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A DFT Model Study about Structure Sensitivity for Benzotriazole Adsorption on Copper Surfaces and Nano Cluster

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Abstract—**As an outstanding corrosion inhibitor for copper, the adsorption behavior of benzotriazole on copper nano cluster has been investigated and compared with copper (111), (100) and (110) surfaces by means of density functional theory (DFT) calculations. Calculations reveal that benzotriazole has chemical adsorption on different copper surfaces and copper nano cluster when its N2-N3 bond is placed down on them. Also, the adsorption energy and closest interatomic distance show strong dependence on the surface structure, which indicates its ability to passivate the reactive under-coordinated surface sites. Relatively strong chemical bond between the copper cluster and the adsorbate is found to form. The chemisorption mechanism and the local structure of benzotriazole on copper surfaces and nano cluster are also discussed and presented.**

Keywords—DFT, benzotriazole, copper cluster, adsorption, surface structure

I. INTRODUCTION

As an excellent interconnection media, copper nanoparticles or microparticles have attracted much attention due to its high electrical and thermal conductivity, good resistance to electro-migration, low cost and so on [1]. Thus, constant research about utilizing copper in electrically conductive sintering pastes has been reported [2]. However, copper has its inherent shortcomings facing corrosion and oxidation in air which limit its further application and performance, thus copper corrosion inhibitors seem to be necessary in such conditions. Among numerous possible inhibitors, benzotriazole (BTAH), as a versatile corrosion inhibitor for copper and correspondent alloys, has been widely used in manufacturing industry [3,4,10]. There are a number of reports concerning the nature of BTAH inhibiting behavior, from which it is found that the adsorption of BTAH on copper surfaces plays a crucial role in corrosion prevention [5]. The adsorption structures of BTAH on copper (111), (100) and (110) have been reported by several groups [6,12,13]. To investigate the interaction behavior between adsorbates and nanoparticle surface, cluster model has been used and reported [14,15]. Even the different positions on Cu_2O were also considered [7]. In addition, the adsorption studies on different specific surfaces of many noble metal nanoparticles have been also reported [8, 9]. However, it is a pity that simulation on both BTAH molecule with different down bonds on copper surface and BTAH molecule reacting with copper nano particles has not been reported yet so far. This study is to focus on absorption behavior of different bonds of BTAH molecule on different copper surfaces as well as on copper nano particle or nano cluster.

In this work, to investigate the BTAH adsorption behavior on the copper surface structure of (111), (110) and (100), a DFT method is carried out with the calculation of adsorption energy (E_a) and charge transfer (ΔQ). The electronic property of charge density difference (CDD) and electron localization function (ELF) are also taken into

consideration. Moreover, the cluster composed of 43 Cu atoms is also studied on its interaction with different BTAH molecular orientations such as C-H down, N-H down and N-N down. The study provides the insight of the BTAH as a good surface protectant for copper nanoparticles.

II. THEORY AND SIMULATIONS

All calculations are based on the package of Materials Studio with the code of Dmol^3 and CASTEP. The energy and electrical property of the models are calculated using the generalized gradient approximation (GGA) of Perdew−Burke−Ernzerhof (PBE) for the exchange correlation function [16]. The Grimme method is introduced into this calculation to describe interlayer Van der Waals correction.

The unit cell of different lattice planes is constructed from four layers of Cu bulk. The vacuum distance is set at least 15Å to reduce the periodic interaction between the layers in the vertical direction. Then $3 \times 3 \times 1$ super cell of the Cu substrate is built to simulate the surface of the different Cu planes. As for the model of the Cu particle, we combine 43 copper atoms to represent the 1 nanometer size copper cluster. In our simulation, the energy cutoff and the k-grid mesh are set as 400 eV and $10 \times 10 \times 1$ for structural relaxation respectively. The geometry is relaxed until the total force on each atom is converged within 0.01 eV Å^{-1}. And the tolerance of energy is set as 1.0 e^{-5} eV per atom. The adsorption energy (E_a) is defined by the following formula as in (1) :

$$E_a = E_{substrate/BTAH} - E_{substrate} - E_{BTAH} \quad (1)$$

where $E_{substrate+BTAH}$, $E_{substrate}$ and E_{BTAH} are the total energies of BTAH/substrate system, Cu substrate and BTAH, respectively.

