Kramers–Kronig analysis of the reflection spectrum disturbed by surface imperfections *

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The influence of surface roughness and oxide layers on the results of Kramers–Kronig analysis is described. The remarkable quantitative changes in extinction coefficient and refractive index curves are found. The negative dip in the extinction coefficient curve, which is an unphysical effect, is noticed. It is suggested that this effect may be used for rms roughness estimation.

1. Introduction

Kramers–Kronig (KK) analysis is one of the most popular method for optical constants determination [1]. In particular, it is widely used for obtaining the optical constants of semiconducting materials (see, for example, [2–4]). In this method reflection spectrum measured in the widest possible energy range is used. Moreover, the measurements of absorption coefficient performed near and below the fundamental absorption edge are employed. Therefore, the results of KK analysis depend on all the factors affecting the reflection spectrum, for instance, surface roughness, oxide layers and internal stresses. The influence of the surface imperfections on the reflection spectrum has been studied by many authors [5–9]. The aim of this paper is to show how the results of KK analysis are affected by the changes in reflection spectrum due to surface roughness and oxide layers. The above study could be performed owing to the precision of the recently developed algorithm for KK analysis [10], [11]. This research makes also possible the application of KK analysis in determining the parameters of surface imperfections, the surface roughness in particular. This possibility was mentioned in [12] while analysing optical constants of Zn_3P_2.

The KK analysis performed for reflection spectra of Zn_3P_2, Zn_3As_2, GaTe, ZnSe, ZnTe as well as for the harmonic oscillator test gave similar results. In this paper the exemplary results for ZnTe are shown. These results are based on the reflection curve taken from [13]. From the measurements, performed according to Cardona and Greenaway [13], at room temperature and at unpolarized light, we have obtained the reflectance spectrum for ZnTe within 2–6.3 eV energy range. The reflectance for the energy ranging from 1 to 2.25 eV was calculated assuming

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that below the fundamental absorption edge, which in this case is equal to 2.25 eV, the absorption coefficient equals zero. Then these two parts of reflection curve being matched together gave the reflection spectrum from 1 to 6.3 eV which may be considered as representative in the case of the ideal surface. Then after the influence of surface roughness or oxide layer on reflectance was simulated, the changes of KK analysis results were taken into consideration.

The question whether these changes are more significant than the error of the calculated optical constants is of interest. This problem is discussed in Sect. 5 of this work.

2. Algorithm for KK analysis

The algorithm for KK analysis used here is described in details elsewhere [10], [11]. Some items of the procedure, important for other parts of this paper, are given below.

The well-known KK integral may be written as follows:

$$\Theta(E_0) = \frac{E_0}{\pi} \int_0^\infty \frac{\ln R(E)}{E_0^2 - E^2} dE \tag{1}$$

where R denotes reflectance, Θ — phase shift of the electromagnetic wave on reflection, E — energy of incident photons. After calculation of the integral (1) the extinction coefficient k and the refractive index n can be determined from the well-known formulae. But, for the KK integral (1) the values of R should be known not only in the measuring $\langle E_a, E_b \rangle$ but in the entire energy range. Hence, there arises the necessity of R extrapolations in both low-energy $(0, E_a)$ and high-energy (E_b, ∞) ranges.

If the R extrapolation is to be determined in the range $(0, E_a)$, then the value of absorption coefficient α in this range must be known. Then the following linear equations system is constructed:

$$\Delta\alpha(E_j) = \sum_{i=1}^N B(E_j, E_i) \Delta R(E_i), \quad j = 1, 2, ..., N \tag{2}$$

where $\Delta\alpha$ denotes the difference between the experimental value of absorption coefficient and that calculated for an arbitrary R extrapolation. From the system of equations (2) we may calculate the required correction ΔR for the initial R extrapolation.

The R extrapolation in the range (E_b, ∞) is described by the following formula:

$$R(E) = R_b x^{(A_1 x^{B_1} + A_2 x^{B_2} + 4)} \tag{3}$$

where $x = E_b/E$ and $R_b = R(E_b)$. The values of the parameters B_1 and B_2 are

chosen almost arbitrarily. Thus, the unavoidable ambiguity in determining the high-energy R extrapolation is manifested. The values of the parameters A_1 and A_2 are calculated under the conditions which must be fulfilled by any high-energy R extrapolation.

