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STM and STS Studies on Platinum Chains in Bis(1,2-Benzoquinonedioximato)Platinum

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We investigated the structure and electric properties of bis(1,2-benzoquinonedioximato)platinum(II) (PTBQD) thin films within a thickness of around 10 nm on highly oriented pyrolytic graphite and molybdenum disulfide substrates. High resolution scanning tunneling microscopy images show regular array of brighter points, corresponding to inter-Pt-chains distance of PTBQD single crystal (α -form). We then measured current-voltage curves by scanning tunneling spectroscopy along a Pt chain vertical to the substrate surface. From the observed features of the curves, the resistivity value was found to be comparable to that of the α -form bulk crystal.

Keywords: bis(1,2-benzoquinonedioximato)platinum(II); STM; STS; thin film

INTRODUCTION

One-dimensional metals in dioximato compounds have been investigated for several decades. They are usually d^8 metal ion complexes which have unique properties such as third harmonic generation of nonlinear optics and high conductivity [1,2]. Bis(1,2-benzoquinonedioximato)platinum(II) (PTBQD, Figure 1(a)) is one of them and its bulk single crystal (α -form [3], Figure 1(b)) shows high conductivity

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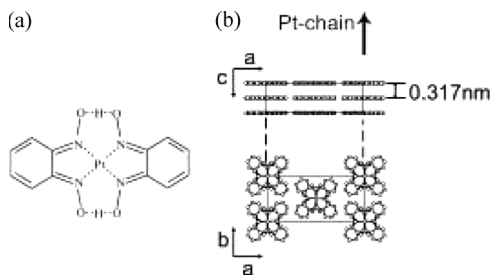


FIGURE 1 (a) The PTBQD chemical formula and (b) the crystal structure of α -form (*Orthorhombic*, space group: *Ibam*, $a = 2.068$ nm, $b = 0.9743$ nm, $c = 0.6346$ nm). The ab -plane indicated in (b) illustrates overlapped two PTBQD molecules with different orientations.

($3 \times 10^2 \Omega\cdot\text{cm}$) along the c -axis (Pt-Pt chain) because of the shortest Pt-Pt distance (0.317 nm) in the crystals among the dioximato family [4]. Recently a phase transition from semiconductor to metal has been found at high pressure along the chain [5], which might be due to the shortest Pt-Pt distance. As for this film formation of PTBQD, thin films were fabricated on a glass substrate by vacuum-deposition, but it could not be directly controlled their chain orientation because of amorphous state of the substrate [6]. Therefore, PTBQD thin films were fabricated on alkali halide single crystalline substrates in order to control their orientation [7,8]. However, in these cases, they often formed other polymorphs which have a longer Pt-Pt distance than that of α -form or even zigzag Pt-chains. Such polymorphs do not exhibit high conductivity as the α -form.

Although the well-oriented α -form thin films could not be directly obtained on the substrates, the polymorphs were found to transform into the α -form crystal by heating [7,9]. In this case, the Pt-Pt chains are oriented vertical to substrates, so that they could be utilized as vertical wires with molecular scale. On the other hand, a horizontal wire to a substrate has been successfully fabricated for different materials already. For example, a one-dimensional molecular wire of polydiacetylene has been directly fabricated with a scanning tunneling microscope (STM) [10] and the electronic property of the wire has been directly investigated by scanning tunneling spectroscopy (STS) [11]. The resistivity was calculated to be about $10^5 \Omega\cdot\text{cm}$.

In this study, our interest is attracted in application to molecular wire for molecular electronics based on this PTBQD molecule. So we attempted to fabricate PTBQD thin films having some conductivity and orientation on other substrates, and directly to evaluate the

electronic property of such a highly-ordered thin film of PTBQD. For that purpose, we fabricated a PTBQD thin film on a substrate of highly oriented pyrolytic graphite (HOPG) or molybdenum disulfide (MoS_2). The structure of the thin films was investigated by using atomic force microscopy (AFM) and STM, and their molecular scale electric properties by STS.

