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Spectroscopic Ellipsometry of Ion-Bombarded Lead Films

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Abstract:

The effects of ion bombardment on the morphology of compact lead films of under 100 nm thickness were investigated by spectroscopic ellipsometry, Auger electron spectroscopy (AES), and scanning electron microscopy (SEM). In contrast to the expected uniform removal of the surface by ion bombardment, on which the determination of composition profiles by AES is based, a nonuniform removal of material with the formation of pits or islands has been found to occur. The pitting is independent of the film preparation or the presence of an oxide overlayer. An optical model of a film distributed as islands was used to interpret spectroscopic ellipsometer measurements. SEM confirmed the island nature of the surface. Spectroscopic ellipsometer and AES measurements agree well when interpreted in terms of surface coverage.

Introduction:

Ion bombardment is extensively used for determining composition profiles of surface layers by Auger electron spectroscopy [1]. For thin films of a few tens of nm thickness, surface roughening is thought to be minor and a uniform removal of material is expected. The present work concerns ion- bombardment of thin lead-films where these assumptions do not apply and composition profiles have to be interpreted differently [2].

Ion-bombardment damage often complicates the determination of composition profiles of thin films. Several forms of ion-bombardment damage have been discussed; surface roughening, preferential sputtering, and recoil implantation [1,3].

Surface roughening, including pitting and rippling, results from uneven sputtering of the surface. Uneven sputtering has been attributed to surface roughness [1], crystallite orientation [3], and composition-dependent sputtering rates [1].

Changes in the surface composition result from preferential sputtering and recoil implantation of surface constituents. Preferential sputtering of a multicomponent surface results in a change in surface composition such that the ratio of the sputtering rates of surface constituents becomes equal to the ratio of their concentrations in the bulk. Recoil implantation results in the implantation of surface atoms into the substrate.

Experimental:

The lead films used in this study were deposited by electrochemical and evaporation methods upon 12.3 mm diameter oxygen-free copper disks. These methods produced films that covered the surface uniformly. The copper substrates were mechanically polished with a final step using 0.05 μm alumina powder in water. Electrodeposition of lead was conducted in an electrolyte consisting of 1.0M $NaClO_4$, 0.005M $Pb(NO_3)_2$, and 10 μm Rhodamine-B chloride adjusted to a pH of 2.4 with perchloric acid. After deposition, the samples were

rinsed quickly with distilled water with excess water being removed by compressed Freon. Vapor deposition of lead films was performed under vacuum, both in the UHV chamber used for AES, and in a commercial evaporator. Both depositions were made by vaporizing high purity lead (99.999%) from a tungsten basket. During vapor deposition, the background pressure in the commercial apparatus was 10^{-4} torr, in the UHV chamber it rose to 10^{-7} torr. The deposits prepared within the commercial apparatus were exposed to air for approximately 10 min. during the transfer to the UHV chamber. The deposits made within the UHV chamber were not exposed to air before ion bombardment. The UHV chamber was equipped with windows which allowed ellipsometry of the sample with a 75° angle of incidence. The windows were oriented normal to the incident and reflected light beams of the ellipsometer. The electron gun for AES, and the ion bombardment gun were also oriented at a 75° angle of incidence of their respective beams but at azimuthal positions of 30° and 60° respectively from the plane of incidence of the ellipsometer beam. Ion bombardment, using a Varian model 981-2043 3kV ion gun, was performed with argon ions at an energy of 1100eV in 5×10^{-5} torr of argon. The ion beam was rastered across the surface for an even bombardment. An electron beam of 1500 eV was used for AES measurements. Optical properties of the film-covered surface were measured with a spectral-scanning ellipsometer. Its construction has been described before[5].

Optical Model:

A dual-film optical model was used to interpret the measured optical properties of the ion-bombarded films (fig 1). The two layers represented the damaged and undamaged regions of the film. To represent surface roughness with dimensions greater than the wavelength of the sampling light, an island layer which partially covers a continuous film was used. In addition the deposited films were assumed to be a composite of either lead and lead oxide, lead and copper, or lead and vacuum. The dual-layer film was bounded by copper and vacuum.

Refractive indices obtained from experiment and literature were used for single component films. The refractive indices for composite films were calculated with the Bruggeman effective media approximation[6,7]. The Bruggeman approximation is a special case of a general rule for mixing the dielectric properties of a multicomponent medium. The approximation results in the following equation for a two component medium.

$$\theta_1 \frac{n_1^2-n^2}{n_1^2+2n^2} + (1-\theta_1)\frac{n_2^2-n^2}{n_2^2+2n^2} = 0 \tag{1}$$

The reflection coefficients of multilayer films were calculated based on a method consistent with the procedure described by Azzam and Bashara [8]. Reflection coefficients are calculated for each film using the apparent optical properties of the underlying surface. In this maner reflection coefficients are successively calculated for each film increment proceding from the substrate to the outer film. The optical properties of the continuous film can be described by an isotropic and homogeneous film model [9]. If the refractive index is known only the thickness is needed to describe the film.

In the case of a pitted film, the reflections from the covered and bare surface are superimposed. Coherent superposition can be assumed when the covered and bare regions have characteristic dimensions smaller than the coherence length of the incident light [6]. The light source used in this study was estimated to have a longitudinal coherence length of 16 μm and a transverse coherence length of 10 μm at a wavelength of 400 nm [10]. With coherent superposition, the overall complex reflection coefficient is the sum, weighted by the coverage of the surface, of reflection coefficients of covered and uncovered regions.

$$r_v = (\theta_f) r_{v,f} + (1-\theta_f) r_{v,s} \tag{2}$$

Five adjustable parameters are used in this model; thickness and composition of both pitted and continuous films and coverage by pits. In each case the values of the adjustable

parameters were chosen in order to minimize the deviation between experimental measurments and model calculations.

