CLAIMS

1. A method of copper electroplating in the manufacture of printed circuit boards, the method comprising the steps of:

a) preparing an electronic substrate to receive copper electroplating thereon, wherein the electronic substrate comprises one or more features, wherein the one or more features comprise one of one or more through-holes and/or one or more micro-vias in the electronic substrate; and

b) electroplating copper in the one or more features by contacting the electronic substrate with an acid copper electroplating solution comprising:

a. a source of copper ions;

b. sulfuric acid;

c. a source of chloride ions;

d. a brightener;

e. a wetter or suppressor; and

f. a leveler;

wherein the acid copper electroplating solution is configured for a single-step process, wherein the same acid copper electroplating solution plates the one or more through-holes and/or the one or more micro-vias using a plating cycle until metallization is complete;

wherein the plating cycle comprises the steps of:

i) pulse plating for a first time period using a plating cycle to accelerate copper plating in the middle of the through-holes and, thereafter

ii) direct current plating using forward current in the same copper electroplating solution to plate the one or more through-holes until the one or more through-holes are completely metallized.

2. The method according to claim 1, wherein the step of preparing the printed circuit board to accept electroplating thereon comprises the step of cleaning the printed circuit board prior to metallizing the one or more through-holes and/or one or more micro-vias.

3. The method according to claim 2, further comprising the step of microetching the cleaned printed circuit board.

4. The method according to claim 1, wherein the one or more metallized through-holes and/or one or more micro-vias do not exhibit any defects.

5. The method according to claim 4, wherein the metallized electroplated copper deposit completely fills the one or more through-holes and/or the one or more micro-vias and deposits a conformal copper deposit on the electronic substrate.

6. The method according to claim 1, wherein the electronic substrate has a thickness of between about 0.005 and about 3 mm.

7. The method according to claim 6, wherein the one or more through-holes and/or one or more micro-vias have a diameter of about 0.005 and about 1 mm.

8. The method according to claim 7, wherein the one or more through-holes and/or one or more micro-vias have a diameter of about 0.01 to about 0.25 mm.

9. The method according to claim 6, wherein the one or more through-holes and/or one or more micro-vias have an aspect ratio of between about 0.5:1 and about 6:1.

10. The method according to claim 5, wherein the conformal deposit has a thickness of between about 5 and about 100 μm.

11. The method according to claim 1, wherein the acid copper electroplating bath is maintained at a temperature of between about 10 and about 50°C.

12. The method according to claim 1, wherein the acid copper electroplating bath comprises: a) 100-300 g/L copper sulfate

b) 10-150 g/L sulfuric acid;

c) 20-200 ppm chloride ions;

d) 0.1-30 ppm brightener;

e) 0.1-50 g/L wetter or suppressor; and

f) 0.001-200 ppm leveler.

13. The method according to claim 1, further comprising the step of direct current plating using forward current for a time period prior to step i).

14. The method according to claim 13, wherein direct current plating for the first time period deposits a flash copper layer on the surfaces of the one or through-holes and/or one or more micro-vias.

15. The method according to claim 1, wherein pulse plating for the first time period accelerates filling of the middle of the one or more through-holes while minimizing an amount of surface copper plated.

16. The method according to claim 15, wherein as the center of the one or more through holes closes, the wave form transitions to direct current in the same acid copper plating solution to completely fill the one or more through-holes.

17. The method according to claim 1, wherein the electronic substrate is contacted with the acid copper electroplating solution by a method selected from the group consisting of spraying, wiping, dipping, and immersing.

18. The method according to claim 17, wherein the electronic substrate is contacted with the acid copper electroplating solution by immersing the electronic substrate in the acid copper plating bath.

19. The method according to claim 1, wherein the pulse plating cycle comprises a first pulse plating cycle with a first pulse plating waveform on a first side of the electronic substrate and a second pulse plating cycle with a second pulse plating waveform on a second side of the electronic substrate.

20. The method according to claim 19, wherein the first pulse plating waveform and the second pulse plating waveform exhibit a phase shift.

21. The method according to claim 19, wherein the first pulse plating cycle and the second pulse plating cycle each comprise a repeating series of one or more forward current pulses, one or more reverse current pulses, and one or more rest periods.

22. The method according to claim 21, wherein the duration of the one or more reverse current pulses is in a range of 100 to 250 ms.

23. The method according to claim 1 wherein the acid copper electroplating bath comprises:

a. 100-300 g/L of a source of copper ions;
b. 10-150 g/L of an acid;
c. 20 to 200 ppm of a a source of chloride ions;
d. 0.1-30 ppm of a brightener, wherein said brightener is selected from the group consisting of 3-(benzothiazolyl-2-thio)-propyl sulfonic acid, sodium salt; 3-mercaptopropane-1-sulfonic acid, sodium salt; bis-(p-sulfophenyl)-disulfide, disodium salt; bis-(ω-sulfobutyl)-disulfide, disodium salt; bis-(ω-sulfohydroxypropyl)-disulfide, disodium salt; bis-(ω-sulfopropyl)-disulfide, disodium salt; bis-(ω-sulfopropyl)-sulfide, disodium salt; O-ethyldithio-carbonic acid-S-(ω-sulfopropyl)-ester, potassium salt; thioglycolic acid; thiophosphoric acid-O-ethyl-bis-(ω-sulfopropyl)-ester, disodium salt; and thiophosphoric acid-(ω-sulfopropyl)-ester, trisodium salt;
e. 0.1-50 g/L of a wetter or suppressor selected from the group consisting of carboxymethylcellulose, nonylphenolpolyglycolether, octandiol-bis-

(polyalkylene glycol ether), octanol polyalkylene glycol ether, oleic acid polyglycol ester, polyethylene glycol polypropylene glycol copolymerisate, polyethylene glycol, polyethylene glycol dimethylether, polypropylene glycol, polyvinylalcohol, β-naphthyl polyglycol ether, stearic acid polyglycol ester, stearic acid alcohol polyglycolether, and copolymers of propylene glycol and ethylene glycol; and

f. 0.001-200 ppm of a leveler selected from the group consisting of polyamines, ethoxylated polyamines, polypyridine, polyimidazole, polyvinyl pyridine, polyvinyl imidazole, ethoxylated polyvinyl pyridine, and ethoxylated polyvinyl imidazole.