A comprehensive in situ spectroscopic study of 2-mercaptobenzothiazole as a corrosion inhibitor for copper

Dissertation

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Zusammenfassung

Abstract

2-Mercaptobenzothiazole (MBT) is known as one of the most effective organic corrosion inhibitors of copper. MBT has been described to react with copper forming a passivating polymeric copper MBT complex to prevent dissolution. Open questions remain on how the passivating layer forms, and different views exist as to its internal structure. In this work, the interaction of MBT with copper in alkaline solution was investigated by in situ infrared (IR), Raman, and ellipsometric spectroscopy, coupled to cyclic voltammetry (CV). In situ work was complemented by detailed ex situ analysis, in particular detailed analysis of X-ray photoelectron spectra (XPS). At negative potentials, MBT monolayers form by adsorption to the oxide free metal surface. These monolayers relax on a minute time scale through MBT reorientation, leading to MBT-copper binding via the exocyclic S and N-atoms. After copper dissolution becomes thermodynamically feasible, including at open circuit, formation of a multilayer CuMBT complex sets in, in which the thiol form dominates over the thione form. Cu$^+$ is exclusively present in these films. As the electrode potential increased, multilayer film formed and effectively inhibited oxide formation; oxide related peaks have been absent in the CVs and in Raman spectra. Instead of formation of copper oxide or copper dissolution, at positive potentials, MBT oxidatively dimerises to 2,2$'$-dibenzothiazole disulfide (DBTA), which remains protective. While MBT also adsorbs to oxide-covered copper surfaces, there is no evidence from the in situ experiments performed that the presence of an initial oxide layer is needed for adsorption of MBT to occur. The effect of aging of the copper substrate was investigated on the structure of the formed copper MBT complex film, and its ability to inhibit oxide formation. On freshly prepared surfaces, adsorption proceeded in the typical flat geometry, which inhibited oxide formation despite polarization to positive potentials. After few weeks of storing the samples, adsorption geometry appears more disordered, and inhibition of oxide formation is no longer possible. After analysis of a number of samples, three different scenarios were identified. Characteristic Raman peaks of the copper MBT complex may serve as an initial indicator on whether the com-
plex layer inhibits oxide formation or not. Overall, this work stresses the different roles a corrosion inhibitor has to possess in order to be effective.
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1 Motivation and Approach

2-Mercaptobenzothiazole (MBT) has been well known as one of the most effective corrosion inhibitors for decades, amongst others for copper \(^{[1]}\). It has been proposed that MBT reacts with Cu and forms a CuMBT polymeric complex layer on the Cu surface to prevent corrosion \(^{[2]}\). Compared with other effective corrosion inhibitors with similar electronic structure, MBT has a particularly superior performance \(^{[3]}\). It is thus important to study the interaction between Cu and MBT in detail to elucidate the interaction mechanism and find the “key factors” of MBT corrosion inhibition. This approach will provide a foundation for knowledge-based development of effective corrosion inhibitors. Only few works exist which focus on the molecular details of the interaction between copper and MBT \(^{[4,5]}\). Therefore, there are arguments about the reaction mechanism, such as which atoms are involved in this interaction, and what the structure is of this CuMBT polymeric complex. In situ spectroscopic studies can provide a variety of detailed structural information during reactions, and are consequently powerful techniques to propose a reaction mechanisms. So far, only patchy in situ studies exist \(^{[6,7]}\), focusing on the application of a single technique. No detailed in situ studies are available allowing to disentangle the role of inhibitor adsorption, metal dissolution, and oxide formation. By combining the results from several in situ techniques, a clearer comprehensive view of the reaction mechanism can be expected. One important aspect is also the competition between oxide film formation and inhibitor film formation. This competition has not been investigated at all in situ. A study focusing on this competition can nevertheless help to understand how oxide affects the formation of the complex layer.
Chapter 1. Motivation and Approach

In this work, three different complementary in situ spectroscopic techniques were applied to study the interaction of MBT with Cu in 1 mM MBT alkaline solution. In situ surface enhanced ATR-IR and in situ Raman spectroscopy were used to investigate the molecular structure of CuMBT complex, the binding of MBT to Cu surface and its inhibition of oxide formation on copper. In situ ellipsometric spectroscopy was used to determine the thickness of the forming interfacial layer. Both Raman and ellipsometry experiments were conducted during cyclic voltammetry (CV) and at controlled constant electrode potential, while ATR-IR spectroscopy was conducted at controlled constant electrode potential and open circuit potential (OCP). Ex situ studies complement the in situ data. X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), X-ray diffraction (XRD), IR spectroscopy and ellipsometric spectroscopy were conducted to assist identifications of materials and provide references for in situ studies.
2 Introduction

2.1 The application of Cu

Copper and its alloys have a wide range of application in industry because of high thermal and electrical conductivity, formability and other outstanding mechanical properties\(^8\). In addition, compared with most other metals, it is more resistant to the irritants from environment due to thermodynamic stability so that it can provide comparatively stable performance in practical use. Copper is used in electronics such as the production of wires, sheets and tubes. It is also used as essential material for water system in marine environment\(^9\)\(^1\)\(^0\) and for nuclear waste containers\(^1\)\(^1\).

To store radioactive waste, the corrosion resistance of the container is principally required. The material should be inert to most environmental condition. It should be able to form protective surface layer to slow down further corrosion. Besides, the corrosion rate should be predictable, so that the thickness of the container can be designed properly\(^1\)\(^2\). Copper has all the advantages mentioned above. It is stable under well understood conditions and comparatively cheaper than other inert metal such as gold, silver and platinum. Besides, in air, Cu oxidized to Cu\(_2\)O\(^1\)\(^3\). As a passivating layer, a Cu\(_2\)O layer can prevent it from further corrosion\(^1\)\(^3\). The rate of Cu corrosion depends on environment, such as moisture, temperature, pH value and the presence of aggressive species such as Cl\(^-\)\(^1\)\(^4\). A previous report showed that the rates of corrosion for 20-year exposure in air were 1 \(\mu\text{m/year}\) for industrial use, 0.8 \(\mu\text{m/year}\) in marine and 0.5 \(\mu\text{m/year}\) for rural atmosphere which are predictable for long term use\(^1\)\(^2\).
Chapter 2. Introduction

In addition, Cu has high ductibility and fabricability to make it an ideal material for large amount of production. In the U.S. and Canada, Cu-coated carbon steel vessels are already in practical use for nuclear waste. In Europe, it is planned to place radioactive waste hundreds of metres underground by 2025 where the planned sites will be in Sweden, Finland and France. Sealed disposal canisters with 5 cm Cu shell are proposed to be used due its high resistance to corrosion.

2.2 The corrosion of Cu

Despite the nobility of copper, it is susceptible to corrode in acidic media or when chloride ions are present in the environment. Besides, as temperature rises, the rate of corrosion increases. The heat generated by radioactive waste increases not only the temperature but also the humidity around the canister. It can facilitate corrosion, which is originally expected to be a very slow process. The corroded canister causes leakage of radioactive substances and may adversely affect our environment and living species.

In addition to nuclear danger, the corrosion of copper plays an important role in industry. The damage of facilities produce large economic costs, and it also leads to safety concerns. The collapse of corroded materials bring about the damage of properties and lives.

Corrosion is a heterogeneous process defined as gradual degradation of material due to an electrochemical reaction in which electron transfer is involved. It is usually found occurring at the interface between metal and environment. Corrosion has been intensively studied in water containing environments and aqueous solution. With dissolved ions and oxygen in water, metals oxidize and release electrons and metal ions followed by a series of electron transfer processes. As metal dissolved as ions in water, accompanied soluble or insoluble products are formed. Dissolution leads to degradation of materials. It changes not only the surface morphology but also the structure of metals. The weakening of their
mechanic properties and the damage of materials are usually concomitant\cite{20}.

In aqueous solution, the anodic reaction is generally the oxidation of metals which releases metal ions. As anodic reaction occurs, a cathodic reaction is always accompanied. In aqueous solution, the common reduction reactions are hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR).

In air or water containing environment, the oxidation of copper starts to form Cu$_2$O. Three stages of copper oxide growth were proposed in the work of Platzman et al.: (a) the formation of a Cu$_2$O layer, (b) the formation of a Cu(OH)$_2$ metastable layer, and (c) the transformation of the Cu(OH)$_2$ layer to more stable CuO layer\cite{25,26}.

Before the Cu(OH)$_2$ metastable layer forms, Cu$_2$O is usually considered as a passivating substance preventing further oxidation. It was shown that only a $\approx 1.6$ nm--thick Cu$_2$O layer formed after exposure at ambient condition for 800 h\cite{13}. Under an aggressive environment, further oxidation occurs with production of different copper oxide. CuO is finally formed\cite{20}. In aqueous solution, the oxidation of Cu becomes more complicated. It is affected by electrode potential and pH value. The theoretical corrosion products are usually described by a Pourbaix diagram\cite{14,29} (Fig. 2.1). In the presence of other ions, such as Cl$^-$, the corrosion product of copper will change. Besides, localized pitting corrosion may occur as well\cite{28}.

Large economic costs and damage resulted from corrosion\cite{29}. Therefore, how to control and prevent corrosion have been an important issue for decades. Corrosion of Cu was studied under a lot of conditions because the rate of corrosion relates to environmental factors, such as humidity, temperature, and the presence of aggressive ions\cite{10,19,28,30,33}. Besides, the prevention of corrosion was extensively investigated, such as a protecting coating on the Cu surface\cite{33,36} and the use of inhibitors\cite{37,39}.
2.3 Corrosion inhibitors

With the concerns of cost, efficiency and safety, the inhibition of Cu corrosion has been an important issue for decades. The use of corrosion inhibitors is an efficient and effective way to prevent metal corrosion, including temporary protection during storage and transport and localized protection. In industry, corrosion inhibitors have been widely used due to excellent anti-corrosive properties.

For example, in petroleum production, long-chain nitrogeous organic inhibitors, including amines and amides were used to inhibit corrosion of metallic containers due to the presence in an aqueous phase. As amphiphiles, these inhibitors are attached to metal via their polar groups and form a film on the surface, while the non-polar groups are physically absorbed by hydrocarbon. Therefore, the thickness of the protective film is increased and the inhibition of corrosion is facilitated. Moreover, water in cooling system contains several metal and non-metal ions and it leads to a corrosion of pipes. This corrosion can be controlled by inhibitors such as nitrate and chromate. For automobiles, inhibitors like nitrites,
phosphates, silicates and benzoates are added into antifreeze to reduce the corrosion of heat exchange or other system with flowing liquids. Phosphonates and carboxylates are applied to protect the metal surfaces exposed to atmosphere [41–44].

The corrosion inhibitor efficiency is given by the follow equation:

\[ E_f = \frac{R_o - R_i}{R_o} \times 100\% \]  

where \( E_f \) is the inhibitor efficiency in percentage, \( R_o \) is corrosion rate without application of inhibitors and \( R_i \) is corrosion rate with inhibitors [39].

Corrosion inhibitors can be classified by mechanism as anodic, cathodic and anodic-cathodic mix types [39]. It can also be classified by chemical nature as inorganic and organic inhibitors. The functions of most of the corrosion inhibitors are similar. A coating layer, usually a passivation layer, forms on the metal surface to block the access of oxidants, water or ions to the metal, so that corrosion is retarded [36–45].

### 2.3.1 Anodic and cathodic inhibitors

**Anodic inhibitors**  Anodic inhibitors, sometimes referred to passivators, act by reducing the rate of the anodic reaction. They react with metal ions released from the anode and form a passivating layer on the anode to block its reaction. Under the application of anodic inhibitors, the corrosion potential of the metal would be shifted to a more positive value, and corrosion current would decrease [39–41].

**Cathodic inhibitors**  Cathodic inhibitors work by reducing the rate of cathodic reaction. Usually, insoluble substances precipitate on the cathodic site and limit the diffusion of reducible species. Under the application of cathodic inhibitors, the corrosion potential of the metal would be shifted to a more negative value, while the corrosion current would decrease [39–41].

**Mixed type**  Mixed type inhibitors act by reducing both rates of anodic and cathodic reactions. They usually form a film covering on the surface and block both
anodic and cathodic sites to hinder both cathode and anode reactions. After using mixed type inhibitors, the corrosion potential of the metal would not change but corrosion currents decrease [39–41].

### 2.3.2 Inorganic and organic inhibitors for Cu

#### Inorganic inhibitors

One of the most studied inorganic inhibitors for Cu is chromate CrO$_4^{2-}$. Chromate can be reduced and form a passive Cr$_2$O$_3$ film on the Cu surface. Besides, it can also be reduced on the Cu surface to decrease corrosion current density. However, the toxicity of chromium ions leads to a dispute. The search of alternative compounds which are more environmentally friendly but equally efficient is currently going on [5].

#### Organic inhibitors

Organic inhibitors such as azoles [9,47], amines [48], amino acids [49] and their derivatives have been studied for decades since they provide outstanding inhibitions and they are widely used in industry nowadays. The presence of heteroatoms such as nitrogen and sulfur in organic compounds usually promotes the compound’s adsorption to a metal surface, hence facilitates effective corrosion inhibition. The presence of functional groups can also help the chemisorption on the Cu surface. In addition, if rings with conjugation bonds present, the π electrons can form coordinate bonds with vacant d orbital of Cu and promote the chemisorption as well [37,45,50–52].

With all the above characteristics, benzotriazole (BTA) [Fig. 2.2(a)] and its thiolated form MBT [Fig. 2.2(b)] are well known organic corrosion inhibitors, amongst others, for copper [53]. Both BTA and MBT can react with copper ions to form a polymeric complex film covering the metal surface [54,55].

### 2.4 2-Mercaptobenzothiazole as corrosion inhibitor

2-Mercaptobenzothiazole (MBT), with a molecular weight of 167.25 g/mol, has two forms at room temperature, which are shown in Fig. 2.2(b) as thiol form or
2.4. 2-Mercaptobenzothiazole as corrosion inhibitor

Figure 2.2: The molecular structure of (a) benzotriazole (BTA) and (b) 2-mercaptobenzothiazole (MBT). Left: thiol form. Right: thione form.

MBT is an effective inhibitor to prevent Cu from corrosion and have been applied in industry for decades \[^1\]. It has been known that it can react with Cu and a CuMBT layer form on the Cu surface to protect it from corrosion \[^57\]. Potentiodynamic electrochemical experiments showed that MBT acts as a mixed-type inhibitor, i.e. inhibiting both cathodic and anodic processes on the surface \[^4,57\]. In the study of Subramanian et al., it showed that MBT had the highest surface coverage compared with other corrosion inhibitors in all applied concentration. They tried to calculate surface coverage of the electrode surface under application of corrosion inhibitors with different concentrations. By trying to fit the coverage-concentration data to different adsorption isotherms, it was found that the data can be best fitted to the Langmuir adsorption isotherm. Based on their results, the highest value of surface coverage of MBT was 0.89 with the concentration of 2 mM \[^9\]. Besides, MBT has been found an effective corrosion inhibitor also to zinc \[^58,59\] and aluminium alloys \[^60\].

In some electrochemical impedance spectroscopic studies, it was shown that MBT has higher inhibition efficiency than commonly used BTA \[^3,47\]. However, compared to BTA \[^9,61\], there were only few studies focusing on mechanism of MBT-Cu interaction \[^2,4,5,57,59,62,64\].

