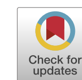
Computational Materials Science 147 (2018) 95–102

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

A comparison of typical additives for copper electroplating based on theoretical computation



Zhiqiang Lai [a], Shouxu Wang [a], Chong Wang [a], Yan Hong [a], Guoyun Zhou [a], Yuanming Chen [a], Wei He [a,c,*], Yongqiang Peng [b], Dingjun Xiao [c]

[a] State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China
[b] Research and Development Department, Netron Soft-Tech (Zhuhai) Co., LTD, Zhuhai 519040, China
[c] Research and Development Department, Guangdong Guanghua Sci-Tech Co., Ltd., Shantou 515000, China

A R T I C L E I N F O

Article history:
Received 8 July 2017
Received in revised form 18 October 2017
Accepted 27 November 2017

Keywords:
Additives
Copper electroplating
Quantum chemistry
Molecular dynamics simulation

A B S T R A C T

Electronic parameters of four additives for copper electroplating including accelerators, mercaptopropane sulfonic acid (MPS) and bis-(acid-sulfopropyl)-disulfide (SPS), inhibitor polyethylene glycol (PEG)and leveler Janus Green B (JGB). They were computed by using DFT/B3LYP method based on the 6-311G + (d, p) basis set. The quantum chemical parameters, which were most relevant to the interaction between the additives and copper surface, were calculated in the gas and aqueous phases for comparison. The condensed Fukui function analysis, molecular electrostatic potential plots and the average local ionization energy plots were applied to predict the most active site(s) of those molecules. Molecular dynamic simulations were also employed to examine the adsorption energies and the adsorption configurations of these additives on Cu (1 1 1) surface under the water environment at 298 K and 323 K conditions. As a result, compared with the other additives in copper electroplating, the unsaturated functional group is an essential factor to levelers. Hence, we predict a novel additive structure according to our calculation results.

© 2017 Published by Elsevier B.V.

1. Introduction

By copper electroplating, the metallization of the micro-vias and through-holes plays an important role in interconnecting the layers of multilayer printed circuit boards (PCBs). Subsequently, the reliability of PCBs depends on the properties of the plating layers [1,2]. An effective method to obtain qualified plating layer is introducing multiple additive-system composing three parts [3]: (1) Accelerators, such as mercaptopropane sulfonic acid (MPS) and bis-(acid-sulfopropyl)-disulfide (SPS), (2) Inhibitors, such as polyethylene glycol (PEG), (3) Levelers, such as Janus Green B (JGB) [3–5].

However, the current additive-system could not meet the future manufacture demands, such as PCBs with high aspect ratio through-holes. Therefore, there is an urgent demand of better performance additives. However, it is a significant challenge to obtain novel additives by traditional experimental methods which are a time and money consuming work. And what really matters in designing novel additives is to figure out their mechanisms in copper plating. The inhibiting mechanism raised by Yokoi [6] was well acknowledged that the oxygen atom of PEG coordinated with a Cu^+, which also coordinated with a Cl^-. And the adsorption of Cl^- on copper surface led to the inhibition of PEG. For accelerating mechanism, Dow et al. [7] claimed that the —SH group of MPS could chemically adsorb on copper surface. Then the $—SO_3$ group would attract the Cu^{2+} to approach the cathode to accelerate the reduction with the assistance of Cl^-. However, it is difficult to investigate the leveling mechanism on the basis of the complex structure of the leveler. Li et al. [8] hypothesized that what really works in leveling was the decomposition products of JGB instead of JGB itself. The mechanism was the N═N group of JGB was prone to electro-reduction at high current density region, leading to a complete electro-reduction with the copper ions. The slowly electro-reduction rate of copper ions at high current region was crucial for an equipotential deposition which led to obtain a uniform deposition layer. But neither consumption of JGB nor current efficiency of copper deposition supports this conclusion.

Quantum chemical methods are ideal tools for investigating electronic parameters, which are relevant to the reactivity of additives. These methods are adept in interpreting the adsorption behavior and detecting the interaction between different mole-

* Corresponding author at: State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China.

E-mail address: heweiz@uestc.edu.cn (W. He).

https://doi.org/10.1016/j.commatsci.2017.11.049
0927-0256/© 2017 Published by Elsevier B.V.

cules [9]. Over the last two decades, Quantum chemical calculation has been widely applied in varied fields, especially in the study of metal corrosion inhibitors [10]. Density functional theory (DFT) has been well accepted as an appropriate and inexpensive method to predict the properties of molecules in various chemical systems because of its accuracy and rapidity of calculation [11]. Meanwhile, molecular dynamic (MD) simulation is another effective tool to evaluate the addictive-metal-surface interaction and to explain the experimental results [12]. Recently, Wang et al. [13] used DFT to calculate JGB and Safranine T (ST). They concluded that JGB performed stronger adsorption on copper surface and the N=N region of JGB was the probable reactive site for the adsorption on the copper surface by comparing their frontier molecular orbitals (FMO) and Fukui function distributions. In addition, they claimed quantum chemical calculation would be used as a powerful tool for screening additives for electroplating. However, only calculating the leveler (JGB) is not sufficient to understand the complex synergistic mechanism of additives. Considering that the results of condensed Fukui function based on various atomic charge are quite diverged on determining the reactive sites, we choose Hirshfeld charge to calculate condensed Fukui function whose rationality and accuracy has been verified [14]. What's more, Zhang et al. [15] used DFT and MD to verify the practicability of using 4, 6-Dimethyl-2-mercaptopyrimidine as a potential leveler. Lei et al. [16] used DFT to compare three tetrazole derivatives (TDs), concluding the energy gaps (ΔE) of TDs correlated negatively with $\Delta\eta$. Therefore, quantum chemical methods are practicable to investigate the mechanisms and to help to design novel additives.

