Moiré Structure of the 2-Mercaptobenzothiazole Corrosion Inhibitor Adsorbed on a (111)-Oriented Copper Surface

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ABSTRACT: The adsorption of 2-mercaptobenzothiazole (2-MBT) vapor on a Cu(111) surface under ultra-low pressure was investigated. For an exposure of 45 L at 150 °C, a Moiré pattern was observed as a result of the superposition of an underlying \((\sqrt{3} \times \sqrt{3})R30°\) structure and an outer layer compressed by 18% and rotated by 1.2°. The Moiré pattern was rich in S bonded to Cu as a result of molecular decomposition and partial desorption and was transformed to a \((\sqrt{7} \times \sqrt{7})R19.1°\) structure when the sample temperature was increased above 250 °C during deposition. This pre-adsorbed Moiré structure led to the sharp decrease of the oxidation kinetics, which better protects copper against corrosion than the non-ordered 2-MBT monolayer formed at room temperature. Upon further exposure to 2-MBT at room temperature, an equivalent monolayer of the molecule was adsorbed on the Moiré structure at saturation whereas a multilayer was formed for the direct deposition on Cu(111) at room temperature.

INTRODUCTION

2-Mercaptobenzothiazole (2-MBT) is used commercially in oils, greases, and cooling fluids as a corrosion inhibitor for copper and its alloys. The molecule may be heated during application, so it is of great importance to elucidate the adsorption of 2-MBT not only at room temperature but also at higher temperatures. However, the interaction of 2-MBT with the copper surface is not well understood, since in practice empirical tests are performed to evaluate the effectiveness of different compounds for industrial applications. Several studies have been carried out in order to investigate the inhibiting effect of 2-MBT on copper corrosion.\(^1\)\(^-\)\(^3\) It is believed that 2-MBT forms a complex layer on copper through bonding with sulfur or nitrogen or both atoms, which can protect the copper from corrosion. However, the inhibition mechanism of the molecular layer is still debated.

The structural aspects of the molecular adsorption at model interfaces is thus of great interest. Our previous study on 2-MBT adsorption by sublimation at ultra-low pressure on Cu(111) at room temperature presented the formation of a non-ordered monolayer followed by flat-lying multilayers at saturation.\(^4\) It has been shown that 2-MBT forms a self-assembled monolayer from the liquid phase with flat-lying molecules on the Au(111) surface.\(^5\)\(^-\)\(^7\) A Moiré pattern was observed for the adsorption of sulfate anions on the Cu(111) surface, which was accompanied by a reconstruction of the Cu(111) substrate.\(^8\) Moreover, the adsorption of S on Cu(111) under ultra-high vacuum (UHV) has been widely studied, with the formation of various structures, including \((\sqrt{3} \times \sqrt{3})R30°\) and \((\sqrt{7} \times \sqrt{7})R19.1°\) structures, depending on the S coverage.\(^9\)\(^-\)\(^11\) A reconstruction to form a pseudo-(100) structure was also observed for the adsorption of nitrogen on Cu(111).\(^12\)\(^,\)\(^13\)

In this work, 2-MBT exposure on a Cu(111) surface by sublimation at ultra-low pressure and 150 °C and the resulting formation of an interfacial layer characterized by a Moiré pattern (hereafter denoted as a “Moiré structure”) were investigated. The inhibition efficiency of the Moiré structure was studied by exposure to gaseous oxygen and ambient air at room temperature as well as its effect on the buildup of a 2-MBT multilayer at room temperature. The sample surfaces were characterized by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). The influence of temperature on the molecular deposition was also studied. The results provide new insight on the chemical and structural interaction between the inhibitor molecule and the copper surface and contribute to the design of new inhibitors that better protect the metals.

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EXPERIMENTAL SECTION

Experiments were carried out in an UHV system with base pressure in the $10^{-10}$ mbar that was equipped with a reactor for 2-MBT evaporation. The following surface analytical techniques were used: STM (Omicron, STM1 with a SCALA system), AES (Omicron, CMA-100), and LEED (Omicron, SpectaLEED). The sample was a high purity (99.999%) Cu(111) single crystal. It was mechanically polished to 0.25 μm (diamond paste), electropolished in phosphoric acid, and then prepared in the UHV system by cycles of ion sputtering ($P_{Ar} = 1 \times 10^{-5}$ mbar, 600 V, and 20 mA for 30 min) and annealing (600°C for 30 min) until a clean copper surface was obtained, i.e., no contamination was shown by AES, a sharp (1 × 1) pattern was observed by LEED, and large and flat terraces were observed by STM.