To date, most available studies on the interaction of copper with MBT have used surface modification and ex situ analysis after transfer of the sample through an oxygen containing atmosphere \[^2,59\]. Ex situ x-ray photoelectron spectroscopy (XPS) after sample transfer through air has been widely used to understand the nature of the MBT layer forming on Cu. Kazansky et al. \[^4,59,63\] suggested that a
thin Cu$_2$O layer on Cu surface was required for the formation of a CuMBT film. The forming CuMBT layer became thicker if Cu was immersed longer in the MBT solution. Studies from Finšgar et al.\cite{57} showed by angle dependent XPS that the nitrogen and exocyclic sulfur atom MBT were involved in the adsorption to Cu. Moreover, no Cu$^{2+}$ species were detected, neither in the CuMBT complex layer, nor on the Cu surface after Cu was treated with MBT. This observation implies that the CuMBT complex contains only Cu$^+$. The same result was shown in the work of Ohsawa et al.\cite{1}. They prepared CuMBT in direct reaction to MBT with CuCl$_2$ as starting material. However, a mixture of Cu$^+$ complex and oxidized product of MBT, DBTA (Fig. 2.3) in 2 : 1 molar ratio was obtained. It was proposed that if Cu$^{2+}$ salts were used, in order to form the Cu$^+$ product, Cu$^{2+}$ needs to reduce to Cu$^+$. As a result, the oxidation of MBT to DBTA (Fig. 2.3) is taking place. Based on results from XPS, Kazansky et al. proposed a probable structure of CuMBT complex layer\cite{2}, in which each Cu$^+$ cation is surrounded by three exo-S atoms and one N atom as a tetrahedron. However, this statement was not directly proven, and left the exact structure of CuMBT complex still in a fog.

Figure 2.3: The molecular structure of 2,2’-dibenzothiazole disulfide (DBTA)

Other surface analysis techniques were also applied to investigate the behavior of MBT in different solutions\cite{1,4,53,64–66}. Non-destructive in situ spectroscopies are also introduced in this field. They can provide immediate information while an electrochemical reaction occurs, and have more insights to its mechanism and structure. Woods et al.\cite{6} used surface enhanced Raman spectroscopy (SERS) to investigate the adsorption of MBT molecules on Cu, Ag and Au. In situ SERS was recorded for Cu at controlled electrode potential in solutions containing MBT at different pH values. Based on in situ Raman spectra, in alkaline solution (pH 9.2), MBT bonded to Cu surface via exocyclic S atom. However, in acid medium (pH 4.6), the adsorption resulted from $\pi-$bonding between the Cu surface and the aro-
2.4. 2-Mercaptobenzothiazole as corrosion inhibitor

The spectra also revealed that MBT interacted with Cu in the thiol form. Huo et al. [7] obtained similar results using electrochemical surface-enhanced infrared (IR) spectroscopy in attenuated total reflection (ATR) mode. In the work, the interaction between MBT and Cu was investigated in 0.1 M NaClO₄. A Cu-coated ATR Si crystal was used as working electrode. It was found that at lower electrode potential (< 0 V), MBT vertically adsorbed on the Cu surface in the form of a thiolate via exocyclic S atom. At higher electrode potential (> 0 V), electron transfer between Cu and MBT occurred, nitrogen atom and exocyclic sulfur atom coordinates to Cu⁺ to form complex polymer on the surface [7] (Fig. 2.4). However, in Tan's work [55], they claimed that the adsorption was mainly via exo S atom and N atom was not included based on the analysis of XPS result (Fig. 2.4). In spite of varying approaches used, the adsorption mechanism of MBT on the Cu surface still remains unclear and all the hypotheses need to be further proven.

![Figure 2.4: The proposed adsorption of MBT on Cu / Cu₂O surface](image)

Besides, in previous studies, it was assumed that a Cu₂O layer is essential for CuMBT layer formation [1,57,59] (Fig. 2.4). This Cu₂O layer was estimated around 2 nm, determined by XP spectra [41,59]. However, in these studies, samples were transported through air, which led to the possibility of post-preparation oxidation. In addition, with similar electronic structure to MBT and as corrosion inhibitor to Cu, BTA was found to be able to adsorb on both Cu oxide and oxide-free surface and still had inhibition of oxide formation [9]. In Hashemi’s work, BTA was also found to form a polymeric complex layer on a CuCl substrate [67] and inhibited oxide formation. Therefore, the interaction of MBT with Cu and Cu₂O still needs to
investigate. In addition, it is also important to study whether the oxide originally on the surface would affect the application of corrosion inhibitors and further influence the inhibition of oxide formation.
3 Experimental section

3.1 Surface characterization technique

3.1.1 Attenuated total reflection-Infrared (ATR-IR) spectroscopy

IR spectroscopy is an absorption spectroscopy which vibrational or rotational transitions are excited. Molecules with change in dipole moment can absorb radiation. Due to the specific absorption frequency, certain bondings can be identified from which the conformation and orientation of molecules can be further proposed. IR spectroscopy can be applied to study molecules in gas, solid and liquid phase. However, in aqueous solution, highly absorbing media, such as water, would make the detection of other molecules difficult. In order to measure the reaction occurring at the interface and avoid interference of water absorption, attenuated total reflection (ATR) technique is introduced. Fig. 3.1 shows the concept of ATR technique. A beam passing through an ATR crystal creates multiple reflections at an internal surface, at which evanescent waves are produced. These waves are absorbed by the sample. This technique can offer high sensitivity of detection to the reaction at the interface. In addition, with limited light path of evanescent wave, the problem of strong absorption of water can be avoided.

In this work, a Bruker Vertex 70v Fourier transform IR spectrometer (Bruker Optik GmbH, Ettlingen, Germany) equipped with a middle band mercury cadmium telluride (MCT) detector was used. IR spectroscopy was used to identify the synthesized product, the structural change of MBT molecules and CuMBT complex at the interface.
Chapter 3. Experimental section

3.1.2 Raman spectroscopy

Raman spectroscopy is a complementary technique to IR spectroscopy to investigate vibrational and rotation information in a system. Different from IR absorption, in Raman processes, the excited molecule is proposed to be in a so-called virtual state, and then re-emits photons and back into higher (Stokes) or lower (anti-Stokes) vibrational states. This phenomenon happens when molecules have a change in polarizability during transition. It is a useful non-destructive technique to study inorganic and organic materials [68, 70].

In this work, a Labram confocal Raman microscope (Horiba Jobin Yvon), with an excitation wavelength of 632 nm of a HeNe laser was used. The resulting spectra were analyzed on a CCD detector. It was used to study the structural change of CuMBT complex and the formation of copper oxide at the interface.

3.1.3 Ellipsometry

Ellipsometry is an optical technique to study the dielectric properties of thin films. It measures the change in the ratio of amplitude reflection coefficients of p and s-polarized light after an incident beam reflects on the surface. In an ellipsometric experiment, two parameters, the amplitude component $\Psi$ and the phase difference $\Delta$, can be obtained. Through the model, not only optical parameters, but also thickness and roughness can be characterized [71].

In this work, to determine the thickness of CuMBT layer and copper oxide, an SE800 UV/Vis spectroscopic ellipsometer (Sentech Instruments), with a xenon source, in the wavelength range of 300–820 nm, at an angle of incidence of 70°
3.1. Surface characterization technique

was used. The thickness of Cu oxide and the CuMBT layer was analyzed by a method described previously\[72\], using calculated values of differences in the ellipsometric parameter $\Delta$ averaged over a wavelength range from 700 nm to 750 nm for a given thickness as calibration. It was assumed that the refractive index of Cu oxides roughly equals the one of the CuMBT complex. No data was available for the refractive index of CuMBT. As transition metal complex, it is likely to be higher than the refractive index of pure MBT, which was reported as 1.785\[73\]. Uncertainties were estimated via Gaussian uncertainty propagation; the standard deviation of the ellipsometric parameter $\Delta$ was estimated in a region at low potential when it was expected to be stable, and used to estimate the standard deviation of the thickness. Uncertainties are reported as single standard deviation. In Sec. 7.2, the thickness of the oxide layer was simulated by SpectraRay using fixed refractive index and absorption as layer type. For Cu, the constants of the refractive index ($n$) and extinction ($k$) are 0.25 and 3.41, respectively. For Cu$_2$O, $n$ and $k$ are 2.94 and 0.11, respectively\[74\].

3.1.4 X-ray photoelectron spectroscopy (XPS)

XPS is a spectroscopic technique which is used to characterize the surface of materials. An XP spectrum was obtained by bombarding the surface of a sample with X-rays having a specific energy. By measuring the kinetic energy of the emitted electrons, the corresponding electron binding energy can be determined. The binding energy differs in different elements and chemical environment. Therefore, it can give information about elemental composition, chemical and electronic states of elements in a material. In angle resolved XPS, by changing the detection angle, the surface sensitivity differs. Smaller angle includes information closer to surface\[75\].

In this work, a Quantum 2000 XPS (Physical Electronics) with a monochromatic Al K$_\alpha$ source was used. The pass energy is 26.5 eV and the energy resolution is 0.1 eV. The XPS data were analyzed by using the software CasaXPS. All the binding energies were calibrated based on the C 1s peak at 284.8 eV. XPS was used to
study the oxidation state of Cu and identify the reaction site of MBT with Cu. The samples as powder were measured by being pressed into an indium foil with a purity of 99.999% (Goodfellow).

### 3.1.5 Atomic force microscopy (AFM)

AFM is a type of scanning probe microscopy which can be used to investigate the topography of a given surface. It is based on the force between the sample and a probe known as cantilever. When a cantilever is displaced due to a force induced by interaction with a surface, the reflection of the laser beam is displaced as well. The height variation is obtained by calculating this displacement, resulting in the information about surface topography[76].

In this work, AFM was used to study the surface roughness and morphology of the samples. AFM images were obtained with a Digital Instruments Dimension 3100 AFM microscope in tapping mode. AFM measurements were conducted with assistance of Petra Ebbinghaus.

### 3.1.6 X-ray diffraction (XRD)

XRD is a technique which can determine the crystal structure, orientation and composition of a material. Illuminated with an X-ray beam, crystalline components produce specific diffraction pattern. By measuring the angles and intensity of the pattern, the information of the crystal structure is obtained[77].

In this work, XRD was used to determine the crystal orientation of Cu deposited on a Si wafer which prepared from physical vapor deposition (PVD) method. XRD measurements were performed by a diffractometer Bruker XS WS with Cu K$_\alpha$ as X-ray source. Data were analyzed by BEARTEX 2012x. Measurements were performed by Benjamin Breitbach.
3.2 Materials

3.2.1 ATR-IR Ge crystal

ATR Ge crystal was prepared from a double side polished Ge(100) crystal with a thickness of 0.5 mm (Crystal GmbH) which was cut into a size of 52 mm·20 mm, and both shorter sides were polished to an angle of 30° to be used for ATR measurement at 60° angle of incidence \[^{78}\]. For cleaning, a well-polished crystal was immersed in neutral Extran lab detergent (VWR) for 1 h, and then washed with ultrapure water for several times, followed by an immersion in 2-propanol (99.5 %, VWR) for 1 h. The crystal was then washed with a large amount of ultrapure water, and then dried in a N\textsubscript{2} stream.

3.2.2 Cu sample for in situ ATR-IR measurements

For in situ IR spectroscopic experiments, an ATR-IR crystal with Cu coating was required. To prepare this sample, physical vapor depositions was firstly used. Different thicknesses of Cu layer (10 nm, 15 nm, 70 nm, and 80 nm) with 10 nm titanium adhesion layer were physically deposited on a well-polished ATR Ge crystal. However, no IR absorbance at the detector was obtained. Avoiding the interference of the Ti layer, different thicknesses of the Cu layer were deposited on the Ge crystal without the titanium adhesion layer. However, there was still no IR absorbance obtained. In addition, without adhesion layer, deposited layer was easily peeled-off from crystal surface as electrode potential was applied.

As solution, a method of chemical deposition was used to prepare a Cu layer on Ge crystal. Based on an established recipe \[^{79}\], 0.2547 g CuSO\textsubscript{4}·H\textsubscript{2}O (Sigma-Aldrich), 1.2579 g potassium sodium tartrate, C\textsubscript{4}H\textsubscript{4}O\textsubscript{6}KNa·4H\textsubscript{2}O (Sigma-Aldrich) and 0.4318 g NaOH (Merck) were dissolved in 50 mL ultrapure water. After all the solid was dissolved, 1 mL formaldehyde, HCHO, (Sigma-Aldrich) was added into the solution. The pH was adjusted to 13 with concentrated HCl to give a clear blue solution. The copper layer was prepared by dropping the solution prepared
as described above on the cleaned germanium crystal such that it covers the area to be sampled subsequently. The crystal was placed on an ATR-IR unit to monitor the process of Cu layer formation.

Figure 3.2: Time-dependent IR spectra recorded during the chemical deposition of a Cu layer. Time refers to the time after the solution was dropped on the ATR Ge crystal.

Fig. 3.2 showed a series of time dependent in situ IR spectra recorded after the prepared solution was left on an ATR Ge crystal. At 30 s, three peaks at 1640 cm\(^{-1}\), 2240 cm\(^{-1}\) and 3300 cm\(^{-1}\) were observed. They are assigned to a bending mode of a water molecules, carbon dioxide from atmosphere and a stretching mode of water molecules, respectively\(^{80,81}\). As time increased, small features appeared on the peak at 3300 cm\(^{-1}\) due to total absorption. The shape of the water peak became sharper as well. In addition, the baseline shifted with time. The shift of the baseline indicated the formation of Cu layer on the ATR Ge crystal. In order to be able to observe the interaction between the Cu layer and MBT molecule, the blue deposition solution was removed before the interested region 1000–1500 cm\(^{-1}\) was affected by baseline shift. The solution was removed from the crystal by washing with a large amount of ultrapure water then dried with flowing N\(_2\). A visible shiny brown Cu layer can be seen on the crystal surface. The whole process
3.2. Materials

usually took 3–5 min, depending on the activity of the deposition solution. The freshly prepared surface was used for subsequent experiments immediately.

3.2.3 Cu sample for in situ Raman and ellipsometric spectroscopy experiments

For in situ Raman and spectroscopic ellipsometry experiments, evaporated Cu on Si(100) wafers was used. Si(100) wafers (Siegert Wafer) were washed with isopropanol and ultrapure water then dried with flowing N₂. First, a 10 nm titanium adhesion layer was e-beam evaporated. Then a 200 nm copper layer was deposited, with the evaporation rate of 1 Å/s. The prepared samples were stored in a dessicator to prevent interaction with the atmosphere. The crystal orientation of a deposited Cu layer was examined with XRD. Fig. 3.3 shows that a Cu(111) layer was obtained. In addition, Si(111) wafer (Siegert Wafer) with 200 nm deposited Cu layer was prepared under the same condition. Its crystal orientation was identified as (111) with XRD as well [Fig. 3.4]. It indicated that the crystal orientation of the Si wafer didn’t affect the crystal orientation of deposited Cu layer. In this work, only Si(100) wafers were used to prepare samples.

![Figure 3.3: XRD pattern of deposited Cu layer on a Si(100) wafer.](image-url)
In Sec. 4.3, Au samples were used as reference. The gold layer was prepared with the same method mentioned above. A 200 nm gold layer with a 10 nm titanium adhesion layer was physically deposited on a Si(100) wafers.

Figure 3.5: AFM images of the Cu layer from two preparation method; (a) chemically deposited on a Ge(100) wafer and (b) physical-vapor-deposited on a Si(100) wafer.

Table 3.1: The statistics for Cu layers prepared from different methods

<table>
<thead>
<tr>
<th>Preparation method</th>
<th>Average height</th>
<th>Maximum height</th>
<th>$R_{ms}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical deposition</td>
<td>52.3 nm</td>
<td>139.2 nm</td>
<td>15.1 nm</td>
</tr>
<tr>
<td>PVD</td>
<td>5.16 nm</td>
<td>13.05 nm</td>
<td>2.59 nm</td>
</tr>
</tbody>
</table>
3.2. Materials

The Cu samples from both preparations were examined by AFM as well. As shown in Fig. 3.5, the Cu layer prepared from chemical deposition has more and smaller grains and larger roughness resulting from uneven Cu deposition (Table 3.1). It is proposed that an effect similar to surface enhancement was obtained due to the rougher surface. Therefore, the IR absorbance was only obtained when the Cu layer was chemically deposited on ATR Ge crystal.

