Electroplating with a polycarboxylate ether supressor

The present invention relates to a process for depositing a metal layer on a substrate by contacting the substrate with a metal plating bath comprising a metal ion source and a suppressor, and applying a current density to the substrate, where the suppressor is a polycarboxylate ether as described below. The invention further relates to a metal plating bath comprising a metal ion source and the suppressor which is a polycarboxylate ether; and to a use of the polycarboxylate ether in a metal plating bath for depositing a metal layer on a substrate.

Electroplating has several problems which need to be solved: The plating bath should have a high electrochemical stability because additives tend to degrade over time. This is important for an cost-effective electroplating process. The metal layer which is deposited on the substrate should have a smooth and uniform layer thickness, and it should have a high gloss. The electroplating should have good leveling properties, in particular provide substantially planar metal layer and filling features on the nanometer and on the micrometer scale without substantially forming defects.

In an aspect, there is provided a process for depositing a metal layer on a substrate by

a) contacting the substrate with a metal plating bath comprising a metal ion source and a suppressor, and
b) applying a current density to the substrate,

where the suppressor is a polycarboxylate ether obtainable by polymerizing a mixture of monomers comprising

(I) at least one ethylenically unsaturated monomer (I) which comprises at least one radical from the series carboxylic acid, carboxylic salt, carboxylic ester, carboxylic amide, carboxylic anhydride, and carboxylic imide; and
(II) at least one ethylenically unsaturated monomer (II) having a polyalkylene oxide radical.

In an example, there is provided a metal plating bath comprising a metal ion source and the suppressor which is a polycarboxylate ether as defined above.

In another aspect, there is provided a use of the supressor which is the polycarboxylate ether as defined above in a metal plating bath for depositing a metal layer on a substrate.

The **process** for depositing the metal layer on the substrate is usually **electroplating**. Typically, substrates are electroplated by immersing the substrate in the metal plating bath And contacting

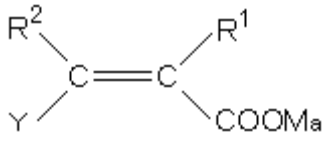
Claims

1. A process for depositing a metal layer on a substrate by
   a) contacting the substrate with a metal plating bath comprising a metal ion source and a suppressor, and
   b) applying a current density to the substrate,

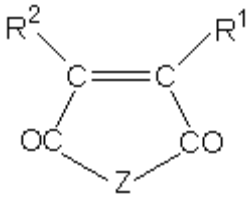
   where the suppressor is a polycarboxylate ether obtainable by polymerizing a mixture of monomers comprising
   (I) at least one ethylenically unsaturated monomer (I) which comprises at least one radical from the series carboxylic acid, carboxylic salt, carboxylic ester, carboxylic amide, carboxylic anhydride, and carboxylic imide; and
   (II) at least one ethylenically unsaturated monomer (II) having a polyalkylene oxide radical.

2. The process according to claim 1 where the ethylenically unsaturated monomer (I) comprises at least one radical from the series carboxylic acid, carboxylic salt, and carboxylic amide.

3. The process according to claim 1 or 2 where the ethylenically unsaturated monomer (I) is represented by at least one of the following general formulae from the group (Ia), (Ib), and (Ic)



(Ia)



(Ib)

   where

   R^1 and R^2 independently of one another are hydrogen or an aliphatic hydrocarbon radical having 1 to 20 C atoms,

   Y is H, $-COOM_a$, $-CO-O(C_qH_{2q}O)_r-R^3$, or $-CO-NH-(C_qH_{2q}O)_r-R^3$,

   M is hydrogen, a mono- or divalent metal cation, ammonium ion, or an organic amine radical,

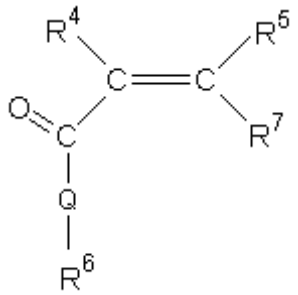
   a is ½ or 1,

   R^3 is hydrogen, an aliphatic hydrocarbon radical having 1 to 20 C atoms, a cycloaliphatic hydrocarbon radical having 5 to 8 C atoms, or an optionally substituted aryl radical having 6 to 14 C atoms,

q independently at each occurrence for each ($C_qH_{2q}O$) unit is identical or different and is 2, 3, or 4,

r is 0 to 200, and

Z is O or NR^3,



(Ic)

where

R^4 and R^5 independently of one another are hydrogen or an aliphatic hydrocarbon radical having 1 to 20 C atoms, a cycloaliphatic hydrocarbon radical having 5 to 8 C atoms, or an optionally substituted aryl radical having 6 to 14 C atoms,

