

## CLAIMS

*What is claimed is:*

1. A method of electroplating a metal into features of a substrate, the method comprising:  
contacting a substrate with an electroplating solution comprising:  
an aqueous solution of pH greater than 7,  
about 0.1 to 60 g/L copper salt dissolved in the aqueous solution,  
a copper (II) complexing ligand, and  
combination of a suppressor and an accelerator selected from the group consisting of (i) a polyallylamine (suppressor) and thiourea (accelerator); (ii) polyallylamine (suppressor) and ammonium thiocyanate (accelerator), and (iii) saccharin (suppressor) and thiourea (accelerator); and  
electroplating copper metal from the electroplating solution into features of the substrate.
2. A method of electroplating a metal into features of a substrate, the method comprising:  
contacting a substrate with an electroplating solution comprising:  
an aqueous solution of pH greater than 7,  
about 0.1 to 60 g/L copper salt dissolved in the aqueous solution,  
a copper (II) complexing ligand,  
an accelerator comprising a thiocyanate salt; and  
a suppressor; and  
electroplating copper metal from the electroplating solution into features of the substrate.
3. The method of claim 1 or 2, wherein electroplating copper metal comprises a superconformal fill of the copper metal into the features of the substrate.
4. The method of claim 1 or 2, wherein electroplating copper metal is performed while rotating the substrate in the electroplating solution.
5. The method of claim 1 or 2, wherein electroplating copper metal is performed while flowing the electroplating solution through a cell containing the substrate.

6. The method of claim 1 or 2 further comprising, prior to contacting the substrate with the electroplating solution, annealing the substrate in inert or reducing atmosphere at a temperature of about 30 to 600 degrees C for a period of about 30 seconds to one hour.
7. The method of claim 1 or 2, further comprising, prior to contacting the substrate with the electroplating solution, annealing the substrate in the presence of a remote reducing plasma while heated the substrate a temperature about 30C to 600C for a period of about 30 seconds to one hour.
8. The method of claim 1 or 2, further comprising, prior to contacting the substrate with the electroplating solution, contacting the substrate with a pretreatment bath for about 1 to 600 seconds.
9. The method of claim 8, further comprising electrically polarizing the substrate in the pretreatment bath.
10. The method of claim 8, wherein the pretreatment bath contains no constituent chemicals not also present in the electroplating solution.
11. The method of claim 10, further comprising, after a pretreatment period of time, modifying the composition of the pretreatment bath to produce the electroplating solution.
12. The method of claim 1 or 2, wherein the electroplating fills features of the substrate having a critical dimension of about 20 nm or less.
13. The method of claim 1 or 2, wherein the features of the substrate comprise a diffusion barrier that is about 1 to 5 nm thick.
14. The method of claim 13, wherein the diffusion barrier comprises a tantalum nitride.
15. The method of claim 1 or 2, wherein the features of the substrate comprise a conductive liner that is about 1 to 5 nm thick.
16. The method of claim 15, wherein the conductive liner comprises cobalt, molybdenum, titanium, or any combination thereof.

17. The method of claim 1 or 2, further comprising, after contacting the substrate with the electroplating solution, holding the substrate at an electrical potential of about 0 to about -1.5V relative to a copper pseudoreference electrode.
18. The method of claim 17, wherein the substrate is held at the electrical potential of about 0 to -1.5V relative to a copper pseudoreference electrode for a time of about 0 to about 10 seconds.
19. The method of claim 1 or 2, further comprising, after contacting the substrate with the electroplating solution, controlling current so about 0 A flows between the substrate and the electroplating solution.
20. The method of claim 1 or 2, wherein electroplating copper metal comprises controlling current to provide a current density on an electroplating face of the substrate of about 0.25 mA/cm<sup>2</sup> to about 40 mA/cm<sup>2</sup>.
21. The method of claim 1 or 2, wherein electroplating copper metal comprises controlling current between the substrate and the electroplating solution such that the current increases from a low value to a high value or decreases from a high value to low value.
22. The method of claim 21, wherein the current is controlled to provide a current density on an electroplating face of the substrate of about 1 to about 60 mA/cm<sup>2</sup> for a period of about 0.1 to about 10 seconds, and then decreasing the current density on the electroplating face of the substrate.
23. The method of claim 1 or 2, wherein electroplating copper metal comprises controlling current between the substrate and the electroplating solution using a series of current pulses.
24. The method of claims 1 or 2, wherein electroplating copper metal comprises controlling the potential of the substrate.
25. An electroplating solution comprising:  
an aqueous solution of pH greater than 7;  
about 0.1 to 60 g/L Cu(II) supplied as a copper salt dissolved in the aqueous solution;  
a copper (II) complexing ligand; and

combination of a suppressor and an accelerator selected from the group consisting of (a) a polyallylamine (suppressor) and thiourea (accelerator); (b) polyallylamine (suppressor) and ammonium thiocyanate (accelerator), and (c) saccharin (suppressor) and thiourea (accelerator).

- 5    26.    An electroplating solution comprising:  
an aqueous solution of pH greater than 7;  
about 0.1 to 60 g/L Cu(II) supplied as a copper salt dissolved in the aqueous solution;  
a copper (II) complexing ligand;  
an accelerator comprising a thiocyanate salt; and  
10        a suppressor.

27.    The electroplating solution of claim 25 or 26, wherein the copper (II) complexing agent is present in the aqueous solution at concentration sufficient to prevent copper hydroxide precipitation.

- 15    28.    The electroplating solution of claim 25 or 26, further comprising a pH adjustment agent or buffer sufficient to maintain the pH above 7 during electroplating of copper from the electroplating solution.

29.    The electroplating solution of claim 25 or 26, further comprising a leveler.

30.    The electroplating solution of claim 25 or 26, further comprising a copper (I) complexing ligand

- 20    31.    The electroplating solution of claim 30, further comprising a component that reduces the ability of the copper (I) ligand to prevent Cu(I) reduction during electroplating.

32.    The electroplating solution of claim 25 or 26, further comprising a sacrificial oxidant.