Results and Discussion:

The spectral dependence of the refractive index was measured by ellipsometry for both copper and lead. The derived refractive indices were then used as input for numerical modeling of the optical properties of lead films following ion bombardment. Refractive indices were measured under vacuum. Prior to measurement, the surfaces were cleaned by ion-bombardment to remove any oxides or contaminants. The refractive indices were calculated based on the assumption that the interface between the metal and vacuum was optically smooth and that the metal was isotropic.

The optical properties of the copper surface became stable durring ion bombardment after removal of the oxide layer. In addition, the optical properties were reproducible between different copper samples. Figure 2 shows the measured refractive indices and some reported values from literature [11].

A vapor-deposited lead film was made sufficiently thick ($>$ 40 nm) such that optical reflection was equivalent to that from an infinite medium. A light ion-bombardment was used to remove the oxide without significantly pitting the film. The optical constants for a lead vapor deposit, determined by ellipsometry, are shown with some literature values [12] in figure 3. The ellipsometer measurements from thick electrochemical lead deposits could be interpreted by use of these optical constants under the asumption of a 20% porosity.

The development of surface roughness due to ion bombardment was monitored by ellipsometry. An optimization routine, for the optical model described, was used to obtain information on the structure of the surface from the ellipsometer measurements (fig. 4,5)(Table 1).

The optical properties of an electrochemically deposited lead film of 0.039 C/cm^2 (37 nm compact) were measured intermittently throughout 125 min of ion bombardment with

1100 eV Ar^+ ions. Up to 5 min of ion bombardment, the surface was modeled as a lead film of 20% porosity with an overlying uniform oxide layer (fig. 4a). The refractive index of the oxide was taken to be 2.5 - 0.0i, which was approximated from literature values of PbO minerals [13]. The oxide thickness was determined to be 3.1 nm at the beginning of ion bombardment.

Between 15 and 35 min of sputtering, the measured optical properties of the surface were modeled with a pitted porous film (fig. 4b). Following 15 min the copper was optically detected through locally thinned regions of the pit bottoms as is indicated by the ellipsometer data at a wavelength of 560nm (fig. 5). The porosity of the film was again determined to be 20%. A comparison of the measured delta and psi parameters with those calculated by the pitted porous-film model are shown in figure 6 for the lead film following 35 min of ion bombardment. The slight discrepancy between the calculated and measured spectra may result from a distribution of pit depths about an average pit depth.

Following 45 min of ion bombardment, the copper substrate became exposed as was indicated by AES and ellipsometer measurements (Table 1)(fig 4c). Exposure of substrate by pits increased further with ion bombardment times between 45 and 125 min. Figure 7 shows the agreement between lead coverage of copper as derived from ellipsometer and AES measurements, if the latter were interpreted in terms of coverage rather than composition. Following 125 min of ion bombardment, Auger spectroscopic measurements indicate a 1% coverage of lead which is in good agreement with the ellipsometer-derived result of a bare copper surface.

In an effort to determine whether the method of deposition was a factor in pitting under ion bombardment, vapor deposits of lead were investigated. The following results are for a vapor deposit approximately 1 μm thick. The lead deposit was optically opaque. The optical properties of the film before ion bombardment indicated an oxide layer of 3.5 nm. Auger electron spectroscopy also indicated the presence of oxygen before ion bombardment. Ion bombardment was performed with 1100 eV Ar^+ ions. The vapor deposit was ion bombarded

for 45 min at which point AES indicated a 67 % coverage of Pb. Interpretation of the optical properties by the island film model indicated a 66% coverage of lead, in good agreement with AES results. The effect of ion bombardment was the same for electrochemical and vapor deposits.

An attempt was made to determine the effects of lead oxide and carbon contamination on ion-bombardment damage. An oxide free lead film was vapor deposited within the same UHV chamber in which AES and ellipsometry were performed. A transfer of the sample involving an exposure to air was thus avoided. Morphological changes which were induced by ion bombardment were similar to those observed on previous films. No correlations to the presence of oxide or carbon films could be determined.

Scanning electron microscopy of ion bombarded films was performed to obtain an independent indication of the surface topography. The micrographs were taken of vapor and electrochemical deposits exposed to several different durations of ion bombardment. Figure 8 is a scanning electron micrograph of a vapor deposit following the 45 min of ion bombardment. The presence of pits 1 μm in diameter can be seen. There is no apparent orientation of the pits with respect to the direction of ion bombardment. There was no visible distinction between ion bombarded vapor and electrochemical deposits. Scanning electron microscopy of the lead films before ion bombardment showed a featureless, pit free surface. The results support the optical model used for the interpretation of ellipsometer measurments although in the early stages of ion bombardment the pits could not be resolved by SEM.

Conclusion:

Thin uniform lead films on copper are not uniformly removed by ion bombardment. The films become pitted following bombardment by 1100-eV Ar^+ ions. Pit formation does not seem to depend on the presence of an oxide layer, rather it appears to be a result of the

sputtering process. This study demonstrates posible problems associated with using ion bombardment to obtain composition profiles of thin films.

The development of pits was confirmed at later stages of ion bombardment by scanning electron microscopy. The present measurments comfirm the validity of the island film optical model for interpreting the optical properties of ion bombarded lead films. The island film model is based on the coherent superposition of the polarization states of light reflected from bare and film covered surface elements. Auger electron spectroscopy and spectroscopic ellipsometer measurements interpreted in terms of lead coverage agreed well.

