

# Electroless silver deposition on ABS plastic using Co(II) as reducing agent

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An unconventional way of plating Ag by electroless means is by using the oxidation process of Co(II) to Co(III) in an ammonia complex to reduce the ionic Ag to metal. The present work deals with electroless Ag deposition on acrylonitrile butadiene styrene (ABS) plastic. Detailed studies on the effect of bath constituents, bath operating conditions and addition agents on the deposition rate, quality of the Ag deposit and crystalline nature of the deposit on ABS plastic discs were carried out and the results discussed.

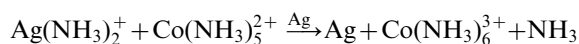
**Keywords:** Electroless Ag deposition, Ammonia Co(II) complex reducer, Plating on ABS plastic, SEM, XRD

## Introduction

Ag, a grey white and lustrous metal with the highest thermal and electrical conductivities of all the metals, has been extensively used in jewellery, silverware, fuses and medical instruments. It has been used as a base coating and converted to form an Ag/AgCl electrode for electrocardiograph application.<sup>1</sup> Instead of a solid Ag electrode, a Ag coated plastic is used as a disposable Ag/AgCl electrode for electrocardiograph application. In this regard electroless Ag plating is used to provide a Ag layer on plastic discs to form the Ag/AgCl electrode by a chloridisation method. Conventional electroless Ag plating is normally carried out from cyanide baths with a common reducing agent such as formaldehyde. A recent trend in electroless plating is to avoid toxic cyanide and hazardous formaldehyde; damage to lungs and irritation to eyes and throat occurs upon exposure to formaldehyde and, of course, sufficient exposure to cyanide is fatal. An unconventional way of plating Ag by electroless means is by using the oxidation process of Co(II) to Co(III) in an ammonia complex as the reducing agent.

Pearlstein *et al.*<sup>2</sup> investigated the electroless deposition of Ag using dimethylamine borane as the reducing agent. Mandich *et al.*<sup>3</sup> investigated an electroless Ag plating solution incorporating a novel reducing agent, a combination of thiosulphate and sulphite. Vaskelis *et al.*<sup>4</sup> carried out SEM and X-ray diffraction (XRD) investigations of a Ag coating obtained from novel solutions for electroless Ag plating, where Co(II) complexes with ammonia served as the reducing agent. The structural characteristics of these coatings and electrodeposited coatings were compared. Vaskelis *et al.*<sup>5</sup> investigated electroless Cu and Ag deposition using similar unconventional reducing agents, e.g. Co(II) complexes. Co(II) complexes with ammonia and some other ligands were found to be efficient reducing

agents in Ag deposition. Ammonia in this case is the ligand for both Ag(I) and Co(II) ions, with the reduction process taking place stoichiometrically as



Vaskelis *et al.*<sup>6</sup> investigated the electrochemical oxidation of Co(II) on Ag, a partial reaction of the electroless Ag plating process and studied this in ammonia, ammonia + ethylenediamine and ethylenediamine solution (pH 9–12) by voltammetry using a rotating disc electrode and electrochemical quartz microgravimetry. In  $\text{NH}_3 + (\text{NH}_4)_2\text{SO}_4$  solutions Co(II) (0.01M) oxidation takes place simultaneously with  $\text{Ag}^+$  ion reduction.

Norkus *et al.*<sup>7</sup> studied the kinetics of electroless Ag deposition from solutions containing Co(II)–ammonia complex compounds as reducing agents at 20 and 50°C. The process rate depends on the solution pH value and the concentration of Ag(I), Co(II) and ammonia species. Under the optimum operating conditions selected, a Ag deposition rate up to  $1.2 \mu\text{m h}^{-1}$  can be obtained at 20°C with high solution stability. At an elevated temperature of 50°C the rate increases and reaches  $\sim 3 \mu\text{m h}^{-1}$ . The Ag coatings obtained were of high quality, compact and bright.

