Technical Paper

Microscopic Ellipsometry of Ferric Hydroxide Films*

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A new type ellipsometer was constructed for the microscopic measurement of a film of uneven thickness. The modification of the ellipsometer consisted of the attaching of an objective lens between the specimen and analyzer, the formation of a magnified image of the specimen, the focal plane of which was limited with an aperture, and the photoelectric measurement of light passing through the aperture. The minimum measurable area on the specimen was about $30 \times 50 \mu\text{m}$. A He-Ne gas laser as a light source provided light intensity sufficient for the determination of the ellipsometer null point by using a photomultiplier. The modified ellipsometer allowed to determine the refractive index and local thickness of uneven films. It also provided fringe patterns based on the ellipsometer equation. The modified ellipsometer was applied to the measurement of anodically deposited ferric hydroxide films resulted from pitting corrosion. The relation between the deposited ferric hydroxide films and anionic species in a solution is also discussed.

1 Introduction

A number of investigators have applied ellipsometric technique to the measurement of anodic films. The studies have been mainly concerned with thin films of uniform thickness, because conventional ellipsometers allow only macroscopic measurement, in which measured area on a specimen is determined by the diameter of parallel light beam. In the study of corrosion of passive metals, it is often of greater concern of many investigators to know the local change of a surface film rather than the accurate value of the thickness and optical constants of a film. In an attempt to apply the ellipsometric technique to localized corrosion, a new type ellipsometer was developed for microscopic measurement. Although the method utilized in the present experiment causes a decrease in the accuracy of ellipsometer readings it allows photometric measurement of an area of $30 \times 50 \mu\text{m}$, and provides fringe patterns based on the ellipsometer equation.

In the previous paper⁽¹⁾, the author has shown that iron suffers pitting corrosion in neutral solutions containing sulfate ion and that the pit is accompanied by the formation of an amorphous ferric hydroxide film. The new ellipsometric technique was applied to the ferric hydroxide film which was not uniform in thickness, and the refractive index and thickness profile were obtained. Similar measurements were also per-

formed for a deposited film as a result of pitting in a neutral solution containing chloride ion. The relation between crystalline structure of the film and the anionic species in the solution is also discussed. In the modified ellipsometer, these films showed fringe patterns resulted from the nonuniformity. The pattern has proved to be very useful for the qualitative understanding of localized corrosion.

2 Instrumentation

A conventional ellipsometer was modified for the purpose of microscopic measurement. The optical arrangement is shown in Fig. 1. A He-Ne gas laser (1 mW, single mode, and without polarization property) was used as a monochromatic light source ($6328 \text{ \AA}$), the parallel light beam of which was about 2 mm in diameter, and the light beam was directed to a specimen without further collimation. In order to obtain a magnified image of a specimen, an objective lens was attached between the specimen and analyzer. The lens used was an $\times 6$ objective of a metallurgical microscope. The objective should be attached in such a way that it can be moved on the optical axis for bringing the specimen into focus. In view of the depth of field and working distance, the focal length of the objective should be greater than 25 mm; thus large magnification cannot be attained. The combination of the telescope originally attached to the ellipsometer with the objective formed a microscope, with which either of the viewing observation, photomicrography, or photoelectric measurement was possible by changing the

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Fig. 1 Optical arrangement of an ellipsometer for microscopic measurement

(1) : He-Ne gas laser, (2) : Polarizer, (3) : Quarter wave plate, (4) : Specimen, (5) : Objective ($f \approx 30$ mm), (6) : Analyzer, (7) and (8) : Telescope, (9) : Camera, (10) : Diaphragm, (11) : Photomultiplier. The real image of a specimen is formed either on the camera or on the diaphragm

optical path. In the case of photoelectric measurement, a diaphragm with a variable aperture was located on the focal plane of the image, thus the measured area of the specimen being limited. The light passing through the aperture corresponds to an elliptic area on the specimen. The major axis of the ellipse, b , is expressed in the form:

$$b = a / \cos \varphi$$

where a is the minor axis of the ellipse and φ is the angle of incidence. The value of a is given by the magnifying power of the microscope multiplied by the aperture radius. The minimum value of $2a$ obtained in the present experiment was about $30 \mu\text{m}$.

3 Experimental

Iron specimens used for electrochemical and ellipsometric experiments in SO_4^{2-} solutions were prepared from electrolytic iron, which was vacuum melted and was hot-rolled to 1 mm thick. Specimens for the experiments in Cl^- -containing solution were also prepared from electrolytic iron, but they were deformed as much as 8%, followed by annealing in wet hydrogen atmosphere at 850°C for 12 hours. In the latter case large grained samples were obtained. The specimens were first abraded with emery papers and were finally polished with fine alumina gel.

