Morphological Observation of Tetracyanoquinodimethane Deposited from Solution onto the Atomically Smooth Native Oxide Surface of an Al(111) Film by Atomic Force Microscopy

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Morphology of tetracyanoquinodimethane (TCNQ) deposited from solutions onto atomically smooth native oxide surfaces of Al(111) films was observed for the first time by atomic force microscopy (AFM). The bearing analysis of the AFM images showed that TCNQ is adsorbed onto the surfaces of the oxidized Al films as both a uniform film on a nm scale and micron sized particles with many morphologies.

AFM enables us to investigate material surfaces in situ and nondestructively on an atomic scale.[1] Atomically smooth substrates are important to obtain molecular images of adsorbed species. TCNQ is a strong electron acceptor and forms various charge-transfer complexes with donors. The vibrational spectra of TCNQ on alumina surfaces of tunneling junctions have been recorded and studied by inelastic electron tunneling spectroscopy (IETS).[2,3] The tunneling spectra show that the monoanion of TCNQ is the dominant species on alumina.[2,3] However, X-ray photoelectron spectroscopy (XPS) suggested that neutral TCNQ predominates on the alumina surface.[4] This difference could be due to the morphology of the adsorbed TCNQ. IETS is sensitive only to areas having sub- to 2 mono-layer coverage. XPS, on the other hand, probes all the material within a few tens of nm of the surface. Thus, morphological observation of TCNQ is an essential ingredient for understanding the spectroscopic results. In this study, we determine the actual morphology of TCNQ adsorbed from solution onto oxidized aluminum.

The atomically smooth Al films were prepared as reported previously.[5] The Al films were oxidized in an oxygen ac glow discharge. TCNQ (purified by recrystallization) was adsorbed onto the oxidized Al films with various solutions, concentrations, and spin times at room temperature (20°C) by the spin doping technique as used in IETS.[2,3] One drop of the solutions was dropped onto surfaces of the oxidized Al films and excess solution was removed by spinning. After doping TCNQ on the surfaces, the samples were pumped at 10^{-6} Torr. The AFM images of the adsorbed TCNQ were taken with a Digital Instruments NanoScope III operating in a contact mode (narrow, 200 μm long cantilevers having a mean force constant of 0.06 N/m) in air.

The AFM top view (a) and the bearing histogram (b) of the image of an oxidized Al film doped from 0.50 mg/ml CH_3CN solution using a 5 s spin time are shown with those (c, d) of the film doped from 0.20 mg/ml solution in Figure 1. The image size is 10 μm wide and 100 nm gray scale. It was found that TCNQ is deposited on the oxidized Al films as particles. Images with sizes of 100 and 30 μm wide and taken on other places of these films indicate that the particles are uniformly present on the surfaces. The morphology of the deposited particles changes slightly with the spin time (5 - 25 s) and the concentration (0.20 - 0.50 mg/ml). The particle size has a range of 0.1 - 1 μm in length. The bearing analysis provides a method of plotting and analyzing the distribution of surface height over a sample. The histogram of a rough surface distributes in a wider range than that of a smooth surface. Thus, the full width at half maximum (W) of the histogram of the film is a good measure of the surface roughness. The bearing histogram indicates the height distributions of the deposited TCNQ particles and the surface of the oxidized Al film. The heights of the deposited particles distribute in

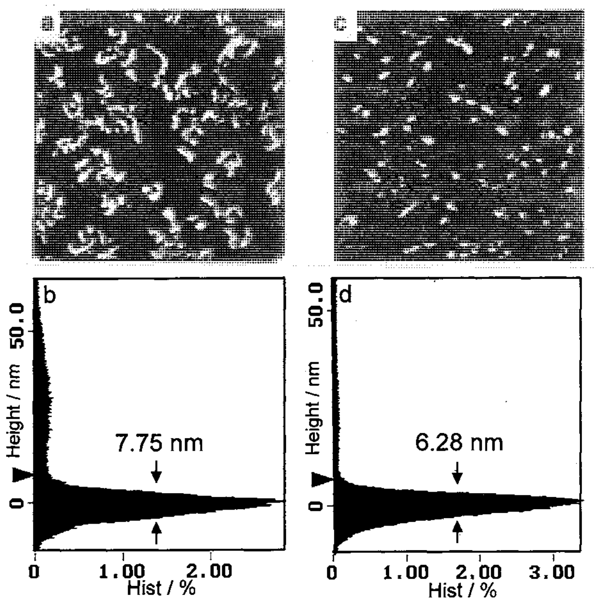

Figure 1. AFM top view (a) and bearing histogram (b) of the TCNQ-deposited oxidized Al film from 0.50 mg/ml CH_3CN solution. Those (c, d) from 0.20 mg/ml solution are also shown. Spin time: 5 s. Image size: 10 μm wide and 100 nm gray scale.

