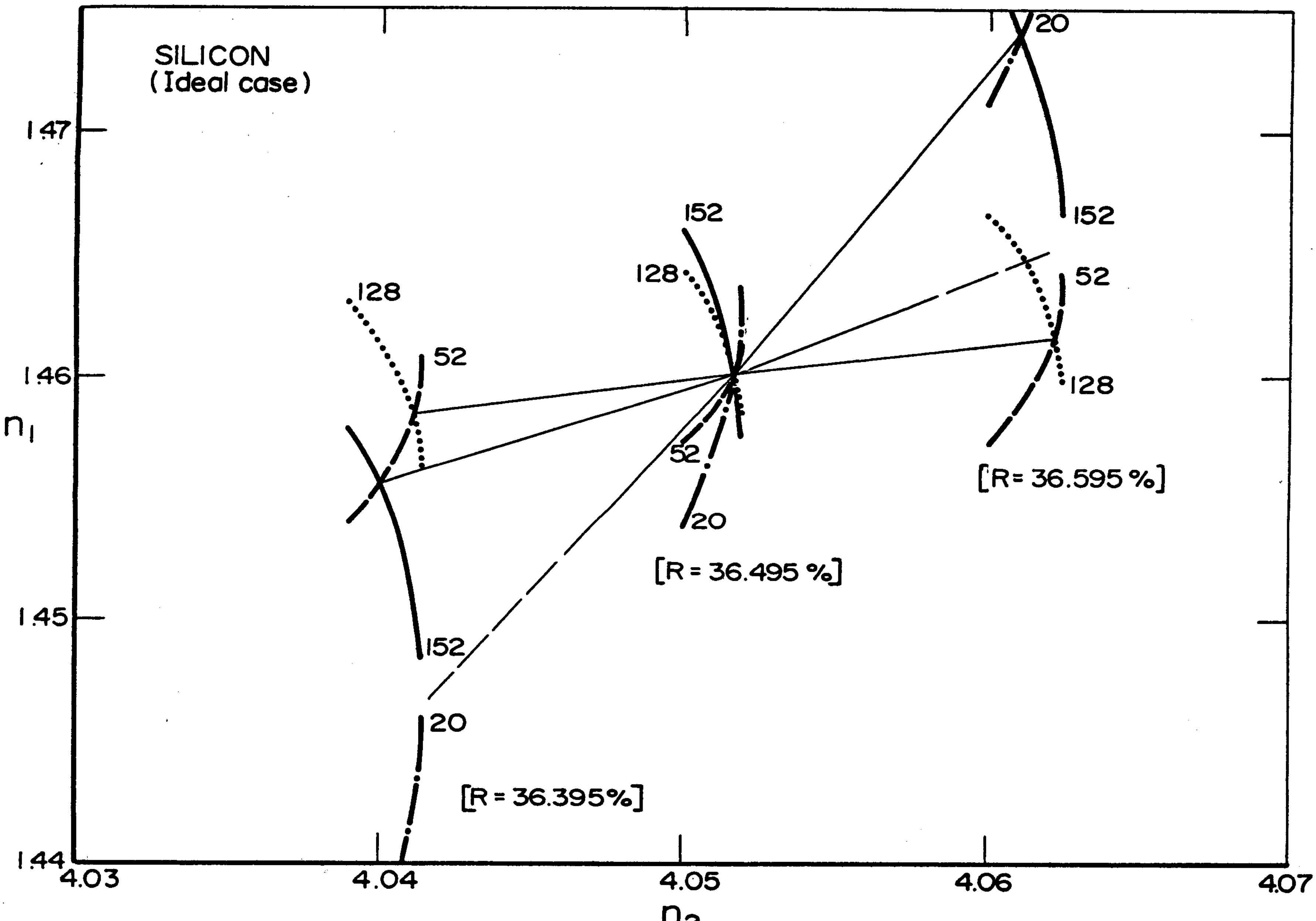

Fig.8 Three groups of calculated values of n_1 vs. n_2 corresponding to three different reflectivities R for various values of film thickness in the Silicon ideal case. The intersections between individual curves are plotted by the thin straight lines and all intersect in a point which defines the true (and in this case assumed) optical parameters of the system. Dashed interconnecting lines indicate regions where there is no longer an intersection between two given curves. An interconnecting line becomes a dashed line at that point at which those ends of the two curves corresponding to $k_2 = 0$ just barely intersect.

