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# Effect of Corrosion Inhibitors on Copper Etching to Form Thick Copper Line of PCB in Acidic Etching Solution

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**Abstract:** The chemical compounds of 2-mercaptobenzothiazole (2-MBT), benzotriazole (BTA) and phenoxyethanol (MSDS) as corrosion inhibitors were used to inhibit the copper etching to form the thick copper line of PCB in the acidic etching solution. The inhibition status was characterized with contact angle measurement, electrochemical test and etch factor calculation, while the corrosion morphology of copper surface was studied by scanning electron microscope. The adsorption mechanism of corrosion inhibitors on copper surface is analyzed by molecular dynamics and quantum chemistry calculations. The results indicated that the synergistic function of the two inhibitors could effectively promote their adsorption on the copper surface in parallel, while their adsorption energy could be higher than that of the single inhibitor. The etch factor of the thick copper line with about 33 μm in thickness increased to 6.59 from the etching solution with 2-MBT and MSDS for good agreement of PCB manufacture.

**Key words:** corrosion inhibitor; synergistic function; thick copper line; acidic etching solution

## 1 Introduction

Printed circuit board (PCB) tends to produce high precision and high-density interconnection to match the development of electronic products miniaturization, lightweight, high speed and multi-function[1]. Subtraction process of copper foil for copper line manufacture has been widely used in PCB production, however, low etch factor is a challenge to fabricate thick copper lines. Organic corrosion inhibitor as an important part of etching potion can significantly increase the etch factor for good quality of copper lines[2].

Generally, organic corrosion inhibitor has been widely used in copper corrosion control due to its low cost and low additive amount[3]. Organic nitrogen-based heterocyclic compounds containing π bonds or heterocyclic atoms (N, P, S, O) have multiple active adsorption sites, making them easily adsorbed on metal surfaces to form protective films and to inhibit corrosion. Triazoles, thiazoles, imidazole, quinoline, pyridine, amines and amino acids are usually selected as corrosion inhibitors. Early works have reported the use of corrosion inhibitor to improve the etch factor of copper line in an acid etching solution. Papapanayiotou et al.[4] developed an acidic etching solution with corrosion inhibitor to obtain the etch factor of 3.0. According to the effects on the etching of copper, a high etch factor could be obtained from the etching solution with high temperature, and the suitable concentrations of $CuCl_2$ etchant and additives[5].

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Chen et al.[6] found out that the etch factor of fine line for IC substrates was only 3.7 from semi-additive process. Zhong et al.[7] added corrosion inhibitors into the common acidic etching solution to increase the etch factor to more than 4.0. However, in order to improve the signal transmission integrity of thick copper lines, good corrosion inhibitors should be discovered to add into the etching solution for the increase of etch factor. The inhibition mechanism and adsorption behavior of three purine derivatives (guanine, adenine and hypoxanthine) were investigated on the corrosion of copper in alkaline artificial seawater[8]. The results showed that the three inhibitors all delayed corrosion by indicating a protective film on the copper surface as well as the three inhibitors all obeyed the Langmuir adsorption model and belonged to a mixed physicochemical adsorption. Additionally, 2-mercaptobenzothiazole (2-MBT) and benzotriazole (BTA) are also excellent inhibitors for copper corrosion because they both have included π bond, and N atom could combine with vacant orbitals on copper surface to form coordination and achieve good adsorption[9-12]. Huang et al.[13] studied the corrosion inhibition of copper by BTA, benzimidazole (BIMH), and benzothiadiazole (BTH) in 3.5wt.% NaCl solution at 30 ºC. The results showed that BTA exhibited the best inhibition effect due to the larger adsorption energy, obtaining the inhibition efficiencies of 99.52% in 3.5wt.% NaCl solution. Chiter et al. [14] reported that the corrosion inhibition properties and adsorption mechanism of 2-MBT as an efficient corrosion inhibitor on copper surface. 2-MBT was found to be strongly adsorbed on copper in the way of ultra-thin oxide film for eventual corrosion inhibition of copper. In addition, the N atoms on thiazole rings and amino groups in phenoxyethanol (MSDS) could exhibit lone pair electrons to contribute to binding empty of copper surface rails, while the benzene ring could work as resist media on the metal surface. Therefore, the organic compounds including BTA, 2-MBT and MSDS could be suitable to be selected as corrosion inhibitors to study the inhibition performances of copper in PCB acidic etching solution.

In this study, 2-MBT, BTA and MSDS as corrosion inhibitors were added into the acidic etching solution to form thick copper line of PCB. Electrochemical testing, quantum chemical computation and molecular dynamics calculation were used to investigate the influence of above molecules on corrosion inhibition behavior.

