# Anthraquinone-2-carboxylic Acid Deposited from Solution onto Native Oxide Surfaces of Al Films Characterized by Inelastic Electron Tunneling Spectroscopy, X-ray Photoelectron Spectroscopy, and Atomic Force Microscopy

Morihide Higo,*[1] Takeshi Miake,[1] Masaru Mitsushio,[1] Toshifumi Yoshidome,[1] and Yoshihisa Ozono[2]
[1]*Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University,*
*1-21-40 Korimoto, Kagoshima 890-0065*
[2]*Center for Instrumental Analysis, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065*

(Received September 20, 2005; CL-051203; E-mail: higo@apc.kagoshima-u.ac.jp)

Anthraquinone-2-carboxylic acid (AQ-2-COOH) deposited from acetone solutions onto native oxide surfaces of Al films was characterized by inelastic electron tunneling spectroscopy (IETS), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). These surface analyses show that AQ-2-COOH is adsorbed on the oxide as both a uniform film of anions on a nanometer scale and micron-sized particles of neutral molecules.

---

IETS is a unique analytical technique of a thin (nm) insulator film of a metal/insulator/metal (MIM) tunneling junction and reveals the vibrational spectrum of the insulator at cryogenic temperatures.[1–3] The high sensitivity and resolution as well as the wide spectral range enable us to obtain a detailed vibrational spectrum of adsorbed species on the oxide surface of the metal electrode. Aluminum is widely used as the metal electrode because of chemical, physical, and electric stability of the oxide.[1–3] Thus, IETS is a powerful surface analytical technique and has been used in many fields of chemistry.[1–3] In the present letter, we report the tunneling spectra of AQ-2-COOH on the oxide surfaces of Al films for the first time. The tunneling spectra were compared with the vibrational spectra of AQ-2-COOH on Ag[4,5] and Au[6] by reflection absorption infrared spectroscopy (RAIR). The adsorption state and the morphology of AQ-2-COOH on the oxide surfaces of Al films were also investigated by XPS and AFM, respectively.

Aluminum (99.999%) was evaporated on a glass slide ($13 \times 37 \times 1\,\mathrm{mm}^3$) at room temperature to form strips (1 mm wide) in a high vacuum ($10^{-3}$ Pa) and the surfaces were oxidized to form the oxide (alumina) in an oxygen dc glow discharge. One drop of acetone solutions ($0.01$–$0.02\,\mathrm{mg\,mL^{-1}}$) of AQ-2-COOH (Tokyo Kasei, >99.0%) was dropped on the strips and excess solution was spun off. The junctions were completed with an evaporated Pb cross strip (1 mm wide). Tunneling spectra were measured at the liquid-helium temperature (4.2 K) with the tunneling spectrometer already reported.[2,3] Aluminum was evaporated on mica sheets ($13 \times 13 \times 0.1\,\mathrm{mm}^3$) and the surfaces were also oxidized. AQ-2-COOH was deposited on the alumina surfaces from acetone solutions of $0.01$–$0.10\,\mathrm{mg\,mL^{-1}}$ at room temperature by the spin doping.[7,8] The deposited AQ-2-COOH was investigated by XPS (Shimadzu ESCA-1000, Mg K$\alpha$ radiation)[8] and AFM (Digital Instruments NanoScope III, contact mode).[7,8]

The tunneling spectrum of AQ-2-COOH doped from an acetone solution ($0.02\,\mathrm{mg\,mL^{-1}}$) and that of the alumina doped from acetone are shown in Figure 1. The spectrum of the acetone-doped alumina is identical to that of undoped alumina,[1–3] showing that acetone is an appropriate solvent for measuring the tunneling spectra of AQ-2-COOH on alumina. Though the tunneling spectrum of AQ-2-COOH shows the peak of the quinone carbonyl groups (C=O) at $1630\,\mathrm{cm^{-1}}$, it shows no peaks of the carboxylic acid group. On the other hand, it has the peak of the symmetrical stretching mode of the carboxylate group ($\nu_s\mathrm{COO^-}$) at $1390\,\mathrm{cm^{-1}}$, showing that AQ-2-COOH is adsorbed on the alumina as the carboxylate anion. The peak position of the $\nu_s\mathrm{COO^-}$ agreed well with those of the corresponding peaks in the RAIR spectra on Ag ($1392$–$1394\,\mathrm{cm^{-1}}$)[4,5] and Au (1382 $\mathrm{cm^{-1}}$).[6] Both the tunneling spectra and the RAIR spectra of AQ-2-COOH have no peak of the asymmetrical stretching mode of the carboxylate group ($\nu_{as}\mathrm{COO^-}$) because of the selection rule on the metal surfaces,[1–6] suggesting that the two oxygen atoms of the $\mathrm{COO^-}$ group are bonded to these metal surfaces symmetrically. The peak positions of CH and CC bonds in the tunneling spectra agreed well with those of the corresponding peaks in the RAIR spectra.[4–6] The resistances of the junctions doped from higher concentrations more than $0.02\,\mathrm{mg\,mL^{-1}}$ were too large to measure the tunneling spectra.