lines joining the various intersection points between similar curves but with different $\bar{R}$s (thin straight lines in Fig. 8), it is seen that they converge to a point at the true value of $\bar{R}$ and at the proper combination of n_2 (k_2) and n_1. Of course this convergence to a point would occur only in the ideal case. In an actual experimental case, however, the lines would converge to a minimum separation at the true value of $\bar{R}$, as shown in Fig. 9 for a typical case of cleaved silicon sample.

In the case of cleaved silicon samples the value of $\bar{R}$ was found to be 37.30 ± 0.10% by the method described in section II (v). It is seen that this value is considerably different from 36.495% obtained in the case of chemically polished samples. By extrapolating from Fig. 9, the final value of $\bar{R}$ was taken as 37.33%. Having thus obtained the final value of $\bar{R}$ it is an easy matter to recompute the data for the final plot between n_2 (k_2) and n_1 as shown in Fig. 10 to yield the true optical parameters of silicon and the film as $n_2 = 4.141$, $k_2 = 0.024$ and $n_1 = 1.46_8$.

Similar measurements and computations have been performed on two other specimens at the present stage and the final data are assembled in Table III. It is seen that the value of the optical parameters of silicon

TABLE III

Sample No.	Resistivity Ω cm	n_2	k_2	n_1
CS1	93	4.14_0	0.02_4	1.47_1
CS2	171	4.14_0	0.05_7	1.46_6
CS3	154	4.14_3	0.01_8	1.47_2