## 2 Experimental Section

The base etching solution consisted of 85 g·L$^{-1}$ cupric chloride dihydrate ($CuCl_2·2H_2O$), 0.1 mol·L$^{-1}$ hydrochloric acid (HCl) and 25 g·L$^{-1}$ ammonium chloride ($NH_4Cl$). 2-MBT, BTA and MSDS as selective corrosion inhibitors were added into the base etching solution. The chemical structures of 2-MBT, BTA and MSDS are shown in Figure 1. All drugs were of analytical grade. The mixture of 2-MBT and MSDS is represented by 2-MBT + MSDS, while the mixture of BTA and MSDS is represented by BTA + MSDS. Above etching solution formulations with above corrosion inhibitors were used in etching experiments and electrochemical tests.

The copper samples used in weightlessness test were copper-clad laminate with about 33 μm-thick copper foil. The samples were cleaned with the removing solution of acid oil and then dried with hot air after distilled water washing. Thereafter, the copper samples were pressed with etchant resist film. After exposure and developing of etchant resist film, the copper samples were statically etched for 6 min at 50

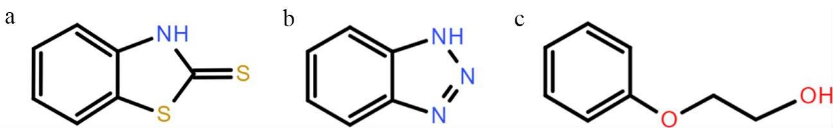


**Figure 1** Molecular structures of the three studied inhibitors: (a) 2-mercaptobenzothiazole (2-MBT), (b) Benzotriazole (BTA), (c) Phenoxyethanol (MSDS). (color on line)

ºC, and the copper lines were obtained by stripping the etchant resist film, as shown in Figure 2. According to 2-MBT and BTA adsorption rules and MSDS concentration test[15], the optimal concentrations of 2-MBT and BTA were 8 mg·L$^{-1}$ and 16 mg·L$^{-1}$, respectively, and the optimal concentration of MSDS was 1 g·L$^{-1}$.

Electrochemical experiments were carried out in a conventional three-electrode glass cell at 50 ºC, using an Autolab electrochemical workstation (PGSTAT302N, Switzerland Metrohm). Copper foil served as the working electrode, with a 2 cm$^2$ effective contact area. The reference and counter eletrodes were a saturated mercurous sulfate electrode (SSE) and a platinum electrode, respectively. The electrochemical experimental solutions were PCB acidic etching solution with different corrosion inhibitors. All impedance experiments were performed in the frequency range of 10$^5$ ~ 10$^{-2}$ Hz with an amplitude of 10 mV. The polarization test started with a sweep from the open circuit potential direction to +0.85 V and then from the open circuit potential to -0.85 V at a scan rate of 0.005 V·s$^{-1}$.

The surface morphology was observed with scanning electron microscope (SEM) (JSM-6060, JEOL), and the contact angle was measured by optical contact angle measuring instrument (JY Pha, Zhengye Technology). Cross section of copper lines was observed with metallographic microscope (BX-51, OLYMPUS). In order to research the structure and geometry of the inhibitor molecules to study the inhibition mechanism, the adsorption energies of acidic etching solution inhibitors 2-MBT and BTA were simulated by the Forcite module of Materials Studio, then MSDS was added into the etching solution to calculate the adsorption energy of the synergistic action between corrosion inhibitors. And then Dmol3 module is used to build the initial model and optimize the molecular configuration. The relationship between inhibitors molecule structures and their inhibition performances is investigated through the Gaussian software calculation to determine the energy value of the lowest unoccupied molecular orbital ($E_{LUMO}$), the highest occupied molecular orbital ($E_{HOMO}$), and the energy gap ($\Delta E$) between the two frontline orbitals. Cu(111) surface with stable and low Miller index is usually used to research the inhibition adsorption[16]. In order to achieve the optimal corrosion inhibitor performance, the adsorption characteristics of three corrosion inhibitor molecules on copper surfaces, as well as the adsorption configuration and behavior of the corrosion inhibitors are simulated and compared.

