Characterization of pitting corrosion in aluminum films by light scattering

Y.-P. Zhao,[a] C.-F. Cheng,[b] G.-C. Wang, and T.-M. Lu
Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180-3590

(Received 16 June 1998; accepted for publication 27 August 1998)

We report a detailed study of the morphology of pits formed by corrosion of aluminum thin films using an in-plane light scattering technique. We show that the corrosion front of the Al thin film can be treated as a quasi-two-level random rough surface. Based on an elastic diffraction theory, we are able to determine the average depth, the area, and the density of pits, as well as the fractal dimension of the surface. Using the advantages of light scattering, one can quantify the morphological parameters of corroded films *in situ* and nondestructively.
[S0003-6951(98)02743-0]

Pitting corrosion results in extremely localized holes in metals.[1] Recently, pitting of thin films has received extensive attention because thin films are widely used in electronic and magnetic recording industries as well as other industries. The pitting of thin films also provides a convenient opportunity for studying the phenomenon of pitting.[2] Many models have been developed to describe the morphological aspects of pitting corrosion, especially using the concept of fractal geometry.[3–6] Recent experiments have found that, for the open-circuit pitting of evaporated Al thin layers in NaCl and $Fe_2(SO_4)_3$, the shape of the pitting patterns depends on the thickness of the film, the pH value of the corrosion medium, the concentrations of aggressive anions (Cl^-) and the oxidizing agent (Fe^{3+}).[2]

One of the conventional methods for studying pitting corrosion is to use a microscope *ex situ* to monitor the propagation of pits. Data can be obtained at various stages during the corrosion process. Recent use of the charge-coupled device (CCD) camera attached to a microscope allows one to monitor the entire corrosion process in real time, which greatly improves the temporal resolution.[2] However, the information of the pit depth is lost, and a certain contrast in the image is required for the observation. Light scattering is another non-destructive technique with the advantage that it can provide the statistical information directly through the scattering profile. The statistics can be very good if the illuminated sample area is sufficiently large. Hunderi first used light scattering to monitor the corrosion processes *in situ*.[7] He related the change of the reflectivity directly to the pitting area. Recently, we performed a real-time light scattering experiment to monitor the wet etching process in Si(100), using a linear diode array with a 30 ms temporal resolution.[8] By measuring the scattering profile, we can obtain morphological parameters such as the lateral correlation length and pit depth in addition to the pitting area.

In this letter, we present a two-dimensional scattering theory based on a quasi-two-level random rough surface model to describe quantitatively the corroded surfaces of the Al thin films. According to the theory, we can obtain detailed information about the corrosion front.

The commercial p-type Si(100) substrates were degreased with organic solutions in an ultrasonic bath, followed by a rinse in deionized (DI) water. About 750 nm of Al was deposited using the electron beam evaporation technique. Under an open-circuit condition, the sample was immersed into a 0.04 M $FeCl_3$ solution at room temperature for 200–480 min. Then the sample was taken out from the solution and was rinsed thoroughly in DI water. After drying, the sample was characterized by atomic force microscopy (AFM) and light scattering *ex situ*. All the samples we characterized give similar results.

Figure 1 shows one sample image and the surface height distribution obtained from AFM. Clearly the surface consists of islands, and the height distribution [Fig. 1(b)] has two peaks. The separation between these two peaks is 690 ± 50 nm, giving the height of the islands. The area of the upper level distribution is 45% of the total area of the height distribution, indicating the fraction of the upper level area is about 0.45. The average fraction of the upper level for five AFM images is 0.38 ± 0.07. These facts lead us to believe that the pitting morphology can be described by a quasi-two-level system. (For an exact two-level surface, one would have two δ-function peaks in the height distribution.)

The light scattering system was described in detail previously.[8–10] In current experiments, the incident laser beam was circular polarized. Figure 2(a) shows six representative light scattering profiles collected at various incident angles: 12°, 28°, 42°, 48°, 54°, and 62° with respect to the surface normal of a Al film after 250 min of corrosion. Two features can be immediately seen: (1) Each profile has a sharp δ function like peak sitting on a diffuse broad profile, and the shapes of all the broad profiles are quite similar. (2) The peak intensity oscillates with the incident angle θ. In Fig. 3 we plot the peak intensity as a function of $k_\perp$, the momentum transfer perpendicular to the surface, $k_\perp \approx (4\pi/\lambda)\cos\theta$.

In order to understand the light scattering results, we write the intensity profile based on the Kirchhoff approximation:[11,12]

[a]Electronic mail: zhaoy@rpi.edu
[b]On leave from Shandong Normal University, People's Republic of China.