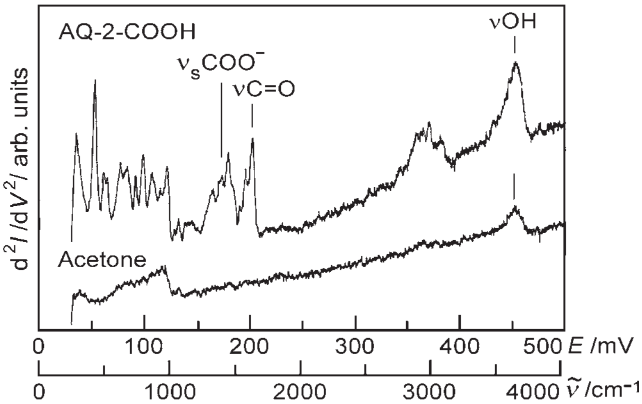

**Figure 1.** Tunneling spectrum of AQ-2-COOH on alumina doped from an acetone solution of $0.02\,\mathrm{mg\,mL^{-1}}$. The spectrum of the alumina doped from acetone is also shown.

The XP spectra over the C1s region of the deposited AQ-2-COOH on alumina from the solutions of 0.10 and $0.02\,\mathrm{mg\,mL^{-1}}$ are shown in Figure 2. A Gaussian shape was used to deconvolute these peaks. The spectra have three peaks at 284.6, 287.2, and 288.7–288.9 eV, and these peaks are due to the C1s of the rings, the quinone carbonyl groups, and the carboxylic acid and/or the carboxylate group of AQ-2-COOH, respectively.[6] Uncertainties of the peak positions are less than ±0.1 eV. The

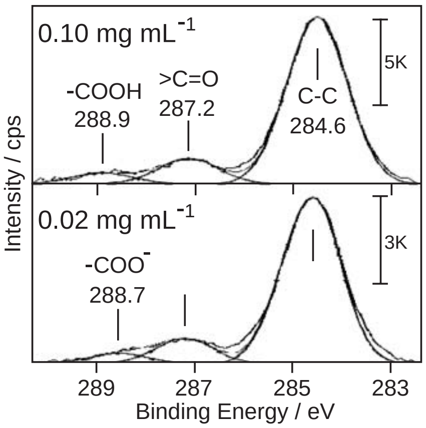

**Figure 2.** XP spectra of C1s of AQ-2-COOH deposited on alumina from acetone solutions of 0.10 and 0.02 mg mL$^{-1}$.

peak positions and the relative intensities of the spectra of the deposited AQ-2-COOH from the solutions of 0.05–0.10 mg mL$^{-1}$ are very similar to those of the spectrum of neutral powder of AQ-2-COOH,[6] suggesting that AQ-2-COOH is deposited as the neutral state on alumina. On the other hand, the spectra of the deposited AQ-2-COOH from the solutions of 0.01–0.02 mg mL$^{-1}$ show the peak of the COO$^-$ at the lower binding energy (288.7 eV). The XP spectra of the deposited AQ-2-COOH from the solutions of 0.01–0.02 mg mL$^{-1}$ are consistent with the corresponding tunneling spectra.

After the XPS measurements, the morphology of the deposited AQ-2-COOH on the surfaces of all the samples was observed by AFM. The observation and analysis were made on two to four randomly selected places in a sample. Typical examples of the images and their bearing histograms are shown in Figure 3. The image size is 30 µm wide and 100 nm gray scale. The AFM images of the deposited AQ-2-COOH from the solutions of 0.01–0.02 mg mL$^{-1}$ show smooth surfaces and no particles on the surfaces, suggesting the presence of a very thin and a uniform film of the AQ-2-COOH anions on the surfaces. On the other hand, the images of the deposited AQ-2-COOH from the solutions of 0.05–0.10 mg mL$^{-1}$ show particles of AQ-2-COOH on the surfaces. The particles are uniformly distributed on the surfaces and the size is of the order of 1 µm in length. The heights of the deposited particles increase with the concentration. It is considered that the particles are the deposited neutral AQ-2-COOH molecules.