## 3 Results and Discussion

### 3.1 Corrosion Inhibition Behavior for Copper Lines

It can be seen from Figure 3 that the systems with

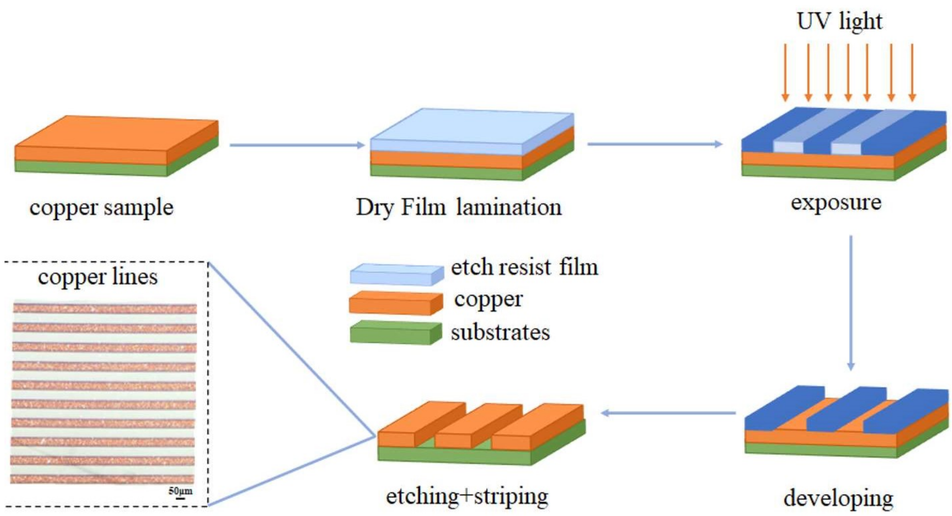


**Figure 2** Flowchart showing process of copper line fabrication after etching (color on line)

the above corrosion inhibitors have different inhibition effects on copper sample in etching solution. With the addition of corrosion inhibitor, the inhibition efficiency of copper sample increased gradually, and reached the maximum value in 2-MBT + MSDS system. Etch factor was calculated from the section diagram in Figure 4 according to Equation (1).

$$\text{Etch factor} = \frac{2h}{b-a} \tag{1}$$

where $h$ is the thickness of copper, $a$ is the length of top copper and $b$ is the length of bottom copper.

A single corrosion inhibitor like 2-MBT or BTA added into the base etching solution weakened corrosion effect, only leading to the etch factor of 4.02 or 4.68, respectively. However, when the inhibitor system with 2-MBT + MSDS was added into the etching solution, the etch factor reached a maximum value of 6.59. During copper etching, MSDS as both functions of corrosion inhibition and wetting agent enhanced the corrosion inhibition effects of 2-MBT and BTA, but 2-MBT + MSDS had the largest corrosion inhibition effect on copper to realize fine copper line manufacturing.

Figure 5 shows the SEM results of copper after immersing in the acidic etching solution containing inhibitor and without inhibitor at 50 ºC for 1 min. It could be observed that the surface of copper foil before corrosion was smooth and uniform. As can be seen from Figure 5(b), in the absence of corrosion inhibitor, the surface of the copper sample was severely corroded and many corrosion cracks were observed, indicating that the corrosion of copper was relatively serious. When 2-MBT and BTA inhibitors were added separately, the surface of copper presented clear fracture traces, but the number of cracks decreased as compared with that from blank solution. In addition, the corrosion pit became shallow, because 2-MBT and BTA had a slight effect on inhibiting copper corrosion. Furthermore, after adding 2-MBT + MSDS and BTA+MSDS in the etching solution, there were some visible corrosion marks on the surface of copper, but the corrosion cracks on the surface of copper decreased obviously, indicating that 2-MBT + MSDS and BTA + MSDS effectively inhibited the corrosion of copper. Therefore, the SEM surface morphology further confirmed that the inhibition effect of the two corrosion inhibitors on copper could be better than that of the single corrosion inhibitor. Meanwhile, 2-MBT + MSDS had the best inhibition effect on copper in the etching solution.

Contact angle tests of the etching solution were done to explain the adsorption effect of corrosion inhibitor molecules and wetting agent molecules on copper surface. Figure 6 shows the contact angle re-

