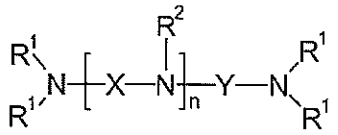
Claims

1. A composition for filling submicrometer sized features having an aperture size of 30 nanometers or less comprising a source of copper ions, and at least one suppressing agent selected from compounds of formula I



(I)

wherein

- the R^1 radicals are each independently selected from a copolymer of ethylene oxide and at least one further C3 to C4 alkylene oxide, said copolymer being a random copolymer.
- the R^2 radicals are each independently selected from R^1 or alkyl.
- X and Y are spacer groups independently, and X for each repeating unit independently, selected from C1 to C6 alkylen and $Z-(O-Z)_m$ wherein the Z radicals are each independently selected from C2 to C6 alkylen,
- n is an integer equal to or greater than 0.
- m is an integer equal to or greater than 1.

2. The composition according to claim 1, wherein X and Y are independently, and X for each repeating unit independently, selected from C1 to C4 alkylen.

3. The composition according to anyone of the preceding claims, wherein the amine compound is selected from methylamine, ethylamine, propylamine, isopropylamine, n-butylamine, tert-butylamine, hexylamine, dimethylamine, diethylamine, cyclopentylamine, cyclohexylamine, ethanolamine, diethanolamine, triethanolamine, ethylene diamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, neopentanediamine, isophoronediamine, 4,9-dioxadecane-1,12-diamine, 4,7,10-trioxyatridecane-1,13-diamine, triethylene glycol diamine, diethylene triamine, (3-(2-aminoethyl)aminopropylamine, 3,3´-iminodi(propylamine), N,N-bis(3-aminopropyl)methylamine, bis(3-dimethylaminopropyl)amine, triethylenetetraamine and N,N´-bis(3-aminopropyl)ethylenediamine.

4. The composition according to anyone of the preceding claims, wherein the C3 to C4 alkylene oxide is selected from propylene oxide.

5. The composition according to anyone of the preceding claims, wherein the content of ethylene oxide in the copolymer of ethylene oxide and the further C3 to C4 alkylene oxide is from 30 to 70 %.

6. The composition according to anyone of the preceding claims, wherein the molecular weight M_w of the suppressing agent is 6000 g/mol or more.

7. The composition according to claim 6, wherein the molecular weight M_w of the suppressing agent is from 7000 to 19000 g/mol.

8. The composition according to claim 6, wherein the molecular weight M_w of the suppressing agent is from 9000 to 18000 g/mol.

9. The composition according to anyone of the preceding claims, wherein amine compound comprising active amino functional groups comprises at least 3 active amino groups.

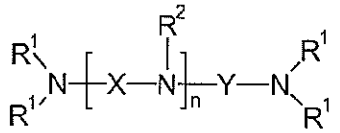
10. The composition according to anyone of the preceding claims, further comprising one or more accelerating agent.

11. The composition according to anyone of the preceding claims, further comprising one or more leveling agent.

12. Use of a copper plating bath comprising a composition according to anyone of the preceding claims for depositing the copper on substrates comprising features having an aperture size of 30 nanometers or less.

13. A process for electrodepositing copper on a substrate comprising submicrometer sized features having an aperture size of 30 nanometers or less, the process comprising

a) contacting a copper plating bath comprising a copper ion source, one or more accelerators, and one or more suppressing agents selected from compounds of formula I



(I)

wherein

- the R^1 radicals are each independently selected from a copolymer of ethylene oxide and at least one further C3 to C4 alkylene oxide, said copolymer being a random copolymer.

- the R^2 radicals are each independently selected from R^1 or alkyl.

- X and Y are spacer groups independently, and X for each repeating unit independently, selected from C1 to C6 alkylen and $Z-(O-Z)_m$ wherein the Z radicals are each independently selected from C2 to C6 alkylen,

- n is an integer equal to or greater than 0.

- m is an integer equal to or greater than 1, particularly m = 1-10.

with the substrate, and

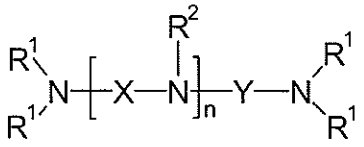
b) applying a current density to the substrate for a time sufficient to fill the submicron size feature with copper.

14. The process according to claim 13, wherein the features have an aspect ratio of 4 or more.

Claims

1. A process for electrodepositing copper on a substrate comprising submicrometer sized features having an aperture size of 30 nanometers or less, the process comprising

a) contacting a copper plating bath comprising a copper ion source, one or more accelerators, and one or more suppressing agents selected from compounds of formula I



(I)

Wherein

- the suppressing agent is obtainable by reacting an amine compound with a mixture of ethylene oxide and at least one compound selected from C3 and C4 alkylene oxides.

- the R^1 radicals are each independently selected from a copolymer of ethylene oxide and at least one further C3 to C4 alkylene oxide, said copolymer being a random copolymer.

- the R^2 radicals are each independently selected from R^1 or alkyl.

- X and Y are spacer groups independently, and X for each repeating unit independently, selected from C1 to C6 alkylen and $Z-(O-Z)_m$ wherein the Z radicals are each independently selected from C2 to C6 alkylen,

- n is an integer of from 0 to 10.

- m is an integer equal to or greater than 1, particularly m = 1-10,

- the content of ethylene oxide in the copolymer of ethylene oxide and the further C3 to C4 alkylene oxide is from 30 to 70 % by weight

with the substrate, and

b) applying a current density to the substrate for a time sufficient to fill the submicron size feature with copper.

2. The process according to claim 1, wherein X and Y are independently, and X for each repeating unit independently, selected from C1 to C4 alkylen.

3. The process according to anyone of the preceding claims, wherein the amine compound is selected from ethylene diamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, neopentanediamine, isophoronediamine, 4,9-dioxadecane-1,12-diamine, 4,7,10-trioxyatridecane-1,13-diamine, triethylene glycol diamine, diethylene triamine, (3-(2-aminoethyl)aminopropylamine, 3,3´-iminodi(propylamine), N,N-bis(3-aminopropyl)methylamine, bis(3-dimethylaminopropyl)amine, triethylenetetraamine and N,N´-bis(3-aminopropyl)ethylenediamine.

4. The process according to anyone of the preceding claims, wherein the C3 to C4 alkylene oxide is selected from propylene oxide.

5. The process according to anyone of the preceding claims, wherein the molecular weight M_w of the suppressing agent is 6000 g/mol or more.

6. The process according to claim 5, wherein the molecular weight M_w of the suppressing agent is from 7000 to 19000 g/mol.

7. The process according to claim 5, wherein the molecular weight M_w of the suppressing agent is from 9000 to 18000 g/mol.

8. The process according to anyone of the preceding claims, wherein the amine compound comprising active amino functional groups comprises of from 3 to 7 active amino groups.

9. The process according to anyone of the preceding claims, said copper plating bath further comprising one or more leveling agent.

10. The process according to anyone of the preceding claims, wherein the features have an aspect ratio of 4 or more.