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Interference Attenuated Total Reflectance On Tin-Oxide Glass Substrates

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The application of Attenuated Total Reflectance spectroscopy has been used for the study of interfacial phenomena.[1] The specific application of this technique to identify and to study species formed during an electrochemical process has been successfully demonstrated by Hansen, Kuwana, and Osteryoung.[2] The conducting surface for the electrochemical process may be either a thin metallic film or a thin layer of "doped" tinoxide on glass substrate. To obtain the spectrum of the species under study, the difference in the values of the reflectance abosrbance with and without the generated species at the surface, was plotted against wavelength. As noticed by these authors, the shape of the spectra depended on the thickness of the films. It was assumed that the film (tinoxide) acted merely as a neutral filter. However this approach is not valid as will be shown. The approach presented in this paper is based on Murmann-Forsterling formula for reflection of light from thin films.[3]

Experimental:

Reagent grade chemicals were used and the solutions were made with doubly distilled water. Tinoxide coated glass plates were obtained from Corning Glass Co. Spectra were obtained on a Cary Model 15 spectrophotometer. Thin films of gold were deposited on glass plates by vacuum evaporation method. The design of the cell was similar to the one previously described.[2]

The Univac 1107 computor using algol system was used for computations.

Theory:

The problem is divided into two sections. First the Fresnel reflective coefficients are calculated for reflections at the interface of two absorbing media. Then these values are used in the general formula for reflection from thin films, first derived by Forsterling for normal reflection, but modified to include any angle of incidence.

Fresnel Reflective Coefficients:

The equation for Fresnel reflective coefficient, r_1, for perpendicularly polarized light at the interface of two absorbing media is

$$r_1 = \frac{\hat{n}_1\cos\phi_1 - \hat{n}_2\cos\phi_2}{\hat{n}_1\cos\phi_1 + \hat{n}_2\cos\phi_2} \qquad (1)$$

where $\hat{n}_1$ and $\hat{n}_2$ are the complex refractive indices, with $\hat{n}_1$ equal to $n_1 - i\kappa_g$ and $\hat{n}_2$ equal to $n_2 - i\kappa_2$ where n_1 and n_2 are the refractive indices and κ_1 and κ_2 are the attenuation indices of tinoxide film and solution respectively. ϕ_1 and ϕ_2

are the angle of incidence and the angle of refraction for the light beam entering from the glass substrate. In the above equation, the angles are also complex, but they can be replaced in terms of the real experimental quantities, ϕ_0 the angle of incidence of the light beam on the transparent glass substrate and it refractive index n_0, using Snell's law.

$$n_0 \sin \phi_0 = \hat{n}_1 \sin \phi_1 = \hat{n}_2 \sin \phi_2 \qquad (2)$$

Simplification of equation (1) leads to the Fresnel reflective coefficient

$$r_1 = \left[\frac{\xi - \eta}{\xi + \eta}\right]^{1/2} \qquad (3)$$

where

$$\xi = x^2+y^2+p^2+q^2 \qquad \text{and}$$

$$\eta = 2(px+qy)$$

with

$$x = 1/\sqrt{2}\sqrt{(N_1^2 - N_1^2\kappa_1^2 - \sin^2\phi_0) + \sqrt{(N_1^2 - N_1^2\kappa_1^2 - \sin^2\phi_0) + (2N_1^2\kappa_1)^2}}$$

$$y = -1/\sqrt{2}\sqrt{-(N_1^2 - N_1^2\kappa_1^2 - \sin^2\phi_0) + \sqrt{(N_1^2 - N_1^2\kappa_1^2 - \sin^2\phi_0) + (2N_1^2\kappa_1)^2}}$$

$$p = 1/\sqrt{2}\sqrt{(N_2^2 - N_2^2\kappa_2^2 - \sin^2\phi_0) + \sqrt{(N_2^2 - N_2^2\kappa_2^2 - \sin^2\phi_0) + (2N_2^2 k_2)^2}}$$

$$q = -1/\sqrt{2}\sqrt{-(N_2^2 - N_2^2\kappa_2^2 - \sin^2\phi_0) + \sqrt{(N_2^2 - N_2^2\kappa_2^2 - \sin^2\phi_0) + (2N_2^2\kappa_2)^2}}$$

The signs for the square roots are dictated by the condition that the reflectivity always be equal or less than unity. Further $N_1 = n_1/n_o$ and $N_2 = n_2/n_o$.

