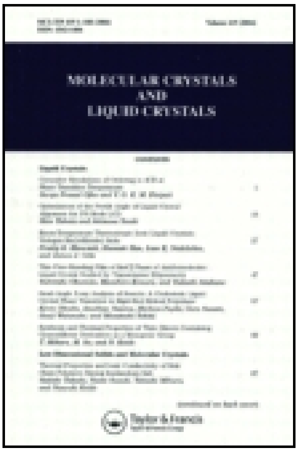

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STM Imaging and Surface Modifications on Thin Films and Single Crystals of the Conducting Metal-Organic Complex: Cu(2,5-DM-DCNQI)$_2$

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STM IMAGING AND SURFACE MODIFICATIONS ON THIN FILMS AND SINGLE CRYSTALS OF THE CONDUCTING METAL-ORGANIC COMPLEX : $Cu(2,5\text{-}DM\text{-}DCNQI)_2$

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Abstract Single crystals and thin films of a highly conducting transition metal complex, copper bis(2,5-dimethyl-N,N'-dicyanoquinonediimine) have been imaged and modified using the scanning tunneling microscopy (STM). Applications for the nanometer lithography were demonstrated.

INTRODUCTION

Scanning tunneling microscopy (STM) and scanning probe microscopy (SPM) are widely used to visualize the surface structure of various materials at atomic or molecular level resolution. Since Aumüller et al.[1] first reported on the highly conducting copper salt of 2,5-dimethyl-N,N'-dicyano-quinonediimine : $Cu(2,5\text{-}DM\text{-}DCNQI)_2$, many analogs have been synthesized and characterized in an effort to understand the origin of their high conductivity stable to 0.45K. We have recently described the first STM study on a unique conducting metal complex, $Cu(2,5\text{-}DM\text{-}DCNQI)_2$.[2] The STM produced images of the surface of $Cu(2,5\text{-}DM\text{-}DCNQI)_2$ single crystals with molecular resolution. The STM images of $Ag(2,5\text{-}DM\text{-}DCNQI)_2$ was also reported recently.[3-4] Present optical storage systems store 1 bit of data on approximately 1 μm spots. This limitation is associated with the wavelength λ of the visible semiconductor laser diode device and the optical diffraction limit (~λ/2) for visible light (approximately 200 nm). This limitation of current optical storage to approximately 10^9 bit/in^2 may be surpassed by using the above mentioned STM or SPM technology.[5-6] Very high density information storage densities can be demonstrated in the laboratory when STM or SPM technology is applied to store 1 bit of data at the nanometer scale. In this paper, we present the first nanometer scale surface modification of $Cu(2,5\text{-}DM\text{-}DCNQI)_2$ using an STM that may be applicable to future information storage devices.

EXPERIMENTAL

$Cu(2,5\text{-}DM\text{-}DCNQI)_2$ single crystals were synthesized by a slow-diffusion method from pure Cu plates and neutral 2,5-DM-DCNQI dissolved in an H-tube.[2] $Cu(2,5\text{-}DM\text{-}DCNQI)_2$ thin films were prepared according to the procedure that has previously been reported.[3] Single crystal KBr substrates were used for the infrared microspectroscopic study and the highly oriented pyrolytic graphite (HOPG ZYA grade, Union Carbide) substrates were used for the STM study. Formation of $Cu(2,5\text{-}DM\text{-}DCNQI)_2$ was confirmed by UV-VI and FT-IR spectroscopy. The details of STM experimental conditions used in this study are described in our earlier paper.[2] The constant current mode was used to record STM images. Both an external pulse generator (HP 8116A) and an internal voltage source were used for the surface modifications. The dc conductivity was measured by a four-point probe resistivity technique (Mitsubishi Petrochemical, Loresta AP). Resistivity geometrical correction factors for finite samples (very thin films on the small substrates) were calculated based on the Yamashita's method[7] and verified experimentally.[8] Temperature dependence of the conductivity was measured by in-house measurement system. A Bomem MB-122 infrared spectrometer equipped with Spectra Tech IR-Plan microscope using 15x reflachromat lens has been used for the infrared microspectroscopic study.