3.2.4 Chemicals

For electrochemical measurements, 0.1 M aqueous NaOH was prepared from NaOH (Merck) and ultrapure water. In the 0.1 M NaOH, a 1 mM solution of MBT (Sigma-Aldrich) was prepared.

3.2.5 The preparation of CuMBT complex for ex situ studies

Syntheses from Cu salts  CuMBT complex was synthesized based on previous literature[82]. Two Cu salts (CuCl, CuSO$_4$·5H$_2$O) with different oxidation states (Cu$^+$ and Cu$^{2+}$, respectively) were used as starting materials.

CuCl (0.36 g, 3.6 mmol) was dissolved in 40 mL H$_2$O, and then a few drops of concentrated HCl were added into it to give a greenish blurred solution. MBT (0.5 g, 3 mmol) was dissolved in 15 mL ethanol. The two solutions were then mixed to give a blackish green solution. After being stirred for 10 min, the solution was filtered to yield green precipitates and a light blue filtrate. The solid was washed with a large amount of ultrapure water, ethanol and acetone to give a product CuMBT (I) as yellow solid.

CuSO$_4$·5H$_2$O (0.5 g, 2 mmol) was dissolved in 50 mL H$_2$O. MBT (0.67 g, 4 mmol) was dissolved in 20 mL ethanol. The two solution were then mixed to give a blackish green solution. After being stirred for 10 min, the solution became yellowish blurred and was filtered to yield yellow precipitates and a light blue filtrate. The solid was washed with a large amount of ultrapure water, ethanol and acetone to give a product CuMBT (II) as yellowish orange solid.
Preparation from immersion in 1 mM MBT  Cu layers on Si wafer prepared from PVD were immersed in 1 mM MBT / 0.1 M NaOH solution in air for different times. The solution was purged with Argon for 30 min and the immersed samples were placed in a beaker with parafilm covering the opening. After the immersion finished, samples were taken out and washed with isopropanol and ultra pure water several times, then dried with flowing Argon. In Sec. 4.2, the sample was immersed in a solution for 27 h. In Sec. 4.3, the samples were immersed in solution for 2 h, 8 h and 24 h, respectively.

3.3 Spectroelectrochemical cell set-ups for in situ measurements

3.3.1 In situ ATR-IR spectroscopy

A home-built three electrode electrochemical cell \[^{[78,83]}\] with electrode area of 4 cm\(^2\) was placed on a Cu-covering ATR Ge crystal prepared in Sec. 3.2.2 in a sample chamber of an IR spectrometer. The electrodes were placed as illustrated in Fig. 3.6. The MCT detector was cooled with liquid nitrogen for 1 h before measurements. All IR spectra were obtained after accumulating 100 scans with a spectral resolution of 4 cm\(^{-1}\). Light source without passing through a polarizer was used for all measurements. For potential-dependent measurements, electrode potential was controlled by a potentiostat (Palmsens). The conditions of the electrochemical experiments would be described in Sec. 3.4.

3.3.2 In situ Raman spectroscopy

For monitoring electrochemical processes, a home-built three electrode electrochemical cell was used, with electrode area of 0.785 cm\(^2\) \[^{[31,84]}\]. The setup is shown in Fig. 3.7. The cell was placed on a Cu-covered Si wafer prepared in Sec. 3.2.3 with a flow system. An objective with magnification 10\(\times\) and numerical aperture 0.25 was used to illuminate the sample with a spot of 10 µm diameter. The elec-
3.3. Spectroelectrochemical cell set-ups for in situ measurements

Figure 3.6: Scheme of the electrochemical setup used for in situ ATR-IR measurements.

The electrode potential was controlled by a potentiostat (Palmsens). The Raman spectra were recorded with an integration time of \(\approx 32\) s continuously after the reduction potential (-1.0 V) was applied. The details of the electrochemical experiments are illustrated in Sec. 3.4.

Figure 3.7: Scheme of the electrochemical setup used for in situ Raman measurements.

3.3.3 In situ ellipsometric spectroscopy

Concurrent electrochemical experiments were conducted in a home-built three electrode electrochemical cell with electrode area of 2.5 cm\(^2\). The cell was placed on a Cu-covering Si wafer prepared in Sec. 3.2.3 with a flow system as shown in
The instrumental parameters used were illustrated in Sec. 3.1.3. The illuminated area on the working electrode was 0.7 cm$^2$. Electrode potential was controlled by a Compact potentiostat (Ivium Technologies). Recording one ellipsometric spectrum required $\approx 35$ s. The ellipsometric spectra were recorded continuously after the application of a reduction potential of -1.0 V. The details of the electrochemical experiments are described in the next section.

![Scheme of an electrochemical setup used for in situ spectroscopic ellipsometric measurements.](image)

**3.4 Electrochemical experiments**

In this work, the electrode potential $E$ is reported with reference to Ag|AgCl|3 M KCl. The current was normalized to the electrode area and is reported as current density $j$. An Ag|AgCl|3 M KCl microreference electrode (World Precision Instruments) was used in all experiments. A graphite rod was used as counter electrode in Raman spectroscopy measurements, while a Pt mesh was used in IR and ellipsometric spectroscopy measurements. In in situ IR measurements, chemically deposited copper (Sec. 3.2.2) was used as working electrode, while in in situ Raman and ellipsometric spectroscopy experiments, evaporated Cu (Sec. 3.2.3) was used. Before experiments started, all the solutions were purged with Argon for 30 min.
3.4. Electrochemical experiments

3.4.1 MBT treated Cu with 1 mM MBT in 0.1 M NaOH as electrolyte

For in situ IR measurements, chemically deposited copper (Sec. 3.2.2) was used as working electrode. In time dependent in situ IR measurements, after preparation, the prepared Cu layer was immediately used for experiments. The 1 mM MBT solution in 0.1 M NaOH was directly introduced into the cell. The reference spectrum was taken ≈5 min after MBT in NaOH was introduced into the cell under open circuit conditions. Afterwards, spectra were continuously recorded. In potential dependent in situ IR measurements, the 1 mM MBT solution in 0.1 M NaOH was also directly introduced into the cell. The electrode potential of -1.0 V was applied for 2 min while the reference spectrum was recorded. Stepwise electrode potential was applied, starting from -0.8 V to +0.6 V then back to -1.0 V with a potential step of 0.2 V and an applied time of 115 s. The IR spectra were recorded after the electrode potential was applied for 10 s. Reference experiments on pure Cu in pure 0.1 M NaOH were performed as well.

For potential dependent in situ Raman and spectroscopic ellipsometry experiments, evaporated Cu was used as working electrode. First, a potential of -1.0 V in 0.1 M NaOH was applied for 10 min to reduce the oxide on the surface. Reference experiments on pure Cu in pure 0.1 M NaOH were performed. To prepare a CuMBT film on the Cu surface, after reduction, 1 mM MBT in 0.1 M NaOH was introduced into a cell by a flow system, while the electrode potential was kept at -1.0 V for 30 min. A cyclic voltammogram (CV) was recorded subsequently in both reference and MBT experiments, from -1.0 V to 0.5 V, with starting electrode potential -1.0 V and scan rate 1 mV/s.

3.4.2 MBT treated Cu with 0.1 M NaOH as electrolyte

The experiments were performed mainly via in situ Raman experiments. The samples used were stored in a desiccator for different periods of time (4 days [Case I], 8 days [Case II] and 15 days [Case III], respectively) after freshly prepared. The
Chapter 3. Experimental section

CuMBT film was prepared in a way the same as the procedure mentioned above. After the film formed on the surface, 0.1 M NaOH was introduced again to replace the electrolyte in cell. During the replacement, the electrode potential was kept at -1.0 V. It took roughly 30 minutes to reduce the concentration of MBT lower than 0.005 mM, which was examined by UV-Vis spectra. Fig. 3.9 shows a UV spectrum of 0.005 mM MBT / 0.1 M NaOH which has a peak at 309 nm with absorbance of 0.06, which was almost the same as previous studies 67, 68. The UV spectra of replaced electrolytes in this series of experiments were all measured to make sure that the absorbance was lower than 0.06, then subsequent electrochemical experiments were applied. The same CV measurements mentioned above were performed but using 0.1 M NaOH as electrolyte.

![Figure 3.9](image)

Figure 3.9: UV spectrum of 0.005 mM MBT / 0.1 M NaOH.
4 Ex situ studies of CuMBT complexes as powders and thin film

4.1 Introduction

For the reference to the following in situ experiments, the structure of CuMBT complexes was examined in more detail ex situ. In this chapter, CuMBT were prepared in two different ways: (a) chemical syntheses and (b) immersion of a Cu sample in 1 mM MBT solution. The prepared CuMBT were identified with IR spectroscopy and XPS. Commercial MBT powder and its oxidized product DBTA were characterized as well. The results were compared with the data in previous literature reports [1,7,82,89]. In time-dependent studies, the time of immersion of Cu in the MBT solution was discussed. Angle resolved XPS and depth-profiling XPS measurements were performed to study the CuMBT layer at different depths. AFM was used to examine the morphology.

4.2 Characterization of MBT, CuMBT complexes and DBTA

IR spectra Fig. 4.1 shows the IR spectra of MBT related compounds. The IR spectrum of commercially available MBT powder was obtained with the ATR technique (Sec. 3.1.1). CuMBTs obtained with three different approaches (Sec. 3.2.5) were measured. CuMBT(PVD) was obtained by the immersion of a Cu layer de-
posited on a Si wafer in a 1 mM MBT solution. The IR spectrum was measured in external reflection. CuMBT (I) and CuMBT (II) were synthesized from Cu$^+$ and Cu$^{2+}$ salts, respectively. The products as powder were measured with the ATR technique (Sec. 3.1.1). DBTA was obtained as a thin layer from oxidizing MBT on a Cu electrode. The IR spectrum was measured in external reflection.

Figure 4.1: IR spectra of (a) commercial MBT powder, (b) CuMBT synthesized from Cu$^+$ salt, (c) CuMBT synthesized from Cu$^{2+}$ salt, (d) CuMBT prepared from an immersion of a Cu sample in 1 mM MBT / 0.1 M NaOH and (e) DBTA film obtained from oxidizing MBT on a Cu electrode. Spectra (a), (b) and (c) were measured with the ATR technique. Spectra (d) and (e) were measured in external reflection.

Figure 4.2: The molecular structure of (a) MBT with two forms at room temperature and (b) DBTA. $S^1$ and $S^2$ indicate exo- and endo-S atoms in both MBT and DBTA, respectively.
4.2. Characterization of MBT, CuMBT complexes and DBTA

Table 4.1: characteristic IR absorbance of MBT compound.

Exp. = the data obtained in this work. Ref. = the experimental data obtained by Huo et al. [7].
calc. = the calculated vibrational frequencies by Altun et al. [89].

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Ref.</th>
<th>calc. thiol</th>
<th>Approx. assignment</th>
<th>cm⁻¹</th>
<th>calc. thione</th>
<th>Approx. assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1012</td>
<td>1012 s</td>
<td>1017</td>
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<td>C=S¹ str.</td>
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</tr>
<tr>
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<td>1034 vs</td>
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<td></td>
<td>1079</td>
<td>Bz ring rock</td>
<td></td>
</tr>
<tr>
<td>1076</td>
<td>1078 m</td>
<td>1076</td>
<td>Bz ring bending</td>
<td></td>
<td></td>
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<tr>
<td>1246</td>
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<td>1246</td>
<td>CNS¹ str.</td>
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<tr>
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<td>1286</td>
<td>C=C str.</td>
<td>1280</td>
<td>CN str.</td>
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<td>Bz ring str.</td>
<td>1334</td>
<td>Bz ring str.</td>
<td></td>
</tr>
<tr>
<td>1425</td>
<td>1427 vs</td>
<td></td>
<td></td>
<td>1426</td>
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<tr>
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<td>Bz ring str.; CH rock</td>
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<td>1502</td>
<td>Bz ring str.; CH rock</td>
<td>1495</td>
<td>Bz ring str.; CH rock</td>
<td></td>
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<tr>
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<td>1597 w</td>
<td></td>
<td></td>
<td>1601</td>
<td>Bz ring str.</td>
<td></td>
</tr>
</tbody>
</table>

S¹ and S² indicate exo- and endo-S atoms in CuMBT, respectively [Fig. 4.2(a)].

The assignment of characteristic peaks of MBT is listed in Table 4.1. With two resonance forms under room temperature, the calculated vibrational value of both thiol and thione forms are shown. The characteristic peaks of two forms are the peaks at 1012 cm⁻¹ and 1033 cm⁻¹, which are assigned to single bond and double bond stretching between C and exo-S atom, respectively.

After MBT oxidized to DBTA, three strong peaks were found at 1007 cm⁻¹, 1429 cm⁻¹ and 1470 cm⁻¹ in Fig. 4.1. The disappearance of the peak at 1033 cm⁻¹, assigned to C=S stretching in thione form, implies the formation of disulfide bond. According to assignment (Table 4.2), it shows that after dimerization, not only heterocyclic ring but also benzene ring were affected. The peaks at 1429 cm⁻¹ and 1470 cm⁻¹ were shifted and their IR absorbances increased.
Table 4.2: characteristic IR absorbance of DBTA

Exp. = the data obtained in this work. Ref. = the experimental data obtained by Huo et al. [7].
calc. = the calculated vibrational frequencies by Altun et al. [89].

<table>
<thead>
<tr>
<th>cm⁻¹</th>
<th>Exp.</th>
<th>Ref.</th>
<th>calc.</th>
<th>Approx. assignment</th>
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<tbody>
<tr>
<td>1007</td>
<td>1012</td>
<td>s</td>
<td>1019</td>
<td>CH bending; CS¹ str.</td>
</tr>
<tr>
<td>1022</td>
<td>1022</td>
<td>w</td>
<td>1039</td>
<td>CH deformation; CS² str.</td>
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<td>1276</td>
<td>m</td>
<td>1279</td>
<td>CH in-plane bending</td>
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<td>vs</td>
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<td>1551</td>
<td>w</td>
<td>1526</td>
<td>NCS² str.; CN str.</td>
</tr>
</tbody>
</table>

S¹ and S² indicate exo- and endo-S atoms in DBTA, respectively [Fig. 4.2(b)].

Table 4.3 shows the assignments of vibrational modes related to all CuMBTs. The IR absorbances of CuMBT(PVD) and CuMBT(I) are almost the same. Their vibrational frequencies also agree with the value in literature [17], and confirm the formation of CuMBT. For CuMBT(II), two additional strong peaks at 1429 cm⁻¹ and 1468 cm⁻¹ were present. These two peaks were found as characteristic peaks of DBTA (Table 4.2). It indicates that CuMBT(II) was the mixture of CuMBT and DBTA. Previously, the same result was obtained as well [1]. It was proposed that CuMBT only contains Cu⁺ ions. If Cu²⁺ salts were used, Cu²⁺ would reduce to Cu⁺ which would make the oxidation of MBT to DBTA occur. Therefore, a mixture of CuMBT and DBTA was obtained (Sec. 2.4).

The Raman spectra were also measured. However, for samples as powder [MBT, CuMBT(I) and CuMBT(II)], strong photoluminescence was shown and no data was obtained. For samples as thin layer [CuMBT(PVD) and DBTA], no related peak was observed. Therefore, the assignment of peaks in the Raman spectra...
would be based on previous literatures\cite{6,89}.

