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Electroless deposition of copper in acidic solutions using hypophosphite reducing agent

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Abstract

A new bath formulation was developed, which allowed deposition of copper-rich Cu–Ni–P alloys in electroless acidic solutions in the absence of formaldehyde. The reducing agent was sodium hypophosphite. Though cupric ions do not catalyse the oxidation of hypophosphite, we show that, in the presence of a low concentration of Ni(II) species, it is possible, even at low pHs, to induce the reduction of the cupric species. A very strong preferential deposition of copper was observed, which gives Cu–Ni–P layers with copper content up to 97 wt%. The phosphorus content decreased from 13% to 1% with increasing copper content. The plating rate decreased when the copper sulfate concentration in the solution increased. It increased with increasing pH or temperature, but the influence was less pronounced than in alkaline solutions. Compact layers were obtained with a nodular morphology which did not markedly changed with composition.

1. Introduction

Thin film copper deposition technologies for ultra-large scale integrated technology (ULSI) are being intensively investigated and electroless-plating is one of the routes explored [1–9]. Indeed copper offers low specific resistance and high resistance to electromigration [2, 3]. Electroless copper may also be used for various metallization processes such as carbon nanotubes or hollow metal spheres [10]. It is a low-cost technique, which leads to conformal, high-quality films with good via/trench filling [11].

Traditional electroless deposition uses formaldehyde or its derivatives as reducing agent. This has two main drawbacks: first formaldehyde is mainly efficient for pH values above 11, this high pH is incompatible with most forms of photoresists [12, 13]. In addition this compound is considered as hazardous to health. It is a volatile, flammable and possibly carcinogen liquid. Hence researches are developing towards alternative reducing agents such as borohydride [14], amine borane [15], glyoxylic alcohol or glyoxylate [4, 16]; or, most commonly, sodium hypophosphite [17–22], which is widely used as reducing agent for electroless nickel deposition [13, 23]. However, the main difficulty results from the fact that the oxidation of hypophosphite is not catalyzed by copper [12, 16–18]. In alkaline solutions, this drawback is overcome by using additional catalysts, such as organic compounds or small amounts of mediators such as Ni^{2+} or Pd^{2+} ions [16–18]. In acid solutions, several difficulties still remain, especially a low deposition rate due to slow oxidation of hypophosphite at these pHs and the corrosion of the deposited copper layer [18]. So far, mainly Ni–Cu–P alloys have been obtained; however, high nickel contents reduce the conductivity of the layers [20, 21]. In the present work copper electroless deposition is investigated in acid hypophosphite solutions and a new bath formulation is developed which leads to nearly pure copper films.

2. Experimental procedure

A 200 ml cell thermostated at 78 °C was used. The substrates were iron plates (3 cm^2), mechanically polished down to 1200 SiC paper, degreased in acetone, etched in 10% dilute sulfuric acid and rinsed with water, prior to the experiment. Steel coupons previously coated with a Ni–P electrolessly deposited layer were also investigated. The deposition rate was estimated from the weight gain after a given immersion time (1–2 h).

The morphology of the deposits was examined by Scanning Electron Microscopy, the composition

estimated by EDX analysis and the crystalline structure by X-ray diffraction using a cobalt anticathode.

3. Results

3.1. *Influence of the constituents of the plating solution*

Electroless deposition of copper has been mainly carried out from solutions containing formaldehyde as reducing agent [13], less frequently borohydride [14] or glyoxylic acid [4, 16]. Copper, which does not catalyze hydrogen evolution, is not expected to be electrolessly deposited from hypophosphite baths [12, 13]. Ternary Ni–Cu–P alloys have been obtained from hypophosphite solutions containing small amounts of cupric ions in neutral or alkaline solutions [17–20]. In acid solutions, very low copper contents (2–4 at %) were obtained [21]. The cupric ions are considered to increase the plating rate at low concentration [18, 20]. According to Armyanov et al., the accelerating effect is due to the catalytic properties of Ni–Cu alloys [20]. In addition the cupric ions also act as stabilizers [20].

