

REVIEW

Synthesis and Evaluation of Organic Additives for Copper Electroplating of Interconnects

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Abstract

Copper interconnects are essential to the functionality, performance, power efficiency, reliability, and fabrication yield of electronic devices. They are widely found in chips, packaging substrates and printed circuit boards, and are often produced by copper electroplating in an acidic aqueous solution. Organic additives play a decisive role in regulating copper deposition to fill micro-trenches, and micro-vias to form fine lines and interlayer interconnects. Generally, an additive package consists of three components (brightener, suppressor, and leveler), which have a synergistic effect of super-filling on electroplating copper when the concentration ratio is appropriate. Many works of literature have discussed the mechanism of super filling and the electrochemical behavior of representative additive molecules; however, few articles discussed the chemical structure and preparation of the additives. Herein, this paper focuses on the preparation method and the rapid electrochemical screening of each additive component to provide an idea for the future development of copper electroplating additives.

Keywords: Acid copper electroplating; Copper interconnect; Suppressor; Brightener; Leveler

1. Introduction

The acid copper electroplating with sulfuric acid and copper sulfate systems was first used in 1988 for the metallization of through-holes in double-sided printed circuit boards (PCBs) and followed by a rapid expansion in most of the electronic component industry [1–3]. The acid copper electroplating bath is working at room temperature between 15 and 30 °C, and has high stability, dispersion, and electroplating current efficiency [4,5]. Electrodeposited copper is obtained by acid copper electroplating solution with high purity, good electrical conductivity, excellent extensibility, and high-tensile strength, which is beneficial for signal and power transmission [6,7].

A typical acid copper-plating bath involves organic additives and a virgin make-up solution

(VMS) containing sulfuric acid, copper sulfate, and chloride ions. Furthermore, the organic additive package includes three parts: suppressor, brightener, and leveler [8–10]. By adjusting VMS and organic additives, plating conditions of current density and convection intensity, etc., geometries ranging from tens nm to hundreds μm can be filled during electroplating [11,12]. Copper electroplating technology mainly applies to interconnect fabrication of integrated chips [13], package substrates [14,15] and PCBs [16,17], such as Damascene electroplating [18], Via Filling (VF) [19], Through Silicon Via plating (TSV) [20], Copper Pillar plating [21], Through Hole Filling (THF) [22], High Aspect Ratio TH plating (HAR) [23], Panel Plating, Pattern Plating and so on.

Several mg/L amounts of organic additives in the bath significantly change electrochemical

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behaviors and properties of the deposited copper. Organic additives not only reduce surface profile and exhibit mirror brightness on the macroscopic scale, but also present the micro-leveling ability to fill micro-nanostructured vias and trenches. Thus, organic additives have always been the core research and development subject of copper electrodeposition [24–30]. However, academic papers currently focus on the mechanism of super-filling, electrochemical properties of typical additives, analytical methods, interfacial interaction mechanisms, etc. [31–39], few of them has introduced chemical structure and synthesis of advanced organic additives. Most additives are monopolized by a few American and Japanese companies [40,41].

By collating academic papers and patents, and combining the authors' decades of developing copper plating additives, this paper summarizes the latest and most comprehensive synthesis and evaluation methods of acid copper additives, which might provide reference to the development of copper plating organic additives.

2. Suppressor

Previous research reveals that the adsorption of suppressors on copper surfaces in chloride ion-free plating solutions is electrostatic, showing potential-dependent characteristics. However, when chloride ion exists, the suppressor exhibits good inhibition properties and effectively prevents copper electrodeposition on the cathode [42,43]. Suppressors are mainly polyethers (PEG, PPG, EO/PO), as illustrated in Fig. 1 [44]. Epoxides (EO, PO, BO, etc.) are used as raw materials for the preparation of polyethers [45].

In previous studies, the molecular weight, arrangement, ratio of EO and PO groups, and end-capping functional groups are the most crucial impacts on the electrochemical performance of a suppressor. The research and development of novel suppressors are also mainly focused on these points.

The methods for polymerization of polyether include oxyanions polymerization [46], coordination polymerization [47,48] and cationic polymerization (Fig. 2) [45]. Among the above methods,

oxyanions polymerization commonly adopts to synthesize PEG, PPG, and EO/PO of low molecular weight (MPPG $w < 15,000 \text{ g}\cdot\text{mol}^{-1}$, MPEG $w < 50,000 \text{ g}\cdot\text{mol}^{-1}$, MEO/PO $w < 5000 \text{ g}\cdot\text{mol}^{-1}$). Oxyanion polymerization uses nucleophiles (alkali metal hydrides, alkyls, aryls, hydroxides, alkoxides, and amides, etc.) and polar non-protonic solvents (tetrahydrofuran, dioxane, dimethyl sulfide, etc.) to drive the reaction. And it is necessary to add a modicum of phosphate, oxalic acid or other reagents to terminate the polymerization reaction [49]. Target production obtained by oxyanion polymerization is a hydroxyl group at one end. And the other end group is determined by the structure of the initiating system. Different initiation systems and reaction conditions (temperature, pressure, reaction solvent, etc.) significantly affect the activity and the degree of oxyanion polymerization. The molecular weight and dispersion coefficient of PEG, PPG, and EO/PO can alter by changing the initiation system and reaction conditions.