RESULTS AND DISCUSSION

We reported molecular images of the conducting transition metal complex, $Cu(2,5\text{-}DM\text{-}DCNQI)_2$ using the STM.[2] The crystal face imaged by the STM showed structural periodicities of 1.1 nm and 0.4 nm along orthogonal directions. This surface structure agrees with the ac plane of the reported bulk crystal structure of $Cu(2,5\text{-}DM\text{-}DCNQI)_2$.[9] We have concluded that distorted rhombic cells in the STM image can be drawn by connecting four adjacent high contrast sites which most likely are the cyano functional groups of surface terminating 2,5-DM-DCNQI ligands (by molecular orbital calculations). During this STM study, we found a dark fissure on the surface when we allowed the tip of the STM to sit above the sample under feed back control condition for about 1 hour without scans (constant current mode, bias voltage (Vt) +0.1V, tip positive, tunneling current (It) 1 nA). We also observed this phenomenon during I/V spectroscopic experiments. When we swept a voltage from - 0.2 V to + 0.2 V, we always observed non-ohmic spectra and similar dark spots at the place where we took spectro-

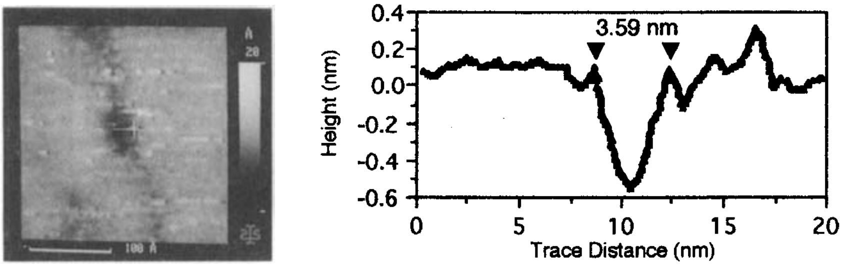

FIGURE 1 3.6nm diameter spot that was appeared after I/V spectroscopy. (left, 25x25 nm, Vt+0.20V, It 1.0nA) Topography along the line in the photograph (right).

scopic measurements on the next regular STM scans. The diameter of dark spots was as small as 3.6 nm which corresponds to an area of 23 Cu(2,5-DM- DCNQI)$_2$ molecules as shown in Figure 1. We have previously reported upon the laser-induced optical phase transition in the copper and silver 2,5-DM-DCNQI complexes which are well known in the family of metal-TCNQ complexes.[3] The results reported in this paper suggest that Cu(2,5-DM-DCNQI)$_2$ may be undergoing a similar electric field-induced phase transition.[10] It has motivated us to continue to explore Cu(2,5-DM-DCNQI)$_2$ system to make nanometer scale modifications using the STM.

We chose the flat single crystal surfaces (ac planes) to investigate the STM tip induced phase transition on the Cu(2,5-DM-DCNQI)$_2$. An initial 100 nm x 100 nm scan with +0.17V (tip positive) bias voltage and 1.0 nA is shown in Figure 2a. This photograph shows a very flat surface with monolayer steps. This topography was stable until

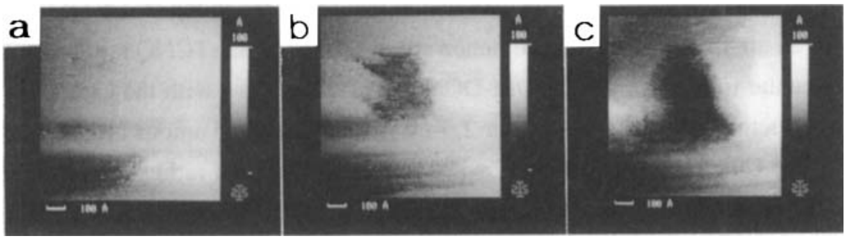

FIGURE 2 Nanometer scale surface modification of Cu(2,5-DM-DCNQI)$_2$ using STM under constant current mode. (100 x 100 nm, Vt +0.17V, It 1.0 nA)
a. Before applying a positive pulse (left) b. After +2V, 1s pulse (center)
c. After +3V, 1s pulse (right) (2d to 2f on next page)