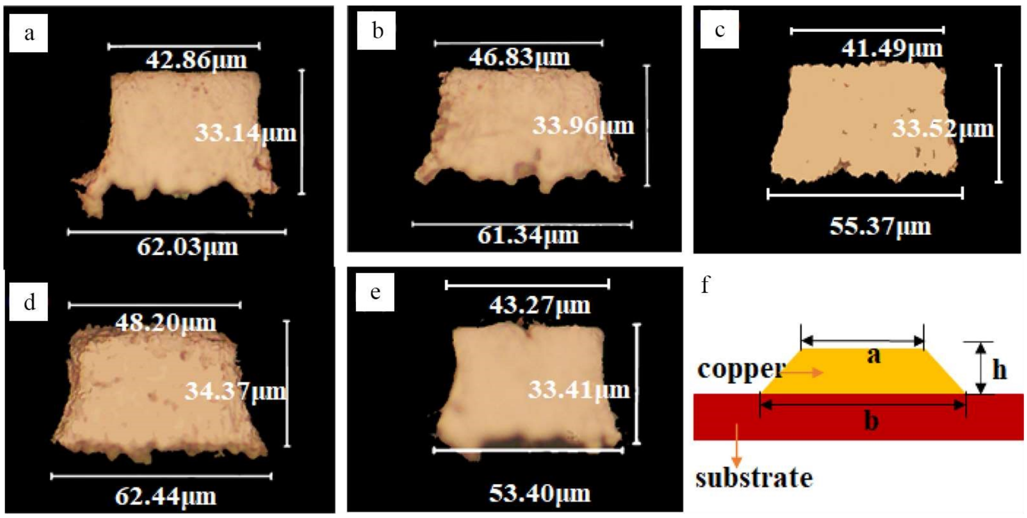


**Figure 3** Section diagram of copper in the etching solutions without and with various inhibitors. (a) no inhibitor, (b) 2-MBT, (c) BTA, (d) BTA + MSDS, (e) 2-MBT + MSDS, (f) Section diagram of copper line (color on line)

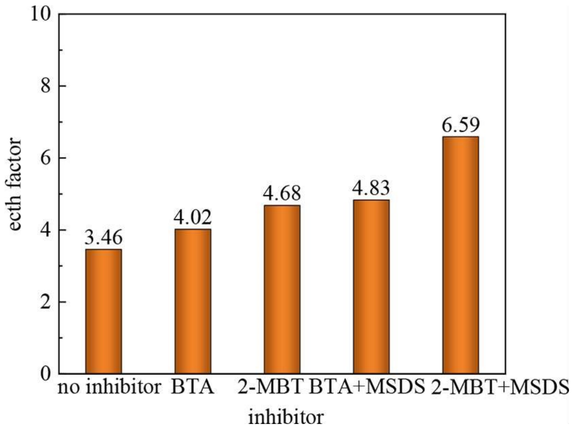


**Figure 4** Etch factor of copper in the etching solution without and with various inhibitors (color on line)

sults on copper surface in acidic etching solution. The contact angle of pure copper sample treated with the etching solution without inhibitor was 64.3°, compared to those of the etching solutions with 2-MBT for 69.8°, BTA for 71.6°, 2-MBT+MSDS for 75.7° and BTA + MSDS for 76.1°. It is observed that the contact angle can be increased after the addition of corrosion inhibitors, indicating that corrosion inhibitors could induce effective adsorption performance on copper surface to enhance the corrosion inhibition. Furthermore, the contact angle rised after adding MSDS and a single inhibitor to the etching solution, showing that the adsorption action on the copper surface is improved.

## 3.2 Analysis of Corrosion Inhibition Mechanism

### 3.2.1 Theoretical Calculations

In order to analyze the relationship between the structure of three inhibitors and the inhibition performance, quantum chemical computation and molecular dynamics calculation are carried out on the three inhibitors. Density functional theory (DFT) is used to calculate the quantum chemistry of inhibitors, and the calculation method of Eqation (2) is introduced according to the frontier molecular orbital theory[17]:

$$\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} \tag{2}$$

where $E_{\mathrm{HOMO}}$ is the highest occupied orbital energy, $E_{\mathrm{LUMO}}$ is the lowest vacant orbital energy and $\Delta E$ is the difference between $E_{\mathrm{HOMO}}$ and $E_{\mathrm{LUMO}}$.

Figure 7 shows the HOMO and LUMO diagrams of the three inhibitors. According to the frontier orbital theory of quantum chemistry, higher HOMO level could result in stronger ability of the inhibitor molecule to provide electrons to the molecular orbital, while lower LUMO level cause stronger ability of the inhibitor molecule to accept electrons[18]. Therefore, HOMO and LUMO levels determine the ability of a corrosion inhibitor molecule to gain and lose electrons. Moreover, energy gap ($\Delta E$) between LUMO and HOMO reflects the stability of the inhibitor