Acknowledgment:

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Nomenclature:

n	Complex refractive index for composite material
n_i	Complex refractive index for i^{th} component
r_v	Effective Fresnel reflection coefficient for polarization v (s or p)
$r_{v,f}$	Fresnel reflection coefficient for film-covered surface
$r_{v,s}$	Fresnel reflection coefficient for bare surface
t_{con}	Thickness of continuous film
t_{ox}	Thickness of oxide film
t_{Pb}	Thickness of lead film
t_{pit}	Thickness of pitted film (pit depth)
θ_i	Volume fraction of component i
θ_f	Fraction of surface covered by film

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Film Model Parameters						
Time (min)	Model	Porosity (%)	Coverage By Pits (%)	Thickness of Pitted Film t_{pit} (nm)	Thickness of Continuous Film t_{Pb} and t_{con} (nm)	Thickness of Oxide Film t_{ox} (nm)
0	a	20.	NA	NA	OP	3.1
5	a	20.	NA	NA	OP	1.1
15	b	18.	18.	OP	11.0	0
25	b	16.	22.	OP	7.7	0
35	b	19.	26.	OP	3.0	0
45	c	19.	32.	OP	0	0
55	c	20.	50.	OP	0	0
65	c	20.	70.	OP	0	0
75	c	18.	86.	OP	0	0
85	c	19.	92.	OP	0	0
95	c	16.	96.	OP	0	0
105	c	23.	98.	OP	0	0
115	c	0	99.	36.	0	0
125	c	NA	0	0	0	0

OP -- Opaque, the model is insensitive to thickness since the light is absorbed by the film.
NA -- Not Applicable

Table 1. Parameter values used in modeling ellipsometric measurments of an 1.1 keV Ar ion-bombarded lead film. The model parameters are tabulated as a function of ion-bombardment duration. The lead film was an electrochemical deposit of 0.039 C/cm^2 (37 nm compact). The models a, b, and c are shown in figure 4.

Fig. 1. Dual-film optical model surface used for interpreting spectroscopic ellipsometer measurements. a)dual-component discontinuous film, b) dual-component continuous film, c) substrate. (XBL 883-10156)

Fig. 2. Spectral dependence of the refractive index, n, and extinction coefficient, k, of bulk copper. ____ present measurements, • Johson and Christy [10], ■ Hass and Hadley [12]. (XBL 844-10454A)

Fig. 3. Spectral dependence of the refractive index, n, and the extinction coefficient, k, of vapor deposited lead. ..... present measurements, • Lifenvall, Mathewson, and Myers [11]. (XBL 847-9851A)

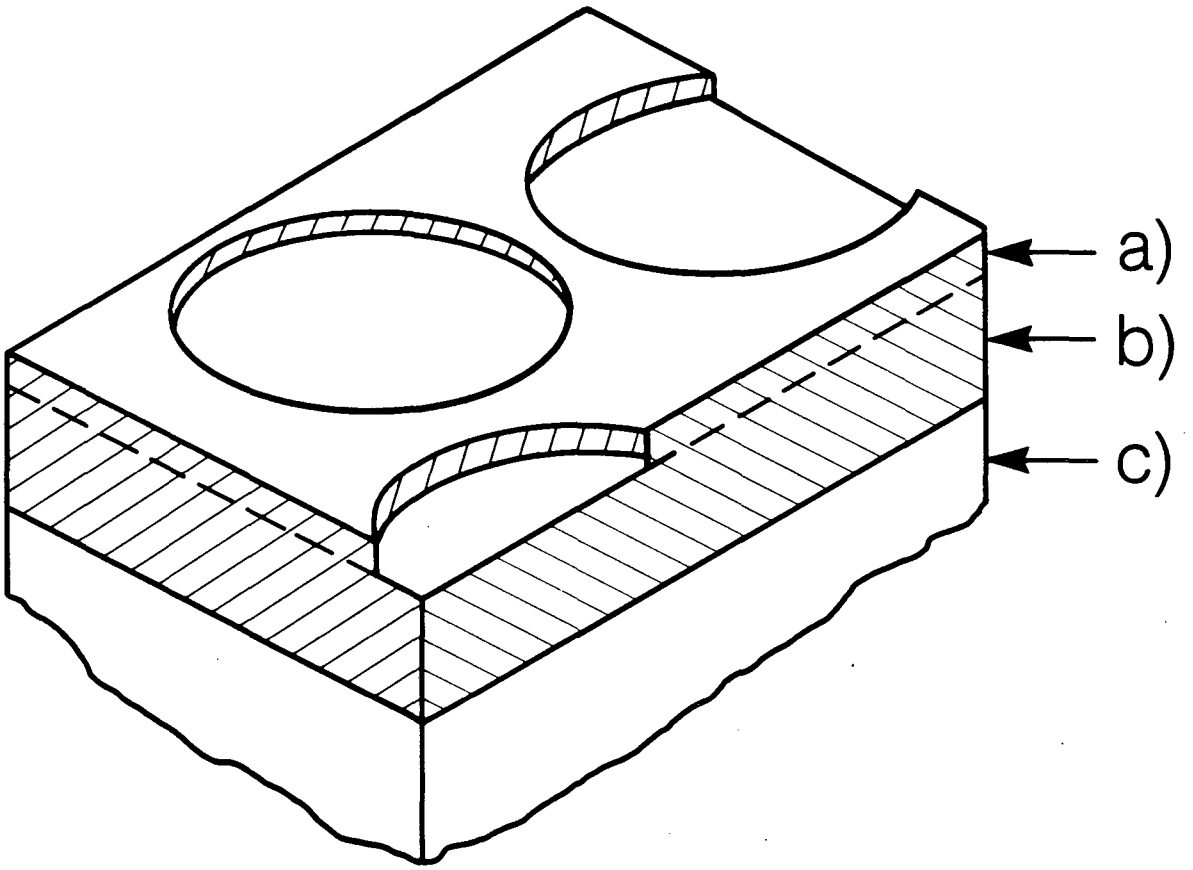
Fig. 4. Schematic of model surfaces used in interpreting the ellipsometer measurements of ion-bombardment damaged lead films. a) oxide covered porous lead film, b) porous lead film with shallow pits, and c) porous lead film with deep pits extending through the film. t_{con} – thickness of continuous film, t_{ox} – thickness of lead oxide film, t_{Pb} – thickness of lead film, t_{pit} – thickness of pitted film (pit depth). (XBL 883-10157)

