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GAS ADSORPTION STUDIES BY ELLIPSOMETRY IN COMBINATION WITH LOW
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Gas Adsorption Studies By Ellipsometry In Combination With Low
Energy Electron Diffraction and Mass Spectrometry*

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ABSTRACT

Isotherms for physical adsorption on a silver single crystal surface from ultrahigh vacuum have been determined by ellipsometry. Molecular volumes, derived from the optically determined monolayer film thickness, indicate that the classical macroscopic theory of ellipsometry for film covered surfaces is surprisingly well suited for physically adsorbed coverages of molecular dimensions. For a fractional monolayer coverage, the electron diffraction pattern has been found to remain characteristic of the clean substrate surface. The results also show the difficulties in the preparation and definition of clean solid surfaces, and indicate a sensitivity of the ellipsometer for surface roughness on an atomic level.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

Ellipsometry and low energy electron diffraction (LEED) have some complimentary properties, which make it desirable to combine¹ the two for resolving uncertainties inherent in both techniques when employed separately. For use in adsorption studies, ellipsometry is basically coverage sensitive while LEED is structure sensitive. Two recurring problems in ellipsometry may profit from such a combination of capabilities, namely:

- (1) The question as to when a clean surface has been obtained and what its optical properties are, and
- (2) The question as to how well the classical theory of ellipsometry, which is based on a continuum model of matter and employs macroscopic physical properties, applies to films of molecular coverage.

In recent years, a considerable technology has been developed for the preparation of single crystal surfaces, determined to be atomically clean in ultrahigh vacuum by low energy electron diffraction. It appeared desirable to employ these techniques for preparing ellipsometer reference surfaces. On the basis of additional diffraction features, ordered adsorption can often be ascribed to one or more possible coverages. A comparison of these coverages with simultaneous ellipsometer results may result in a preferred alternative and thus, provide valuable cross-checks between both techniques. The measurement of disordered adsorbed layers by ellipsometry, at present not quantitatively observable by LEED, would further the interpretation of diffraction data from such surfaces.

Equipment

The equipment built for this study² is sketched in Fig. 1. Ellipsometer

components from a commercial instrument have been mounted on a Table E which can be rolled over part of the LEED apparatus N and is reproducibly positioned by means of spacers and tapered pins between both frames. This arrangement avoids repetition of the time-consuming optical alignment process every time the ellipsometer has to be removed for baking out the vacuum system. One can recognize the collimator with the polarizer circle F followed by the compensator G, and the telescope with the analyzer circle K. A mercury arc C with glass filters has mostly been used as a light source. The beam is modulated with a rotating chopper D which provides a reference signal for a phase-sensitive detector A which in turn measures the signal from the photomultiplier L. Except for minor adjustments, collimator and compensator are mounted in fixed positions. The telescope is provided with rotatory and translatory degrees of freedom in vertical and horizontal direction for optical alignment, and can be laterally moved out of the way on the carrier O for observation of the diffraction pattern through the front window of the vacuum chamber. The optical arrangements allows azimuth measurements, as determined from two off-minimum readings, which are reproducible to $\pm 0.01^\circ$.

The LEED system has been laboratory-built from commercially available components. The chamber H (Fig. 1) contains the electron optics and the specimen on a specially built holder, which allows temperature variation between about -195° and $+200^\circ\text{C}$. Gases to be adsorbed are admitted by a variable leak valve; the resulting atmosphere, as well as the residual vacuum constituents, are monitored with a quadrupole mass spectrometer, connected to the flange M on the bottom of the LEED chamber below the specimen.

The windows on the LEED chamber are made of Corning 7056 borosilicate glass, selected for lack of birefringence and optical inhomogenities. A frequently neglected problem of ellipsometry concerns the orientation of chamber windows with respect to the light beam. Measurements with the unmounted 3/8" thick windows are shown in Fig. 2. They demonstrate that within one degree of normal incidence ($\phi = 0^\circ$), the measured relative phase and amplitude parameters Δ and ψ are affected by less than 0.01° by the presence of a window. Its alignment is, therefore, not very critical as long as it is oriented normal to the optic axis. However, any non-normal orientation would have to be determined with extreme accuracy, in order to quantitatively account for the effect of windows on the measurements.

Specimen Preparation

The preparation of crystal surfaces for the simultaneous use in ellipsometry and low energy electron diffraction can present considerable problems, because the chemical etching, routinely used in LEED studies to expose the undisturbed lattice, does not result in the flat, optically polished surfaces desirable for ellipsometry. Adequate³ silver surfaces have been obtained by chemical polishing with mechanically controlled mass transfer.⁴

Bare Substrate

Basic to any adsorption experiment are the properties of the bare substrate. For measurements by ellipsometry, the optical constants of the bare substrate must be known at the temperatures to be employed. Optical constants of metals, particularly of silver,⁵ found in the literature, show considerable scatter and very little data on temperature depen-

dence⁶ are available. For surfaces shown to be clean by electron diffraction, the determination of optical constants by ellipsometry was expected to give unambiguous results. However, different complicating factors have been encountered in this measurement. Two of them, namely the problems of surface contamination and topography, will be discussed here, because they relate to important questions in ellipsometry. The results⁷ shown in Fig. 3 have been obtained with one particular surface under the best possible exclusion of contamination effects.⁹

It is useful to remember that, even in ultrahigh vacuum, an ideally clean surface becomes contaminated in a finite period of time. These times can approximately be calculated for low specimen temperatures, where the sticking coefficient for the impinging gas molecules can be assumed to approach unity and to be independent of coverage. Then the rate of condensation R (milligrams/cm² sec) is given by

$$R = (p/1.72 \times 10^{-2}) \times \sqrt{M/T}$$

where p - (atm) pressure in torr, M - molecular weight, T - gas temperature in °K. Results obtained by this expression for butane and water are shown in Fig. 4 in the form of the time required for monolayer formation as a function of gas pressure. It can be seen that with 4×10^{-10} torr of water a monolayer is formed in thirty minutes. A cold surface can, therefore, be expected to remain clean only for times in the order of three minutes, when 0.1 monolayer, the approximate detection limit in these experiments, has been formed.¹⁰

An instructive example of contamination is documented by the next three figures. Figure 5 shows the increase in film thickness computed from the ellipsometer measurements. The origin of time and thickness

(curve 5) could therefore be mistaken as that of a clean surface (curve 1).

Apart from contamination, surface topography may affect the optical constants of bare substrates determined by ellipsometry. The (110) face of silver crystals is known to be unstable.⁴ Facets of (111) and (100) orientation have been shown in the literature to appear upon prolonged heating in vacuum above 600°C, and this process is accelerated by the presence of certain gases.¹² It appears that ellipsometry is able to detect a precursor to this microscopically visible faceting after much milder treatments: A systematic difference in the relative phase change Δ of 0.3° has been found in the optical properties of clean silver (110) surfaces, depending on whether they had been heated below 85° or above 140° in the cleaning process. The exposure of other crystal faces by this treatment can also be inferred from surface-Debye temperatures derived from LEED intensity measurements. The results from such measurements, shown in Fig. 9, fall into two categories which coincide with the different surface treatments.

If the optical effects of surface roughness on a scale below the wavelength of light can be represented as a transitional layer between the bulk substrate and the vacuum, with optical properties intermediate between the two phases and a thickness corresponding to a mean variation in the surface profile, the expected effect of surface roughness on the measured relative phase change Δ can be computed. In this model of surface roughness, a smooth surface with few grooves is represented by a transitional layer of more metal-like properties (large fractional metallic properties) while few protrusions from a plane are described by more vacuum like properties of this hypothetical layer.¹³ Results of computations for different fractional metallic properties of the transitional layer, deter-

mined with the Clausius-Mosotti equation,¹⁴ are given in Fig. 10.¹⁵ It can be seen that the observed change in Δ of 0.3° corresponds to changes in surface roughness in the Angstrom range for all assumed optical properties of the transitional layer.

If the above interpretations are correct, then two conclusions with serious consequences for the use of ellipsometry must be drawn:

(1) Ellipsometry may not be a suitable technique for the precise determination of optical constants of solid materials, even if all the instrumental sources of error for absolute measurements were eliminated.

(2) The cleanliness of a surface cannot be judged a priori from the measured ψ and Δ values.

In the case of our measurements on silver, an uncertainty of 0.3° in Δ , presumably due to minute changes in surface roughness, corresponds to errors in n of 3% and in κ of 2%, as can be derived from Fig. 11. Instrumental factors which affect the absolute accuracy of ellipsometer measurements, particularly non-ideal compensator,¹⁶ are analyzed in detail in the literature. Little attention has been given, however, to azimuth errors of the fixed ellipsometer element, which are not diminished by the simple four zone averaging procedure, and to deviation from the nominal angle of incidence, particularly the spread of angles due to finite source size. Birefringence in cell windows can also result in absolute errors of several degrees. While the absence of birefringence in windows can be established with reasonable certainty by comparing the azimuth circle alignments¹⁷ with and without windows, the effect of inadvertently present birefringence is difficult to account for. A possible technique for this purpose involves the use of an environment-independent reflecting surface, for which a metallized totally reflecting prism has been

used with good success.