Due to the limitations of the oxyanions polymerization, the higher molecular weight polyethers with narrow dispersion coefficients can be prepared by coordination polymerization [45,47]. Catalysts used for coordination polymerization include organometallic compounds, protic compounds containing active metal-heteroatom (Mt-X, Mt=Al, Zn and Cd, and X = O, S, N, Cl) bonds, porphyrin salts (Al and Zn), double metal cyanide complexes, alkali metal derivatives, quaternary onium salts, and phosphazene bases. However, most of the catalysts for coordination polymerization are high-cost, hardly stored, and tough to remove from the target polymer. These drawbacks limit the commercial application of the coordination polymerization technique. Besides oxyanions polymerization and coordination polymerization, polyether can also be synthesized by cationic polymerization. It is worth noting that cationic polymerization is rarely used for the polymerization of EO or PO caused by the formation of considerable amounts of cyclic polyether byproducts. And it is more commonly used to prepare commercial poly(oxyethylene). In conclusion, classical oxyanion polymerization is still superior to all other controlled or living polymerization techniques.

Inhibitors have the ability to enhance cathodic polarization and refine the grains of copper deposits, Hull cell electroplating and electrochemical experiments are generally employed to evaluate suppressor candidates. The plating bath of Hull cell electroplating contains $0.5\text{--}1 \text{ g}\cdot\text{L}^{-1}$ suppressor in 250 mL VMS. By examining the deposited layer

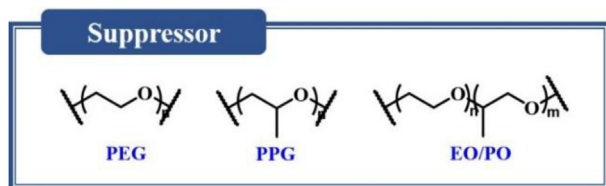


Fig. 1. Chemical structures of common suppressors [44].

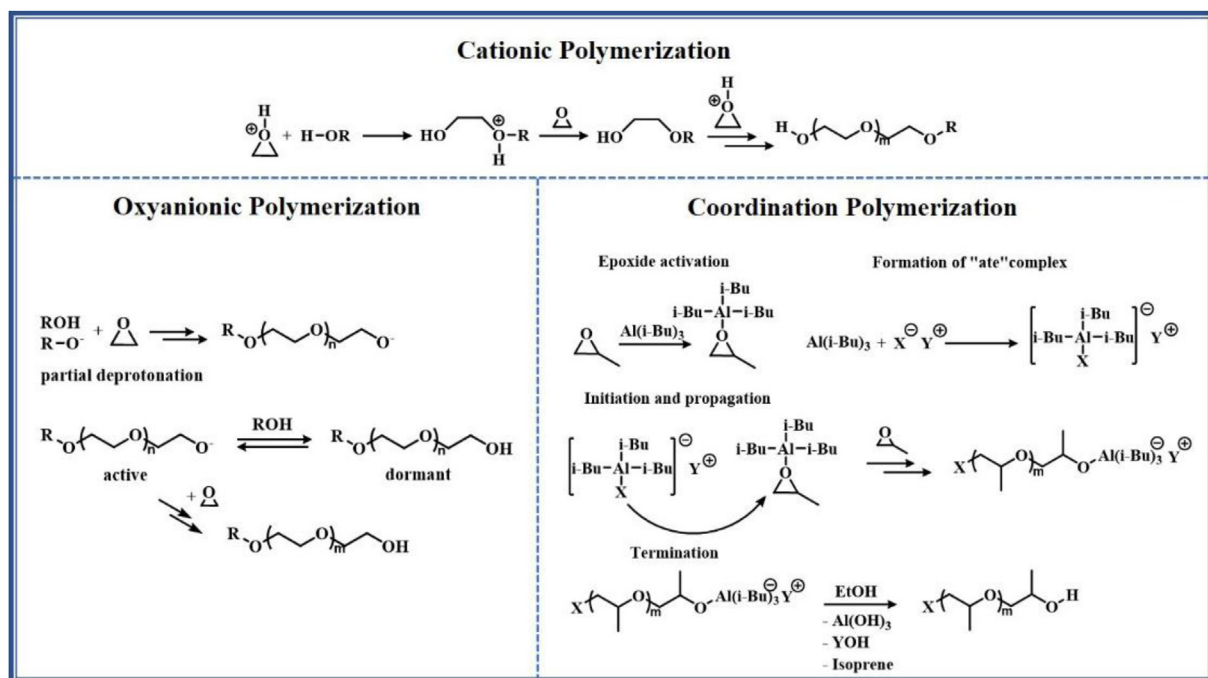


Fig. 2. Three proposed reactions of polyethers reported in the literature [45].

on brass test coupon after 10 min plating at 2A cathodic current, the grain sizes, nodules and width of the burnt area can be evaluated. Further, $1 \text{ mg} \cdot \text{L}^{-1}$ brightener is added to the bath before plating to measure the width of the mirrored bright area. For electrochemical measurement experiments of inhibitor properties, both cyclic voltammetry stripping (CVS) and constant current measurement (GM) methods are appropriate [50,51]. Fig. 3a presents the variation of stripping peak area with the concentration of suppressor candidates and the different inhibitory abilities of some suppressor candidates in CVS experiments.