Table 4.3: characteristic IR absorbance of CuMBT

<table>
<thead>
<tr>
<th>Exp. (cm(^{-1}))</th>
<th>Ref. (cm(^{-1}))</th>
<th>Approx. assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVD I II</td>
<td>1  2  3</td>
<td></td>
</tr>
<tr>
<td>1011 1009 1009</td>
<td>994 w 1010 vs 1009 vs</td>
<td>C=S(^1) str.</td>
</tr>
<tr>
<td>1024 1022 1022</td>
<td>1025 m 1021 vs 1021 s</td>
<td>C=S(^1) str.</td>
</tr>
<tr>
<td>1080 1080 1080</td>
<td>1086 w 1080 w 1079 m</td>
<td>Bz ring bending; CH rock</td>
</tr>
<tr>
<td>1246 1244 1244</td>
<td>1249 w 1244 w 1244 m</td>
<td>Bz ring bending; CNS(^1) str.</td>
</tr>
<tr>
<td>1279 1276 1276</td>
<td>1279 vw 1279 vw 1280 w</td>
<td>C=C str.</td>
</tr>
<tr>
<td>1313 1313 1313</td>
<td>1316 w 1312 w 1313 m</td>
<td>C=C str.; CN str.; CH rock</td>
</tr>
<tr>
<td>1410 1408 1408</td>
<td>1398 s 1409 vs 1406 vs</td>
<td>NCS(^2) ring str.</td>
</tr>
<tr>
<td>1429</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1454 1454 1454</td>
<td>1452 m 1452 w 1452 m</td>
<td>Bz ring bending; CH rock</td>
</tr>
<tr>
<td>1468</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S\(^1\) and S\(^2\) indicate exo- and endo-S atoms in MBT molecules, respectively [Fig. 4.2(a)].

**XP spectra** XP spectra were used for further identification. The binding energy region of S 2p is shown in Fig. 4.3(a). For MBT, two peaks with binding energies 162.2 eV and 164.3 eV were observed. They are assigned to S\(^1\) (162.2 eV) and S\(^2\) atom (164.3 eV), respectively\cite{2,57}. For CuMBT(I), after MBT reacted with Cu salts, the binding energy of endo-S atom didn’t change a lot, however, the binding energy of the exo-S atom increased \(\approx 0.5\) eV to 162.7 eV. It indicates that exo-S atom was involved in CuMBT formation. The interaction with Cu decreased the electron density on exo-S atom due to the attraction of comparatively electronegative Cu atom which led to an increase of binding energy of exo S atoms. For CuMBT(II) and CuMBT(PVD), the same shifts were also observed. The shapes of
Chapter 4. Ex situ studies of CuMBT complexes as powders and thin film

the peaks for CuMBT(II) were different from the other two, because DBTA was included in its product. Therefore, this spectrum was not analyzed in detail.

Figure 4.3: XP spectra (a) S 2p and (b) N 1s of MBT powder and CuMBT from different preparations: CuMBT (PVD) = CuMBT prepared from an immersion of a Cu sample in 1 mM MBT / 0.1 M NaOH; CuMBT (I) = CuMBT synthesized from Cu$^+$ salt; CuMBT (II) = CuMBT synthesized from Cu$^{2+}$ salt.

In N 1s spectra [Fig. 4.3(b)], a shift of binding energy from 400.5 eV to 399.2 eV was also observed, showing that the N atom was also involved in CuMBT formation. However, different from exo-S atom, the binding energy of N atom had a 1.3 eV decrease. It is proposed that after MBT binding with Cu, the resonance between thiol form and thione form may corrupt. The failure of electron delocalization increased the electrondensity on N atom and led to a decrease of
binding energy. Besides, in the N 1s spectrum of CuMBT(II), which contained both CuMBT and DBTA, only one peak at 399.2 eV was detected. After DBTA formed, the resonance between thiol and thione forms can not take place because of the formation of disulfide bond [Fig. 4.2(b)], so the $\pi$ electrons on C=N bond can not be delocalized. Therefore, the electron density of N atom increased which led to a binding energy decrease.

Figure 4.4: XP spectra (a) Cu 2p and (b) Cu LMM of CuMBT from different preparations: CuMBT (I) = CuMBT synthesized from Cu$^+$ salt; CuMBT (II) = CuMBT synthesized from Cu$^{2+}$ salt; CuMBT (PVD) = CuMBT prepared from an immersion of a Cu sample in 1 mM MBT / 0.1 M NaOH; Cu = sputter-cleaned bare Cu.

Fig. 4.4(a) shows the binding energy region of Cu 2p. All the spectra have two peaks located at 932.6 eV and 952.5 eV, which belong to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$, respectively. It shows that Cu 2p doesn’t change after reacting with MBT. For Cu$^{2+}$ ion, there was no strong satellite peak observed at 943 eV. For Cu$^+$ ion, there was also no broad satellite peak observed at 945 eV. However, it is possible that
these satellite peaks were too weak and too broad to be detected.

To distinguish pure Cu, Cu$^+$ and Cu$^{2+}$, Cu LMM spectra were measured as well. Fig. 4.4(b) shows their Cu LMM spectra, only one peak at 915.7 eV was observed in all CuMBT related spectra. This peak is assigned to Cu$^+$ ion in CuMBT. In the spectrum of sputter-cleaned bare Cu, four peaks at 914.2, 916.2, 918.7 and 921.4 eV were observed. Assigned to pure Cu, these four peaks were not found in the spectra of CuMBT. It shows no pure Cu and Cu$^{2+}$, only Cu$^+$ ion was involved in CuMBT. It proves that even though Cu$^{2+}$ salts were used as starting material, no Cu$^{2+}$ product formed, or was not stable.

4.3 Time-dependent studies

4.3.1 The growth of CuMBT complex

Figure 4.5: Ex situ IR spectra of Cu samples immersed in 1 mM MBT / 0.1 M NaOH for 2 h, 8 h and 24 h respectively under Ar.

The external reflection IR spectra of Cu layers immersed in 1 mM MBT for 2 h,
4.3. Time-dependent studies

8 h and 24 h were measured [Fig. 4.5]. The characteristic peaks of the CuMBT layer at 1010 cm$^{-1}$, 1022 cm$^{-1}$, 1080 cm$^{-1}$, 1246 cm$^{-1}$ and 1408 cm$^{-1}$ were visible. The intensity of these peaks increased as immersion time increased. This increase can be attributed to either the growth or the change of orientation of CuMBT, which needs further investigation.

XP spectra were used to investigate the time effect. Cu samples were exposed to MBT for 2 h and 48 h, respectively. The spectra of Cu 2p, Cu LMM, N 1s and S 2p of two immersed Cu samples were shown in Fig. 4.6. Compared with Fig. 4.3 and Fig. 4.4, the formation of CuMBT on both 2 h and 48 h samples was confirmed.

![Figure 4.6: XP spectra of a Cu layer after immersed in 1 mM MBT / 0.1 M NaOH for 2 h and 48 h: (a) Cu 2p, (b) Cu LMM, (c) N 1s and (d) S 2p.](image)

Fig. 4.7 shows the AFM images of Cu layers after exposure to MBT for 2 h and 48 h, respectively. The characteristics of the Cu surface are listed in Table 4.4. As immersion time was longer, the average height became larger and the surface...
became rougher, showing that some substances formed on the Cu surface with Cu dissolution which led to an increase of average height and roughness.

The same experiment using PVD prepared Au layer as sample was performed as well. The Au layer was immersed in 1 mM MBT / 0.1 M NaOH for 40 h and then was investigated by AFM. In Fig. 4.8 and Table 4.4 it shows that after 40 h immersion, the height had a $\approx 0.9$ nm increase.

In previous literature, MBT molecules were found to adsorb to Au surface to form a AuMBT monolayer\textsuperscript{[91]}. Molecular dimensions of MBT were reported as length of $\approx 0.70$ nm and width of $\approx 0.50$ nm\textsuperscript{[91,92]}. After 40 h immersion, the average height was found to have an increase of 0.9 nm. This value agreed with the reported length, 0.70 nm. Therefore, the formation of a AuMBT monolayer on Au surface can be proposed. However, compared with Cu case, it had a 2 nm increase after 2 h immersion and the thickness reached to 20 nm after 48 h immersion.

Table 4.4: The characteristics of Cu / Au surfaces exposed to 1 mM MBT for different times. The parameters of AFM images were analyzed from Gwyddion. The minimum data values were shifted to zero.

<table>
<thead>
<tr>
<th>Immersion time</th>
<th>Average height</th>
<th>Maximum height</th>
<th>$R_{\text{ms}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu 0 h [Fig. 4.7(a)]</td>
<td>5.16 nm</td>
<td>13.05 nm</td>
<td>2.59 nm</td>
</tr>
<tr>
<td>2 h [Fig. 4.7(b)]</td>
<td>7.12 nm</td>
<td>16.72 nm</td>
<td>2.05 nm</td>
</tr>
<tr>
<td>48 h [Fig. 4.7(c)]</td>
<td>19.82 nm</td>
<td>53.38 nm</td>
<td>9.88 nm</td>
</tr>
<tr>
<td>Au 0 h [Fig. 4.8(a)]</td>
<td>3.05 nm</td>
<td>6.96 nm</td>
<td>1.06 nm</td>
</tr>
<tr>
<td>40 h [Fig. 4.8(b)]</td>
<td>3.97 nm</td>
<td>8.64 nm</td>
<td>1.21 nm</td>
</tr>
</tbody>
</table>
4.3. Time-dependent studies

Figure 4.7: AFM images of the Cu layer after immersion in 1 mM MBT / 0.1 M NaOH for different times: (a) 0 h, (b) 2 h and (c) 48 h under Ar.

Figure 4.8: AFM images of the Au layer, (a) before and (b) after immersion in 1 mM MBT / 0.1 M NaOH for 40 h under Ar.
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All the immersions were performed under Ar, therefore, this increase was not related to Cu oxide formation. Combined with the observation in IR spectra and XP spectra, it can be proposed that this time-dependent increase was resulted from the growth of CuMBT on the Cu surface. Besides, in XPS, there was no obvious shifts of peaks observed after immersion for longer time. It indicates that the elemental composition and chemical environment of CuMBT surface remained the same after the growth.

4.3.2 Internal structure of CuMBT layer

Angle resolved spectra were shown in Fig. 4.9 for 2 h immersion sample and in Fig. 4.10 for 48 h immersion sample. In this measurement, detection angles of 20°, 30°, 45°, 60°, 75° and 90° were used. In Cu 2p [Fig. 4.9(a) and Fig. 4.10(a)] and N 1s [Fig. 4.9(c) and Fig. 4.10(c)] spectra of both immersed samples, as the angle changed, there was no obvious difference.

In Cu LMM spectra, a shoulder at 918.6 eV gradually appeared with increasing detection angle. The kinetic energy at 918.6 eV was assigned to pure Cu [90]. With the largest 90° as detection angle, the information of the deepest part from surface can be detected, which makes it possible to detect the pure Cu layer under CuMBT complex. In the 2 h case [Fig. 4.9(b)], progress of the shoulder peak at 918.6 eV was clearly observed. However, in the 48 h case [Fig. 4.10(b)], although this peak was detected as well, it was less obvious than that in 2 h, showing that the pure Cu layer was in deeper part from the surface of 48 h sample. This result indicates a thicker CuMBT layer formed on the 48-hour-immersed Cu sample. It also agrees with the time-dependent growth of CuMBT observed in IR and AFM studies.

In both S 2p spectra [Fig. 4.9(d) and Fig. 4.10(d)], as detecting angle increased, the shoulder at ≈162.6 eV becomes more obvious. Assigned to exocyclic S atom, the increase of peak indicates exocyclic S atom is closer to the surface. It implies that MBT molecules may adsorb to Cu surface mostly via exo-S atom.

Depth profile spectra were applied to further investigation. With a sputtering energy of 1000 V applied for 1 min, CuMBT layers in both 2 h and 48 h case
4.3. Time-dependent studies

Figure 4.9: Angle resolved XP spectra of (a) Cu 2p, (b) Cu LMM, (c) N 1s and (d) S 2p analyzed at $\theta = 20, 30, 45, 60, 75$ and $90^\circ$. The Cu sample was treated with 1 mM MBT / 0.1 M NaOH for 2 h. As the angle increased, a shoulder peak gradually appeared in both (b) Cu LMM and (d) S 2p.

were completely depleted. To study different depths, the sputtering energy was lowered to 200 V and applied for 1 min each time. Based on the settings of the instrument, a depth of 3.27 nm was expected to be depleted under application of 200 V for 1 min. Nevertheless, the exact value differs from materials. For organics, the molecules may rearrange during measurement. Therefore, the real depth of the CuMBT layer was not studied here. With the same depleted material, only the comparison of two samples was discussed.

Fig. 4.11 and Fig. 4.12 show the result of XP depth-profiling measurement of CuMBT layer formed from immersion in 1 mM MBT solution for 2 h and 48 h, respectively. The intensities of Cu LMM spectra have been vertically offset for clarity, and to compare the evolution of peaks.

In Cu LMM spectra, as the depth became deeper, the evolution of the peak at 918.5 eV was shown in 2 h case [Fig. 4.11(a)]. Assigned to pure Cu, this peak was detected due to the approach to pure Cu surface. However, in 48 h case
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Figure 4.10: Angle resolved XP spectra of (a) Cu 2p, (b) Cu LMM, (c) N 1s and (d) S 2p analyzed at θ = 20, 30, 45, 60, 75 and 90°. The Cu sample was treated with 1 mM MBT / 0.1 M NaOH for 48 h. As the angle increased, a shoulder peak gradually appeared in both (b) Cu LMM and (d) S 2p.

[Fig. 4.12(a)], different from 2 h case, the progress of shoulder peak at 918.5 eV was not seen obviously. With thicker CuMBT layer on the surface, the Cu sample immersed in solution for 48 h still have large amount of CuMBT remained on the surface after three sputtering cycles. Therefore, pure Cu was not detected.

In both Cu 2p spectra [Fig. 4.11(b) and Fig. 4.12(b)], the intensity of peaks increased as depth. It indicates gradual depletion of CuMBT layer and pure Cu surface was gradually exposed.

In N 1s spectra [Fig. 4.11(c) and Fig. 4.12(c)], the intensity of the peak decreased with depth due to the gradual depletion of the CuMBT layer. After the third sputtering, the signal of N 1s almost disappeared in the 2 h case [Fig. 4.11(c)] . In addition, a peak shift from 399.3 eV to 398.7 V was observed after the first sputtering. The peak at 397 eV is close to the binding energy of N 1s for metal nitrides \[90\]. As approaching to copper surface, it is proposed that the nitrogen atom was affected by the copper surface more and a nitride-like bonding formed
Figure 4.11: XP spectra of (a) Cu LMM, (b) Cu 2p, (c) N 1s and (d) S 2p before and after 1st, 2nd and 3rd sputtering. The sputtering energy was 200 V with sputtering time of 1 min. The Cu sample was treated with 1 mM MBT / 0.1 M NaOH for 2 h.

in between which made the binding energy lower. In the 48 h case [Fig. 4.12(c)], both the decrease of intensity and the shift of peak were detected. Due to thicker complex layer on the surface, the N 1s peak was still shown after the third sputtering. Besides, the transition of two peaks was observed. Both the peaks at 399.3 eV and 398.7 V were detected after the first sputtering.

In both S 2p spectra [Fig. 4.11(d) and Fig. 4.12(d)], a shift of peaks was detected. The peak at 164.2 eV shifted to 163.8 eV and the peak at 162.6 eV shifted to 162.1 eV. This decrease can be attributed to the influence from Cu surface as well. The reported binding energy of the metal sulfide is $\approx 161.5$ eV\textsuperscript{90}. Like the case in nitrogen, a sulfide-like bonding may lead to an increase of electron density of sulfur atom which lowers its binding energy.

