Title

SPECTROSCOPIC ELLIPSOMETRY OF RHODAMINE-B ADSORBED ON PLATINUM, SILVER AND COPPER

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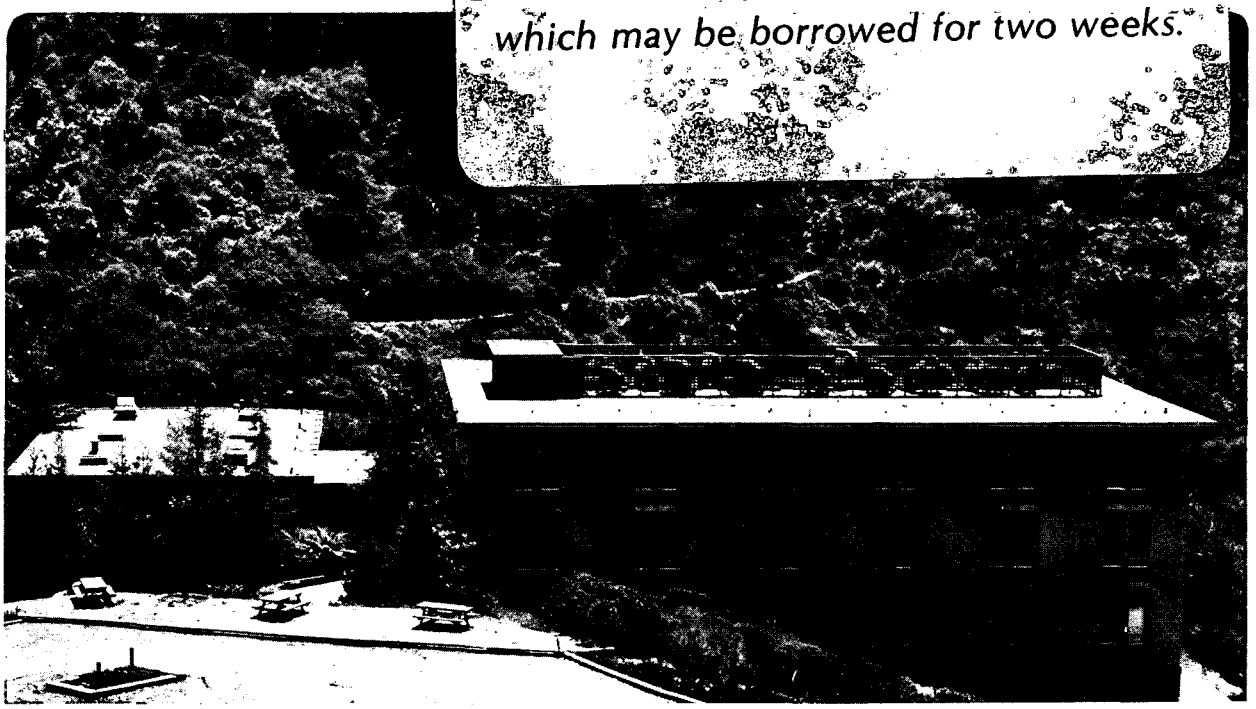

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DISCLAIMER

SPECTROSCOPIC ELLIPSOMETRY OF RHODAMINE-B ADSORBED ON PLATINUM, SILVER AND COPPER

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The use of spectroscopic ellipsometry has been investigated for the determination of number and orientation of dye molecules adsorbed from solution, and to find whether a specific orientation is responsible for the inhibiting effect in cathodic metal deposition. Rhodamine-B, shown schematically in Fig. 1, was chosen as dye because it is well-characterized optically (1) and structurally and available in high purity at low cost. Its electronic transition moment for light absorption lies in the plane of the aromatic rings. In solution, it absorbs light in the spectral range (370-720 nm) accessible to a spectroscopic ellipsometer (2). Among 30 model inhibitors tested, Rhodamine-B showed the largest electrochemical effect for the electrodeposition of Pb. Substrates used were Pt, Ag, and Cu. The electrolyte was 1 M $NaClO_4$, 5 mM $Pb(NO_3)_2$, and 0.5 to 20 μM dye, acidified to a pH of 3 with $HClO_4$.

The ellipsometer was also used to determine the effect of this adsorbed organic material on the micromorphology of electrolytic metal deposits (3) from the first few atomic layers to films of 2000 Å thickness (4). The optical model used in this work for the adsorbate layer is that of a homogeneous, uniaxially anisotropic film with optic axis normal to the surface of the substrate (5). Changes of coverage (number density) by adsorbed molecules are represented by changes in the optical constants of a film of fixed (molecular) thickness. This optical treatment is based on the use of a macroscopic optical model extrapolated to molecular dimensions. Such models have been remarkably successful in interpreting ellipsometer measurements of sub-monolayer films (6-8).

