



## Influences of bath chemistry and complexing agent on plating rate in electroless copper methane sulphonate bath

T. Manikanda Kumaran<sup>a</sup>, S. Jothilakshmi<sup>b</sup> and S. Rekha<sup>\*c</sup>

<sup>a</sup>R&D, Bharathiar University, Coimbatore-641 046, Tamil Nadu, India

<sup>b</sup>RMK College of Engineering and Technology, Pudukkottai, Chennai-601 206, India

<sup>c</sup>RMD Engineering College, Kavaraiyattai, Chennai-601 206, India

E-mail: rekhaaperichiappan@gmail.com

Manuscript received online 12 October 2020, revised and accepted 27 November 2020

In electroless bath the ingredient which can change the kinetics of the plating process is called a complexing agent. The complexing agent slows down the rate of deposition and improves the deposit qualities. Diethylene triamine pentaacetic acid (DTPA) is used as complexing agent. It shows high stability and rate of deposition, as it is an octadendate ligand compared to EDTA. The novel electroless plating bath is optimized with copper methane sulphonate, formaldehyde and DTPA as complexing agent and rate of deposition is studied by gravimetry. The formation of complex with metal ion greatly influences reduction of cupric ion in a strong base. The complex formed between ligand and metal ion alters the mixed potential and affects the copper deposition rate. In present study, the new bath is investigated with DTPA and compared with traditional EDTA bath by weight gain method.

Keywords: Electroless plating, copper plating, diethylene triamine pentaacetic acid (DTPA), complexing agent, copper methane sulphonate.

### Introduction

Narcus in 1947 first proposed electroless copper<sup>1</sup> deposition. In 1957 Cahill found the electroless copper plating bath utilizing formaldehyde to reduce cupric ion with sodium, potassium tartarate as complexing agent<sup>2</sup>. Printed circuit board hole metallization technique<sup>3,4</sup> further promoted the considerable improvement in electroless copper plating technology with respect to plating rate and stability of bath. The improvement enhanced its application fields. Electroless copper plating<sup>5,6</sup> is defined as the process of chemical reduction of cupric ions from solution to copper atoms on the activated substrate with the help of the reducing agent. No current is applied in the process. It is an autocatalytic redox reaction where the nascent copper atom deposited act as auto catalyst, thus layer over layer deposition occurs. The nature of plating substrate is not a criterion for electroless plating. Further, the electroless plating can be carried out on substrate with any size, shape and conductivity of the substrate. Another advantage is that it forms uniform depos-

its irrespective of shape unlike electroplating. Hence, electroless deposition is an effective tool, through which noble metal can be plated on substrates like plastics, ceramics etc. Further modified formulations<sup>7,8</sup> recently developed has shown high rate of deposition with high bath stability, thus working under a wide operating range. Its simple technique of forming thin metal film has emerged new way for integrated circuit fabrication and electromagnetic interference shielding. Electroless copper plating process is mainly employed for the manufacture of printed and integrated circuit boards<sup>9-12</sup>, ultra large scale integration (ULSI) circuit applications<sup>13-16</sup> etc.

Methane sulphonic acid (MSA) was first made available commercially by Guertin in 1964<sup>17</sup>. It is considered as a 'green' electrolyte due its readily biodegradable properties and it is easy to store and transport; being environmental friendly as no disposal problems<sup>18</sup>. The high solubility and electrolytic conductivity property of MSA is the attractive features for electroless plating bath<sup>19</sup>. Metallic salts like copper,

nickel, silver, lead shows high solubility in MSA<sup>20</sup>. Further studies have been carried out using copper methane sulphonate for electroless copper deposition<sup>21–23</sup>.

The plating bath mainly contains copper salt, complexing or chelating agents<sup>24–28</sup> for cupric ion complex formation, NaOH or KOH as pH adjuster and a reducing agent. In general well established complexing agent for electroless copper plating baths is ethylene diamine tetra acetic acid (EDTA)<sup>29–31</sup>.

In this present investigation a new electroplating bath based on DTPA as complexing agent was investigated and the bath was compared with traditional EDTA bath. The rate of deposition and deposited metal properties of copper electroless plating is mainly governed by the complexing salt as it performs four<sup>32,33</sup> important functions in the plating bath: (a) it exerts a buffering action that prevents the pH of the bath from changing too fast, (b) prevents the precipitation of copper ions as hydroxides since complexing agents forms complexes with ions, (c) reduces the concentration of free copper ions for deposition and (d) avoids powdery deposit and improves good adherence.

