Optical constants of polyimide films in the soft x-ray region from reflection and transmission measurements

R. Wolf, H.-G. Birken, and C. Kunz

Measurements were performed with synchrotron radiation on free-standing, ~ 300 -nm-thick polyimide films in the photon energy range of 40–1350 eV. We evaluated optical constants both from transmission measurements with the Kramers–Kronig analysis and from multiangle reflection measurements by fitting Fresnel equations modified by two different roughness factors for both sides of the film. A thorough error analysis was carried out for both methods. The results agree well within the error bars thereby strengthening confidence in the applied theoretical formalism as well as in the experimental method in this difficult spectral region.

Key words: Optical constants, soft x-ray, polyimide, synchrotron radiation.

1. Introduction

Experimental determination of optical constants, while difficult in all spectral regions, becomes exceptionally cumbersome in the spectral region beyond the UV. The reasons may differ from case to case, but they usually result from the need to experiment in a vacuum the adverse effect of even thin surface contaminants, the extremely high-absorption coefficients encountered, the disturbing effects of surface roughness when the wavelength becomes short, and the difficulty with substances that are unstable in air and need to be prepared *in situ* in vacuum.

Commonly two methods are used in this spectral region: angular-dependent reflectance measurements that are evaluated when Fresnel's equations are applied¹ and transmittance measurements of thin films that are evaluated by means of a Kramers-Kronig analysis.² We recently introduced a third method, which works in the case of metals and metal films, namely, the determination of the photoelectric yield as a function of the angle of incidence.^{3,4} This method is not important in the context of this paper, where we deal with an insulating material, polyimide.

Whenever optical constants in this spectral region are available from different measurements, the discrepancies between the results are astonishingly large. In many cases they can be attributed to differences in preparing the samples. There are, however, also indications of systematic differences between optical constants determined from reflectance and transmittance measurements. Lukirskii et al.⁵ find for Au and Al differences in the region of 110-525 eV of the order of $\sim 30\%$. The optical constants of Au and Ag determined from transmittance measurements by Hagemann et al.² yield normal-incidence reflectances at 20 eV, which are more than 50% lower than the values measured by Canfield et al.⁶ and by Ehrenreich and Philipp.⁷ It is extremely difficult to make a critical assessment of these discrepancies since a sound quantitative analysis of possible error is almost never available. In cases where error bars are plotted they often comprise only one type of error or they are estimates not justified in detail.

The goal of our investigation was the elimination of all those errors that originate from differences in the composition of samples. Therefore we perform reflectance and transmittance measurements on the same thin film. This is possible since we could obtain sufficiently flat polyimide films of uniform thicknesses. Our investigation is divided into two steps. First a measurement of the bare polyimide film followed by a careful analysis of the results from both types of measurement is carried out. This is the contents of this paper. In a second step Au was evaporated on top of this film, and again transmittance and reflec-

When this study was done all authors were with the II. Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, D-2000 Hamburg 50, Germany. R. Wolf is now with Robert Bosch GmbH, K8/EIS, Tübinger Strasse 123, D-7410 Reutlingen, Germany.

Received 7 August 1991.

^{0003-6935/92/347313-15\$05.00/0.}

^{© 1992} Optical Society of America.

tance were measured. The analysis in this case applied a two-layer model. These results on Au will be published in a consecutive paper. All our measurements were carried out on an experimental station, which covers a large range of photon energies and which was optimized during the past six years for exactly such measurements.^{8,9} Among other features this station is well characterized with respect to the spectral purity of the radiation used; it has an extremely good collimation of the beam and the capability of preparing and measuring samples in ultra high vacuum whenever necessary.

In Section 2 we summarize briefly the theoretical basis of our analysis, citing mainly the equations used since most of the theory is readily accessible in the literature. Only our method, which allows for two different roughnesses on the two sides of the polyimide film, needs a more detailed justification. The experimental procedure is described in Section 3, while the experimental results, the evaluation of the data, the error analysis, and the final optical constants are given in Section 4. This section also includes a comparison and discussion of the two sets of data.

2. Theoretical Background

A. Multilayer Reflection and Transmission

Most of the theoretical background needed to analyze our measurements is obtained from standard Fresnel theory for multilayer reflection and transmission. Here we follow quite closely the notation of Pepper.¹⁰ For our analysis, however, we modified the final equations by attaching individual interface roughnesses to the different boundaries according to an approximation first introduced by Spiller and Rosenbluth.¹¹ Since here we want to give also the theoretical background for the case of Au on polyimide, we present the results for the generalized case of m interfaces beween m + 1 media (see Fig. 1).

The isotropic dielectric function $\epsilon = \epsilon_j(E)$, (j = 0, ..., m) characterizes each layer j by a complex function of photon energy E:

$$\epsilon(E) = \operatorname{Re} \epsilon(E) + i \operatorname{Im} \epsilon(E).$$
 (1)

The index of refraction n(E) and the extinction coefficient k(E) are defined as

$$[\epsilon(E)]^{1/2} = n(E) + ik(E).$$
 (2)

They are connected by the Kramers–Kronig transformations:

$$\operatorname{Re} \epsilon(E) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{E' \operatorname{Im} \epsilon(E')}{E'^2 - E^2} dE',$$
$$\operatorname{Im} \epsilon(E) - \frac{h\sigma_0}{2\pi\epsilon_v E} = -\frac{2E}{\pi} P \int_0^\infty \frac{\operatorname{Re} \epsilon(E') - 1}{E'^2 - E^2} dE',$$

$$n(E) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{E' k(E')}{E'^2 - E^2} dE',$$

$$k(E) = -\frac{2E}{\pi} P \int_0^\infty \frac{n(E') - 1}{E'^2 - E^2} dE', \quad (3)$$

where *P* denotes Cauchy's principal value of the integral, σ_0 is the dc conductivity, ϵ_v is the dielectric constant of vacuum, and *h* is Planck's constant.

There are several methods described in the literature for deriving the (intensity) reflectances R_s and R_p and the (intensity) transmittances T_s and T_p . Here the indices s and p denote the two different types of linear polarization. If P is the degree of polarization of the incident light, the measured reflectance R and transmittance T are given by

$$R = \frac{1-P}{2}R_s + \frac{1+P}{2}R_p;$$

$$T = \frac{1-P}{2}T_s + \frac{1+P}{2}T_p.$$
 (4)

 $R_a (a = s, p)$ is derived from the amplitude reflectivity $R_{a,1}^+$ from a stack with *m* interfaces bounded on both sides by vacuum. The general case with ϵ_0 , $\epsilon_m \neq 1$ is treated in Ref. 12. T_a is derived from the amplitude transmissivity $T_{a,1}^+$ of this stack as

$$R_a = |R_{a,1}^+|^2, \qquad T_a = |T_{a,1}^+|^2. \tag{5}$$

The indices + and 1 denote a wave traveling in the positive y direction that is incident on interface 1 (see also Fig. 1).

To calculate these quantities we apply an iterative approach here. We assume that the problem is solved for the stack of interfaces $2, \ldots, m$, which yields amplitude reflectivity $R_{a,2}^+$ and amplitude transmissivity $T_{a,2}^+$ for any wave incident on the stack. Then the top layer (1) is added to the stack. With the help of the Fresnel amplitude reflectivities and transmissivities $r_{a,1}^\pm$ and $t_{a,1}^\pm$ at the added interface, we obtain the quantities $R_{a,1}^+$ and $T_{a,1}^+$ by summing up over an infinite series.