Fig. 5. Spectroscopic ellipsometer measurments from an electrochemical lead deposit of 0.039 C/cm^2 (34 nm) for times up to 125 min of 1.1 keV Ar ion-bombardment. The changes in the optical properties reflect the removal of oxide for the first 15 min and the generation of pits throughout the 125 min of sputtering. a) delta, b) psi. (XBL 844-10453A)

Fig. 6. Comparison of the measured and calculated delta and psi for a 0.039 C/cm^2 electrochemically deposited lead film following 35 min. of ion-bombardment. The optical model consists of a 0.74 coverage of lead islands with an underlying 30 A lead film. Both the island and continuous film have a porosity of 0.2. The substrate is bulk copper. a) delta, b)psi. (XBL 848-8659)

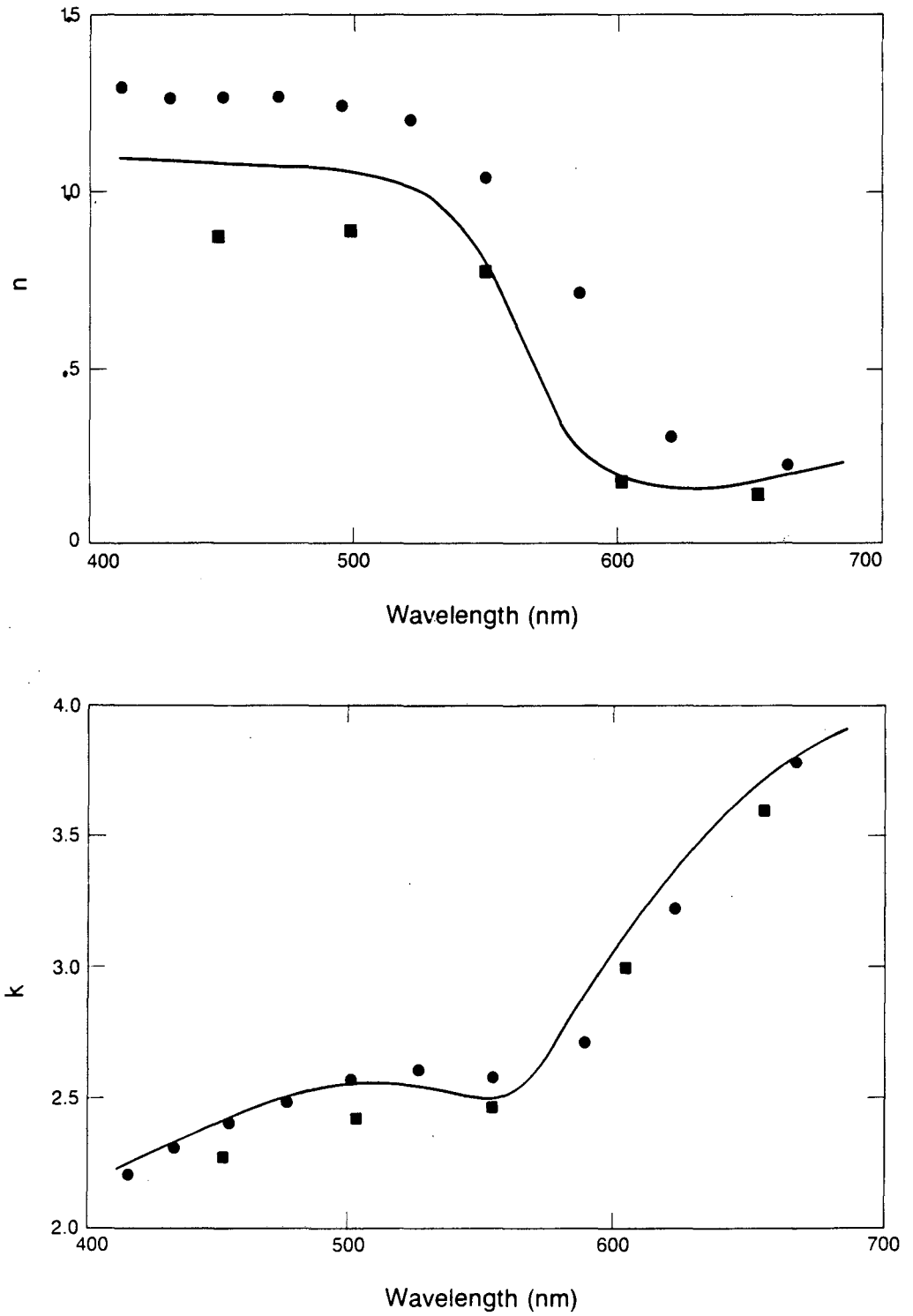
Fig. 7. Fraction of the copper surface covered by a lead film, derived from spectroscopic ellipsometer and AES measurments, as a function of sputter duration. The lead film was a 0.039 C/cm^2 (37 nm compact) electrochemical deposit. (XBL 847-9848)

Fig. 8. Scanning electron micrograph of a Pb vapor deposit after 45 min. of 1 keV Ar ion-bombardment. Spectroscopic ellipsometry measurements fitted with a coherent superposition model of the pits indicates a 68% coverage by lead with a thickness greater than 45 nm. The dark areas are copper and light areas are lead. (XBB 844-2539A)