No bath composition has been proposed so far for the electroless deposition of copper from acid hypophosphite solutions, except for very low copper content [16, 18, 20]. Very low plating rates were obtained at pH 5.3 [16]. We started from the electrolyte previously developed for Ni–P plating [24] and added increasing amounts of copper sulfate. The composition of the solutions is given in Table 1. The electrolytes contained nickel sulfate, copper sulfate and sodium hypophosphite as reducing agent. The solution pH was adjusted by adding acetic acid or ammonia. Table 2 shows the deposit compositions and the plating rates.

Due to the large difference in the deposition potentials of nickel and copper, complexing agents are necessary for their codeposition. Trisodium citrate is the most widely used complexing agent [16, 17, 26]. Ammonium acetate acts as both complexing and stabilizing agent. In alkaline Ni–P solutions it has been previously shown that the solution stability was increased in the presence of ammonium acetate or chloride [25]. It may be noticed that when the concentration of the copper sulfate is increased up to 8×10^{-4} mol dm^{-3}, in the absence of ammonium acetate, the solution decomposes spontaneously. In addition, Table 2 shows that the copper content increases markedly from 1.5 wt% to 10 wt% due to the addition of ammonium acetate (electrolytes 2 and 3).

Table 2. Composition of the deposited alloys (Ni balance), deposition potential and deposition rate

Solution	Cu / wt%	P / wt%	Ed / mV vs. SCE	v / μm h^{-1}
1	0	13		5
2	1.5	13.5		6.5
3	10	11		5
4	15	11		4
5	40	15	−650	2
6	70	10	−730	1
7	90	1.5	−760	1
8	97	1	−760	1

3.2. *Film composition*

With these acid electroless solutions, Ni–Cu–P layers with copper content from 1.5 wt% to 97 wt% were obtained (Table 2). When the copper sulfate concentration in the solution is increased, the copper content increases and both nickel and phosphorus contents decrease (Figure 1).

Figure 2 shows the Cu/Ni ratio (at %) as a function of the molar ratio in the solution on a semi-logarithmic scale. A quasi-exponential dependence is observed. The dashed line represents the reference line, i.e. the same ratio in the deposit as in the solution. For all the solutions, the Cu/Ni ratio in the deposit is markedly above the reference curve. This confirms that, due to its higher deposition potential, copper is preferentially deposited, as already pointed out in alkaline solutions [17, 20, 22]. However this preferential deposition is much more pronounced than in alkaline solutions, probably because of the lower complexing effect of citrate in acidic solutions.

3.3. *Deposition rate*

Electroless deposition was carried out either on bare steel plates or on plates previously coated with an electrolessly deposited Ni–P layer and the plating rate estimated from the weight gain. In both cases the deposition rates were identical. As already pointed out, small additions of copper sulfate lead to a slight increase in the plating rate [20]. For larger additions, the plating rate decreases rapidly when the copper sulfate concentration increases and becomes as low as 1 μm h^{-1} for the

Table 1. Composition of the solutions (mol dm^{-3}), which contain in addition 0.28 mol dm^{-3} $NaH_2PO_2\cdot H_2O$ and the pH is 5

Solution	$NiSO_4\cdot 7H_2O$	$CuSO_4\cdot 5H_2O$	$Na_3C_6H_5O_7\cdot 2H_2O$	$NH_4CH_3CO_2$
1	0.10	0	0	0
2	0.10	0.4 10^{-3}	0.20	0
3	0.10	0.4 10^{-3}	0.20	0.50
4	0.10	0.8 10^{-3}	0.20	0.50
5	0.10	1.0 10^{-3}	0.20	0.50
6	0.10	1.6 10^{-3}	0.30	1.0
7	0.085	1.6 10^{-3}	0.25	1.0
8	0.085	1.6 10^{-3}	0.30	1.0