#### Chemical reactions involved:

Electroless copper deposition takes place at pH (>12) with chelated metal and reducing agent.

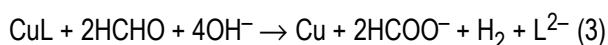
Anodic half cell reaction:



Cathodic half cell reaction: L denotes ligand



Overall reaction:



From the above equation we infer that one mole of deposition of copper, evolves one mole of hydrogen gas. Hydrogen evolution is an integral part of the plating process. And it is found that ductility of electroless plated copper (3.5%) is less than electroplated copper (12.5–16.5%)<sup>34</sup>. This accounted to the entrapped hydrogen molecule in the copper film, as interstitial atom or gas bubbles<sup>35</sup>.

The hydrogen embrittlement leads to change in property like decrease in ductility, tensile strength and density of the deposit. Deposited copper shows a density of  $8.861 \pm 0.012$ <sup>36</sup>, which is less than bulk copper 8.92. Hydrogen occlusion is reported to be high on copper surface than on plastic sur-

faces<sup>37</sup>. Okinaka *et al.*<sup>36</sup> observed two types of hydrogen occlusion viz. diffusible hydrogen and residual hydrogen, in which the residual hydrogen can be removed by annealing at lower temperature of 150°C for 24 h, which improves ductility (6.5%) of the deposits. No change in residual hydrogen is found. It is also observed that with time (6 months) the ductility of copper film increases due to diffusion of copper by interstitial mechanism out of copper film<sup>38</sup>. Thus the plated surface need to be annealed before using it as PCB. The ductility in the range of 4–7% elongation are characterized by crack free deposits<sup>39</sup>. The ductility of the deposits can be increased by the addition of stabilizer, which reduces plating rate<sup>40</sup>. Thus pore, void and crack free deposit is observed in electroless copper deposition. Thin film of copper deposits having ductility in the above said range is acceptable for PCB industries.

## Experimental

### Preparation of stock solution:

To prepare copper methane sulphonate, about 50 g of copper carbonate is weighed and taken in a 500 ml beaker. To this required quantity of methane sulphonic acid is added and approximately 100 ml of water is added and stirred until CO<sub>2</sub> is expelled completely. The suspended impurities present in the solution were removed by filtration. The solution is then made upto 500 ml with distilled water in a standard measuring flask. The solution was stored in a clean closed container. The stock solution was analyzed for the copper methane sulphonate concentration iodometrically.

### Pretreatment of substrate:

The substrate surface pretreatment is essential to ensure good adherence and pore free deposits. In addition to above requirement the surface need to be pretreated to activate the surface for metal reduction reaction preferentially to take place on the substrate surface.

In the present study, the following procedure is followed for pretreatment of copper panel of size 1 sq. inch (both sides) as shown in Fig. 3.

The substrate rubbed with emery to remove oxide layer on the copper surface. It is degreased to remove oil/grease dirt from the surface to ensure adherence. The substrate it dipped in acidified PdCl<sub>2</sub> solution for 30 s for activating the surface. Here the Pd ions get adsorbed on to the surface.

The panel is washed thoroughly to ensure the removal of any excess Pd ion, otherwise it may lead to bath decomposition. Now the substrate is ready for plating.

The following compounds calcium carbonate, methane sulphonic acid, thiourea, DTPA and EDTA, A.R. grade were used in the present study. The structure of DTPA is given below.

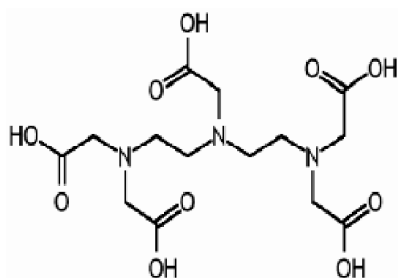


Fig. 1. Structure of DTPA.

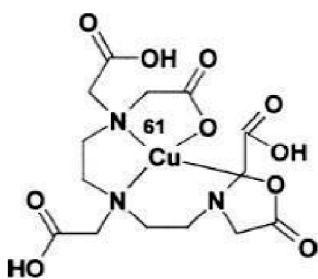


Fig. 2. Structure of Cu-DTPA complex.