The principal feature of the adsorbed dye layer is its large extinction coefficient at the wavelength of maximum adsorption; at other wavelengths its optical constants are similar to those of the solvent, with a very small extinction coefficient. Oriented adsorbed dye molecules produce dichroism in the adsorbate layer because the electric field vector parallel to the electronic transition moment of the dye molecule is attenuated to a much greater extent than that normal to it. The extinction coefficients in the ordinary (parallel) and extraordinary (normal) directions are therefore different.

Spectroscopic ellipsometer measurements of adsorbed Rhodamine-B are illustrated in Fig. 2 with an Ag(111) substrate for different dye

concentrations in solution. It was concluded that the surface becomes saturated with Rhodamine-B at a concentration of approximately 1.2 micromolar; increases in peak response above the 1.2 micromolar level may be due to an artefact caused by light absorption in the solution (11).

Experimental spectroscopic ellipsometer measurements were interpreted on the basis of spectroscopic simulations. Molecular orientations and number densities were estimated from the thickness and the ordinary and extraordinary complex refractive indices of the adsorbed layer derived from the measurements. Coverages of close to 50% of close packing were found with primarily normal orientation for Ag and mixed orientations for Pt and Cu.

Spectroscopic ellipsometer measurements of Rhodamine-B adsorbed on polycrystalline Pt are illustrated in Fig. 3 . Two peaks are caused by the presence of the adsorbed dye, a small peak at 470 nm (positive for delta, negative for psi) and a broad band centered at about 570 nm (negative for delta and psi). Based upon the optical simulations, the broad band has been interpreted as being due to adsorbed dye molecules with electronic transition moments oriented normal to the surface; only slight chemical shifting of the peak from the wavelength of maximum absorption for the dissolved dye is observed. The smaller peak has been interpreted as a chemically shifted absorption due to a strongly chemisorbed species having its transition moment parallel to the surface.

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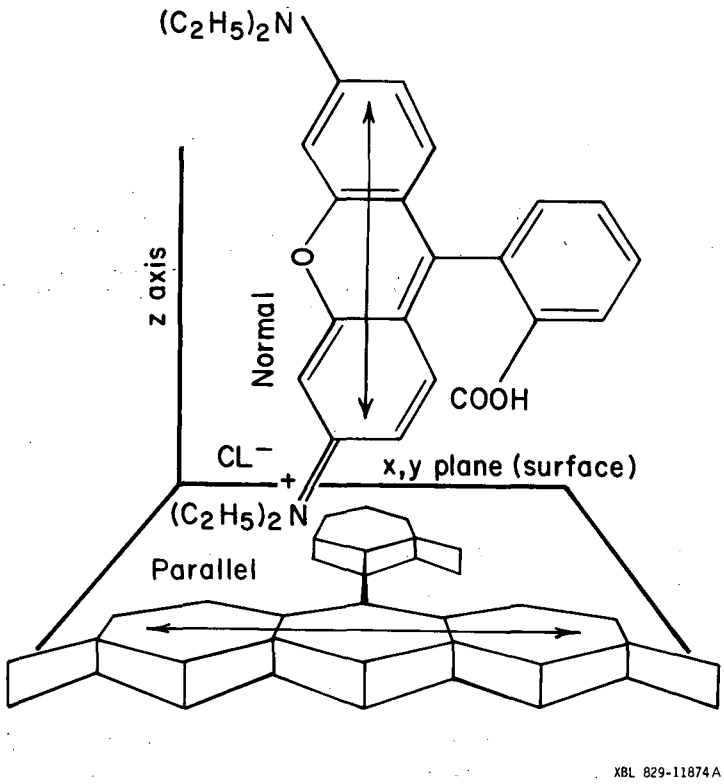

Fig. 1

Limiting orientations of adsorbed Rhoadmine-B molecules with electronic transition moment, shown by arrows, normal or parallel to the electrode surface, represented by the x-y plane.