Besides, the proportion of intensity of exo-S and endo-S atom changed with depth. In Table\textsuperscript{4.5} as closer to Cu surface, the relative intensity of exo-S atom was much larger than that of endo-S atom. It indicates that exo-S atom mostly involved
Figure 4.12: XP spectra of (a) Cu LMM, (b) Cu 2p, (c) N 1s and (d) S 2p before and after 1st, 2nd and 3rd sputtering. The sputtering energy was 200 V with sputtering time of 1 min. The Cu sample was treated with 1 mM MBT / 0.1 M NaOH for 48 h.

in the adsorption to Cu surface, which also agrees with the result obtained in angle resolved measurements.

Table 4.5: The ratio of intensity of exo-/endo-S atom

<table>
<thead>
<tr>
<th>Immersion time</th>
<th>Before sputtering</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 h</td>
<td>0.94 ± 0.01</td>
<td>4.02 ± 0.18</td>
<td>8.80 ± 0.46</td>
<td>13.94 ± 1.36</td>
</tr>
<tr>
<td>48 h</td>
<td>1.02 ± 0.11</td>
<td>2.41 ± 0.03</td>
<td>3.64 ± 0.24</td>
<td>4.86 ± 0.48</td>
</tr>
</tbody>
</table>

1st, 2nd and 3rd indicate after 1st, 2nd and 3rd sputtering.

4.4 Summary

MBT powder, DBTA films, CuMBT complex powders and a CuMBT complex layer on Cu were prepared and charaterized ex situ by IR and XP spectroscopy. In
agreement with previous studies\cite{42,157}, only complexes including Cu$^+$ ions were observed. If Cu$^{2+}$ salts were used as starting materials, no Cu$^{2+}$ complex was obtained, however, the formation of an oxidation product of MBT, DBTA, was observed. Comparing XP spectra of the complex to the one of MBT shows that after the complex formed, the N 1s peak shifted to lower binding energy. However, in S 2p spectra, only binding energy of exo-S atom was affected and shifted to higher value, while the binding energy of endo-S atom remained the same.

The influence of immersion time at open circuit in preparing CuMBT layer was also studied. In IR spectra, CuMBT complex was found to grow as a function of time. In AFM images, an increase of average height and roughness were observed at the same time. In the XP spectra, the Cu sample with longer immersion showed a higher complex layer thickness on the surface, both when using angle dependent XPS as well as with depth profiling. The increasing proportion of the peak assigned to the exo-S atom as angle and depth increased shows that the exo-S atoms were closer to Cu surface than the endo-S atom. Shifts to lower binding energies were observed in N 1s spectra and S 2p spectra at lower depths.

These observations indicate that both exo-S and N atom of MBT molecule are participating in the adsorption to the Cu surface. In addition, the chemical environment closer to the Cu surface must be different. These differences can either result from the influence of the Cu surface on the spectra, or from structural difference between adsorbed MBT and CuMBT complex inside the thin film.
Chapter 4. Ex situ studies of CuMBT complexes as powders and thin film
The formation and growth of a CuMBT layer on a Cu surface*

5.1 Introduction

As discussed in chapter 4, a time-dependent growth of CuMBT was observed. In this chapter, this growth was further studied in situ by IR spectroscopy. Besides, results from in situ Raman and in situ ellipsometric spectroscopy were combined to investigate the adsorption mechanism of MBT on the Cu surface. The in situ experiments were conducted in 1 mM MBT / 0.1 M NaOH.

5.2 Time-dependent growth of CuMBT layer

Fig. 5.1 shows time-lapse IR spectra recorded at open circuit potential (Sec. 3.4). As immersion time increased, a baseline shift was observed. Besides, an increase of negative absorbance at 3300 cm\(^{-1}\) and appearance of peaks in the region between 900 cm\(^{-1}\) to 1800 cm\(^{-1}\) were detected, indicating an interfacial change.

Fig. 5.2 shows enlarged time-lapse IR spectra of Fig. 5.1 to explore the interaction between Cu and MBT. In Fig. 5.2(b), the peaks at 1009 cm\(^{-1}\), 1032 cm\(^{-1}\), 1200 cm\(^{-1}\), 1385 cm\(^{-1}\) and 1454 cm\(^{-1}\) were detected. The absorbance of these peaks

increased as immersion time increased. Four peaks at 1009 cm$^{-1}$, 1032 cm$^{-1}$, 1385 cm$^{-1}$ and 1454 cm$^{-1}$ appeared, assigned to characteristic peaks of CuMBT (Sec. 4.2), indicating a time-dependent growth of CuMBT. A broad peak which centered at 1200 cm$^{-1}$ was detected as well. However, no appropriate assignment related to MBT, CuMBT, Cu or water was found for this peak. It may result from
5.2. Time-dependent growth of CuMBT layer

Figure 5.2: Partially enlarged time-dependent ATR-IR spectra of Fig. 5.1 in a region of 900 cm\(^{-1}\) to 1800 cm\(^{-1}\). (a) Large time scale from 60 min to 375 min; (b) small time scale from 6 min to 18 min.
Chapter 5. The formation and growth of a CuMBT layer on a Cu surface*

the solution used in chemical deposition (Sec. 3.2.2), which still remained on the Cu surface.

As the immersion time became longer, the absorbance continuously increased and indicated a progressive formation of CuMBT layer. In addition, progressive negative absorbance was detected at \( \approx 1640 \text{ cm}^{-1} \) and \( 3300 \text{ cm}^{-1} \), which are assigned to the bending mode\(^{80,81}\) and stretching mode of water molecules\(^{93}\), respectively. It indicates a decrease of water molecules at the interface. This observation agreed with the growth of the CuMBT layer as well. Because of the formation of CuMBT layer, water molecules were pushed away from the Cu surface and it led to a decrease of absorbance of water. In Fig. 5.2(a), at 220 min, new peaks at \( 1078 \text{ cm}^{-1} \), \( 1244 \text{ cm}^{-1} \), and \( 1319 \text{ cm}^{-1} \), assigned to CuMBT (Table 4.1), appeared. Besides, the absorbance of water became more negative. All of the observations indicated the continuous growth of CuMBT.

Figure 5.3: Partially enlarged time-dependent ATR-IR spectra of Fig. 5.1 (a) Peaks in the region of \( 1000 \text{ cm}^{-1} - 1050 \text{ cm}^{-1} \) from 60 min to 375 min; (b) Peaks in the region around \( 1400 \text{ cm}^{-1} \) from 6 min to 375 min.

Moreover, shifts of two peaks were observed. The peak originally at \( 1032 \text{ cm}^{-1} \) at 60 min shifted to \( 1022 \text{ cm}^{-1} \) at 375 min [Fig. 5.3(a)] and the peak originally
5.2. Time-dependent growth of CuMBT layer

at 1385 cm\(^{-1}\) at 14 min shifted to 1404 cm\(^{-1}\) at the end [Fig. 5.3(b)]. Based on
the identification in Sec. 4.2, 1022 cm\(^{-1}\) and 1404 cm\(^{-1}\) are assigned to CuMBT.
1032 cm\(^{-1}\) can be assigned to MBT. There was no appropriate assignment found
for 1385 cm\(^{-1}\). However, in previous Raman studies\(^6\), this peak was found varying from 1379 cm\(^{-1}\) to 1405 cm\(^{-1}\). Therefore, it can be assigned to CuMBT as well.

This shift shows that there are some differences between initial and final product. The final product at 375 min is more like the CuMBT obtained in Sec. 4.2.

The shift can be ascribed to both the growth and structural transition of CuMBT layer. When MBT adsorbed on the Cu surface, the first layer which was bound
directly to the Cu surface may be affected by Cu surface and lead to a shift of peak (1022 cm\(^{-1}\) to 1032 cm\(^{-1}\)). The subsequent layers which were not bound
to Cu surface were not affected, so that their peaks were not shifted. Therefore, as CuMBT layer became thicker, a gradual shift of the peak at 1032 cm\(^{-1}\) to
1022 cm\(^{-1}\) was observed.

As for structural transition, the peak at 1032 cm\(^{-1}\) is assigned to C=S thione
stretching of MBT molecules (Sec. 4.2). It is proposed that in Fig. 5.2(b) not a
CuMBT but an intermediate has formed. Therefore, both characteristic peaks of
MBT (1032 cm\(^{-1}\)) and CuMBT (1385 cm\(^{-1}\)) showed at the same time. As time
went on, the formation of CuMBT completed. Therefore, the characteristic peak
of MBT at 1032 cm\(^{-1}\) disappeared, followed by the appearance of CuMBT charac-
teristic peak at 1022 cm\(^{-1}\). Besides, the peak at 1385 cm\(^{-1}\) shifted to 1404 cm\(^{-1}\) as well.

In addition, it was observed that the absorbance increase of the peaks at 1009 cm\(^{-1}\)
and 1022 cm\(^{-1}\) did not proceed in the same manner (Fig. 5.3(a)). Initially, both
peaks had approximately the same absorbance, however, in the course of the ex-
periment, the 1009 cm\(^{-1}\) peak significantly gained in absorbance. At the end,
absorbance at 1009 cm\(^{-1}\), characteristic for the thiol form, was higher than that at
1022 cm\(^{-1}\), characteristic for the thione form (Sec. 4.2). Based on this observation,
we infer that the thiol form is dominant in the formed CuMBT layer. However, the
thione form is also present. It also implies that there was a structural transition during the establishment of CuMBT layer.

5.3 Formation of a CuMBT film

In this section, adsorption of MBT to a reduced, oxide free Cu surface at negative potential was investigated. The formation of a CuMBT film was further studied at controlled electrode potential by in situ Raman and ellipsometric spectroscopy. Ellipsometric data in Fig. 5.4 shows that after -1.0 V was applied, a rapid decrease in thickness was detected due to a reduction of the copper oxide. After reduction for \( \approx 10 \) min, MBT was introduced into the cell at time = 0 in Fig. 5.4, and a gradual increase of thickness to 1 nm was observed. It indicated the formation of a CuMBT layer on the Cu surface. Thickness stopped to increase \( \approx 7 \) min after introduction of MBT, and started to decrease, implying a structural change at the metal / solution interface. The thickness continued decreasing as time increased, and it reached \( \approx 0.5 \) nm after \( \approx 20 \) min, then the thickness remained at 0.5 nm until the end.

Fig. 5.5 shows the related in situ Raman spectra. Immediately after MBT addition, two peaks at 1244 cm\(^{-1}\) and 1382 cm\(^{-1}\) were observed, both of which were assigned to CuMBT \(^{[6,89]}\), indicating the formation of a CuMBT film. At the second minute, a peak at 1071 cm\(^{-1}\) started to be observed, assigned to an asymmetric stretching of both benzene and NCS ring \(^{[6,89]}\). As time increased, the intensity of the peaks at 1244 cm\(^{-1}\) and 1382 cm\(^{-1}\) didn’t change significantly. Nevertheless, the peak at 1071 cm\(^{-1}\) grew with time.

Based on the intensity increase of the peak at 1071 cm\(^{-1}\) and the observed decrease in layer thickness, we propose a reorientation at the metal / solution interface. MBT molecules are proposed to adsorb initially on the Cu surface vertically with the exo-S atom (Fig. 5.6 left). In later stages, as precursor for the formation of a CuMBT film, MBT changes its orientation as illustrated (Fig. 5.6 right), such that both N and exo-S atoms were in contact with the Cu surface.
5.3. Formation of a CuMBT film

Figure 5.4: Thickness of interfacial layer from ellipsometry in 0.1 M NaOH and 1 mM MBT / 0.1 M NaOH. The electrode potential was constantly at -1.0 V during the whole process. Time was set to 0 at injection of MBT.

Such an interpretation is in agreement to the structure reported from ex situ XP spectra, in which N and exo-S atoms were involved in the formation of the CuMBT layer [Sec. 4.2 and Fig. 4.3(b)]. This reorientation leads to the decrease of interfacial thickness at constant potential. Molecular dimensions of MBT were reported as length of ≈0.70 nm and width of 0.50 nm \cite{91,92}. It agreed with our observation of interfacial thickness, which was initially 1 nm and reached 0.5 nm at the end.

In addition, we observed a shift of the peak initially at 1382 cm$^{-1}$ to 1387 cm$^{-1}$. Similar shift was observed previously \cite{6}. In their case \cite{6}, a peak at 1379 cm$^{-1}$, proposed from surface CuMBT complex, was detected in buffer solution of pH 9.2 at -0.7 V and then shifted to 1383 cm$^{-1}$ at -0.5 V. The shift in the aforementioned Raman peak with time indicated a change in the interaction between the copper surface and MBT, which further supports our hypothesis of reorientation. In Sec. 5.2, this shift was also observed in time dependent in situ IR measurement. In Fig. 5.3(b), the peak originally at 1385 cm$^{-1}$ shifted to 1404 cm$^{-1}$ after MBT solution was introduced for 1 h. In Sec. 5.2, we related the shift to the structural
Chapter 5. The formation and growth of a CuMBT layer on a Cu surface

Figure 5.5: Time dependent in situ Raman spectra for Cu in 1 mM MBT / 0.1 M NaOH at -1.0 V. The spectrum at OCP was collected before reduction and spectrum labelled “Reduction” was recorded before introducing MBT. Times refer to the time after introduction of MBT.

Figure 5.6: Proposed mechanism of MBT adsorption on Cu under reducing conditions in NaOH.

change of CuMBT layer. Combined with the observation in both ellipsometric and Raman data here, the structural change observed in situ IR spectra can further be attributed to reorientation of MBT molecules at the metal / solution interface.

In addition, in ex situ Raman data, the peak at 1387 cm$^{-1}$ was found at 1405 cm$^{-1}$ of a synthesized CuMBT in solid state\textsuperscript{[6]}. This red shift was also found in the work of Woods et al.\textsuperscript{[6]}. It can be attributed to the influence of Cu surface. The interfacial thickness indicates that only a monolayer film formed on the sur-
face. Bound to a Cu surface, the electron density in the MBT ring would reduce due to the attraction of comparatively electron-deficient Cu atoms\(^6\). Therefore, it led to the reduction of the double bond character of NCS ring, and resulted in the shift to lower wavenumber of NCS ring stretching peak\(^6\).

It was shown that this monolayer film didn’t grow with time under reducing conditions. Unlike in situ IR spectroscopy which was monitored at open circuit potential, Raman and ellipsometry measurement were performed at -1.0 V. This electrode potential was too low for Cu dissolution to occur hence to permit multilayer formation of CuMBT. In previous studies, based on post mortem analysis, formation of a Cu\(_2\)O layer on Cu was suggested to be crucial to the subsequent formation of CuMBT complexes\(^2\,^5\,^9\,^6\,^2\). In this case, we expect most of the oxide to be removed after 10 min polarization at -1.0 V. Moreover, there was no Cu\(_2\)O related peak detected in the in situ Raman spectra. Consequently, from the in situ data gathered here, there is no evidence that Cu\(_2\)O is essential for CuMBT complex formation. However, it is still possible that fractions of the oxide were not removed, and were not detected in Raman spectra.

### 5.4 Summary

The interaction between Cu and MBT was studied by in situ time-dependent ATR-IR spectroscopy at open circuit potential and in situ Raman and ellipsometric spectroscopy at controlled electrode potential.

