Tetracyanoquinodimethane Deposited from Solution onto the Atomically Smooth Native Oxide Surface of an Al(111) Film Characterized by X-ray Photoelectron Spectroscopy and Atomic Force Microscopy

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Tetracyanoquinodimethane (TCNQ) deposited from acetonitrile solutions onto atomically smooth native oxide surfaces of Al(111) films was characterized by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The XP spectra and the bearing analysis of the AFM images show that TCNQ is adsorbed onto the oxide surface as both a uniform film of anions on a nanometer scale and micron sized particles of neutral molecules.

TCNQ is a strong electron acceptor and forms a variety of charge-transfer complexes with inorganic and organic donors. The characterization of TCNQ on alumina surfaces has been done by inelastic electron tunneling spectroscopy (IETS)[1,2] and XPS.[3] These electron spectroscopies showed that TCNQ is adsorbed on the surfaces as both anions and neutral molecules. However, the relative intensities of both the TCNQ species obtained by these spectroscopies were different significantly probably because of differences in the sensitivity and selectivity of these spectroscopies to the morphology of the adsorbed TCNQ. Thus, knowledge of the morphology of TCNQ on alumina is critical to interpret these spectroscopic results correctly. In our previous papers,[4] we have reported the preparation of very smooth Al films on a nanometer scale over a wide surface area. Such atomically smooth films enabled us to perform a detailed morphological observation of TCNQ on alumina by AFM.[5] The analysis of the AFM images showed that TCNQ is adsorbed onto the surfaces as both a uniform film on a nanometer scale and micron sized particles with many morphologies.[5] In the present letter, we report both the XPS and AFM studies of TCNQ deposited from various concentrations onto atomically smooth native oxide surfaces grown on poly-crystalline Al(111) films.

The atomically smooth Al films with a thickness of 150 nm were prepared at a temperature of 350 °C and at a pressure of 10^{-4} Pa by vacuum evaporation of Al (99.999%) onto previously cleaved and heated (550 °C) mica substrates (9 × 12 mm wide).[4] The Al films were oxidized in an oxygen dc glow discharge (10 Pa, 5 mA, 30 s). TCNQ (Tokyo Kasei, powder, >98%) was deposited onto the oxidized Al films with various concentrations (0.04–1.03 mg mL^{-1}) of acetonitrile solutions at a room temperature (14–17 °C) and at a humidity of about 53% by the spin doping technique.[5] The XP spectra of the adsorbed TCNQ on the oxidized Al films and the TCNQ powder on a conductive tape were measured with a Shimadzu ESCA-1000 with a resolution of 1.0 eV using Mg Kα radiation. The AFM images of the adsorbed TCNQ were taken with a Digital Instruments NanoScope III operating in contact mode in air.

The XP spectra of TCNQ over the N 1s region of the powder and a TCNQ-deposited oxidized Al film from 1.03 mg mL^{-1} CH_3CN solution are shown in Figure 1. A Gaussian shape was used to deconvolute these peaks. The spectrum of the powder has two peaks at 399.7 and 402.3 eV, and these peaks are due to the N 1s of neutral TCNQ ($TCNQ^0$) and the shake-up satellite, respectively.[3,6] The full width at half maximum of the neutral TCNQ peak is 1.2 eV. The peak positions and relative intensities of these peaks agree well with those of the peaks in the high resolution XP spectrum measured by Lindquist and Hemminger.[6] The peak width of the adsorbed TCNQ on the oxidized Al film is larger than 1.2 eV and the peak consists of three components. The main peak near 400 eV is due to neutral TCNQ and was deconvoluted using a peak width of 1.2 eV. The peak near 399 eV has a chemical shift of about 1 eV and is assigned to ionized TCNQ ($TCNQ^{x-}$) on the surface.[3] The peak width is wider than that of the neutral TCNQ. The neutral peak may have a contribution from the satellite of $TCNQ^{x-}$; its intensity is estimated to be about 20% of that of $TCNQ^{x-}$. The satellite peak of $TCNQ^0$ lies near 401 eV.

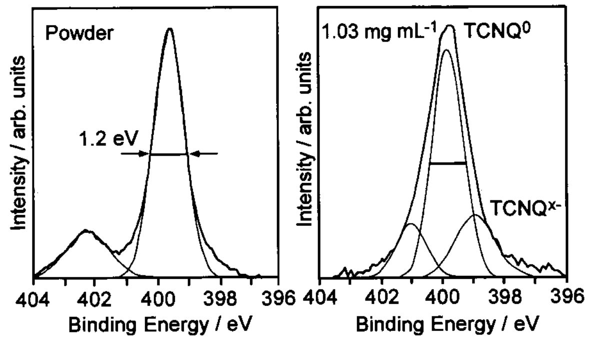

Figure 1. N 1s spectra of the TCNQ powder and the deposit on the oxidized Al film from 1.03 mg mL^{-1} CH_3CN solution.