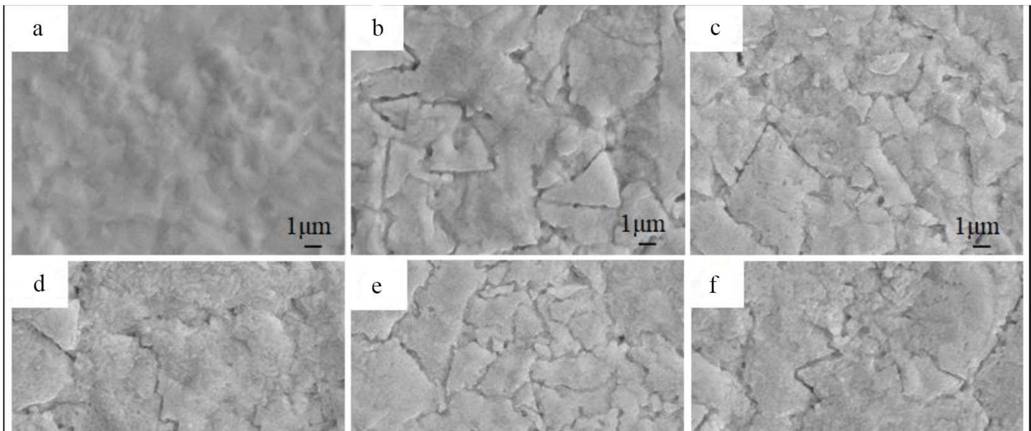


**Figure 5** Surface morphologies of copper samples before (a) and after immersing the etching solution without or with various inhibitors. (b) no inhibitor, (c) BTA, (d) BTA + MSDS, (e) 2-MBT, (f) 2-MBT + MSDS

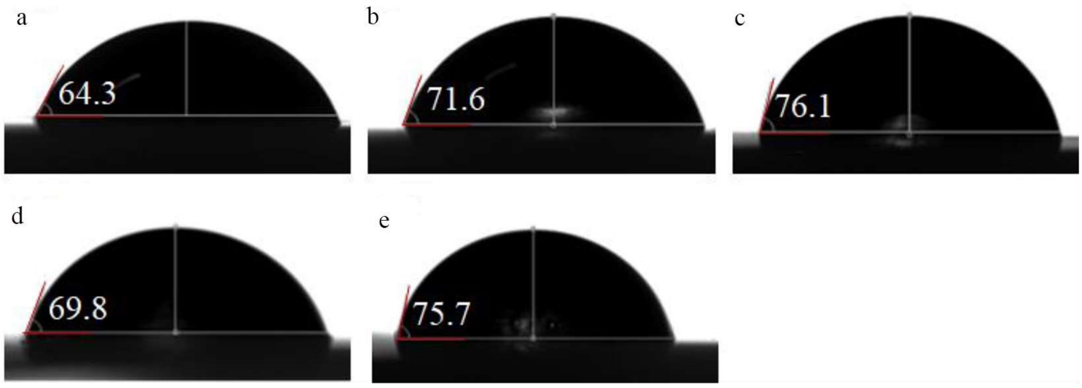


**Figure 6** Contact angles of copper sample in the etching solution without and with various inhibitors: (a) no inhibitor, (b) BTA, (c) BTA + MSDS, (d) 2-MBT, (e) 2-MBT + MSDS

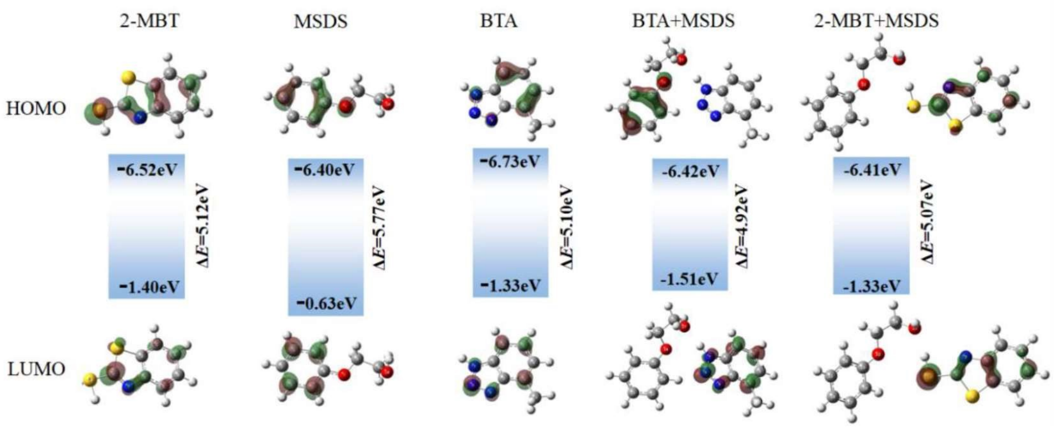


**Figure 7** HOMO and LUMO calculation results for different inhibitors (color on line)

molecule. If $\Delta E$ value is lower, inhibitor molecules could contribute to easier surface adsorption. The $\Delta E$ values of 2-MBT + MSDS and BTA + MSDS are lower than that of single corrosion inhibitor, indicating that MSDS could enhance the inhibition effect of single inhibitor. Small difference is found by comparing the $\Delta E$ values of 2-MBT + MSDS and BTA + MSDS. The $E_{\mathrm{HOMO}}$ values of the 2-MBT + MSDS and BTA + MSDS are almost the same, but the $E_{\mathrm{LUMO}}$ value of 2-MBT + MSDS is lower for easy electrons acceptance. The interaction between etching solution and copper surface is mainly to electron donating effect, thus, 2-MBT + MSDS could be more easily adsorbed on copper surface to achieve stable corrosion inhibition.