III. RESULTS AND DISCUSSION

To study the interaction between the different planes of Cu with the BTAH molecule, we first optimize the bulk Cu and the lattice parameter of Cu is 3.59 Å, which is less than 1% compared with the experimental value [11]. Then the four layers of (111), (110) and (100) planes are cut off respectively from the optimized bulk Cu. And we get the final super cell of $3 \times 3 \times 1$ with the coverage of 1/16 (ML) to continue our study. There are four different initial sites for the Cu (111) , which are Bridge, Fcc, Hcp, Bridge. However, normally the adsorption strength of top site is larger than the site of Bridge, Fcc and Hcp respectively. Therefore, top site Cu atom interacting with different BTAH (, $C_6H_5N_3$) molecular orientations, as shown in Fig. 1, becomes the main object of this paper for study. Three molecular orientations of the BTAH are considered, including the bond of C-H down, N-H down and N-N down (i.e. N2-N3 in Fig. 1(e)). All of these systems are relaxed in the same method.

As given in TABLE 1, we consider the adsorption conditions of nine models, including detail adsorption energy (E_a), charge transfer (ΔQ) and adsorption distance (d) which is the shortest distance between the adsorbate and the Cu surface. In the case of Cu(111), the adsorption energy for C-H bond on Cu surface is -0.72 eV, which is much smaller than that of N-H (-1.68 eV) and N-N (-1.21 eV). Correspondingly, the ΔQ for N-H (0.034 e) and N-N (-0.104

e) bonds are larger than that for C-H (-0.017 e). It is can be seen that the adsorption for C-H bond may be much weaker than the other two bonds. Furthermore, the closest distance is between Cu and N in the case of N-N bond which is 2.054 Å, close to the chemical bond length between Cu and N (about 2.03 Å). As for the N-H case, the closest distance to the Cu atom is about 2.78Å but from the C atom. With such a long distance, chemical bond is difficult to form in this system. In this case, C atom is the closest to the Cu surface because the BTAH molecule appears nearly parallel to the Cu (111) plane instead of the vertical way at its beginning.
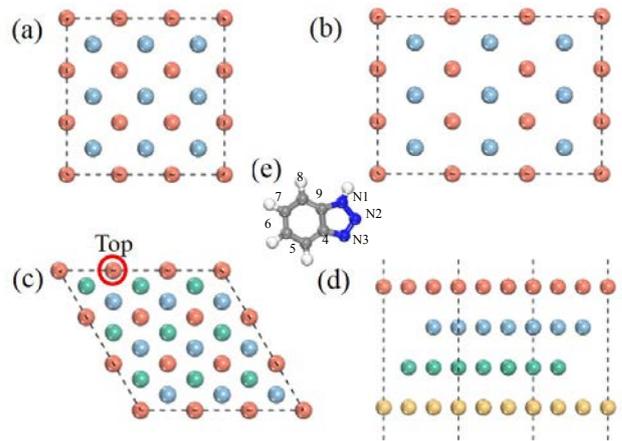
Fig. 1. Top view of (a) Cu(100), (b) Cu(110), (c) Cu(111) surface; (d) side view of Cu(111) surface where the first, second, third and fourth layer are labeled with light red, blue, green and yellow respectively;（e）top view of BTAH molecule.

TABLE 1. Adsorption energy (E_a), adsorption distance (d), and charge transfer (ΔQ) of the three BTAH bonds on the copper surfaces.

Model		E_a (eV)	d (Å)	ΔQ (e)
Cu (111)	C-H	-0.725	2.091$_{(Cu-H)}$	-0.017
	N-H	-1.681	2.783$_{(Cu-C)}$	-0.104
	N-N	-1.217	2.054$_{(Cu-N)}$	0.034
Cu (110)	C-H	-0.549	2.016$_{(Cu-H)}$	-0.091
	N-H	-1.799	2.186$_{(Cu-C)}$	-0.192
	N-N	-1.691	1.986$_{(Cu-N)}$	0.077
Cu (100)	C-H	-0.621	2.051$_{(Cu-H)}$	-0.107
	N-H	-0.639	2.160$_{(Cu-H)}$	-0.143
	N-N	-1.242	2.016$_{(Cu-N)}$	0.105

