Arachidate Layers on Ag and Au Substrates Detected by the ATR Method

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Monolayers of cadmium arachidate (thickness 26.8 Å) are deposited on Ag and Au substrates. They can be detected by the resonance excitation of surface plasmons (ATR method). The number of monolayers is correlated with the displacement of the reflection minimum. The observed values of the position of the minima as well as the shape of the reflection curve are in agreement with the calculated ones, using a refractive index of cadmium arachidate of 1.52 in agreement with other measurements.

1. Introduction

The Langmuir-Blodgett [1] method allows to deposit stepwise single layers of fatty acid of known thickness on a metal surface. Therefore we have used the ATR method (excitation of surface plasmons by light) to study the change of the resonance minimum as a function of the number of layers of cadmium arachidate on silver (gold) surfaces [2]. Earlier experiments have demonstrated that the ATR method is sensitive enough to detect very thin (< 5 Å) dielectric coatings [3], [4]. Steiger has performed similar measurements with the ellipsometric method [5].

2. Measuring Method and Preparation

Surface plasmon oscillations (SPO) can be excited at the boundary metal-air (metal-coating) using the experimental arrangement of Figure 1. In the case of resonance the maximum of the electromagnetic field is located in the boundary and decreases on both sides exponentially.

An Ag (Au) film is deposited on a quartz slide and brought into optical contact with the base of a prism with the refractive index of 1.48. We measured the reflected p-polarized light intensity Rp versus angle of incidence θ. Excitation of surface plasmons is detected as a resonant minimum in the reflected light.

The Langmuir-Blodgett method as described by Kuhn and coworkers can be used to deposit various monolayers on solid substrate [6, 7]. A fatty acid in an organic solvent is spread on water containing 30×10^{-4} mol $CdCl_2$ at pH = 6.4. After evaporation of the solvent a surface pressure is applied to obtain a density packed monolayer. The appropriate pressure, 30 dyne/cm, is taken from compression isotherms. This monolayer can be transferred to a solid substrate by dipping the solid slowly through the monolayers into the water (see Figure 2). In the

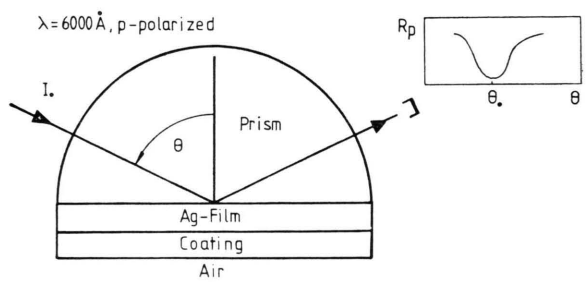

Fig. 1. Experimental Arrangement: Incoming light of intensity I_0 (p-polarizised, 6000 Å wavelength) is reflected at the boundary quartz-silver and detected with a photomultiplier. If the dispersion relation is fulfilled, surface plasmons are excited at the boundary silver-air. This excitation is detected as a minimum in the reflected light.

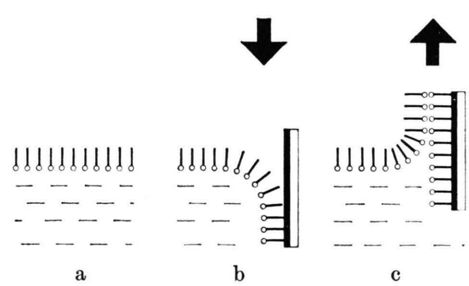

Fig. 2. Langmuir-Blodgett Dipping Technique: (○—: the circle represents the hydrophylic head, the bar the carbon chain of the molecule).

Fig. 2a. Monolayer on water surface.

Fig. 2b. First dipping of a metal substrate with hydrophobic surface into the water.

Fig. 2c. Drawing the substrate out of the water.

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case of hydrophobic surface the monolayer is attached to it with the methyl end group of the fatty acid molecules. Therefore, the first monolayer has its carbon chain next to the metal film. On drawing the substrate slowly out of the water the second monolayer is transferred with its hydrophilic head onto the first one. Thus we get organized films with thicknesses in steps of two monolayer thicknesses. The silver (gold) films are 500 Å thick films deposited by vaporization at a rate of 5 Å/s on quartz slides. Five slides were covered with silver (gold) in one evaporation process. The cadmium-arachidate layers of different thicknesses are deposited on four substrates, whereas the optical properties of the fifth one is measured without being covered and serves as a reference substrate.