The Fresnel (amplitude) coefficients are given as follows:

$$r_{s,j}^{+} = \frac{\xi_{j-1} - \xi_j}{\xi_{j-1} + \xi_j}, \qquad r_{p,j}^{+} = \frac{\epsilon_j \xi_{j-1} - \epsilon_{j-1} \xi_j}{\epsilon_j \xi_{j-1} + \epsilon_{j-1} \xi_j}, r_{a,j}^{-} = -r_{a,j}^{+}, \qquad t_{a,j}^{\pm} = 1 + r_{a,j}^{\pm}, \qquad (6)$$

where

$$\xi_j = rac{2\pi}{\lambda_{v
m sbx}} \, (\epsilon_j - \sin^2 heta)^{1/2}$$

is the complex normal component of the wave vector, while λ_v is the wavelength in vacuum and θ is the angle of incidence on the topmost interface. The summation over all multiply reflected and transmitted waves according to Fig. 1 yields the general result



Fig. 1. Notation for calculating the multilayer reflection and transmission process by means of an iterative algorithm. A four-boundary system is shown. The left-hand side gives the notation for the individual layers, the middle section explains the notation for the Fresnel coefficients at an individual interface (between layers 1 and 2), the right-hand side explains the combination of reflectances and transmittances inside a subsystem to a total $R_{a,j}^+$ and $T_{a,j}^+$.

for arbitrary j = 1, ..., m - 1, where d_j is the thickness of the individual layers:

$$\begin{aligned} R_{a,j}^{+} &= r_{a,j}^{+} + t_{a,j}^{-} t_{a,j}^{+} \sum_{k=1}^{\infty} (R_{a,j+1}^{+})^{k} \\ &\times \exp(2ikd_{j}\xi_{j})(r_{a,j}^{-})^{k-1}, \\ T_{a,j}^{+} &= t_{a,j}^{+} T_{a,j+1}^{+} \exp(id_{j}\xi_{j}) \sum_{k=0}^{\infty} (R_{a,j+1}^{+})^{k} \\ &\times \exp(2ikd_{j}\xi_{j})(r_{a,j}^{-})^{k}, \end{aligned}$$
(7)

while for j = m

$$R_{a,m}^{+} = r_{a,m}^{+}, \qquad T_{a,m}^{+} = t_{a,m}^{+} = 1 + r_{a,m}^{+}.$$
 (8)

Evaluating the sums and using Eqs. (6) finally yield for j = 1, ..., m - 1

$$R_{a,j}^{+} = r_{a,j}^{+} + \frac{(1 - (r_{a,j}^{+})^2)R_{a,j+1}^{+} \exp(2id_j\xi_j)}{1 + r_{a,j}^{+}R_{a,j+1}^{+} \exp(2id_j\xi_j)}.$$
 (9)

Equations (4), (5), (8), and (9) give an accurate solution to the problem of smooth interfaces.

B. Inclusion of Roughness

The theory of reflection from a single (m = 1) rough interface is treated extensively by Beckmann and Spizzichino¹³ within the framework of the scalar theory. Any attempt to include a modern vector theory of scattering in our analysis had to be rejected because of the impossibility of including these complicated equations in the fit procedure. While the scalar theory has natural limitations they are important in the analysis of scattered radiation rather than in the loss of intensity in the specular beam. It yields

$$R_a = |r_{a,1}^+|^2 \exp(-4\sigma_1^2 \xi_0^2), \tag{10}$$

where σ_1 is the rms roughness.

How is this result to be generalized for the case of multilayers with individual roughnesses at the different interfaces? Spiller and Rosenbluth¹¹ propose the following substitutions, which are justified in detail in Ref. 12:

$$r_{a,j}^{+} \to r_{a,j}^{+} \exp(-2\sigma_{j}^{2}\xi_{j-1}^{2}),$$

$$r_{a,j}^{-} \to r_{a,j}^{-} \exp(-2\sigma_{j}^{2}\xi_{j}^{2}).$$
(11)

They yield instead of Eqs. (7), (8), and (9)

$$\tilde{R}_{a,j}^{+} = r_{a,j}^{+} \exp(-2\sigma_{j}^{2}\xi_{j-1}^{2}) + t_{a,j}^{-}t_{a,j}^{+} \sum_{k=1}^{\infty} (\tilde{R}_{a,j+1}^{+})^{k}$$

$$\times \exp(2ikd_j\xi_j)[r_{a,j}^- \exp(-2\sigma_j^2\xi_j^2)]^{k-1}, \quad (12)$$

$$R_{a,m}^{+} = r_{a,m}^{+} \exp(-2\sigma_m^2 \xi_{m-1}^2), \qquad (13)$$

$$\tilde{R}_{a,j}^{+} = r_{a,j}^{+} \exp(-2\sigma_{j}^{2}\xi_{j-1}^{2}) + \frac{[1 - (r_{a,j}^{+})^{2}]\tilde{R}_{a,j+1}^{+} \exp(2id_{j}\xi_{j})}{1 + r_{a,j}^{+} \exp(-2\sigma_{j}^{2}\xi_{j}^{2})\tilde{R}_{a,j+1}^{+} \exp(2id_{j}\xi_{j})}$$
(14)

and for the (intensity) reflectance holds:

$$\tilde{R} = \frac{1-P}{2} |\tilde{R}_{s,1}^{+}|^2 + \frac{1+P}{2} |\tilde{R}_{p,1}^{+}|^2.$$
(15)

As obvious as this treatment of multilayer roughness might appear to be, we should mention here that it is not valid in all circumstances; e.g., the case of identical roughness structures at each interace (a waviness of the whole multilayer) and reflection close to normal incidence [Eq. (15)] is not applicable. Instead the reflectance is described by Eq. (10).¹⁴

The phenomenological effect of different interface roughnesses on the reflectance can be quite spectacular. Assume a layered system whose top interface is smooth while the second interface is rough. In this case the interference structures are damped. We note in this context that a diminished interference contrast is often traced back to other effects, e.g., the inhomogeneous film thickness and the energy spread of the radiation used. In the opposite case the top interface is rough while the second interface is smooth; however, the relative amplitude of the interference structures is enhanced compared with Eq. (10). This difference turned out to be important in the case of thin Au films evaporated onto polished substrates or onto the polyimide foils described here.

C. Evaluation of the Reflectance Data

In our experiments the reflectance R is measured at many different angles θ_n , usually 100 or more, with individual statistical errors $\delta(\theta_n)$. According to the method of smallest quadratic deviations, we minimize the function

$$\chi^{2} = \sum_{\theta_{n} \ge \theta_{\min}}^{\theta_{n} \le \theta_{\max}} \frac{[R_{\text{theo}}(\theta_{n}) - R_{\exp}(\theta_{n})]^{2}}{\delta(\theta_{n})^{2}} \cdot$$
(16)

The theoretical reflectance $R_{\text{theo}}(\theta_n)$ in our computer program is based on Eq. (15). It may contain up to three layers (m = 3) and may involve the following parameters:

$$R_{\text{theo}}(\theta_n) = \tilde{R}(\theta_n; \sigma_1, \epsilon_1, d_1, \sigma_2, \epsilon_2, d_2, \sigma_3, \epsilon_3; E, P). \quad (17)$$

To parameterize the statistical error in a reasonable form we set

$$\delta(\theta_n) = \alpha + \beta R_{\exp}(\theta_n). \tag{18}$$

This appears to be justified since we measure the signals with extremely sensitive electrometers. Typically we set $\alpha = 0.0001$ and $\beta = 0.01$.

When we evaluate data with small values of the imaginary of the dielectric function, it is necessary to take into consideration the divergency of the incoming radiation. In this case the theoretical reflectance in Eq. (17) is replaced by the following convolution:

$$R_{\text{theo}}'(\theta_n) = \int_{-\infty}^{\infty} R_{\text{theo}}(\theta_n - \theta'') f(\theta'') d\theta''.$$
(19)

The distribution of directions $f(\theta'')$ in the incoming beam is approximated by a Gaussian distribution with parameters approximating the actual situation. In this case the number of fit parameters needs to be reduced in some cases because of computer time limitations.