The bearing analysis provides a method of plotting and analyzing the histogram of surface heights over a sample. A surface area and a volume above a certain height are calculated.[7,8] The main peak in the histogram represents the surface height distribution and its width (full width at half maximum: $W$) is a good measure of the surface roughness.[7,8] The surface heights of the AQ-2-COOH deposited samples from the solutions of 0.01–0.02 mg mL$^{-1}$ ($W = 1.02$–$1.62$ nm) agreed well with those of the undoped samples ($W = 1.30 \pm 0.34$ nm), showing a presence of very thin and uniform films of the AQ-2-COOH anions on the surfaces. On the other hand, the surface heights of the AQ-2-COOH deposited samples from the solutions of 0.05–0.10 mg mL$^{-1}$ are 1.47–8.81 nm, suggesting a contribution from surface roughening and/or very small surface reaction products of the AQ-2-COOH anions. The bearing histograms distribute up to 50 nm, showing the presence of the neutral AQ-2-COOH particles having the heights on the surfaces. The histograms of the images of the AQ-2-COOH deposited samples from the solutions of 0.05–0.10 mg mL$^{-1}$ gives the volumes of the deposited particles to be about 1 µm$^3$ and they increase further with the concentration.

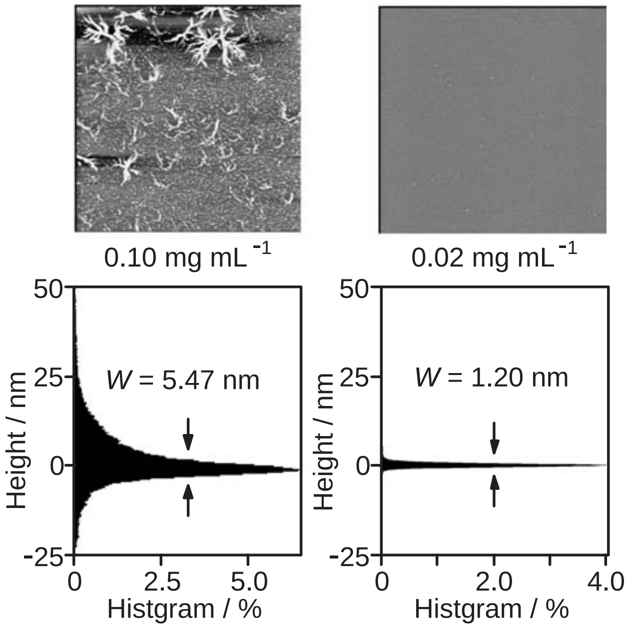

**Figure 3.** AFM top views and bearing histograms of the AQ-2-COOH-deposited alumina from acetone solutions of 0.10 and 0.02 mg mL$^{-1}$. Image size: 30 µm wide and 100 nm gray scale.

This is the first report on the adsorption state and the morphology of the deposited AQ-2-COOH on the native oxide surfaces of Al films. We conclude that AQ-2-COOH is adsorbed on alumina as both a uniform film of anions on a nanometer scale and micron-sized particles with the height of a few tenth nanometer of neutral molecules. The IETS and XPS characterization and the AFM morphology observation of the deposited AQ-2-COOH on the surfaces provide a clear information on the adsorbed species and the mechanism.

The present study was partially supported by a Grant-in-Aid for Scientific Research (No. 16550080) from the Ministry of Education, Culture, Sports, Science and Technology and the Light Metal Educational Foundation.

## References

1 P. K. Hansma, *Tunneling Spectroscopy*, Plenum, New York, **1982**.
2 M. Higo, *Bunseki Kagaku* **2001**, *50*, 637.
3 M. Higo, S. Kamata, *Anal. Sci.* **2002**, *18*, 227.
4 M. Osawa, K. Ataka, K. Yoshii, T. Yotsuyanagi, *J. Electron Spectrosc. Relat. Phenom.* **1993**, *64–65*, 371.
5 S. W. Han, T. H. Ha, C. H. Kim, K. Kim, *Langmuir* **1998**, *14*, 6113.
6 S. W. Han, S. W. Joo, T. H. Ha, Y. Kim, K. Kim, *J. Phys. Chem.* **2000**, *B104*, 11987.
7 M. Higo, X. Lu, U. Mazur, K. W. Hipps, *Thin Solid Films* **2001**, *384*, 90.
8 M. Higo, T. Futagawa, M. Mitsushio, T. Yoshidome, Y. Ozono, *J. Phys. Chem.* **2003**, *B107*, 5871.

Published on the web (Advance View) December 3, 2005; DOI 10.1246/cl.2006.48