For some purposes we may assume that the extrapolation is given by the simple formula

$$R(E) = R_x = \text{const}, \quad E > E_b. \tag{4}$$

The parameter R_x may be interpreted as the mean value of R for energies higher than E_b. The value of R_∞ can be calculated for any extrapolation; for the extrapolation given by the Eq. (3), it is as follows:

$$R_\infty = R_b \exp\left[-\frac{A_1}{(1+B_1)^2} - \frac{A_2}{(1+B_2)^2} - 4 \right]. \tag{5}$$

The results of KK analysis for ZnTe presented below are obtained for the following input data: R in the energy range 1–6.3 eV, $\alpha(E) = 0$ for $0 < E \leqslant 1$ eV, $B_1 = 0$, and $B_2 = 10$.

3. Surface roughness

Polished optical surfaces are usually described by a statistical model. In many cases the Gaussian approximation was found valid for the height distribution function and for the autocorrelation function [14], [15]. Thus, the surface roughness can be described with the two parameters: rms roughness σ and the correlation length T.

The influence of the surface roughness on reflectance was found from Kirchhoff diffraction formula [16]. The well-known solution is that proposed by PORTEUS [8]. Unfortunately, for a short wavelength range, it does not give a good agreement with the experimental results. Therefore, in this work the Beckmann formula [17] is applied to surface roughness simulation (see Fig. 1). For small values of the acceptance angle β this formula may be written as follows:
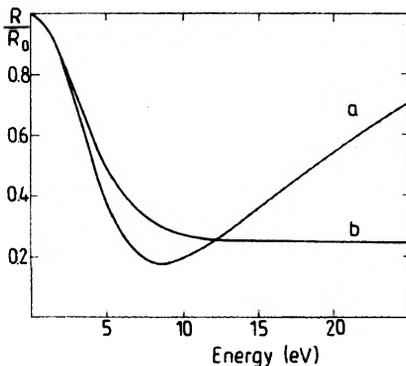

Fig. 1. Influence of surface roughness on reflectance (a) according to the Porteus theory [8], and (b) – to the Beckmann theory [17]. The two curves are for the same parameters $\sigma = 200$ Å, $T = 2000$ Å

$$R/R_0 = \exp(-4k^2\sigma^2)\left[1 + \frac{\sqrt{\pi}\,T\beta}{LR_0}\sum_{m=1}^{\infty}\frac{(2k\sigma)^{2m}}{m!\,\sqrt{m}}\exp(-k^2\,T^2\,\beta^2/4m)\right] \qquad (6)$$

where $k = 2\pi/\lambda = 2\pi E/hc$, R_0 is the reflectance for an ideal surface and L is the dimension of the surface.

In calculations described below, the value of σ varies from 0 to 175 Å which, according to [12], [15], seems to be reasonable. It is also assumed that $\beta = 5°$ and $T = 10\sigma$.

The ideal reflection curve for ZnTe as well as the ones affected by the surface roughness are presented in Fig. 2. The KK analysis of these curves gives us results
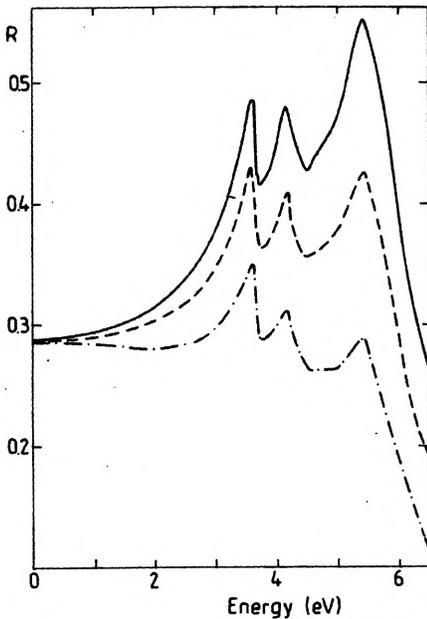

Fig. 2. Reflectance for ZnTe [13] (solid line) and after lowering for the surface roughness with $\sigma = 100$ Å (dashed line) and $\sigma = 175$ Å (dotted-dashed line)

which are shown in Fig. 3. Taking into account the refractive index spectrum, it can be noticed that in the major part of the considered energy range the value of n decreases when σ increases. At the same time the n curve becomes more flat. For $E \to 0$ the value of n is almost constant and equal to 3.30 ± 0.01.