EXPERIMENTAL

The samples were PTBQD thin films grown on the (001) surface of HOPG or MoS_2 by vapor deposition. The vacuum pressure was approximately 1×10^{-4} Pa. The temperature of the substrates was kept at 60°C during the deposition. Thickness of the thin films was controlled at deposition rate of 0.1 nm/s by using a quartz oscillator.

Morphology of the thin films was observed by AFM (Veeco Instruments, NanoScope IIIa) under tapping mode with a commercial Si tip. Since the fabricated thin films have some conductivity as described below, high resolution imaging were performed on the thin films by STM (NanoScope IIIa) equipped with a low current converter at constant current mode. An STM tip used was Pt/Ir (Pt:Ir = 80%:20%) wire which was cut mechanically with a nipper. The bias voltage was applied to the sample in a condition that the tip is grounded. At positive bias voltages, electrons tunnel from the tip to the substrate.

Electrical properties of these films were measured by STS mode in STM (NanoScope IIIa). The sign of the bias voltage and the direction of the tunneling electrons are the same in the STM measurement mentioned above. STS spectra are obtained as current-voltage (I - V) curves which were recorded at a fixed sample location and a constant distance between tip and sample (feedback loop is open during the spectrum measurement). The bias voltage was swept from -1.5 V to $+1.5 \text{ V}$ under a sweeping rate of $16\text{--}20 \text{ Hz}$ per a data point for securing stability in spectra measurement. The recorded I - V curves were averaged after acquiring a spectrum $15\text{--}20$ times. The tunneling conductance as the derivative of I - V curve was calculated numerically. All the measurements of AFM, STM and STS were performed at room temperature in air.

RESULTS AND DISCUSSION

Morphology of PTBQD Thin Films

Figure 2(a) shows an AFM image of PTBQD thin film on HOPG. The morphology of the film is plate-like with a size of several μm wide and

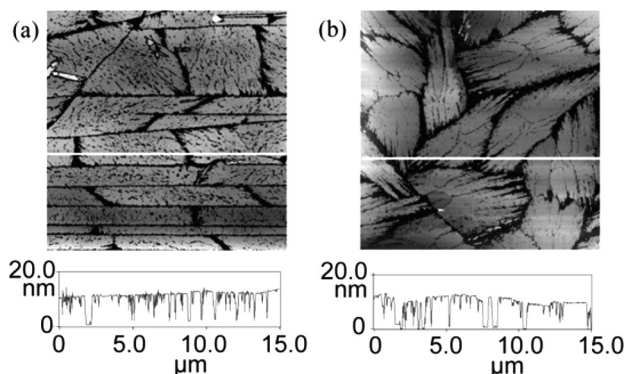


FIGURE 2 Typical AFM images of PTBQD thin films on (a) HOPG and (b) MoS_2 (scan area $15\ \mu\text{m} \times 15\ \mu\text{m}$). Each white line in the figures is the location of a profile shown below for the respective Figures.

almost constant height of 10 nm. The plates have many grains which is the same feature as bis(dimethylglyoximate)platinum(II), one of one-dimensional platinum complexes, when grown on a potassium chloride single crystal substrate by vacuum-deposition [12]. In that case, the Pt-chain column is also normal to the substrate. In case of MoS_2 substrate, the same morphology was observed but different orientation with respect to the substrate (Fig. 2(b)). The plate-like growth with a constant height was always observed disregarding the substrates used.