The clean metallic Cu(111) surface was exposed to the 2-MBT vapor at ultra-low pressure (2 × 10^{-9} mbar) in the UHV reactor. Exposures are expressed in langmuirs (1 L = 1 × 10^{-6} Torr·s). The 2-MBT powder (99% purity, Sigma-Aldrich) was placed in a vacuum-sealed glass mounted on the reactor. The pressure in the reactor was limited by the vapor pressure of 2-MBT at room temperature. The Cu(111) sample was heated to 150°C during molecule deposition. The temperature was selected to avoid the total desorption of molecules from the surface and to allow the reorganization of the molecular layer. The STM characterization was carried out at room temperature and in the constant current mode. A W tip was prepared by electrochemical attack in a NaOH solution followed by voltage pulses under UHV. Image processing was performed using WSxM software (5.0 develop 9.1). No filtering was applied. All images were corrected by plane subtraction.

Quantitative chemical analysis was performed by quickly transferring the sample to another UHV system equipped with a spectrometer for XPS analysis (Thermo Electron Corporation, ESCALAB 250) with a base pressure of 10^{-10} mbar. A monochromatic Al Kα source (1486.6 eV) was used. The survey spectra were recorded with a pass energy of 100 eV corresponding to an overall resolution of 1.8 eV, and the high resolution spectra were recorded with a pass energy of 20 eV corresponding to an overall resolution of 360 meV. The XPS measurements were performed at a takeoff angle of 90°, and the data analysis was preformed using the CasaXPS software (ver. 2.3.19).

Exposure to 2-MBT vapor at ultra-low pressure (2 × 10^{-9} mbar) in the UHV reactor. Exposures are expressed in langmuirs (1 L = 1 × 10^{-6} Torr·s). The 2-MBT powder (99% purity, Sigma-Aldrich) was placed in a vacuum-sealed glass mounted on the reactor. The pressure in the reactor was limited by the vapor pressure of 2-MBT at room temperature. The Cu(111) sample was heated to 150°C during molecule deposition. The temperature was selected to avoid the total desorption of molecules from the surface and to allow the reorganization of the molecular layer. The STM characterization was carried out at room temperature and in the constant current mode. A W tip was prepared by electrochemical attack in a NaOH solution followed by voltage pulses under UHV. Image processing was performed using WSxM software (5.0 develop 9.1). No filtering was applied. All images were corrected by plane subtraction.

In order to verify the inhibition properties of the adsorbed Moiré layer formed at 150°C further exposure to 2-MBT at room temperature and 2 × 10^{-9} mbar was performed as well as exposure of the surface with the Moiré structure to oxygen at a low pressure (1 × 10^{-5} mbar) for up to 1 h 30 min and to ambient air at atmospheric pressure. Finally, to investigate the influence of temperature on the adsorption of 2-MBT, exposure was also performed at a higher temperature.

RESULTS AND DISCUSSION

Exposure at 150°C: Moiré Structure Formation. STM images of the Cu(111) surface before and after exposure to 2-MBT at 150°C are shown in Figure 1. On clean Cu(111), the step edges were aligned according to the disorientation of the single-crystal, with multistepic steps (1–3 atomic planes), as shown in Figure 1a. The step edges appear to be fuzzy because of the high mobility of copper atoms at room temperature. After exposure to 2-MBT at 150°C (45 L), as shown in Figure 1b, the step edges became straight, suggesting a reduced surface mobility of Cu atoms after exposure to 2-MBT. Moreover, they were reoriented in three directions, forming a 120° angle with each other. Large terraces are favored by the formation of higher multiatomic steps (1–6 atomic planes). The terraces remained atomically flat, suggesting the formation of an organized layer after exposure to 2-MBT.

By zooming in on the terraces obtained after 2-MBT exposure, a Moiré structure was observed with the presence of two hexagonal structures, as indicated in Figure 2a and modeled in Figure 2b. The short-range hexagonal unit cell is marked in blue with a lattice parameter of 3.5 ± 0.5 Å and a rotation of 31 ± 4° with respect to the directions of the substrate. This was also confirmed by fast Fourier transform subtraction.