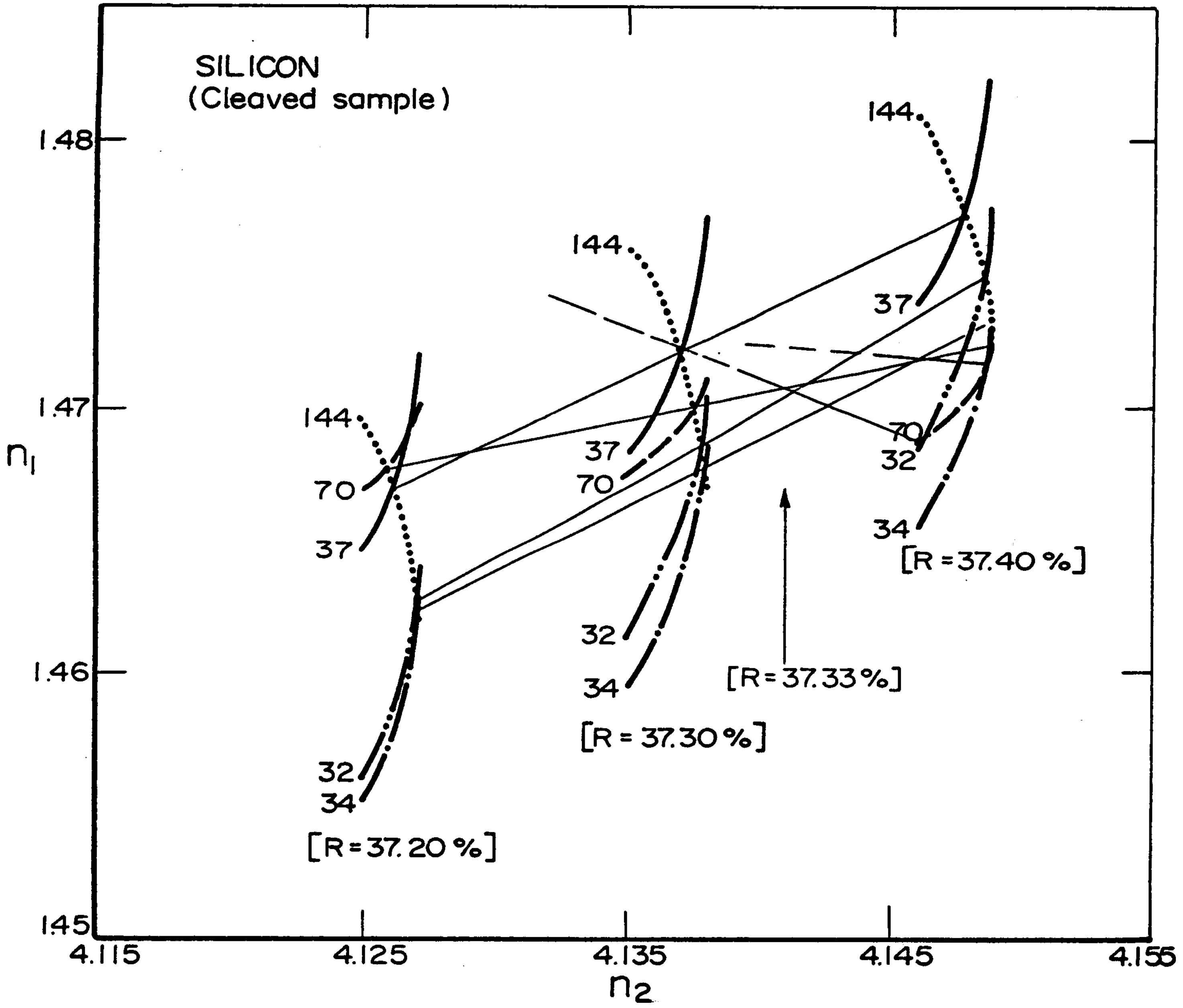

Fig. 9 Three groups of calculated values of n_1 vs. n_2 corresponding to three different reflectivities R for various values of film thickness δ in the case of cleaved Silicon sample. The intersections between individual δ curves are plotted by the thin straight lines and all intersect in a point which defines the true optical parameters of the system. Dashed interconnecting lines indicate regions where there is no longer an intersection between two given curves. An interconnecting line becomes a dashed line at that point at which those ends of the two curves corresponding to $k_2 = 0$ just barely intersect.