The peak intensities (peak areas) of the N 1s spectra of the neutral and anionic TCNQ on the oxidized Al films doped from the various concentrations were measured and the result is shown in Figure 2. The intensities of both the species on the surfaces doped from lower concentrations are weak and almost equal. The intensity of the anionic TCNQ increases slowly with the concentration. On the other hand, the intensity of the neutral TCNQ increases rapidly with the concentration and becomes about three times larger than that of the ionized TCNQ at 1.0 mg mL^{-1}. The result of XPS shows that the quantities of the neutral and anionic TCNQ deposited onto the oxidized Al films strongly

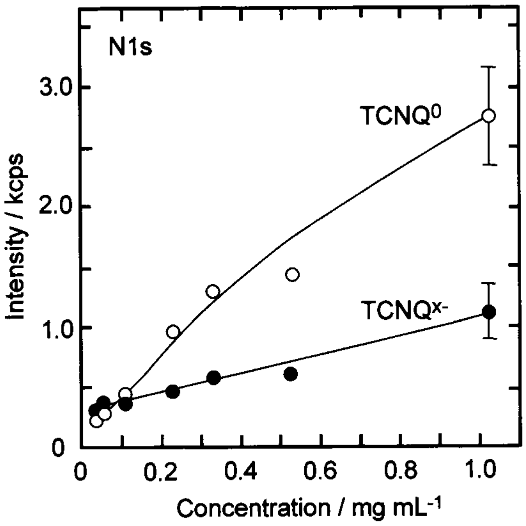

Figure 2. Intensities of the N 1s peaks of neutral and anionic TCNQ of the TCNQ-deposited oxidized Al films from various concentrations of CH_3CN solutions.

depend on the solution concentration used.

After the XPS measurements, the morphology of the deposited TCNQ on the surfaces of all the samples was observed by AFM. The observation and bearing analysis were done on 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 show the particles of TCNQ on the surfaces. The particles are uniformly distributed on the surfaces and the size is of the order of 1 μm in length. The morphology of the deposited particles changes slightly with the concentration. The number of the particles increases as the concentration increases, but the size is almost independent of the concentration.

The bearing analysis provides a method of plotting and analyzing the histogram of surface height over a sample. 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 roughness.[5] If the peak has a Gaussian shape with a standard deviation σ, W corresponds to 2.36 σ and most (>95%) areas are in the $2W$ region between $-W$ and W. We define the bearing volume (V) as the volume in the bearing curve in this $2W$ region. The surface heights of the TCNQ-deposited films from 1.03 and 0.23 mg mL^{-1} solutions distribute in a wider range (W = 4.68 and 4.32 nm, respectively) than that of the undoped film (W = 3.20 ± 0.69 nm) because of a contribution from surface roughening and/or very small (a few nm height) surface reaction products of TCNQ. The heights of the large deposited particles from 1.03 and 0.23 mg mL^{-1} solutions distribute over 70 and 20 nm, respectively. The histogram of the TCNQ-deposited film from 1.03 mg mL^{-1} solution is separated at above 4.68 nm (indicated by the marker) from the center of the distribution of the surface, and it gives the volumes of the deposited large and small TCNQ particles to be 2.58 and 1.86 μm^3, respectively. The volumes of the large and small TCNQ particles deposited from 0.23 mg mL^{-1} solution are 0.89 and 1.15 μm^3, respectively. The bearing analysis shows that the volume of the large particles increases rapidly as the concentration increases, but that of the small particles increases slowly with the concentration. The changes in the volumes of both types of particles on the surfaces upon the concentration correlate well with the intensities of the neutral and anionic TCNQ obtained by XPS. This correlation between the separated volumes and intensities of the surface species strongly suggests that large and small particles are the neutral and anionic TCNQ on the surface, respectively. Thus, we can conclude that TCNQ is adsorbed onto the oxidized Al films 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. Both the XPS characterization and AFM morphology observation of the deposited TCNQ on the surfaces provide a clear information on the adsorbed state.

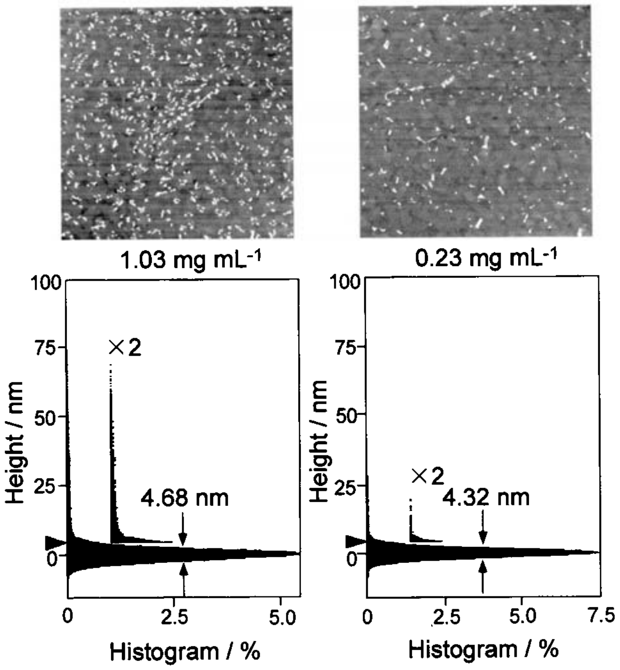

Figure 3. AFM top views and bearing histograms of the TCNQ-deposited oxidized Al films from 1.03 and 0.23 mgmL^{-1} CH_3CN solutions. Image size: 30 μm wide and 100 nm gray scale.

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