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Adsorption and deposition of anthraquinone-2-carboxylic acid on alumina studied by inelastic electron tunneling spectroscopy, infrared reflection absorption spectroscopy, X-ray photoelectron spectroscopy, and atomic force microscopy

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Abstract

The adsorption state of anthraquinone-2-carboxylic acid (AQ-2-COOH) deposited from acetone solutions (0.01–1.00 mg/ml) on native oxide surfaces of Al films was characterized by inelastic electron tunneling spectroscopy, infrared reflection absorption spectroscopy, and X-ray photoelectron spectroscopy. The oxide was prepared on evaporated Al films at room temperature in an oxygen-dc glow discharge. The morphology of the deposited AQ-2-COOH on the oxide surfaces was observed and analyzed by atomic force microscopy. These surface analyses showed that AQ-2-COOH is adsorbed predominantly as a uniform nanometer-scale film of carboxylate anions on the oxide surfaces deposited from solutions with concentrations lower than or equal to 0.02 mg/ml. It was found that AQ-2-COOH is adsorbed as both a uniform film of anions and as micron-sized particles of neutral molecules with heights of a few tens of nanometers when AQ-2-COOH is deposited from solutions with concentrations higher than 0.02 mg/ml. A comparison of the results obtained by these surface analytical techniques clearly shows the features and advantages of these analytical techniques.

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1. Introduction

Inelastic electron tunneling spectroscopy (IETS) is a unique analytical technique for investigating a thin (nm) insulator film of a metal/insulator/metal (MIM) tunneling junction, providing vibrational information about the insulator at cryogenic temperatures [1–9]. The insulator typically consists of a metal oxide layer with adsorbed species on the surface. The high sensitivity, good resolution, and wide spectral range of IETS enable one to obtain a detailed vibrational spectrum of the adsorbed species on the oxide surface of the metal electrode. Since the dipole and induced dipole moments couple to tunneling electrons, both infrared-active and Raman-active vibrational modes are observed in the IETS spectrum. IETS has an orientational preference: an oscillating dipole moment perpendicular to the oxide surface generally couples to tunneling electrons more strongly than that parallel to the surface. The junction is prepared sequentially by metal evaporation, oxidation, sample adsorption, and top electrode evaporation. Aluminum is widely used as the metal electrode, not only because of the excellent chemical, physical, and electrical stability of the oxide, but also because of its ease of

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formation. Lead is used as a good top electrode, because of its relatively low reactivity and large atomic size. Moreover, lead is superconducting at cryogenic temperatures thereby improving the sensitivity and resolution of the IETS spectrum. The tunneling spectra of evaporated thin (nm) films of Si and Ge on the oxides of Al have also been obtained [7,8]. Thus, IETS is a powerful surface analytical technique for investigating oxides and semiconductors, and its application to many fields of science and technology has been reviewed [2,3,5–9]. A collection of tunneling spectra of more than 200 chemical species published from 1966 to 1984 is available in the literature [4]. IETS has been used in the present study to investigate the adsorption state of anthraquinone-2-carboxylic acid (AQ-2-COOH) on oxidized Al films.

Plasma oxidation of Al produces a dense self-limiting growth oxide film that is chemically similar to alumina used in industry [10–14]. Surface-oxidized Al has served as a model for catalytic oxides, and is much easier to characterize than conventional high surface area powders [15–18]. Oxidized Al films are useful for IETS studies, while the junction is a good model system for oxide catalysts, electronic devices, and solid state sensors, etc. Information about the adsorption states and chemical reactions of adsorbed species occurring on alumina can be obtained through analyses of the tunneling spectra. It has been found that the surface hydroxyl (OH) groups on alumina play an important role for the reactions of organic acids, esters, and amides, where the anions formed from these reactions are adsorbed on the Lewis-acid sites (Al^+) on the alumina surface [7,8]. We have also employed atomic force microscopy (AFM) to observe the surface morphology of Al films evaporated at various temperatures on mica [19–26]. The surface of the Al films prepared at room temperature under high vacuum consists of spherical grains having diameters of about 100 nm, while the Al films evaporated onto heated mica at 250–350 °C show atomically-smooth surfaces. We have used AFM and X-ray photoelectron spectroscopy (XPS) to characterize the morphology and adsorption state of tetracyanoquinodimethane (TCNQ) deposited from various solutions onto the atomically-smooth oxide surfaces of Al films [21–24].

