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Adhesion improvement of electroless copper coatings by polymer additives

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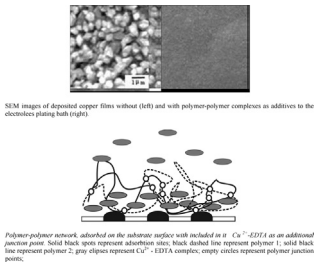
HIGHLIGHTS

- A polymer–polymer complexes for copper electroless deposition approach is developed.
- Polymer mixtures PEG + EC and PEG + PDMAPS are tested.
- Improved adhesion in the presence of the polymer–polymer complexes was achieved.

GRAPHICAL ABSTRACT



SEM images of deposited copper films without (left) and with polymer-polymer complexes as additives to the electroless plating bath (right).

Polymer-polymer network, adsorbed on the substrate surface with included in it Cu^{2+}-EDTA as an additional junction point. Solid black spots represent adsorbtion sites; black dashed line represent polymer 1; solid black line represent polymer 2; gray elipses represent Cu^{2+} - EDTA complex; empty circles represent polymer junction points;

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ABSTRACT

An original approach for copper electroless deposition without the use of the palladium catalysts is developed. The mixture of two hydrophilic polymers, forming polymer–polymer complex and an assembly with ethylenediaminetetraacetic acid (EDTA)–Cu(II) one is the essential element of the method proposed. Two pairs compatible polymer mixtures (polyethylene glycol (PEG) – ethyl cellulose (EC) and PEG – poly(dimethylaminoethylmethacryloyl propanesulfonate), (PDMAPS) are tested. It is shown that these polymer additives do not change the UV- and EPR-spectra, as well as the current–voltage curve characteristics, which is related to the fact that in the presence of these polymer additives there is not the formation of new compounds with absorbance in the UV- and visible regions and new paramagnetic centers, as well as that they don't influence the formaldehyde oxidation potential and Cu(II) reduction one. At the same time, these polymer additives decrease the deposition rate, improve the homogeneity, surface coverage and adhesion of the copper film to the substrate. These results correlate with the nonlinear viscosity elevation of the electroless bath with polymer additives, as well as with the maximal values of the critical angle for the first movement of the drop on the inclined substrate plane and of the difference between front and back contact angles of the drop from the electroless bath with polymer additives too. This correlation is related to the formation of the polymer–polymer complex, cross-linked with Cu(II)–EDTA as physical junction points, multisite adsorption of this enriched with Cu(II) network on the substrate surface, the precondition for a autocatalytic copper electroless deposition, more smooth substrate coverage, and improved adhesion of the copper film to the substrate surface.

1. Introduction

Electroless deposition is a heterogeneous electrochemical process of coating with the aid of a chemical reducing agent in solution, without the application of external electrical power [1]. It is therefore applicable to nonconductive flexible surfaces, as well as on

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metals and semiconductors. A wide range of applications has been found for electroless plating, including the preparation of chip interconnects and other electronic elements [2–8]. Probably, this is a result of the fact that in contrast to electroplated copper, which requires a global seed layer, electroless copper is readily selectively deposited on patterned dielectric surfaces (usually with dispersed, sub-colloidal palladium) [9–18]. Generally, carriers for the Pd immobilization are different water-soluble homo- and co-polymers. Hydrophilic polyelectrolyte brushers on the selected regions of the substrate surfaces as polymer carriers are produced by atom transfer radical polymerization or by UV-, γ- and plasma-activated graft copolymerization [19]. The possibility of using environmentally friendly natural polyhydroxylic alcohols (xylitol, D-mannitol and D-sorbitol) as Cu(II) ligands instead ethylenediaminetetraacetic acid to this aim is demonstrated also [20].

However, based on the traditional palladium catalyst, these approaches are unacceptable for the application of the copper electroless deposition to extremely small, and closely-spaced features in the nanoelectronics. Initial efforts to obtain electroless copper deposits without the use of palladium catalyst, have yielded encouraging results in the case of the application of water-soluble, nitrogen-containing polymer in an electroless copper plating solution together with glyoxylic acid and/or phosphinic acid as reducing agents instead formaldehyde. The tested nitrogen-containing polymers are polyacrylamide, polyethylene imine, polyglycine, poly(allylamine), polyaniline (sulfonated), polyurea, poly(melamine-*co*-formaldehyde), polyaminoamides, polyalkanolamines, polyvinylpyridine, polyvinylimidazole, polyvinylpyrrolidone, polybiguanide, poly(vinylimidazole-*co*-vinylpyrollidone) with weight average molecular weight at least 10^5 Da [21–28]. The consistency of the nitrogen atoms in the adsorbed macromolecule provides the bridge connection between the substrate surface and copper ions in the electroless plating bath, the autocatalytic mechanism of this process, and an excellent adhesion between the surface and deposited copper layer. An effective nonformaldehyde electroless copper plating without the use of the palladium catalyst is established also with such reducing agents as sodium hypophosphite in a combination with thiourea [29], ascorbic acid together with proteins and acetic acid [30], potassium ferrocianide with polyethylene glycol 6000 [31], dimethylamineborane (DMAB) with sodium citrate as a complexing agent [32]. Using DMAB, a promising approach for direct electroless patterning of copper films without catalysts (denoted as "Seedless copper microparterning process", SCMP) is developed on the basis of the NH_2- and SH-terminated self-assembled monolayers (SAMs) on silicon wafers [32–34]. However, the laborious of this multistep process inspires a search for its alternatives. Recently [21], it was established that the application of the mixed potential theory [35,36] to the electroless copper deposition using glyoxylic acid as reducing agent leads to erroneous predictions of the deposition rate and surface mixed potential. These shortcomings in the application of this theory is related to autocatalysis during the electroless copper plating using glyoxalic acid or mentioned above reducing agents instead formaldehyde. Exactly this positive feedback loop provides the necessary copper electroless deposition without the use of palladium catalyst. It is noteworthy that mentioned above bridge connection function of the nitrogen-containing macromolecules is a crucial precondition for the discussed autocatalysis and hence, for the electroless plating without catalyst.