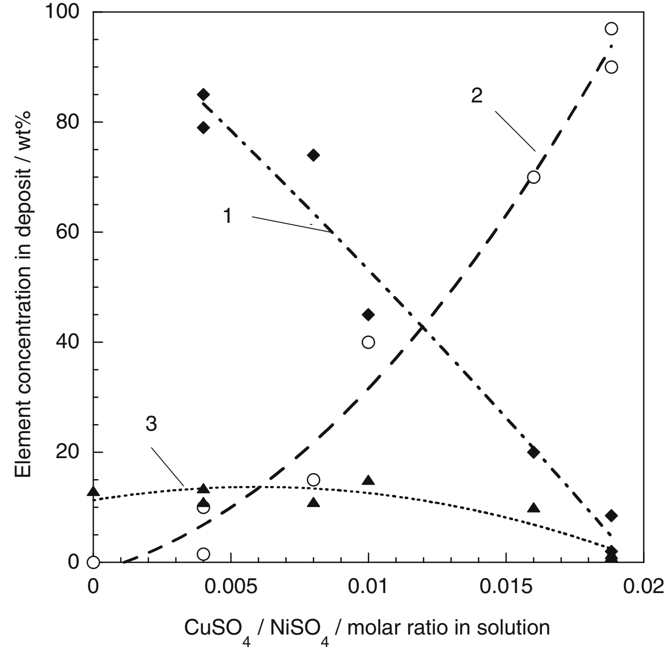

Fig. 1. Influence of the copper sulfate vs. nickel sulfate molar ratio in solution on: Curve 1: Ni content in deposit (wt%), Curve 2: Cu content in deposit (wt%), Curve 3: P content in deposit (wt%).

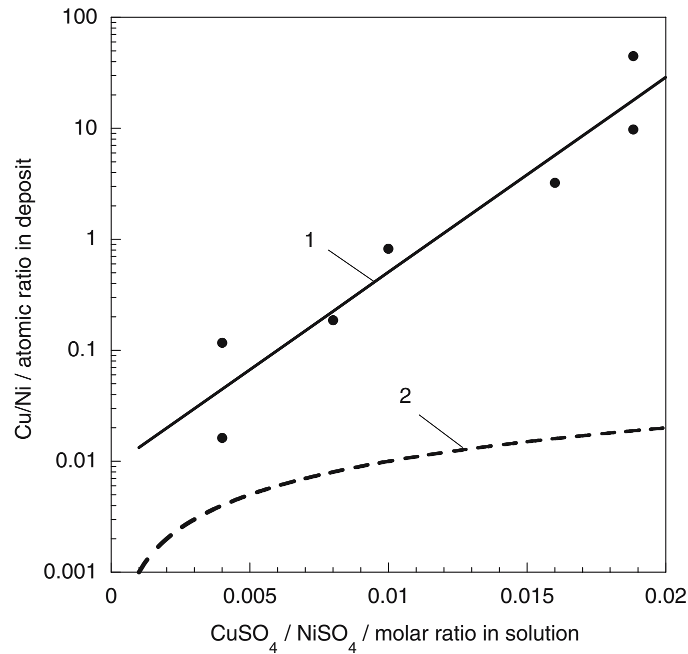

Fig. 2. Cu/Ni atomic ratio in deposit as a function of copper sulfate vs. nickel sulfate molar ratio in solution. Curve 1: Cu/Ni atomic ratio in deposit, Curve 2: Reference curve: Cu/Ni ratio atomic ratio in deposit equal to the ratio in the solution.

copper-rich layers (Figure 3). The deposition potential is constant throughout the experiment; it decreases with increasing copper content (Table 2).

To increase the deposition rate, some organic additives were investigated such as thiourea [26, 27]. In our case, addition of 1 ppm thiourea to electrolyte 5 leads to a rate increase up to 3.5 μm h^{-1}; however black powdery deposits are obtained. For contents greater than 1 ppm the baths decompose spontaneously.

