

Combined grazing-angle and normal-incidence reflectometry of absorbing media

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We have studied the grazing-incidence differential-reflectance method for obtaining the dielectric function of absorbing media in terms of the derivatives R'_p and R'_s of the polarized light reflectances and found that it does not guarantee adequate accuracy for almost any values of the optical parameters. Therefore we modify that approach and describe what we believe is a novel method for the unambiguous determination of the optical constants n and k of a metal and other absorbing materials in terms of the ratio of the derivatives $\alpha = R'_p/R'_s$ at the grazing incidence and the normal incidence reflection coefficient R . Moreover, it is possible to express α through the logarithmic derivatives $(1/R)R'$ in the vicinity of the grazing angle. The possibility of performing measurements at the unspecified angle without knowledge of the explicit value of this angle is an evident advantage of this technique. For the great majority of metals and semiconductors the relative errors in the optical constants are comparable to or less than the relative errors in the experimentally measured parameters. © 1999 Optical Society of America [S0740-3232(99)01302-2]

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1. INTRODUCTION

The soaring interest in thin-film technology has created a new demand for routine techniques for determining the refractive index n and the extinction coefficient k of coatings and bulk absorbing materials over a wide range of wavelengths.¹⁻³ Polarized-light reflectometry is well suited for determining the optical constants of absorbing materials. This approach is fast and relatively easily implemented. A number of methods exist for determining these constants from measurements of the intensity reflectances R_p and R_s of p - and s -polarized light, respectively, at both normal and oblique incidence. These methods were listed by Humphreys-Owen⁴ (and in a modified form by Hunter)³ and may be divided into two general categories: (1) reflectance measurements at one or two arbitrary angles of incidence³⁻⁷ and (2) measurements of the pseudo-Brewster angle and R_p, R_s (or ratio R_p/R_s at this or the so-called second pseudo-Brewster angle, where the ratio R_p/R_s is minimum).^{3,4,7,8} A particular case of this category consists of measuring of the pseudo-Brewster angle and the reflectivity at normal incidence.⁹ The variety of the proposed methods stems from the need to improve sensitivity and overcome ambiguities in the solutions. Such ambiguities arise when the experimentally measured values are compatible with several physically reasonable pairs of the optical constants. They may be inherent in a given method or be merely fictitious, i.e., arising from experimental inaccuracies and substrate imperfections.¹⁰⁻¹² The inherent ambiguities were considered in Refs. 10 and 11 by means of Jacobian formalism, and the problem of the influence of error on ambiguity in the determination of optical constants was treated in Ref. 12 by an error-analysis approach. Therefore there is a general demand in any concrete problem to find a set of experimental parameters that are most sen-

sitive to changes in the optical constants and to determine for what ranges of n and k each method is experimentally useful. Although a knowledge of the pseudo-Brewster angle and the value of the ratio R_p/R_s is sufficient to give an explicit analytical determination of the optical parameters, that technique is sensitive only for not-so-great values of the ratio R_p/R_s (Refs. 7 and 8), i.e., not-so-great k . As for Query's explicit analytical inversion method⁵ of determining n and k by measuring the reflectances R_p and R_s at a given angle of incidence, its applicability is limited to the region $n < 3$ and $k < 3.2$ even if the measurements are performed at the optimum angle.⁶ Recently, Lekner did a similar inversion for the real ϵ' and imaginary ϵ'' parts of the dielectric function.¹³ He showed that even at the optimum angle of incidence a minimum-error multiplier, i.e., an increase in the common value of the root-mean-square error in ϵ' and ϵ'' in comparison with such errors in the experimentally measured reflectance and incident angle θ for a typical metal is excessively large ($\sim 10^4-10^5$). As a result, he concludes that "one might well be skeptical about optical constants derived from inversion of θ, R_p , and R_s measurements" for a metal and other absorbing materials (p. 1358).

However, this limitation does not concern the measurement of the derivatives R'_p and R'_s , which remain informative in the vicinity of the grazing angle. The greatest sensitivity of the polarometric methods in near-grazing-incidence region for a large value of the optical constants was demonstrated in Ref. 14 by numerical calculations. Abelès was probably first to suggest the use of the slope of R_p and R_s coefficients as a function of θ at the grazing angle to determine the refractive index of a dielectric film.¹⁵ Later Azzam suggested a grazing-incidence differential-reflectance method¹⁶ for explicit determina-