MBT molecules firstly adsorbed on the Cu surface as initial step as shown in Fig. 5.7. As time went on, this intermediate rearranged and a CuMBT monolayer formed. This rearrangement of the first adsorbed layer was found under controlled potential as a reorientation of the MBT molecules at the metal / solution interface. Based on the increase of the peak at 1071 cm\(^{-1}\) in Raman spectra and the decrease of thickness analyzed from ellipsometric spectra, it is proposed that MBT molecules initially vertically adsorbed on the Cu surface only with exocyclic S atom. They later reorientated and attached to the surface obliquely with both exo-
Figure 5.7: Proposed mechanism of the formation and growth of CuMBT complex on Cu surface in 1 mM MBT / 0.1 M NaOH. Under controlled potential, MBT molecules attached to Cu surface via exo-S atom vertically, and then reoriented to attach to the Cu surface via both exo-S and N atoms. At open circuit potential, a time-dependent growth of CuMBT layer took place.

cyclic S atom and N atom. In addition, CuMBT layer was found to grow with time at open circuit potential, in which the thiol form of MBT is dominant in complex layer.
6 Inhibition of Cu oxide formation

6.1 Introduction

As a corrosion inhibitor to copper, the inhibition of Cu oxide formation of MBT was investigated in this chapter. Non destructive in situ IR, Raman and ellipsometric spectroscopies were used to observe oxide formation after exposure to MBT. In previous work, in situ ellipsometric spectroscopy was used to investigate the interaction of BTA with Cu[94], and inhibition of BTA to Cu corrosion[95,96]. Nevertheless, there is no MBT related studies so far. In this chapter, the interaction between Cu and MBT was studied under controlled electrode potential. Experiments were also performed in 0.1 M NaOH as reference. All the experiments were performed under Ar.

6.2 Potential-dependent in situ IR spectra

In this section, the interaction between Cu and MBT was studied by in situ IR spectroscopy. Initially, three reference experiments were described: The interactions of the ATR crystal material Ge with NaOH (Sec.6.2.1) and MBT in NaOH (Sec.6.2.2) were studied. Furthermore, the interaction of Cu with NaOH was investigated (Sec.6.2.3), before proceeding to a study of the full system, Cu with MBT in NaOH (Sec.6.2.4).
6.2.1 Ge in NaOH

In the first experiment, ATR Ge crystal was used as working electrode with 0.1 M NaOH as electrolyte. Fig. 6.1 showed the related in situ IR spectra recorded at different electrode potentials. In previous studies, it was shown that as potential decreased, the Ge surface gradually changes from OH terminated to H-terminated, and vice versa. The more hydrophilic Ge surface led to an increase of absorbance of water at the interface. In Fig. 6.1(a), this trend was observed. As the potential increased, the absorbance of a broad peak centered at 1650 cm\(^{-1}\) increased, assigned to the OH\(_2\) bending mode of water\[^93\]. An increase of absorbance of a broad peak from 3000 to 3500 cm\(^{-1}\) was also observed. Due to total absorption in the region of 3200 to 3400 cm\(^{-1}\), the peak can not be identified. Nevertheless, this region is related to an OH stretching mode of water\[^93\]. Both observations indicate an increase of water molecules at the Ge / electrolyte interface.

![Figure 6.1: IR spectra recorded at different electrode potentials for Ge in 0.1 M NaOH in Ar in direction of (a) increasing and (b) decreasing potential. The reference spectrum was taken at open circuit potential before polarization. Corresponding j are displayed in Fig. 6.3.](image)

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Figure 6.2: Enlarged IR spectra of Fig. 6.1 with a region of 900–1900 cm$^{-1}$ in direction of (a) increasing and (b) decreasing potential. The reference spectrum was taken at open circuit potential before polarization. Corresponding $j$ are displayed in Fig. 6.3.

Figure 6.3: Current density $j$ of Ge as function of applied electrode potential in 0.1 M NaOH acquired during IR measurement (Fig. 6.1 / 6.2).

In addition, a progressive negative absorbance at 1084 cm$^{-1}$ was observed as well. However, no appropriate assignment was found. Besides, this peak is not
important in the scope of this work, as focus is on CuMBT. It is possibly related
to product formed when Ge reacted with basic media at high potential. After the
experiment finished, white substances and scratchs were found on the Ge surface.

Fig. 6.3 shows the current density detected during in situ IR measurement. In
anodic direction, from -1.0 V to -0.6 V, the current density was zero. At -0.4 V,
a current density of 10 $\mu$A cm$^{-2}$ was detected. It agrees with in situ IR spectra,
in which the changes of absorbance at 1084 cm$^{-1}$ and 1650 cm$^{-1}$ were observed
from -0.4 V as well.

### 6.2.2 Ge in MBT

In the second reference experiment, an ATR Ge crystal was still used as working
electrode while 1 mM MBT / 0.1 M NaOH was used as electrolyte. In Fig. 6.4,
the increases of absorbance at 1650 cm$^{-1}$ and 3300 cm$^{-1}$ were observed. This
pattern was observed in Sec. 6.2.1 as well, indicating an increase of absorbance
of water at the Ge / electrolyte interface. However, no peak at 1084 cm$^{-1}$ was
observed. It is proposed that slightly acidic MBT molecules reduced the basicity
of solution and hindered the reaction of Ge in basic media. There was also no
residue found on the Ge surface after the experiment. Moreover, in Fig. 6.5, no
MBT related peaks can be identified. It can be attributed to low concentration of
MBT solution. Besides, no interaction of MBT with Ge was detected. In that way,
it can be ignored in the interpretation of the spectra of Cu in MBT.

Fig. 6.6 shows the current density detected during in situ IR measurement. The
trend is the same as Fig. 6.3.
6.2. Potential-dependent in situ IR spectra

Figure 6.4: IR spectra recorded at different electrode potentials for Ge in 1 mM MBT / 0.1 M NaOH in Ar in direction of (a) increasing and (b) decreasing potential. The reference spectrum was taken at open circuit potential before polarization. Corresponding $j$ are displayed in Fig. 6.6.

Figure 6.5: Enlarged IR spectra of Fig. 6.4 with a region of 900–1900 cm$^{-1}$ in direction of (a) increasing and (b) decreasing potential. The reference spectrum was taken at open circuit potential before polarization. Corresponding $j$ are displayed in Fig. 6.6.
Chapter 6. Inhibition of Cu oxide formation

6.2.3 Cu in NaOH

In the last reference experiment, ATR Ge crystal with Cu layer prepared from chemical deposition (Sec. 3.2.2) was used as working electrode and 0.1 M NaOH was used as electrolyte. In Fig. 6.7(a), a baseline shift was observed, implying that the condition of Cu surface was different from the one at the beginning.

In Fig. 6.9(a), as electrode potential increased, different from previous two reference experiments in Sec. 6.2.1 and Sec. 6.2.2, the absorbance of a peak at 1640 cm$^{-1}$ related to OH$_2$ bending mode decreased. This decrease can be attributed to the formation of Cu oxide on the surface. The Cu oxide occupied on the surface indirectly pushed electrolyte away from ATR crystal which made the absorbance of water become negative. In Fig. 6.9(b), as electrode potential decreased, there was no obvious change in IR spectra. In all spectra, there were small peaks observed in the region of 1000 to 1500 cm$^{-1}$. These absorbances may resulted from the residue of solution used in chemical deposition.

Fig. 6.10 shows the current density detected during in situ IR measurement. Different from previous two experiments, when the same electrode potential (> 0 V) was applied, the current density measured during anodic direction was al-
6.2. Potential-dependent in situ IR spectra

Figure 6.7: Non-offset IR spectra recorded at different electrode potentials for Cu in 0.1 M NaOH in Ar in direction of (a) increasing and (b) decreasing potential. The reference spectrum was taken at open circuit potential before polarization. Corresponding $j$ are displayed in Fig. 6.10.

Figure 6.8: Offset IR spectra of Fig. 6.7 recorded at different electrode potentials for Cu in 0.1 M NaOH in Ar in direction of (a) increasing and (b) decreasing potential. The reference spectrum was taken at open circuit potential before polarization. Corresponding $j$ are displayed in Fig. 6.10.
Figure 6.9: Enlarged IR spectra of Fig. 6.8 with a region of 900–1900 cm\(^{-1}\) in direction of (a) increasing and (b) decreasing potential. The reference spectrum was taken at open circuit potential before polarization. Corresponding \( j \) are displayed in Fig. 6.10.

Figure 6.10: Current density of Cu as function of applied electrode potential in 0.1 M NaOH acquired during IR measurement (Fig. 6.7 / 6.8 / 6.9).

ways larger than the one measured during cathodic direction. This observation can be attributed to the formation of Cu oxide postulated in IR experiment. Cu oxide formed on the surface during anodic direction and the conductivity of Cu
6.2 Potential-dependent in situ IR spectra

surface was affected. Therefore, different current density was detected when the same electrode potential was applied during cathodic direction.

6.2.4 Cu in MBT

In this experiment, the interaction between Cu and MBT was studied. In Fig. 6.11(a), a baseline shift was observed, implying a change of the Cu surface. Fig. 6.13(a) showed that from -0.2 V, negative absorbances were detected at 1009 cm$^{-1}$, 1076 cm$^{-1}$, 1238 cm$^{-1}$, 1396 cm$^{-1}$ and 1450 cm$^{-1}$, assigned to characteristic peaks of CuMBT complex (Sec. 4.2). In addition, a negative absorbance at 1640 cm$^{-1}$ related to the OH$_2$ bending mode was observed as well.

Figure 6.11: Non-offset IR spectra recorded at different electrode potentials for Cu in 1 mM / 0.1 M NaOH in Ar in direction of (a) increasing and (b) decreasing potential. The reference spectrum was taken at open circuit potential before polarization. Corresponding $j$ are displayed in Fig. 6.14.

Negative absorbance can mean either a decrease of the amount or a reorientation of molecules on the surface. However, in this series of spectra, all the characteristic peaks decreased in the same manner. Therefore, the negative absorbance
Figure 6.12: Offset IR spectra of Fig. 6.11 recorded at different electrode potentials for Cu in 1 mM / 0.1 M NaOH in Ar in direction of (a) increasing and (b) decreasing potential. The reference spectrum was taken at open circuit potential before polarization. Corresponding \( j \) are displayed in Fig. 6.14.

most likely resulted from a decrease of amount of substance on the surface. It is proposed that as potential increased to -0.2 V, the dissolution of Cu surface caused the linkage between Cu surface and CuMBT layer break. Therefore, the complex layer desorbed from the surface and it led to a decrease of absorbance. The electrolyte above the complex was pushed away as well. Therefore, negative absorbance at 1640 cm\(^{-1}\) was observed. As the electrode potential continued to increase, the absorbance related to CuMBT decreased more. Conversely, the absorbance of water peak increased. It is proposed that at higher potential, as the dissolution of Cu surface continuously took place. The electrolyte between CuMBT layer and Cu surface become more which led to an increase of water absorbance.

In Fig. 6.13(b) as the electrode potential decreased, there was no obvious change on water peak and most of CuMBT peaks. Because the space was already occupied by electrolyte, it was impossible for the complex layer to approach the surface again, so absorbances of both water and complex remained the same.
6.2. Potential-dependent in situ IR spectra

Figure 6.13: Enlarged IR spectra of Fig. 6.12 with a region of 900–1900 cm\(^{-1}\) in direction of (a) increasing and (b) decreasing potential. The reference spectrum was taken at open circuit potential before polarization. Corresponding \(j\) are displayed in Fig. 6.14.

Figure 6.14: Current density of Cu as function of applied electrode potential in 1 mM MBT / 0.1 M NaOH acquired during IR measurement (Fig. 6.11 / 6.12 / 6.13).
However, the changes of absorbance at 1009 cm\(^{-1}\) and 1022 cm\(^{-1}\) were observed. The two peaks are assigned to characteristic peak of thiol form and thione form of CuMBT complex, respectively (Sec. 4.2). In Fig. 6.13(a), at -0.2 V, a negative absorbance at 1009 cm\(^{-1}\) was first observed. However, as potential increased and as potential decreased in Fig. 6.13(b), this negative absorbance gradually disappeared. When back to -1.0 V, the negative absorbance at 1009 cm\(^{-1}\) almost disappeared. Conversely, the absorbance at 1022 cm\(^{-1}\) consistently decreased, and reached the most negative value at the end.

It is proposed that MBT molecules used thiol form to adsorb on Cu surface in Sec. 5.2. Therefore, as the layer desorbed, the decrease of absorbance at 1009 cm\(^{-1}\) was shown at the beginning. However, in the following process, a continuous increase of absorbance at 1009 cm\(^{-1}\) and a continuous decrease of absorbance at 1022 cm\(^{-1}\) were observed. In Sec. 5.2, the same trend was shown as well, which was attributed to a structural transition during the formation of a CuMBT layer. Therefore, the change here also ascribes to the same reason. During the whole process, not only the interaction between Cu, CuMBT complex layer and electrolye happened, but also the internal rearrangement of layer occurred simultaneously.

Fig. 6.14 shows the current density measured during in situ IR measurement. The current density remained unchanged in both anodic and cathodic direction, implying no oxide formed during the whole process under protection of CuMBT layer. This statement can also be supported by IR spectra. Although it is hard to observe oxide related peaks directly in IR spectra. However, from the increase of water peak in anodic reaction and invariant absorbance in the subsequent cathodic reaction, it can be proposed there should be almost no oxide formed during whole process. Further studies on inhibition of oxide formation were shown in next section.
6.3 Oxide formation and inhibition observed by in situ ellipsometric and Raman spectroscopy

6.3.1 The formation of Cu oxide in 0.1 M NaOH

Oxide formation on Cu in the absence of MBT was initially investigated as reference. Fig. 6.15 shows the CV and corresponding thickness change obtained from analysing ellipsometric spectra. In the CV, three anodic peaks and three cathodic peaks were observed. The anodic peaks at -0.4 V and 0.0 V were attributed to the formation of Cu$_2$O and CuO, respectively. During the anodic reaction, two steps with increase of thickness were observed. The first thickness increase started at -0.4 V, and reached 9 nm at -0.2 V. The second increase started at -0.1 V, and reached 16 nm at +0.1 V. Above +0.1 V, there was no obvious thickness increase, and the thickness remained at $\approx$16 nm. The two stages of thickness increase agreed in potential to anodic peaks observed in the CV, refering to the formation of Cu oxide. In the cathodic reaction, the cathodic peaks at -0.4 V and -0.9 V were assigned to the reduction of CuO and Cu$_2$O, respectively. However, there was no obvious decrease in thickness at -0.4 V. As the electrode potential reached -0.8 V that the thickness started to decrease, and it reached 2 nm at -1.0 V. Surface roughening during anodic and cathodic process may lead to an apparent thickness larger than 0.

In Raman spectra in the absence of MBT [Fig. 6.16(a)], at -1.0 V, only the water peak at 1640 cm$^{-1}$ was observed. When the electrode potential reached 0.0 V in the experiments with increasing potential, a peak at 523 cm$^{-1}$ appeared, which was assigned to the $A_{1g}$ mode of Cu$_4$O$_3$ , implying the formation of copper oxide. The appearance of this peak was consistent with the thickness increase.

*This section contains results submitted as a scientific article: Y.-H. Chen et al. The multiple roles of an organic corrosion inhibitor on copper investigated by a combination of electrochemistry-coupled optical in situ spectroscopies. Corrosion Science, submitted
Figure 6.15: CV of evaporated Cu layer in 0.1 M NaOH during ellipsometric experiment and corresponding thickness of interfacial layer as function of applied electrode potential. Scan rate: 1 mV / s.

Figure 6.16: Raman spectra recorded during CV for Cu in 0.1 M NaOH in direction of (a) increasing and (b) decreasing potential. The CV was similar to the one obtained in ellipsometric experiment which was displayed in Fig. 6.15.
6.3. Oxide formation and inhibition observed by in situ ellipsometric and Raman spectroscopy

observed at 0.0 V. However, at -0.4 V, the position of the first anodic peak, there was no obvious change in spectra. We didn’t observe CuO and Cu$_2$O related peaks in any Raman spectra. It is possible that amorphous oxide was formed, so that the peaks were too broad to be observed. With increasing electrode potential, both water and Cu$_4$O$_3$ peaks decreased. The decrease of water peak can be attributed to oxide formation on the surface. The decrease of Cu$_4$O$_3$ peak is interpreted as transformation of Cu$_4$O$_3$ to other copper oxides, presumably CuO, at higher electrode potential. (Alternatively, soluble Cu$^{2+}$ species may also form.) During the negative scan [Fig. 6.16(b)], the peak at 523 cm$^{-1}$ increased, implying the reformation of Cu$_4$O$_3$. A very strong increase at 700 cm$^{-1}$ was observed when the electrode potential reached -0.8 V. Peaks in this range have been assigned to Cu$-$OH species formed after reduction.