The solution pH is an important parameter in electroless deposition. It affects both anodic and cathodic reactions as well as the nature of the complexed species. It is well known that the oxidation of hypophosphite is enhanced by the presence of hydroxyl ions

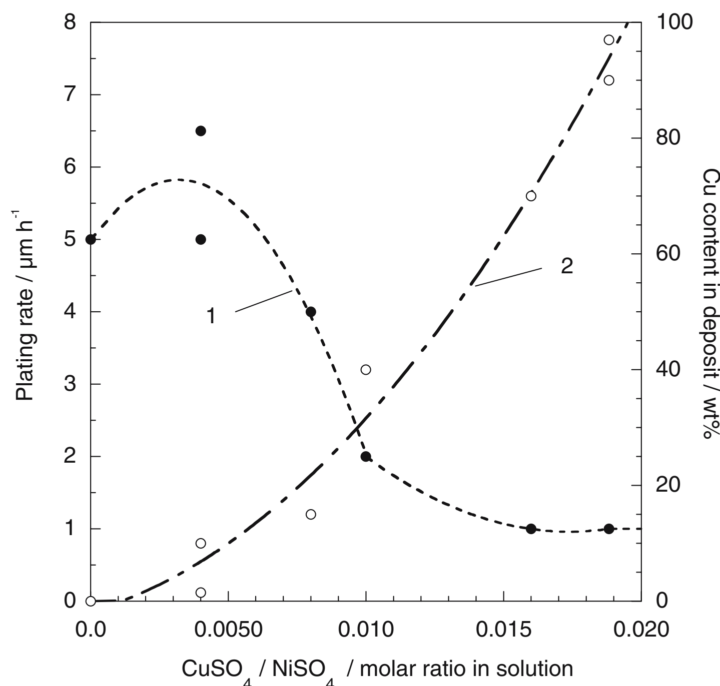

Fig. 3. Plating rate (curve 1) and copper content (curve 2) in deposit as a function of the copper sulfate vs. nickel sulfate molar ratio in solution.

[12, 16]. For the various solutions, when the pH is raised from 5 to 8, in every case the plating rate increases (Figure 4). It increases as a power function of the hydroxyl ion concentration with an exponent close to 0.10. The exponent is slightly greater (0.12) for electrolyte 5 than for electrolytes 6 to 8 (0.10 ± 0.01). This reaction order is much lower than the value of 0.25 found by [12] for the anodic oxidation of hypophosphite in cupric salt solutions at pH 9.0. The effect of pH is much less pronounced in these solutions.

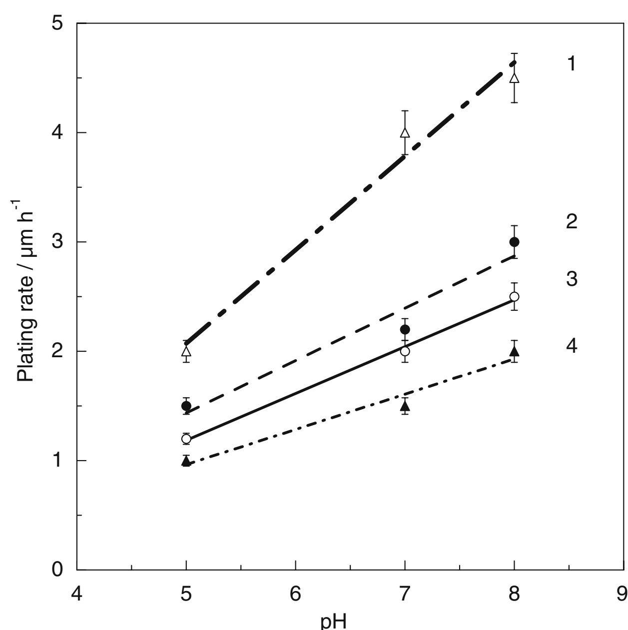

Fig. 4. Influence of the pH of the electrolyte on the plating rate. Curve 1: Electrolyte 5, Curve 2: Electrolyte 6, Curve 3: Electrolyte 7, Curve 4: Electrolyte 8.