tion of the complex dielectric function of an absorbing medium in terms of R'_p and R'_s . Unfortunately, as will be shown in Section 2, the sensitivity of the method is not sufficient for its practical application to any material with appreciable absorption. In spite of this, the combination of the ratio R'_p/R'_s and the Brewster-angle measurements are useful for determining the parameters of a dielectric substrate, in particular an optical anisotropy.^{17,18} Unlike the dielectrics, the distinctness of the pseudo-Brewster angle for the absorbing materials deteriorates with increasing absorption, while the normal-incidence reflection coefficient $R(0)$ for the absorbing materials remains sensitive to both the optical constants. This suggests the adoption, instead of the pseudo-Brewster-angle measurements, the measurement of $R(0)$ in combination with the ratio $\alpha = R'_p/R'_s$ at the grazing angle. In Section 3 we develop such an approach and demonstrate that it allows an unambiguous determination of the optical parameters of absorbing materials with high sensitivity for almost all values n and k . For the practical utilization of this method it is essential that although originally the parameter α is introduced in terms of the derivatives exactly at the grazing angle, where measurements are extremely difficult or impossible, this difficulty may be avoided. In reality, owing to the specific exact relationship [see Eq. (16)] between the derivatives at the grazing angle, one may shift all the measurements by an unspecified angle $\Delta\theta$. As a result, instead of the practically inaccessible measurements of the derivatives R'_p and R'_s at the grazing incidence, one should measure only the ratio of the logarithmic derivatives $(\ln R'_p)'$ and $(\ln R'_s)'$ at the near-grazing-incidence angle $\theta = \pi/2 - \Delta\theta$. In this case Hunderi's well-known technique¹⁹ may be applied.

2. DIELECTRIC FUNCTION $\varepsilon = \varepsilon' - i\varepsilon''$ IN TERMS OF α AND R'_s

The intensity reflection coefficients of p - and s -polarized light at the planar interface between vacuum and a linear, isotropic medium with the dielectric constant ε are given in Ref. 20:

$$R_p = \frac{\left| \frac{\varepsilon \cos \theta - \sqrt{\varepsilon - \sin^2 \theta}}{\varepsilon \cos \theta + \sqrt{\varepsilon - \sin^2 \theta}} \right|^2}{\left| \frac{\cos \theta - \sqrt{\varepsilon - \sin^2 \theta}}{\cos \theta + \sqrt{\varepsilon - \sin^2 \theta}} \right|^2}, \quad (1)$$

where θ is the angle of incidence. From Eqs. (1) by a straightforward calculation one obtains

$$R'_p = 2 \left(\frac{\varepsilon}{\sqrt{\varepsilon - 1}} + \frac{\varepsilon^*}{\sqrt{\varepsilon^* - 1}} \right) \quad (2)$$

$$R'_s = 2 \left(\frac{1}{\sqrt{\varepsilon - 1}} + \frac{1}{\sqrt{\varepsilon^* - 1}} \right), \quad (3)$$

where $R'_{p,s} \equiv R'_{p,s}(\theta = \pi/2)$. By combining Eqs. (2) and (3), after a few algebraic steps we obtain

$$\alpha = R'_p/R'_s = 1 + |\varepsilon - 1|. \quad (4)$$

Now Eqs. (3) and (4) can easily be inverted to give the real ε' and the imaginary ε'' parts of the dielectric constant in terms of α and R'_s :

$$\varepsilon' = R_s'^2 \frac{(\alpha - 1)^2}{8} - \alpha + 2, \quad (5)$$

$$\varepsilon'' = \frac{(\alpha - 1)^2 R_s'}{8} \left[\frac{16}{\alpha - 1} - R_s'^2 \right]^{1/2}.$$

Equations (5) are a compact form of Eqs. (11)–(17) in Ref. 16. Let us now test the ambiguity and the sensitivity of this approach. In Fig. 1 the region of physical significance $\varepsilon'' > 0$ and $|\varepsilon| > 1$ (if only the incident medium is a vacuum) in the plane α, R'_s is shown. It is delineated by the curves

$$(A) \quad \varepsilon'' = 0, \quad (\alpha - 1 = 16/R_s'^2)$$

and

$$(B) \quad |\varepsilon| = 1, \quad \left(\alpha - 1 = \frac{2}{1 + R_s'^2/4} \right). \quad (6)$$

Loci have also been plotted in Figs. 1(a) and 1(b) for which ε' and ε'' are fixed. The “bunching” of these loci occurs at $\alpha \gg 1$ [for $R'_s \geq 1$ in Fig. 1(a) and near the dielectric boundary A in Fig. 1(b)], where they are so close together that an accurate determination of ε from measurements of α and R'_s is impossible. One may notice that most of the metals in the visible are situated fairly far from these unfavorable domains, so there are potential opportunities for application of the method to such materials. Now we investigate such possibilities.