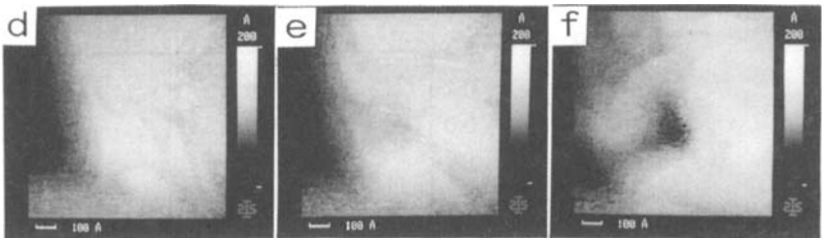

FIGURE 2 (Continued) d. Before applying a negative pulse (left) e. After -2V, 1s pulse (center) f. After -3V, 1s pulse (right)

we applied voltage pulses sufficient to chemically/physically modify the surface. No significant change occurred when a +1V square pulse (with respect to the tip) for 1 second was applied through the tip to the sample surface. However, we observed dramatic surface changes, shown in Figure 2b, when a +2V square pulse was applied to the sample for 1 second. The approximate size of this feature was 40 nm x 20 nm with a 0.9 - 1.1 nm depth under the constant current mode that corresponds to a monolayer of the Cu(2,5-DM-DCNQI)$_2$ crystal. Figure 2c shows a surface after we applied +3V pulse for 1 second pulse in addition to the +2V pulse. The feature was further expanded to 55 nm x 40 nm with a 4.2 - 4.6 nm depth. These modifications were reproducible and the spots could also be made using a negative bias. When we applied negative voltage pulses, no significant change occurred until a -3V square pulse for 1 second was applied as shown in Figure 2d to 2f. The feature created on the surface was also smaller (approximately 10 nm diameter) than that created by the same amplitude pulse with positive polarity. When we applied an additional -4V pulse for 1 second pulse in addition to the -3V pulse, the feature was further expanded to approximately 30 nm.

This bias dependence can be understood that redox reactions of 2,5-DM-DCNQI radical anion are involved this phenomenon similar to the metal-TCNQ system.[10] The STM molecular images on Cu(2,5-DM-DCNQI)$_2$ crystals agree with the unreconstructed ac planes structure terminated with four 2,5-DM-DCNQI radical anions around the near surface of the Cu atoms.[2] The surface exposed 2,5-DM-DCNQI radical anions in Cu(2,5-DM-DCNQI)$_2$ crystal and negatively charged (-0.67 per one 2,5-DM-DCNQI molecule was reported[11]) in order to neutralize the positively charged Cu cation (+1.3 average charge on Cu was reported[11]). When we applied positive pulses, neutral DCNQI was produced by the electron transfer from the Cu(2,5-DM-DCNQI)$_2$ surface to the tip. The neutral DCNQI molecules were then removed by the next STM tip scans, because neutral DCNQI molecules are insulating. Only a very thin layer of neutral DCNQI molecules were permitted to stay on the conducting $Cu(2,5\text{-}DM\text{-}DCNQI)_2$ surface by the operational mechanism of the STM.

When we applied negative pulses, more DCNQI radical anions and dianions were produced by the electron transfer from the tip to the $Cu(2,5\text{-}DM\text{-}DCNQI)_2$ surface. It is harder to transfer the electrons from the STM tip to the negatively charged 2,5-DM-DCNQI radical anions than that from the negatively charged 2,5-DM-DCNQI radical anions to the tip. Not only is this due to the electron-electron repulsion, but it is also due to the large difference between the first and the second redox potentials (E_1 -0.38V, E_2 +0.21).[12] The reason why the negative-pulsed area appears dark may be due to the reduced conductivity of $Cu(2,5\text{-}DM\text{-}DCNQI)_2$ surface which is the result of the destruction of conducting column by the reduction of $Cu(2,5\text{-}DM\text{-}DCNQI)_2$. This proposed mechanism adequately explains the bias dependence of the STM induced modifications.

Figure 3a shows a drawing of a "baby face" on the $Cu(2,5\text{-}DM\text{-}DCNQI)_2$ single crystal surface using the STM tip pulse technique. We first created a 18 nm diameter dark spot by applying +2V square pulse for 20 seconds and then sequentially created a 28 nm diameter dark spot by applying +2V square pulse for 60 seconds, a 37 nm diameter dark spot by applying +2V square pulse for 30 seconds, a 61 nm diameter dark spot by applying +3V pulse for 30 seconds and a 49 nm diameter dark spot by applying +4V pulse for 5 seconds. We also "drew" the number "7" on the same $Cu(2,5\text{-}DM\text{-}DCNQI)_2$ single crystal surface using a nanometer scale lithography technique with continuous +2V square pulse from the external pulse generator as shown in Figure 3b . Tip movement was controlled by the STM control software. We have also shown in Figure 3 that we can control the STM to make artificial features on $Cu(2,5\text{-}DM\text{-}DCNQI)_2$ single crystal surface using the pulse technique.