D. Evaluation of the Transmittance Data

Our measurements need to be augmented by results from other authors and by extrapolations to lower and higher energies before the Kramers–Kronig relations can be applied. Furthermore the program used extrapolates the data point at the lowest given energy to E = 0, and from the highest given energy to $E = \infty$ it sets $k \propto E^{-3}$ according to an oscillator model or any other general theory. The measured transmittance of a sample depends on both k and n. An iterative procedure suggested by Hagemann *et al.*² is applied. The extinction coefficient $k_{1,i+1}$ of the first medium in the i + 1st iteration is calculated as

$$k_{1,i+1}(E) = k_{1,i}(E) + \frac{\lambda_v}{4\pi d_1} \ln[T[\epsilon_{1,i}(E); d_1, \\ \epsilon_2(E), d_2, \dots; \theta] / T_{\exp}(E; \theta)], \quad i = 0, \dots, \quad (20)$$

where $T_{\exp}(E; \theta)$ is the experimentally determined transmittance and $\theta = 0$ for our measurements. $T[\epsilon_{1,i}(E); d_1, \epsilon_2(E), d_2, \ldots; \theta]$ is the transmittance according to Eqs. (4), (5), and (7) and optical constants from the *i*th iteration. The dielectric function $\epsilon_{1,i}$ is calculated from $k_{1,i}(E)$ and from the index of refraction $n_{1,i}(E)$. The latter is obtained by Kramers-Kronig transforming $k_{1,i}(E)$. The optical constants and the thicknesses of all the other layers need to be known. Because of possible interference effects the determination of optical constants from transmittance measurements may not be unique. Therefore appropriate initial values must be inserted. This, however, is of no importance in our spectral region. Interface roughness also is irrelevant here.

3. Experimental

A. Measuring System

The experiments were carried out at the reflectometer station with synchrotron radiation from the storage ring DORIS at HASYLAB in Hamburg. The station's specialities are reflection, transmission, stray light, and other fundamental optical measurements. It consists of the monochromator, Bumble Bee,⁹ which in principle covers the energy range of 15–1500 eV and which in certain subregions is highly efficient in suppressing higher-order and other false light contributions. The reflectometer⁸ operates in UHV with high precision differentially pumped feed-



Fig. 2. Schematic arrangement of the reflectometer station at HASYLAB.

throughs. The arrangement is restricted to operation in s polarization only. It is sketched in Fig. 2.

The spectral purity of the radiation used in reflectance and transmittance measurements is decisive for the accuracy of the results. The way in which this propagates into the final error is quite intricate and can be significantly different in different spectral regions. For the type of measurement described here, spectral purity can be influenced by the mode of operation of the monochromator,⁹ which allows for the use of two different gratings (1200 and 300 lines/mm) combined with two different premirrors (gold coated or Kanigen, a nickel alloy). Furthermore, the same photon energy can be monochromatized at different angles of incidence on a premirror and a grating with different optimizations either for maximum flux which allows for the best use of additional filters, or for good rejection of higher-order radiation already without filters. In addition the detector with its efficiency and spectral characteristics comes into play. Two different detectors have been used here, an open photomultiplier (Johnson MM-2) with an Al₂O₃-covered cathode and GaAsP Schottky diodes.¹⁵ The latter were the detectors of choice at the end of the experiment because of their high stability. The rising efficiency with higher photon energy is favorable for the suppression of longwavelength stray light, while the enhancement of higher-order radiation is compensated for by the use of filters and/or the operation of the monochromator in special modes.

The details of the different modes of operation are given in the original papers. As a general rule the contribution of false light to the primary signal could be kept at 1% or below in the energy range of 40-1000 eV. An estimate of this contribution is incorporated into the error analysis (see below).

B. Sample Preparation and Mounting

Polyimide films were used for our measurements for several reasons. We were looking for a film that could be mounted flat over a large area, that has a sufficiently high transmission in our spectral range, and that would stand a certain heat load without wrinkling during the evaporation of Au, which, as mentioned above, is the topic of a consecutive paper.

We obtained our films from the Göttingen x-ray microscopy group, which uses them among other applications as supports for holographic zone plates. They are produced by distributing a drop of polyimide acid solution on a spinning glass plate. By a process of several heat treatments and other treatments, polymerization sets in.¹⁶ Finally a ring is glued on the film as shown in Fig. 3. The inner ring touches only the foil while it is glued on the slightly lowerlying outer ring. Thereafter the glass is dissolved in hydrofluoric acid. As a result flat 0.3-µm-thick polyimide films 22-mm in diameter are obtained with a diameter of 15 mm for the unsupported region. As our measurements show, homogeneity is excellent. While a well-known polyimide is sold under the name Kapton by Du Pont, our material originates from Hitachi under the name PIQ 13.¹⁷ Transmittance is higher than 0.1 in most of our spectral region but drops fast at lower energies.

The rings are mounted reproducibly in a sample holder, which can be aligned in the reflectometer. An excentrically mounted razor blade can be moved into the beam instead of the foil and allows control of the extremely sensitive alignment of the beam rela-



Fig. 3. Special sample holder for the polyimide foils. The plane of incidence of the beam is perpendicular to the paper. First, we aligned the sample surface to the axis of rotation by rotating the sample holder by 180°. In shifting the sample holder to intercept the beam at the razor blade, which is located behind the plane of the drawing, the location of the axis of rotation can be aligned with respect to the incoming beam.

tive to the axis of rotation. Indeed with only 15-mmwide samples this alignment is decisive for obtaining reliable data at grazing incidence. Therefore a careful analysis of the remaining misalignments was made with each sample and taken into consideration in the evaluation of the data.

Our measurements were performed with a reduced entrance aperture of 0.4 mm compared with that described in Ref. 18. This resulted in beam heights of 0.29 and 0.21 mm (full width at half-maximum) in two different alignments. The centers of the beam lay 0.24 mm below and 0.02 mm above the axis of rotation of the sample, respectively. This leads to corrections on the measured angle of incidence. Furthermore the width and displacement limit the maximum angle of incidence, which can be included in the evaluation. Applying the criterion that 99% of the incoming intensity should hit homogeneous and



Fig. 4. (a), (b) Reflectance R as a function of the angle of incidence θ at two different photon energies E. The open circles are the measurement at foil P86a; the dashed line is the result of a fit according to Eq. (14). The deviations of the fit are plotted around the central line (right scale) in units of $\delta_n = 0.0001 + 0.01R$.

planar parts of the film limits the angles of incidence to 86.6° and 88.2°, respectively.

C. Characterization of the Samples

The homogeneity of the samples was determined by measuring their transmittance at 123-eV photon energy at different points. In a central region of 7.5-mm diameter the transmittance, which is ~0.5, fluctuates by at most $\pm 0.4\%$.

For us to perform meaningful measurements of the reflectance, the films must be planar to a certain extent. We measured the planarity by mounting the films in a Michelson interferometer after a layer of gold had evaporated on them (see Ref. 12). The Au layer could have added at most additional distortion. The interference patterns show that the films have a saddlelike distortion around the center. At distances of 2, 4, and 6 mm from the center the deviations from a plane amount to ± 0.3 , ± 2.8 , and $\pm 8.5 \mu m$. Along the symmetry lines of the distortion the radii of curvature are several meters. Even along those lines at 2 mm from the center, the tangent angle is $<0.02^{\circ}$. This must be compared with the horizontal and vertical divergencies of our beam, which are 0.28° and 0.09°, respectively. We therefore consider the samples as being sufficiently plane for the purpose of our measurements.