A. Unambiguity of the Method

As is known, ambiguities of any inversion, in this case from α and R'_s to ε' and ε'' , occur only if the Jacobian $J(\varepsilon', \varepsilon'') = (\partial R'_s / \partial \varepsilon')_{\varepsilon''} (\partial \alpha / \partial \varepsilon'')_{\varepsilon'}$ $- (\partial R'_s / \partial \varepsilon'')_{\varepsilon'} (\partial \alpha / \partial \varepsilon')_{\varepsilon''}$ changes its sign.^{10,11} After not very tedious calculations one obtains from Eqs. (5)

$$J(\varepsilon', \varepsilon'') = \frac{\sqrt{2\varepsilon''}}{(\varepsilon' - 1)^2 + \varepsilon''^2} [\varepsilon' - 1 + \sqrt{(\varepsilon' - 1)^2 + 4\varepsilon''^2}]^{-1/2} > 0. \quad (7)$$

Therefore the method is unambiguous, i.e., the measured quantities α and R'_s are compatible with only one pair of the optical parameters ε' and ε'' . When ε'' tends to zero the Jacobian [Eq. (7)] tends to zero as well, and this corresponds to the bunching effect along line A in Fig. 1(b). We should like to emphasize that this bunching takes place only for ε'' loci, whereas ε' loci remain unbunched [see Fig. 1(a)]. One can see that the Jacobian has a maximum in the vacuum ($\varepsilon' = 1, \varepsilon'' = 0$) limit, where it tends to infinity: region $\alpha \rightarrow 0, R'_s \rightarrow \infty$ in Fig. 1.

B. Sensitivity of the Method

From the practical point of view it is of interest to determine (1) which experimentally measured values give the best sensitivity to changes in the ε' and ε'' and (2) for what ranges of ε' and ε'' the method is sufficiently accurate. The accuracy of the determination of the optical parameters of the material depends strongly on the materi-

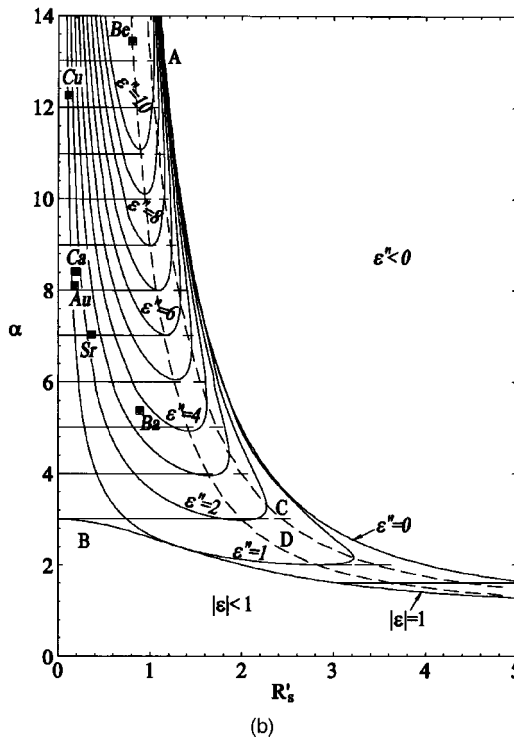
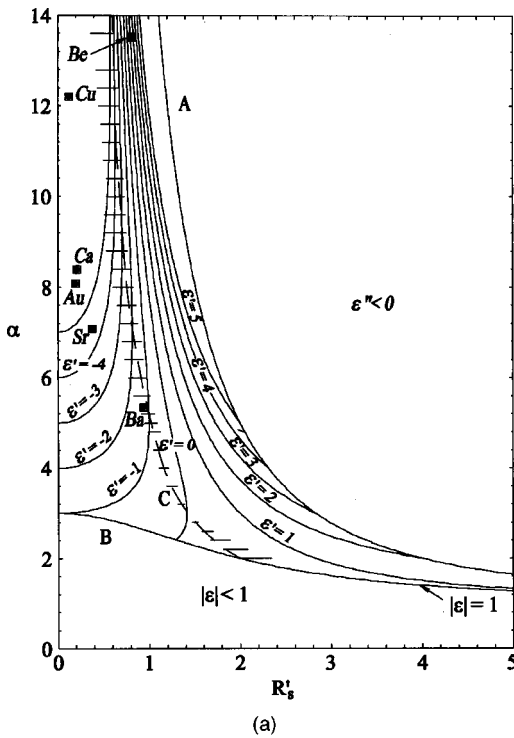


Fig. 1. (a) Distribution of ϵ' loci in terms of the ratio $\alpha = R_p/R_s'$ and the derivative R_s' . Curves A ($\epsilon'' = 0$) and B ($|\epsilon| = 1$) outline the domain of physical significance, assuming that the incidence medium is a vacuum. The horizontally hatched region around the curve C ($\alpha - 1 = 4/R_s'^2$) corresponds to the condition that prefactor of $d\alpha/\alpha$ in Eq. (7) is of the order of unity or less. A bunching effect takes place at $\alpha \gg 1$, $R_s' \gg 1$. The points represent some metals in the visible. (b) Distribution of ϵ'' loci in terms of α and R_s' . Dashed curves C and D are given by Eq. (9). In the horizontally hatched regions, prefactors of da/α and dR_s'/R_s' in Eq. (8) are not greater than unity. A strong bunching occurs near a perfect dielectric boundary.