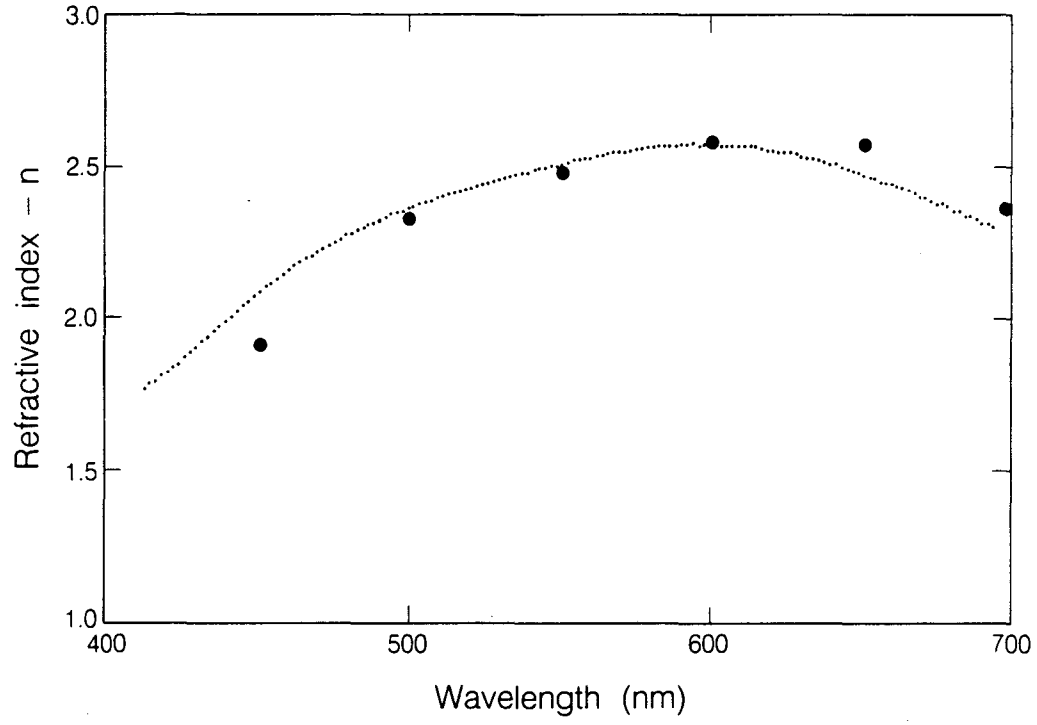
XBL 883-10156

Fig. 1



XBL 844-10454A

Fig. 2


3.0
2.5
2.0
1.5
1.0
Refractive index – n
400
500
600
700
Wavelength (nm)