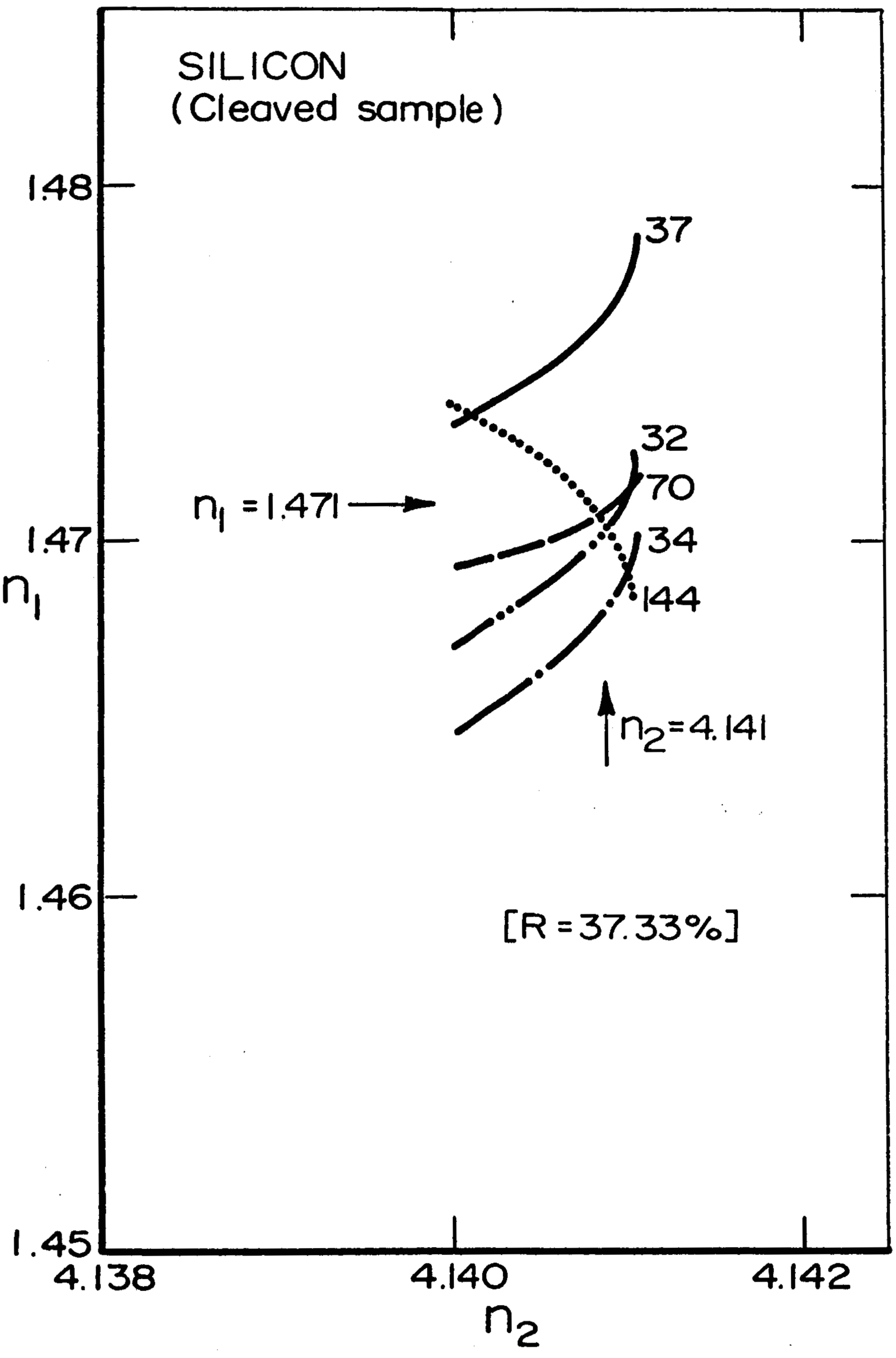

Fig. 10 Calculated values of n_1 vs. n_2 for various values of film thickness δ in the case of cleaved Silicon (experimental). The calculation was performed for that value of R which was determined by the intersections of Fig. 9.

is quite different from the often quoted values $n_2 = 4.050$ and $k_2 = 0.028$. As mentioned earlier these values correspond to the chemically polished specimens and hence cannot be treated as representing the true values of the pure material.

The data of the etched samples were also subjected to recomputation to take into account the possible error in $\bar{R}$ as described above, the final result being for the chemically etched samples $n_2 = 4.06_5$ and $k_2 = 0.02_8$, which are essentially the same as obtained by other workers.

Here it is relevant to point out that, even though the real part of the refractive index n_2 of silicon can be determined with great precision, the corresponding results on the imaginary part of the refractive index k_2 is far from satisfactory. For example it is seen from Table II, that if the value n_2 is altered from 4.0517 to 4.0518 then the value of k_2 must also be altered from 0.029 to 0.022 in order to satisfy the criterion of constancy of the reflectivity $\bar{R}$. In other words in a weakly absorbing material like silicon it is advisable to use the new method for determining only the value of n_2, and to determine the value of k_2 it is better to employ the well known optical absorption technique [11,12] .

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PERSONNEL

Dr. E. Schmidt of Purkyne University, Brno, Czechoslovakia joined this project in February 1968 as a Research Associate. Dr. Schmidt is not new to this field since he has been working on ellipsometry as well as the kinetics of oxidation of silicon for a number of years and hence his collaboration is certainly a welcome addition. Besides this, there has been one other change in the personnel working on this project, Mr. J. Labenski has rejoined as a part time technician, in place of Mr. Dennis Williams who has left for other occupation.

