Electronic Supplementary Material

Effects of Hydroxyl and Trifluoromethyl Substituents on the Corrosion Inhibition of Benzotriazole Derivatives in Copper Surface Planarization

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Materials and Methods

1. Materials and slurry preparation

Benzotriazole (BTA), 1-Hydroxybenzotriazole (n-OH-BTA), and 1-Hydroxy-6-trifluoromethylbenzotriazole (n-OH-BTA-4CF_3) are sourced from Tansoole Co., Ltd. (China). Hydrogen peroxide (H_2O_2, 30 wt% aqueous solution) and dilute hydrochloric acid (0.1 M HCl) are acquired from Sinopharm Chemical Reagent Co., Ltd. and Godow Technology Co., Ltd., respectively. Spherical silicon dioxide nanoparticles (SiO_2, nominal diameter: 20 nm) are supplied by Zhongye Nanomaterials Co., Ltd. All reagents are used as received without further purification unless explicitly stated. The chemical mechanical planarization (CMP) slurries are formulated with fixed concentrations of H_2O_2 (1.0 wt%) and SiO_2 (5 wt%), while the concentrations of BTA and its derivatives (n-OH-BTA, n-OH-BTA-4CF_3) are standardized at 0.001 $mol\cdot L^{-1}$. A solubilizer (Polysorbate-80, 1wt%) is introduced in all slurries to enhance the solubility of corrosion inhibitors. Slurry preparation involves sequential mixing under mechanical agitation: (1) SiO_2 nanoparticles and polysorbate-80 are dispersed in deionized water via 10 min ultrasonication and 30 min magnetic stirring to ensure homogeneity; (2) BTA derivatives are dissolved into the colloidal suspension by 10 min ultrasonication and 15 min magnetic stirring; (3) H_2O_2 is introduced to initiate redox activation; (4) pH adjustment to 5.5 ± 0.1 is achieved through titrated addition of dilute HCl.

2. Electrochemical analysis and physical characterization

White light interferometer (Contour X, Bruker) is employed to measure surface roughness and surface morphology of copper after CMP. Electrochemical tests are recorded on an electrochemical workstation (CHI660e, ChengHua Co., Shanghai) using three electrode system, in which copper wafer (2 × 2 cm), Ag/AgCl (saturated KCl), and platinum wire are served as working electrode, reference electrode, and counter electrode, respectively. Electrochemical impedance spectroscopy (EIS) and Tafel plots are performed in CMP slurries that contain different corrosion inhibitors (0.001 moL L^{-1}). For all EIS tests, the scanning frequency range and the amplitude potential are 0.1-1×10^6 Hz and 5 mV, respectively. The characteristic equivalent electrocircuit are utilized to analyze the obtained Nyquist plots. Before Tafel tests, the open circuit potential (OCP) should be carried out first. Prior to electrochemical tests, all copper wafers are treated with acetic acid for 5 min to remove the surface oxides. The corrosion inhibition efficiency can be calculated using the following equations $Eq.$ S1-2:

$$\eta_{Tafel} = \frac{I_{corr}^{o} - I_{corr}}{I_{corr}^{o}} \times 100\% \qquad Eq. S1$$

$$\eta_{EIS} = \frac{R_p - R_p^o}{R_p} \times 100\% \qquad Eq. S2$$

Where η_{Tafel} and η_{EIS} mean the corrosion inhibition efficiency associated with Tafel and EIS, respectively. I_{corr} and I_{corr}^{o} represent the corrosion currents that are obtained with and without corrosion inhibitors, respectively. R_p and R_p^o represent the polarization resistances that are achieved with and without corrosion inhibitors, respectively. Since corrosion inhibitors has a dominant effect on both passivation film resistance (R_{pf}) and charge transfer resistance (R_{ct}), R_p should be the sum of them.

3. Theoretical calculations

ESP and Huckel charges were investigated via density functional theory (DFT) calculations using the Gaussian 16 software package, with the B3LYP hybrid exchange-correlation functional consistently adopted across all calculations. The geometries of all studied compounds are first optimized at the def2-SVP basis set level, followed by vibrational frequency analyses to confirm the absence of imaginary frequencies and obtain converged equilibrium configurations. The energy accuracy is refined through single-point calculations at the singlet electronic state, which are subsequently performed using the larger def2-TZVP basis set. Dispersion interactions are rigorously addressed through the DFT-D3(BJ) method, incorporating Becke-Johnson damping for improved treatment of long-range non-covalent forces. The Multiwfn software package is then utilized to compute frontier molecular orbital energies and generate three-dimensional electrostatic potential (ESP) surface maps for the purpose of electronic property analysis.