We imaged 100 nm thick $Cu(2,5\text{-}DM\text{-}DCNQI)_2$ thin films prepared by a new technique: acetonitrile vapor assisted charge-transfer of vacuum deposited films. Before

FIGURE 3 Nanometer scale lithography on $Cu(2,5\text{-}DM\text{-}DCNQI)_2$
a: Left : "Baby face" (500 x 500 nm, Vt +0.10V It 1.0 nA)
b: Right : "Number 7" (250 x 250 nm, Vt +0.10V It 1.0 nA)

we started the STM experiments, conductivity measurements were performed by a four point-probe method. The in-plane conductivity of thin film was 2.0 x 10^{-1} S/cm. It is lower by three order of magnitude than that of single crystals (c-axis 4.7 x 10^{2} S/cm) at room temperature. The films shows a semiconducting conductivity-temperature dependence in contrast to the single crystals that show a metallic conductivity-temperature dependence as shown in Figure 4. These differences of electrical properties between the single crystals and the thin films were also reported for M(2,5-DM-DCNQI)$_2$ (M=Li, Na, K, Rb, Cs) thin films synthesized by a solid state diffusion technique.[13-14] The calculated band gap from the conductivity-temperature dependence was 0.40 eV. This number is close to 0.3eV, the semiconducting gap of amorphous Cu(2,5-DM-DCNQI)$_2$ thin film on Cu foil observed by XPS and UPS.[15] Figure 5 shows the STM image of polycrystalline films that consists of 20-100nm long small grains. We performed the surface modification experiments by the STM on this film using the same conditions that were used for the single crystals. We observed similar dark regions created with higher voltage pulses (+2-5V), however, the size of the dark regions was larger (typically 30 - 300 nm diameter) than that on the single crystals (10 - 50 nm diameter). Two factors can contribute to these differences. The first factor is the orientation of crystallites in the films. Cu(2,5-DM-DCNQI)$_2$ thin films were polycrystalline films, whereas the ac plane was exposed to the STM tip on the single crystal of Cu(2,5-DM-DCNQI)$_2$. This modification may preferentially occur on the ac plane. The second factor is the in-plane conductivity of samples. Since grain boundaries reduce the mobility in the films, we expected to see

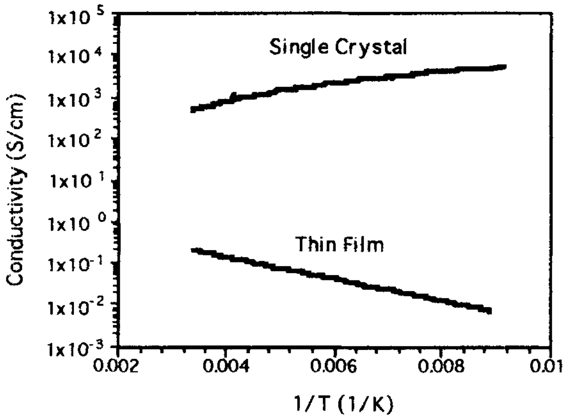

FIGURE 4 Conductivity of a Cu(2,5-DM-DCNQI)$_2$ film and a single crystal as a function of theinverse temperature

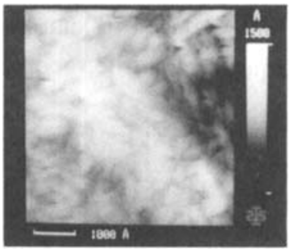

FIGURE 5 STM image of 100nm thick Cu(2,5-DM-DCNQI)$_2$ film on HOPG (500 x 500 nm, Vt -0.03V, It 0.92 nA)

the activated behavior over the temperature range down to 100K. Ohmic loss on the films is larger by three order of magnitude than that on the single crystals and it may explain the increase in the threshold voltage on the STM surface modification experiments.

We observed a color change from deep blue (original color of Cu(2,5-DM-DCNQI)$_2$ charge transfer complex film) to yellow brown (color of neutral 2,5-DM-DCNQI film) on the films of Cu(2,5-DM-DCNQI)$_2$ surrounding the current probe after 4-point probe resistivity measurements were performed. The color change occurred when we set a probe free from the surface. Voltages larger than a set voltage might applied because the power supply in the resistivity meter automatically increased the voltage until the set current was detected before the probe was completely detached. As shown in Fig.6a, infrared microspectroscopic data on this sample showed that the yellow brown area had more than doubled the transmittance (about 25 -30 %) in comparison with the original Cu(2,5-DM- DCNQI)$_2$ area. We assigned a peak centered at 2170 cm^{-1} to the C≡N peak (2168 cm^{-1}) of neutral 2,5-DM-DCNQI (on the yellow brown area). The Cu(2,5-DM- DCNQI)$_2$ area of the film had low transmittance (about 12 %) and no peak around 2165 cm^{-1} (figure 6b) as previously reported.[3] Very similar spectrum changes had been observed before and after exposure of Cu(2,5-DM- DCNQI)$_2$ to the laser irradiation.[3] Under constant current STM conditions, the darker regions are less conductive. The dark region which appeared after the STM pulsing may contain neutral