3. Results of Measurements with Silver Film

The cadmium arachidate monolayers are detected by the displacement of the minimum of the totally reflected light as is expected from earlier work. Since the thickness of one layer is known (26.8 Å) and the number of layers can be chosen, the ATR method with its sensitivity can be applied to control the thickness of the monolayer and its

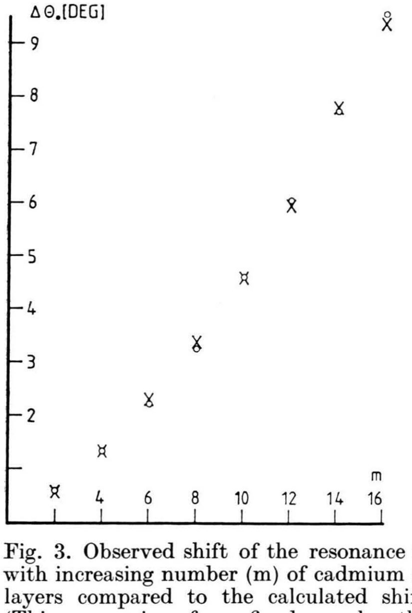

Fig. 3. Observed shift of the resonance minimum $\triangle\theta_0(x)$ with increasing number (m) of cadmium arachidate monolayers compared to the calculated shift (o) (see text). (This curve gives for a fixed wavelength the dependence of the thickness of the coating film, versus the angle of incidence θ_0 and is identical with the lower part of the curve "Surface mode" of Fig. 17 in [3].

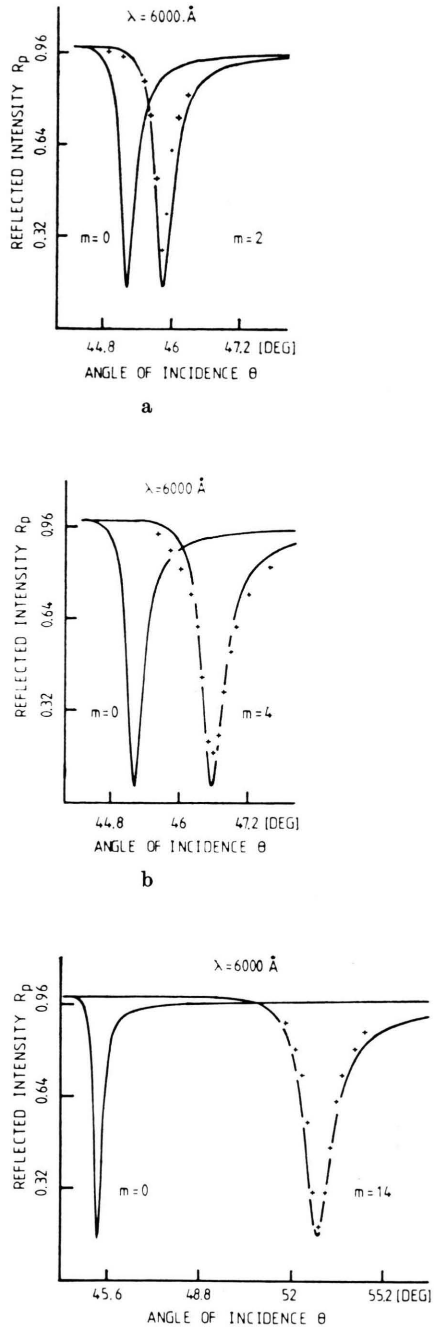

Fig. 4. Reflection curves obtained with the ATR method: The first minimum represents the uncovered silver film. The second one belongs to the coated calculated silver substrate. The crosses are experimental points. The figures are examples of a) two monolayers (reference film: Ag/III), b) four monolayers (Ag/I) and c) fourteen monolayers (Ag/II). The data of the reference films are listed in Table 1.

refractive index. The reflection as a function of angle of incidence θ can be calculated by the relation $R_p = |r_{210}|^2$ (see [8]). r_{210} is a function of the data of the multilayer system (quartz prism/Ag/cadmium arachidate /air), thickness and dielectric functions of the layers, wavelength, polarization and of angle of incidence θ. Using the data of the Ag reference film, the known thickness of the cadmium arachidate films ($m \times 26.8$ Å) and assuming that the organic coating is nonabsorbing we calculated the function $R_p(\theta)$ for various values of the refractive index of the film. Figure 3 shows the shift $\Delta\theta_0$ with increasing number (m) of monolayers. The circle represent the calculated displacement of the minima. The crosses are measured points. As Figure 3 shows the shift of the minimum follows the calculated curve rather well. The value of the refractive index comes out as 1.52 at best fitting.

It has been controlled whether the ATR method describes the shape of the minimum too. Therefore we have plotted the calculated reflection curve using the data of the Ag reference and of the organic films as determined above. Figure 4 displays the cases of two, four and fourteen monolayers on Ag. The first minimum represents the uncovered Ag film, whereas the second one the cadmium arachidate monolayers on Ag films. Calculated minima (full line) are compared to the measured curves (crosses). They show a fairly good agreement for a refractive index of $n = 1.52$.

In order to test the accuracy of the measurements we have derived the optical constants of several Ag films (uncovered substrates) from their reflection curves by fitting them to the Fresnel coefficient R_p. Table 1 shows the variations of the optical constants of the different films. Further we measured the position of the minimum of the reflection curve on different points of the substrate (Table 2). Comparing the optical constants of Table 1 and 2, we see

Table 1. Optical data of different Ag references.