Figure 8 shows the equilibrium adsorption configurations of corrosion inhibitor molecules and the interaction between corrosion inhibitor molecules on copper surface. The results show that the corrosion inhibitor molecules are adsorbed on copper surfaces parallel and vertically before the equilibrium, however, they tend to be adsorbed on copper surfaces horizontally after the equilibrium. Parallel adsorption of corrosion inhibitor is beneficial to maximize surface coverage[19] and protect the copper surface, leading to good corrosion inhibition effect.

Adsorption energy is an important index to measure the binding abilities of corrosion inhibitor and metal surface. The calculation formula of adsorption energy is shown in Equation (3)[20]:

$$E_{\mathrm{Cu-inhibitor}} = E_{\mathrm{total}} - (E_{\mathrm{Cu}} + E_{\mathrm{inhibitor}}) \quad (3)$$

where $E_{\mathrm{Cu}}$ and $E_{\mathrm{inhibitor}}$ represent the energies of the copper surface and the inhibitor surface, respectively. $E_{\mathrm{total}}$ represents the total energy of the inhibitor and

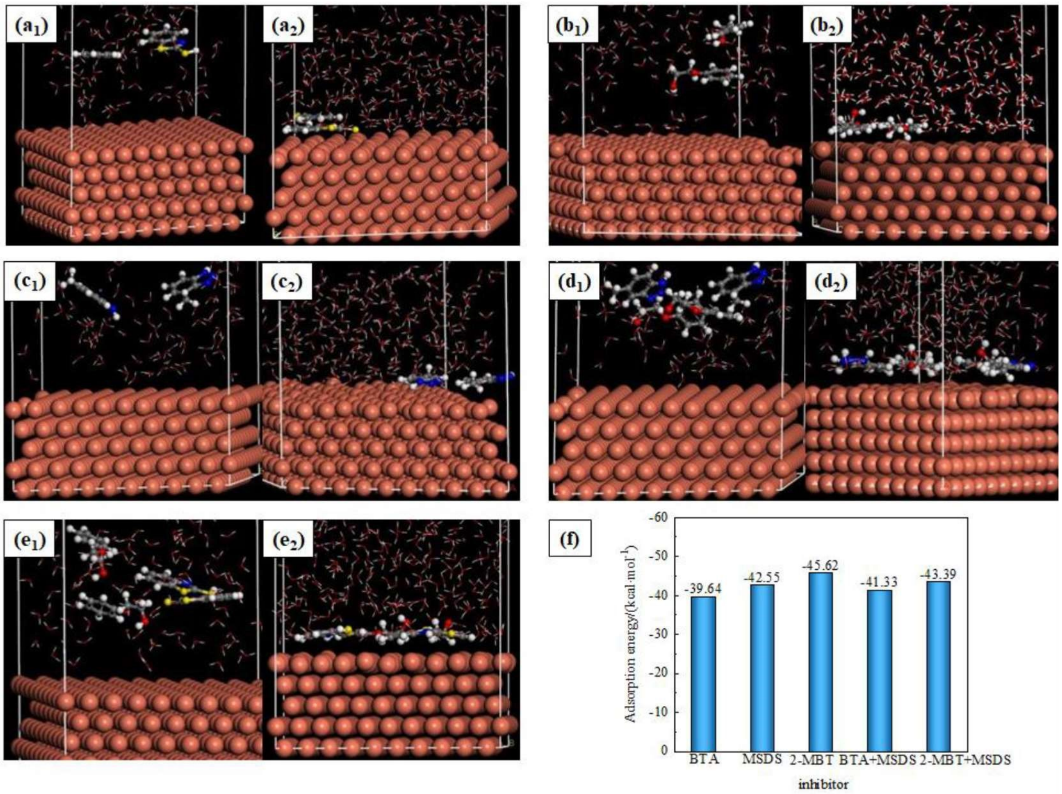


**Figure 8** The equilibrium configurations on copper before and after the adsorption of corrosion inhibitor system: ($a_1$ and $a_2$) 2-MBT; ($b_1$ and $b_2$) MSDS; ($c_1$ and $c_2$) BTA; ($d_1$ and $d_2$) BTA + MSDS; ($e_1$ and $e_2$) 2-MBT + MSDS; and (f) calculative adsorption energy of corrosion inhibitor system. (color on line)

the metal surface.