Fig. 3b plots the over-potential for chrono-galvanometric lines of some suppressor candidates at a constant current density of 2 ASD.

3. Brightener

Brightener, essential for obtaining a mirror-bright coating, is usually an organic compound containing sulfur. In VMS, it courses a weak polarizing effect in the absence of chloride ion (Cl^-) in VMS, but in combination with the suppressor and Cl^- , it shows a depolarizing effect. Therefore, the brightener is also known as the accelerator. Fig. 4 lists some

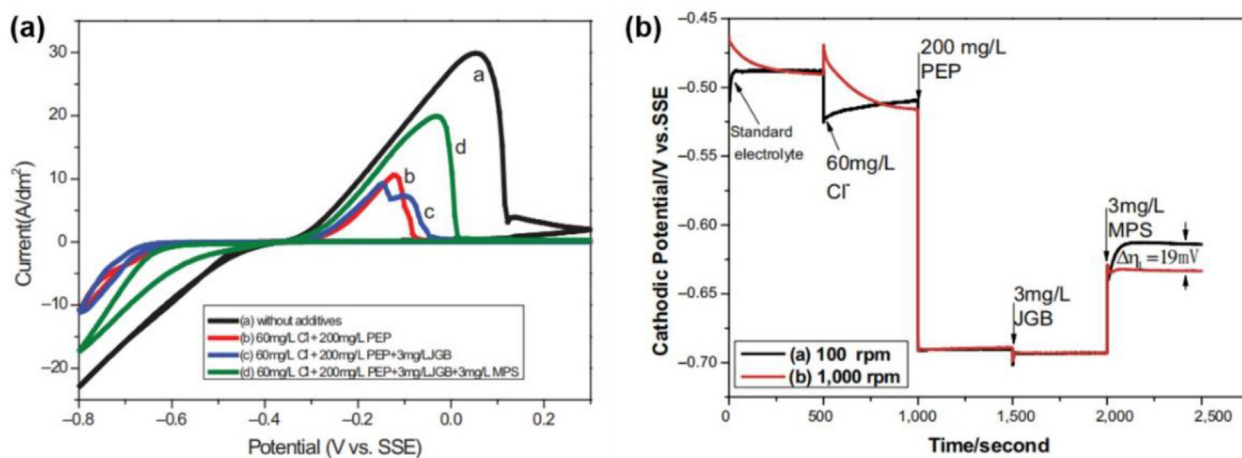


Fig. 3. (a) Cyclic voltammometry stripping (CVS) curves and (b) cathodic potential-time curves by galvanostatic measurement (GM) reported in the literature [51]. Reproduced with permission of Ref. [51], copyright Emerald.

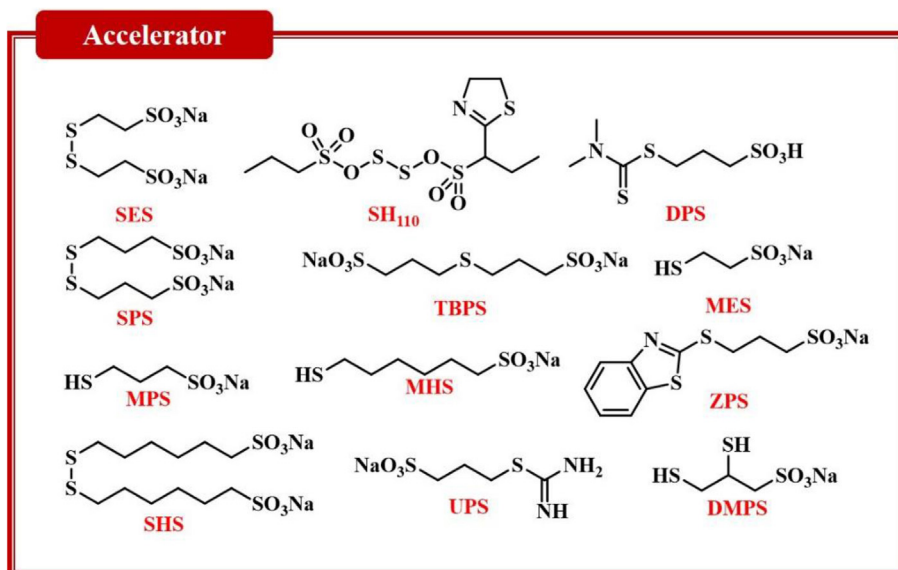


Fig. 4. Chemical structures of accelerators reported in the literature [52–56].

abbreviated names and chemical structures of the brighteners reported in the literature. Among them, Bis-(3-sulfopropyl) disulfide (SPS) is the preferred brightener for acid copper plating baths nowadays, and a few brighteners are derivatives of SPS [52–56]. There are two main synthetic routes of industrial SPS [57].