The mentioned polymer functions depend on the polymer concentration and the nature of the macromolecular functional groups, providing both the multisite macromolecular adsorption on the substrate surface, the local uptake of the viscosity and coordinated copper ions in the boundary layer between solution and substrate. From the available literature it does not found information about the application of mixtures of the hydrophilic polymers with different functional groups, providing the formation of the water-soluble polymer–polymer complexes. In this communication the first results for the influence of two pairs polymer mixtures, polyethylene–glycol (PEG) – ethyl cellulose (EC) and PEG – poly(dimethylaminoethylmethacryloyl propanesulfonate), (PDMAPS), on the copper electroless deposition with formaldhyde as a reducing agent, but without Pd catalysts, are presented. The application of the polymer–polymer complexes in the copper electroless solutions favors not only the autocatalysis, but contributes the adhesion of the deposited copper layer to the substrate surface, as well as the tunable uptake of the electroless bath viscosity and thixotropy. The latter is of primary importance for the copper electroless plating of moving or inclined substrates by screen or inkjet printing methods, affording the patterning domains with high spatial resolution [37].

2. Materials and procedures

Ethyl cellulose (Dow Chemical, Ethocel Std.10 Premium FP, EC) with 48% ethoxy groups (EC) and poly(ethylene glycol) with weight average molecular weight 4000 Da (PEG 4000, Sigma-Aldrich) are used without additional chemical modifications. For the acceleration of the EC dissolution in water it is wetted at first with ethyl alcohol. Polyzwitterion, (PDMAPS), is synthesized by radical polymerization of 10% (wt) aqueous solution of DMAPS with 2% (wt) ammonium persulfate as an initiator at 45 °C in argon atmosphere for 6 h. The residual monomer and initiator are separation by dialysis through cellulose membrane with average cut-off molecular weight 2000 Da against distilled water for 24 h. The PDMAPS as a white powder is produced by the freeze-drying of its aqueous solution, obtained after dialysis. Its average molecular weight, determined by laser scattering method (Malvern-System 4600) is 76,000 Da. Copper(II) sulfate pentahydrate (98%, Sigma Aldrich), sodium hydroxide (Pure Substances Co), formaldehyde (Sigma Aldrich, 37% in water), potassium tetracyanonickelate(II) (99.9%, Sigma Aldrich), ethylenediaminetetraacetic acid disodium salt (Complexon III, Alafa Aesar) and dimethylaminoethylmethacryloyl propanesulfonate (Merck) are used without additional purification.

The chemical copper bath contains 12–15 g/L $CuSO_4{\cdot}5H_2O$, 30 g/L Complexon III, 10–12 g/L NaOH (pH = 12.6), 10 g/L CH_2O, 0.006 g/L $K_2[Ni(CN)_4]$ and 0.02 g/L PEG 4000. The optimal concentrations of the polymer additives are 3.6 mg/L EC and 1.2 mg/L polyzwitterion (PZ). The working temperature interval is 25–50 °C. Substrates for copper electroless plating are glass, epoxy fiber glasses and stainless steel with smooth (not rugged) surfaces.

UV- and EPR-spectra are registered by Specord UV/Vis and Bruker ELEXSYS-II spectrometers, respectively. Viscosity of copper electroless bathes is determined using an Ubbelohde viscometer. SEM images are registered by JEOL JSM-5510 apparatus. Current-voltage curve measurements are performed by Agilent Source/Measure Unit E5260/70.

The peel-off testing is a quantitative method to assess the strength of adhesion between the deposited copper film and substrate [38]. It was used for determination of the optimal concentrations of the polymer additives also. To this aim the firmly pressed Scotch tape into contact with the electrolessly deposited copper film is peeled-off the adhesive tape at a nearly constant rate. The amount of the transferred to the tape copper is a measure of the adhesive strength of the film. The comparative assessments of the adhesive strengths of the films, produced by electroless plating with and without polymer additives, are performed using this method.

The surface tension of the aqueous solutions of copper complex with polymer additives was measured by Wilhelmi plate method

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