Adsorption

The adsorption experiments to be reported have all been conducted under conditions of physical adsorption, i.e. weak interaction between film and substrate. Because of the contamination of vacuum chamber and electron optics and the release of previously pumped constituents, particularly CO, Ar and H₂ from the ion pump, the pressures employed have usually been restricted to below 10⁻⁶ torr. The lowest temperature used has been limited by contamination rates from the residual atmosphere and chosen to be -70°C. At this temperature, the effect of contamination remained below the detection limit of the ellipsometer during about 15 minutes. For the interpretation of adsorption measurements, it is important to differentiate between the usually rapidly reached equilibrium thickness of the adsorbed layer of admitted gas and a steady state thickness primarily due to contaminants and reached after much longer times. All the film thicknesses were computed from the ellipsometer measurements according to the classical theory with refractive indices for the bulk liquid phase^{18,19} at the temperatures involved (Table I). From the first step of film thickness-time relationships, like the one shown in Fig. 12, adsorption isotherms in terms of optical thickness have been derived. Typical results for krypton, oxygen and acetylene are given in Fig. 13. Every data point has been obtained by first desorbing contaminants from the crystal at 85° in vacuum, then admitting a given gas pressure and rapidly cooling the specimen to the desired temperature. From families of isotherms, heats of adsorption as a function of coverage have been derived by use of the Clausius-Clapeyron relation (Fig. 14). The results confirm the weak interaction between adsorbate and substrate. Thus, thermodynamic

data for single crystal surfaces can be obtained by ellipsometry.

Correction of the indicated pressure by a constant factor, to account for a possible pressure gradient between specimen and gauge, will shift the adsorption isotherms but not affect the heats of adsorption. Errors in the absolute values of ψ and Δ , although serious in the determination of optical constants, are not of importance for film thickness determinations within any likely error limits. Computations given in Fig. 15 show that the thickness of an n-butane film, derived from relative Δ measurements, is affected by only 7% by the substantial variations in substrate optical constants which result from an absolute error in Δ of 7° .

A comparison of coverages by adsorbed molecules, as determined by ellipsometry and LEED has not been possible because no ordered adsorptions have been obtained so far. Another, less direct test of the classical theory of ellipsometry has been carried out and seems to confirm the measured monolayer film thicknesses: If one determines the monolayer film thickness from the pressure-independent part of the adsorption isotherm, and derives the molecular area in the film⁴ by use of the bulk density of the adsorbed material (Table I), the results compare well with literature data from volumetric adsorption work (Table II) based on nitrogen as a standard. Similar conclusions on the applicability of the classical theory of ellipsometry for determining the amount of the material in partial monolayers have been drawn by Smith¹⁸ and Bootsma and Meyer.²⁰

Discussion

Ellipsometry has been successfully employed for the determination of

adsorption isotherms, heats of adsorption and molecular areas of different gases at low temperatures on a single crystal surface. The sensitivity of ellipsometry to fractional monolayer coverages, expected on theoretical grounds and found with other systems^{18,21} has been confirmed. However, ellipsometer measurements seem to depend also on surface roughness and it may be possible to develop submicroscopic roughness measurements from this dependence.

An important conclusion from this study is that the preparation of clean surfaces, even in ultrahigh vacuum environment, is by no means a trivial problem. The principal limitation of the optical arrangement used lies in the 45° angle of incidence, which is due to the arrangement of window ports in the LEED chamber. Computations illustrated in Figs. 16 and 17 show that for both, the determination of optical constants of the bare substrate and the thickness of dielectric films, a three times higher sensitivity can be obtained at an angle of incidence of 80° .

A possible explanation for the apparent lack of sensitivity of the low energy electron diffraction technique to fractional monolayers of physically adsorbed species lies in a patch coverage of the surface. Within certain limits, the size of such patches may be amenable to analysis by ellipsometry with variable lateral coherence of the incident beam.

TABLE I.

Physical Properties of Adsorbates
Used in Computations

Gas	Temperature, °C	Density	Refractive Index
Kr	-63.8	0.908	1.26
Xe	-70	2.8	1.46
O ₂	-118.8	0.43	1.22
CH ₄	-72	0.22	1.13
C ₂ H ₄	-66	0.51	1.32
C ₂ H ₂	-84	0.62	1.36
n-C ₄ H ₁₀	-42	0.64	1.37

TABLE II.

Cross sectional areas of adsorbed molecules. Comparison of results derived from ellipsometer measurements with literature values ($\text{\AA}^2/\text{molecule}$)

Gas	Ellipsometry	Literature
Kr	25.6	21.5
Xe	19.6	22.5
O ₂	26	17.4
C ₂ H ₂	18.3	22.0
n-C ₄ H ₁₀	42	43.4

Footnotes

1. A combination of ellipsometry with LEED has recently been reported by: A. J. Melmed, H. P. Layer, and J. Kruger, Surface Sci. 9, 476 (1968).
2. R. H. Muller, Rev. Sci. Instr. 39, 1440 (1968).
3. Micro-roughness approx. 800 \AA , as determined by double beam interference microscopy, numerical aperture of objective 0.63.
4. J. Morabito, R. Steiger, R. Muller and G. Somorjai, Proc. Fourth Intl. Materials Symposium, Univ. of Calif. Berkeley, June 19-21 (1968), Wiley (to be published).
5. L. G. Schutz, J. Opt. Soc. Amer. 44, 357 (1954); L. G. Schutz and F. R. Tangherlini, J. Opt. Soc. Amer. 44, 362 (1954).
6. T. Smith, J. Opt. Soc. Amer. 57, 1207 (1967).
7. The conventions and definitions employed in this work are those preferred elsewhere in this volume,⁸ except for the positive coordinate direction of the reflected p-component where the second alternative has been used.
8. R. H. Muller, Conventions and Definitions in Ellipsometry, this volume.
9. The optical constants shown must still be considered approximate because the effect of strain-induced birefringence in one of the chamber windows, determined with a prism reference surface after the conclusion of the experiments, had to be applied as a correction to the measurements. The room temperature results are in reasonable agreement with values reported by Schulz.⁵

10. Due to the simplifying assumptions used in this computation, somewhat longer times can be expected in practice.
11. A. J. Van Bommel and F. Meyer, *Surface Sci.* 8, 381 (1967).
12. A. J. W. Moore, *Thermal Faceting, Metal Surfaces*, Am. Soc. Metals (1963).
13. A more sophisticated approach of this kind, which employs continually changing optical properties, represented by multiple layers, has been reported by Fenstermaker and McCrackin.¹⁴
14. C. A. Fenstermaker and F. L. McCrackin, *Errors Caused by Surface Roughness in Refractive Index Measurements by Ellipsometry*, this volume.
15. Qualitatively the same results have been obtained with optical constants for the transitional layer derived by linear interpolation of n and κ between metal and vacuum.
16. D. A. Holmes, *J. Opt. Soc. Amer.* 54, 1115 (1964).
17. F. L. McCrackin, E. Passaglin, R. R. Stromberg and H. L. Steinberg, *J. Res. Natl. Bur. Standards* 67A, 363 (1963).
18. T. Smith, *J. Opt. Soc. Amer.* 58, 1069 (1968).
19. J. Kruger and W. J. Ambs, *J. Opt. Soc. Amer.* 49, 1195 (1959).
20. G. A. Bootsma and F. Meyer, *Surface Sci.*, to be published.
21. R. O. Archer, *Ellipsometry in the Measurement of Surfaces and Thin Films*, E. Passaglia, R. R. Stromberg and J. Kruger, Eds. National Bur. Standards, Misc. Publication 256 (1964).
22. E. R. Jones, J. T. McKinney and M. B. Webb, *Phys. Rev.* 151, 476 (1966).

Figure Captions

Fig. 1. Ellipsometer for attachment to LEED equipment.

- A. Phase sensitive detector
- B. Remote read-out for A
- C. Mercury arc light source
- D. Light chopper
- E. Top of movable ellipsometer table
- F. Polarizer azimuth circle on collimator
- G. Compensator azimuth circle
- H. LEED chamber
- I. Specimen holder
- K. Analyzer azimuth circle on telescope
- L. Photomultiplier housing
- M. Flange on LEED chamber for connecting mass spectrometer
- N. Table top of LEED apparatus
- O. Telescope carrier with lateral translation
- P. Retractable swivel casters
- Q. Adjustable legs

Fig. 2. Errors in ellipsometer measurements ψ and Δ due to non-normal incidence ϕ on a plano parallel window of $3/8$ " thick glass (Corning 7056).

Fig. 3. Complex refractive index $n(1 + i \kappa)$ of a silver (110) surface for wavelengths of 5461\AA and 5893\AA .

Fig. 4. Low temperature contamination of silver (110) computed for sticking coefficient = 1, gas temperature 25°C , monolayer coverages

Ag:H₂O = 2:1, Ag:butane = 4:1, number of silver atoms $8.5 \times 10^{14}/\text{cm}^2$

Fig. 5. Water contamination of a silver (110) surface at -195°C, indicated pressure, 4×10^{-10} torr, refractive index used 1.309.

Fig. 6. Water content of residual atmosphere during formation of contamination layer in Fig. 5, indicated pressure 4×10^{-10} torr.

Fig. 7. Specular reflection of 94 Volt electrons during formation of contamination layer in Fig. 5. Optical intensity measurement of the zero order diffraction spot by means of a telephotometer.

Fig. 8. Specular reflection of electrons during formation of contamination layer

Curve	Time (min.)	Temp.(°C)
1	0	26
2	25	-196
3	40	-196
4	75	-196
5	105	-196
6	135	-196
7	150	-196

Fig. 9. Surface Debye temperatures for a silver (110) face after different surface treatments, indicating precursor to faceting due to heating above 140°C. Broken line literature data for (111) face. Bulk Debye temperature = 225°K.

Fig.10. Surface roughness of silver ($n = 0.082$, $\kappa = 44.0$) treated as transitional layer with optical properties intermediate between

metal and vacuum. Wavelength 5461 \AA , angle of incidence 45° .

Fraction of metallic properties of transitional layer indicated on the curves.