In the present study, preconditioning treatments have been devised to deposit Ag electrolessly on acrylonitrile butadiene styrene (ABS) plastic discs used for a disposable Ag/AgCl electrode. Ag(I) and Co(II) ions in ammonia complex along with ammonium chloride as buffering salt were used for electroless Ag deposition. The effects of bath constituents, additives and operating conditions on the deposition rate have been studied. The effects of plating time, additives, pH, temperature and impurities on the topography of the deposit have also been studied using SEM. The crystalline nature of electroless Ag on ABS plastic was studied using SEM and XRD.

## Experimental

All the chemicals used were of laboratory reagent grade. Plastic discs of ABS, 10 mm in diameter with a stem of 3 mm diameter and 5 mm length at the centre of one

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side having a total area of 2 cm<sup>2</sup> were used as the substrate material. The substrate was subjected to preconditioning treatments comprising of:

- (i) etching in a solution containing 100 g L<sup>-1</sup> potassium dichromate and 900 mL L<sup>-1</sup> concentrated sulphuric acid for 120 s
- (ii) sensitisation in a solution containing 10 g L<sup>-1</sup> stannous chloride and 40 mL L<sup>-1</sup> hydrochloric acid
- (iii) activation in a solution containing 5 g L<sup>-1</sup> of ammoniacal Ag nitrate.

After the preconditioning treatments with intermediate wash and rinsing in demineralised water, electroless Ag plating was carried out in a solution containing ammoniacal Co chloride, ammoniacal Ag nitrate and ammonium chloride.

### Electroless plating solution

Predetermined quantities of Ag nitrate, Co chloride and ammonium chloride were dissolved in deionised water separately. Ammonia solution was added slowly to dissolve the precipitate and excess ammonia solution added to obtain clear solutions of both Co and Ag salt. These solutions were filtered through Wattman 40 filter paper and made up to the required volumes and used for the studies. The required amounts of ammoniacal Co chloride, ammoniacal Ag nitrate and ammonium chloride were mixed, the volume adjusted and pH value fixed by adding ammonia solution. The bath composition range studied is given in Table 1.

A teflon coated magnetic stirrer pellet was used for continuous agitating or stirring the electrolyte, which was held in a glass beaker. The activated and washed/rinsed plastic test buttons (of known number) were added to the agitating solution and kept immersed for 30 min or other required duration. After the desired duration of plating, the plated buttons were removed from the solution by filtration/decantation, washed, rinsed and dried, and a number of them weighed to determine deposition rates.

### Deposition rate

The Ag coating was dissolved in 10% HNO<sub>3</sub> solution and washed, and the ABS test buttons were rinsed, dried and weighed. The difference in weight is the deposit weight. Knowing the weight of the deposit, total area of the plastic buttons, density of Ag and time of plating, the deposition rate (μm h<sup>-1</sup>) was calculated as follows

$$\text{Deposition rate} = \frac{W \times 10^4 \times 60}{ADt}$$

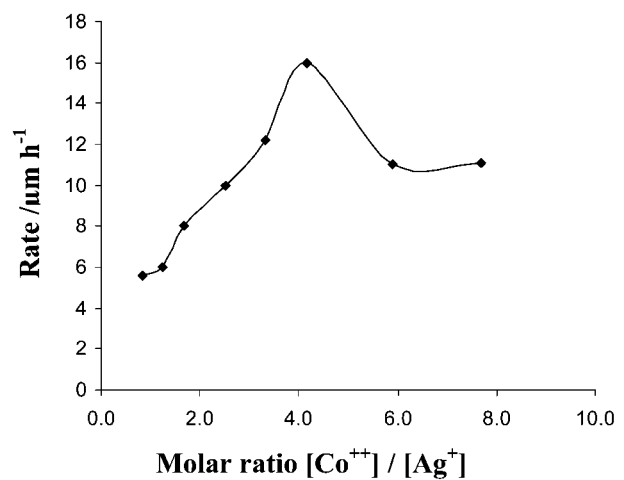
where  $W$  is weight of deposit (g),  $A$  is total area of the substrate (cm<sup>2</sup>),  $D$  is density of the Ag (g cm<sup>-3</sup>) and  $t$  is the time (min).