APPENDIX

```
      IMPLICIT REAL*8 (A-H,O-Z)
      RAD(A)=A*3.1415927D0/180.D0
      DEG(A)=(A*180.D0)/3.1415927D0
      DIMENSIONINTT(20),DEL(2,180),DELTA(2,180),PSI(2,180),XP(180),
     1YP(180),RNXB(20),RNXT(20),RKT(20),          PTT(20),DTT(20),RZR(20),
     1RZD(20),RZP(20),RXD(20),RXP(20)
      INTEGERSRN
      READ100,NA,NN,SRN
100   FORMAT(3I4)
C  PHI=70.0 DEGREES AND THE AMBIENT IS AIR FOR THIS DECK
C  INTD=INITIAL VALUE OF SMALL DELTA FOR EACH SET DELTA AND PSI
C  PTT ARE EXPERIMENTALLY DETERMINED PSI ANGLES.
C  DTT ARE EXPERIMENTALLY DETERMINED DELTA ANGLES
C   NN=NO. OF FILM N'S
C  SRN=NO. OF SUBSTRATE N'S
C  NA=NO. OF DELTA, PSI AND INTD SETS
      READ130,(PTT(LM),LM=1,NA)
      READ140,(DTT(LN),LN=1,NA)
      READ145,(INTT(LK),LK=1,NA)
      READ150,(RNXT(LI),LI=1,SRN)
      READ160,(RKT(LJ),LJ=1,SRN)
      READ102,(RNXB(JJ),JJ=1,NN)
130   FORMAT(8F10.3)
140   FORMAT(8F10.3)
145   FORMAT(8I4)
150   FORMAT(8F10.6)
160   FORMAT(8F10.6)
102   FORMAT(8F10.6)
      DO5000 LI=1,SRN
      RK2=RKT(LI)
      RNX2=RNXT(LI)
      RNXA1=1.
      DCLC=DELEX
      PRINT200,RNX2,RK2,RNXA1
200   FORMAT('1'T5,'N OF SUBSTRATE='F9.6,T35,'K OF SUBSTRATE='F9.6,T65'N
     1 OF AMBIENT='F9.6/'0'T20,'PSI',T30,'DELTA',T55,'SMALL',T78,'SMALL'
     1/T12,'PHI',T20,'EXP.',T30,'EXP.',T43,'N1',T55,'DELTA',T65,'DELTA',
     1T78,'DELTA',T88,'PSI',T112,'XA'/)
      DO6000 LK=1,NA
      AT=70.0
      A=RAD(AT)
      PSIEX=PTT(LK)
      DELEX=DTT(LK)
      INTD=INTT(LK)
      SINA=DSIN  (A)
      COSA=DCOS  (A)
      ALPHA1=(RNX2**2)-(RK2**2)-(SINA**2)
      ALPHA2=2.D0*RNX2*RK2
      RNO=DSQRT (ALPHA1**2+ALPHA2**2)
      APHI=-DATAN (ALPHA2/ALPHA1)
      R1NO=DSQRT (RNX2**2+RK2**2)
      APHI1=-DATAN (RK2/RNX2)
      R2NO=DSQRT (RNO)/R1NO
      APHI2=APHI/2.0D0-APHI1
      ALPHA3=R2NO*DCOS   (APHI2)
      ALPHA4=R2NO*DSIN   (APHI2)
      DEL(1,1)=1.0D0
      DEL(2,1)=RAD(2.D0*DEL(1,1))
      DO201 K=1,179
      DEL(1,K+1)=DEL(1,K)+1.0D0
```

```
201     DEL(2,K+1)=RAD(2.D0*DEL(1,K+1))
        KV=0
307     DO6000 JJ=1.NN
        RNX1=RNXB(JJ)
        XYZ=SINA*RNXA1/RNX1
        IF(XYZ-1.0D0)310,310,308
308     PRINT309,RNX1
309     FORMAT('1'T12,'TOTAL EXTERNAL REFLECTION.  N1='F6.3)
        GO TO 6000
310     COSB=DCOS   (DARSIN(XYZ))
        RD=RNX1*ALPHA3-RNX2*COSB