When the value of σ increases there appear many important changes in the extinction coefficient spectrum. First of all the values of k significantly decrease, and for the three main maxima (k_1, k_2, k_3) they are listed in Tab. 1. With the decreasing values of k, the positions of peaks shift towards higher energies. For example, when the value of σ is equal to 175 Å, for the first peak this shift is equal to about 0.05 eV, and for the third one it amounts to 0.3 eV.

For low energies an unphysical effect, namely negative values of k, can be observed [12]. This effect, the so-called "dip", is shown more clearly in Fig. 4. Certainly, due to the dip in the k curve the appropriate dip occurs in the α curve. The latter may be described by the minimum value of absorption coefficient α_{min} (see Tab. 1).
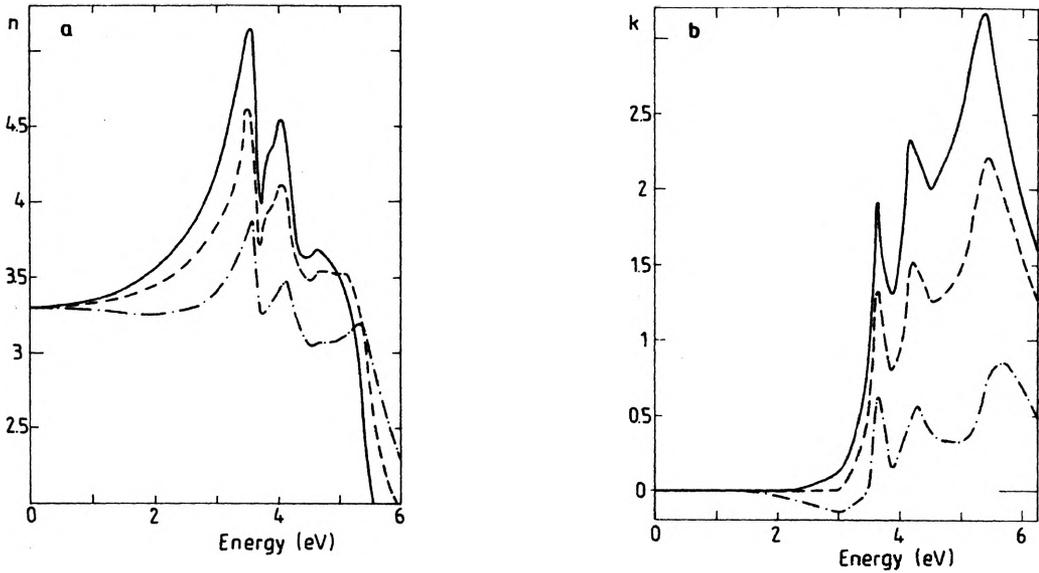
Fig. 3. Refractive index (a) and extinction coefficient (b) curves for ZnTe obtained according to the method described in Sec. 2. Results for the ideal surface (solid line) and for the surface roughness with $\sigma = 100$ Å (dashed line) and $\sigma = 175$ Å (dotted-dashed line)

Taking into account the surface roughness, it may be stated that the high-energy R extrapolation is also changed. When σ increases the value of the parameter R_{γ} rapidly increases. For some values of σ the value of R_{∞} is even greater that R_b, the value of R at the last measuring point. In some cases R_{∞} may be even greater than 1. The ratio R_{∞}/R_b is listed in Tab. 1. In calculations made for ZnTe reflection spectrum measured up to 6.3 eV, we do not expect that for the energies higher than 6.3 eV the mean value of R is greater that R (6.3 eV). If our calculation gives another result, this effect is unphysical.
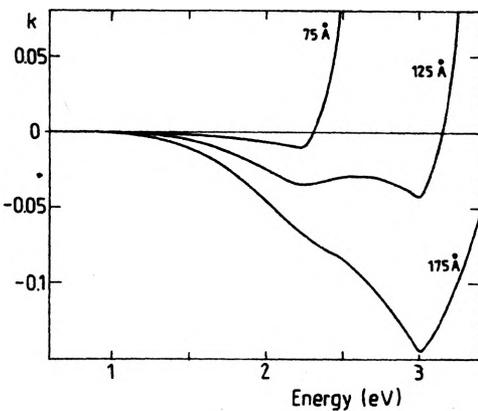