Figure 8 The equilibrium configurations on copper before and after the adsorption of corrosion inhibitor system: ($a_1$ and $a_2$) 2-MBT; ($b_1$ and $b_2$) MSDS; ($c_1$ and $c_2$) BTA; ($d_1$ and $d_2$) BTA + MSDS; ($e_1$ and $e_2$) 2-MBT + MSDS; and (f) calculative adsorption energy of corrosion inhibitor system.

3.2.2 Electrochemical Measurements

Electrochemical impedance spectroscopy (EIS) and polarization curve test were used to further study the inhibition mechanism of corrosion inhibitor on copper surface in an acidic etching solution. Figure 9(a) shows the impedance spectra of copper electrodes in acidic etching solutions without and with different inhibitors at 50 ºC. It can be seen from Figure 9(a) that the impedance spectra without and with various corrosion inhibitors are mainly represented as a semi-circle capacitive reactance arc. With the addition of the corrosion inhibitor, the capacitance arc radius increased, and the electrical impedance value and charge transfer resistance increased[21]. Therefore, the addition of corrosion inhibitor inhibits the charge transfer between copper electrode and etching solution, and the results indicating that the adsorption of corrosion inhibitor molecules on the surface of copper electrode can inhibit copper corrosion. 2-MBT + MSDS significantly reduced the copper corrosion in the etching solution, displaying the maximum capacitance reactance arc.

The polarization curves of copper electrodes with different corrosion inhibitors in acidic etching solutions are shown in Figure 9(b). As shown in Figure 9 (b), compared with the one without corrosion inhibitor, the addition of 2-MBT and BTA resulted in a change of corrosion potential, but the influence trend was not significant. It can be inferred that 2-MBT and BTA have an inhibition effect on copper corrosion and are mixed corrosion inhibitors[22] . The corrosion inhibition efficiency is calculated as Equation (4):

$$IE_{(i)} = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100\% \quad (4)$$

where $IE_{(i)}$ represents the corrosion inhibition efficiency, and $I_{corr}$ and $I_{Corr(inh)}$ represent the self-corrosion currents of the copper and the inhibitor, respectively.

The Tafel linear region of the polarization curve was extrapolated to the self-corrosion potential $E$ to obtain the $I_{corr}$ and $I_{corr(inh)}$, and the corrosion inhibition efficiency $IE_{(i)}$ as calculated by the corrosion currents before and after the addition of corro sion inhibitor are observed in Figure 9(c). According to the data measured, compared with the corrosion current density of the etching solution without corrosion inhibitor, the corrosion current densities of 2-MBT and BTA decreased to 3.7 mA·cm$^{-2}$ and 3.9 mA·cm$^{-2}$, respectively, indicating that both 2-MBT and BTA can inhibit the dissolution of copper electrodes by etching solution. At the same time, the above corrosion inhibitors and MSDS were both added to further reduce the corrosion current density, and the corrosion inhibition rate increased to 31.1% and 22.2%, respectively. These values indicate that the synergistic action of corrosion inhibitors can further impede the dissolution reaction of copper electrodes and improve the corrosion inhibition effect of copper, while the combination of 2-MBT + MSDS has the best corrosion inhibition.

In summary, the results of the electrochemical experiments further proved that the three corrosion inhibitors can have good corrosion inhibition effect on copper surface, consistent with the above results of copper etching and simulation. Especially, the acid etching solution with 2-MBT + MSDS presented the best corrosion inhibition for good fabrication of copper line with the greatest etch factor, compared to the cases of the acid etching solution with other corrosion inhibitor systems.