al's position in the α, R_s' plane. From Eqs. (5), one can connect the relative errors in determining ϵ' and ϵ'' with the experimental precisions in α and R_s' :

$$\frac{d\epsilon'}{\epsilon'} = - \frac{\alpha \left[1 - \frac{(\alpha - 1)R_s'^2}{4} \right]}{(\alpha - 1)^2 R_s'^2 - \alpha + 2} \frac{d\alpha}{\alpha} + \frac{\frac{(\alpha - 1)^2 R_s'^2}{4}}{(\alpha - 1)^2 R_s'^2 - \alpha + 2} \frac{dR_s'}{R_s'} \tag{8}$$

$$\frac{d\epsilon''}{\epsilon''} = \frac{3\alpha \left[1 - \frac{(\alpha - 1)R_s'^2}{12} \right]}{2(\alpha - 1) \left[1 - \frac{(\alpha - 1)R_s'^2}{16} \right]} \frac{d\alpha}{\alpha} + \frac{1 - \frac{(\alpha - 1)R_s'^2}{8}}{1 - \frac{(\alpha - 1)R_s'^2}{16}} \frac{dR_s'}{R_s'} \tag{9}$$

Figure 1 helps to analyze these expressions.

1. Real Part [Fig. 1(a)]

The most favorable experimental situation for determining the real part of the dielectric permittivity is realized when both derivatives $(\partial\epsilon'/\partial\alpha)_{R_s'}$ and $(\partial\epsilon'/\partial R_s')_{\alpha}$ are small. The region where the prefactor multiplying quantity $d\alpha/\alpha$ is of the order of unity or less is shown in Fig. 1(a) by the horizontal hatching around line C ($\alpha - 1 = 4/R_s'^2$), whereas prefactor multiplying dR_s'/R_s' is of the order of unity almost everywhere. Therefore both of these conditions hold true only in the very narrow hatched region. This means that to guarantee, for example, an accuracy of 1% in the measurement of ϵ' , it is necessary to measure the parameter α with α times better precision, which seems unrealistic. The sole exception is a region $\alpha \geq 1$ and $R_s' > 1$, where $\epsilon' \ll 1$ and $\epsilon'' \geq 1$ (this corresponds to materials with $n \approx k \approx 1$). To obtain the value of ϵ' with a prescribed precision in this region, it is sufficient to measure the parameters α and R_s' with the same accuracy. Unfortunately, almost all metals, with the exception of Ba, are located far outside this domain.

2. Imaginary Part [Fig. 1(b)]

With respect to the imaginary part ϵ'' of the dielectric permittivity, the most favorable regions, where α and R_s' are sensitive to the ϵ'' value [horizontal hatchings in Fig. 1(b)], lie in the vicinities of the curves

$$(C) \quad \alpha - 1 = \frac{12}{R_s'^2}$$

and

$$(D) \alpha - 1 = \frac{8}{R_s'^2}, \quad (10)$$

where the derivatives $(\partial \varepsilon''/\partial \alpha)_{R_s'}$ and $(\partial \varepsilon''/\partial R_s')_\alpha$ become zero. Only in the intercrossed domain of these regions will the sensitivity in determining ε'' be comparable with the precision of the experimental parameters α and R_s' . However, as is shown in Fig. 1(b), the hatched region around curve C is vanishingly narrow, so such an overlapping takes place merely in the domain $\alpha < 2, R_s' \geq 3$, corresponding to values of $|\varepsilon| \geq 1$ ($n > 1, k \ll 1$), which has no great practical significance (all metals lie far away from it).

It may be concluded that the grazing-incidence differential-reflection method is not sufficiently sensitive to changes in dielectric permittivity and cannot be applied to highly absorbing materials. In addition it should be noted that the procedures of measuring the values α and R_s' in themselves are essentially different. In reality, since α is the ratio of the derivatives, then to find it one should not make any absolute angular measurements (provided only that they have been accomplished sufficiently close to the grazing angle). On the contrary, to find R_s' , one should perform very exact angular and photometric measurements in the vicinity of the grazing angle. Bearing this in mind, we can proceed in a different way and choose, instead of R_s' , any other experimental parameter. To be exact, by reasoning similar to the Darcie-Whalen approach in the case of the pseudo-Brewster-angle measurements,⁹ one can suggest an idea for combining the grazing-angle parameter α with the normal-incidence reflectance $R(0)$.