Boric-borate buffer solution (pH 8.45) was used as a standard electrolyte in all experiments. Sulfate and chloride ions were added to the electrolyte in the form of their sodium salts.

The process of the electrolysis for SO_4^{2-} solution was the same as described in the previous paper¹⁾. In experiments of chloride pitting, sodium chloride

solution was injected to the standard buffer solution, after a specimen had undergone perfect-passivation treatment at 0 mV vs. S.C.E. for 1 hour.

A pitted specimen was mounted to a two-directionally movable stage that was attached to the ellipsometer. Each ellipsometric measurement was carried out by means of photomultiplier after the specimen being moved by 0.05 to 0.1 mm in the direction perpendicular to the plane of incidence. If a sample with nonuniform film is used, the single sample gives a number of ellipsometer values, thus forming an ellipsometer curve in ψ - Δ diagram.

The angle of incidence used in the present measurements was 55° . This value is relatively smaller than that employed in ordinary ellipsometric experiments, for the maximal sensitivity in ellipsometric measurement can usually be attained at around 70° ²⁾. The larger value of the angle of incidence, in this case, causes deterioration in the image, because the specimen is so mounted as it is inclined to the optical axis. The procedure in determining the photoelectric null point was the same as the case of a conventional ellipsometer. In the present experiment, ellipsometric measurements were made with the specimens exposed to the air.

4 Results and Discussion

Iron specimens suffer pitting corrosion when polarized in neutral sulfate or chloride solutions³⁾⁻⁵⁾. The pit is surrounded by a ferric hydroxide film which is formed as a result of anodic deposition of Fe^{2+} ions supplied from the pit. The schematic illustration of the pit is given in Fig. 2. The anodically deposited

Fig. 2 A schematic illustration of a pit and deposited ferric hydroxide film formed in a neutral solution

film is considered to play the role of inhibiting the lateral growth of the pit. The present experiment is mainly concerned with the deposited film.

A photomicrograph of a pitted specimen is shown in Photo. 1. The iron specimen was anodically polarized in a 0.1 M SO_4^{2-} solution buffered at pH 8.45. This micrograph was taken under monochromatic illumination of $5461 \text{ \AA}$, produced with a narrow band filter. Fringes around the pit are caused by the interference of the light reflected from film surface and film/metal interface. The change in reflectivity in

Photo. 1 Monochromatic light micrograph (5461 Å) of iron pitted in a borate solution containing SO_4^{2-} . Fringes around the pit are explained by Fig. 3

the presence of a thin film can be estimated from Fresnel's equation. Fig. 3 shows calculated reflectivity as a function of film thickness for vertical incidence of light, in which the refractive indices of iron

Fig. 3 Reflectivity change for iron as a function of the thickness or optical length expressed in phase shift ($\delta = 4\pi n_2 d_2 / \lambda$) of a surface film

The curve was calculated by assuming the refractive indices of iron and film: $n_s = 3.35 - 3.84j$ and $n_2 = 1.7$, respectively; and the wave length of light; $\lambda = 5461 \text{ Å}$, for normal incidence

and film are assumed as $n_s = 3.35 - 3.84j$ and $n_2 = 1.7$, respectively. The minimum of the reflectivity is as much as 23%, while the ratio of the minimum to the maximum is 38%; hence only a very diffuse fringe pattern is obtained by the conventional interference method.

Similar fringe patterns were obtained by using the modified ellipsometer, as shown in Photo. 2. The area shown in Photo. 2 is the same as that of Photo. 1. In the ellipsometer fringe pattern, the light intensity as a function of film thickness is given by ellip-

Photo. 2 Ellipsometric images (6328 Å) of iron pitted in a borate solution containing SO_4^{2-} , by using the modified ellipsometer

Two micrographs indicate the change of polarizer azimuths: Photo. 2-a and 2-b were obtained when ellipsometer values were set at angles indicated by points A and B in Fig. 4, respectively

someter equation; the fringes are, therefore, moved by rotating polarizers (Photo. 2-a and 2-b). Ideally, the film thickness that satisfies ellipsometer equation for a given set of polarizer azimuths gives perfect extinction of light. Thus the ellipsometer image gives very contrasted fringes. The gas laser, however, caused unexpected speckle patterns due to its excellent coherency, which made the image less sharp. It should also be noted that the scales given in Photo. 2 vary depending on vertical and horizontal directions because of the unavoidable angle of incidence.