The phase angle β associated with the above electric vector is calculated to be

$$\sin \beta = 2(py-qx)/(\xi^2 \eta^2) \qquad (4)$$

Table I

Comparison Between Experimental and Simulated Spectra

	Experimental	Simulated +
Maxima	390 mμ	390 mμ
	458 "	460 "
	748 "	760 "
Minima	415 "	420 "
	508 "	510 "
	635 "	655 "

The thickness of the film is taken to be 960 mμ.

For individual cases of reflection, the amplitude and the phase angle can be evaluated from equations (3) and (4).

Murmann-Forsterling Formula:

The reflections from thin films give rise to maxima and minima, the distance between the peaks being dependent upon the thickness of the film. The ray of light entering the glass substrate is partially reflected with a Fresnel coefficient r_1 and phase angle γ, at the film-glass interface. The transmitted part travels through the film with thickness d being attenuated by a factor α and undergoes a phase lag of δ . This ray is further reflected with a Fresnel coefficient r_2 and a phase angle β at the film-solution interface. Thus the progressively attenuated rays undergo multiple reflections in the thin film. These partially emergent electric vectors may constructively or destructively interfere with the first reflected ray. The net addition of these vectors and subsequent manipulation with the complex conjucate gives

$$\text{Reflectivity}=I/I_o = \frac{r_1^2 + (\alpha r_2)^2 + 2\alpha r_1 r_2 \cos(\gamma-(\beta-\delta))}{1 + (\alpha r_1 r_2)^2 + 2\alpha r_1 r_2 \cos(\gamma+(\beta-\delta))} \qquad (5)$$

where

$$\alpha = \exp \frac{4\pi d n_o y}{2\lambda}$$

and

$$\delta = \frac{4\pi d n_o x}{2\lambda}$$

λ being the wavelength.

Experimental Results and Discussion:

In figure 1. experimental reflectance spectra for the tinoxide-air and tinoxide-water interfaces with perpendicularly polarized light are shown. Absorbance is defined as -log Reflectivity.

The validity of equation (5) was checked by the computor by simulating the spectrum with substituted values. The value of κ_1, the attenuation index for tinoxide, was evaluated as 0.0035. The value for the thickness of the film was chosen to be 960 mμ, as this number gave similuated spectra similar to experimental ones as may be seen in Table I. This value is near the value of 1 micron quoted by the manufactures. Further agreement at all wavelengths is not expected because of the assumed constant value for the refractive index.

The refractive index for tinoxide and glass were taken as 1.88 and 1.49 respectively. The angle incidence ϕ_o was 72°.

An important conclusion drawn from the results is that the change in refractive index affects the position as well as the heights of the absorbance peaks.

The second interesting aspect of these spectra is the following. In A.T.R. if the absorbance of the species is independent of wavelength, the spectrum would be a straight line parallel to the wavelength axis. In the interference A.T.R. non-linear effect of κ_2, the attenuation index of species in solution is seen on the spectrum. For a constant κ_2, the maximum of absorbance for species coincides with the maximum due to the interference A.T.R. In figure 2 the relative change of absorbance is plotted as a function of wavelength with $\kappa_2 =$ 0.005. It is clear that the shape of the spectrum for the species at the solution-film interface is greatly dependent on the optical properties of the film.

Figure 3A is the A.T.R. spectrum of Eosin-Y with the tinoxide coated plate replaced by a plastic one. There is no evidence for adsorption of Eosin-Y on this surface. The peak occurs at 521 mμ. Using formulas (1) and (3), the κ_2 values are calculated for different wavelengths and then substituted into equation (5). The computor calculations give the resultant absorbance which is shown in Figure 3B. Figure 3C is the experimentally determined absorbance curve for Eosin-Y with the tinoxide coated cell. It is clear that the A.T.R. thin film simulated spectrum is in agreement with the experimental spectrum but shifted to longer wavelengths with respect to the experimental A.T.R. spectrum without the thin film.