3. OPTICAL CONSTANTS n AND k IN TERMS OF α AND R

With such a choice of experimentally measured parameters, it is more convenient to pass the optical parameters n and k . From Eqs. (1) and (4) after unsophisticated calculations, one obtains

$$n^2 = \frac{(\alpha - 1)^2(1 - R)^2}{16R},$$

$$k^2 = \frac{(\alpha - 1)}{\sqrt{R}} - \left[\frac{(\alpha - 1)(1 - R)}{4\sqrt{R}} + 1 \right]^2, \quad (11)$$

where we denote $R(0) = R$. The distributions of n and k loci are shown in Figs. 2(a) and 2(b), respectively. The region of physical significance is bounded by the curves A and B:

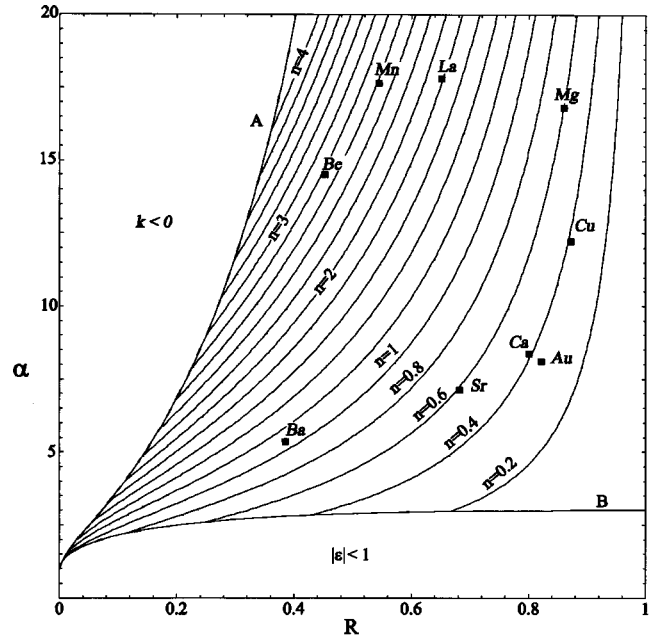
$$(A) \quad k = 0, \quad \left[\alpha - 1 = \frac{4\sqrt{R}}{(1 - \sqrt{R})^2} \right],$$

$$(B) \quad |\varepsilon| = 1, \quad \left(\alpha - 1 = \frac{4\sqrt{R}}{1 + R} \right). \quad (12)$$

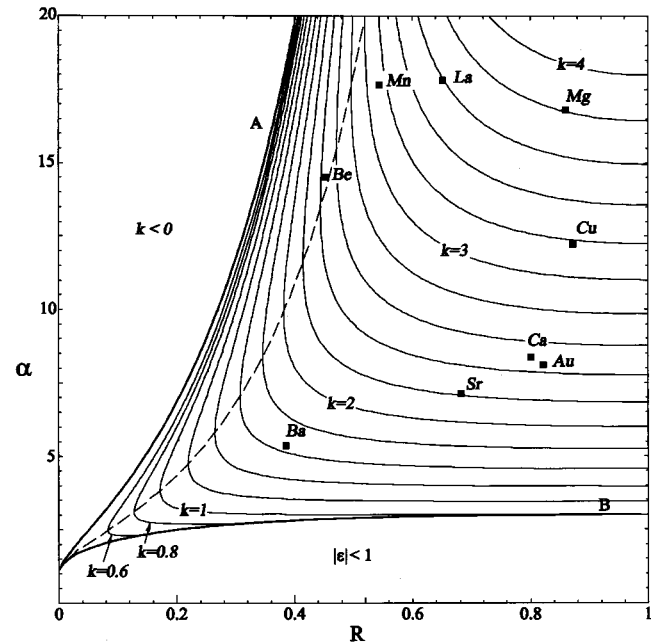
There is no bunching of n loci, whereas for k loci some bunching takes place only near the dielectric boundary under $k < 1$.

A. Unambiguity of the Method

From Eqs. (11) it immediately follows that the Jacobian



(a)



(b)

Fig. 2. (a) Distribution of n loci in terms of α and R within the physical region delineated by curves A ($k = 0$) and B ($|\varepsilon| = 1$). There is no visible bunching in this case. The points represent some metals in the visible. (b) Distribution of k loci within the physical region [the same as in (a)]. The bunching effect is noticeable near the dielectric boundary at $k \ll 1$. The dashed curve $\alpha - 1 = [4\sqrt{R}(1 + R)]/(1 - R)^2$ corresponds to the condition $(\partial k/\partial \alpha)_R = 0$.