Both chemical and electrochemical reactions depend on electrolyte temperature. Figure 5 shows that the plating rate increases quasi linearly with the reciprocal temperature. The activation energy, in the case of solutions 5 and 7 lies, between 20 and 25 kJ mol^{-1}, which is significantly smaller than for solution 8, for which it is around 58 kJ mol^{-1}. These values may be compared with the values mentioned, for the oxidation of hypophosphite at pH 9, which lye in the range 33–88 kJ mol^{-1} depending on the nature of the substrate (46 kJ mol^{-1} on Ni) [12].

3.4. *Morphology and structure*

The layers have a nodular morphology when examined by SEM (Figures 6, 7). The roughness of the layers increases when the copper content increases: a grey background is observed on which bright aggregates emerge. An increased copper content is observed on these protuberances, which confirms that copper is discharged under diffusion control, as expected from the low copper sulfate concentration in the electrolyte. This feature is even more pronounced in electrolyte 7, in which the global copper content reaches 90% (Figure 7).

Figure 8 shows the XRD diffraction pattern of a film deposited from electrolyte 8. The EDX analysis (Table 2) shows that it is nearly pure copper. Indeed it has the characteristic face-centred cubic structure of copper with a parameter slightly larger than that of 04-0836 JCPDS file (0.363 nm instead of 0.3615 nm).

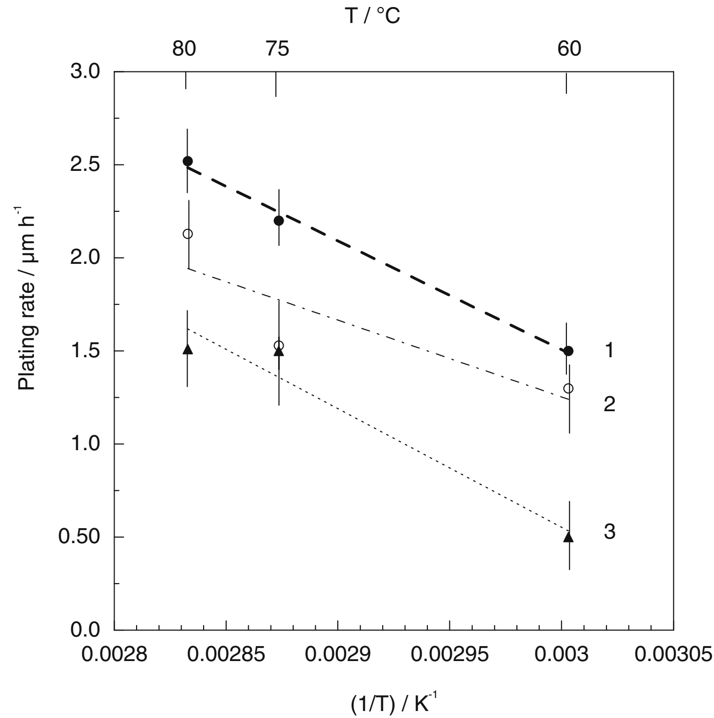

Fig. 5. Influence of the electrolyte temperature on the plating rate. Curve 1: Electrolyte 5, Curve 2: Electrolyte 7, Curve 3: Electrolyte 8.

4. Conclusion

In the present work, we developed a new composition of solutions for the electroless deposition of copper films at low pH in the absence of formaldehyde. The reducing agent is sodium hypophosphite. Though the cupric ions do not catalyse the oxidation of hypophosphite, their reduction is induced by the presence of small concentrations of nickel species. This remarkable feature relies on the strong preferential deposition of copper, usual in these types of solutions, but which is increased here by the addition of ammonium acetate. Nearly pure copper thin layers containing less than 10 wt% nickel and a few per cent phosphorus are obtained. The layers exhibit a