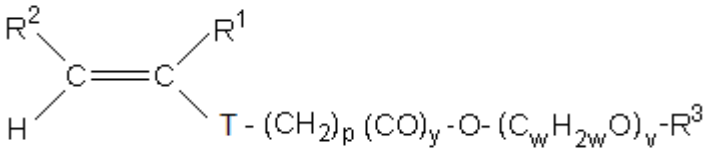
Q is identical or different and is represented by NH, NR^3, or O, where R^3 possesses the definition stated above,

R^6 is identical or different and is represented by (C_nH_{2n})-SO_3H with n = 0, 1, 2, 3, or 4, (C_nH_{2n})-OH with n = 0, 1, 2, 3, or 4; (C_nH_{2n})-PO_3H_2 with n = 0, 1, 2, 3, or 4, (C_nH_{2n})-OPO_3H_2 with n= 0, 1, 2, 3, or 4, (C_6H_4)-SO_3H, (C_6H_4)-PO_3H_2, (C_6H_4)-OPO_3H_2, and (C_nH_{2n})-NR^8_b with n = 0, 1, 2, 3, or 4 and b = 2 or 3,

R^7 is H, -$COOM_a$, -CO-O$(C_qH_{2q}O)_r$-R^3, -CO-NH-$(C_qH_{2q}O)_r$-R^3, where M_a, R^3, q, and r possess definitions stated above,

R^8 is hydrogen, an aliphatic hydrocarbon radical having 1 to 10 C atoms, a cycloaliphatic hydrocarbon radical having 5 to 8 C atoms, or an optionally substituted aryl radical having 6 to 14 C atoms.

4. The process according to any of claims 1 to 3 where the ethylenically unsaturated monomer (II) is represented by the following general formula



(II)

in which

p is an integer between 0 and 6,

y is 0 or 1,

v is an integer between 3 and 500,

w independently at each occurrence for each ($C_wH_{2w}O$) unit is identical or different and is an integer between 2 and 18,

T is oxygen or a chemical bond,

where R^1, R^2, and R^3 possess the definition stated above.

5. The process according to claim 4 where in the ethylenically unsaturated monomer (II) p is an integer between 0 and 4, v is an integer between 5 and 250, and w independently at each occurrence for each ($C_wH_{2w}O$) unit is identical or different and is 2 or 3.

6. The process according to claim 4 or 5 where in the ethylenically unsaturated monomer (II) the R^3 is an aliphatic hydrocarbon radical having 1 to 20 C atoms.

7. The process according to any of claims 1 to 6 where the ethylenically unsaturated monomer (II) has a molecular weight of 500 to 10 000 g/mol.

8. The process according to any of claims 1 to 7 where the polycarboxylate ether has a molecular weight of 1 000 to 100 000 g/mol.

9. The process according to any of claims 1 to 8 where the fraction of the monomer (I) in the copolymer is 5 to 95 mol%.

10. The process according to any of claims 1 to 9 where the monomer (I) is a carboxylic amide, such as N,N-dimethylacrylamide, N,N-dimethylmetacrylamide, N,N-diethylacrylamide, or N,N-diethylmethacrylamide.

11. The process according to any of claims 1 to 10 where the fraction of the monomer (II) in the copolymer is 1 to 89 mol%.

12. The process according to any of claims 1 to 11 where the polycarboxylate ether is present in the range from 1 to 10 000 mg/l based on the weight of the bath.

13. The process according to any of claims 1 to 12 where the metal ion source comprises a copper salt.

14. The process according to any of claims 1 to 13 where the metal plating bath comprises an accelerator which is a compound comprising one or more sulphur atom and a sulfonic/phosphonic acid or their salts.

15. A use of a supressor which is a polycarboxylate ether as defined in any of claims 1 to 14 in a metal plating bath for depositing a metal layer on a substrate.