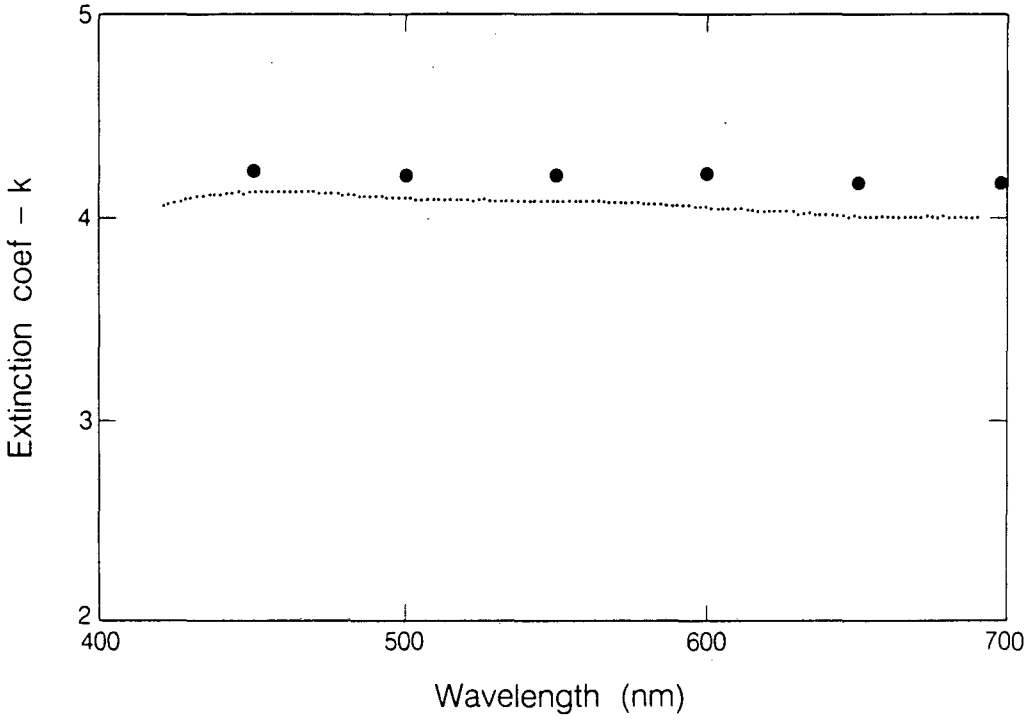
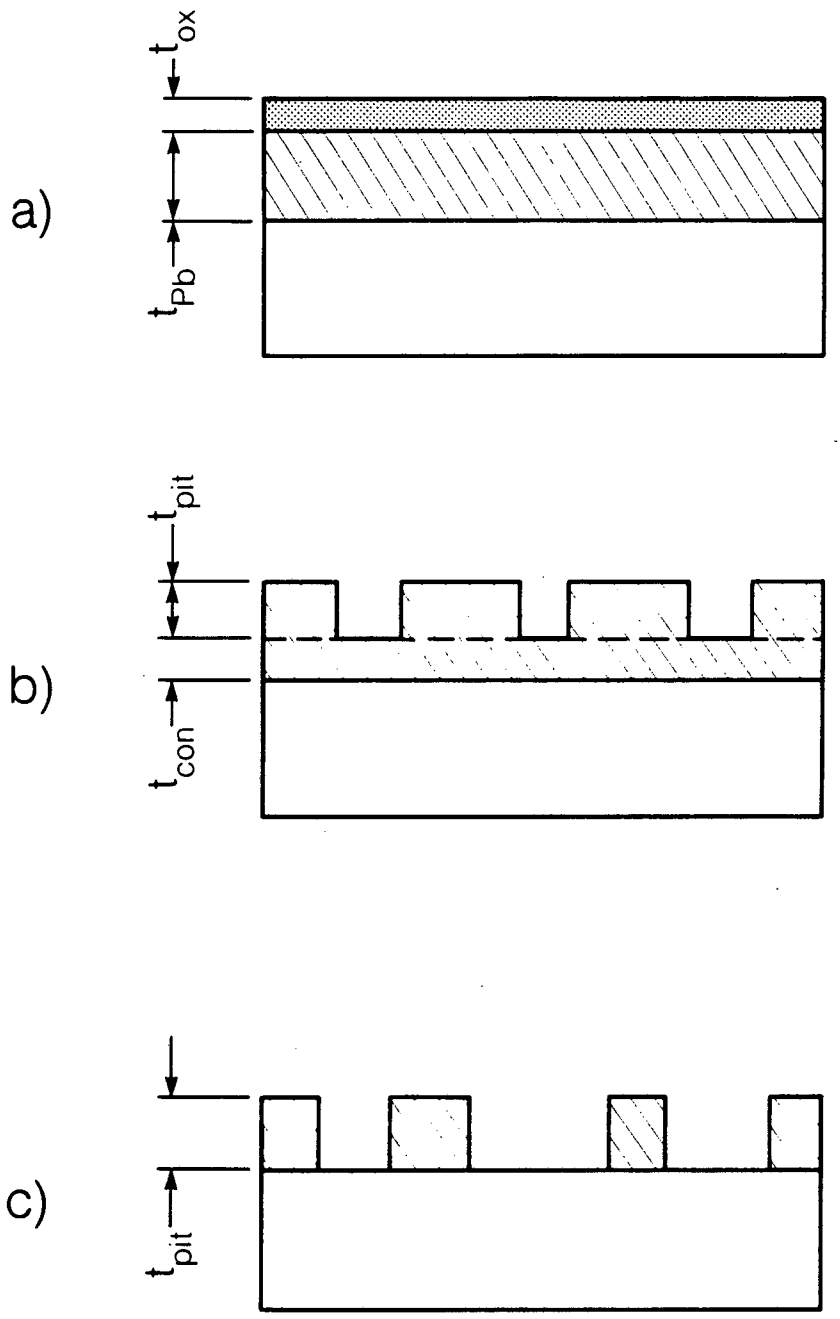
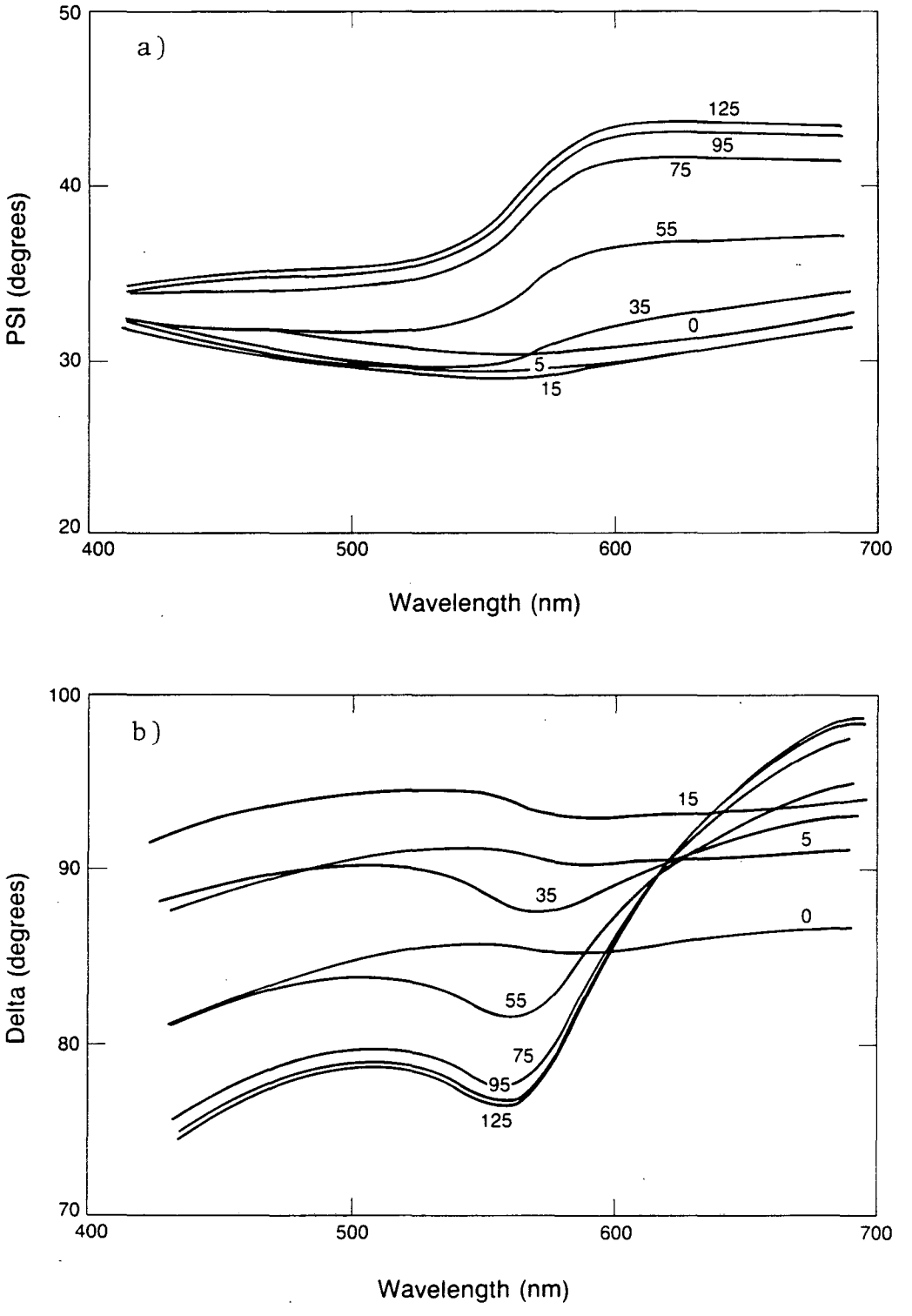