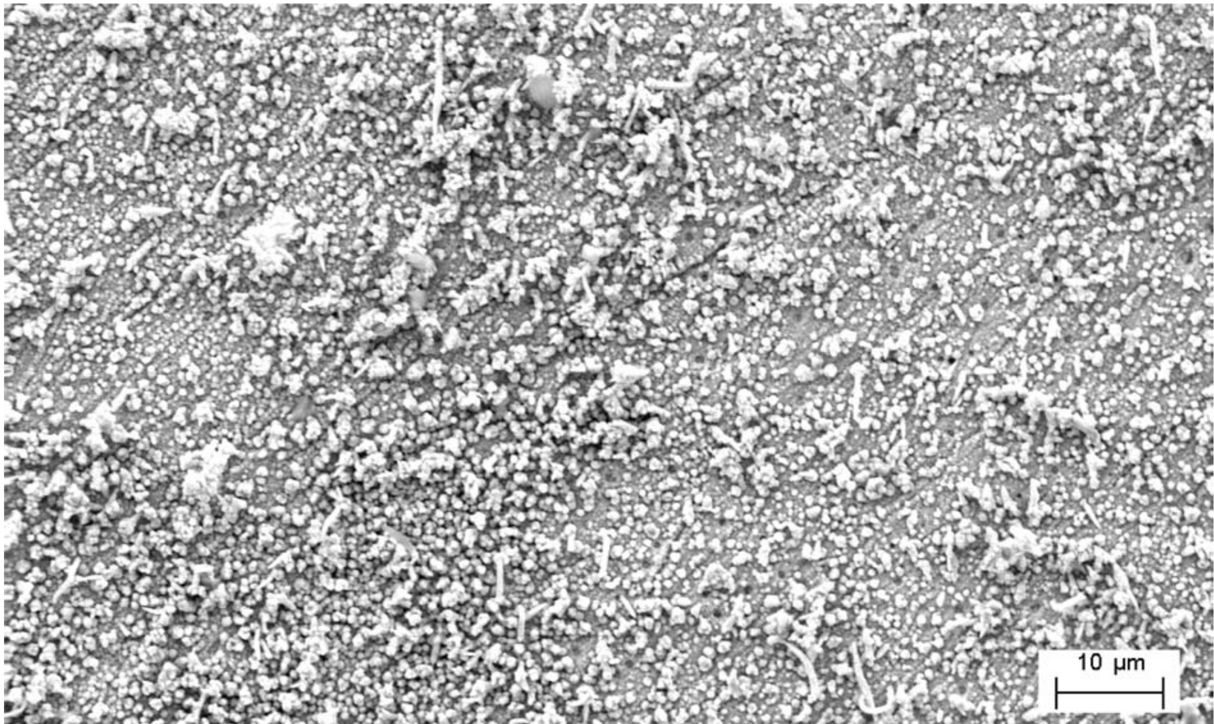

Fig. 6. SEM micrograph of a film deposited from electrolyte 6 (global composition 70 wt% Cu, 20 wt% Ni, 10 wt% P).