### Surface topography

The surface topography of the deposit on the ABS discs was determined by studying the plated sample surface using SEM (Hitachi 3000H, JSM 35 CF JEOL) under

**Table 1 Electroless Ag plating solution**

Co <sup>2+</sup>	0.05–0.2M
Ag <sup>+</sup>	0.02–0.08M
NH <sub>4</sub> Cl	0.5–1M
Ammonia	pH 10–11
Temperature	30–50°C



**1 Molar ratio of [Co<sup>2+</sup>]/[Ag<sup>+</sup>] on deposition rate**

magnification of ×3000 and comparing it with electroless Ag deposited from a cyanide bath. The crystalline nature of the Ag, deposited by the electroless method from the present cyanide free solution, was assessed from the XRD data (Philips, model X'pert PRO).

## Results and discussion

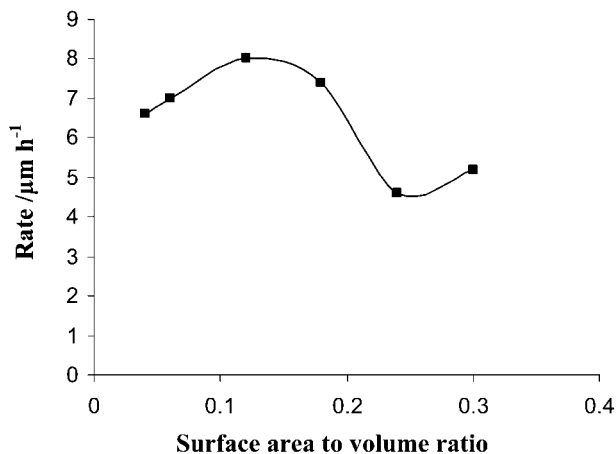
### Effect of molar ratio of Co<sup>2+</sup> to Ag<sup>+</sup> ion on deposition rate

Molar ratio of Co<sup>2+</sup> to Ag<sup>+</sup> ion was varied from one to eight with other parameters at a constant value. The effect of Co/Ag ion ratio is presented in Fig. 1. It indicates that a Co<sup>2+</sup>/Ag<sup>+</sup> molar concentration ratio of 4.2 gives a maximum deposition rate (16 μm h<sup>-1</sup>). Although the conversion rate of Co(II) into Co(III) determines the reduction rate of Ag<sup>+</sup> into Ag, the deposition rate mainly depends on the surface catalytic nucleation points. The availability of Ag ion also determines its deposition rate. Above the concentration of 0.12M Ag in the solution it has no effect on the increase in deposition rate; instead it reduces the rate. At a higher concentration of Ag ion, there is a formation of Ag powder in the solution. At the same time as nucleation at catalytic points on the surface of the base material the excess presence of Ag ion leads to non-adherent Ag particle formation which detached from the surface and contaminated the solution. Hence, for further studies a concentration of 0.06M Ag ions and 0.1M Co ions of 1.7 mole ratio ([Co<sup>2+</sup>]/[Ag<sup>+</sup>]) were used.

### Effect of area of substrate on deposition rate

In the present study, the area of the substrate was varied between 2 and 30 cm<sup>2</sup> in a 50 mL electroless plating solution under constant magnetic stirring speed for all the experiments. Figure 2 shows the effect of area to volume ratio on the deposition rate. It shows that 6 cm<sup>2</sup> area of the substrate, equivalent to an area to volume ratio of 0.12, gives a maximum deposition rate (8 μm h<sup>-1</sup>).