The electrochemical behaviors of additives in copper electroplating have been investigated extensively by electrochemical and spectrum methods [17–27]. However, the explanation of the electrochemical observations is lack of theoretical support. Thus it is necessary to investigate the basic properties of these three typical types' additives. Below, some crucial issues have been discussed: (1) The properties of these four molecules (MPS, SPS, PEG and JGB) relating to their effects. (2) The preferred reactive sites relating to their synergistic effect, antagonistic effect. (3) The adsorption on Cu surface. This paper, which offers a more detailed insight into the mechanisms of additives in copper electroplating, aims at studying the differences of four additives on the quantum chemical parameters (QCPs), the preferred reactive sites and the adsorption energies on copper surface by calculations based on DFT and MD. Meanwhile, the obtained structure parameters are very useful for us to design the structure of a novel additive. Thus, we predict a novel additive based on our work.

2. Computational details

The calculations were performed using the Gaussian 09 program package [28]. The geometry optimizations were conducted by DFT using B3LYP method and 6-311G+ (d p) basis set [29]. The effect of solvent is necessary to be placed into the computation model since the electroplating always occurs in the liquid phase. Self-consistent reaction field (SCRF) theory [30], with Tomasi's polarized continuum model (PCM), was utilized to perform the calculations in a solution with a uniform dielectric constant of 78.5. The frequency calculations were performed to characterize all structures in energy and achieve the relevant zero point energy. The calculations of Hirshfeld charge, the electrostatic potential (ESP) and the average local ionization energy (ALIE) were performed using Multiwfn program package [31].

It is necessary to illustrate the QCPs which help us to discuss the reactivity of the four molecules. The energies of the highest occupied molecular orbital (E_{HOMO}) and the energies of the lowest unoccupied molecular orbital (E_{LUMO}) of the molecules depend on the ionization potential, IE, and the electron affinity, EA, respectively, by the following two equations

$$IE = -E_{HOMO} \tag{1}$$

$$EA = -E_{LUMO} \tag{2}$$

The absolute electronegativity, χ, the absolute hardness, η, and the global chemical softness S are given in the following equations [32].

$$\chi = \frac{IE + EA}{2} \tag{3}$$

$$\eta = \frac{IE - EA}{2} \tag{4}$$

$$S = (2\eta)^{-1} = \frac{1}{IE - EA} \tag{5}$$

The number of transferred electrons, ΔN, is calculated with the following equation [33].

$$\Delta N = \frac{\chi_{Cu} - \chi_{ad}}{2(\eta_{Cu} + \eta_{ad})} \tag{6}$$

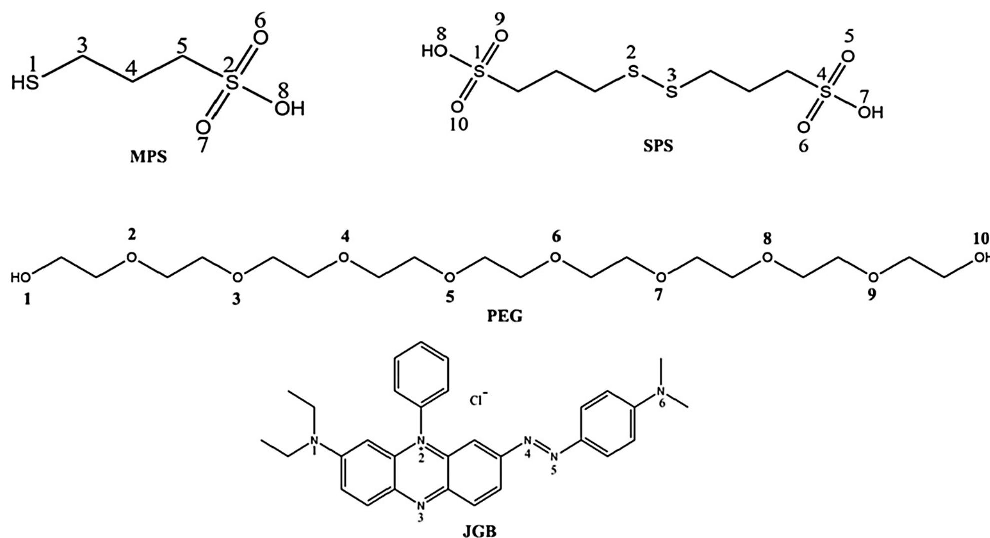


Fig. 1. The molecular structure and atomic label of MPS, SPS, PEG and JGB.

Download English Version:

https://daneshyari.com/en/article/7957741

Download Persian Version:

https://daneshyari.com/article/7957741

Daneshyari.com