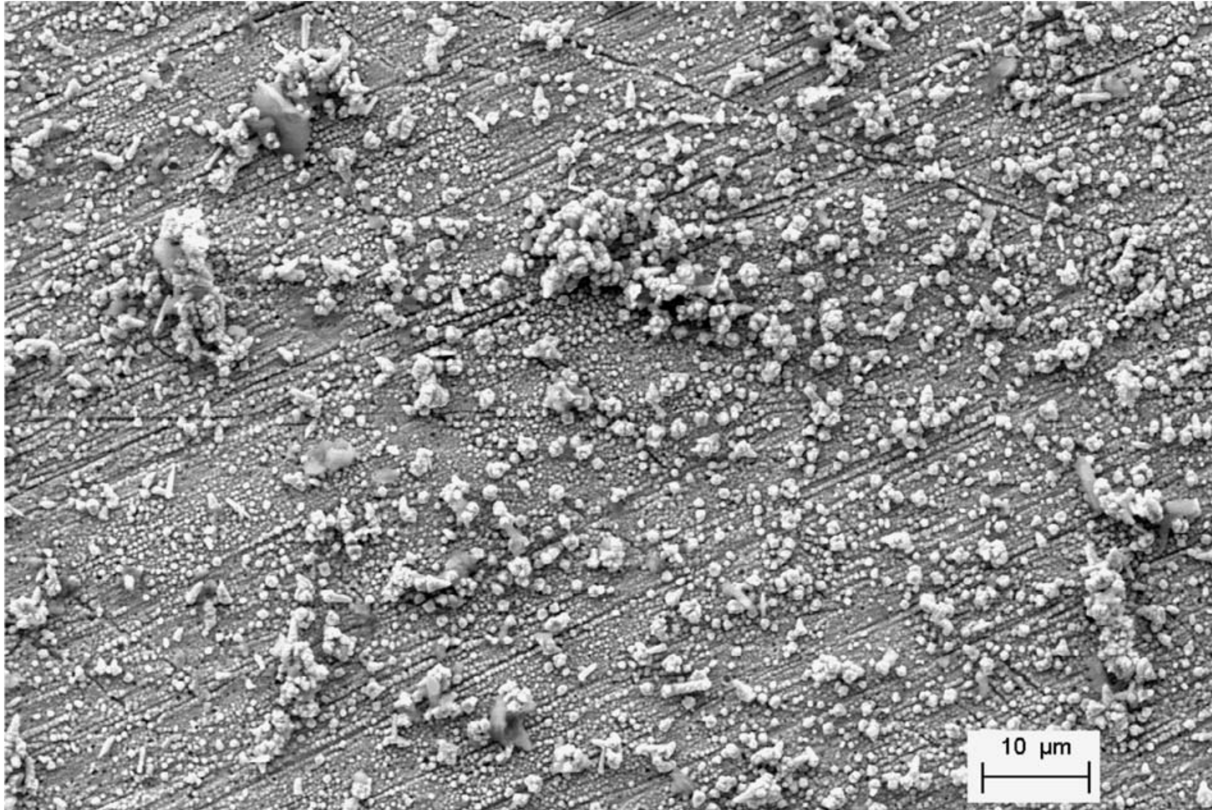

Fig. 7. SEM micrograph of a film deposited from electrolyte 7 (90 wt% Cu, 8.5 wt% Ni, 1.5 wt% P).

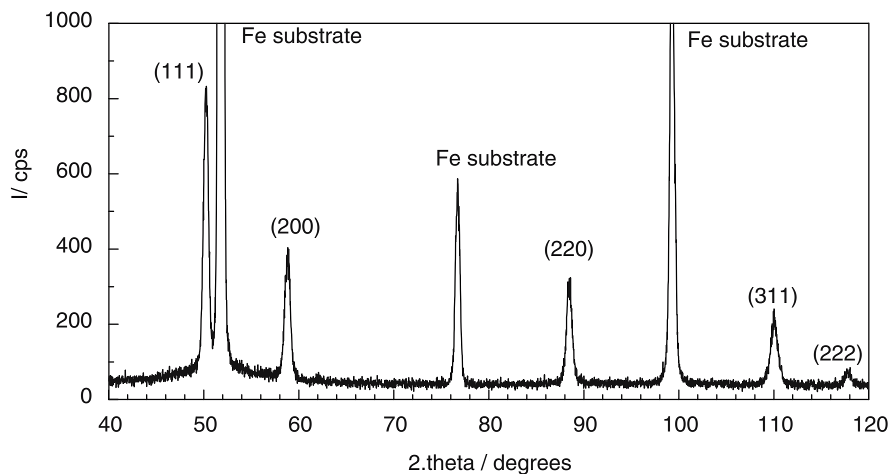

Fig. 8. X-ray diffraction pattern of a film deposited from electrolyte 8.

compact nodular morphology. However several difficulties still remain, especially the low deposition rate due to slow oxidation of hypophosphite in acid solution.

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