An increasingly lustrous nature of the coating was obtained when reducing the area of the substrate. From this experiment it can be concluded that 6 cm<sup>2</sup> is the optimum area for a 50 mL electroless plating solution from the point of view of maximum rate and finish. For



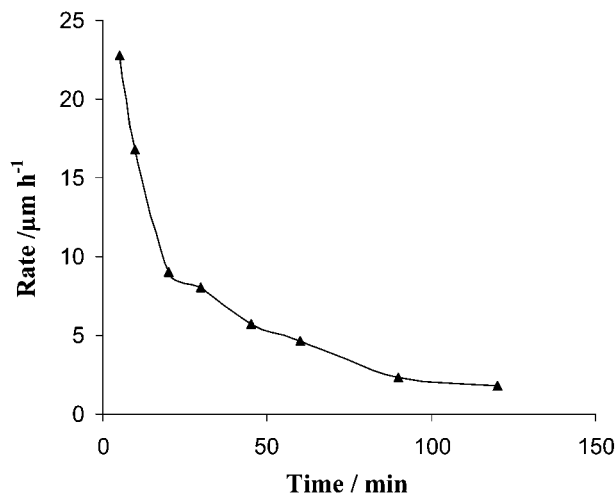
2 Effect of surface area to volume ratio on deposition rate

all the further studies, a 6 cm<sup>2</sup> area, equivalent to three buttons, was used.

Generally, to get the maximum deposition rate from a known volume of the electroless plating solution, an optimum area of the substrate should be used. Under the agitating condition of the electroless plating solution the area to be plated may be increased. When increasing the area of the substrate for a fixed volume of the electrolyte, there will be a reduction in the deposition rate as well as an inferior finish of the coating. Small substrate area increases the lustrous nature of the coating.

### Effect of plating time on deposition rate

The deposition time was varied from 5 to 120 min by keeping the solution pH value (10.8) and temperature (30°C) constant. Figure 3 shows the deposition rate with plating time. For 5 min there is a rate of 22.8  $\mu\text{m h}^{-1}$  and reduction in rate is observed at 20–30 min and, furthermore, there is a continuous reduction in rate to a value of 1.8  $\mu\text{m h}^{-1}$  for 120 min plating. During electroless deposition, there is always a continuous change in concentration of reducer and the metal ion to be deposited out with time. In particular, during electroless deposition on non-conductors, deposition occurs first on catalysed activated particles on the surface. Generally, the oxidation rate of reducing agent



3 Effect of plating time on deposition rate

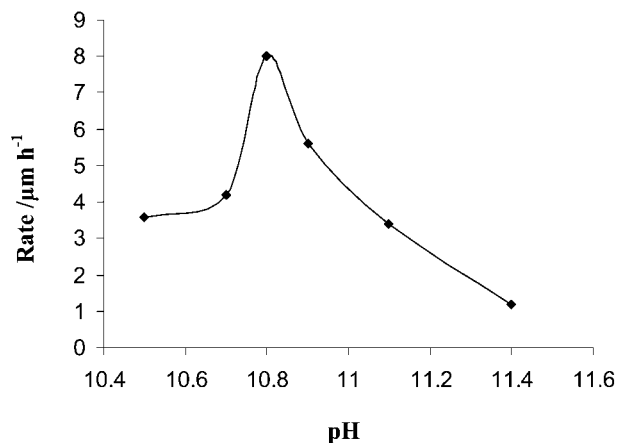
depends on the nature of the catalytic activity of the metal particles formed on a non-conductor during activation treatments. Naturally, at the initial stage the deposition rate will be in high order due to catalytic activity of the particles formed during the activation treatment.<sup>8</sup> Although the deposition rate of 22.8  $\mu\text{m h}^{-1}$  was observed for 5 min plating time the finish of the coating was grey in colour. A compromise of 30 min for the plating time to give an acceptable known plating rate was chosen for further studies.