![Figure 1. STM images of (a) the clean Cu(111) surface (100 × 100 nm², V = 0.7 V, and I = 0.2 nA) and (b) the Cu(111) surface exposed to 45 L of 2-MBT at 150°C (100 × 100 nm², V = 0.1 V, and I = 2.5 nA).](https://dx.doi.org/10.1021/acs.jpcc.0c04083)
(FFT) (Figure 2c) and LEED (Figure 2d) measurements, which show the same direction and gives a lattice parameter of 3.7 Å. Moreover, two overlapped mirror domains were observed by LEED. The long-range hexagonal lattice (Moiré structure) is indicated in black with a lattice parameter 5.6 times larger (19.6 ± 0.6 Å) than that of the short-range structure and a rotation of 6.4° (25 ± 5° with respect to the substrate). According to Moiré pattern mathematical formalism,16 we found that the observed Moiré structure may be explained by the superposition of the following two molecular layers: the 3.5 Å lattice observed in the STM image and an underlying hexagonal lattice not observed in the STM image, with a lattice parameter mismatch of 18% and a rotation of 1.2° between the two, as shown in Figure 2b. The lattice parameter for the underlying layer is 4.1 ± 0.6 Å, corresponding to \(\sqrt{3} \times \sqrt{3} \)R30° structure.

AES peak-to-peak height ratios of S (151 eV) and N (380 eV) to C (271 eV) signals were calculated for the Moiré structure, and their relative ratios were corrected using the relative sensitivities of the Auger transitions. The results give a S:C atomic ratio of 3.57, which is about 12.5 times the theoretical (molecule stoichiometry) value (2:7), and a N:C atomic ratio of 0.05, which is about 0.4 times the theoretical value (1:7). These differences suggest that the Moiré structure is rich in S as the result of a partial decomposition of the 2-MBT by the cleavage of the C=S or C=S bonds during exposure at 150 °C, probably due to the high affinity of sulfur to copper.17–21 The Moiré structure also appears to be poor in N, suggesting the desorption of molecular fragments after decomposition.

The surface with this Moiré structure was then transferred to the XPS system for quantitative analysis, and the results are shown in Figure 3. For the peak fitting of S 2p spectra, spin–orbit doublets S 2p1/2 and S 2p3/2 with a branching ratio of 0.5 and a spin–orbit splitting of 1.18 eV were considered.23,24 The Moiré structure is mainly composed of a S3 component with S 2p3/2 at 161.7 eV. This component is slightly shifted to a higher binding energy (0.2 eV) compared to that of the \(\sqrt{3} \times \sqrt{3} \)R19.1° S/Cu(111) surface obtained by exposing the clean Cu(111) surface to H2S, which may be explained by an interaction with oxygen during the transfer in air. The S3 component is assigned to the S bonded to the metallic copper.22 A N 1s component at 399.0 eV was observed, corresponding to N in the non-bonded molecule. XPS spectra obtained from the 2-MBT monolayer formed on Cu(111) at room temperature are also shown for comparison. The intensity of the S 2p spectrum was found to be 0.6 times that obtained from the Moiré structure, and the intensity of the N 1s spectrum was found to be 1.3 times that obtained from the Moiré structure, suggesting that the Moiré structure is richer in S than the 2-MBT monolayer formed at room temperature.

The atomic ratios of S and N vs C were calculated for the Moiré structure. We found a S to C atomic ratio 1.4 times the theoretical value for the stoichiometry of the molecule (2:7) and a N to C atomic ratio 0.4 times the theoretical value (1:7), confirming the decomposition of the molecule. We assumed three types of carbon, C2, C3, and C4, for the peak fitting of the C 1s spectrum. The full width at half maximum (FWHM) values (1.3 eV) of the C2 and C3 components were set to be the same, and the fit is in agreement with the measured spectrum. The C4 component at a binding energy of 288.2 eV

![Figure 3. XPS spectra of the S 2p, N 1s, and C 1s core levels for Cu(111) that was exposed to 45 L of 2-MBT at 150 °C (Moiré structure) and 15 L of 2-MBT at RT (2-MBT monolayer) for comparison. The S 2p spectrum for a \(\sqrt{3} \times \sqrt{3} \)R19.1° S/Cu(111) surface is also shown for comparison.22](https://dx.doi.org/10.1021/acs.jpcc.0c04083)
indicates the presence of carboxylic groups (air contamination), which explains the difference in the atomic ratios of S and N to C obtained by AES. The C$_2$ and C$_3$ components at binding energies of 285.8 ± 0.2 and 284.7 ± 0.1 eV correspond to C−N bond and the remaining C atoms in the benzene ring, respectively. The intensity of C$_3$ is 5−6 times that of C$_2$. This confirms the decomposition of 2-MBT by the cleavage of the C=S and C−S bonds.