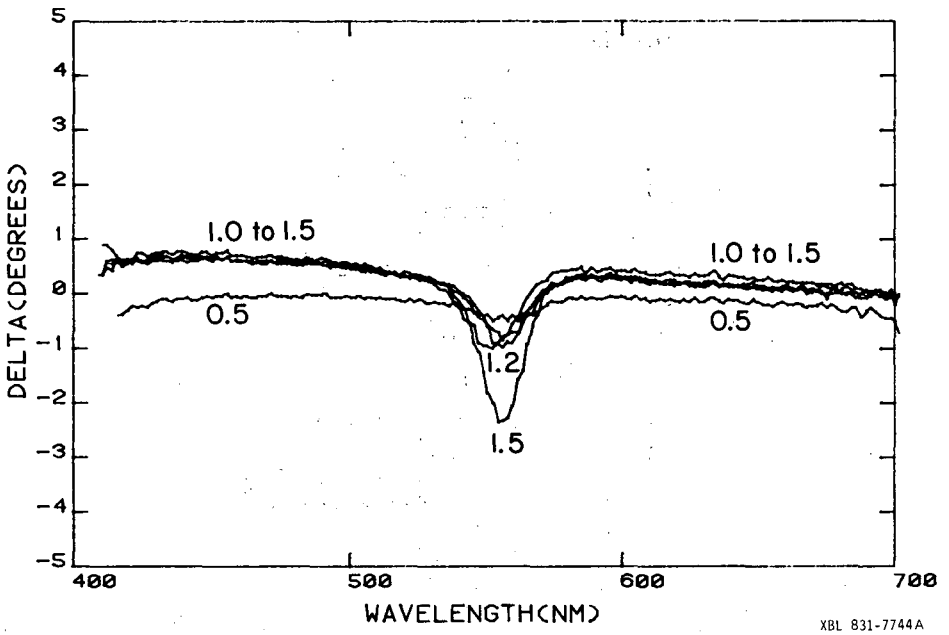

Fig. 2

Experimental spectroscopic ellipsometer measurements of Rhodamine-B adsorbed on Ag(111) from solutions of 0.5, 1.0, 1.1, 1.2 and 1.5 micromolar dye concentrations containing 5 mM $Pb(NO_3)_2$ and 1 M $NaClO_4$ at pH 3. Difference spectra for delta relative to bare surface. Surface saturated with adsorbed Rhodamine-B of preferential normal orientation at a concentration of about 1.2 micromolar; changes in delta at higher concentrations due to variations in instrument gain (absorption in solution).

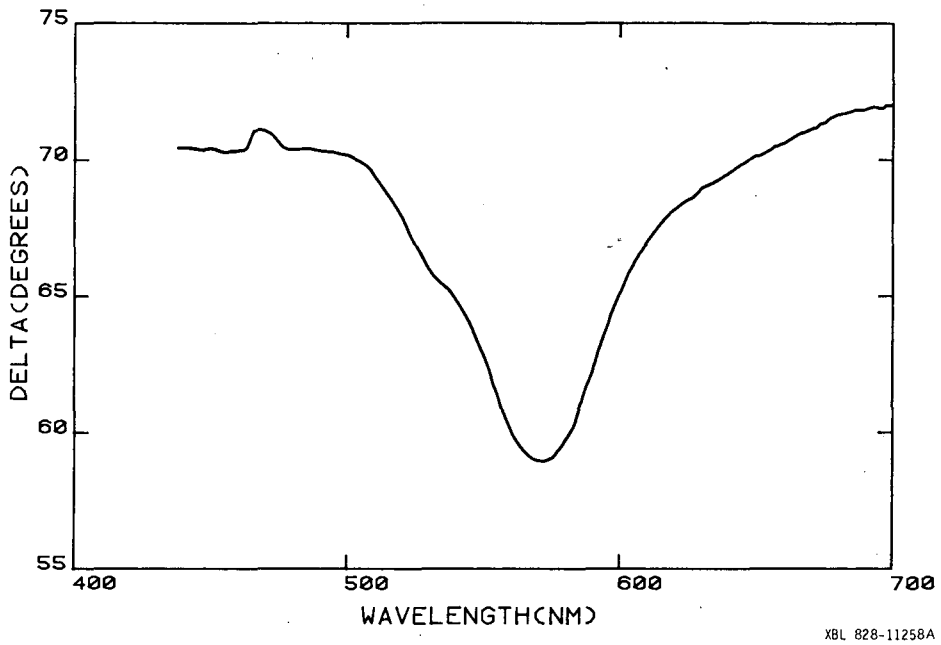

Fig. 3

Experimental spectroscopic ellipsometer measurements of Rhodamine-B adsorbed on Pt from a 20 micromolar solution containing 5 mM $Pb(NO_3)_2$ and 1 M $NaClO_4$ at pH 3. Absolute values of delta vs. wavelength. Broad minimum between 500 and 600 nm attributed to normal orientation of the electronic transition moment, small maximum at about 420 nm attributed to parallel orientation of the transition moment and strong electronic interaction with the surface.

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