(1) A sodium disulfide is first prepared by reaction with sodium sulfide and sulfur, and then sodium disulfide reacts with 1,3-propanesulfonic acid lactone to give SPS (Fig. 5a).

(2) MPS is obtained by hydrolyzing thioacetate-functional alkyl sulfonate under acidic conditions, and then SPS is obtained by oxidization of MPS (Fig. 5b).

The first method exhibits the advantages of a simple process and low production cost. Nevertheless, the side reactions occur during the

initiation step (Fig. 5b). Due to the polysulfide impurities, the SPS yield remains at around 80%. The second method provides reasonable product quality for SPS, but the whole process of production becomes complicated, which ultimately reduces the SPS yield (ca. 20%) and increases the production cost. The relevant production route of SPS remains to be further optimized.

Considering the higher yield and more implementable process based on the first synthetic route of SPS, several types of research have been published for this synthetic route and have made some achievements in recent years. For instance, Lu et al. [58] discovers that the disproportionation of the by-product sodium polysulphide with the hydroxide produced sodium persulphide and sodium thiosulphate. Subsequently, sodium thiosulfate reacted with 1,3-propane sulfonate under the

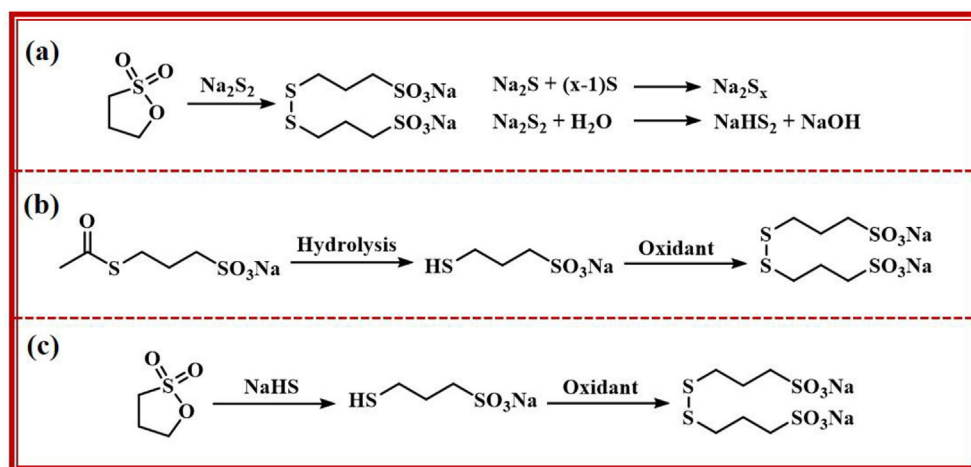


Fig. 5. Three synthesis routes of SPS reported in the literature [57–59].

action of an oxidizing agent to form the target product SPS, resulting in an improved yield of SPS. In addition, sodium persulfide in water undergoes a degree of hydrolysis, and adding sodium hydroxide could inhibit this process and further enhance the productivity of SPS. Song et al. [59] considered that sodium sulfide is prone to oxidation and deterioration in O_2 , replacing sodium sulfide with sodium hydrogen sulfide can avoid this problem. The synthetic route is shown below: MPS is prepared by sodium hydrosulfide and 1,3-propane sulfonic acid lactone, and then oxidized to produce SPS (Fig. 5c). The authors determined that this stable synthetic route has high commercial application value.

The evaluation method of the brightener is similar to that of the suppressor, in which depolarization with the existence of the suppressor on the GM curve and mirrored bright area on the Hull cell plating coupon are the two main indexes. SPS has been mass-produced domestically, which is only about half the price of the Raschig imports from Germany. Although the successful application of SPS retards the global research and development of new brighteners, batch stability and purity of the domestically produced SPS are still an issue, and development of a purification method will be the main subject in the coming years.

4. Leveler

Leveler is the most mysterious and complex part among the additives, which often has nitrogen-

content functional groups and a positive charge in the acid electroplating solution. Leveler also has the property of enhancing polarization of copper electrodeposition, so it is also known as a type II suppressor [60]. However, the most significant difference between a typical leveler and an ordinary suppressor (a type I suppressor) is that the leveler has significant convection-dependent polarization. The polarization of levelers positively correlates with convection. In other words, the leveler is adsorbed on the cathode in the high-density charge region to inhibit copper deposition and level the copper surface profile. The essential role of the leveler in superfilling and its application in advanced interconnect fabrication also has been well studied [61–68]. So far, the leveler can be classified into polyethyleneimine (PEI) and derivatives, organic small molecule levelers, and other polymer levelers (containing electron-absorbing unsaturated bonds). However, the ideal chemical structures and their preparation methods of commercial levelers are still top secrets under the protection of patents.