1/4	-	$n = 1.54, \kappa = 0.0045$
1/2	-	$n = 2.47, \kappa = 0.012$
3/4	-	$n = 7.05, \kappa = 0.092$

Fig. 11. Computed relationship between ellipsometer parameters ψ and Δ and optical constants n and κ of a bare, smooth reflecting surface.

Angle of incidence 45° , complex refractive index $n(1 + i\kappa)$.

Fig. 12. Contamination of a 6 \AA thick monolayer of krypton on silver (100) by residual hydrocarbons, 5×10^{-10} torr, -53°C .

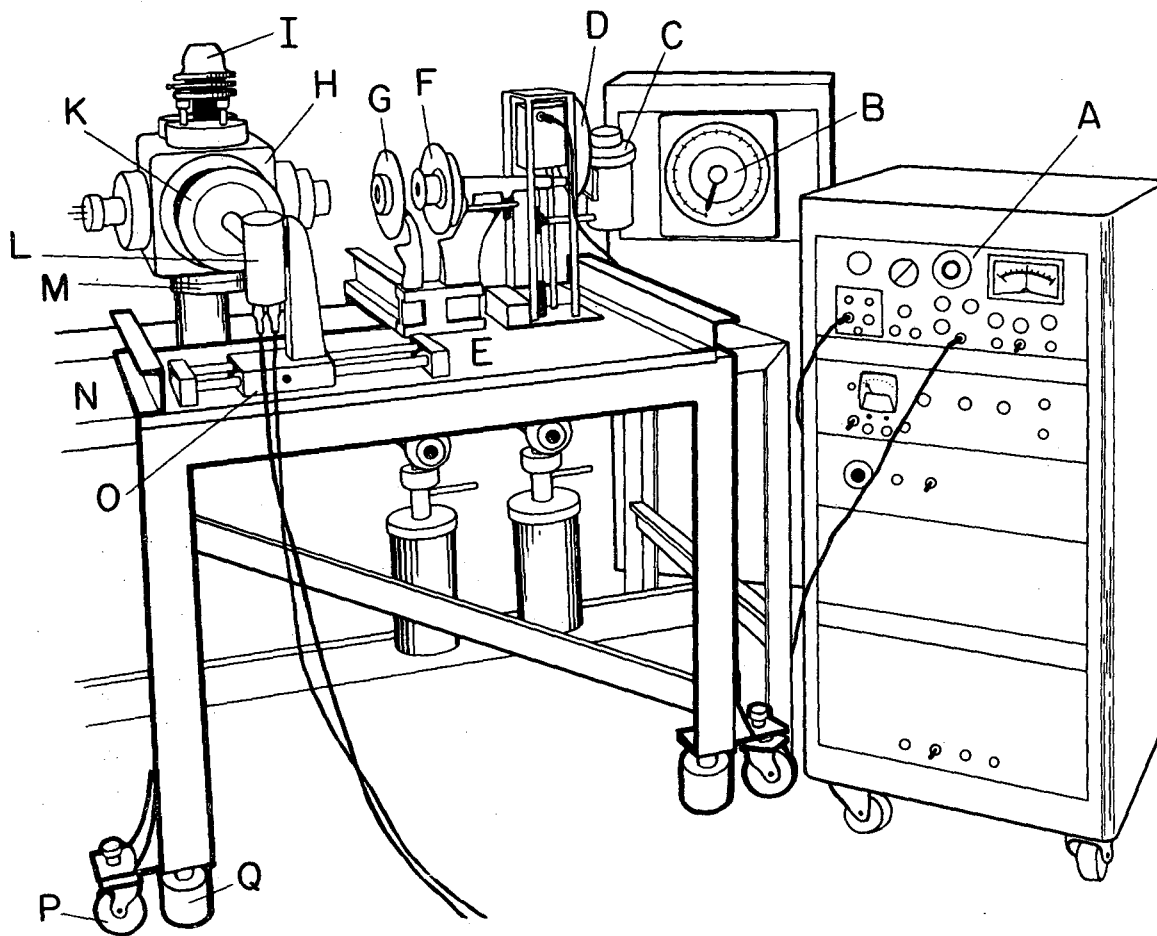
Fig. 13. Adsorption isotherms of krypton, oxygen and acetylene on silver (110) in terms of film thickness determined by ellipsometry.

Fig. 14. Isosteric heats of adsorption derived from adsorption isotherms with extrapolation to zero coverage.

Fig. 15. Effect of a 7° error in the absolute value of Δ on the optical constants n and κ of a silver substrate and the measured film thickness of n-butane ($n = 1.3$) derived from the change in Δ due to the adsorption.

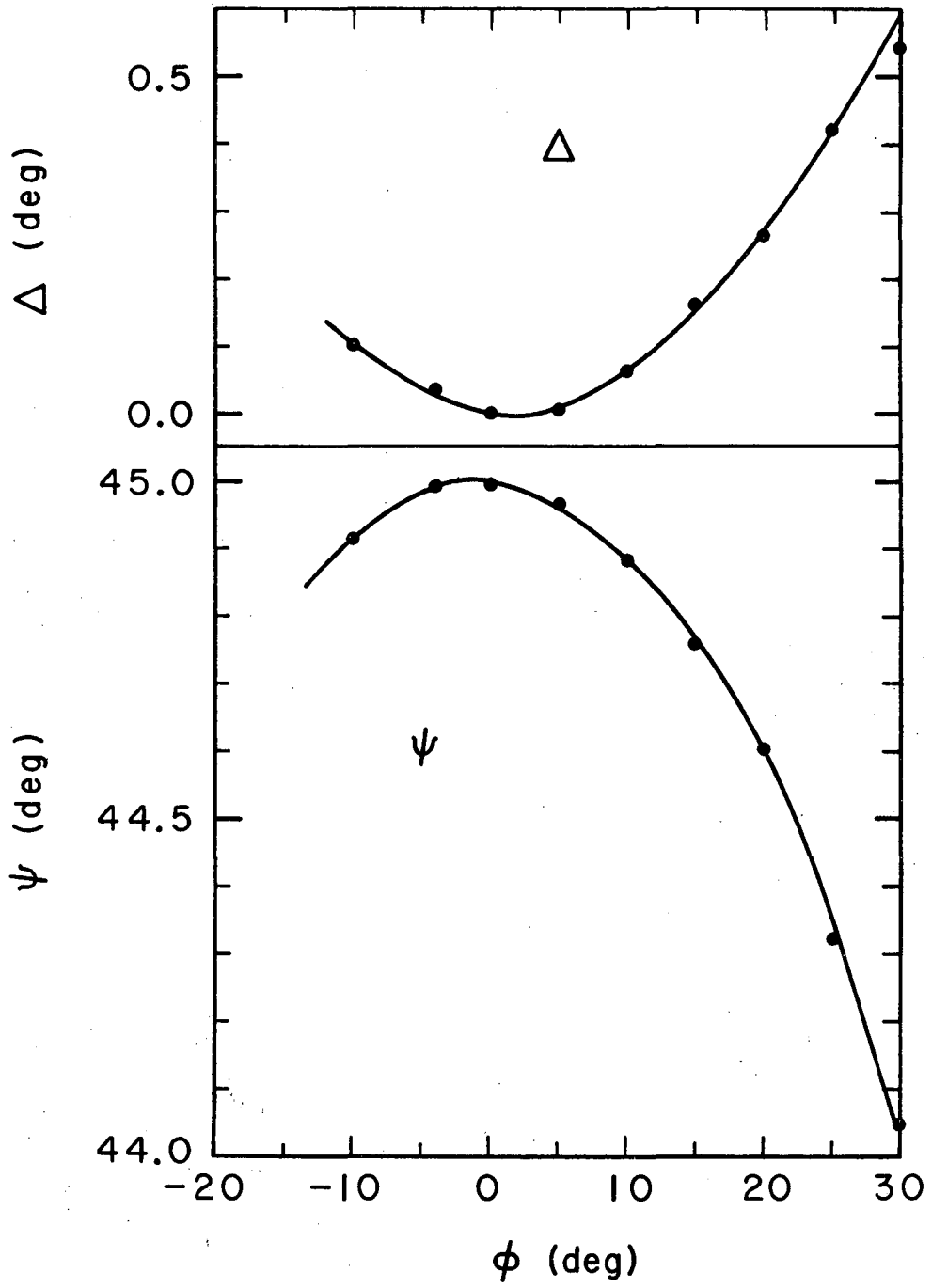
Fig. 16. Sensitivity for the determination of the optical constants of bare silver ($n = 0.14, \kappa = 34.0$) from ellipsometer measurement of ψ and Δ .

Fig. 17. Sensitivity for the determination of the thickness of a dielectric film ($n = 1.35$) on a silver substrate ($n = 0.14, \kappa = 34.0$) from ellipsometer measurement of ψ and Δ .