        RE=RNX1*ALPHA4+RK2*COSB
        RF=RNX1*ALPHA3+RNX2*COSB
        RG=RNX1*ALPHA4-RK2*COSB
        RI=RNX1*COSB-RNX2*ALPHA3-RK2*ALPHA4
        RJ=RK2*ALPHA3-RNX2*ALPHA4
        RK=RNX1*COSB+RNX2*ALPHA3+RK2*ALPHA4
        RN=RNX2*ALPHA4-RK2*ALPHA3
        SCH1=RNXA1*COSB
        SCH2=RNXA1*COSA
        CALLPOLMOR(RD,RE,RF,RG,SCH1,COSA,RL,RO,RP,RNX1)
        CALLPOLMOR(RI,RJ,RK,RN,SCH2,COSB,RM,RO,RR,RNX1)
        JPSI=0
        JDEL=0
        JPDOB=0
        DO303 J=INTD,180
        IF(JDEL)3023,3023,3020
3020    IF(JPSI)3023,3023,3021
3021    JPDOB=JPDOB+1
        IF(JPDOB-5)3023,3022,3022
3022    IF(DABS(DEL(1,JDEL-1)-DEL(1,JPSI-1))- 5.)3023,3066,3066
3023    CS2D=DCOS   (DEL(2,J))
        SN2D=DSIN   (DEL(2,J))
        CALLSTUVWX(RL,RO,RP,CS2D,SN2D,W,X)
        CALLSTUVWX(RM,RO,RR,CS2D,SN2D,W1,X1)
        DENR=W1**2+X1**2
        Y=(W*W1+X*X1)/DENR
        Z=(X*W1-W*X1)/DENR
        DELTA(1,J)=DATAN (Z/Y)
        PSI(1,J)=DATAN (Y/DCOS   (DELTA(1,J)))
        DELTA(2,J)=DEG(DELTA(1,J))
        PSI(2,J)=DEG(PSI(1,J))
        IF(PSI(2,J))500,401,401
500     PSI(2,J)=-PSI(2,J)
        DELTA(2,J)=DELTA(2,J)+360.D0
        IF(DELTA(2,J)-360.0D0)402,402,700
700     DELTA(2,J)=DELTA(2,J)-360.D0
402     GO TO 298
401     DELTA(2,J)=DELTA(2,J)+180.D0
298     IF(JPSI)4015,4015,29950
4015    IF(J-INTD-1)303,303,2985
2985    IF(PSI(2,J-1)-PSI(2,J))2991,2991,299
299     IF(PSI(2,J)-PSIFX)29915,29915,29930
2991    IF(PSIFX-PSI(2,J))29915,29915,29930
29915   JPSI=J
        PSGAP=PSI(2,JPSI)-PSI(2,JPSI-1)
        PSNT=PSIFX-PSI(2,JPSI-1)
        YA=DABS   (PSNT/PSGAP)
        DCLC=DELTA(2,JPSI-1)+YA*(DELTA(2,JPSI)-DELTA(2,JPSI-1))
        D1CLC=DEL(1,JPSI-1)+YA*(DEL(1,JPSI)-DEL(1,JPSI-1))
```

```
      GO TO 29950
29930 IF(J-180)29950.29931,29931
29931 DCLC=0.
      D1CLC=0.
29950 IF(JDEL)3033,3033,30655
3033  JP=J
      IF(JP-INTO-1)303,303,3034
3034  IF(DABS(DELTA(2,JP)-DELTA(2,JP-1))-300)3035,303,303
3035  IF(DELTA(2,JP)-DELTA(2,JP-1))304,303,305
304   IF(DELTA(2,JP-1)-DELEX)3042,303,3041
305   IF(DELTA(2,JP-1)-DELEX)3052,303,3051
3041  IF(DELTA(2,JP)-DELEX)306,306,303
3042  IF(DELTA(2,JP)-DELEX)303,306,306
3051  IF(DELTA(2,JP)-DELEX)306,306,303
3052  IF(DELTA(2,JP)-DELEX)303,306,306
306   JDEL=J
30655 IF(JPSI)303,303,301
303   CONTINUE
3066  D1CAL=0.