4.1. Small molecule leveler

Based on the characteristic of molecular structures, organic small molecule levelers involve two categories: non-heterocyclic levelers and heterocyclic levelers (including dyes) (Fig. 7). And some synthesis routes of levelers have been reported in part of the literature displayed in Fig. 6. Due to the high price of synthetic monomers and complex synthesis routes, only a few organic small molecule levelers can be manufactured commercially (such

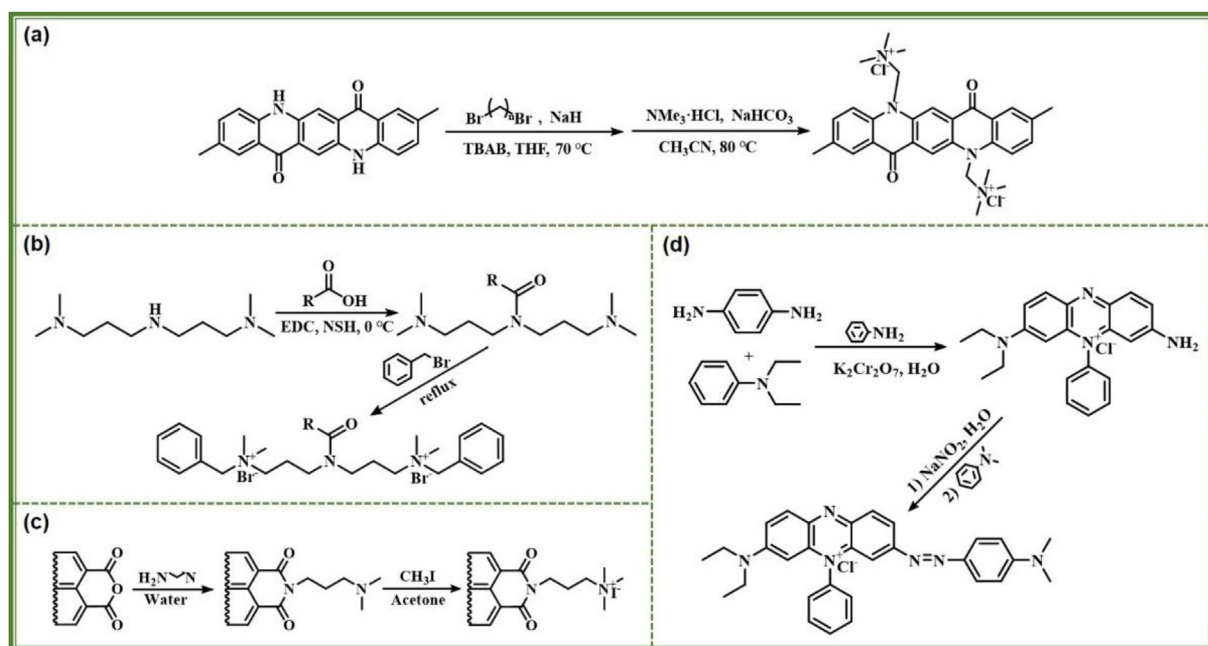


Fig. 6. Some synthetic organic small molecule levelers reported in the literature [61,62,64].