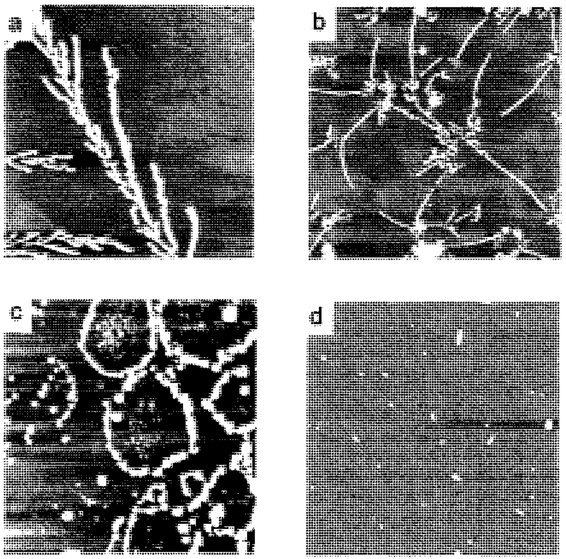

Figure 2. AFM top views of the TCNQ-deposited Al_2O_3 films from 0.10 mg/ml CH_3CN (a), $(CH_3)_2C{=}O$ (b), and CH_3OH (c) solutions. The AFM top view of the TCNQ-deposited mica sheet (d) from 0.10 mg/ml CH_3CN solution is also shown. Spin time: 5 s. Image size: 10 μm wide and 100 nm gray scale.

a range of 10 - 60 nm and the average height is about 30 nm. The surface heights of the oxidized Al films distribute in a wider range (W = 7.75 and 6.28 nm) than the undoped, acetonitrile-, acetone-, methanol-, and water-doped oxidized Al films (W = 2.43 ± 0.85 nm) because of a contribution from surface roughening and/or very small (a few nm high) surface reaction products of TCNQ. If the histogram (b) is separated at above 7.75 nm (indicated by the marker) from the center of the distribution of the surface, we can calculate the volumes of the deposited large and small TCNQ particles to be 0.50 and 0.61 μm^3, respectively using the standard NanoScope III software. The volumes of the large and small TCNQ particles doped from 0.20 mg/ml solution are 0.18 and 0.38 μm^3, respectively.

The AFM top views of the oxidized Al films doped from 0.10 mg/ml CH_3CN (a), $(CH_3)_2C{=}O$ (b), and CH_3OH (c) solutions are shown with that of the TCNQ-deposited mica (d) in Figure 2. The image size is 10 μm wide and 100 nm gray scale. There are particles with many morphologies on the oxidized Al surfaces doped from these solutions. The size of the particles is of the order of 1 μm in length. The widths of the histograms of the surfaces doped from 0.10 mg/ml CH_3CN and $(CH_3)_2C{=}O$ solutions are 7.69 and 5.19 nm, respectively. The heights of the large particles distribute in a range of 10 - 50 nm. The surface height of the film doped from the CH_3OH solution (c) distributes in a more wider range (W = 17.29 nm) and the heights of the large particles distribute in a range of 10 - 100 nm. The morphology of the particles strongly depends on the solvent, concentration (0.05 - 0.10 mg/ml), and spin time (5 - 25 s) in these doping conditions. After the observation, the TCNQ-deposited oxidized Al film was pumped at a pressure of 10^{-6} Torr for 5 min and observed again. However, the morphology of the particles or the bearing histogram had no change and showed that the TCNQ particles are stable on the surfaces. The AFM image of the TCNQ-doped mica sheet (d) shows smaller and fewer particles on the surfaces. The morphology of the particles is simple oval with a diameter of the order of 0.1 μm. The height of the particles distributes in a range of 5 - 50 nm. The particles are uniformly present on the mica surfaces and the volume of the deposited particles is of the order of 0.01 μm^3. This is a clear contrast with that on the oxidized Al films.

The atomically smooth oxidized Al films enable us to analyze the morphology, height distribution, and volume of the deposited particles on the surfaces. TCNQ was found to be deposited from the solutions onto the surfaces of the oxidized Al films as both a uniform film on a nm scale and micron sized particles with the height distribution from 10 to 100 nm. Since the volatility of TCNQ is relatively low, it is easily deposited on the surfaces as particles. The morphology of the deposited TCNQ particles on the oxidized Al films changes with variation in the doping conditions (solvent, concentration, and spin time). The discrepancy in IETS and XPS results is now clear. The tunneling spectrum is coming from the thin uniform film, while the XPS signal is heavily weighted towards the particles. In the limit of decreasing concentration, it is expected that the particles would disappear and the XPS results would parallel those of IETS. A more general point to be learned from this study is that a knowledge of the morphology of the adsorbate is a critical element in analyzing surface spectroscopy data. AFM of adsorbates on atomically smooth surfaces provides a means of determining the morphology.

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