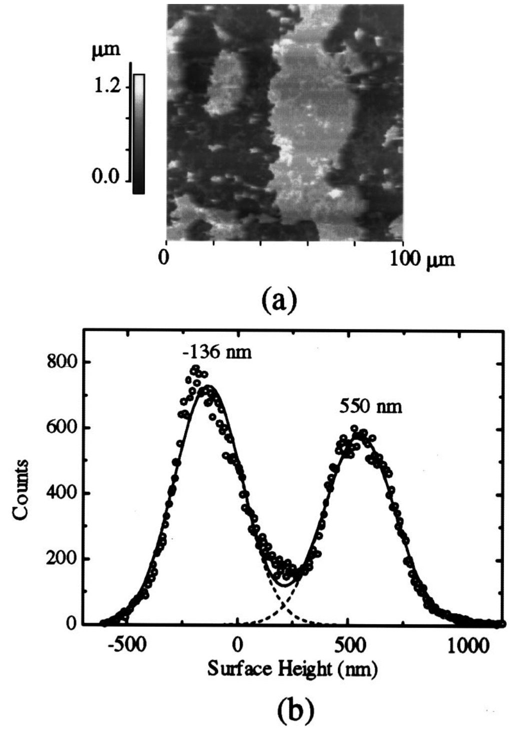

FIG. 1. (a) AFM image obtained from 250 min corroded Al film and (b) the surface height distribution of Al film on Si. Note that there are two peaks in the surface height distribution with a separation of about 690 nm. The solid curves in the height distribution are best Gaussian fits. The area under the upper level height distribution is 45% of the total area of the height distribution.

$$I(k_\perp,\mathbf{k}_\parallel)=RFP*\int e^{i\mathbf{k}_\parallel\cdot\mathbf{r}}\langle e^{ik_\perp[h(\mathbf{r})-h(0)]}\rangle d\mathbf{r}, \qquad (1)$$

where R is the surface reflectivity, F is an angular factor, and P is the system point spread function. According to Beckmann and Spizzichino,[13] for the diffraction from a rough metal surface,

$$F=\frac{1+\cos^2\theta-\sin^2\theta\cos\gamma}{2\cos^2\theta}.$$

In our experiments, since the in-plane scattering angle γ is small, $F\approx 1$. Therefore, we will ignore these factors in the following discussion. The surface height at position $\mathbf{r}$ is $h(\mathbf{r})$. The notations * and $\langle ...\rangle$ denote a convolution and an ensemble average, respectively. For a quasi-two-level surface, the ensemble average in the integrand in Eq. (1) can generally be written as[14]

$$\langle e^{ik_\perp[h(\mathbf{r})-h(0)]}\rangle=\left[1-4\Theta\sin^2\left(\frac{k_\perp d}{2}\right)\right]+4\Theta\sin\left(\frac{k_\perp d}{2}\right)P_{11}(\mathbf{r}), \qquad (2)$$

where Θ is the fraction of the upper level area, d is the distance between the upper level and the lower level, or the average pit depth, and $P_{11}(\mathbf{r})$ is the probability of an upper level at position $\mathbf{r}$ given an upper level at position $\mathbf{0}$. In general, $P_{11}(0)=1$ and $P_{11}(|\mathbf{r}|\to\infty)=\Theta$. For an isotropic surface, we assume $P_{11}(\mathbf{r})$ has the following form:

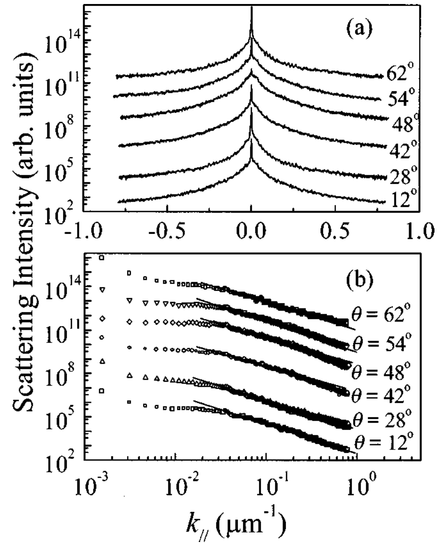

FIG. 2. (a) Light scattering profiles obtained from 250 min corroded Al film at different incident angles: 12°, 28°, 42°, 48°, 54°, and 62°. These angles correspond to $k_\perp=19.4$, 17.5, 14.8, 13.3, 11.7, and 9.3 μm^{-1}. Note that all the curves are shifted in order to avoid any overlapping. Note that every profile has a sharp δ-function like peak sitting on a diffuse broad profile, and the shape of all the broad profiles are quite similar. The peak intensity changes and oscillates while the incident angle θ varies; (b) The log-log plot of the tail part of scattering profiles at different incident angles. Note that the straight-line fits of the tails are quite parallel, giving a slope of -2.10 ± 0.06.