$$J(n, k) = \left(\frac{\partial R}{\partial k} \right)_n \left(\frac{\partial \alpha}{\partial n} \right)_k - \left(\frac{\partial R}{\partial n} \right)_k \left(\frac{\partial \alpha}{\partial k} \right)_n$$

$$= \frac{8k}{(n+1)^2 + k^2} \left[\frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \right]^{1/2} > 0 \quad (13)$$

never changes its sign, so that the method is unambiguous. The sensitivity of the determination of n in terms of the experimentally measured values is given by the relation

$$\frac{dn}{n} = \frac{\alpha}{\alpha-1} \frac{d\alpha}{\alpha} - \frac{1+R}{2(1-R)} \frac{dR}{R}. \quad (14)$$

In almost all of the physical region (excepting a narrow strip $1-R \ll 1$, where $n \ll 1$) the relative error in n is comparable with the experimental precision of the measured parameters α and R . Similarly, for the absorption coefficient k one gets

$$\frac{dk}{k} = \frac{\alpha(1+R)}{4k^2\sqrt{R}} \left[1 - \frac{(\alpha-1)(1-R)^2}{4\sqrt{R}(1+R)} \right] \frac{d\alpha}{\alpha}$$

$$+ \frac{(\alpha-1)(1-R)}{8k^2\sqrt{R}} \left[\frac{(\alpha-1)(1+R)}{4\sqrt{R}} - 1 \right] \frac{dR}{R}. \quad (15)$$

The optimum situation relative to the α -parameter measurements ($\partial k/\partial \alpha_R = 0$) is shown in Fig. 2(b) by the dashed curve. It is interesting that the analogous curve ($\partial k/\partial R)_\alpha = 0$) coincides with the boundary of the physical region [Eq. (12), curve B]. With the help of Eqs. (11) it is easy to demonstrate that the prefactor of $d\alpha/\alpha$ is not more than unity in all of the physical region except a narrow vicinity near the dielectric boundary $k = 0$. For absorbing materials, if $n < k$ and then $\varepsilon \approx k^2$, the estimate of the prefactor of dR/R is $(\varepsilon^2 - 1)/8k^2(1-R)/(1+R) \approx \varepsilon/8(1-R)/(1+R) < 1$.

Therefore, in almost all of the region characteristic of a metal, the sensitivity of the method in the determination of the absorption coefficient k is the same as or better than the experimental precision in measurements of α and R . Since measurements of the normal-incidence reflection coefficient R may be performed very exactly,⁹ this gives a simple practical method for determining of the complex refractive index of a metal and absorbing media. The only exception is the region $1-R \ll 1$ (in terms of n and k this relates to the materials with $n \ll 1$ and $k > 1$, i.e., for example, a metal in the vacuum ultraviolet spectral region) and the vicinity of the dielectric boundary A, i.e., materials with $k \ll 1$. In both of these cases the Jacobian [Eq. (13)] tends to zero, which leads to a fall in sensitivity. For the dielectric boundary this is a characteristic of all the reflection methods.¹⁰ But even in these unfavorable cases our method encounters a difficulty in the determination only of *one of two* optical parameters. In reality, in the region $1-R \ll 1$ the sensitivity in n is large and in k is small, whereas in the vicinity of the dielectric boundary the situation is exactly the opposite.

B. Experimental Requirement for the Proximity of the Incidence Angle to $\pi/2$

The viability of the method may be essentially improved if the logarithmic derivatives, not the derivatives, are measured. Indeed, the more we approach the grazing angle, the more difficult the measurements become. Therefore one should obtain a necessary condition on the proximity of the incidence angle $\theta = \pi/2 - \Delta\theta$ to $\pi/2$. Since all angular measurements in the near-grazing region are extremely difficult, it is very important to suggest a procedure that will be angular independent in this region. For the parameter α the necessary condition of this requirement is $\Delta\theta R'_{p,s} \ll 1$, which means that $\Delta\theta \ll 1/R'_{p,s}$, since always $R'_s < R'_p$. Often when $R'_p \sim 1$, this restriction on $\Delta\theta$ is not very onerous. However, for $R'_p \gg 1$, even grazing angle $\theta = 89^\circ$, i.e., $\Delta\theta = 1^\circ$, is not enough to achieve a suitable 1% accuracy. Fortunately, the accuracy of the method may be readily improved by the use of a certain important exact relationship between the derivatives at grazing incidence. In fact, after a straightforward calculation from Eqs. (1)–(3), one can obtain the relations

$$R''_{p,s} = R'^2_{p,s} \quad (16)$$

[compare with Eq. (1) in Ref. 16]. Then we find a connection between the theoretical parameter $\alpha = [R'_p(\pi/2)]/[R'_s(\pi/2)]$ and the experimentally measured value $\alpha(\theta) = [R'_p(\theta)]/[R'_s(\theta)]$ of this parameter at the given angle θ . Then, by expanding $\alpha(\theta)$ in a power series of the parameters $\Delta\theta R'_{p,s}$, one obtains to the first order in $\Delta\theta$

$$\alpha(\theta) = \frac{R'_p(\pi/2) - \Delta\theta R''_p(\pi/2)}{R'_s(\pi/2) - \Delta\theta R''_s(\pi/2)}$$

$$= \frac{R'_p(\pi/2)[1 - \Delta\theta R'_p(\pi/2)]}{R'_s(\pi/2)[1 - \Delta\theta R'_s(\pi/2)]}$$

$$= \alpha \frac{1 - [1 - R_p(\theta)]}{1 - [1 - R_s(\theta)]} = \alpha \frac{R_p(\theta)}{R_s(\theta)}. \quad (17)$$