STM Imaging of PTBQD Thin Films

The plate-like morphology with grains imaged by AFM was also observed by STM (Fig. 3(a) and (b)). Heights of the plate in STM image agree well to those of AFM results. The thin films, therefore, have certain conductivity perpendicular to the substrates at least, suggesting a perpendicular orientation of the Pt-chain to the substrate surfaces. High resolution STM images were observed to analyze molecular-scale structures in the plate. Images of PTBQD thin film on HOPG show that the surface of the plate is composed of regular array of brighter contrast points, although the image does not figure out the molecule itself (Fig. 3(c)). Images of PTBQD thin film on MoS_2 show also the same result, even though the image is not as clear as that on HOPG. In the images, some defects are observed with darker contrast on surface (Fig. 3(d)). It was failed to determine the crystallographic orientation of the array with respect to the substrate surface by imaging

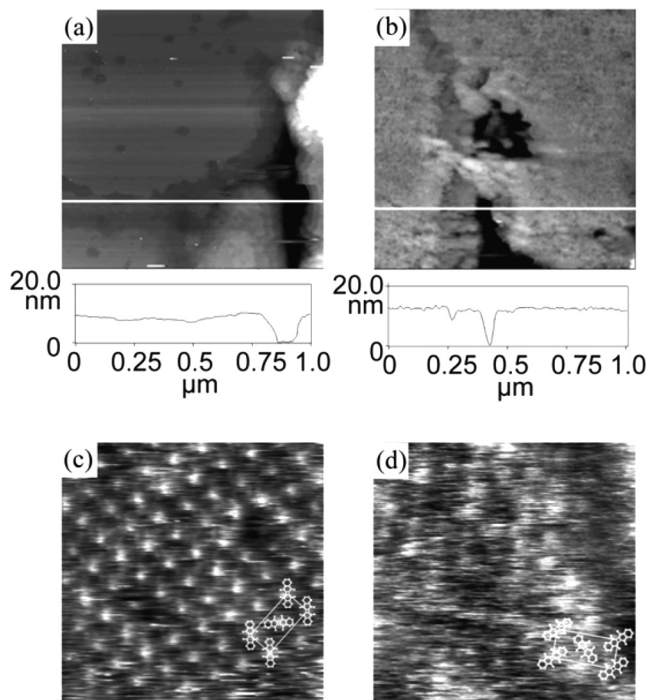


FIGURE 3 STM images of PTBQD thin films on (a) HOPG (scan area: $1\ \mu\text{m} \times 1\ \mu\text{m}$, bias: 150 mV, current: 5.3 pA, scan rate: 0.5 Hz) and (b) MoS₂ (scan area: $1\ \mu\text{m} \times 1\ \mu\text{m}$, bias: 500 mV, current: 1 pA, scan rate: 1.2 Hz). Each white line in the upper figures is the location of a profile shown below the (a) and (b). The corresponding high resolution images of the thin films on (c) HOPG (scan area: $10\ \text{nm} \times 10\ \text{nm}$, bias: $-300\ \text{mV}$, current: 6.6 pA, scan rate: 24.4 Hz) and (d) MoS₂ (scan area: $10\ \text{nm} \times 10\ \text{nm}$, bias: 300 mV, current: 5.2 pA, scan rate: 8 Hz).

the underlying substrate through the crystal. Usually adsorbed monomolecular layers can be analyzed on their crystallographic orientation with respect to substrates in such a method to measure both molecular and substrate surface images by adjusting bias voltage and tunneling current. However, we could not carry out such a method since the present films were too thick to do so. As for the structure, we compared the repeating feature of bright spots with the known crystal structures of PTBQD under an assumption that the bright spots should correspond to the Pt-chains. As a result, the periods of the points arrays almost well correspond to inter-Pt-chains distance of the *ab*-plane of PTBQD α -form crystal (Fig. 1). Since the α -form crystal has conductive

property along the Pt-chain, it is plausible to assign the structure to the α -form. Therefore, we can conclude that the thin films are the α -form crystal and their Pt chain (the c -axis) is vertical to the substrates.