4. Results and Discussion

In this chapter both the angular-dependent reflectance and the energy-dependent transmittance measurements are presented. They lead to optical constants by fitting the Fresnel equations or by performing a Kramers-Kronig analysis, respectively (see Section 2). Finally in Section 4.C we compare the two independent data sets with each other.

We consider the fact that the evaluation of the data accompanied by an extensive error analysis is of utmost importance. Since the primary goal of this work was to present data with well-founded error bars, we investigated the different sources of errors from the beginning. Several measurements in the course of the investigations had to be discarded, and many improvements on the measurements, the instrument, and the analysis were introduced. These data, although not presented here, were helpful in assessing primary sources of errors and estimating the orders of magnitude of the systematic errors needed to perform the final analysis. A more detailed description of this is in Ref. 12.

Table 1.	Results of the	R(A)	Measurements	on Pol	vimide	Film	P86a ^a
10010 11	ricourto or the	,,,,,,	measurements	0111 01	ymmac		1 000

	$1 - \operatorname{Re} \epsilon$	Im e			
<i>E</i> (eV)	(0.001)	(0.001)	<i>d</i> (nm)	σ_1 (nm)	$\sigma_2 (nm)$
42.34 ± 0.42	200.5 ± 1.7	114.4 ± 3.4		0.316 + 0.474 / -0.316	
50.18	154.4	74.32		0.698	
50.44	152.1	72.84		0.849	
58.33	119.4	48.69		0.708	
69.58	88.10	28.79	291.1	0.794	1.00
69.89	87.24	28.68	291.3	0.786	
82.90	63.62	16.09	290.9	0.892	0.193
83.26	62.98	16.05	291.0	0.879	0.006
98.59 ± 0.49	44.47 ± 0.18	8.995 ± 0.225	292.0 ± 1.5	0.853 ± 0.085	0.875 ± 0.788
118.1	30.85	5.151	291.5	0.864	0.957
118.1	30.83	5.143	291.5	0.853	0.874
136.2	23.01	3.274	291.6	0.877	1.10
139.4	21.91	3.039	291.5	0.883	0.898
166.6	15.00	1.700	291.3	0.877	0.821
197.4	10.21	1.022	291.5	0.807	1.04
235.6 ± 1.2	6.546 ± 0.059	0.5852 ± 0.018	290.6 ± 1.5	0.790 ± 0.114	1.05 ± 0.43
235.6 ± 1.2	6.546 ± 0.059	0.5852 ± 0.018	290.6 ± 1.5	0.790 ± 0.114	1.05 ± 0.43
235.6	6.573	0.5973	290.5	0.879	1.04
269.6	3.675	0.3719	290.1	0.546	1.26
269.6	3.639	0.3857	290.3	0.339	1.42
270.7	3.542	0.3782	290.1	0.573	1.25
333.4	4.375	2.228		0.786	
333.4	4.344	2.273		0.801	
333.4	4.357	2.298		0.808	
397.7	3.154	1.256	290.1	0.721	0.949
470.2 ± 2.4	2.467 ± 0.035	0.7387 ± 0.039	290.1	0.842 ± 0.034	
560.4	1.852	0.5971	288.8	0.793	
668.8	1.376	0.3252	296.6	0.792	
794.5	0.9898	0.1952	286.7	0.744	
950.4	0.7115	0.0988	293.4	0.672	0.137
950.4 ± 4.8	0.7058 ± 0.035	0.1056 ± 0.047	293.2 ± 2.1	0.657 ± 0.184	0.001

^aThe significance of the blanks is that these parameters were set in the fit.

A. Reflection Measurements

1. Results

Typical angular-dependent reflectance measurements are presented in Fig. 4. We obtained them by measuring point by point the detector signal. To normalize this signal, we removed the sample from the beam; in a separate measurement the beam hits the detector directly. Fluctuation of the incoming intensity is compensated for by a reference detector.¹⁸ In this way absolute values of the reflectance R are measured.

The curve in Fig. 4(a) clearly displays the sharp decrease in reflectance below the critical angle of total reflection at 79° . Both curves show pronounced interference structures caused by the finite thickness of the film.

The measured curves are fitted with theoretical curves according to Eqs. (4), (5), (14), and (16). When we minimize the χ^2 function according to Eq. (16), the measured points are weighted through their

statistical errors according to Eq. (18), $\alpha = 0.0001$ and $\beta = 0.01$. To show the deviation between R_{theo} and R_{exp} , we display this deviation separately with a scale given on the right-hand side in units of $\delta(\theta_n)$, the statistical error of each point. This is ~1% of R_{exp} for the highest reflectance values.

When we performed the fit the degree of polarization P of the radiation was determined theoretically from the acceptance of the monochromator with respect to the plane of the storage ring. Furthermore, the vertical angular width of the beam of 0.087° full width at half-maximum is convoluted with the theoretical reflectivity for photon energies above 139 eV while this could be neglected below. The region in θ , which was included in the fit, is shown in Fig. 4 by plusses. The upper limit is determined by the considerations explained in Section 3.B. The lower limit was chosen individually for each photon energy. Too low a limit is sometimes adverse because of computer-time considerations or inclusion of background because of long-wavelength stray light.

Table 2. Contributions to the Error Analysis for Five Selected Photon Energies^a

	$\Delta(1 - \operatorname{Re} \epsilon)/(1 - \operatorname{Re} \epsilon)$	ΔIm ε/Im ε	$\Delta d/d$	$\Delta \sigma_1 / \sigma_1$	$\Delta\sigma_2/\sigma_2$
42.34 eV ±1%					
Fit	± 0.0023	± 0.0055		± 0.3504	
ΔN	+0.0020	-0.0131		-0.8006	
$+\Delta\theta_0$	-0.0015	0.0000		-0.0741	
$+\Delta P$	-0.0014	-0.0021		-0.1549	
$+\Delta\sigma(\theta)$	0.0000	0.0000		0.0000	
$+\Delta E$	0.0000	0.0000		-0.0117	
$(\Sigma\Delta^2)^{1/2}$	± 0.0037	±0.0144		± 0.8907	
+0.0050 R(25 eV)	+0.0052	+0.0234		-0.9999	
+0.0070 R(2E)	-0.0020	+0.0032		+0.1639	
Δ_{tot}	± 0.0085	± 0.0300		+1.5/-1.0	
50.55 EV ±0.5%	± 0.0011	± 0.0053	± 0.0009	± 0.0228	± 0.6997
ΔN	+0.0009	-0.0171	+0.0001	-0.0449	+0.2869
$+\Delta \theta_0$	-0.0030	+0.0001	+0.0004	-0.0120	-0.0233
$+\Delta P$	+0.0002	-0.0015	0.0000	+0.0336	+0.0609
$+\Delta\sigma(\theta)$	0.0000	0.0000	0.0000	0.0000	-0.0029
$+\Delta E$	0.0000	0.0000	-0.0049	-0.0049	-0.0043
$(\Sigma\Delta^2)^{1/2}$	± 0.0033	±0.0180	±0.0050	±0.0619	± 0.7591
+0.0004 R(E/2)	-0.0003	+0.0032	0.0000	-0.0468	+0.0090
+0.0050 R(2E)	-0.0006	+0.0063	-0.0001	+0.0181	-0.1308
$\Delta_{ ext{tot}}$	± 0.0040	± 0.0250	± 0.0050	± 0.1000	± 0.9000
$235.6 \text{ eV} \pm 0.5\%$					
Fit	± 0.0008	± 0.0075	± 0.0002	± 0.0289	± 0.1406
ΔN	+0.0008	-0.0156	+0.0001	-0.0716	+0.1597
$+\Delta \theta_0$	-0.0087	-0.0012	+0.0013	-0.0656	-0.0256
$+\Delta P$	0.0000	-0.0004	0.0000	+0.0087	+0.0126
$\sigma(\theta) + \Delta \sigma(\theta)$	-0.0001	-0.0104	0.0000	+0.0239	-0.2675
$+\Delta E$	0.0000	0.0000	-0.0049	-0.0050	-0.0043
$(\Sigma\Delta^2)^{1/2}$	± 0.0088	± 0.0202	± 0.0051	± 0.1046	± 0.3430
$+0.0020 R(E/2)^{b}$	+0.0004	+0.0514	+0.0001	-0.9994	-0.2282
+0.0040 R(2E)	-0.0003	+0.0060	0.0000	+0.0246	-0.0664
Δ_{tot}	±0.0090	±0.0300	±0.0050	±0.1300	±0.4100