Fig. 4. Negative dip in the extinction coefficient curve of ZnTe for rms roughness equal to 75, 125 and 175 Å

Table 1. Parameters obtained within the KK analysis for different values of rms roughness

$\sigma(\text{Å})$	0	50	75	100	125	150	175
k_1	1.87	1.71	1.53	1.32	1.08	0.84	0.61
k_2	2.20	1.98	1.74	1.46	1.15	0.85	0.60
k_3	3.11	2.91	2.61	2.21	1.75	1.28	0.86
$\alpha_{min}(\text{cm}^{-1})$	$>-10^2$	-1.17×10^4	-2.19×10^4	-4.79×10^4	-1.27×10^5	-2.89×10^5	-4.49×10^5
R_α/R_b	0.389	0.472	0.581	0.776	1.08	1.56	2.29

Table 2. Parameters obtained within the KK analysis for different values of oxide layer thickness

$\sigma(\text{Å})$	0	20	40	60	80	100
k_1	1.87	2.04	2.15	2.25	2.29	2.31
k_2	2.20	2.30	2.33	2.31	2.26	2.17
k_3	3.11	2.95	2.79	2.60	2.38	2.15
R_α/R_b	0.389	0.422	0.481	0.575	0.726	0.972

Summing up, we can conclude that the results of KK analysis are very sensitive quantitatively to the presence of the surface roughness. If at certain energies the exact values of k and n are not known, this effect cannot be used for surface roughness estimation. In the optical spectra there occur also the quantitative changes. Here, the unphysical dip in absorption coefficient curve must be mentioned. The correction of the reflection curve towards vanishing of the dip allows us to determine the value of σ. We can say that a much simpler way of determining σ is to compare the reflection curves measured for different surfaces. It is, however, a relative method, while that mentioned above is absolute.

4. Oxide layer

Let us assume that an oxide layer of thickness σ is grown on the ideal crystal surface. Taking into account multiple reflections, the reflectance for the oxide-crystal wafer is given by the well-known formula

$$R = \left| \frac{\tilde{r}_0 + \tilde{r}_1\, e^{i\Delta}}{1 + \tilde{r}_0\, \tilde{r}_1\, e^{i\Delta}} \right|^2 \tag{7}$$

where

$$\tilde{r}_0 = \frac{\tilde{n}_1 - 1}{\tilde{n}_1 + 1}, \qquad \tilde{r}_1 = \frac{\tilde{n}_2 - \tilde{n}_1}{\tilde{n}_2 + \tilde{n}_1},$$

and

$$\Delta = \frac{4\pi}{hc} \tilde{n}_2\, \sigma E.$$

The symbols $\tilde{n}_1 = n_1 + ik_1$ and $\tilde{n}_2 = n_2 + ik_2$ denote the complex refractive indices of the oxide layer and the base material, respectively.

For the purpose of our calculations it is assumed that the layer of ZnO is grown on the ZnTe crystal. The layer thickness varies from 0 to 100 Å which seems to be reasonable for unintentionally grown oxide layer. The optical constants of ZnO are taken from [18], whereas those of ZnTe are calculated from the ideal reflection curve.