5
4
3
2
Extinction coef – k
400
500
600
700
Wavelength (nm)

Fig. 3



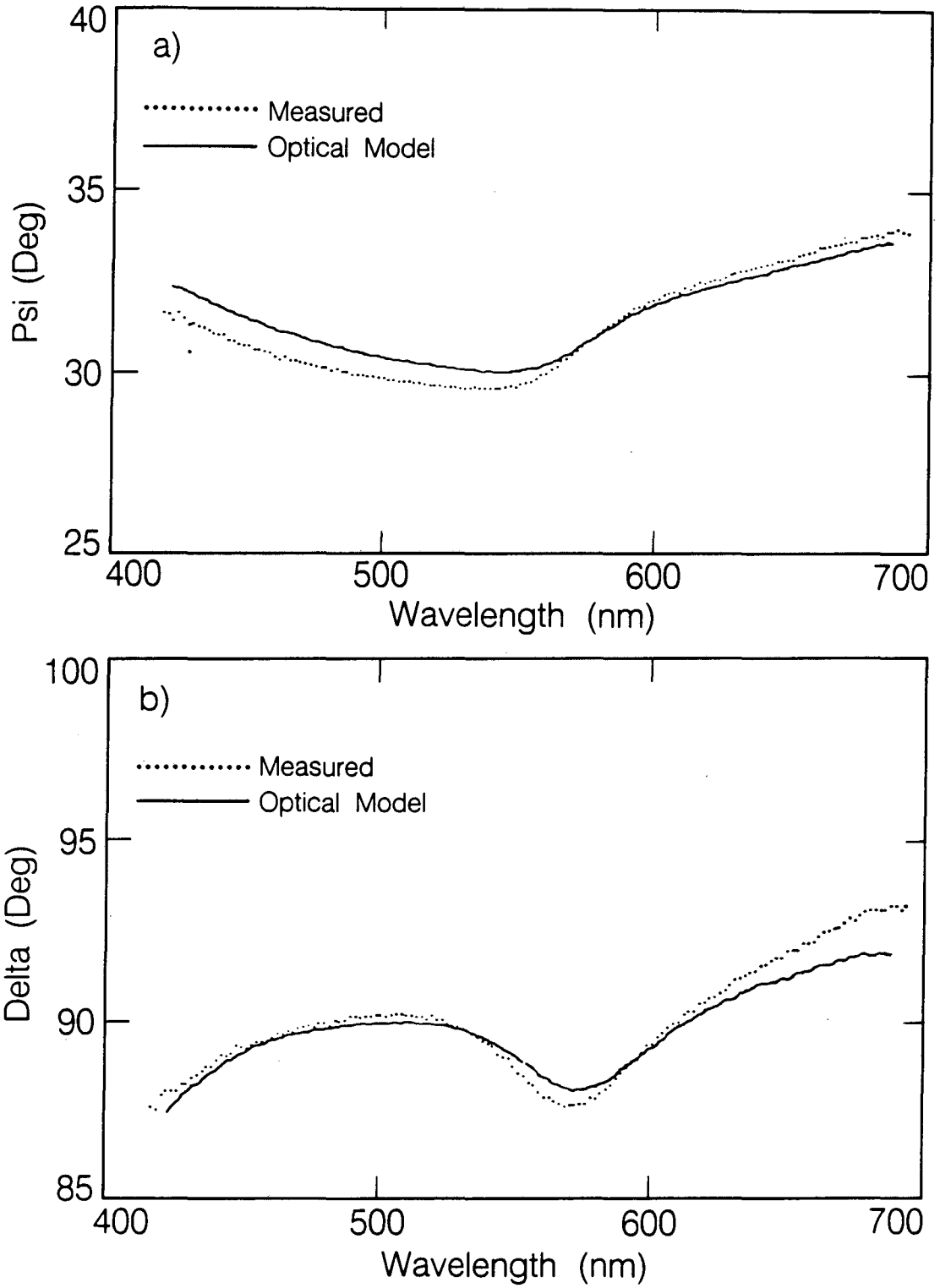
XBL 883-10157

Fig. 4



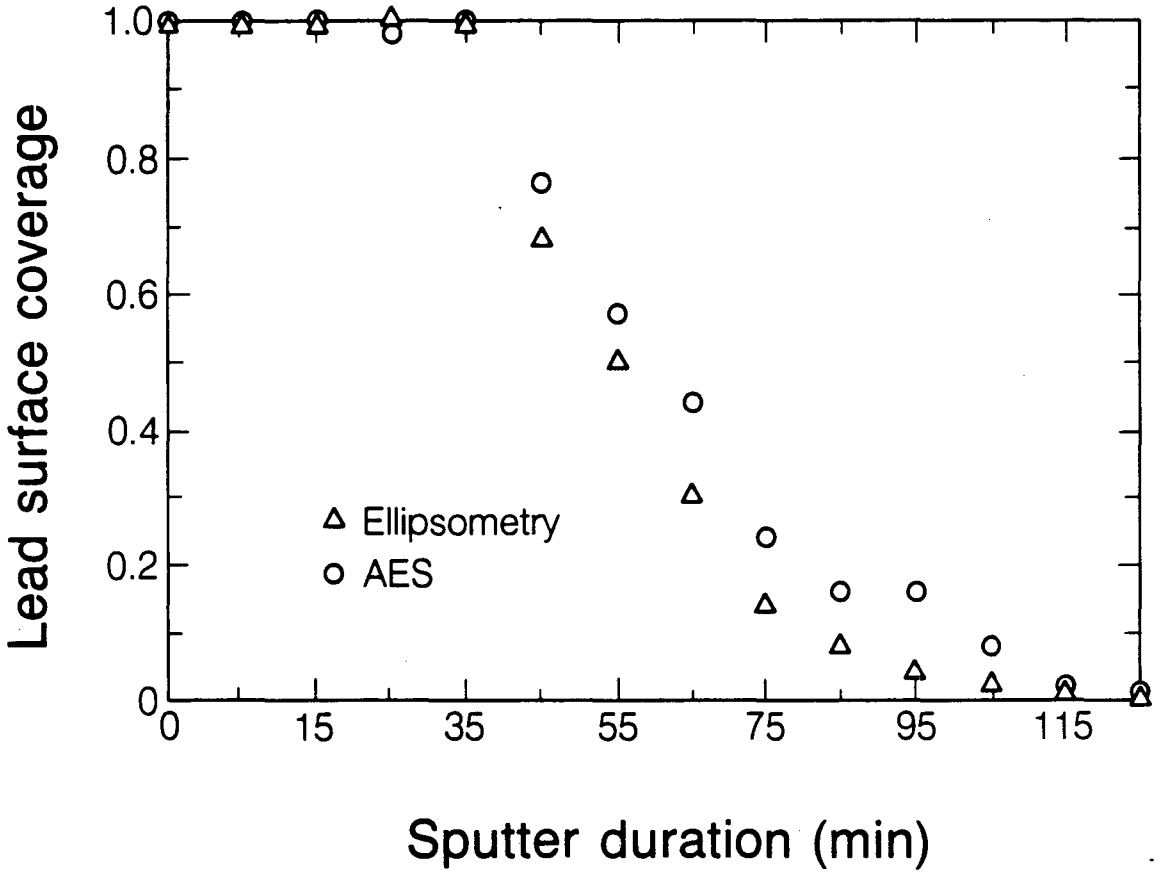