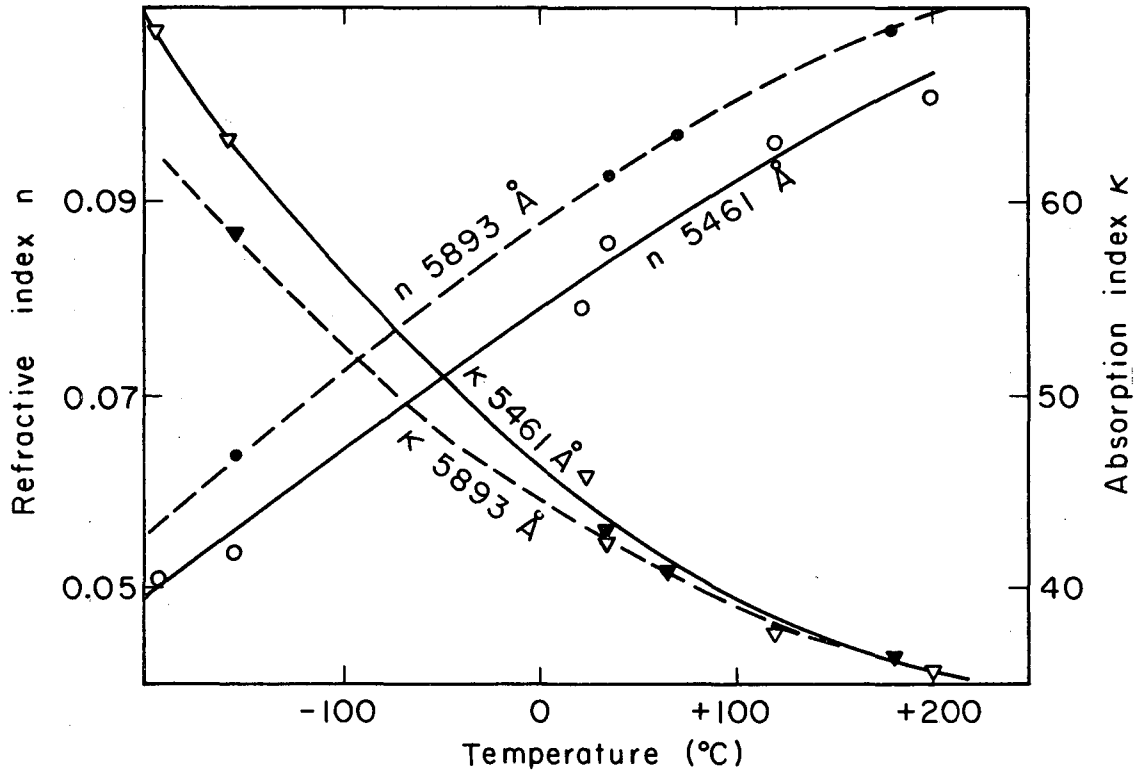
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Figure 1



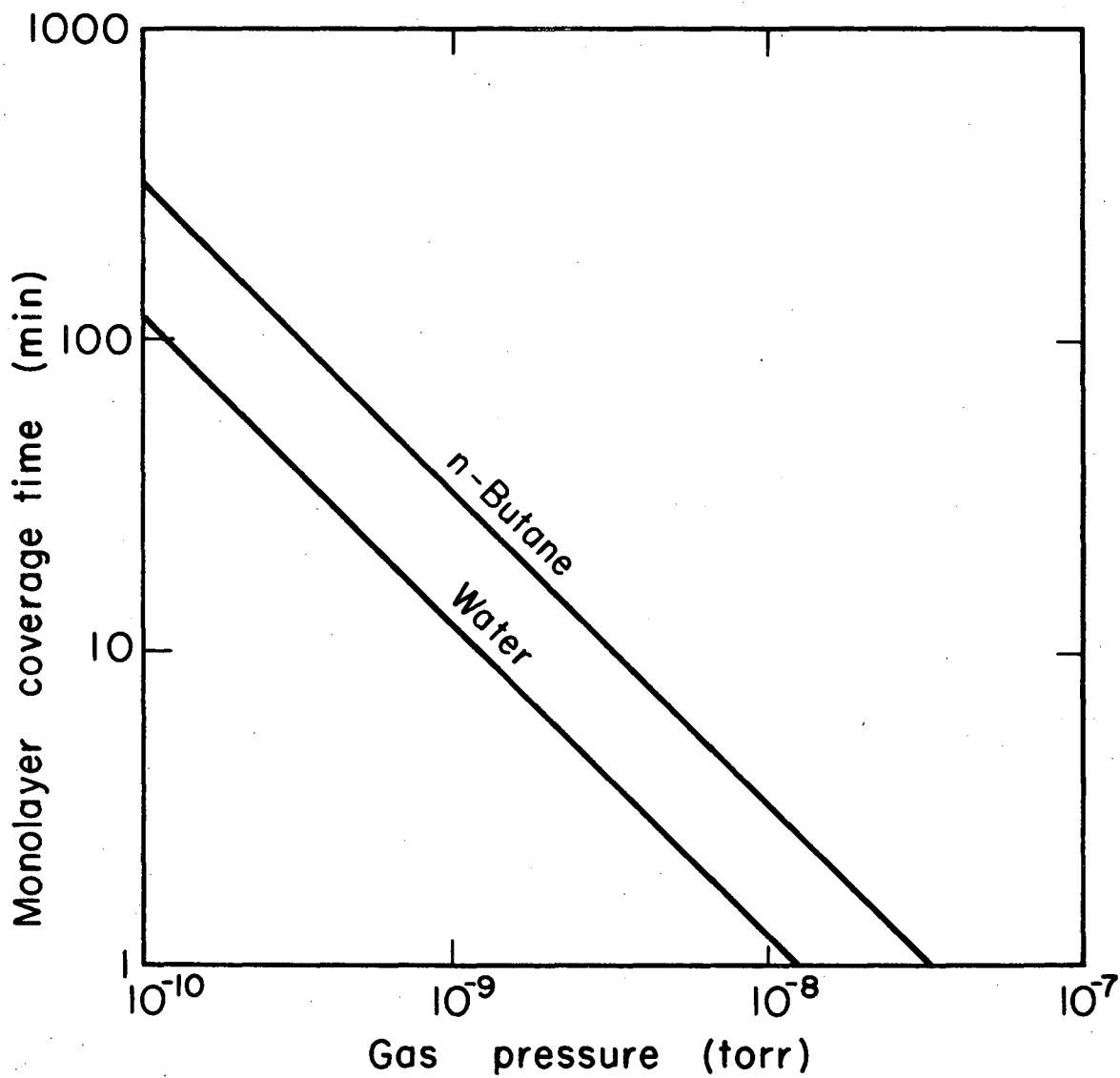
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Figure 2



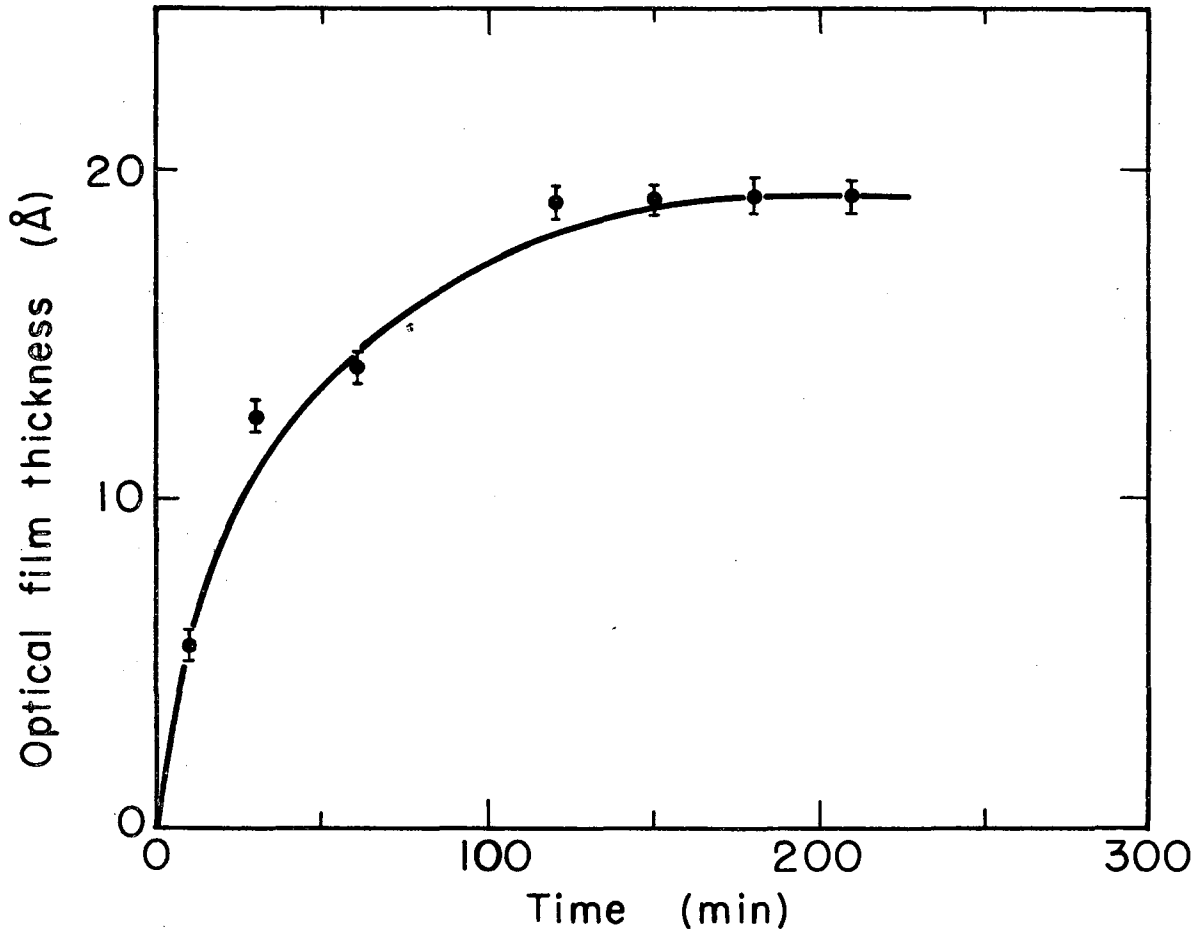
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Figure 3