(Table continued)

Table 2. continued

	$\Delta(1 - \operatorname{Re} \epsilon)/(1 - \operatorname{Re} \epsilon)$	$\Delta \text{Im }\epsilon/\text{Im }\epsilon$	$\Delta d/d$	$\Delta\sigma_1/\sigma_1$	$\Delta\sigma_2/\sigma_2$
$470.2 \text{ eV} \pm 0.5\%$					
Fit	± 0.0015	± 0.0217	± 0.0038	± 0.0250	
ΔN	+0.0030	+0.0059		-0.0072	
$+\Delta\theta_0$	-0.0124	+0.0082		-0.0231	
$+\Delta P$	0.0000	0.0000		+0.0022	
$+\Delta\sigma(\theta)$	-0.0004	-0.0005		-0.0021	
$+\Delta E$	0.0000	0.0000		-0.0049	
$(\Sigma\Delta^2)^{1/2}$	± 0.0129	± 0.0239		± 0.0353	
+0.0006 R(E/2)	+0.0034	+0.0446		+0.0094	
+0.0030 R(2E)	-0.0008	-0.0016		+0.0018	
$\Delta_{ m tot}$	± 0.0140	± 0.0530		± 0.0400	
$950.4 \text{ eV} \pm 0.5\%$					
Fit	± 0.0134	± 0.1832	± 0.0025	± 0.0908	
ΔN	+0.0039	+0.0045	+0.0002	-0.0040	
$+\Delta\theta_0$	-0.0177	+0.0300	+0.0038	-0.0377	
$+\Delta P$	0.0000	+0.0020	0.0000	+0.0015	
$+\Delta\sigma(\theta)$	+0.0260	-0.3962	+0.0023	+0.2520	
$+\Delta E$	0.0000	-0.0013	-0.0049	-0.0043	
$(\Sigma\Delta^2)^{1/2}$	± 0.0344	± 0.4376	± 0.0071	± 0.2706	
+0.0020 R(E/2)	+0.0320	+0.0453	+0.0021	+0.0467	
Δ_{tot}	± 0.0500	± 0.4400	±0.0070	±0.2800	

^aFit means the error resulting from the mean-square deviation of the fit, ΔN is the error of the normalization signal obtained with the sample removed, $\Delta \theta_0$ is the error in the angle of incidence, ΔP is the error in the degree of polarization, $\Delta \sigma(\theta)$ is the error in the assumed vertical divergence of the beam, ΔE is the error in the energy calibration of the monochromator. $(\Sigma \Delta^2)^{1/2}$ is the result of the quadratic superposition of these first six errors. The following error sources have their origin in contributions of wrong photon energies: R(25 eV), R(E/2) is the contribution of long-wavelength light, R(2E) is the contribution of second harmonic light. We obtain Δ_{tot} by adding up all errors quadratically while we take R(2E) into account linearily in order to stress the relative importance of this contribution.

^{*b*}Not included in Δ_{tot} since it is obviously overestimated.

The free-fit parameters are Re ϵ , Im ϵ , d, σ_1 , and σ_2 . The photon energy-independent parameters d, σ_1 , and σ_2 were in some cases kept fixed at the values already determined at other photon energies. The measurements of four different polyimide films were evaluated. Here we present the final results on film 86a only, for which the most careful measurements were performed yielding the least errors in the final results.

Table 1 shows the results for photon energies between 42 and 950 eV. For lower photon energies sufficient spectral purity could not be achieved. Even 1% and less false light (depending on other parameters) can spoil the data. Measurements were also performed at 1130 and 1345 eV, but in spite of reducing the number of free parameters the fit calculations did not converge to unique values. This is a result of the pronounced curvature in the logarithmic R versus Θ plot, which is closely correlated with Im ϵ , coming to lie far beyond our upper evaluation limit. Nevertheless we want to mention that, even at 1345eV, interference oscillations show up in the measured curves.

For the thickness d of the film the maximum deviation from the mean value of 290.8 nm is 0.4% up to 470 eV. The values for higher photon energies deviate by an integer number of the respective wavelength, which demonstrates that the fit procedure has problems in finding the correct order number of the interference oscillations if they are spaced too closely.

The roughness σ_1 is that of the top of the film, which was originally in contact with the glass substrate, and σ_2 is that of the back surface, which was originally the free surface. It makes sense that the surface that ought to be a replica of the polished glass substrate is smoother. The σ_1 can be determined from the fit with good accuracy while the sensitivity on σ_2 is rather vague.

2. Error Analysis

Table 2 gives the result of an extensive analysis of the errors of the final data. Because of the wide range of photon energies a uniform error analysis in closed form is not possible. We give an analysis for five different photon energies, which are representative also for adjacent photon energies.

Eight different sources of errors were considered as explained in footnote a of Table 2. The determination of these errors required extensive model calculations, keeping all other parameters fixed and varying only a single input value or varying the whole spectrum as was necessary for determining the effects of R(E/2) and R(2/E).

The first six error sources were determined as follows: The error in the fit procedure on each free parameter is calculated by statistical methods. $\Delta N/N$

is determined to be reproducible within 1%. $\Delta \theta_0$ is taken to be 0.02°, which arises mainly from an uncertainty of 0.015° in fixing the absolute scale. The uncertainty in the degree of polarization was estimated to be 20% of the calculated deviation from a complete s polarization. The vertical divergency was assumed to have an error $\Delta \sigma(\theta)$, which is 20% of its value. The uncertainty of the energy calibration has to be assumed to be as large as 0.5% because of frequent changes in the operating modes of the monochromator. Adding the first six errors quadratically yields $(\Sigma \Delta^2)^{1/2}$, which is an error not yet involving any uncertainty of the spectral composition of the radiation. The latter influence is much harder to determine and needs a much more difficult-to-justify model calculation. This is discussed at the end of this section.

We now analyze the results in $(\Sigma\Delta^2)^{1/2}$ in order to identify the dominant contributions. The uncertainty in 1 – Re ϵ of 0.3–3.5% originates at 42 eV from the uncertainty in the fit and the normalization, at 99, 236, and 470 eV almost exclusively from the uncertainty of the angle of incidence, and at 950 eV from the uncertainty from the angle of incidence and its vertical divergence. The uncertainty in Im ϵ of 1.4–44% originates at 42 and 99 eV from the uncertainty of the normalization, at 236 eV in addition from the vertical divergence, at 470 eV from the uncertainty in the fit, and at 950 eV again from the uncertainty in the vertical divergence.