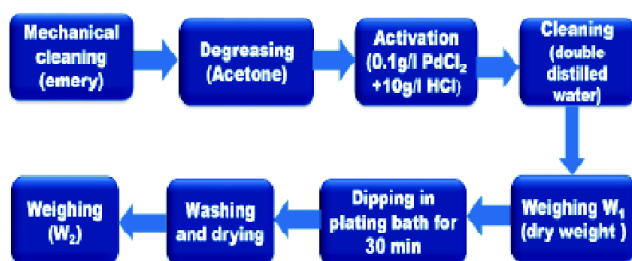


Fig. 3. Procedure for plating.

The optimized bath used in the present study has the following composition.

Copper methane sulphonate – 12 g/L; DTPA – 20 g/L; formaldehyde – 10 g/L;

NaOH to adjust pH.

Experiments were performed at various pH and various concentration of copper. The pretreated and pre weighed panel is immersed in bath for half an hour. The plated panel is removed washed with distilled water, dried and weighed. The rate of plating is calculated from the weight gain of copper deposition. The deposition rate is calculated by using the gravimetric formula.

$$\text{Rate of deposition } (\mu\text{m h}^{-1}) = W \times 10^4 / DA t,$$

where  $W$  = weight gain of the deposit (g)  $D$  = deposit metal density ( $\text{g cm}^{-3}$ );  $t$  = plating period (h);  $A$  = deposited surface of the panel ( $\text{cm}^2$ ). Copper specimens of dimensions  $2.5 \times 2.5 \text{ cm}^2$  were employed for weight gain experiment.

## Results and discussion

### Effect of pH:

The plating was performed at room temperature in various pH ranges 12, 12.5, 13, 13.5 and rate of deposition were calculated and tabulated in Table 1. Both for EDTA and DTPA the rate of electroless plating showed an increase with rise in pH and the bath were also stable. The bath containing EDTA decomposed at pH 13.5 while plating and the bath containing DTPA had some copper nucleation on the wall's of beaker which decomposed when kept overnight. This indicates DTPA is more stabilizing the bath than EDTA. This behavior can be accounted with the number of ligands it possesses. DTPA being octadentate in nature complexes  $\text{Cu}^{2+}$  ion better than EDTA being hexadentate. The stability constant of  $\text{Cu}^{2+}$  ion with EDTA is 18 and DTPA is  $21^{41}$ .

With DTPA as complexing agent, it is found that the deposition rate is greater than the EDTA with better bath stability proving itself to be a good complexing agent for electroless plating. Yi-mao lin and Shi-chen yen<sup>42</sup> in their studies have

Table 1. Rate of copper electroless plating process with pH, at room temperature  $28 \pm 0.2^\circ\text{C}$

EDTA		DTPA	
Rate of deposition ( $\text{mm h}^{-1}$ )	Stability of bath	Rate of plating ( $\text{mm h}^{-1}$ )	Stability of bath
0.53	Stable	0.71	Stable
2.11	Stable	2.50	Stable
3.33	Stable	3.87	Stable
3.52	Decomposes	4.07	Less stable

shown that EDTA has better plating rate than ethylene diamine. This is due to better adsorption of ethylene diamine on the plating surface, hence retarding plating with similar analogy DTPA being larger molecule the degree of adsorption is less compared to EDTA on the metal surface, hence rate of deposition is higher for DTPA.

pH affects copper electroless deposition in two distinct ways. First,  $\text{OH}^-$  ions from eq. (3) act as reactants in the overall reaction and for the partial anodic oxidation reaction from eq. (1) and thus base influence these electroless deposition reactions directly (primary pH effects). In the second way, pH affects various phenomena including (i) adsorption, (ii) the structure of the double layer, (iii) the structure of the copper species in the solution, and (iv) the ionic strength of the solution in an indirect way (secondary pH effects). The primary pH effect is generally expressed graphically as rate of deposition against  $\text{pH}^{43}$ .

Plots of the experimentally observed plating rates against pH show a linear increase initially with a rise of pH with EDTA and DTPA as complexing agent. Above a pH of 13 the rate curve flattens and the bath decomposes. DTPA showing a higher rate of deposition which shows better complexing ability.