In order to study the influence of temperature on the adsorption of 2-MBT, exposures were carried out on Cu(111) at different temperatures, and the surface structure was characterized by LEED. The Moiré structure formed at 150 °C was transformed to a ($\sqrt{7} \times \sqrt{7}$)R19.1° structure when the deposition temperature was increased to 250 °C.

Growth of the 2-MBT Layer on a Pre-Adsorbed Moiré Structure at Room Temperature. The surface with the Moiré structure was then exposed to 2-MBT under ultra-low pressure (2 × 10$^{-9}$ mbar) at room temperature, and the AES peak-to-peak height ratios of S (151 eV), C (271 eV), and N (380 eV) to the Cu (920 eV) signals were calculated and plotted as a function of the exposure (Figure 4). The values at 0 L correspond to those for the Moiré structure.

![Figure 4](https://example.com/figure4)

Figure 4. Growth of the 2-MBT layer on a pre-adsorbed Moiré structure at 2 × 10$^{-9}$ mbar and RT. Change in the AES peak-to-peak height ratios of $h_S/h_{Cu}$, $h_C/h_{Cu}$, and $h_N/h_{Cu}$ as a function of the 2-MBT exposure.

After exposure to 65 L of 2-MBT, a slight decrease of the S signal was first observed. This may be explained by the attenuation of the Moiré structure (rich in S) by the adsorbing 2-MBT molecules. On the contrary, N and C signals were observed to increase, confirming the adsorption of molecules on the surface. Further exposure of 2-MBT up to 4000 L showed no obvious increase in the S, C, and N signals. By comparing the AES peak-to-peak height ratios to those obtained for 2-MBT deposited on the clean Cu(111) surface, we estimated that only one equivalent monolayer of 2-MBT was adsorbed; meanwhile, 2-MBT multilayers were grown on the clean Cu(111) surface.

The sample was also analyzed by XPS to obtain information on the chemical composition (Figure 5). The S 2p spectrum shows that the growth of 2-MBT on the Moiré structure at room temperature gives rise to two other components, S$_1$ and S$_2$, with 2p$_{3/2}$ peaks at 164.2 and 162.8 eV corresponding to the endocyclic and exocyclic S atoms in the 2-MBT molecule not bonded to copper, respectively. This confirms the adsorption of molecules on the Moiré structure. The comparison of the intensity of the XPS spectra with those obtained from Cu(111) with the pre-adsorbed 2-MBT monolayer confirmed the formation of one equivalent 2-MBT monolayer on the Moiré structure at room temperature. The binding energies of the S$_1$ and S$_2$ components were found to be slightly superior to those found in our previous study on 2-MBT, which may be explained in this case by the influence of the exposure to air during the transfer to XPS. An increase in the intensities of C and N was also observed, with a slight shift to a higher binding energy (0.3 eV) and a decrease in the FWHM value (1.5 eV) of about 25% for the N 1s spectrum. A component C$_1$ at a binding energy of 286.4 eV is also observed, which was assigned to the C=S bond. Similarly, the C$_4$ component at 288.2 eV was assigned to carboxylic groups (air contamination).

The topography of the surface of the Moiré structure obtained after exposure at room temperature to 2-MBT was characterized by STM and is shown in Figures 6 and 7. After an exposure of 65 L (Figure 6), the surface was homogeneous, with the presence of multilatonic steps with heights of about 7 Å (3–4 atomic planes). The step edges remained straight. By zooming in on the terraces (Figure 6b), we can see that the adsorbed molecular layer is almost complete and is relatively flat with a maximal height difference of around 1.5 Å. The size of the protrusions is 1−2 nm, which could be assigned to the adsorption of 2-MBT molecules. FFT measurements showed no ordered structure.

At higher exposures up to 4000 L, Figure 7a shows that the step edges are reorganized and the surface is always flat and homogeneous, as confirmed by Figure 7b. The molecular layer is very similar to that observed at 65 L, with a maximal height difference of around 1.7 Å and protrusions of 1−2 nm; no ordered local structure was revealed by FFT.