The uncertainty in the roughness of the upper boundary lies between 89% at 42 eV and 3.5% at 470 eV. At 42 eV it originates mainly from the uncertainty in the normalization, at 99 and 235 eV it originates in addition from the uncertainties in the degree of polarization and the angle of incidence, and at 470 eV it originates from the uncertainties in the fit and the angle of incidence. The large error of 27% at 950 eV is mainly caused by the uncertainty in the vertical divergence. The roughness of the lower boundary has larger errors. Where it could be determined at all its uncertainty depends mainly on the uncertainty in the fit, the normalization, and the vertical divergence. The errors in the energy calibration influence only the accuracy in determining the the film thickness where they play the dominant role.

Such an analysis of the errors in detail can serve to guide instrumental developments for future improvement in measuring optical constants. In summary we find that the uncertainty in the angle of incidence is decisive for that of Re ϵ , and the uncertainty of the normalization and the vertical divergence give the main contribution to the error in Im ϵ .

As we mentioned in Section 2.A the operation of the Bumble Bee monochromator is optimized for the suppression of stray light and higher-order radiation. In the range covered here these contributions, as seen by our detector, are kept below 1%. At first sight this appears to be a high spectral purity especially in view of the great energy range covered and the difficulties we encounter in this spectral range when attempting to achieve such a standard. Nevertheless even small contributions of second-order light (2E) and long-wavelength stray light represented here by E/2 distort the angular-dependent reflectance spectra in a systematic way. R(2E) adds contributions that are close to $\theta_i = 90^\circ$, while R(E/2)increases the overall reflectivity at small values of θ_i . The latter influence can be understood easily from looking at Fig. 4. There $R(\theta_i)$ was measured down to only 10^{-4} since false low-energy light falls off less with decreasing θ_i and thus starts to contribute (and finally dominate) the reflectance spectra beyond that level.

The errors in Table 2 because of these effects result from fits of spectra that were calculated by the linear combination of measured spectra and R(E/2) or R(2E) curves. The fractions of false-light contributions are best estimates from various investigations performed with our instrument^{9,19} and do not lend themselves to performing active data correction. The choice of these parameters is discussed in more detail in Ref. 12. How to add statistical errors and systematic errors is a matter of choice. To quote a total error Δ_{tot} , we decided to add quadratically the uncertainty originating from R(E/2), while the better documented R(2E) contribution is added linearily. These additional error contributions influence especially the accuracy with which Im ϵ and σ_1 , σ_2 are determined.

This error analysis leads to a data set as shown in Table 1, which in the field of optical constants is fairly exceptional insofar as the values in Table 1 include error intervals that are well justified. More important, however, the enormous difficulties in obtaining accurate optical constants in the soft x-ray at an accuracy of better than a few percent become obvious. We also clarified in this section the instrumental improvements that are necessary in different spectral regions in order to obtain results with better accuracy. Indeed some of the results are quite remarkable, e.g., the notable influence of small contributions of false light and the fact that the accuracy of the film thickness is just a reflection of the accuracy in the energy calibration of the monochromator.

B. Transmission Measurements

1. Results

Measurements of the transmittance of the same four polyimide films, which were used for the reflectance measurements, were performed between 40 and 1570 eV. Various filters and two different detectors were used. Since the photomultiplier with the Al_2O_3 covered cathode showed saturation effects and instabilities in certain spectral regions, some of the data had to be discarded. Therefore we show only the data of those two films that were measured with the Schottky diode detector. The other data are also evaluated¹² and serve to support the final result.

The edge structures observed in the spectra at 290, 410, and 540 eV originate from the 1s edges of C, N, and O. The absence of any structure at the Si 2p

edge at 100 eV shows that the glass substrate was removed completely when the films were prepared. The expanded data at higher energies (which are not visible in Fig. 5) also display smaller structures at 850 and 1570 eV, which originate from insufficient normalization of the primary spectrum at the Ni 2p and Al 1sedges (the mirror coating and filter).

The extinction coefficient k is calculated from the transmittance data according to the iteration process given in Eq. (20). The film thickness d was taken from the reflectance results. The iteration converges sufficiently well after two steps. The extinction coefficient is the basis of the Kramers-Kronig analysis according to Eq. (3). In order to perform this analysis, we need additional values that are below 40 eV and above 1570 eV. Arakawa et al.20 have published results on polyimide foils (Kapton-H, DuPont) between 0.5 and 70 eV. In the overlapping region their values are higher by 10% than those of our PIQ13 foils (Hitachi). We attribute this difference to differences in the density of the films and assume that the extinction coefficient is proportional to the density. The values of Arakawa et al.²⁰ were multiplied by 0.923. The energy at which the transition to these data is made depends on the quality of our data between 50 and 70 eV for the different samples.

The extrapolation to higher energies is based on the atomic scattering coefficient tabulation of Henke *et al.*²¹ Since the accurate composition of PIQ13 is not published,¹⁷ we used that of Kapton ($C_{22}H_{10}N_2O_5$). The calculation of optical constants as a superposition of the elemental contributions is justified, since all the absorption edges lie way below the region under consideration. The best matching between measured and calculated data is achieved by taking

the density to be 1.40 g/cm³, which is close to the density of Kapton.²² The mismatch at the lower end of our data would suggest, however, a density for PIQ13 of 1.31 g/cm^3 . On the other hand, it is known that Kapton in air can absorb water, thus influencing the density measurements in an unknown way. Above 10,000 eV the extinction coefficient was extrapolated by a power law according to E^{-3} .

The final results for $1 - \text{Re } \epsilon$ and $\text{Im } \epsilon$ are presented in Fig. 6 and Table 3. A remarkable feature is the very low value of $1 - \text{Re } \epsilon$ at the Ca 1s edge. With some of the data $1 - \text{Re } \epsilon$ even changed sign. Within the error margins, as explained below, we attribute no significance to this.

2. Error Analysis

The errors were analyzed by varying the Kramers– Kronig input data according to 12 different sources of error. The total error, which is shown in Fig. 6 by dotted curves as an interval around the final $1 - \text{Re } \epsilon$ and Im ϵ spectra, is obtained by quadratic superposition of the individual errors.

A first group of errors exerts a direct influence on the transmittance data:

(1) Photons of false energy are assumed to influence the data by $\Delta T = 0.001$.

(2) Because of the variation of the beam position in the storage ring between measurements with and without the sample, the reproducibility is 1%.

(3) Energy calibration is uncertain by 0.5%. One should note that this is an important error because of the steep falloff of the optical constants. It poses a special problem at the edges.

(4) The film thickness is uncertain within 0.5%.



Fig. 5. Transmittance T of the polyimide foils P78a (dashed-dotted curve) with d = 252.5 nm and P86a (solid curve), with d = 290.8 nm.

A second group of errors depends on the extrapolations:

(5) The scaling factor in fitting to the data of Arakawa *et al.* is uncertain by 0.5%.

(6) The scaling factor in fitting to the high-energy data is considered to be uncertain by 1%.

(7)/(8) We assumed an increase in the uncertainty of extrapolated values away from the point of fitting as 10%/decade. This agrees at low energies with the error given by Arakawa *et al.*²⁰ at 13 eV as 6%.

(9)/(10) The point at which the transition to the extrapolated values was made could be varied at the upper and lower end of the spectrum.

(11) Extrapolation of the data of Arakawa *et al.*²⁰ to E = 0 could be performed in various ways.

(12) Extrapolation to $E = \infty$ was made as E^{-3} according to free-electron theory, but the data of Henke *et al.*²¹ suggest $E^{-4.3}$ at 10,000 eV.

With the exception of the edge regions [see point (3)] the error in $1 - \text{Re } \epsilon$ decays steadily from 8% at 50 eV to 4% at 1150 eV. The error in Im ϵ is 5% at 50 eV; it drops to 2% at 60 eV, from 120 eV it rises steadily to 4% at 200 eV and reaches 8% just before the C 1s edge. Between the edges it lies around 3%, and from 600 to 1150 eV it rises steadily to 13%. A detailed analysis of the origin of the individual errors is given in Ref. 12.