6.3.2 The inhibition of Cu oxide formation in 1 mM MBT / 0.1 M NaOH

Fig. 6.17 shows the CV and corresponding thickness change obtained from analysing ellipsometric spectra in the presence of MBT. Compared with the NaOH case, both peak current density and thickness were significantly lower, showing that Cu oxidation was effectively inhibited by the presence of MBT. The CV showed only one anodic peak at +0.21 V, while two cathodic peaks at -0.38 V and -0.9 V were detected. The initial thickness was 0.5 nm, which can be attributed to the formation of a CuMBT surface layer. As the electrode potential increased, the thickness increased. Layer thickness also increased in two stages, smeared out over a large potential range. The first stage started at -0.6 V, and reached 3 nm at +0.2 V. The second stage started at +0.2 V and reached 10 nm at the end of the anodic process. The thickness continued to increase until +0.4 V after reversing the scan direction before it started to decrease.
Chapter 6. Inhibition of Cu oxide formation

Figure 6.17: CV of evaporated Cu layer in 1 mM MBT / 0.1 M NaOH during ellipsometric experiment and corresponding thickness of interfacial layer as function of applied electrode potential. Scan rate: 1 mV / s.

Figure 6.18: Raman spectra recorded during CV for Cu in 1 mM MBT / 0.1 M NaOH in direction of (a) increasing and (b) decreasing potential. The CV was similar to the one obtained in ellipsometric experiment which was displayed in Fig. 6.17. The characteristic peaks of DBTA were marked **"** in the figures.
6.3. Oxide formation and inhibition observed by in situ ellipsometric and Raman spectroscopy*

Fig. 6.18 shows in situ Raman spectra in the presence of MBT. At -1.0 V, the peaks at 1071 cm\(^{-1}\), 1244 cm\(^{-1}\) and 1387 cm\(^{-1}\) were observed, related to CuMBT complex formation. As the electrode potential increased, the latter peak shifted to 1400 cm\(^{-1}\), which it reached at -0.2 V [Fig. 6.19(a)]. A peak wavenumber of 1405 cm\(^{-1}\) was obtained for synthesized CuMBT. As discussed in section 5.3, this shift can be attributed to the influence of the copper surface. In addition, peak shift also indicated the formation of a multilayer. Top layers were less affected by the Cu surface, so the position of peaks is closer to synthesized CuMBT. Peak shift for multilayer formation is significantly larger than during reorientation of the molecules in the monolayer discussed in section 5.3.

![Figure 6.19](image-url)

Figure 6.19: Partially-enlarged Raman spectra of Fig. 6.18 in the region of 1350 cm\(^{-1}\)–1450 cm\(^{-1}\) in direction of (a) increasing and (b) decreasing potential.

When the electrode potential reached +0.2 V, peaks at 501 cm\(^{-1}\), 1010 cm\(^{-1}\), 1126 cm\(^{-1}\), 1238 cm\(^{-1}\), 1276 cm\(^{-1}\), 1425 cm\(^{-1}\) and 1463 cm\(^{-1}\) started to appear in the spectra (marked in Fig. 6.18). These peaks indicate the presence of DBTA.
Chapter 6. Inhibition of Cu oxide formation

As the electrode potential increased, the intensity of the DBTA-related peaks increased, indicating an increase in the amount of DBTA on the surface. At the same time, the amount of CuMBT did not change, since there was no obvious change in intensity. When scanning in negative direction [Fig. 6.18(b)], the intensity of DBTA-related peaks continued increasing until +0.2 V was reached, then started to decrease until -1.0 V, where no DBTA was observed any longer. The peaks originating from CuMBT decreased slightly from +0.4 V to -0.4 V. When -0.6 V was reached, the peak at 1400 cm\(^{-1}\) shifted back to 1387 cm\(^{-1}\), implying only the surface CuMBT species remained, and the CuMBT complex in the multilayers on top was removed. However, compared with the spectra recorded at the initial -1.0 V, the intensity was higher after one cycle. Consequently, after electrode potential sweeping, the surface species may change. Comparing these spectra with those measured in NaOH shows the absence of a copper oxide related peak at \(\approx 523\) cm\(^{-1}\). The effective inhibition of copper oxide formation was proven.

The observed two stage layer thickness increase in the ellipsometric CV in the presence of MBT [Fig. 6.17] can hence be excluded to originate from copper oxide formation: neither was there an anodic peak in the CV, nor were copper oxide peaks observed in Raman spectra. The first stage with increasing layer thickness can be attributed to the formation of a CuMBT multilayer. The second stage can be attributed to the formation of DBTA in the surface layer. DBTA formation also manifests in the anodic peak at +0.2 V, indicating the oxidation of MBT molecules.

After reversing scan direction, thickness kept increasing until the potential returned to +0.4 V. Subsequently, thickness decreased until 0.0 V. According to in situ Raman spectra, this decrease was due to the reduction of DBTA. However, there was no cathodic peak observed here. Therefore, the decrease in layer thickness either resulted from depletion, or from a localized molecular electron transfer. Electrochemical reduction of DBTA can be excluded. From 0.0 V to -0.35 V, the thickness remained constant. At \(\approx -0.35\) V, there was a slight increase in thickness, together with appearance of a cathodic peak. We argue that this behaviour may be related to a shift at -0.6 V in Raman spectra, a change of the CuMBT layer. At
6.4 Summary

The potential-dependent interaction between Cu and MBT was studied by in situ ATR-IR, Raman and ellipsometric spectroscopy. Thickness of interfacial layer and current density during CV measurement decreased significantly after the application of corrosion inhibitor, MBT. As the electrode potential increased, it is found that the linkage between CuMBT layer and Cu surface broke, which made the layer desorbed from the surface. At the same time, a multilayer of CuMBT was formed and internal rearrangement of the complex layer occurs. At higher potential, no Cu oxide, but the oxidized product of MBT, DBTA, formed. The CuMBT complex layer together with DBTA layer provide a protection to the Cu surface. Cu oxide related peak was not observed in Raman spectra when experiment was performed in MBT solution. The result shows that the application of MBT can effectively inhibit formation of Cu oxide, even at high potential, where oxide formation with Cu dissolution is expected according to the system’s thermodynamics / Pourbaix diagram.
Chapter 6. Inhibition of Cu oxide formation
7 Effect of post-preparation aging on inhibitor adsorption and oxide formation inhibition

7.1 Introduction

In this chapter, the influence of aging of PVD Cu on the adsorption of MBT and inhibition of oxide formation was investigated by in situ Raman spectroscopy. As previous procedure, a 10 min reduction was applied before the formation of CuMBT layer. However, due to different amount of oxide on the surface due to aging, the roughness of the Cu surface would be different after reduction. Besides, it was also possible that part of the oxide still remains on the surface after reduction. These factors may affect the adsorption of corrosion inhibitors on the surface and their function may be influenced. Here, all the Cu sample were treated with MBT solution to form a CuMBT layer followed by the electrochemical experiments performed in 0.1 M NaOH.

7.2 The growth of oxide on the surface during aging

The thickness of the oxide was obtained from the data measured by ellipsometric spectroscopy (Sec. 3.1.3). It is assumed that only Cu₂O layer formed on Cu
Chapter 7. Effect of post-preparation aging on inhibitor adsorption and oxide formation inhibition

The sample was stored in a vacuumed desiccator under atmosphere. It was taken out for measurement of thickness in the air. Fig. 7.2 shows the time-dependent growth of copper oxide. The oxide formation can be attributed to two reasons. One is the exposure to air during transportation or measurement. In Fig. 7.2 at 0 days, after short period that Cu layer was prepared by PVD method, a thickness $\approx 1.7$ nm of copper oxide was already obtained. The other reason may come from the contamination in the desiccator. Few amount of organic pollutants from air may remain in desiccator and lead to the increase of thickness on the surface. The IR spectra of Cu samples stored in a vacuumed desiccator for 3 days and 10 days, respectively, were measured in external reflection [Fig. 7.1(a)]. The absorbances were detected in regions of 1000–1800 cm$^{-1}$ and 2800–3000 cm$^{-1}$, which usually refer to hydrocarbons. However, in a blank measurement, where no samples was presented, these absorbances were also observed [Fig. 7.1(b)]. It was difficult to determine if these absorbances resulted from contamination of Cu samples. Therefore, the increase of thickness was attributed to the growth of oxide.

Figure 7.1: IR spectra of (a) Cu sample stored in a vacuumed desiccator for 3 days and 10 days, respectively and (b) blank condition. (a) were recorded in external reflection.
7.3. Electrochemical reaction of MBT treated Cu in 0.1 M NaOH

In the following measurements, the electrolyte was replaced to 0.1 M NaOH after Cu surface was exposed to MBT to form CuMBT complex layer (Sec. 3.4.2). Without MBT in the electrolyte, it was assumed that no further CuMBT layer formed on the surface while application of the potential so that the function of the initial layer can be examined. The samples used were stored in a vacuumed desiccator for 4 days (Case I), 8 days (Case II) and 15 days (Case III) before electrochemical experiments. In situ Raman spectra were recorded while a CV was measured.

7.3.1 Case I

In the first case, the sample stored in a desiccator for 4 days was used. It had the least oxide on the surface, which was assumed be completely removed after reduction. Fig. 7.3 and Fig. 7.4 show the related Raman spectra and CV. In
Figure 7.3: Raman spectra recorded at different electrode potentials for Cu stored in a desiccator for 4 days in 0.1 M NaOH after MBT adsorption at -1.0 V in direction of (a) increasing and (b) decreasing potential during CV. Corresponding CV is displayed in Fig. 7.4.

Figure 7.4: CV of MBT-treated Cu in 0.1 M NaOH (Case I) (Fig. 7.3). Scan rate: 1 mV / s.
7.3. Electrochemical reaction of MBT treated Cu in 0.1 M NaOH

Fig. 7.3(a), at an electrode potential of -1.0 V, the peaks at 1071 cm\(^{-1}\), 1244 cm\(^{-1}\) and 1387 cm\(^{-1}\) were observed and assigned to characteristic peaks of CuMBT\(^{[6,89]}\), indicating the formation of a CuMBT layer. In Sec. 5.3, this layer was found to be a monolayer with MBT molecules adsorbed on Cu surface via exo-S and N atom [Fig. 7.5(a)]. The water peak at 1638 cm\(^{-1}\) and a peak at 711 cm\(^{-1}\), assigned to hydroxy group attached to the Cu surface\(^{[98]}\), were observed as well.

As the electrode potential increased, no obvious increase of CuMBT peaks was observed. When -0.2 V was reached, a shift of the peak at 1387 cm\(^{-1}\) to 1400 cm\(^{-1}\) was observed. In Sec. 6.3.2, this shift was interpreted as a result of the formation of a CuMBT multilayer. However, in this experiment, the shift may be not attributed to the growth of CuMBT. With NaOH as electrolyte, there was insufficient MBT in solution. It was proposed that as the electrode potential increased, with dissolution of Cu surface, the linkage between the Cu surface and CuMBT layer broke [Fig. 7.5(b)]. As discussed in Sec. 6.2.4, it led to the peak at 1387 cm\(^{-1}\) shift to higher wavenumber i.e. 1400 cm\(^{-1}\). The dissolution of Cu and the break of the bonding between Cu and CuMBT can also be seen in CV (Fig. 7.4), in which an anodic peak with a current density of 1.3 \(\mu\)A cm\(^{-2}\) was detected at -0.3 V.

As the electrode potential continuously increased, not only the peaks related to CuMBT but also the water peak at 1638 cm\(^{-1}\) and Cu–OH peak at 711 cm\(^{-1}\) decreased. It is proposed that the Cu–OH peak decreased due to the dissolution of the Cu surface. Besides, Cu oxide is proposed to form at the interface [Fig. 7.5(c)]. Without sufficient MBT in the electrolyte, the Cu ions released at high potential were less possible to form more CuMBT complex, but reacted with the electrolyte at the interface to form Cu oxide, leading to a slight decrease of the peak at 711 cm\(^{-1}\). An anodic peak at 0.16 V detected in CV can be attributed to the oxidation of Cu surface as well. With the interference of interfacial Cu product, both the peaks of CuMBT complex and water decreased at higher potential. Although there were no Cu oxide related peaks observed due to amorphous product obtained, it was postulated that only Cu\(^{+}\) oxide existed. With protection of CuMBT complex layer, there should be no additional oxidant accessible at inter-
An anodic peak at 0.4 V was detected in CV (Fig. 7.4). This peak was proposed to relate to the formation of DBTA. The peaks at 1010 cm$^{-1}$, 1129 cm$^{-1}$ and 1590 cm$^{-1}$, assigned to DBTA were observed in [Fig. 7.3(b)]. Although there was limited amount of MBT in electrolyte, the appearance of DBTA indicates the oxidation of MBT, which may originate from electrolyte or the partial dissociation of CuMBT layer.

In the cathodic process [Fig. 7.3(b)], due to the reduction of Cu oxide, CuMBT complex layer approached surface and the peaks gradually increased [Fig. 7.5(d)]. At -0.2 V, the peak at 1400 cm$^{-1}$ shifted back to 1387 cm$^{-1}$, which implied the linkage between CuMBT and Cu surface gradually formed again. However, the relative intensity of three characteristic peaks changed. The peak at 1071 cm$^{-1}$ which had the largest intensity at the beginning almost disappeared at the end of the polarization cycle. On the contrary, the peak at 1387 cm$^{-1}$ had much higher intensity than before.

A distortion of the CuMBT complex layer is proposed. As the electrode potential changed, due to alternate oxidation and reduction, the surface became rougher. Therefore, the molecules were attached to the surface in a way, which was tilted to original surface normal [Fig. 7.5(e)]. Consequently, the benzene ring would be further from the surface. This orientation changed the relative intensity of the peaks. The peak at 1071 cm$^{-1}$ which related to an asymmetric stretching of benzene ring decreased. Conversely, under such influence, the peaks related to thiazole ring stretching gained more intensity.

In Sec. 5.3, the appearance of the peak at 1071 cm$^{-1}$ is proposed to relate to reorientation of MBT molecules from vertical to oriented parallel. It also agrees with the statement here. Besides, as the formed CuMBT layer was distorted, this change may affect the protection of Cu surface. Nevertheless, in the whole process, no Cu oxide related peaks were detected. It showed that the Cu surface was still under protection of CuMBT complex layer.
7.3. Electrochemical reaction of MBT treated Cu in 0.1 M NaOH

The adsorption of MBT on Cu surface. A monolayer was formed.

The dissolution of Cu surface led to break of the linkage between CuMBT layer and Cu surface.

The dissolved Cu ions reacted with the electrolyte and formed Cu oxide.

The reduction of Cu oxide.

The linkage formed again. The layer was distorted due to an uneven reduction on the surface.

Figure 7.5: The schematic diagram of the proposed mechanism in Case I

7.3.2 Case II

In the second case, a sample stored in a desiccator for 8 days was used. Fig. 7.6 and Fig. 7.7 show the Raman spectra and CV, respectively. In Fig. 7.6(a), at -
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Figure 7.6: Raman spectra recorded at different electrode potentials for Cu stored in a desiccator for 8 days in 0.1 M NaOH after MBT adsorption at -1.0 V in direction of (a) increasing and (b) decreasing potential during CV. Corresponding CV is displayed in Fig. 7.7.