The refraction curve obtained for $\sigma = 100$ Å is presented in Fig. 5. We can see that for higher energies the reflectance of ZnO–ZnTe wafer is lower than that of ZnTe. In the low-energy range the differences between these two curves are less significant. The reflectance of the wafer may be higher than that of ZnTe. Aspnes and Studna mentioned [9] that the influence of the oxide layer on reflection is similar to that of the surface roughness of an appropriate thickness. Due to two factors the reflectance decreases. Such a behaviour was observed for oxide–GaAs wafer [9]. The calculations for ZnO–ZnTe wafer indicate that this behaviour strongly depends on the type of the oxide layer and the crystal.
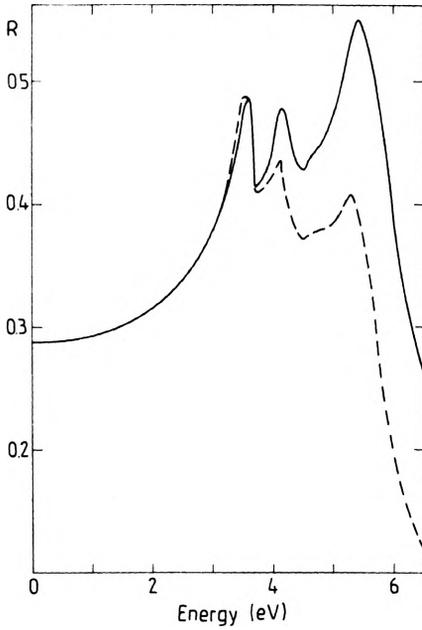
Fig. 5. Reflectance for ZnTe [13] (solid line) and in th presence of ZnO layer with $\sigma = 100$ Å (dashed line
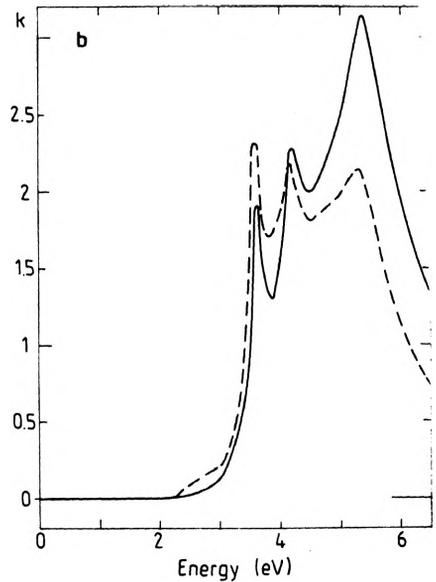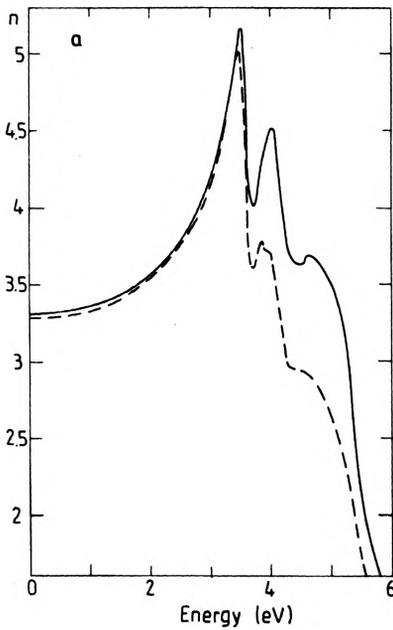

Fig. 6. Refractive index (a) and extinction coefficient (b) curves for ZnTe obtained according to the method described in Sec. 2. Results for the ideal surface (solid line) and for ZnO layer with $\sigma = 100$ Å (dashed line)

Due to the presence of ZnO layer the calculated optical constants are changed (see Fig. 6). In most values within the low-energy range the extinction coefficient increases. Only in the range 1.3–1.9 eV k has negative values and then the unphysical dip is formed. These negative values of k are, however, not high enough to treat dip as a characteristic feature of our results. The shift of the energy gap by about 0.2 eV towards lower energies is such a feature. The peaks in k curve are shifted towards lower energies as well, just in opposite direction as it was with the presence of surface roughness. For these peaks the values of k (k_1, k_2 and k_3, respectively) are listed in Tab. 2.

The decrease of refractive index curve is especially distinct for higher energies. The third main peak for $\sigma = 100$ Å is manifested only by the point of inflection. For $E \rightarrow 0$ the value of n is equal to 3.30 ± 0.01.

The influence of oxide layer on high-energy R extrapolation is described by the ratio R_∞/R_b (see Tab. 2). It increases with σ increasing even faster than for the surface roughness.

It can be summarized that the influence of oxide layer on the results of KK analysis is mainly quantitative. It depends, in a way, on the kind of oxide. When the same thickness of imperfections is considered the influence of the oxide layer is approximately of the same importance as that of surface roughness. In many cases, however, surface roughness is expected to be thicker than the oxide layer, and then it will mainly affect the optical constants.

5. Influence of error on the results

The results of KK analysis involve not only the influence of surface imperfections but also the influence of the experimental error and the error of the applied method. Certainly, these errors will deteriorate the precision of the surface roughness estimation by the method suggested in Sect. 3.