As for Cu(110), the adsorption energy for C-H, N-H, and N-N on the Cu surface are -0.55 eV, -1.80 eV and -1.69 eV respectively, while the corresponding ΔQ is -0.091 e, -0.192e and 0.077 e respectively. They display the same phenomenon as the Cu(111) where the interaction between Cu plane with N-N and N-H bonds are stronger than with C-H bond. The N-N bond has the smallest Cu-N distance to both Cu(110) and Cu(111) and the Cu(110) has larger E_a and ΔQ than the Cu(111) indicating its strong chemical absorption on the Cu(110) surface. In addition, the C atom is also the closest to the Cu atom with distance of 2.186 Å in the N-H case. However, Cu-C distance is still much larger than their interatomic chemical bond length of 2.05 Å (the sum of radius values of Cu and C atoms). In this case, same as Cu(111), the originally vertical BTAH molecule rotated

towards the Cu surface. The position instability of N-H bond could be caused by non-uniform molecular ring structure of the BTAH. Even though in the parallel position, we could not see a strong bonding of C atom with the Cu surface especially on the Cu(111) surface. The physical absorption rather than chemisorption occurs when the BTAH is nearly parallel with the Cu surface, which may be explained by Cu-d electrons transferring to non-bonding π or anti-bonding π^* orbitals of BTAH [18].

On the surface of Cu(100), both the N-H bond and the C-H bond have weaker adsorption on the Cu surface, while the N-N bond still keep stronger adsorption ability with the absorption energy of -1.242 eV and closest atom distance of 2.016 Å. The two values show that the N-N has chemical absorption on the Cu(100), but weaker than on the Cu (110). The N-N bond shows clear dependence of Cu surface structure in its E_a and d with a trend of Cu(110) > Cu(100) > Cu(111). Well, the ΔQ value is positive for N-N case and negative for C-H and N-H.

According to above analysis, the adsorption lattice plane and molecular orientation both have influence on the adsorption ability between the Cu substrate and the BTAH molecule. The enhanced chemisorption strength on the loosely packed copper crystal planes is likely related to their upshifted energy of the d-band center [12].
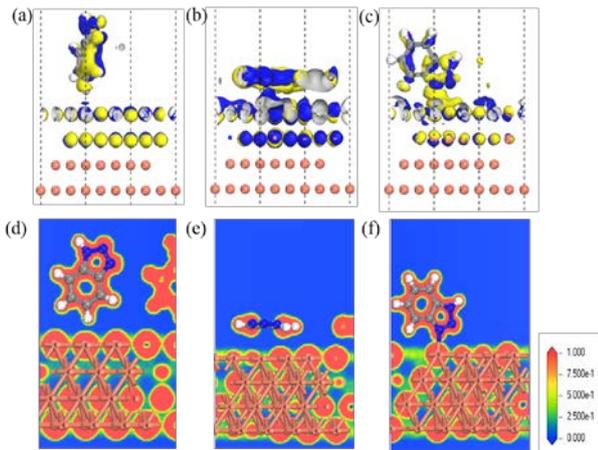
Fig. 2. Charge density difference of (a) C-H, (b) N-H, (c) N-N down bonds on (111) surface. The blue and yellow areas represent where the electron density has been accumulated and dissipated, respectively. The isosurface value is 0.008 e/Å³. Electron localization function of (d) C-H, (e) N-H, (f) N-N on (111) surface, where the red area represent that the electrons are highly localized. The reference bar for the ELF value from 0 to 1 is located on the right side of the figure.