      PSCAL=0
      GO TO 899
301   DGAP=DELTA(2,JDEL-1)-DELTA(2,JDEL)
      DINT=DELEX-DELTA(2,JDEL-1)
      XA=DABS   (DINT/DGAP)
      PSCAL=PSI(2,JDEL-1)+XA*(PSI(2,JDEL)-PSI(2,JDEL-1))
      D1CAL=DEL(1,JDEL-1)+XA*(DEL(1,JDEL)-DEL(1,JDEL-1))
899   PRINT900,AT     ,PSIEX,DELEX,RNX1,D1CLC,DCLC,D1CAL,PSCAL,XA
900   FORMAT(6X4F10.4,3X,2F10.3,3X,2F10.3,14X,F10.3)
      KV=KV+1
      RZR(KV)=RNX1
      RZD(KV)=D1CAL
      RZP(KV)=PSCAL
      RXD(KV)=D1CLC
      RXP(KV)=DCLC
      IF(KV-NN)6000,790,790
790   RXPPO=0.
      DO 795 JSNX=1,KV
      IF(RXP(JSNX))795,795,7905
7905  IF(RXPPO)7906,7906,7907
7906  RXPPO=RXP(JSNX)
7907  IF(RXPPO-DELEX)792,792,791
791   IF(RXP(JSNX)-DELEX)793,793,795
792   IF(RXP(JSNX)-DELEX)795,793,793
793   BAND=RXP(JSNX-1)-RXP(JSNX)
      BANDO=RXP(JSNX-1)-DELEX
      ZAP=BANDO/BAND
      RAFFO=RZR(JSNX-1)+(RZR(JSNX)-RZR(JSNX-1))*ZAP
      DALTO=RXD(JSNX-1)+(RXD(JSNX)-RXD(JSNX-1))*ZAP
      PRINT 796,DALTO,RAFFO
796   FORMAT ('0'10X,'FROM PSI INTERPOLATION, SMALL DELTA=' F7.3,' AND N
     11='F7.5)
      GO TO 890
795   CONTINUE
890   RZPPO=0.
      DO 895 JSN=1,KV
      IF(RZP(JSN))894,894,8905
8905  IF(RZPPO)8906,8906,8907
8906  RZPPO=RZP(JSN)
8907  IF(RZPPO -PSIEX)892,892,891
891   IF(RZP(JSN)-PSIEX)893,893,894
```

```
892   IF(RZP(JSN)-PSIEX)894,893,893
893   BAND=RZP(JSN-1)-RZP(JSN)
      BANDO=RZP(JSN-1)-PSIEX
      ZAP=BANDO/BAND
      RAFFO=RZR(JSN-1)+(RZR(JSN)-RZR(JSN-1))*ZAP
      DALTO=RZD(JSN-1)+(RZD(JSN)-RZD(JSN-1))*ZAP
      PRINT 896,DALTO,RAFFO
896   FORMAT( 1X,I1,'FROM DELTA INTERPOLATION SMALL DELTA=' F7.3,' AND N
     11='F7.5//)
      GO TO 6000
894   IF(JSN.EQ.KV)GO TO 8941
      GO TO 895
8941  PRINT 8942
8942  FORMAT( /)
895   CONTINUE
6000  CONTINUE
5000  CONTINUE
      STOP
      END
      SUBROUTINEPOLMOR(RD,RE,RF,RG,X1,X2,RL,RO,RP,RNX1)
      IMPLICIT REAL*8 (A-H,O-Z)
      RFG=(RF**2+RG**2)
      RL=(X1-RNX1*X2)/(X1+RNX1*X2)
      RO=(RD*RF+RF*RG)/RFG
      RP=(RF*RF-RD*RG)/RFG
      RETURN
      END
      SUBROUTINESTUVWX(RL,RO,RP,CS2D,SN2D,W,X)
      IMPLICIT REAL*8 (A-H,O-Z)
      RS=RL+RO*CS2D+RP*SN2D
      RT=RP*CS2D-RO*SN2D
      RU=1.D0+RL*RO*CS2D+RL*RP*SN2D
      RV=RL*RP*CS2D-RL*RO*SN2D
      RUV=RU**2+RV**2
      W=(RS*RU+RT*RV)/RUV
      X=(RT*RU-RS*RV)/RUV
      RETURN
      END
```