Nr. of Film	Angle θ [DEG]	Thick-ness [Å]	Optical Constants	
			real part	imag. part
Ag/I	45.20	481	−15.772	0.473
Ag/II	45.25	480	−15.418	0.350
Ag/III	45.25	474	−15.744	0.358
Ag/IV	45.19	473	−15.852	0.281
Ag/V	45.17	470	−16.021	0.319

Table 2. Optical data of substrate Ag/VI at different points.

Spot	Angle θ [DEG]	Thick-ness [Å]	Optical Constants	
			real part	imag. part
a	45.17	476	−15.924	0.264
b	45.15	473	−16.172	0.301
c	45.14	455	−16.277	0.295
d	45.18	459	−16.057	0.262

that the variations are of the same order of magnitude: real part $< 5\%$ and imaginary part $< 7\%$.

These variations cause an error of the refractive index of cadmium arachidate of about 1%.

4. Results of Measurements with Gold Film

We have made the same experiments and analysis with Au substrates as described above for Ag-films. In Table 3 the angles of the minima θ_0 are gathered for different numbers of monolayers, the columns α, β, γ represent different measurements. The average shifting $\Delta\theta_0$ is listed in the next column. If we use a refractive index of cadmium arachidate of 1.52, the difference of measured and calculated position of the reflection minimum is of the order of magnitude of experimental error (Table 3). To control the shape of the minimum we plotted the calculated reflection curve using the

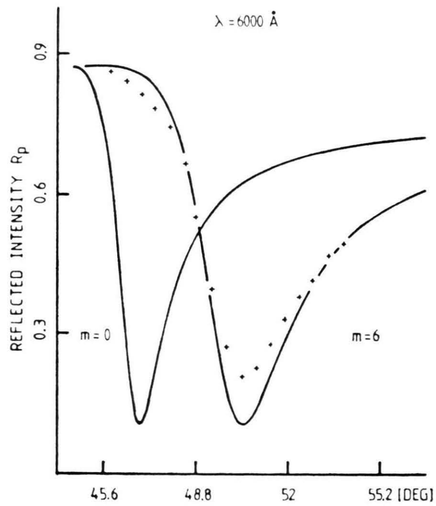

Fig. 5. Reflection curve of Au: The first minimum is calculated for the Au substrate. The second one belongs to the Au substrate coated with 6 monolayers. The crosses are experimental points.

Table 3. Real and imaginary part of the dielectric function of substrate Au/X at wavelength 6000 Å: $-9.06 + j\,1.642$, thickness 548 Å at different points.

	Measurement				Calculation	
Nr. of Layers	Angle of Incidence θ_0 [Deg] α	β	γ	Shift $\Delta\theta_0$ [Deg]	Angle θ_0 [Deg]	Shift $\Delta\theta_0$ [Deg]
0	46.80 ±	0.04			46.82	
2	47.78	47.76	47.78	0.97	47.81	0.99
4	48.97	48.94	48.97	2.16	48.99	2.17
6	50.36	50.40	50.36	3.57	50.40	3.58

Table 4. Optical constants of different Au films.

Nr. of Film	Angle θ_0 [Deg]	Thick-ness [Å]	Optical real part	Constants imag. part
Au 0/V	46.99	574	−8.613	1.356
Au 9/V	46.97	570	−8.665	1.324
Au 0/VI	46.83	543	−9.004	1.549
Au 9/VI	46.86	540	−9.054	1.635

data of the Au reference and of the organic film as determined above (see Table 3). For example we took substrate Au/X with 6 monolayers coating (Figure 5).

Table 5. Optical constants of Substrate Au X at different points.

Spot	Angle θ_0 [Deg]	Thick-ness [Å]	Optical real	Constants imag. part
a	46.89	529	−8.950	1.429
b	46.86	508	−9.120	1.786
c	46.89	555	−9.060	1.782
d	46.84	548	−9.060	1.642

To know the accuracy of the measurements we have derived the optical constants of several Au films (Table 4) and made tests on different points of one reference film (Table 5). The variation of the optical properties cause an error of the refractive index of cadmium arachidate of 1%.

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[1] B. Blodgett and I. Langmuir, Phys. Rev. **51**, 964 (1937).
[2] In the meantime an article on the same subject has appeared (J. G. Gordon II and J. D. Swalen, Opt. Com. **22**, 374 (1977). Further we have obtained a preprint by I. Pockrand, J. G. Gordon, J. D. Swalen and M. R. Philpott. Besides some differences the main results were in agreement with the data reported here. We have to thank these authors for sending us the preprints.
[3] H. Raether, Phys. of Thin Films, **9**, 145 (1977), Academic Press, New York.
[4] I. Pockrand, Surface Science, to be published.
[5] R. Steiger, Helvetica Chimica Acta, **54**, 2645 (1971).
[6] H. Kuhn, D. Moebius, and H. Bücher, Techniques of Chemistry, Vol. 1, Part IIIb, Spectroscopy of Monolayer Assemblies, Chapter VII, Wiley Interscience, New York 1972.
[7] H. Kuhn and D. Moebius, Z. Angewandte Chemie **83**, 672 (1971).
[8] E. Kretschmann, Z. Physik, **241**, 313 (1971).