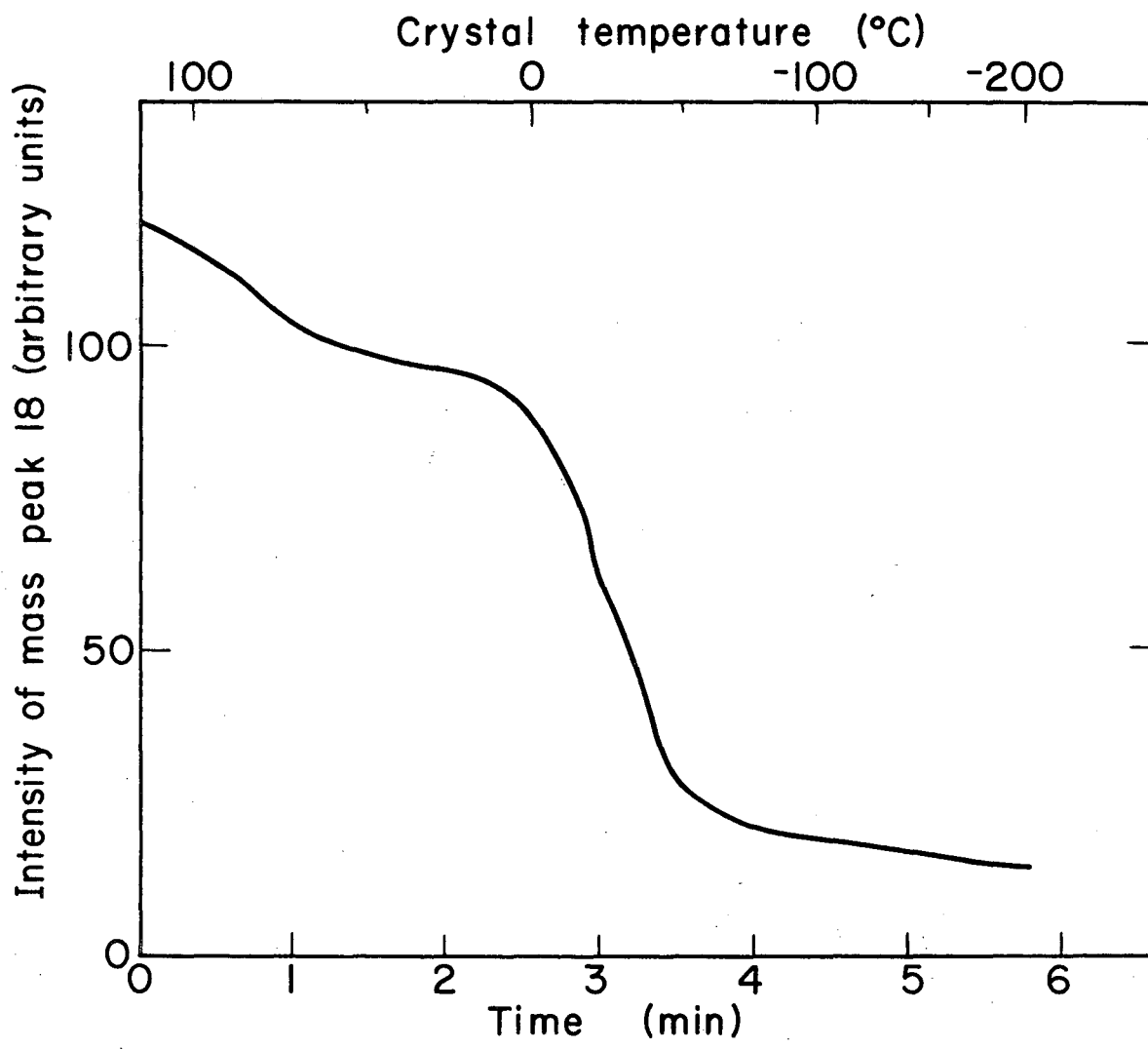
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Figure 4



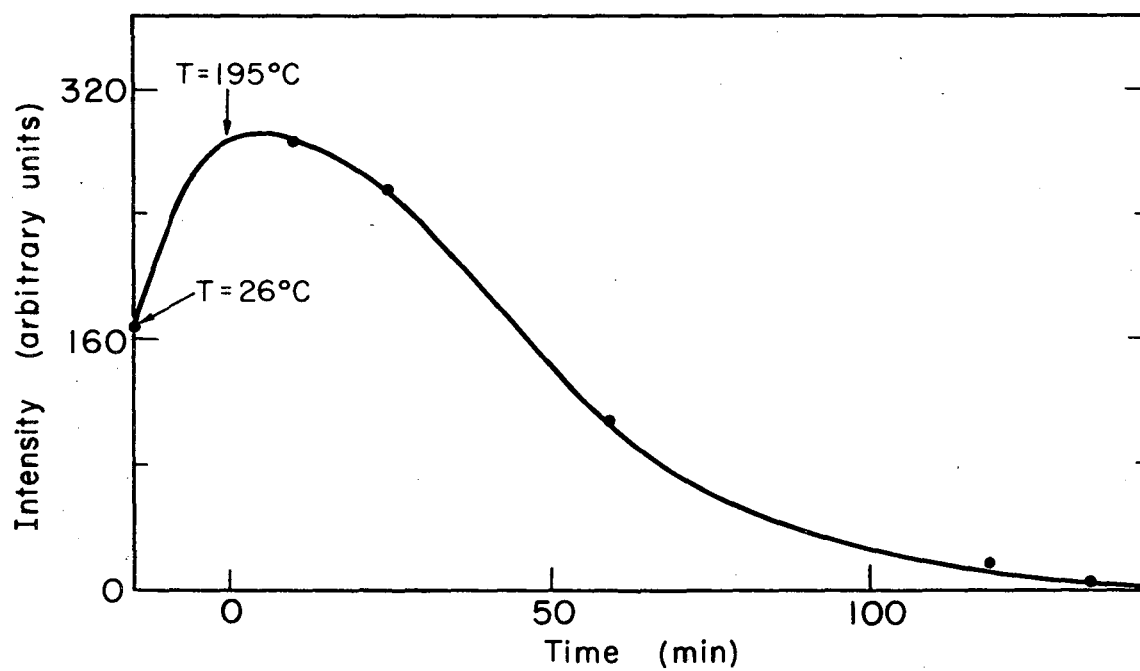
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Figure 5



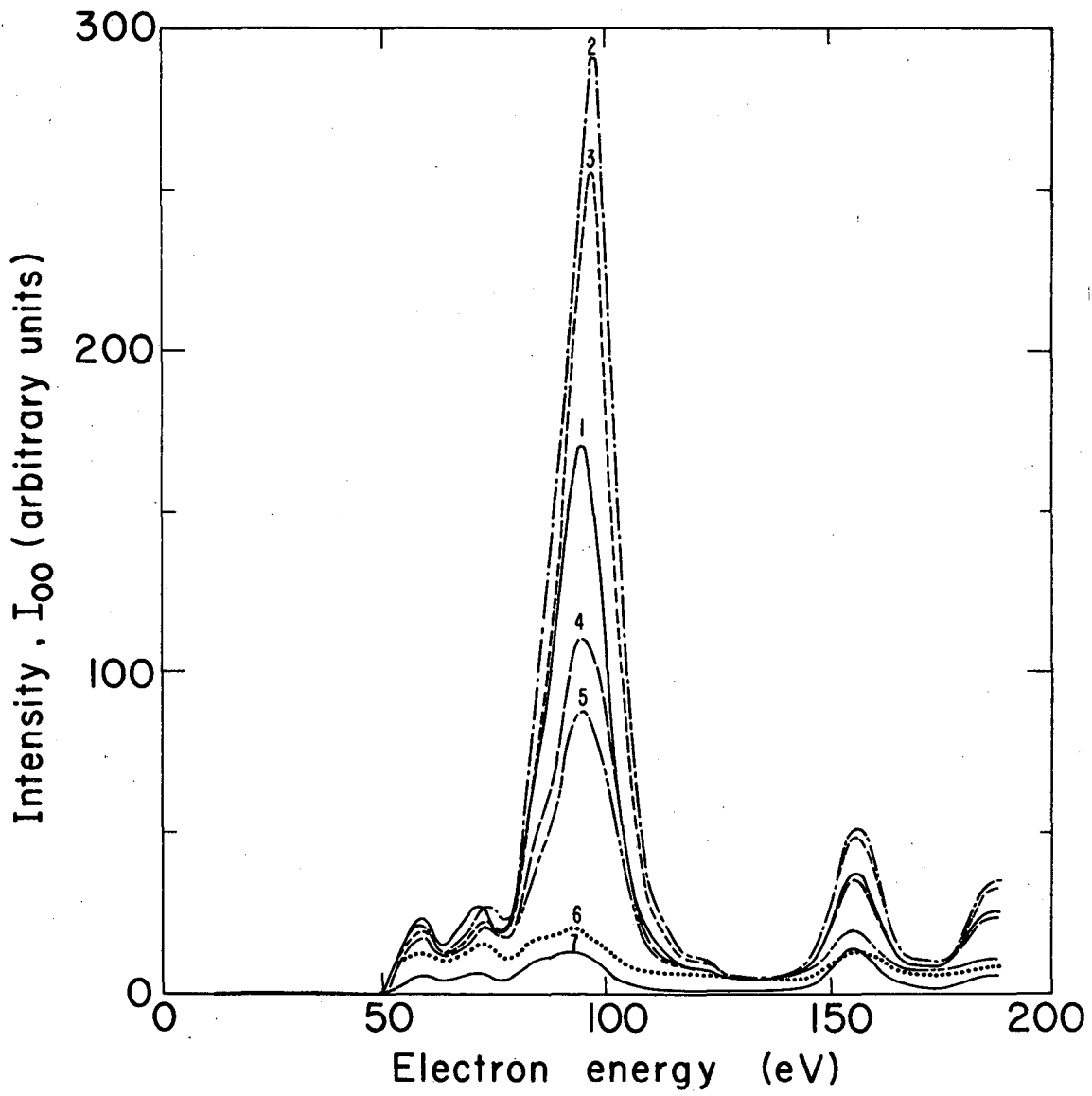
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Figure 6