STS Measurement

We measured current-voltage (I - V) curves by STS (Fig. 4(a), (b)) in order to investigate electronic property of PTBQD thin films at a molecular scale on HOPG and MoS₂ substrates. However, I - V curves could not be measured on only Pt chain but averaged over an area around a fixed location on the PTBQD thin film because of drift during I - V measurement and the radius of curvature of STM tip. In case of HOPG substrate (Fig. 4(a)), the curve has three features. The first is that the curve is somewhat asymmetric for a sign of bias voltage, which could be originated from a resonant tunneling effect in a thin film grown on a substrate [13] because of asymmetric density of state around the Fermi level. The second is a flat region spreading over ca. 1 eV from -0.5 V to $+0.5$ V in the dI/dV - V curve (shown below in Figure (a)). This value of 1 eV corresponds roughly to the optical band gap of d-p transition [14]. The third feature is the resistivity of tunneling conduction. The resistivity in the energy gap region is in the order of $10^3 \Omega\cdot\text{cm}$ on assumption that the cross section and the length of the conduction volume are 1-nm^2 and 10 nm (film thickness) in this case, respectively. The value corresponds well to the macroscopic resistivity obtained for a PTBQD single crystal or a thin film grown on glass substrate before annealing [6]. Furthermore, the resistivity in a region out of the energy gap is in the order of $10^2 \Omega\cdot\text{cm}$ under the same assumption as described above. Although the conduction may include

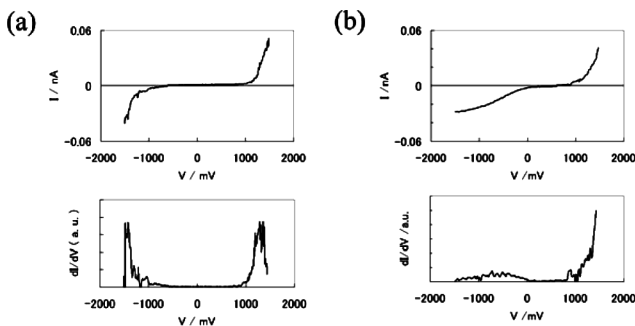


FIGURE 4 Typical STS I - V (above) and dI/dV - V (below) curves of PTBQD thin films on (a) HOPG (bias 250 mV, current: 1 pA, bias sweeping rate: 20 Hz) and (b) MoS₂ (bias: 150 mV, current: 1 pA, bias sweeping rate: 16 Hz).

a tunnel process between the tip to the sample surface, the value is comparable to that of the α -form single crystal.

In case of MoS_2 substrate (Fig. 4(b)), the I - V curve is more asymmetric than that on the HOPG substrate. MoS_2 is a semiconductor which has ca. 1 eV of the energy gap and its I - V curve shows rectifying behavior dependent on surface state [15]. These properties can cause high asymmetric behavior. Another important finding is that energy gap is about 0.8 eV from dI/dV - V curve shown below the figure, which is the similar value to the case of HOPG substrate. Also, the order of resistivities in energy gap region and out of energy gap region are $10^3 \Omega\cdot\text{cm}$ and $10^2 \Omega\cdot\text{cm}$, respectively. These results suggest that PTBQD thin film on MoS_2 can be the same as PTBQD thin film on HOPG substrate, forming well-oriented α -form film.

CONCLUDING REMARKS

We investigated the structure and electronic properties of PTBQD thin film on HOPG and MoS_2 substrates using AFM and STM for structure observation and STS for electronic property analysis. AFM images showed that the thin films are composed of the flat grainy morphology with a size of several μm wide and a constant height. In particular, high resolution STM images show regular array of brighter points, corresponding to inter-Pt-chains distance of the α -form crystal; that is, the location of Pt-chain is conductive to appear bright. Since the Pt-chains are perpendicular to the surface, the PTBQD film has some high conductivity normal to the substrate surfaces. Then measured current-voltage (I - V) curve exhibits some specific features. One is a flat region of ca. 1 eV width in the dI/dV - V curve, corresponding roughly to the optical band gap of d-p transition. The other is the resistivity of the order of $10^2 - 10^3 \Omega\cdot\text{cm}$ which is comparable to that along the c -axis of the α -form bulk crystal. The above results suggest that the PTBQD thin film on HOPG and MoS_2 substrates can be a well-oriented α -form film. We could fabricate the thin film applicable to molecular electronics such as molecular nanowire and molecular switching.

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