XBL 844-10453A

Fig.5



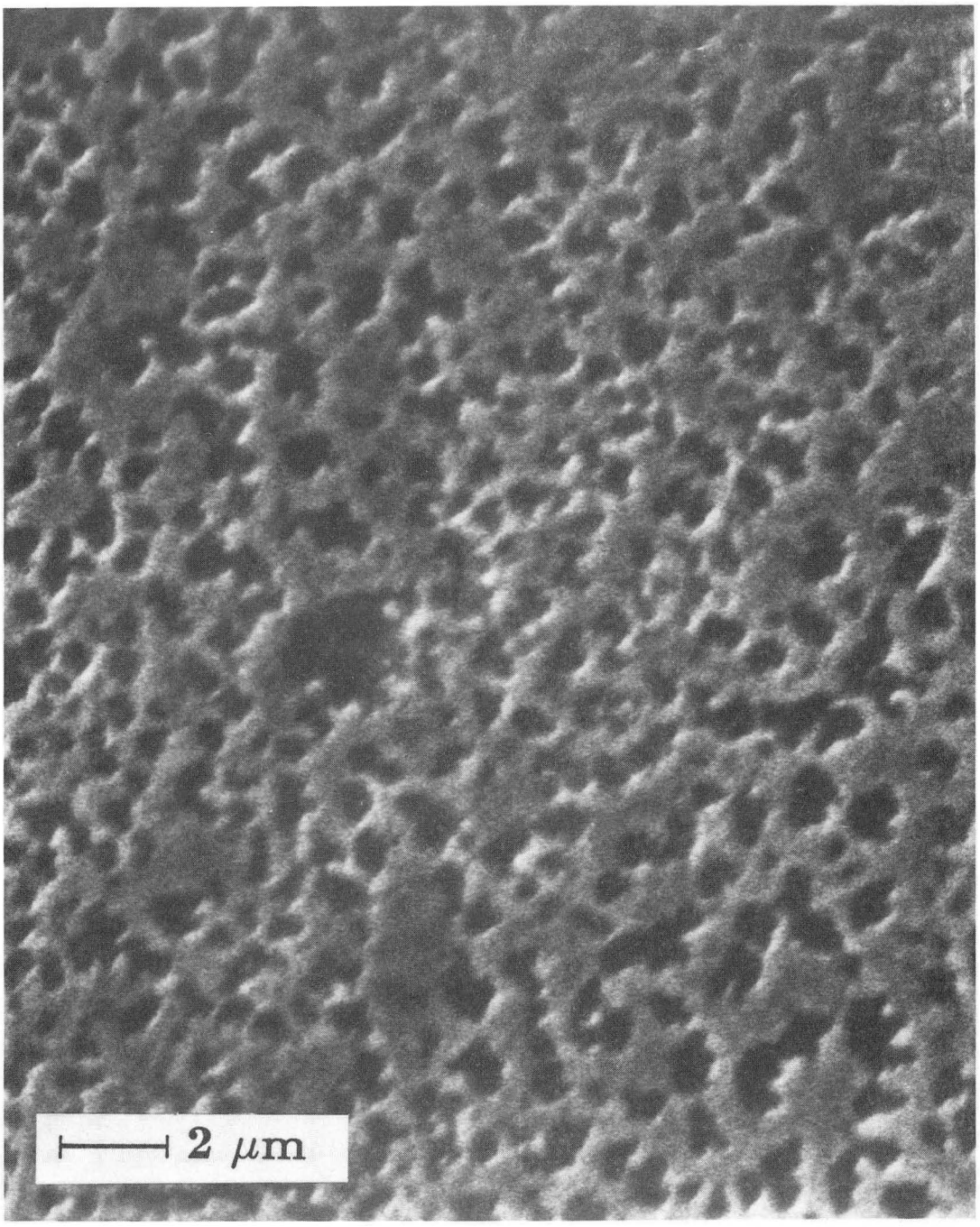
XBL 848-8659

Fig. 6



XBL 847-9848

Fig. 7



XBB 844-2539A

Fig. 8

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