Since the Cu(111) plane is the most densely packed, restructuring generally does not occur. Therefore, we focus on this plane with more specific analysis. As shown in CDD maps (Fig. 2 (a)-(c)), the charge accumulation mainly occurs on the BATH molecule in the N-N, while the BTAH shows the electron consumption in the N-H and C-H, which is in line with the ΔQ value. In Fig. 2(c), the electrons of BTAH and Cu (111) transfer apparently to the area between two layers in the N-N case. Moreover, in Fig. 2(f), there is electron localization between the N and Cu atoms and the orbitals are overlapped, which indicates the formation of chemical bond between them. Inversely, the electron transfer for the N-H is very weak, even there is no obvious charge

transfer between the BTAH and the substrate. Combined with the ELF as shown in Fig. 2(d) and Fig.2(e) where no orbital overlap is seen, we can conclude that the orbits of the copper layer and the BTAH molecule do not hybridize and no chemical bond is formed in the case of N-H and C-H, which is consistent with our previous analysis in this paper.
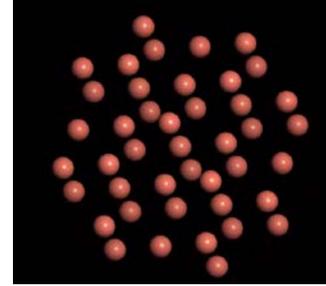
Fig. 3. The Cu nano cluster (Cu₄₃) model used in this study.

Having discussed the adsorption behavior on the Cu surface structure, we now will observe the behavior of a BTAH molecule on a copper-cluster. The Cu₄₃ cluster is constructed in a cubic box of 25 Å to reduce the periodic effect. The cluster is based on 1nm size particle as shown in Fig. 3. The calculation is the same as that used in the adsorption on the surface structure study. The TABLE 2 gives that the E_a of these three bonds are -1.79 eV, -1.41 eV and -2.09 eV respectively. The N-N has more clearly a chemical bond with the Cu cluster surface from its E_a and d values as compared with its absorption on the single orientation crystal planes, while the other two bonds clearly show their non-chemical bond with the cluster surface.

TABLE 2. Adsorption energy (E_a), adsorption distance (d), and charge transfer (ΔQ) of the three BTAH bonds on the cluster Cu₄₃ surface.

Model	E_a (eV)	d (Å)	ΔQ (e)
Cu₄₃-CH	-1.791	3.295 (Cu-H)	-0.047
Cu₄₃-NH	-1.414	2.602 (Cu-H)	-0.199
Cu₄₃-NN	-2.088	1.959 (Cu-N)	0.021

The strong chemical bond between the BTAH and the Cu cluster could be related to the less densely packed planes located on the cluster surface, i.e. (110) and (100) planes as shown in Fig. 4, along with grain boundaries between them on the cluster surface. The N-N distance is slightly longer than typical N=N bond length and chemical bond could be easily formed through nitrogen sp² lone pairs [18]. On the other side, delocalized carbon ring is relatively stable and could be difficult to form chemical bond with the Cu surface. Study on BTAH molecule reacting with Cu clusters of different cluster size including adsorption, desorption and dissociation behaviors would be very interesting and helpful to obtain a copper paste of low sintering temperature.

IV. CONCLUSIONS

In this work, the adsorption of BTAH molecule with different copper surface has been investigated via DFT calculation. The N-N bond shows strong chemical adsorption

on the Cu surface with some dependence of copper surface structure. The lower packing density the crystal plane does have, the higher possibility of forming chemical bond it may have with the BTAH molecule through N2-N3 likely due to delocalized nitrogen sp^2 lone pair. Its bonding strength has the following trend of Cu (110) > Cu(100) > Cu(111). At meanwhile, the C-H and N-H of the BATH are absorbed on the Cu surface through physical absorption. Thus, it can be seen that BTAH has a strong interaction with copper surface due to N-N bond, which makes it become a good candidate for protecting Cu surface. When the N-N bond of BTAH is placed down on the copper cluster surface, a chemical bond of Cu-N is more easily formed between the substrate and the BTAH likely due to (100) and (110) planes located on the cluster surface in this case. Therefore, a Cu nano particle or nano cluster may have different reactions with BTAH molecule based upon different crystal orientations located on its surface. Future effort will be on further study of interacting behavior between BTAH molecule(s) and versatile Cu nano particles using simulation and experiment.
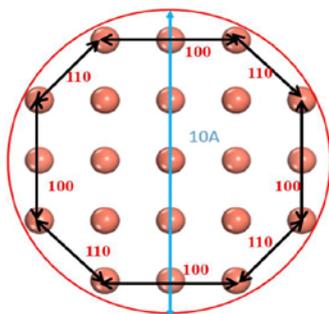
Fig. 4. The crystal planes on the Cu nano cluster surface.