The preliminary calculations for parallel polarized light showed that the Reflectivity was relatively lower than that for perpendicular polarization. The electric vector experiences a field effect as it penetrates the medium and is reflected at the interface. Optical rotation may therefore be expected in an applied electric field. In the absence of any absorbing species (only the supporting electrolyte) the peak height changes with applied potential. It is very important that the future workers report similar observations in addition to giving the effect of potential in the presence of absorbing species. Further, our observation that the Absorbance-time relationship for potentiostatic jump is much longer than the one expected on the basis of diffusion and penetration depth agrees with those reported previously.[2] This time dependence is very difficult to understand by only considering the surface concentration unless there is a time dependent adsorption of the material occurring. Similar time dependence is noticed with only supporting electrolyte (pH 1, HCl buffer) and this may be from the orientation of molecules in the tinoxide film, which leads to the time dependent anisotropic behavior. Figure 4 gives the potentiostatic jump to 0.6 v with respect to s.c.e. with gold and tinoxide films. One might notice the rapid response with the gold film, compared to that of the tinoxide film. Though one cannot discount the effect of film formation totally, it should be borne in mind that the new film will definitely alter the shape of the spectrum, both in the height and the position of the peaks. In Figure 5 the reflectance spectrum of tinoxide plate coated with a thin layer of gold is shown. This spectrum is predicted by Forsterling relationship for reflections from multiple films.

To summarize, extreme care should be exercised in interpreting the chemical phenomenon on surface purely from optical measurements, when thin films are used. The calculation penetration depth is in error because of multiple reflections in the thin film.