## 4 Conclusions

The chemical compounds of 2-MBT, BTA and

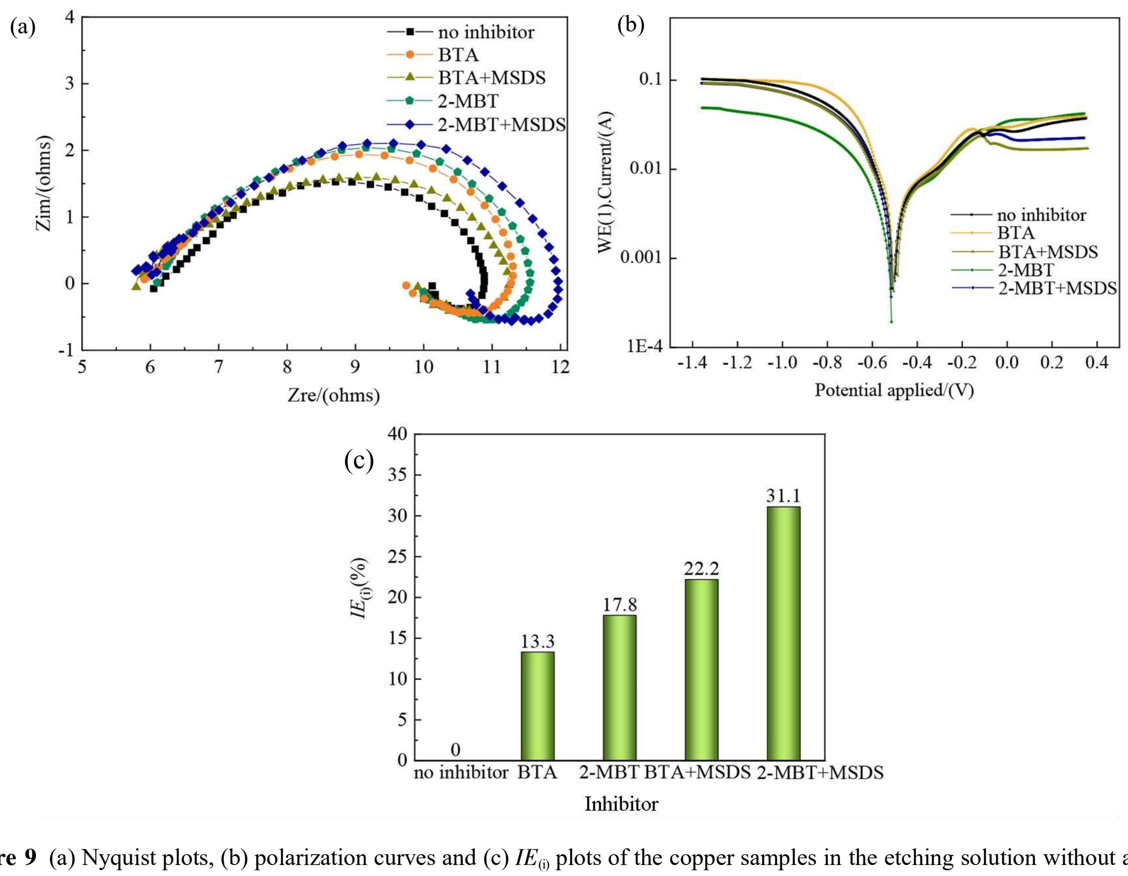


**Figure 9** (a) Nyquist plots, (b) polarization curves and (c) $IE_{(i)}$ plots of the copper samples in the etching solution without and with various inhibitors. (color on line)

MSDS as corrosion inhibitors were added into the acidic etching solution to form the thick copper line of PCB. The inhibition mechanism and adsorption behavior of the corrosion inhibitors were investigated by contact angle measurement, electrochemical test, SEM, quantum chemical calculation and molecular dynamics calculation. The electrochemical tests and simulation results of the corrosion inhibitor proved that the order of the inhibition effect was 2-MBT + MSDS > BTA + MSDS. The 2-MBT, BTA and MS-DS molecules could be adsorbed on the copper surface in parallel coverage, therefore, contributing to good inhibition effect. The etch factor of the thick copper line with about 33 μm in thickness increased to 6.59 from the etching solution with 2-MBT+MS-DS for good quality of PCB interconnection.

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# PCB 酸性蚀刻液中缓蚀剂对厚铜线路制作的影响

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**摘要:** 以 2- 巯基苯并噻唑(2-MBT)、苯并三氮唑(BTA)和苯氧基乙醇(MSDS)作为缓蚀剂, 研究了其加入在酸性蚀刻液后对 PCB 厚铜线路的缓蚀效果。通过接触角测试、电化学测试和蚀刻因子得出缓蚀状态,并结合扫描电子显微镜观察铜表面形貌。通过分子动力学计算和量子化学模拟分析缓蚀剂在铜表面的吸附机理。结果表明, 2-MBT + MSDS 与 BTA + MSDS 的分子结构可有效地平行吸附在铜表面, 且吸附能高于单一缓蚀剂。加入了 2-MBT + MSDS 的蚀刻液, 对厚度约为 33 μm 铜线路进行刻蚀, 铜线路的蚀刻因子提高到 6.59, 可有效应用于 PCB 厚铜线路制作。

**关键词:** 缓蚀剂; 协同作用; 厚铜线路; 酸性蚀刻液