*Influence of copper ions concentration:*

The plating was performed by varying the copper ions concentration and the results were shown in Fig. 4. It is found that as the copper ions concentration is increased the rate of deposition increases sharply, but beyond certain concentration, the bath becomes turbid due to the hydrolysis of  $\text{Cu}^{2+}$  ions. It was found that the rate of deposition found to increase with increase in copper ions from 1 g/L to 5 g/L in DTPA and EDTA bath (Fig. 4). With 1 g/L of copper ion in bath gave a non-uniform deposit i.e. patches of copper deposits were observed this is due to insufficient  $\text{Cu}^{2+}$  ion available for plating in the bath. Deposit quality is improved in 2 and 3 g/L with excellent bath stability.  $\text{Cu}^{2+}$  ion with 4 g/L shows poor deposit qualities like partially powdery deposits in both the baths due to higher concentration of copper ion. 5 g/L of  $\text{Cu}^{2+}$  ion shows poor deposit quality as well as poor stability of bath. So the concentration of copper(II) ion was fixed as 3 g/L for further studies. The Fig. 4 shows that DTPA has better deposition rate than EDTA.

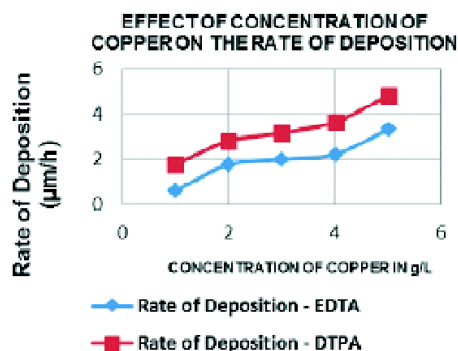


Fig. 4. Rate of copper deposition with varying concentration of copper ions.

*Influence of additive on deposition rate:*

The electroless plating rate of the copper with the thiourea (TU) addition at different concentrations is presented in Fig. 5. It is observed that the deposition rate of the electroless plating process found to increase with the concentration. The curve flattens at higher range indicating that higher concentration it stabilizes the bath. The additive like TU improves the bath stability and also in certain baths accelerate the process at lower concentration and inhibits by its adsorption at the metallic surface<sup>44,45</sup> at higher concentration. Thiourea (TU) has three coordination centers possessing lone pair of electron viz. two N and one S atom, which get adsorb<sup>46,47</sup> to the substrate surface either inhibits or accelerates the process. Han Keping *et al.*<sup>44</sup> proved through XPS analysis that S acts as the dominating coordination center and it can act as an accelerator or inhibitor. In DTPA and EDTA bath thiourea initially accelerate and moves towards stability on increase of concentration. The effect of thiourea

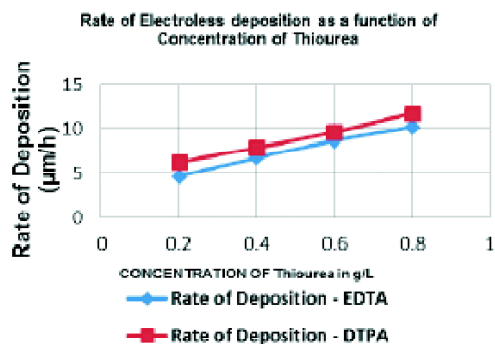
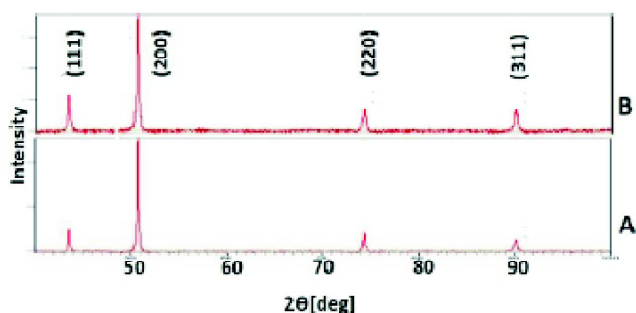


Fig. 5. Copper deposition rate with varying concentration of thiourea.

on both the bath is same, DTPA bath showing increase in rate of deposition than EDTA bath.