$$P_{11}(\mathbf{r})=\Theta+(1-\Theta)\exp\left[-\left(\frac{r}{\xi}\right)^D\right], \qquad (3)$$

where ξ is the lateral correlation length and D is the surface fractal dimension.[15] The diffraction profile can be written as

$$I(k_\perp,\mathbf{k}_\parallel)\propto 4\pi^2\left[1-4\Theta(1-\Theta)\sin^2\left(\frac{k_\perp d}{2}\right)\right]\delta(\mathbf{k}_\parallel)+8\pi\Theta(1-\Theta)\sin^2\left(\frac{k_\perp d}{2}\right)G(k_\parallel), \qquad (4)$$

where $G(k_\parallel)=\int_0^\infty e^{-(r/\xi)^D}rJ_0(k_\parallel r)dr$, and $J_0(x)$ is the zeroth-order Bessel function. Therefore, the diffraction pro-

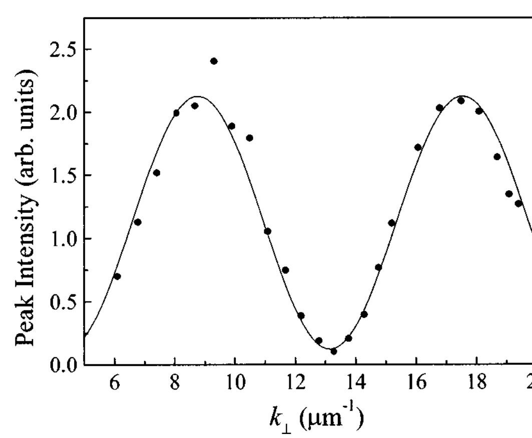

FIG. 3. Peak intensity plotted as a function of the momentum transfer perpendicular to the surface, $k_\perp$. The filled circles are the experimental data obtained from 250 min corroded Al film, and the solid curve is the best fit by using the function $a\cos(k_\perp d)+c$ [equivalent to Eq. (4)]. The fit gives $d=717\pm 3$ nm, $a=1.00\pm 0.04$, $c=1.12\pm 0.03$. The upper level fraction Θ is deduced to be 0.38.

file from a quasi-two-level surface consists of two parts, a δ peak and a broad diffuse peak. The δ-peak intensity would oscillate as a function of $k_\perp$, the period is given by the average pit depth. The diffuse profiles at any $k_\perp$ condition should have the same shape. These predictions describe our experimental observations quite well as shown in Figs. 2 and 3. The period of the oscillation gives the depth of the pits, which is obtained from Fig. 3 to be $d \cong 717 \pm 3$ nm. This is compared to the result $d \cong 690 \pm 50$ nm obtained by the AFM technique. We must bear in mind that the sampling area in the light scattering experiment is much larger than that of the AFM.

The fraction of the pit area, i.e., the fraction of the lower level area, $1-\Theta$, can be determined by two methods. First, it can be obtained through the relative δ-peak intensity ratio,

$$R_\delta = \frac{\int d\mathbf{k}_\parallel I_\delta}{\int d\mathbf{k}_\parallel I_{total}} = 1 - 4\Theta(1-\Theta)\sin^2\left(\frac{k_\perp d}{2}\right),$$

as d has already been obtained through the period of the peak intensity oscillation. The fractional pit area can also be obtained by the peak intensity oscillation. According to Eq. (4), the ratio of the minimum peak intensity and maximum peak intensity can be written as $(1-\Theta)^2$. Therefore, according to the fit in Fig. 3 by Eq. (4), we obtained $\Theta = 0.38$, which is consistent with the value ($=0.38 \pm 0.07$) determined by AFM.

Furthermore, according to Ref. 12, the inverse of the full width at half maximum (FWHM) of the diffuse profile is proportional to the lateral correlation length ξ, and the tail of the profile obeys a power law of $k_\parallel$, $I(k_\parallel) \propto k_\parallel^{-2-D}$. (For our experiments, because of the use of an array of slit detectors, this relation becomes $I(k_\parallel) \propto k_\parallel^{-1-D}$.[10]) From Fig. 1, we obtain $\xi = 21 \pm 3$ μm. Figure 2(b) shows the log-log plot of the scattering angular profiles at different incident angles. From the tails of these profiles, we obtain $D = 1.10 \pm 0.06$. Therefore the surface is slightly fractal. (For a nonfractal structure, D should be 1.)