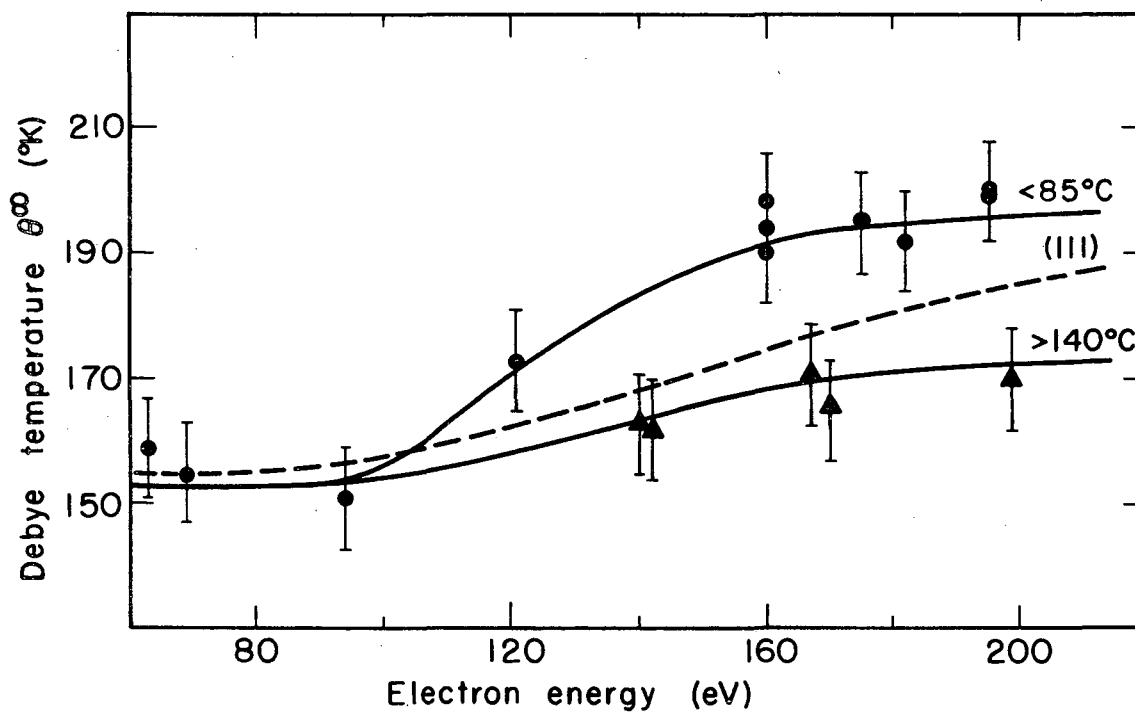
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Figure 7



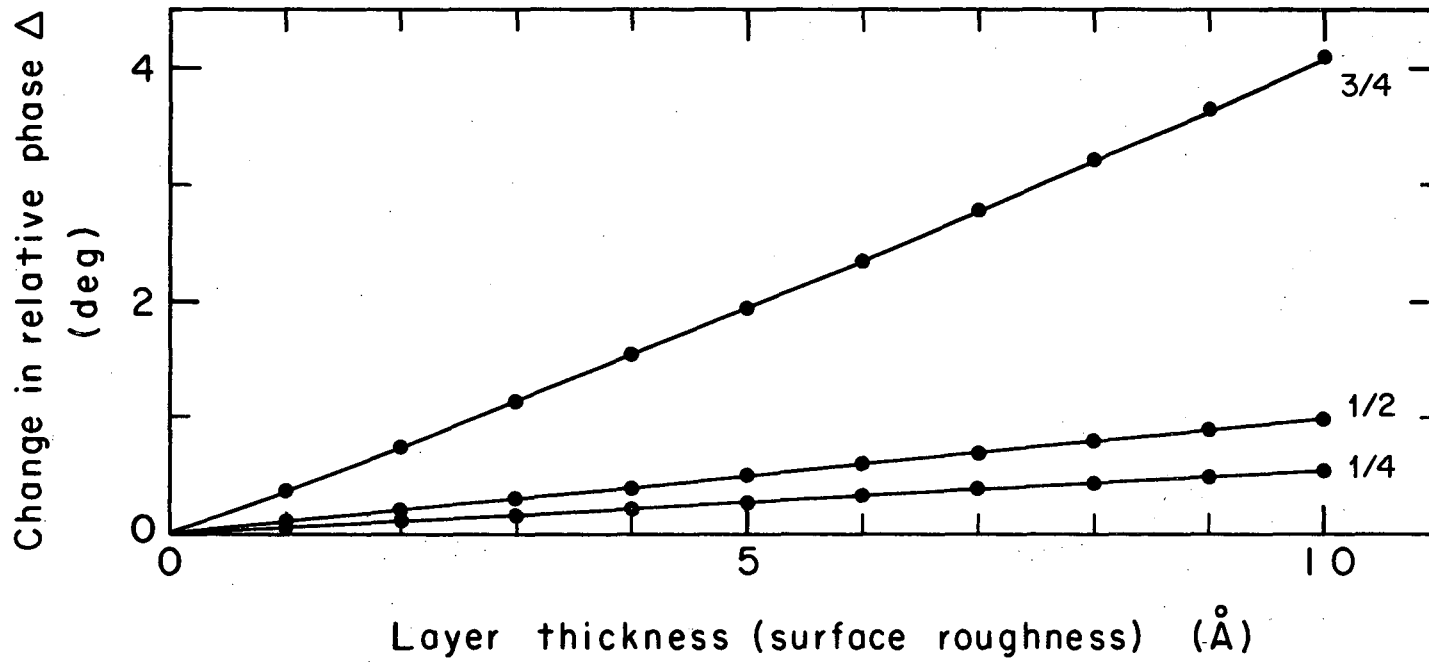
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Figure 8



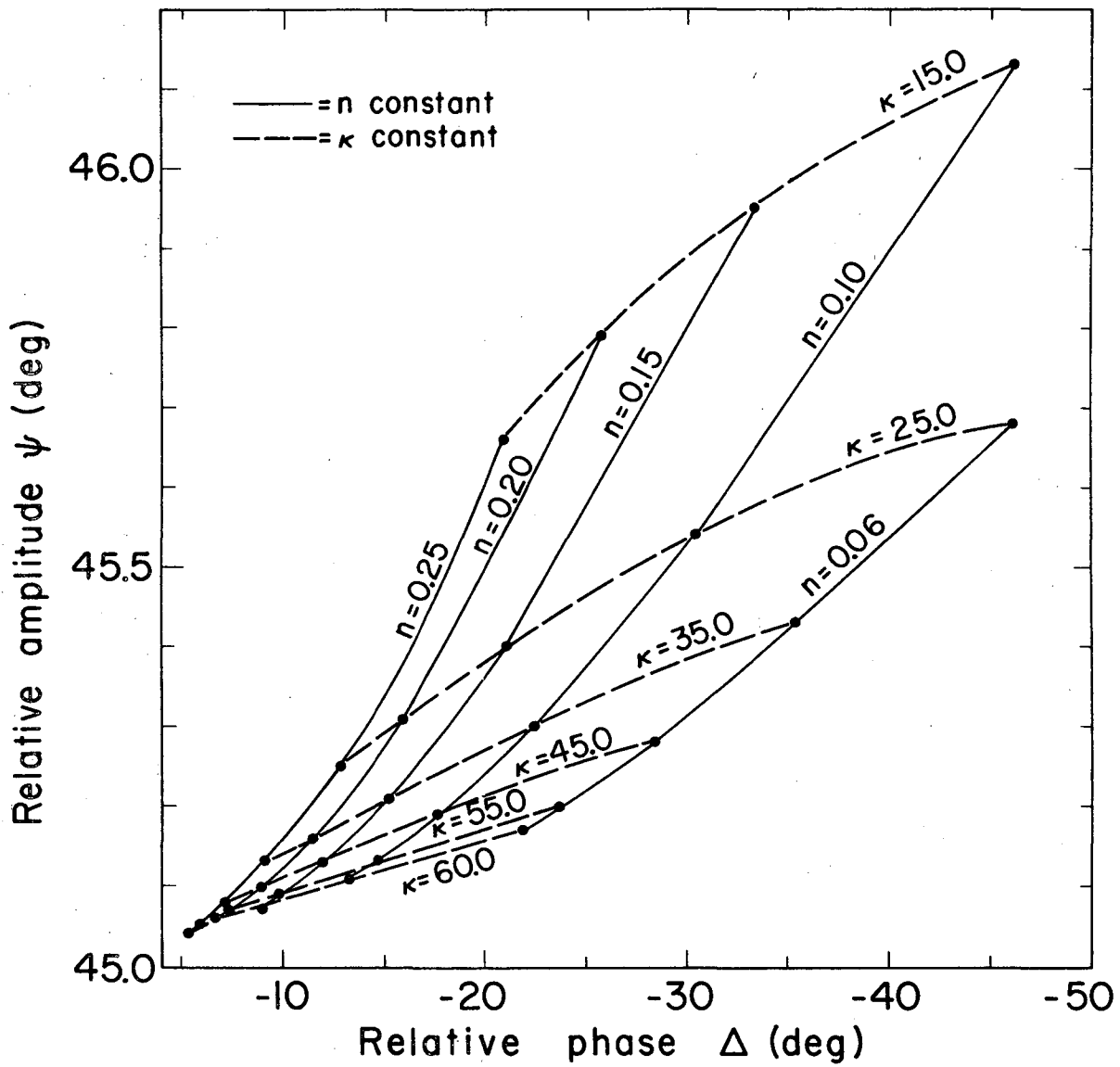
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Figure 9