Therefore

$$\alpha = \frac{R_s(\theta)}{R_p(\theta)} \alpha(\theta) = \frac{R'_p/R_p}{R'_s/R_s} \Big|_{\theta} = \frac{(\ln R_p)'}{(\ln R_s)'} \Big|_{\theta} \quad (18)$$

with an accuracy up to $(\Delta\theta)^2$. Table 1 demonstrates the precision of the α -parameter determination calculated from Eqs. (18) and (4) at an angle of incidence of 89° . The theoretical value of this systematic error is $2k^2(\Delta\theta)^2$. After correction, the error in α is two orders of magnitude less than the precision in the raw measurements and so may be neglected. Therefore to determine α it is sufficient to measure the ratio of the logarithmic derivatives of reflectance in the vicinity of the grazing angle (the appropriate technique is described in Ref. 19). The constancy of Eq. (18) under variation of an incidence angle θ may serve as evidence of the sufficient proximity of θ to $\pi/2$. Factor R_s/R_p between α and $\alpha(\theta)$ in Eq. (18) may be essential for an exact determination of the parameter α . For example, when $\Delta\theta = 2^\circ$ this factor is equal to 1.195 for Al ($n = 1.38, k = 7.61$) and 1.054 for Cu ($n = 0.39, k = 3.16$) so that its neglect leads to an error in

Table 1. Accuracy of the Determination of α Expressed As the Ratio of the Logarithmic Derivatives from Eq. (18) at $\theta = 89^\circ$

Element	$\varepsilon = \varepsilon' - i\varepsilon''$	$\alpha = \frac{R'_P(\pi/2)}{R'_S(\pi/2)}$ Eq. (4)	$\alpha^{(\text{exp})} = \frac{R'_P/R_P}{R'_S/R_S}$ Eq. (18) $\theta=89^\circ$	$\frac{\Delta\alpha}{\alpha} = \frac{\alpha^{(\text{exp})} - \alpha}{\alpha}$ (%)
Ba $k = 1.62$	-1.3-i3.8	5.442	5.435	-0.12
Sr $k = 2.2$	-4.5-i2.65	7.105	7.081	-0.33
Au $k = 2.42$	-5.73-i1.75	7.954	7.917	-0.46
Be $k = 2.45$	+1.85-i13.7	14.726	14.690	-0.24
Mn $k = 3.17$	-2.2-i17.7	18.987	18.871	-0.6
Cu $k = 3.18$	-9.97-i2.9	12.347	12.243	-0.84

α and, according to Eqs. (14) and (15), the errors are $\Delta n/n = 16.6\%$, $\Delta k/k = 8.1\%$ and $\Delta n/n = 5.3\%$, $\Delta k/k = 2.9\%$ for Al and Cu, respectively. It should be noted that such a proximity θ to the grazing angle implies, of course, the availability of a large substrate.

4. SUMMARY AND CONCLUSION

In summary, a robust direct method for optical characterization of absorbing materials based on measurements of the derivatives of the p - and s -polarized light reflection coefficients near the grazing angle has been presented. It is shown that measurements only in vicinity of the grazing angle cannot guarantee acceptable sensitivity in determining the optical parameters. Only by use of the combined near-grazing-angle and near-normal-incidence reflectance measurements can one obtain an acceptable sensitivity in the parameters n and k .

In addition to the conventional intuitive indication of the sensitivity as the spacing between loci, the sensitivity of any method may be investigated easily by consideration of the value of the corresponding Jacobian [Eq. (13)]. In Fig. 3 the value $J(n, k)$ of this Jacobian corresponds to the areas of the parallelograms arising from the intercrossing of n and k loci. Since $J(n, k)$ becomes zero for $k \rightarrow 0$ and $k \rightarrow \infty$, it predicts a maximum that occurs when $(\partial J/\partial k)_n = 0$. This equation can be readily solved as

$$k^2 = 4n + (n^4 + 14n^2 + 1)^{1/2} \quad (19)$$

or $k^2 \approx n(n+4)$ for $n \gg 1$. As is noticeable from Fig. 3, under the motion, starting from the boundaries A or B, along any loci n the areas of the parallelograms at first increase and then decrease. For example, under travel along the contour $n = 1$, the maximum, according to Eq. (17), occurs at $k \approx 2.8$. Therefore, under fixed n the sensitivity is greatest for k given by Eq. (17). On the other hand, with motion along the loci k (starting from $n = 0$, i.e., $R = 1$), one can notice the monotonic decrease in the parallelogram areas. From Eq. (13) we easily get that $(\partial J/\partial n)_k$ becomes zero under the condition