The adsorption energies of benzotriazole (BTA) derivatives on the Cu_2O (111)

surface were investigated via density functional theory (DFT) calculations using VASP 6.3.0. Since the surface of copper (Cu(0)) is rapidly oxidized to form a Cu_2O layer (Cu(I)), this oxide layer will keep covering the Cu(0) surface during the CMP process. Therefore, the corrosion inhibitor is more likely adsorbed on the surface of Cu_2O rather than on Cu(0) in the copper CMP process. Thus, Cu_2O was used in density functional theory (DFT) calculations. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was employed for the exchange-correlation potential, while the RPBE functional was used to describe exchange-correlation interactions. The Projector Augmented Wave (PAW) method was utilized throughout the study. Structural optimizations were performed with a 4 × 4 × 1 k-point grid for Brillouin zone sampling, and a supercell of dimensions 18.0 × 18.0 × 31.0 Å with angles of 90° × 90° × 120° was employed to accurately model the Cu_2O (111) surface. A plane wave cutoff energy of 450 eV and a smearing width of 0.2 eV were set, with a self-consistent field (SCF) convergence criterion of 10^{-5} eV. A significant vacuum region was included to avoid spurious interactions. The adsorption energies were calculated through first-principles simulations, involving adsorption cell setups and subsequent geometric optimizations, with Van der Waals forces being explicitly considered in the entire calculation process. The octanol-water partition coefficient (log P) of three inhibitors is calculated by chemdraw.

4. Operation of chemical mechanical planarization

CMP experiments are performed on an UNIPOL-1202 polishing apparatus (Shenyang Kejing, China) utilizing a satin-frosted leather polishing pad (30 cm in diameter). The platen speed is maintained at 120 rpm, and the down pressure is approximately 2.5 psi. Prior to the start of the CMP, moisten the polishing pad with slurry, and then the flow rate of slurry is kept at 1.5 mL min^{-1} during CMP experiment. Three samples are polished simultaneously as a parallel control group for 2 h. Subsequent to polishing, the samples are cleaned and dried using distilled water and compressed air, respectively. The materials removal rate (MRR) is calculated according to the following equation:

$$MRR = \frac{\Delta m}{\rho \times s \times t} \qquad Eq.S3$$

Where Δm stands for the mass loss of copper wafer after CMP, ρ means the density of copper (8.96 g cm^{-3}), s is the area of the copper substrates, and t stands for the operation time of CMP.

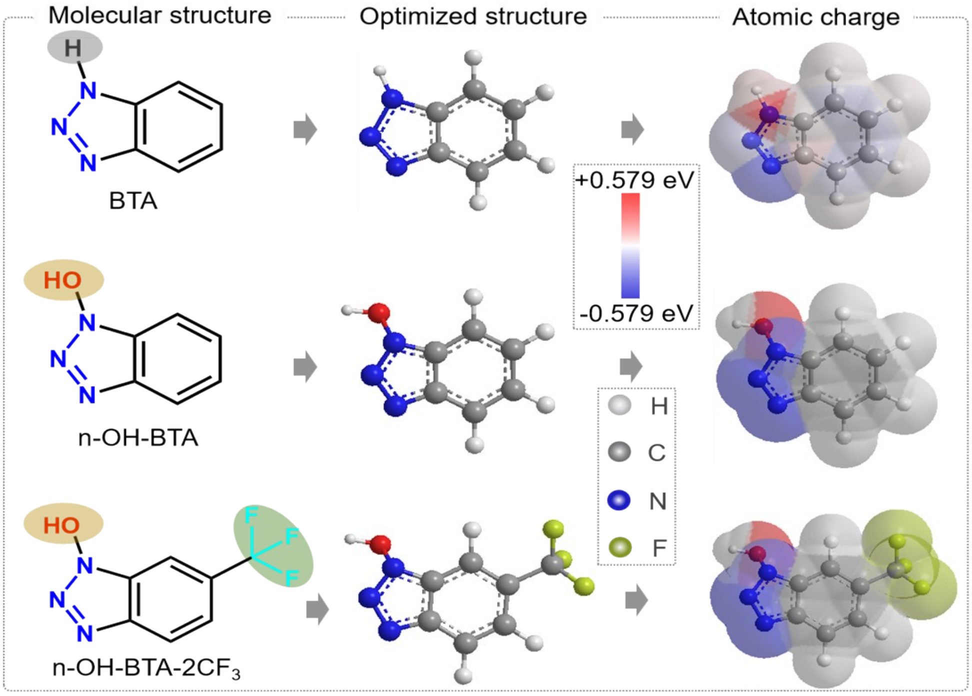

Fig. S1. The optimized structures of BTA derivatives using MM2 Algorithm with minimum energy, and the corresponding atomic charges distribution of BTA derivatives.