Corresponding photoelectric results for $\lambda = 6328 \text{ Å}$ are shown in Fig. 4. Each plot was obtained with the displacement of the specimen at intervals of 0.05 to 0.1 mm. The measured area on the specimen was an elliptic shape of which minor axis was about 30 μm and major axis, 50 μm . The sensitiveness in the null point determination was decreased to a considerable degree compared with conventional ellipsometers. The light intensity of a laser is much less stable than that of a mercury lamp. In order to increase the stability, the gas laser had been warmed up at least for two hours before measurements were made, and it was allowed to operate with a stabilized

power supply and under a thermostated condition. In this case the short-term stability of the laser did not exceed 2% (in 30 sec.). Thus the instability of the laser is not considered to be a major factor that determines the accuracy in ellipsometer readings. Notwithstanding the coherency and instability of light, the laser afforded sufficient light intensity for determining ellipsometer null points by means of a photomultiplier and for quick photographing. The decreased sensitiveness is mainly attributed to the use of the objective placed between the specimen and analyzer. The curvature and optical inhomogeneity of the lense distort linearly polarized light reflected from the specimen to locally elliptic light before it passes through the analyzer, thus resulting in less sharp extinction. In order to minimize misalignment, the objective had not been attached until alinement procedures were completed with a specimen set to the ellipsometer. The misalignment is considered to cause systematic errors rather than the reduced sensitiveness in ellipsometer null point. Taking the above discussion and the relatively small angle of incidence into consideration, it is concluded that the present method for microscopic ellipsometry is not suitable for determining accurate values of the refractive index and thickness of a surface film.

Plots in Fig. 4 form an anti-clockwise loop, in which

Fig. 4 Ellipsometric data obtained from an iron specimen pitted in a borate buffer solution containing SO_4^{2-} ($\lambda = 6328 \text{ \AA}$ and $\phi = 55^\circ$)

Data on the second cycle are indicated by filled circles. A solid line represents a calculated curve for $n_2 = 1.7$

the data on the second cycle are indicated by filled circles. The closure of the loop indicates that the film is transparent (the refractive index is a real number). The ellipsometer values for the "bare" metal is not known in this case, owing to the measurement in the air and the presence of an underlying passive film. It is, however, possible to determine the film refractive index from the entire shape of the loop. A calculated film index ranged between 1.63 to 1.72 even in the region of large value of ϕ . A fairly good fit of the plots to a calculated curve was seen when the film refractive index was assumed as $n_2 = 1.7$. The calculated curve for $n_2 = 1.7$ is given by a solid line in Fig. 4. This value of the refractive index is lower than those of anhydrous oxides and even those of crystalline ferric hydroxides⁹; it is in agreement with that reported for amorphous ferric hydroxide film⁷. The amorphous nature of the film was also confirmed by electron diffraction technique.

Ellipsometer azimuths represented by points A and B in Fig. 4 gave corresponding fringe patterns of Photo. 2-a and 2-b, respectively.

The ellipsometer curve thus measured provided a film-thickness profile as a function of the distance on a specimen. A typical example of the profile is given in Fig. 5. The distance was measured with a vernier attached to the stage.

Fig. 5 Film thickness profile of a pitted iron specimen in a borate buffer solution containing SO_4^{2-}

In the measurements of specimens pitted in a solution containing chloride ion, no reproducible results were obtained. Some typical curves for $\lambda = 6328 \text{ \AA}$ are given in Fig. 6, in which curve A fits to that calculated by assuming $n_2 = 1.7$, while the film refractive index for curve B (probably a complex number)

Fig. 6 Ellipsometric data for iron specimens pitted in a borate buffer solution containing Cl^- ($\lambda=6328 \text{ \AA}$ and $\varphi=55^\circ$)

Difference of symbols indicates the scatter depending on specimens

could not be determined because of a number of adjustable sets of the real and imaginary parts of the index. The electron diffraction patterns for the film consisted of a few, diffuse rings which were identified as $\gamma\text{-FeOOH}$. This shows good contrast with the result of the deposited film formed in SO_4^{2-} solution. Crystalline ferric hydroxides are optically birefringent and the reported values of their refractive indices are larger than that obtained in the present experiment^{6),7)}. The discrepancy between the results of ellipsometry and electron diffraction is attributed

to the partial crystallization of the film formed in the chloride solution. This can be confirmed from curve A of which refractive index agrees with that of amorphous hydroxide. As proposed by Hashimoto and Cohen, complex forming agents participate in the formation of amorphous ferric hydroxide during the process of anodic oxidation of Fe^{2+} ⁸⁾. Since borate buffer is used as a standard solution in the present experiments, borate ion is expected to be introduced into the structure of ferric hydroxide^{9),10)}. It is quite probable that the introduction of such a glass former as borate ion might inhibit the formation of more stable form of $\gamma\text{-FeOOH}$.

A specially designed electrolytic cell for *in situ* ellipsometric measurement was constructed. In the observation of pit formation in chloride solution, the generation of a pit was recognized as a bright spot in the darkened image of a specimen. However, no conclusive information has been yet obtained. The use of the present ellipsometric technique to the *in situ* observation is a problem of future investigation.

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