In conclusion, we report a study of the aluminum pitting morphology by using an in-plane light scattering technique. We show the average pit depth, the pitting area, the pit density, and the fractal dimension of the surface can be determined quantitatively. One notices that even for bulk pitting corrosion, the pit depth is also centered around the average pit depth.[1] Essentially, the pitted surface can also be treated as a quasi-two-level system, and the diffraction model developed above is still suitable for describing the surface morphology. Based on the above discussion, light scattering is potentially useful in the *in situ* study of corrosion fronts for both thin films and bulk materials.[8] Other diffraction techniques can also be used to study the corrosion process in situ. Using x-ray diffraction, recently Sinha *et al.*[16] studied the initial stage of Cu corrosion and found that the pit structures possessed a characteristic length that was not seen in our experiment. X-ray diffraction can detect a much smaller lateral length scale than light scattering. By combining both x-ray diffraction and light scattering one can obtain a more complete understanding of the corrosion process from the initial stage to the later stage.

This work was supported by NSF. The authors thank J. B. Wedding for proofreading the manuscript, and also thank Bin Wang and J. Fortin for preparing the Al films.

[1] M. G. Fontana, *Corrosion Engineering*, 3rd ed. (McGraw–Hill, New York, 1986).
[2] L. Balázs and J.-F. Gouyet, Mater. Res. Soc. Symp. Proc. **407**, 281 (1996), and references therein.
[3] J. M. Costa, F. Sagués, and M. Vilarrasa, Corros. Sci. **32**, 665 (1991).
[4] T. Nagatani, Phys. Rev. A **45**, 2480 (1992); *ibid.* , 6985 (1992); Phys. Rev. Lett. **68**, 1616 (1992).
[5] P. Meakin, T. Jøssang, and J. Feder, Phys. Rev. E **48**, 2906 (1993).
[6] R. Reigada, F. Sagués, and J. M. Costa, J. Chem. Phys. **101**, 2329 (1994).
[7] O. Hunderi, Corros. Sci. **19**, 621 (1979); O. Lunder, K. Nisancioglu, and O. Hunderi, *ibid.* **24**, 965 (1984).
[8] Y.-P. Zhao, Y.-J. Wu, H.-N. Yang, G.-C. Wang, and T.-M. Lu, Appl. Phys. Lett. **69**, 221 (1996).
[9] Y.-P. Zhao, H.-N. Yang, G.-C. Wang, and T.-M. Lu, Appl. Phys. Lett. **68**, 3063 (1996).
[10] Y.-P. Zhao, Irene Wu, C.-F. Cheng, Ueyn Block, G.-C. Wang, and T.-M. Lu, J. Appl. Phys. **84**, 2571 (1998).
[11] E. L. Church, Appl. Opt. **27**, 1518 (1988).
[12] H.-N. Yang, G.-C. Wang, and T.-M. Lu, *Diffraction from Rough Surfaces and Dynamic Growth Fronts* (World Scientific, Singapore, 1993), p. 94.
[13] P. Beckmann and A. Spizzichino, *The Scattering of Electromagnetic Waves from Rough Surfaces* (Macmillan, New York, 1963).
[14] H.-N. Yang, K. Fang, G.-C. Wang, and T.-M. Lu, Europhys. Lett. **19**, 215 (1992); H.-N. Yang, G.-C. Wang, and T.-M. Lu, Phys. Rev. B **51**, 17932 (1995).
[15] The relation between the density-density correlation function, $c(r)$ and $P_{11}(r)$ is $2\pi r c(r)\Delta r = P_{11}(r) - P_{11}(r+\Delta r)$. Therefore $cr \propto r^{D-2} \exp[-(r/\xi)^D]$. According to Vicsek [T. Vicsek, *Fractal Growth Phenomena* (World Scientific, Singapore, 1989), p. 23], D is the fractal dimension.
[16] S. K. Sinha, Y. P. Feng, C. A. Melendres, D. D. Lee, T. P. Russell, S. K. Satija, E. B. Sirota, and M. K. Sanyal, Physica A **231**, 99 (1996); Y. P. Feng, S. K. Sinha, C. A. Melendres, and D. D. Lee, Physica B **221**, 251 (1996).