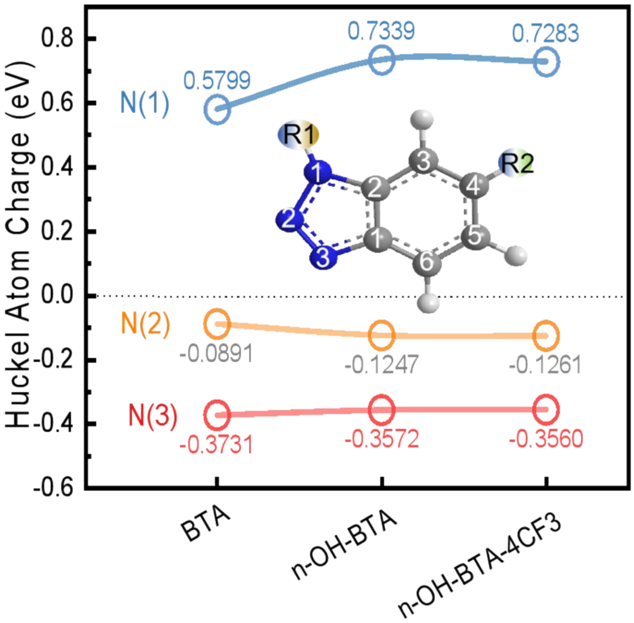

Fig. S2. Charge distribution of N atoms within BTA derivatives.

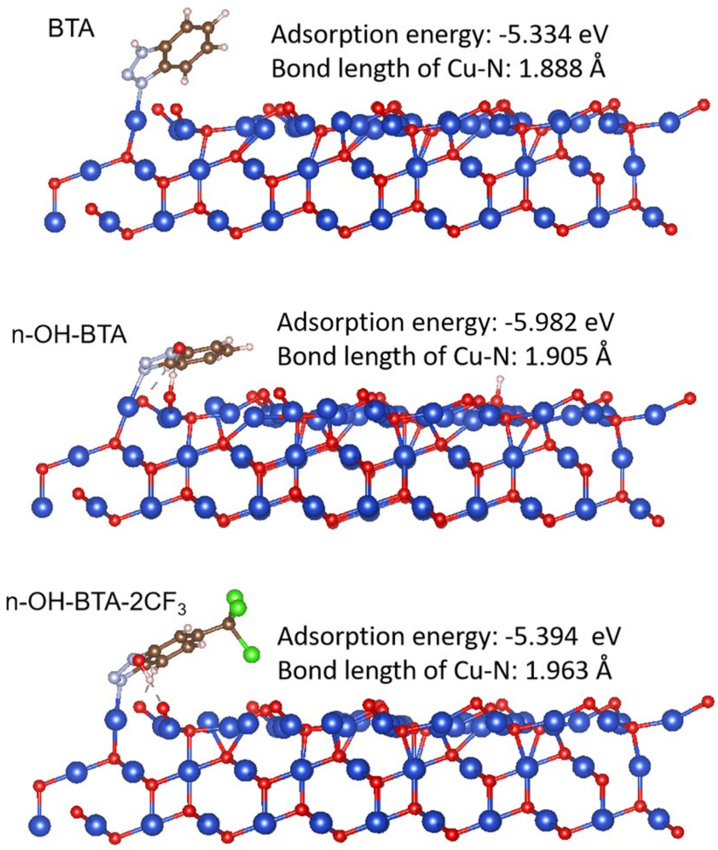

Fig. S3. Adsorption energies and Cu-N bond lengths obtained by first principles calculations.

Table S1. AC impedance and tafel fitting results for different BTA derivatives.

Inhibitos	W/O	BTA	n-OH-BTA	n-OH-BTA-4CF$_3$
R_{pf} (Ω)	318.5	3753	498	856.4
R_{ct} (Ω)	521.2	9356	1631	1820
R_p (Ω)	839.7	13109	2113	2676.4
η_{EIS}	-	93.6%	60.3%	68.6%
I_{corr} ($\times 10^{-6}$ A)	42.25	2.073	16.63	9.523
η_{Tafel}	-	95.1%	60.6%	77.5%

Table S2. The octanol-water partition coefficient of different BTA derivatives.

Inhibitos	BTA	n-OH-BTA	n-OH-BTA-4CF$_3$
logP	1.04	0.51	1.78