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REFERENCES

[1] A. Fateh, M. Aliofkhazraei and A. R. Rezvanian, "Review of corrosive environments for copper and its corrosion inhibitors", Arabian Journal of Chemistry 2020, 13 (1), pp. 481-544.

[2] A Kokalj, S. Peljhan, "Density functional theory study of ATA, BTAH, and BTAOH as copper corrosion inhibitors: adsorption onto Cu(111) from gas phase", Langmuir 2010, 26 (18), pp. 14582-14593.

[3] M. M. Antonijević, S. M. Milić, M. B. Petrović, "Films formed on copper surface in chloride media in the presence of azoles", Corrosion Science 2009, 51 (6), pp. 1228-1237.

[4] K. Schnabl, et al., "Nanocopper based solder-Free electronic assembly. Journal of Electronic Materials", 2014, 43 (12), pp. 4515-4521.

[5] Y. Jianfeng, Z. Guisheng, H. Anming, Y. N. Zhou, "Preparation of PVP coated Cu NPs and the application for low-temperature bonding", Journal of Materials Chemistry", 2011, 21 (40), pp. 15981-15986.

[6] Y. Y. Dai, et al., "Enhanced copper micro/nano-particle mixed paste sintered at low temperature for 3D interconnects", Applied Physics Letters, 2016, pp.108 (26).

[7] A. Kokalj and S. Peljhan, "Density functional theory study of adsorption of benzotriazole on Cu2O surfaces," Journal of Physical Chemistry C, vol. 119, no. 21, 2015, pp. 11625-11635.

[8] A. Kokalj, S. Peljhan, M. Finšgar, I. Milošev, "What determines the inhibition effectiveness of ATA, BTAH, and BTAOH corrosion inhibitors on copper?", Journal of the American Chemical Society, 2010, 132 (46), 16657-16668.

[9] Li, Y.; Gong, M.; Ramji, K.; Li, Y., "Role of Cu−benzotriazole nanoparticles in passivation film formation", Journal of Physical Chemistry C, 2009, 113 (42), pp. 18003-18013.

[10] S. Kapoor, D. K. Palit, T. Mukherjee, "Preparation, characterization and surface modification of Cu metal nanoparticles", Chemical Physics Letters, 2002, 355 (3), pp. 383-387.

[11] Z. Z Tasic, M. M.Antonijevic, M. B. P.Mihajlovic, M. B. Radovanovic, "The influence of synergistic effects of 5-methyl-1H-benzotriazole and potassium sorbate as well as 5-methyl-1H-benzotriazole and gelatin on the copper corrosion in sulphuric acid solution", Journal of Molecular Liquids 2016, 219, pp. 463-473.

[12] S. Peljhan, A. Kokalj, "DFT study of gas-phase adsorption of benzotriazole on Cu(111), Cu(100), Cu(110), and low coordinated defects thereon physical chemistry", Chemical Physics , 2011, 13 (45), pp. 20408-20417.

[13] F. Grillo, D. W. Tee, S. M. Francis, H. Früchtl, N. V Richardson, "Initial stages of benzotriazole adsorption on the Cu(111) surface", Nanoscale, 2013, 5 (12), pp. 5269-5273.

[14] Z. Hu, R. J. Boyd, "Structure sensitivity and cluster size convergence for formate adsorption on copper surfaces: A DFT cluster model study", Journal of Chemical Physics, 2000, 112 (21), pp. 9562-9568.

[15] H. T. Chen, J. G. Chang, S. P. Ju, H. L Chen, "Ethylene epoxidation on a Au Nanoparticle versus a Au(111) surface: A DFT Study", Journal of Physical Chemistry Letters", 2010, 1 (4), pp. 739-742.

[16] J. P. Perdew, K. Burke, M. Ernzerhof, "Generalized gradient approximation made simple", Physical Review Letters, 1996, 77 (18), pp. 3865-3868.

[17] Q. Zhou; et al., "Highly selective adsorption on SiSe monolayer and effect of strain engineering: a DFT study," Sensors, 2020, vol. 20, no. 4, p. 977.

[18] Y. Jiang, J. B. Adams, "First principle calculations of benzotriazole adsorption onto clean Cu(111)", Surface Science, 2003, 529, pp. 428-442.