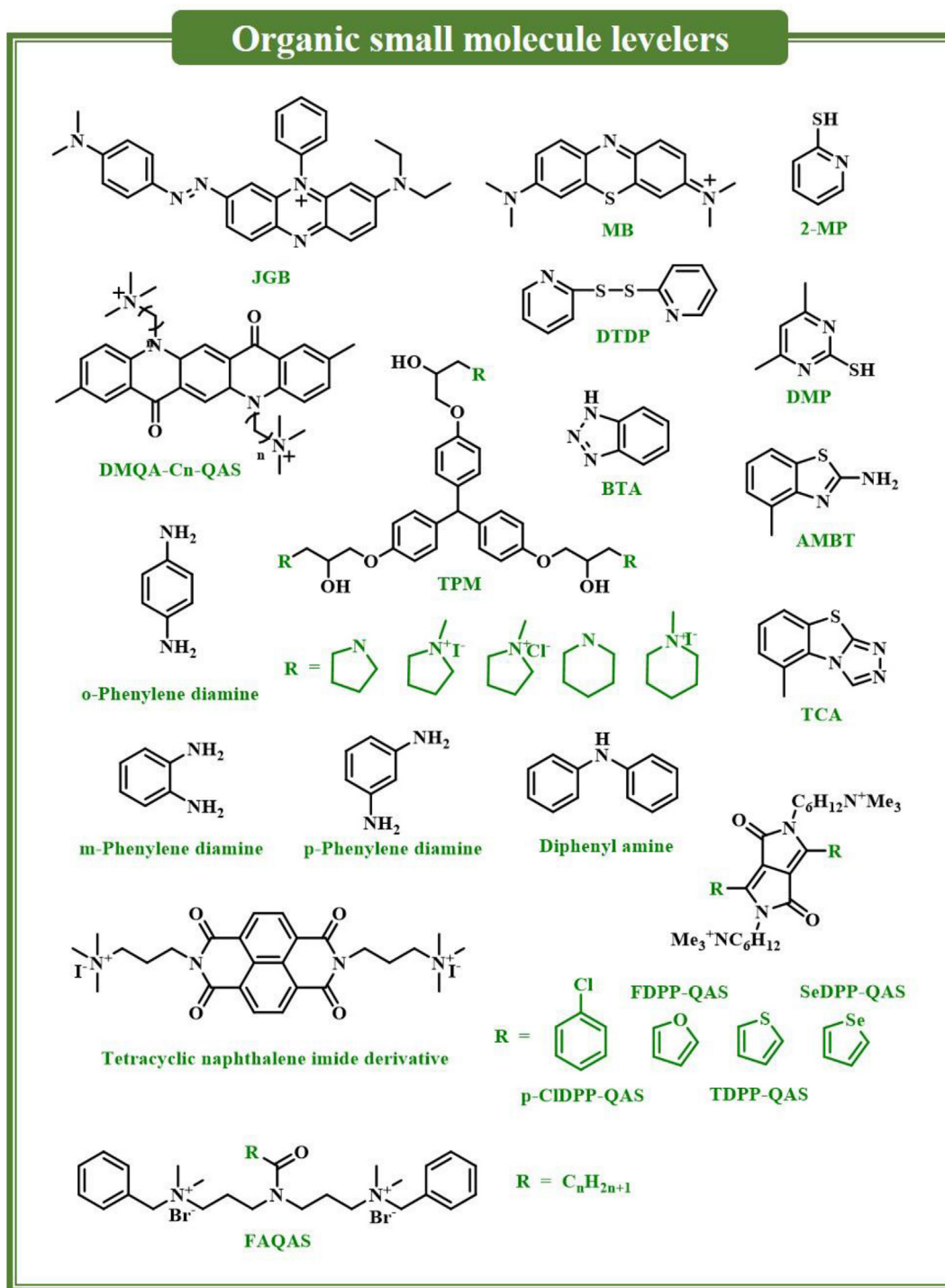


Fig. 7. Chemical structures of organic small molecule levelers reported in the literature [61–68].

as Janus Green Blue, JGB). Hence, the synthesis for organic small molecule levelers does not describe in detail. Up until now, studies related to levelers have focused on JGB. In addition, dye levelers are costly and prone to degradation during the copper electrodeposition, aging the bath solution. Therefore, plenty of novel high-performance levelers candidates are designed and studied.

4.2. Polyethyleneimine and its derivatives

Polyethyleneimine (PEI) is one of the major polymeric levelers used in copper electrodeposition. PEI is prepared by polymerization of ethyleneimine monomer. Based on different approaches of ethyleneimine monomer preparation, synthesis methods of PEI are summarized as follows [69,70]:

(1) The aminoethanol hydrogen sulfate is prepared by a reaction with sodium sulfide and sulfur under the condition of sulfuric acid. Then aminoethanol hydrogen sulfate reacts with sodium hydroxide to obtain ethylene imine aqueous solution. Ethylene imine aqueous solution is added to the reaction and polymerized by introducing hydrogen chloride and carbon dioxide to give an aqueous PEI solution (Fig. 8a).

(2) The ethanolamine hydrochloride is obtained via the reaction of hydrogen chloride and ethanolamine. Subsequently, ethanolamine hydrochloride reacts with sulfoxide chloride to obtain 2-Aminoethanesulfonyl chloride hydrochloride. The product is further treated with alkali to give an aqueous solution of ethyleneimine. And the final product PEI is prepared by ring-opening polymerization of ethyleneimine (Fig. 8b).

(3) Ethanolamine is dehydrated and cyclized to get ethyleneimine, and followed by gas phase polymerization in the presence of an acidic catalyst to give PEI (Fig. 8c).

(4) PEI is prepared by condensation polymerization of ethylene glycol and ethylenediamine under the condition of a transition metal catalyst (Fig. 8d).

(5) Ring-opening polymerization of 2-ethyl-2-oxazoline is initiated by trifluoro methane sulfonate initiator (Fig. 8e).

