Total Internal Reflection Ellipsometry - A Tool for In-situ Corrosion Studies

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Objectives

Ellipsometry has sub-nanometer resolution for thickness determination that can be utilized in sensor applications. The objective here is to demonstrate that ellipsometry in total internal reflection mode can be used for in-situ corrosion monitoring and sensing.

Background and Short Technical Description

Ellipsometry is based on measurements of the change of the polarization state of a light beam reflected from a surface [1]. It has a high surface sensitivity, which makes it powerful for studies of thin films [2]. A complementary technique, total internal reflection, is based on measuring the intensity of a light beam reflected at an interface for which the optical density is higher for the incident medium. The evanescent field associated with total internal reflection can then be used to monitor layers at the interface.

The combination of ellipsometry and total internal reflection becomes a powerful tool for thin film analysis with high sensitivity and precision. We call the technique total internal reflection ellipsometry (TIRE). In addition to the features of ellipsometry, this configuration has the important advantage that the medium that influences the thin layer on the sample can be non-transparent.

The TIRE system is based on a rotating analyzer ellipsometer equipped with a prism and a flow cell designed for total internal reflection measurements of an angle of incidence of 70°. In the flow cell a glass slide with a thin metal layer is mounted in optical contact with the prism. Liquid flowing through the cell may affect the metal layer, causing changes in thickness, roughness or other properties of the layer. These will change the optical conditions at the interface and can be monitored as changes in the ellipsometric angles ψ and Δ. If the refractive indices of the prism, the glass slide and the layer are known, one can quantify the thickness and refractive index changes in the metal layer due to corrosion in a single measurement. A more detailed technical description is given elsewhere [3].

Results

TIRE is a new development and so far only pilot studies have been done. This includes corrosion measurements with thin copper layers exposed to 1-100 mM hydrochloric acid (HCl) in water. These experiments were performed to check the abilities and sensitivity of the system as a corrosion sensor.

The samples used in the measurements were glass slides with 60 nm and 30 nm copper films fabricated by vacuum deposition. Two types of experiments were performed. In the first type a flow of water was switched to HCl during periods in the range 2-15 minutes and then back to water. In the second type a thin copper layer was exposed to HCl for a long time (10 hours). The kinetics of ψ and Δ were recorded at the wavelength of 700 nm during the experiments. Before and after HCl exposures in the first type, and once an hour in the second type, ellipsometric spectra were recorded in the wavelength range 350-1000 nm to make a more detailed analysis possible. Both types of experiments were repeated for the different Cu samples with different thicknesses and for different HCl concentrations.

Spectra recorded during one of experiments of the first type are presented in Fig.1. The experimental conditions were: 60 nm Cu layer, 10 mM HCl, 10 minutes HCl exposures with about 30 minutes water exposures in between.

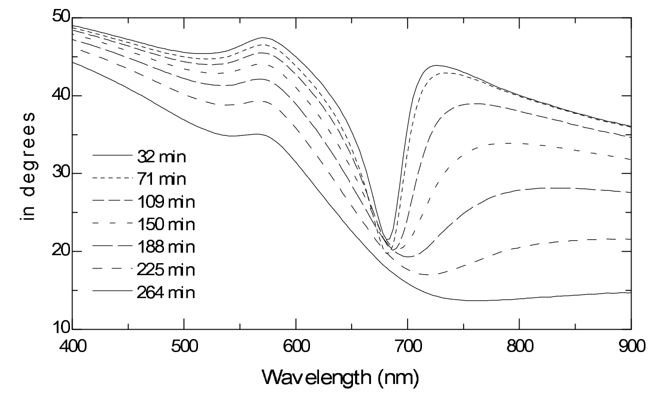

Fig.1. TIRE spectra (ψ only) for a 60 nm Cu layer on glass. The data were recorded between 10 minutes HCl exposures at times as indicated, except the first curve which was recorded after 32 minutes of water exposure.

Differences between the spectra are typically about 5-15%, which corresponds to changes of 7-12 degrees in ψ (the sensitivity of the system is about 0.05 degree). Analysis of the ψ and Δ spectra showed a decrease in the copper layer thickness, an increase of surface roughness and formation of a thin CuO layer on the top of the Cu layer due to the exposure to HCl.

Discussion

Ellipsometry can be used in total internal reflection mode for corrosion studies. The high sensitivity makes it useful in environments where even very slow corrosion takes place. A major advantage is the possibility to use it in non-transparent media. It should also be observed that there is no restriction to thin metal films in which surface plasmons can be generated because ellipsometry is a general optical probe. Being an optical technique, TIRE is perturbation free from an electrical point of view, which is an advantage in corrosion monitoring. Here we have demonstrated the use of TIRE with copper as a sensing layer. However, depending on type of application other metals like iron, titanium, chromium, etc. can be used. Corrosion from gas phase is also possible.

Acknowledgments

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References

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