*X-Ray diffraction (XRD) patterns:*

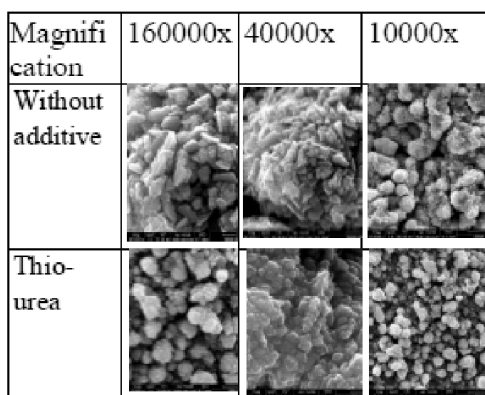
The XRD plot for the copper deposit for thiourea free bath and with thiourea of copper methane sulphonate bath is shown in Fig. 6. The XRD plot shows that the major orientation of copper atom is (200) plane for plain bath and TU added bath; the sharp peak indicates crystalline nature of copper deposit<sup>48</sup>.



**Fig. 6.** XRD plots of copper deposit in (A) stabiliser free bath and (B) with thiourea.

*Scanning electron microscope studies:*

SEM pictures at a magnification of x10000, x40000 and x160000 for electroless copper deposit of specimens with DTPA as complexing agent for plain and TU bath are shown in Fig. 8. The uniform and fine grained deposit surface observed nodular growth of copper crystals in all the specimens. The TU bath shows fine grained deposits than addi-



**Fig. 8.** SEM images with different magnification.

tive free bath. This is due to slowing of the deposition rate. The crystals are organized uniformly and produce smooth deposition on addition of thiourea. The deposits were pore, crack and blister free indicating minimum hydrogen occlusion. The adherence of copper deposits is generally tested with hand scratch test. The deposits showed good adherence.

**Conclusions**

In the present work a new plating bath was formulated and the bath composition and operating conditions were determined in DTPA bath and coherent copper deposits are obtained. As compared with the traditional EDTA plating bath it has equivalent rate of deposition and the following results were obtained:

- (i) The cupric ion concentration has an effect on deposition rate, an increase in free ion increase the rate of deposition but bath stability decreased due to availability of free ion to decompose the bath easily.
- (ii) The electroless copper deposition rate is better at 12.5–13 pH. Above a pH of 13 bath is unstable.
- (iii) Thiourea acts both as accelerator and stabilizer in the electroless copper bath at lower concentration.
- (iv) The optimum bath formulated for DTPA bath can be fixed as 12.5–13.0 pH and cupric ion concentration as 3 g/L and bath stability and rate is increased.
- (v) The study can be further extended by combining the DTPA as a promising complexing agent for electroless copper deposition.

**References**

1. H. Narcus, *Metal Finishing*, 1947, **45**, 64.
2. A. E. Cahill, *American Electrochemical Society Proceedings*, 1957, **44**, 130.
3. R. J. Zeblicky, J. F. McCormack, J. D. Williamson and F. W. Shneble, US Patent, 3,095,309, 1963.
4. S. Shingubara, Z. Wang, O. Yaegashi, *et al.*, Electron Devices Meeting, 2003. IEDM'03 Technical Digest. *IEEE International*. IEEE, 2003, **6.3**, 1.
5. G. O. Mallory and J. B. Hajdu (Eds.), "Electroless Plating: Fundamentals and Applications", American Electroplaters and Surface Finishers Society, Orlando, FL, 1990.
6. J. B. Hajdu, *Plating Surf. Finish.*, 1996, **83**, 29.
7. C. R. Shipley, *Plating*, 1984, **71**, 94.
8. K. F. Blurton and F. J. Nuzzi, *Plating Surf. Finish.*, 1987, **74**, 62.