The above methods obtain various molecular weights of PEI by controlling the reaction conditions (temperature, pressure, and time). Processes (1), (2), and (3) use highly corrosive and toxic ethyleneimine, and these reactions require high-level production equipment. Ethyleneimine also remains in the products and waste solution, which

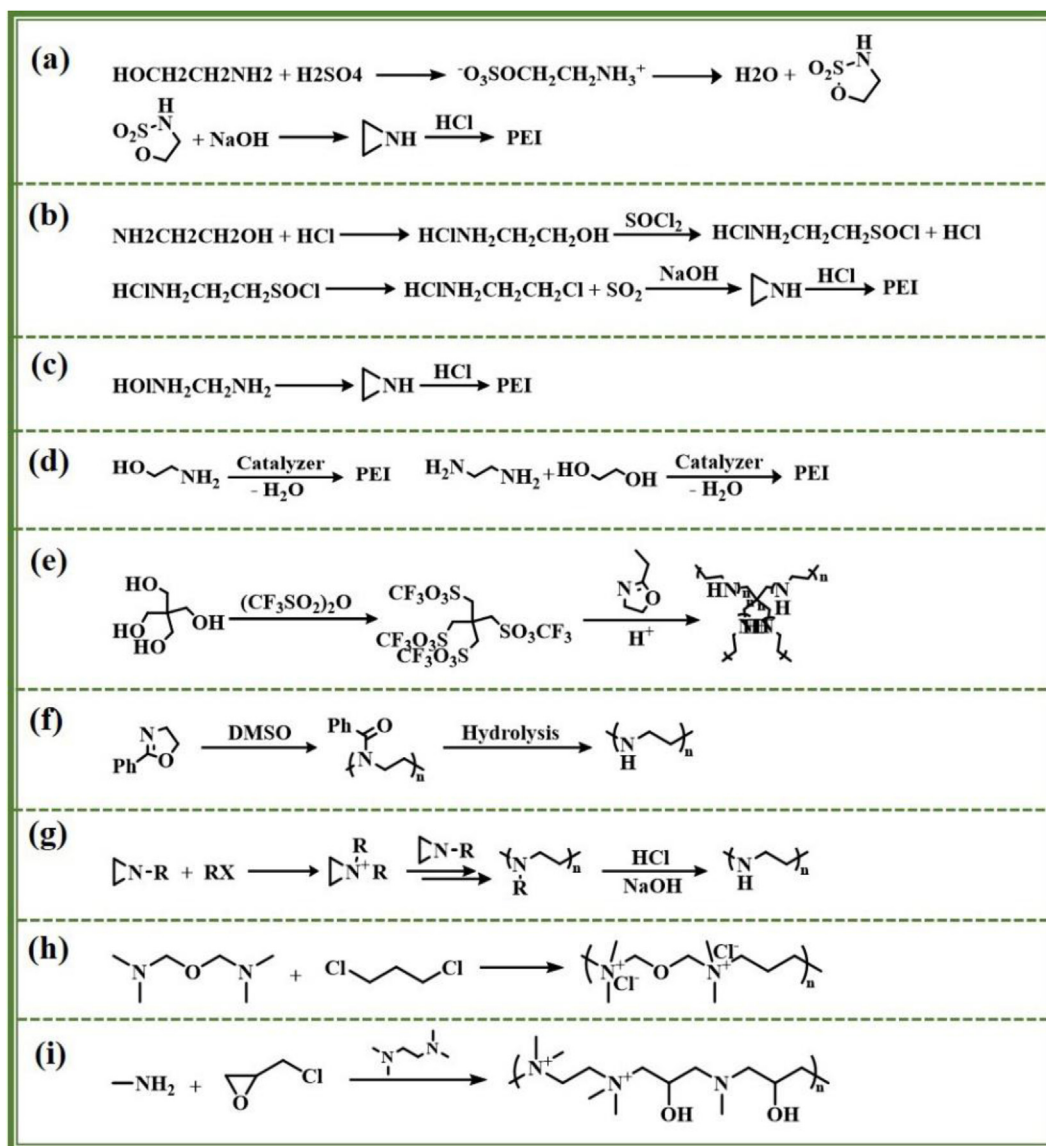


Fig. 8. Common synthesis routes of PEI reported in the literature [69–72].