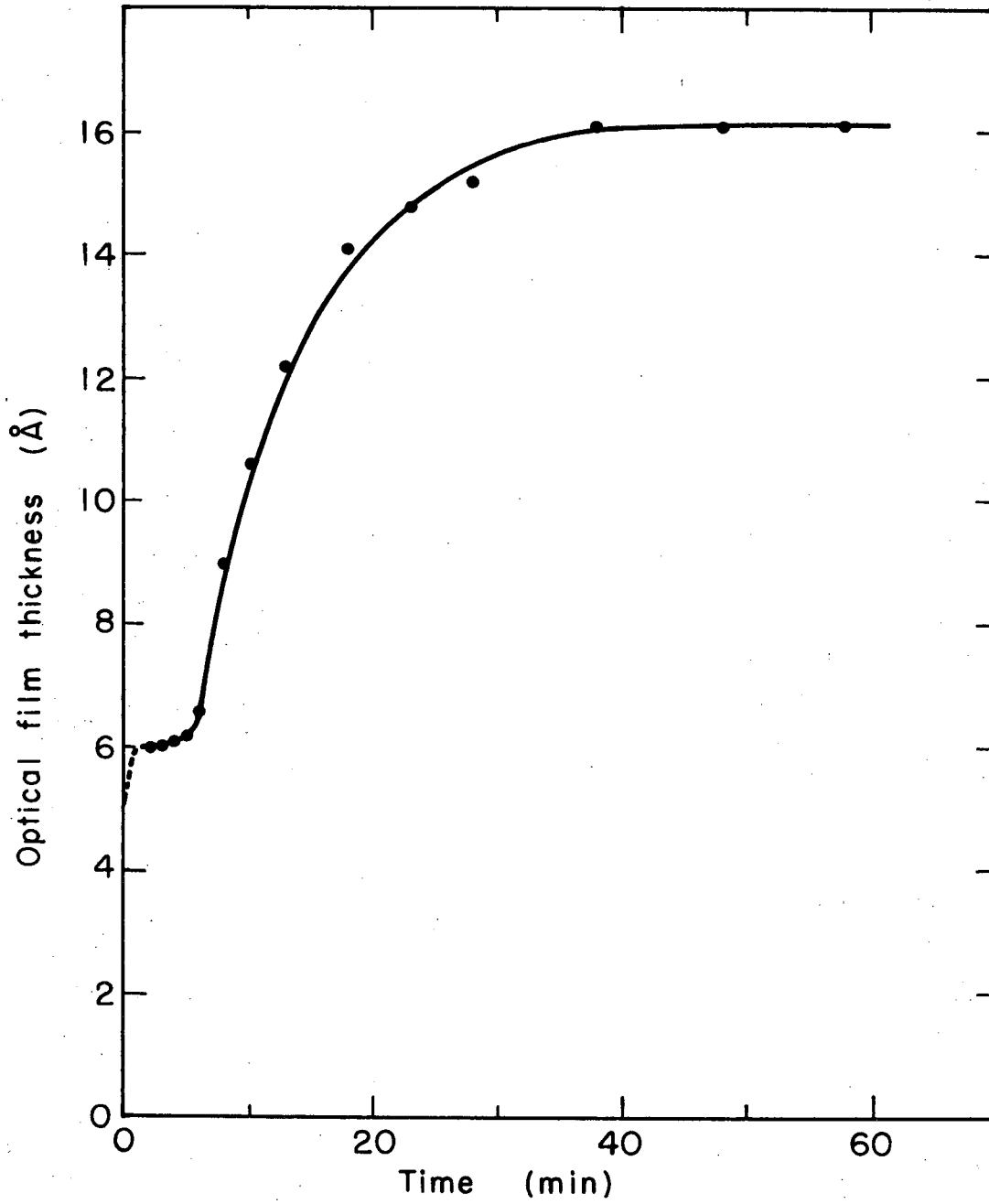
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Figure 10



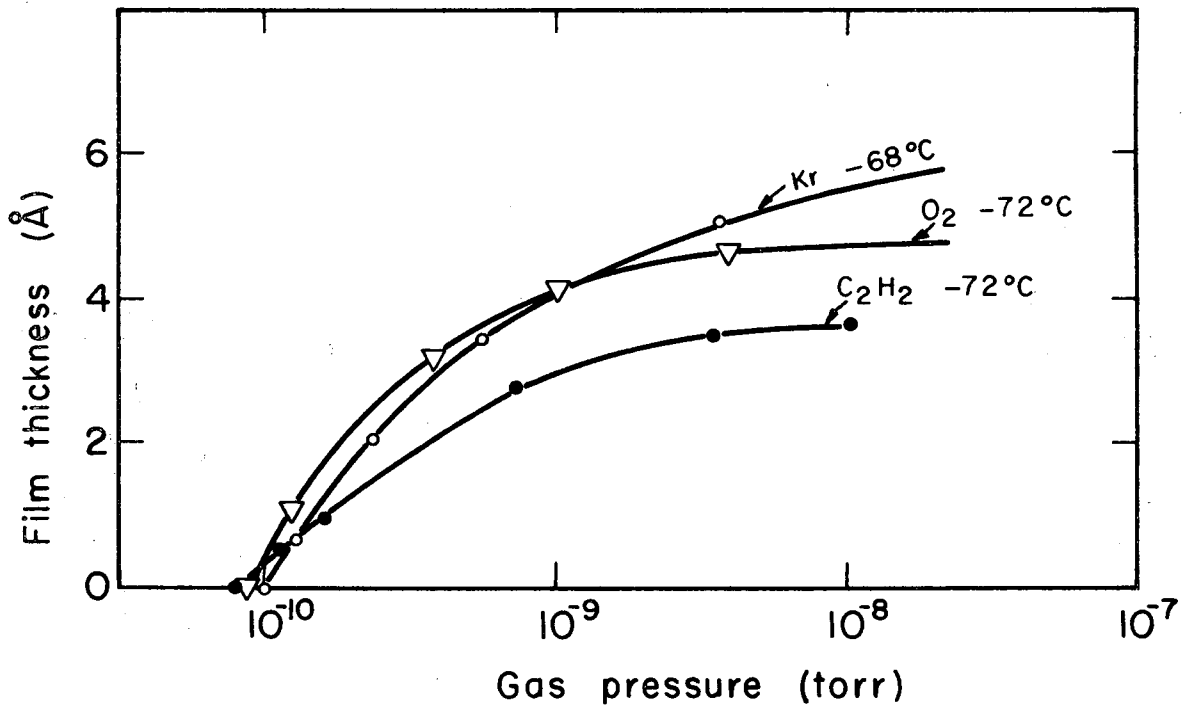
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Figure 11