9. Y. Okinaka and T. Osaka, in: H. Gerischer and C. W. Tobias, "Advances in electrochem Science and Engineering", VCH, Weinheim, 1994, **3**, 55.
10. A. Vaskelis, in: D. Satas and A. A. Tracton (Eds.), "Coatings Technology Handbook", Marcel Dekker, New York, 2001, 213.
11. E. J. O'Sullivan, in: R. C. Alkire and D. M. Kolb (Eds.), "Advances in Electrochem. Science and Engineering", Wiley-VCH, Weinheim, 2002, **7**, 225.
12. A. Vaskelis and E. Norkus, *Electrochim. Acta*, 1999, **44**, 3667.
13. J. W. Schultze and A. Bressel, *Electrochim. Acta*, 2001, **47**, 3.
14. T. Homma, I. Komatsu, A. Tamaki, H. Nakai and T. Osaka, *Electrochim. Acta*, 2001, **47**, 47.
15. T. Hara, S. Kamijima and Y. Shimura, *Electrochem. Solid State Lett.*, 2003, **6**, C8.
16. H. H. Hsu, C. W. Teng, S. J. Lin and J. W. Yeh, *J. Electrochem. Soc.*, 2002, **149**, C143
17. R. Guertin, US Patent. 3,626,004, 1967, assigned to Pennwalt Corporation.
18. M. D. Gernon, M. Wu, T. Buszta and P. Janney, *Green Chem.*, 1999, **1**, 127.
19. D. B. Roitman, J. McAlister and F. L. Oaks, *J. Chem. Eng. Data*, 1994, **39**, 56.
20. Frank C. Walsh and Carlos Ponce de León, *Surface & Coatings Technology*, 2014, **259**, 676.
21. S. Jothilakshmi, *International Journal of Scientific Research and Modern Education (IJSRME)* ISSN (Online): 2455-5630 Special issue (NCRAC-2016).
22. S. Rekha, Published in International Conference on Green technology and environmental Conservation (GTEC-2011), IEEE explore, 2011.
23. S. Rekha, *et al.*, *Materials and Manufacturing Processes*, 2013, **28**, 905.
24. S. Shukla, S. Seal, J. Akesson, R. Oder, R. Carter and Z. Rahman, *Appl. Surf. Sci.*, 2001, **182**, 35.
25. B. Yang, F. Z. Yang, L. Huang, S. K. Xu, G. H. Yao and S. M. Zhou, *J. Electrochem.*, 2007, **13**, 425.
26. J. Li and P. A. Kohl, *Electrochem. Soc.*, 2003, **150**, 558.
27. W. H. Lin, H. F. Chang, *Surf. Coat. Tech.*, 1998, **107**, 48.
28. Y. J. Zheng, W. H. Zou, D. Q. Yi, Z. Q. Gong and X. H. Li, *J. Cent. South. Univ. Tech.*, 2005, **12**, 82.
29. R. E. Acosta and L. T. Romankiw, The Electrochemical Society Extended Abstract, Atlanta, Georgia, Oct., 1977, **77-2**, 9-14, Abstract 277: 736-738.
30. M. Paunovic, *Plating*, 1968, **55**, 1161.
31. M. Paunovic, *J. Electrochem. Soc.*, 1978, **125**, 173.
32. Marc J. Madou, *Manufacturing Techniques for Microfabrication and Nanotechnology*, 2011, **2**, 547.
33. Manish Roy, *Surface Engineering for Enhanced Performance against Wear*, 2013, 198.
34. Jack W. Dini, *Electrodeposition - The Material Science of Coating and Substrates*, 1993, 33.
35. S. Nakahara and Y. Okinaka, *Materials Science and Engineering A*, 1988, **101**, 227.
36. Y. Okinaka and H. K. Straschil, *J. Electrochem. Soc.: Solid-state Science and Technology*, 1986, **133**, 2608.
37. S. Nakahara, C. Y. Mak and Y. Okinaka, *J. Electrochem. Soc.*, 1993, **140**, 533.
38. Perminder Bindra and James R. White, *Fundamental Aspects of Electroless Plating*, 2008, 325.
39. M. Paunovic and R. Zeblysky, *Fundamental Aspects of Electroless Plating*, 1985, **72**, 52.
40. J. J. Grunwald, H. Rhodenizer and L. Slorninski, *Plating*, 1971, **58**, 1004.
41. Kondo, *et al.*, US patent, No. 4, 935,267, 1990.
42. Yi-mao lin and Shi-chern yen, *Appl. Surf. Sci.*, 2001, **178**, 116.
43. F. Hanna, *et al.*, *Materials Lett.*, 2003, **58**, 104.
44. Han Keping and Jing Li Fang, *J. Metal Finishing*, 1997, **95**, 73.
45. M. S. Kang, *et al.*, *Thin Solid Films*, 2008, **516**, 3761.
46. M. Saito, *Journal of the Metal Finish Soc. of Japan*, 1966, **17**, 14.
47. R. T. Loto, C. A. Loto, A. P. I. Popoola, *J. Mater. Environ. Sci.*, 2012, **3**, 816.
48. S. Jothilakshmi, *et al.*, *J. Indian Chem. Soc.*, 2019, **96**, 153.