Inhibition Effect of the Pre-Adsorbed Moiré Structure on the Oxidation of Cu(111). In order to clarify the inhibition properties of the interfacial Moiré structure, the Cu(111) surface with the pre-adsorbed Moiré structure was exposed to oxygen under a low pressure (until 10$^{-5}$ mbar) at room temperature. The oxidation kinetics were followed by AES, as shown in Figure 8. When the copper surface is pre-covered by the Moiré structure there is almost no uptake of oxygen, in contrast to the oxidation kinetics on the clean Cu(111) surface. This confirms the effective protection of copper by the Moiré structure at a low O$_2$ pressure and room temperature. Because of the well-organized pre-adsorbed structure, no residual uptake of oxygen was observed as in the case of Cu(111) with a non-ordered pre-adsorbed 2-MBT monolayer formed at room temperature, suggesting a better protection of copper by the Moiré structure against corrosion.

When exposed to ambient air, the sample surface was slightly oxidized, as indicated by the XPS spectra shown in Figure 9. The results were compared to those obtained on the metallic Cu(111) surface after exposure to air. First, we can see that the intensities of the Cu 2p, O 1s, and Cu LMM core levels were largely decreased in the presence of the pre-adsorbed Moiré structure. The decrease of the Cu 2p intensity can be explained by a strong attenuation of the signal by the
pre-adsorbed Moiré structure. Moreover, weak satellite structures are observed between the 2p1/2 and 2p3/2 peaks, indicating the formation of Cu(II) in two cases.27,28 Analysis of the O 1s spectrum obtained on metallic Cu(111) gives two components O1 and O2 at binding energies of 531.5 and 530.3 eV, respectively. The O1 component may be attributed to the interface OH groups resulting from the dissociative adsorption of water or oxygenated contaminations, while the O2 component is usually assigned to the bulk oxide.29,30 The decrease in the O 1s spectrum (both O1 and O2 components) with the Moiré structure indicates that the metallic Cu(111) sample is more oxidized and contaminated. This confirms that the Moiré pattern offers good protection of copper against oxidation even in ambient air.

In order to elucidate the nature of the oxide formed on the sample surface, decomposition of the Cu LMM spectrum was also carried out using three reference spectra obtained by analyzing the metallic Cu sample and copper oxides.31 The results show the formation of 34% cuprous oxide (Cu2O) and 19% cupric oxide (CuO) on the metallic Cu(111). In the presence of the Moiré structure, the intensities of the Cu(I) and Cu(II) components decrease; however, the relative proportion of the Cu(I) component increases to 76%. This
can be explained by a preferential Cu(I) oxidation occurring upon the formation of the Moiré structure, with the Cu(I) component assigned to the oxidized copper bonded to S in the Moiré structure. The results confirm that the Moiré structure can protect the copper substrate from oxidation when exposed to air.

**CONCLUSIONS**

The adsorption of 2-MBT on Cu(111) at ultra-low pressure was investigated at mild temperature by STM, XPS, AES, and LEED. The STM images show that a Moiré structure was formed from exposure at 150 °C with a short-range unit cell and an underlying superimposed (√3 × √3)R30° structure. XPS spectra show that the Moiré structure is rich in S bonded to Cu as a result of 2-MBT decomposition and partial desorption. When the deposition temperature was increased, the Moiré structure formed at 150 °C was transformed to a (√7 × √7)R19.1° structure at 250 °C, which was assigned to atomic S bonded to Cu.

The corrosion inhibition efficiency of the interfacial Moiré structure was determined by dosing oxygen to the pre-adsorbed Moiré structure. No uptake of oxygen was observed until an oxygen partial pressure of 10⁻⁵ mbar, and the sample was only slightly oxidized when exposed to ambient air. This indicates the good protection by the pre-adsorbed Moiré structure against oxidation of the Cu(111) surface, which is more efficient than a 2-MBT monolayer formed at room temperature.

Upon further exposure of the Moiré structure to 2-MBT at 2 × 10⁻⁹ mbar and room temperature, an equivalent monolayer of molecules was formed, which was flat and homogeneous. However, no further growth was shown until an exposure of 4000 L, suggesting that the pre-adsorbed Moiré structure does not enable the formation of multilayers of 2-MBT that was observed on the clean Cu(111) surface.

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**Notes**

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