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Figure 12



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Figure 13

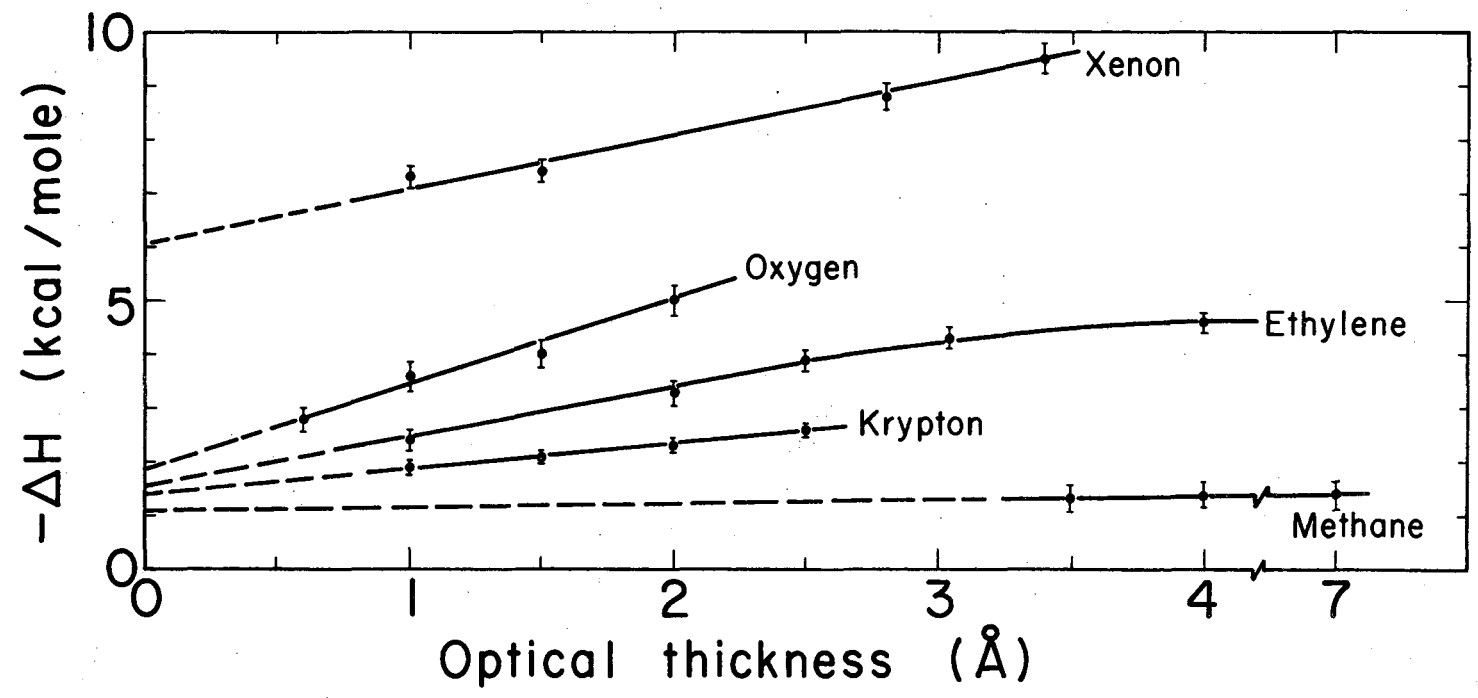
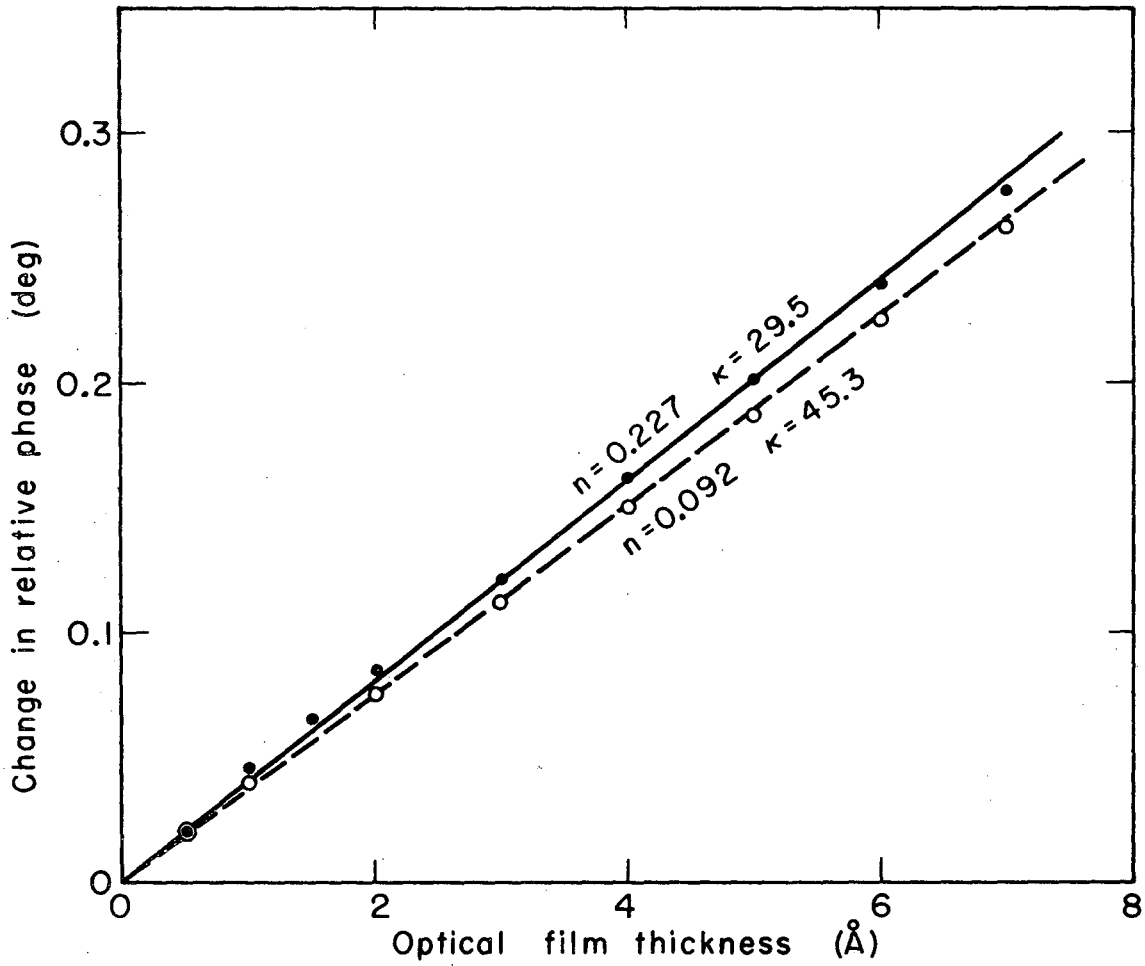


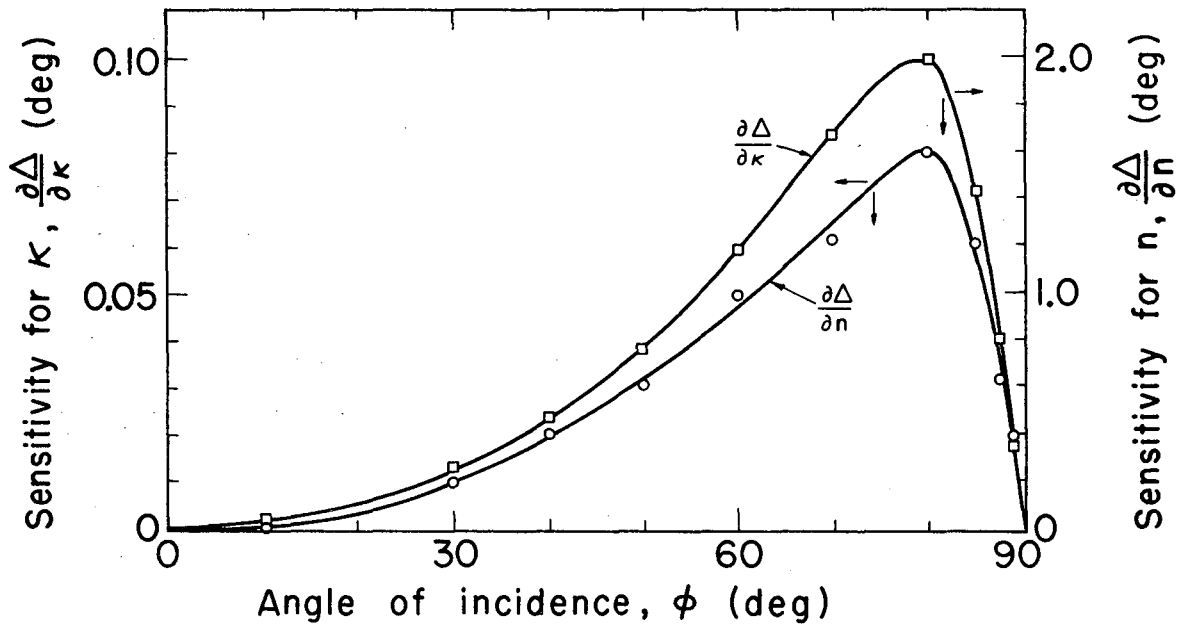
Figure 14

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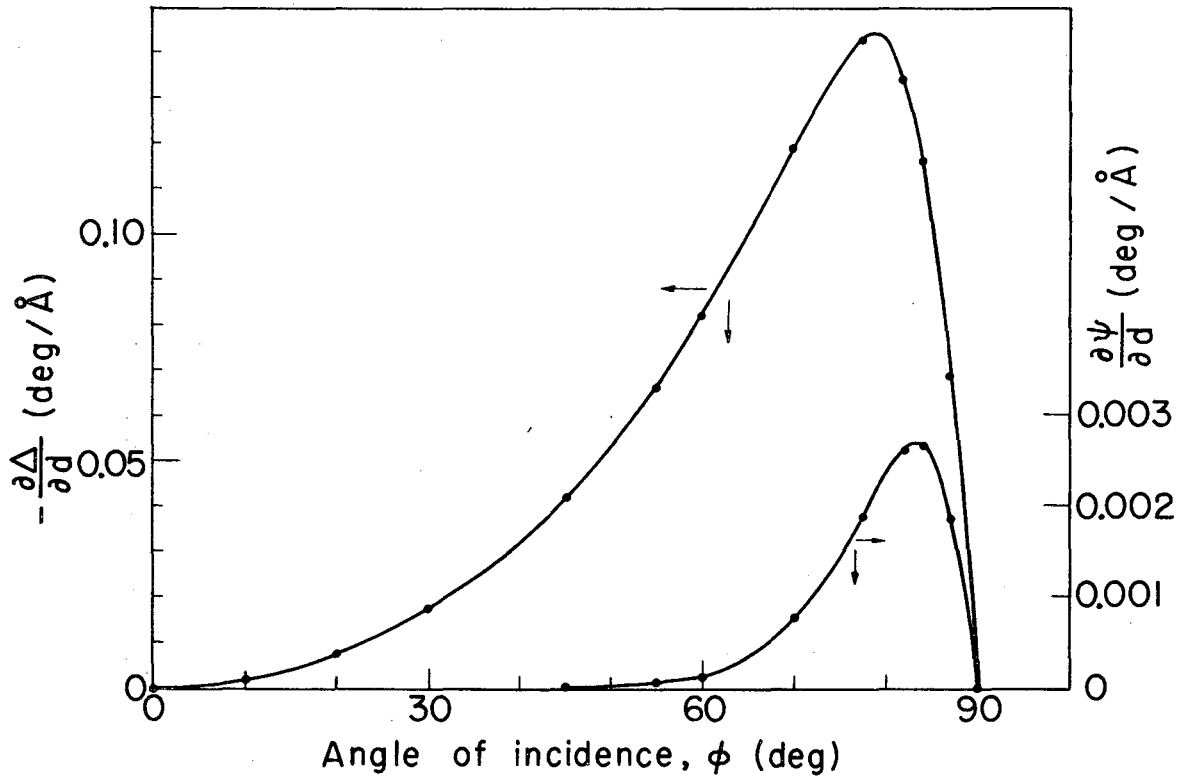
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Figure 15



XBL687-3402

Figure 16



XBL687-3398

Figure 17

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