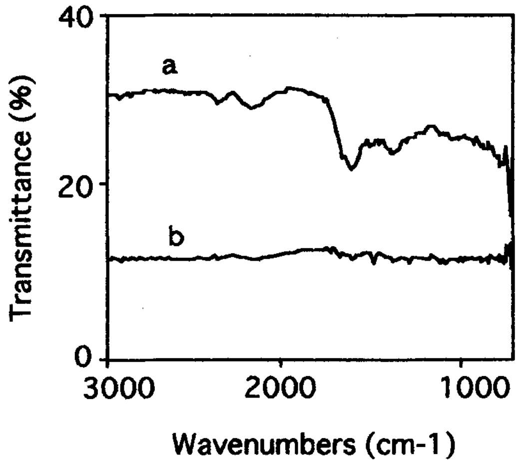

FIGURE 6 Infrared microspectroscopy of 200 nm thick Cu(2,5-DM-DCNQI)$_2$ film on KBr (a:Yellow brown area produced after performing resistivity measurement, b: Original Cu(2,5-DM-DCNQI)$_2$ film area)

2,5-DM-DCNQI. Because neutral 2,5-DM-DCNQI is insulator, this observation supports an electric field induced ionic-neutral phase transition which similar to the mechanism proposed for other metal-TCNQ complexes.[5-6]

From this series of experiments, we have shown that an electric field phase transition contributes to the surface modification of Cu(2,5-DM-DCNQI)$_2$ by the STM. Cu(2,5-DM-DCNQI)$_2$ may be a good candidate for SPM-based information storage material because it has a high STM electric field sensitivity (a low threshold voltage) and it can easily be prepared in thin film form.

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REFERENCES

1. A. Aumüller, P. Erk, G. Klebe, S. Hünig, J.U. von Schütz and H.-P. Werner, Angew. Chem. Int. Ed. Engl., 25, 740 (1986)
2. S. Yamaguchi, T.J. Kistenmacher, C.A. Viands, H.S.-W. Hu and R.S. Potember, Synth. Met., 63 ,61 (1994)
3. S. Yamaguchi, C.A. Viands and R.S. Potember, Synth. Met., 45 , 71 (1991)
4. D. Schmeisser, W.Göpel, H.Fuchs, K.Graf and P.Erk,Phys.Rev.B.,48,4891 (1993)
5. S. Yamaguchi, C.A.Viands and R.S.Potember, J. Vac. Sci. Technol., B9, 1129 (1991)
6. S. Yamaguchi, C. A. Valenzuela and R. S. Potember, Mat. Res. Soc. Symp. Proc., Vol. 276, 265 (1992)
7. M. Yamashita and M. Agu, Jpn. J. Appl. Phys., 23, 1499 (1984)
8. M. Yamashita, S. Yamaguchi, and H. Enjoji, Jpn. J. Appl. Phys., 27, 869 (1988)
9. A. Aumüller, P. Erk, G. Klebe, S. Hünig, J.U. von Schütz and H.-P. Werner, Angew. Chem. Int. Ed. Engl., 25, 740 (1986)
10. R. S. Potember, T. O. Poehler and D. O. Cowan, Appl. Phys. Lett., 34, 405 (1979)
11. H. Kobayashi, A. Miyamoto, H. Moriyama, R. Kato and A. Kobayashi, Chem. Lett., 863 (1991)
12. A. Aumüller and S. Hünig, Liebigs. Ann. Chem., 165 (1986)
13. H. Wachtel, J.U. von Schütz, H. C. Wolf, Synth. Met., 41-43, 1789 (1991)
14. H. Wachtel, J.U. von Schütz, H. C. Wolf, Mol. Cryst. Liq. Cryst., 218, 271 (1992)
15. D. Schmeisser, K. Graf, W. Göpel, J.U. von Schütz, P. Erk and S. Hünig, Chem. Phys. Lett., 148, 423 (1988)