Figure 7.7: CV of MBT-treated Cu in 0.1 M NaOH (Case II) (Fig. 7.6). Scan rate: 1 mV / s.
1.0 V, we observed two peaks at 1244 cm\(^{-1}\) and 1387 cm\(^{-1}\). However, the peak at 1071 cm\(^{-1}\), which related to the benzene ring\(^{[6]}\), was missing. This spectrum was similar to the one at -1.0 V in Fig. 7.3(b). With more oxide covering on the surface in this case, compared with the sample in Case I, the surface would become rougher after reduction. It may affect adsorption of MBT on the Cu surface. Based on the disappearance of the peak at 1071 cm\(^{-1}\) at the beginning, it is proposed that MBT molecules were attached to Cu surface in a more tilted way at the beginning [Fig. 7.8(a)], and a distorted layer may form.

As the electrode potential increased, we still observed the peak at 1387 cm\(^{-1}\) shifted to 1400 cm\(^{-1}\), related to the break of the linkage between CuMBT layer and Cu surface [Fig. 7.8(b)]. Nevertheless, at 0.0 V, the peak at 1400 cm\(^{-1}\) shifted back to 1387 cm\(^{-1}\) with a sudden increase of intensity and a large shift of baseline observed, which may resulted from photoluminescence. The baseline shift became larger at +0.2 V, at which there was no CuMBT related peaks observed. We proposed that the change of CuMBT orientation at the beginning led to a distortion of the CuMBT layer. As a result, the structure of the CuMBT layer became weaker. During the anodic process, when a certain electrode potential was reached, which was 0.0 V here, it is proposed that the film collapsed, resulting in a dramatic change of interfacial structure and caused baseline shift observed in spectra [Fig. 7.8(c)]. At +0.4 V, no CuMBT was observed at the interface. In addition, based on the decrease of water peak and the anodic peak at 0.14 V in CV (Fig. 7.7), the formation of copper oxide was proposed.

In the cathodic process shown in Fig. 7.6(b), a peak at 523 cm\(^{-1}\), assigned to Cu\(_4\)O\(_3\)\(^{[101,102]}\), was observed from -0.2 V. As the mixed oxide contained Cu\(^+\) and Cu\(^{2+}\), the appearance of Cu\(_4\)O\(_3\) revealed further oxidation of Cu\(_2\)O to CuO at the interface. Since complex film collapsed and the protection was lost, it was not surprising to see this Cu\(_4\)O\(_3\) related peak appear. As the electrode potential decreased, the increase of the peak at 523 cm\(^{-1}\) indicates the reformation of Cu\(_4\)O\(_3\) during cathodic process [Fig. 7.8(d)].

At -0.8 V, we started to observe the return of the peaks related to CuMBT at the
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The linkage formed again. The complex bonded to the surface more tilted to surface normal. Some Cu oxide remained on the surface.

A distorted layer formed due to rougher surface.

The dissolution of the Cu surface led to a break of the linkage of the CuMBT layer and the Cu surface.

More oxide formed. The breakdown of CuMBT layer.

The reduction of Cu oxide.

The linkage formed again. The complex bonded to the surface more tilted to surface normal. Some Cu oxide remained on the surface.

Figure 7.8: The schematic diagram of the proposed mechanism in Case II

However, the peak originally at 1387 cm\(^{-1}\) shifted to 1382 cm\(^{-1}\). The Cu surface was expected to be rougher after oxidation and reduction. It affected the readsorption of CuMBT complex and an orientation change of molecules may
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happen. Moreover, due to the breakdown of CuMBT layer during anodic process, the CuMBT observed here was assumed not a layer but clusters of CuMBT. Without the restriction in the layer, CuMBT could freely change their orientation more to attach to the Cu surface. It made the peak shift to lower wavenumber, 1382 cm\(^{-1}\) [Fig. 7.8(e)]. In Sec. 5.3, the same value, 1382 cm\(^{-1}\), was also obtained from proposed vertically absorbed MBT molecules.

In Fig. 7.6(b), the peak at 523 cm\(^{-1}\) indicated Cu oxide still remained on the surface after cathodic process. It is not clear whether MBT molecule was attached to Cu oxide or Cu surface. However, it is proposed that the remained oxide can affect the readsortion of MBT molecules as well.

7.3.3 Case III

In this case, it was assumed to have the most oxide on the surface. After reduction, the surface become even rougher. Due to the rougher surface, the molecules changed their orientation even more. The peak shifted from 1387 cm\(^{-1}\) to even lower wavenumber, 1377 cm\(^{-1}\), and the unusual high intensity of this peak at the beginning in Fig. 7.9(a) were observed. This orientation and the rough surface would make them difficult to form a layer covering on the surface and only attached to the surface separately [Fig. 7.11(a)].

As the electrode potential increased, the peak at 1377 cm\(^{-1}\) shifted to 1385 cm\(^{-1}\), ascribed to the dissolution of the Cu surface and the break of linkage between CuMBT complex and Cu surface [Fig. 7.11(b)]. Different from the Case II, there was neither sudden increase of CuMBT nor baseline shift detected in this case. Besides, the peak at 523 cm\(^{-1}\) assigned to Cu\(_4\)O\(_3\) was detected from +0.0 V in anodic process with an anodic peak at -0.02 V observed in CV (Fig. 7.10).

It is proposed that no layer was formed on the surface. Therefore, there was no baseline shift resulted from collapse of CuMBT layer in anodic process. Moreover, at higher potential, without the protection of CuMBT layer, Cu oxide formed [Fig. 7.11(c)].

However, the intensity of the peak at 523 cm\(^{-1}\) decreased while potential in-
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Figure 7.9: Raman spectra recorded at different electrode potentials for Cu stored in a desiccator for 15 days in 0.1 M NaOH after MBT adsorption at -1.0 V in direction of (a) increasing and (b) decreasing potential during CV. Corresponding CV is displayed in Fig. 7.10.

Figure 7.10: CV of MBT-treated Cu in 0.1 M NaOH (Case III) (Fig. 7.9). Scan rate: 1 mV / s.
7.3. Electrochemical reaction of MBT treated Cu in 0.1 M NaOH

The dissolution of Cu surface led to the desorption of CuMBT clusters.

Figures 7.11: The schematic diagram of the proposed mechanism in Case III

Increasing. It is proposed that Cu$_4$O$_3$ transformed to other type of copper oxide such as CuO at higher potential. In cathodic process [Fig. 7.9(b)], as potential decreased, the increase of the peak at 523 cm$^{-1}$ implied the reformation of Cu$_4$O$_3$.
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[Fig. 7.11(d)]. When the potential reached -0.6 V, CuMBT clusters appeared at the surface again. Due to the much rougher surface after oxidation and reduction, CuMBT clusters were attached to the surface more tilted to surface normal [Fig. 7.11(e)]. The peak shifted to even lower wavenumber, 1367 cm$^{-1}$. The baseline shift and the growth of Cu–OH peak at -0.8 V also revealed the vigorous morphologic change on the surface without proper protection of CuMBT layer. Compared with the spectra of non-protected Cu recorded in 0.1 M NaOH [Fig. 6.16(b)], despite the CuMBT related peaks, two spectra are very similar. It indicates there was no inhibition of oxide formation in this case.

7.3.4 Comparison of different cases of CVs

Figure 7.12: Cyclic voltammograms recorded during different experimental conditions: Red (—) : MBT-treated Cu in 1 mM MBT / 0.1 M NaOH (MBT); orange (—) : MBT-treated Cu in 0.1 M NaOH (Case I); Olive (—) : MBT-treated Cu in 0.1 M NaOH (Case II); Light blue (—) : MBT-treated Cu in 0.1 M NaOH (Case III); Blue (—) : bare Cu in 0.1 M NaOH (NaOH).

From Raman spectra, it shows that the oxide formation was inhibited in Case I and there was almost no inhibition in Case III. This trend was revealed in CV as well. Fig. 7.12 showed 5 CVs which were recorded during different in situ Raman measurements. In the NaOH case, without treatment with MBT, two anodic
7.3. Electrochemical reaction of MBT treated Cu in 0.1 M NaOH

peaks at -0.4 V and -0.06 V were observed, assigned to the formation of Cu$_2$O and CuO, respectively. In case III, the anodic peak at -0.06 V was found shifted to -0.02 V and the current density was smaller as well. Anodic peaks of case II and case I were at 0.14 V and 0.16 V, with even smaller current density respectively. When MBT was present in electrolyte, the current density was very small and the anodic peak at the most positive potential, 0.22 V. The anodic peak at 0.4 V observed in case I was related to oxidation of MBT to DBTA, as discussed in Sec. [7.3.1]

Based on these observations, it can be inferred that if the CuMBT layer can provide protection to the Cu surface, the anodic peak would shift to higher potential, and related current density was also smaller.

### 7.3.5 The investigation of thickness of interfacial layer

![Figure 7.13: CV of MBT-treated Cu in 0.1 M NaOH during ellipsometric experiment and corresponding thickness of interfacial layer as function of applied electrode potential. Scan rate: 1 mV / s.](image)

Fig. 7.13 shows the thickness of interfacial layer during CV of MBT-treated Cu in 0.1 M NaOH. Different from previous electrochemical experiments, the preparation of CuMBT complex film was under higher electrode potential (-0.5 V) for
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30 min. Therefore, a larger value of initial thickness, 2 nm, was obtained, indicating thicker CuMBT layer formed at the beginning. As electrode potential increased, the thickness remained the same until -0.3 V. From -0.3 V, layer thickness increased in two stages. The first stage started at -0.3 V, and reached 13 nm at 0.0 V. The second stage started from -0.07 V and reached 17 nm at the end of the anodic process. These two stages in thickness agree with the CV, in which two anodic peaks at -0.3 V and 0.0 V were detected. The thickness continued to increase in cathodic process which reached 18 nm when back to -1.0 V.

Based on the position of the anodic peaks and cathodic peaks, it is proposed this condition was similar to Case III of in situ Raman experiments. Therefore, it is proposed no CuMBT layer formed. The thicker initial interfacial layer shows more CuMBT complexes were prepared under higher electrode potential. In Sec. 6.3.2, an increase of interfacial thickness from -0.6 V was observed due to continuous formation of CuMBT layer. However, in this case, no increase was observed from -0.6 V, indicating there was no further growth of CuMBT due to lack of MBT molecules in electrolyte. An anodic peak at -0.3 V was attributed to the dissolution of Cu surface which led to the break of linkage between CuMBT and the Cu surface.

In Fig. 7.13, without the formation of a protective layer, the first increase of thickness was related to the formation of Cu oxide. The second increase of thickness at 0.0 V should be related to the formation of CuO, at which the peak at 523 cm⁻¹ was observed in Fig. 7.9(a). In cathodic process, the thickness didn't decrease but had an increase of 1 nm. It can be attributed to uneven reduction on the Cu surface and the return of CuMBT complexes.

7.4 Summary

The influence of copper oxide on the adsorption of MBT molecules and the formation of CuMBT layer was investigated by in situ Raman spectra coupled with electrochemical studies. The results show that it was more difficult to form a pro-
tective CuMBT layer on the surface to inhibit the formation of Cu oxide, if Cu was stored in a desiccator for longer time. It would affect the adsorption of MBT molecules, the formation of CuMBT complex layer and the inhibition of oxide formation.

Based on the results in Raman spectra, it can be inferred that the appearance of the peak at 1071 cm$^{-1}$ and the initial position of the peak around 1387 cm$^{-1}$ can be used as indicator whether a protective CuMBT layer formed. Only when a protective CuMBT complex layer forms, the Cu surface can be protected and the formation of Cu oxide can be inhibited. While protection against dissolution has not been investigated, a complete CuMBT layer covering the surface must also inhibit dissolution.
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8 Conclusion

The formation of copper MBT complex layers on copper in alkaline electrolyte was studied ex situ and in situ in this work. In ex situ studies, the protective layer grew as a function of immersion time. In agreement with previous studies, both N and exo-S atoms were involved in the interaction with the surface of metallic copper, based on the results obtained from XP spectra. In the presence of MBT, copper can be oxidized only up to Cu$^+$; the formation of Cu$^{2+}$ is inhibited by the oxidation of MBT to a dimer. The copper MBT complex layers on copper have an internal structure. According to the shifts observed in depth profile XP spectra and angle resolved XP spectra, there is a structural difference between the MBT directly in contact with the metallic copper, and the copper MBT complex inside the formed CuMBT complex film.

Three different complementary in situ spectroscopic techniques were applied to study the interaction of MBT with Cu in situ, ATR-IR spectroscopy, ellipsometric spectroscopy and Raman spectroscopy. Under open circuit conditions in the final film, the thiol form of MBT dominates over thione form, though the latter is still detectable. Data from the early stage of film formation show that initially MBT adsorbed molecularly in a monolayer that relaxes to a compact geometry with time. This geometry is stable under constant reducing potential, and likely contains MBT bound via both exo-S and N atoms to the copper surface. When polarizing to positive potentials in the presence of MBT in bulk solution, copper dissolution becomes thermodynamically feasible. Thus, the copper MBT complex multilayer film forms on top of the initial multilayer. This film effectively inhibits oxide formation. Instead, formation of the disulfide oxidation product of MBT
was observed. Under open circuit conditions, multilayer film formation containing copper MBT complexes was observed on the hour time scale. From the in situ experiments performed, there is no evidence that the presence of an initial oxide layer is needed for adsorption of MBT to occur. Nevertheless, MBT may also adsorb to oxide-covered Cu surfaces.

The effect of aging of the copper substrate was investigated on the structure of the formed copper MBT complex film, and its ability to inhibit oxide formation. To that end, MBT was adsorbed to free metal surface under reducing conditions, and residual MBT was washed out of the bulk electrolyte. On freshly prepared surfaces, adsorption proceeded in the typical flat geometry, which inhibited oxide formation despite polarization to positive potentials. After few weeks of storing the samples, adsorption geometry appears more disordered, and inhibition of oxide formation is no longer possible. After analysis of a number of samples, three different scenarios were identified. Characteristic Raman peaks of the copper MBT complex may serve as an indicator on whether the complex layer inhibits oxide formation or not.

Overall, this work shows the quite complex role of the molecular corrosion inhibitor, and lets one reflect on design criteria for molecular corrosion inhibitors: they need to form stable but dynamic bounds to the metal surface to be protected via multiple binding sites, they need to be able to form complexes with oxidation products of the metal, and their own oxidation products need to contribute to upholding surface protection. In that manner, MBT acts as a “sacrificial inhibitor”; oxidation of the inhibitor molecule happens instead of oxidation of the metal surface.
Bibliography


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Appendix
**Abbreviations**

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<tr>
<th>Abbreviation</th>
<th>Explanation</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
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<tr>
<td>BTA</td>
<td>Benzotriazole</td>
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<td>CE</td>
<td>Counter electrode</td>
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<tr>
<td>CuMBT</td>
<td>Copper 2-mercaptopbenzothiazole</td>
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<tr>
<td>CV</td>
<td>Cyclic voltammogram; cyclic voltammetry</td>
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<tr>
<td>DBTA</td>
<td>2,2'-Dibenzothiazole disulfide</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
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<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>MBT</td>
<td>2-Mercaptobenzothiazole</td>
</tr>
<tr>
<td>MCT</td>
<td>Mercury cadmium telluride</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
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<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
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<tr>
<td>RE</td>
<td>Reference electrode</td>
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<tr>
<td>SERS</td>
<td>Surface enhanced Raman spectroscopy</td>
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<tr>
<td>UV–Vis</td>
<td>Ultraviolet visible</td>
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<tr>
<td>WE</td>
<td>Working electrode</td>
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<td>X-ray photoelectron spectroscopy</td>
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List of publications


Oral presentations and posters at conferences