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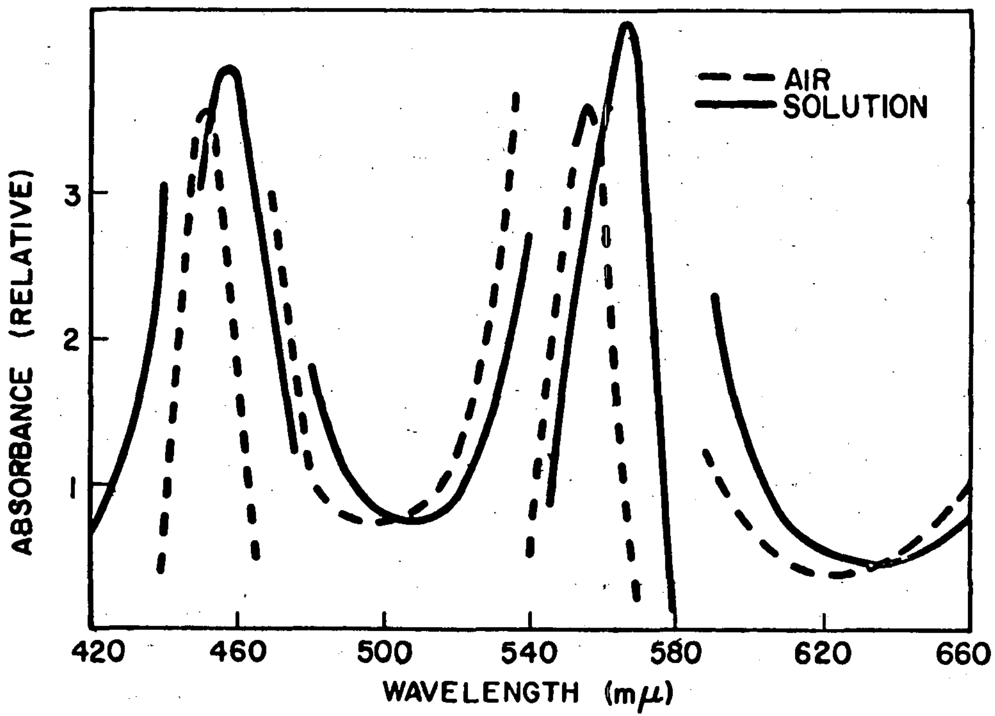
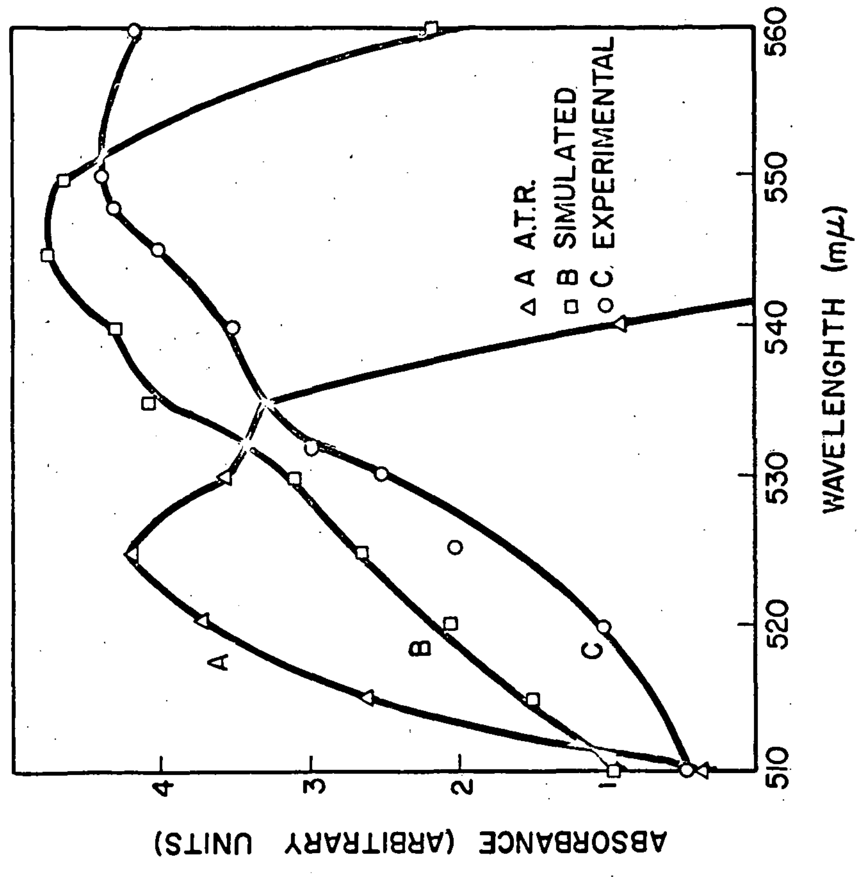
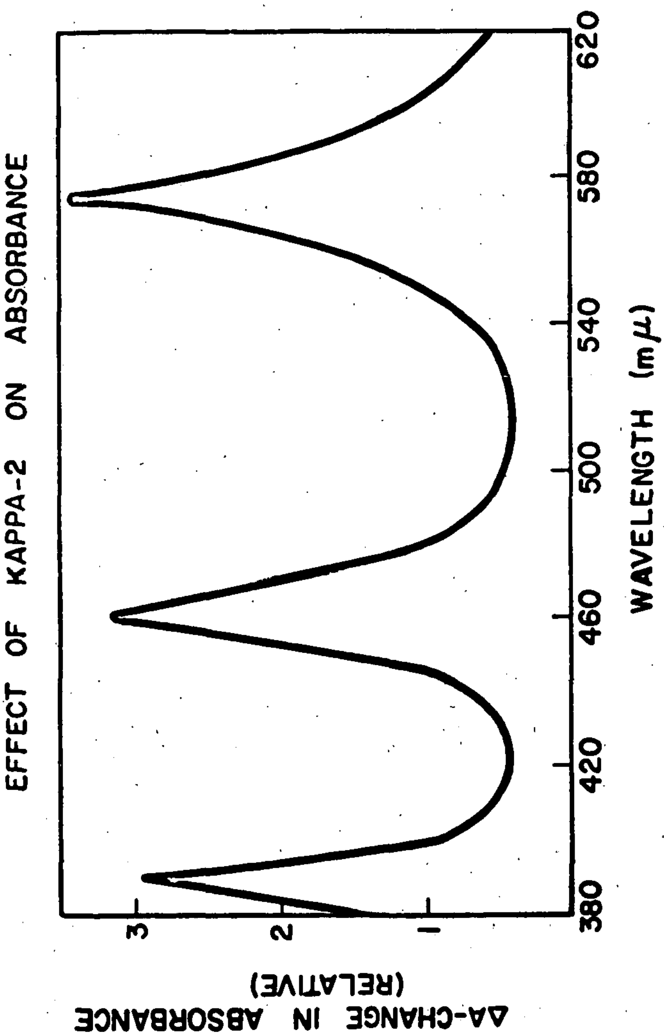
3. Vasicek, A., "Optics of Thin Films", pp. 323-327, North-Holland Publishing Co., Amsterdam (1960).