C. Comparison of Reflectance and Transmittance Results

Figure 6 shows the result of both types of measurement including the error bars and error intervals.

E	$1 - \operatorname{Re} \epsilon$	Im e	E	$1 - \operatorname{Re} \epsilon$	$\operatorname{Im} \epsilon$	E	$1 - \operatorname{Re} \epsilon$	Im e
(ev)	(0.001)	(0.001)	(ev)	(0.001)	(0.001)	(ev)	(0.001)	(0.001)
19.97	553.4	950.1	29.58	356.9	300.5	43.31	195.8	109.6
20.44	560.1	894.9	29.92	350.7	291.5	44.33	188.5	103.0
20.67	563.1	856.4	30.62	338.6	274.4	44.84	184.9	99.87
21.16	552.8	793.9	31.34	327.0	258.2	45.89	177.9	93.82
21.65	548.1	738.8	31.70	321.3	250.5	46.96	171.1	88.12
22.16	538.1	684.3	32.45	310.2	235.8	47.51	167.8	85.40
22.41	531.8	658.6	33.20	299.3	221.9	48.62	161.5	80.19
22.94	517.0	611.3	33.59	294.0	215.3	49.76	155.5	75.27
23.48	500.9	569.0	34.38	283.7	202.6	50.60	151.0	71.68
23.75	492.8	549.8	35.18	273.7	190.7	51.58	145.9	60.09
24.30	476.9	513.8	35.59	268.8	184.9	52.73	140.0	63.82
24.87	461.3	480.9	36.42	259.2	174.0	53.81	135.3	60.52
25.16	453.6	465.4	37.27	249.9	163.7	54.70	131.9	58.18
25.75	438.6	436.4	37.71	245.3	158.8	55.71	127.8	55.21
26.35	423.9	409.5	38.59	236.4	149.3	56.86	123.3	51.11
26.66	416.8	396.8	39.49	227.8	140.4	57.95	118.7	48.85
27.28	402.8	372.8	39.95	223.6	136.2	59.16	114.3	46.25
27.92	389.1	350.3	40.88	215.3	128.0	60.23	110.9	44.20
28.24	382.5	339.7	41.84	207.4	120.3	61.58	106.6	41.70
28.90	369.5	319.5	42.33	203.5	116.7	62.50	104.1	40.02
64.01	99.81	37.47	93.81	48.46	10.63	138.3	21.86	3.106
65.27	96.55	35.28	96.06	46.15	9.862	141.1	20.97	2.901
66.51	93.44	33.51	97.72	44.61	9.338	144.1	20.05	2.699
67.83	90.39	31.49	99.44	43.04	8.806	146.5	19.34	2.558
69.12	87.42	29.73	101.8	40.98	8.172	149.4	18.58	2.409
70.48	84.49	27.79	103.7	39.51	7.732	152.6	17.75	2.240
71.82	81.57	26.20	105.4	38.21	7.327	155.5	17.05	2.106
73.21	78.82	24.54	107.9	36.42	6.821	158.9	16.26	1.964
74.60	76.05	23.10	109.9	35.09	6.460	161.5	15.70	1.866
76.11	73.35	21.57	111.7	33.91	6.117	164.6	15.07	1.762
77.39	70.97	20.34	114.1	32.46	5.720	168.2	14.37	1.643
78.96	68.32	19.10	116.1	31.32	5.427	172.1	13.66	1.522
80.75	65.40	17.60	118.7	29.94	5.069	174.8	13.19	1.469
82.25	63.08	16.58	120.8	28.93	4.797	177.8	12.72	1.381
83.84	60.82	15.48	123.5	27.60	4.461	181.4	12.14	1.294
85.34	58.65	14.58	125.6	26.70	4.251	185.1	11.62	1.233
87.02	56.42	13.69	128.2	25.58	3.971	188.7	11.13	1.149
88.93	54.00	12.67	130.5	24.65	3.739	192.6	10.62	1.083
90.57	52.00	11.94	133.5	23.52	3.476	196.1	10.19	1.024
92.25	50.14	11.26	135.7	22.74	3.305	199.9	9.737	0.9645

Table 3. Results of the T(E) Measurements on Polyimide Film P86a

(Table continued)

Table 3. continued

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	i
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	9
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	15
257.0 4.791 0.4100 378.2 3.310 1.480 557.8 1.768 0.66 261.9 4.403 0.3822 386.0 3.202 1.388 569.8 1.715 0.58 267.7 3.912 0.3519 393.5 3.090 1.304 580.7 1.665 0.55 272.8 3.409 0.3292 401.4 2.913 1.242 591.5 1.624 0.51 278.6 2.670 0.3098 409.4 2.829 1.430 603.0 1.577 0.47 283.3 1.622 0.3138 417.4 2.974 1.272 615.1 1.573 0.44	.6
261.94.4030.3822386.03.2021.388569.81.7150.58267.73.9120.3519393.53.0901.304580.71.6650.55272.83.4090.3292401.42.9131.242591.51.6240.51278.62.6700.3098409.42.8291.430603.01.5770.47283.31.6220.3138417.42.9741.272615.11.5230.44	.5
267.7 3.912 0.3519 393.5 3.090 1.304 580.7 1.665 0.55 272.8 3.409 0.3292 401.4 2.913 1.242 591.5 1.624 0.51 278.6 2.670 0.3098 409.4 2.829 1.430 603.0 1.577 0.47 283.3 1.622 0.3138 417.4 2.974 1.272 615.1 1.523 0.44	3
272.8 3.409 0.3292 401.4 2.913 1.242 591.5 1.624 0.51 278.6 2.670 0.3098 409.4 2.829 1.430 603.0 1.577 0.47 283.3 1.622 0.3138 417.4 2.974 1.272 615.1 1.523 0.44	.4
278.6 2.670 0.3098 409.4 2.829 1.430 603.0 1.577 0.47 283.3 1.622 0.3138 417.4 2.974 1.272 615.1 1.523 0.44	2
983 9 1 699 0 9198 417 4 9 974 1 979 615 1 1 599 0 44	4
200.0 1.022 0.0100 417.4 2.074 1.272 010.1 1.020 0.44	9
289.0 1.083 2.982 425.4 2.891 1.108 627.2 1.472 0.41	51
	•
639.1 1.427 0.3907 941.6 0.6894 0.0960 1392.0 0.3136 0.02	.8
651.4 1.382 0.3658 959.8 0.6642 0.0890	
663.3 1.339 0.3431 977.8 0.6395 0.0833 1426.0 0.2986 0.01	8
675.7 1.296 0.3201 996.6 0.6159 0.0772 1460.0 0.2847 0.01	1
688.8 1.252 0.2990 1015.0 0.5939 0.0721 1496.0 0.2709 0.01	5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0
717.5 1.162 0.2580 1057.0 0.5466 0.0624	_
730.5 1.124 0.2414 1076.0 0.5278 0.0581 1570.0 0.2456 0.01	7
746.9 1.078 0.2236 1096.0 0.5091 0.5500 1609.0 0.2337 0.01	5
761.1 1.040 0.2076 1122.0 0.4860 0.0501 1648.0 0.2226 0.01	.4
775.4 1.003 0.1947 1143.0 0.4681 0.0459 1688.0 0.2120 0.01	4
789.7 0.9699 0.1831	
805.0 0.9329 0.1702 1175.0 0.4424 0.0414 1730.0 0.2017 0.00	5
820.8 0.8997 0.1597 1204.0 0.4210 0.0377 1772.0 0.1921 0.00	6
825.1 0.8901 0.1568 1233.0 0.4011 0.0345 1815.0 0.1830 0.00	9
890.4 0.7702 0.1200 1263.0 0.3821 0.0315 1860.0 0.1742 0.00	1
894.6 0.7636 0.1180 1294.0 0.3637 0.0287 1905.0 0.1660 0.00	5
898.8 0.7567 0.1149	
902.8 0.7497 0.1131 1326.0 0.3461 0.0262 1952.0 0.1581 0.00	9
924.3 0.7160 0.1025 1358.0 0.3298 0.0239 2000.0 0.1507 0.00	4

It is worth mentioning that both methods lead to the same values of the optical constants in the wide energy range covered in this investigation. This is not self-evident since there are many examples in the literature that show considerable discrepancies in optical constants determined by different methods. In most cases, however, the lack of a careful error analysis does not permit the evaluation of the importance of such discrepancies. We demonstrate in a second paper that with Au such discrepancies exist in reality.