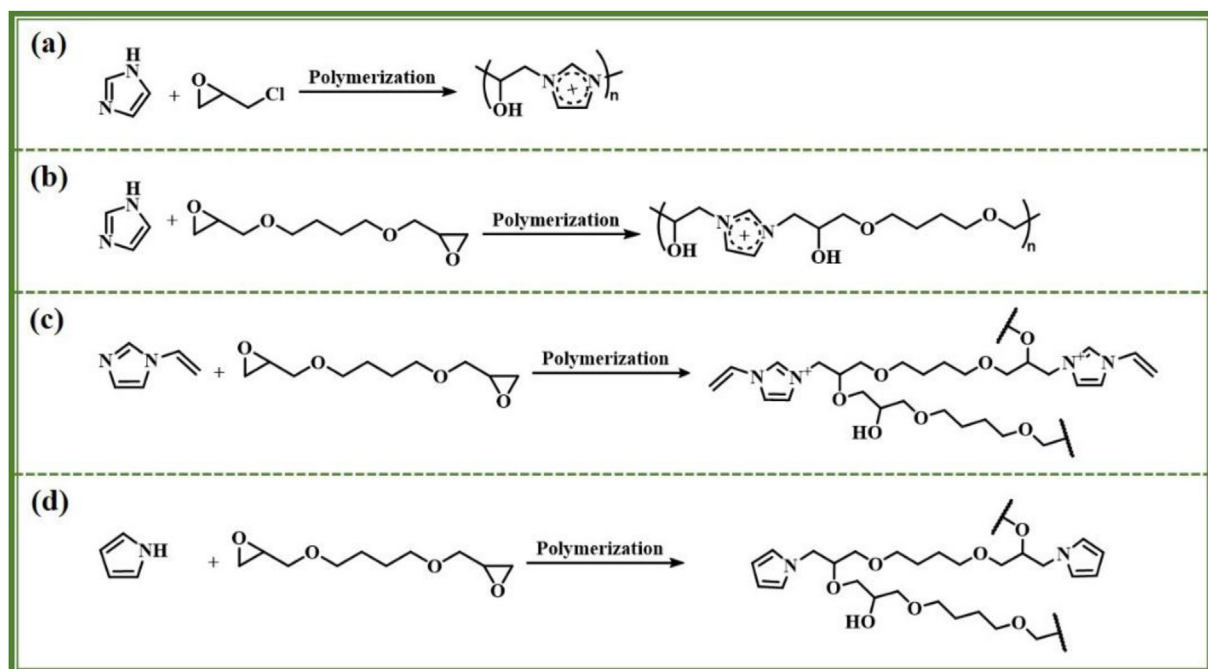


Fig. 9. Some synthesis routes of imidazole polymers and pyrrole polymers reported in the literature [14,77–79].

needs follow-up treatments of the product and waste stream. Besides, cationic ring-opening polymerization of ethyleneimine is uncontrollable, and the main product has a highly branched structure containing primary, secondary and tertiary amino functions. Process (4) avoids the problems posed by ethyleneimine but requires the costly transition metal catalyst for PEI's production, which raises the processing cost of the product. The synthesis of linear polyethyleneimine (LPEI) is summarized as follows [71–73].

(6) 2-Oxazoline undergoes cationic isomerization ring-opening polymerization followed by hydrolysis to give PEI (Fig. 8f).

(7) Polycondensation reaction of N(2-aminoethyl)aziridine in an aqueous medium (Fig. 8g).

Based on the synthetic approach (7) and modification of aziridine structure, PEI derivatives can be obtained with specific functions. Although some literature proves that polyquaternium is an effective leveler in copper plating, it commonly applies in hair conditioners, shampoos, and other detergent products [74,75]. Polyquaternium is mainly prepared by reacting monomers containing tertiary amine groups with dihalide intermediates (Fig. 8h and i) [73,76].

4.3. Other polymer levelers

Aside from PEI and its derivatives, imidazole polymer and pyrrole polymer are other general polymer levelers used in the acid copper-plating

solution. These polymers could be prepared by polymerizations of imidazole/pyrrole monomers and cyclic ether monomers (Fig. 9) [14,77–79]. Due to the high prices of raw materials, complicated synthesis routes, low productivity and other factors, except for some dye levelers and polymer levelers, most levelers could currently only be prepared through the laboratory and cannot be commercially manufactured.

The addition of levelers must not negatively affect the brightness and flatness of the copper layer, and of course, the convection-dependent property is required. More detailed information describing the electrochemical method for evaluating leveler performance by two parameters of potential differences can be found in Reference [15].

5. Conclusions

Due to their ability to influence the microstructure of copper deposits and the macroscopic leveling properties of plating baths, organic additives have received much attention in electroplating. The R&D of a bath formula involves chemical structure design, organic synthesis, electrochemical performance evaluation and electroplating application. It often takes several years to industrialize a new plating bath solution under the cooperation of fine chemicals, solution suppliers and interconnect manufacturers. The study of the chemical structure and preparation process of

organic additives using a systematic approach are essential for further research into the interfacial mechanism of copper electrodeposition and the formulation of an ideal plating bath.

Moreover, the study on the structure-activity relationship between the chemical structure and electrochemical mechanism of the existing organic additives can also contribute to the evolution of other emerging electroplating technologies for the electronic industry, such as single additive copper plating, citrate copper plating, cobalt plating and ruthenium plating.

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铜互连电镀中有机添加剂的合成与分析

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摘要

铜互连是保障电子设备的功能、性能、能效、可靠性以及制备良品率至关重要的一环。铜互连常通过在酸性镀铜液电镀铜实现, 并广泛用于芯片、封装基材和印制电路板中。其中, 有机添加剂在调控铜沉积完成沟槽填充、微孔填充以形成精密线路和实现层间互连方面起着决定性作用。添加剂主要由光亮剂、抑制剂和整平剂三组分组成, 在恰当的浓度配比下, 添加剂对于盲孔超填充具有协同作用。目前, 已报导的文献聚焦于代表性添加剂的超填充机理及其电化学行为, 而对于添加剂的化学结构与制备方法鲜有深入研究。本文重点研究了各添加剂组分的制备工艺和快速电化学筛选方法, 为电镀铜添加剂的未来发展提供理论指导。

关键词: 酸性电镀铜; 铜互连; 抑制剂; 光亮剂; 整平剂