REFLECTANCE SPECTRA OF SnO_2-GLASS

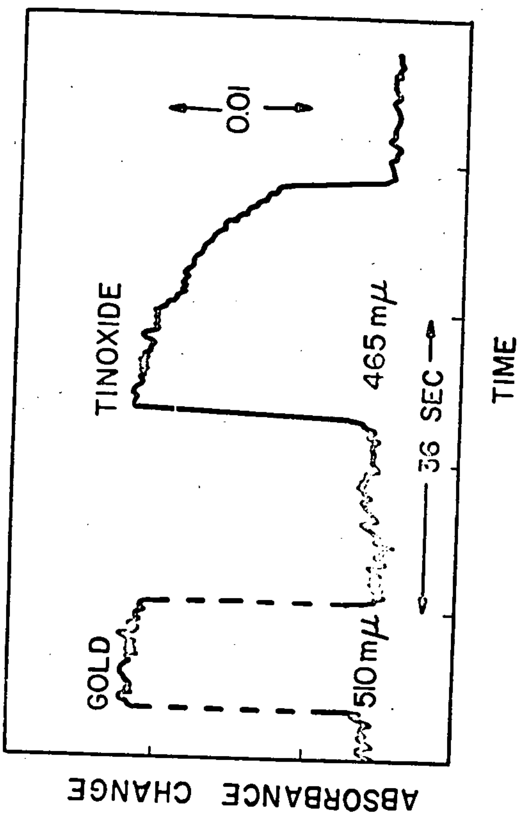


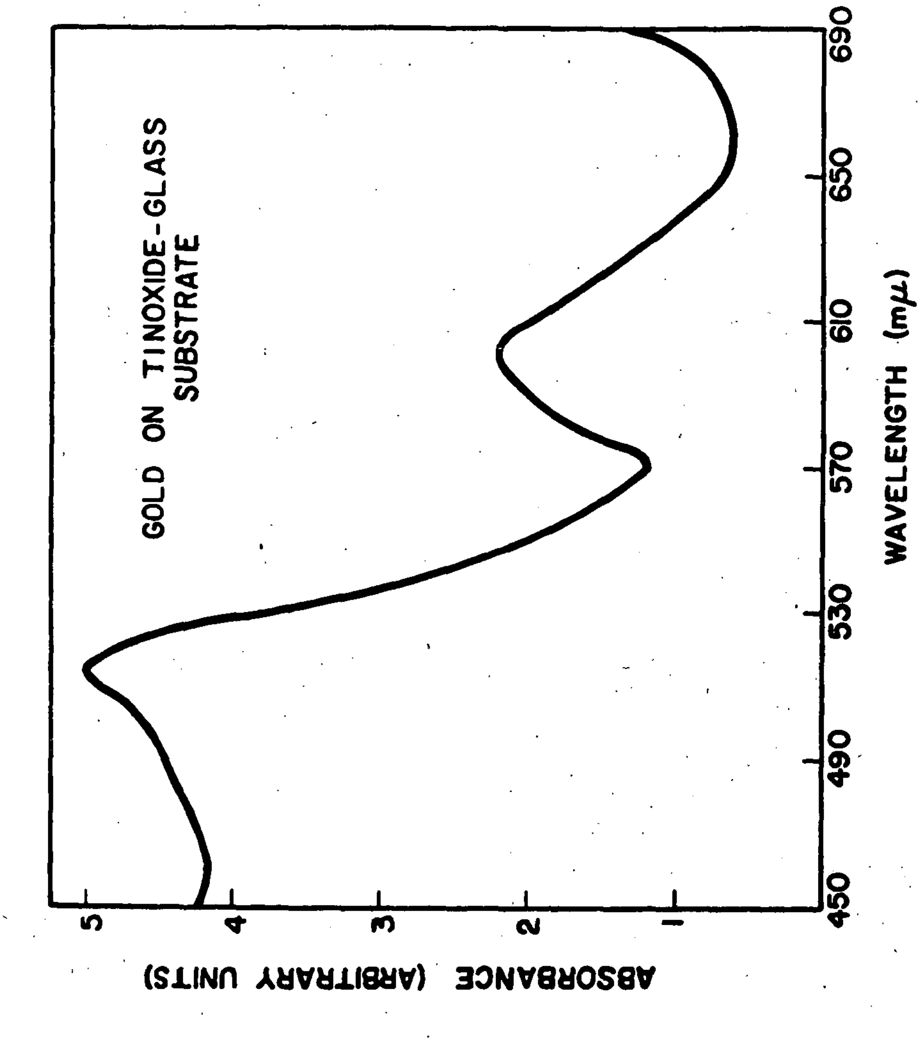
REFLECTANCE SPECTRA OF EOSIN-Y




EFFECT OF KAPPA-2 ON ABSORBANCE
ΔA-CHANGE IN ABSORBANCE
(RELATIVE)
1
2
3
380
420
460
500
540
580
620
WAVELENGTH (mμ)

CHANGE IN ABSORBANCE FOR SUPPORTING ELECTROLYTE




GOLD ON TINOXIDE-GLASS
SUBSTRATE
ABSORBANCE (ARBITRARY UNITS)
WAVELENGTH (mμ)
1
2
3
4
5
450
490
530
570
610
650
690