Within the error margins these are some systematic deviations, the most noteworthy being the discrepancy in Im ϵ below the C 1s edge. No reasonable explanation for the larger 1 – Re ϵ values from reflectance data compared with those from the transmittance data could be found. Some systematic trends at the upper limit of our measuring interval in both Im ϵ and 1 – Re ϵ are not considered to be as surprising since they lie well within the increasing error bars of the reflectance data. Also, there the sizes of systematic errors could be misjudged much more easily.

5. Conclusion

We have demonstrated that applying two fundamentally different methods of determining optical constants in the soft x-ray region with well-defined samples leads to the same results within the error bars. The errors in $1 - \text{Re } \epsilon$ and Im ϵ in general fall below 10%. The error analysis demonstrates, however, quite clearly the great difficulties that occur when measurements aim at accuracies for these quantites at the 1% level.

In addition to the clarification of these more fundamental problems we have obtained a set of reliable optical constants for polyimide, which belongs to a



Fig. 6. (a), (b) Real and imaginary parts of the dielectric constant ϵ weighted in a way that allows an optimum display over the wide energy range. The solid curves are the results of the Kramers–Kronig analysis of the transmission measurements; the dotted curves give an error interval. The open circles are the results of fits to reflectance measurements of the type shown in Fig. 4.

class of substance of considerable importance in x-ray lithography.

We thank O. Christ, G. Rudolph, and G. Schmahl from the Forschungsgruppe Röntgenmikroskopie, Göttingen, for providing the polyimide foils and C. Blessing and M. Krisch for their assistance during the measurements and for fruitful discussions. Technical support by HASYLAB and the workshop of the II. Institute of Experimental Physics is gratefully acknowledged. The project was supported by the Bundesministerium für Forschung und Technologie under project 05 405 AXB TV 5.

References

- M. Born and E. Wolf, *Principles of Optics* (Pergamon, London, 1975).
- 2. H.-J. Hagemann, W. Gudat, and C. Kunz, "Optical constants from the far infrared to the x-ray region: Mg, Al, Cu, Ag, Au, Bi, C, and Al_2O_3 ," J. Opt. Soc. Am. **65**, 742–744 (1975).
- H.-G. Birken, W. Jark, C. Kunz, and R. Wolf, "Angular dependent photoelectric yield and optical constants of Al between 40 and 600 eV," Nucl. Instrum. Methods A 253, 166-170 (1986).
- H.-G. Birken, C. Blessing, and C. Kunz, "Determination of optical constants from angular-dependent photoelectric-yield measurements," in *Optical Constants of Solids*, E. D. Palik, ed. (Academic, Orlando, Fla., 1991), pp. 279–292.
- A. P. Lukirskii, E. P. Savinov, O. A. Ershov, and Yu F. Shepelev, "Reflection coefficients of radiation in the wavelength range from 23.6 to 113 Å for a number of elements and substances and the determination of the refractive index and absorption coefficient," Opt. Spectrosc. (USSR) 16, 168–172 (1964).
- 6. L. R. Canfield, G. Hass, and W. R. Hunter, "The optical properties of evaporated gold in the vacuum ultraviolet from 300 Å to 2000 Å," J. Phys. (Paris) **25**, 124–129 (1964).
- 7. H. Ehrenreich and H. R. Philipp, "Optical properties of Ag and Cu," Phys. Rev. **128**, 1622–1629 (1962).
- H. Hogrefe, D. Giesenberg, R.-P. Haelbich, and C. Kunz, "A new VUV-reflektometer for UHV-applications," Nucl. Instrum. Methods A 208, 415–418 (1983).
- 9. W. Jark and C. Kunz, "Output diagnostics of the grazing incidence plane grating monochromator Bumble Bee (15–1500 eV), Nucl. Instrum. Methods A **246**, 320–326 (1986).
- S. V. Pepper, "Optical analysis of photoemission," J. Opt. Soc. Am. 60, 805–812 (1970).
- E. Spiller and A. E. Rosenbluth, "Determination of thickness errors and boundary roughness from the measured performance of a multilayer coating," in *Applications of Thin-Film Multilayered Structures to Figured X-Ray Optics*, G. F. Marshall, ed. Proc. Soc. Photo-Opt. Instrum. Eng. 563, 221-236 (1985).

- R. Wolf, "Vergleich von optischen Konstanten aus Reflexionsund Transmissionsmessungen im Bereich weicher Röntgenstrahlung am Beispiel von Polyimid und Gold," Ph.D. dissertation (Universität Hamburg, Hamburg, Germany, 1989); Internal Rep., DESY F41, HASYLAB 89-13 (DESY, Hamburg; 1989).
- P. Beckmann and A. Spizzichino, The Scattering of Electromagnetic Waves from Rough Surfaces (Pergamon, London, 1963).
- J. M. Eastman, "Scattering by all-dielectric multilayer bandpass filters and mirrors for lasers," in *Physics of Thin Films*, G. Hass and M. H. Francombe, eds. (Academic, New York, 1978), Vol. 10, pp. 167–226.
- M. Krumrey, E. Tegeler, J. Barth, M. Krisch, F. Schäfers, and R. Wolf, "Schottky type photodiodes as detectors in the VUV and soft x-ray range," Appl. Opt. 27, 4336–4341 (1988).
- G. Schmahl and D. Rudolph, Forschungseinrichtung Röntgenphysik, Universität Göttingen, Geiststrasse II, W-3400 Götingen, Germany (personal communication, 1986).
- Hitachi Chemical data sheet Y-114 (Hitachi Chemical, Tokyo, 1985).
- H.-G. Birken, C. Blessing, C. Kunz, and R. Wolf, "Investigations on the consistency of optical constants in the XUV determined by different methods," Rev. Sci. Instrum. 60, 2223-2226 (1989).
- W. Jark, "Eigenschaften reflektierender optischer Komponenten und deren Zusammenwirken in einem Monochromator für weiche Röntgenstrahlung," Ph.D. dissertation (Universität Hamburg, Hamburg, Germany, 1985); Internal Rep., DESY F41, HASYLAB 85-14 (DESY, Hamburg; 1985).
- E. T. Arakawa, M. W. Williams, J. C. Ashley, and L. R. Painter, "The optical properties of Kapton: measurement and applications," J. Appl. Phys. 52, 3579–3582 (1981).
- B. L. Henke, P. Lee, T. J. Tanaka, R. L. Shimabukuro, and B. K. Fujikawa, "Low energy x-ray interaction coefficients: photoabsorption, scattering, and reflection," At. Data Nucl. Data Tables 27, 1–144 (1982).
- 22. A. Krempel, Eigenschaften von Kapton Typ H, F und HD, Data Sheet (A. Krempel u. Soehne, Stuttgart, Germany, 1989).