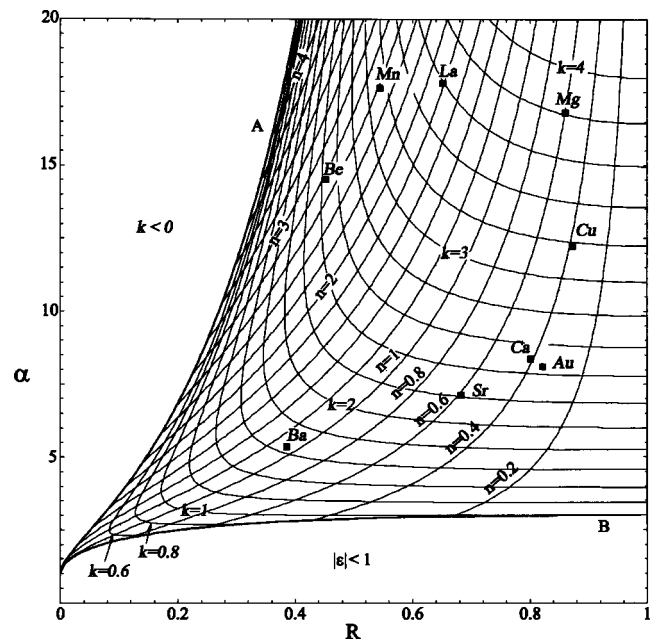


Fig. 3. Distribution of n and k loci in the (α, R) plane. The sizes of the parallelograms show the value of the Jacobian [Eq. (13)] at a given point.

$$k^2 = \frac{(n^2 - 1)(2 - n)}{n + 2}, \quad (20)$$

i.e., only in a very small domain, where $1 < n < 2$ and $k < 0.42$. In Fig. 3 this domain is imperceptible. For $k > 0.42$ the sensitivity of the method always deteriorates with an increase in the refractive index n (see areas of the parallelograms in Fig. 3). A comparison of the method with numerical data of two other— p -polarized light reflectance R_p and pseudo-Brewster-angle θ_B —reflectometric methods for the dielectric constants typical of the interband and intraband region of the noble metals is given in Table 2. Our method gives the maximum sensitivity for measuring ε' when $|\varepsilon'| \gg \varepsilon''$ (i.e., $k \gg n$) and for measuring ε'' when $|\varepsilon'| \ll \varepsilon''$ (i.e., $k \approx n$).

Table 2. Errors in ε' and ε'' in Percent Introduced by a 1% Error in Parameters R , α , $R_p(\theta)$, θ_B

Dielectric Constants					
Method	Parameter	$\varepsilon' = -1.2$	$\varepsilon'' = 6.9$	$\varepsilon' = -11$	$\varepsilon'' = 1.0$
R and α	R	9.9	0.55	0.001	20.3
	α	3.4	1.45	1.18	1.67
R and $R_p(\theta)^a$	R	16.5	5.2	45.0	56.0
	$R_p(\theta)$	10.0	3.1	44.0	57.0
R and θ_B^b	R	0.72	1.55	0.9	19.5
	θ_B	15.1	6.5	15.4	22.4

^aAngle of incidence θ is 60° (from Ref. 19).

^bCalculated by formulas of Ref. 9.

In conclusion, we have described a novel method in grazing-angle reflectometry of absorbing media. It is hard, if not impossible, to measure the derivatives R'_p and R'_s near the grazing angle with the required precision, and therefore the known grazing-incidence differential-reflectance method is inviable. On the other hand, all methods with inversion of R_p and R_s measurements are powerless at the grazing incidence. It is possible, however, to limit oneself to the measurement of only the ratio of the logarithmic derivatives at an unspecified angle in the vicinity of grazing incidence, which is quite feasible. In combination with the normal incidence reflectance this measurement resolves the problem. A suitable range of k to which this method is applicable has been found to be $k \geq 1$; i.e., it includes all the domain where the traditional approaches using the optimum angle reflectance and pseudo-Brewster-angle measurements encounter basic difficulties. Since all the measurements should be performed in two angular regions (near 0° and 90°) without any fine angular adjustment, they may be made rapidly in real time. Therefore, this method can have practical application in measuring simultaneously the refractive index and the extinction coefficient of absorbing materials, and it might readily be incorporated into a system for *in situ* measurements.

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