Anthraquinone-2-carboxylic acid (AQ-2-COOH) was used as a sample molecule for studying the adsorption on alumina in the present study, because its properties and the adsorption on metal surfaces have been investigated as follows. The different crystal forms of AQ-2-COOH were determined by use of various analytical techniques and their physicochemical properties, such as solubilities, partition coefficients, and heats of solution, etc. were investigated [27]. The adsorption of AQ-2-COOH on metal surfaces has been studied by various surface analyses [28–31]. Osawa et al. [28] measured the infrared spectra of AQ-2-COOH adsorbed on Ag electrodes in a $NaClO_4$ aqueous solution by the attenuated-total-reflection (ATR) method, and concluded that AQ-2-COOH is adsorbed on the metal surfaces through the carboxylate group. Han et al. [29] investigated the adsorption of AQ-2-COOH on Ag by infrared reflection absorption spectroscopy (IRAS), quartz crystal microbalance (QCM), and AFM. They also concluded that AQ-2-COOH is adsorbed on Ag as the carboxylate anion with its two oxygen atoms bound symmetrically to the surface. Han et al. [30] also investigated the adsorption of AQ-2-COOH on Au by experiments (IRAS, Raman, XPS, and voltammetry) and quantum mechanical calculations. Although their theoretical considerations failed in the elucidation of the higher adsorptivity of AQ-2-COOH, they reported for the first time that AQ-2-COOH is adsorbed onto Au as the anion having a symmetrical carboxylate group on the surface even without applying positive potentials. We have already published a preliminary report on the tunneling spectra of AQ-2-COOH adsorbed on alumina doped from acetone solutions [31]. In this case, the alumina was prepared on evaporated Al films at room temperature in an oxygen-dc glow discharge. The adsorption state and morphology of AQ-2-COOH on alumina surfaces have also been investigated by XPS and AFM, respectively [31]. AQ-2-COOH was adsorbed onto the alumina surfaces as a uniform film of carboxylate anions deposited from acetone solutions with concentrations of 0.01–0.02 mg/ml. AQ-2-COOH was deposited as micron-sized particles of neutral molecules deposited from an acetone solution with a concentration of 0.10 mg/ml. AQ-2-COOH is a good sample molecule for studying adsorption from submonolayer to multilayer coverage on alumina by use of XPS and AFM. The motivation for the present study is to investigate the adsorption state and morphology of AQ-2-COOH on alumina deposited from AQ-2-COOH solutions of a wide concentration range.

In the present paper, we present for the first time IRAS spectra of AQ-2-COOH on alumina deposited from acetone solutions with various concentrations. These IRAS spectra have been investigated and compared to the tunneling spectra of AQ-2-COOH on alumina under the same experimental conditions. The vibrational frequencies and mode assignments for AQ-2-COOH deposited on alumina are given with those reported on Ag [28,29] and Au [30]. The IRAS spectra, XPS spectra, and AFM images of AQ-2-COOH on alumina, deposited from acetone solutions in the wide concentration range from 0.02 to 1.00 mg/ml, are also presented. This work presents a thorough study of the adsorption state and morphology of AQ-2-COOH deposited on the surfaces of oxidized Al films prepared at room temperature.

2. Experimental

The junction preparation and measurements of tunneling spectra have previously been described in detail [7,8]. Aluminum (Mitsuwa Chemicals, >99.999%) was evaporated from a resistively heated molybdenum boat on a clean glass slide (13 mm × 37 mm × 1 mm) at room temperature (18–28 °C) to form three strips (1 mm wide) in high vacuum (10^{-3} Pa). The surfaces of the strips were oxidized in an oxygen-dc glow discharge (10 Pa, 5 mA, 20–40 s) to form oxides (alumina). About 20 μl of acetone or ethanol solutions (0.01–0.02 mg/ml) of AQ-2-COOH (Tokyo Kasei, >99.0%) was dropwise added onto the surfaces of the strips and the excess solution was spun off. The junctions were completed with an evaporated Pb (Wako Chemicals, >99.999%) cross strip (1 mm wide). The resistances of the measured junctions were in the range of 200–570 Ω. The tunneling spectra were measured at liquid helium temperature