The error of the method may be divided into two categories. The first one, connected with the accuracy of calculation method, can be limited to the level required. The second one, the so-called extrapolation error, cannot be reduced without extending the input data. Figure 7 shows the part of the extinction coefficient curve obtained for $\sigma = 100$ Å and the range of extrapolation error determined for this case by the procedure described in [11]. We can see that the dip is more significant than the extrapolation error. The latter, however, creates the unavoidable limit for the precision of rms roughness estimation. In the case considered above, this limit is equal to about 25 Å.

Taking into account the experimental error, the results of the procedure presented in Sect. 2 are most sensitive to the accuracy of measurement at the two first points of the reflection spectrum. These points are used to determine the parameter of high-energy R extrapolation. In this way, the continuity condition for dR/dE at the first measuring point is fulfilled. Thus, it is not the absolute value of reflectance at the first two points, which plays the main role, but the slope of the

reflection curve. For example, when R (1 eV) is lowered by $\Delta R = 0.00025$ with respect to R (1.2 eV) we obtain the values of Δk which are presented in Fig. 7 The values of Δk are found to be approximately proportional to ΔR.

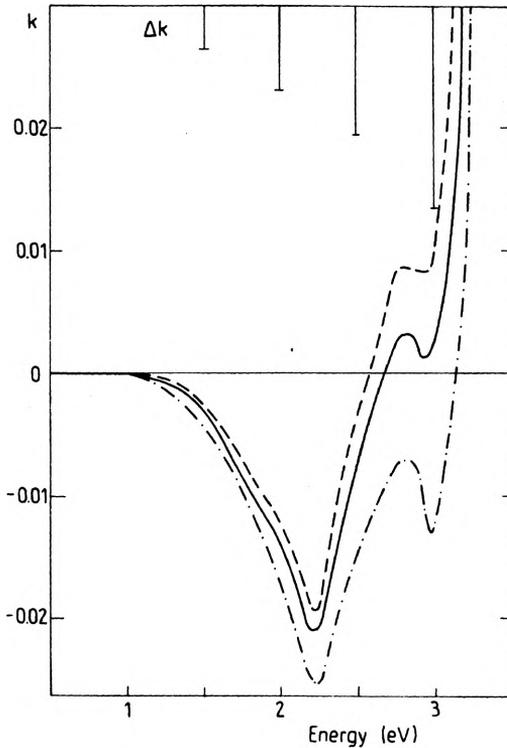
Fig. 7. Negative dip in the extinction coefficient curve of ZnTe for rms roughness $\sigma = 100$ Å (solid line) and the range of extrapolation error (dashed line). The values of Δk are marked in the upper part of the figure (see description in the text)

The random error at the remaining measuring points must be at least of one order greater to give the same values of Δk. Finally, it may be added that the dip structure is not affected by lowering of the whole R curve even by 0.1 R.

6. Conclusions

When the sample surface is not ideal, it causes the changes in the reflectance being measured. Besides very sophisticated surface treatment, these changes are remarkable in the results of KK analysis. Sometimes they may cause the unphysical effects, like negative values of absorption coefficient or very high values of reflectance out of the highest measuring energy point. Therefore, in order to obtain the real values of optical constants of the crystal being investigated, the correction for the sample surface imperfection must be applied. The correction procedure may be based on the other experiments, such as the direct measurements of surface roughness. But the KK analysis itself may be a support in

estimation of surface roughness. However, in this case the achievement of good final results mostly depends on the experimental error in the low-energy range.

It must be added that further experimental as well as theoretical studies are required. First, the account must be taken of the influence of surface roughness on the reflection spectrum in a wide energy range. It would be also worthy to study the case when the surface roughness and oxide layer are present simultaneously. It seems more difficult to study the case of polarized light and other types of surface imperfections.

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Анализ Крамерса–Кронига для коэффициента отражения с учётом несовершенности поверхности

В работе исследовано влияние неровности поверхности и слоя окиси на результаты анализа Краммерса–Кронига. Описано наблюдаемые количественные изменения для кривых коэффициента преломления и коэффициента экстинкции. Описано тоже являющийся нефизическим эффектом отрицательный минимум на кривой экстинкции. Внушают, что этот эффект можно использовать для оценки неровности поверхности данного образца.