### Effect of pH on deposition rate

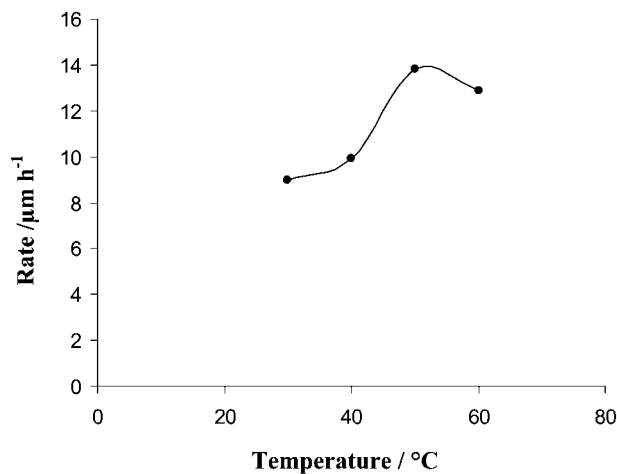
In the present system the pH of the solution was altered within a narrow range from 10.2 to 11.4 by changing the concentration of ammonia solution added to the electrolyte. The other variables were kept at a constant value. The effect of pH on the deposition rate is recorded in Fig. 4. It shows that there is a rise in deposition rate from 6 to 8  $\mu\text{m h}^{-1}$ , followed by a decrease in rate from 8 to 1.2  $\mu\text{m h}^{-1}$  over that pH range. The optimum pH value for the deposition of Ag with a high rate is 10.8. The pH 10.8 corresponds to 400 mL L<sup>-1</sup> of ammonia (30%) solution. Furthermore, at a higher concentration (>600 mL L<sup>-1</sup>) of ammonia the coating is non-uniform and dull in nature. Thus, for all further studies 400 mL L<sup>-1</sup> of ammonia (30%) solution was used. In general, pH of the bath/electrolyte, either in electroplating or in electroless plating, plays a major role in the properties of the deposit and efficiency on the one hand, and deposition rate on the other. In electroless plating most of the oxidation/reduction processes taking place on a catalysed surface are pH dependent.<sup>7-9</sup>

### Effect of temperature on deposition rate

By keeping all the constituents of the bath at a constant level, the author varied the temperature of the solution from 30–60°C in 10°C steps. A thermostatically controlled hot water bath was used for maintaining the temperature. The deposition rate versus temperature is shown in Fig. 5. A maximum rate of 13.8  $\mu\text{m h}^{-1}$  is obtained at 50°C and the rate is reduced slightly at 60°C. In general, the temperature of any reaction medium greatly affects the deposition rate of a reaction; increasing temperature increases the deposition rate.<sup>9</sup> Further reduction in rate at a higher temperature may probably be due to the loss of ammonia in the solution. Increasing temperature also alters the finish of the



4 Effect of pH on deposition rate



5 Effect of temperature on deposition rate

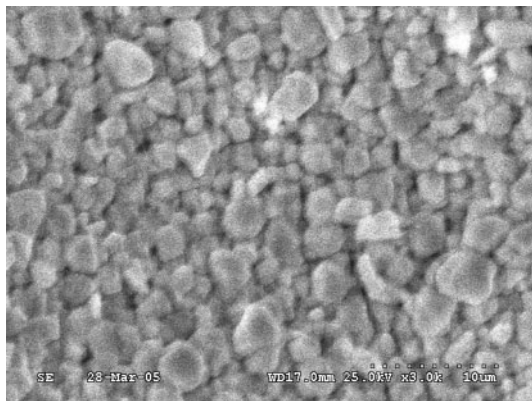
coating, i.e. its lustrous nature is improved. Although a higher temperature produces favourable results such as a higher rate and finer finish, all further experiments were carried out at room temperature (30°C).

Effect of addition agents

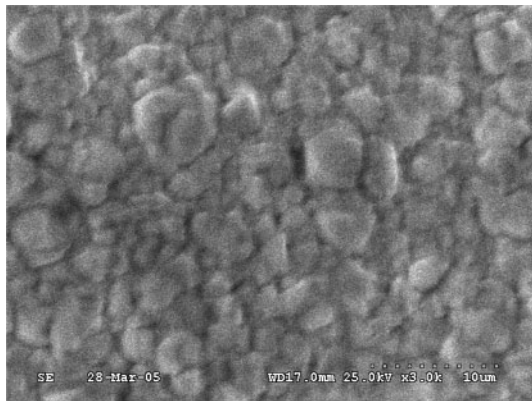
Gelatin, saccharin and naphthalene-2-sulphonic acid were added to determine their effects on grain refinement. Addition agents in the present studies were added with the additional need to know their effects on deposition rate as well as on the finish of the Ag deposit. The effect of additives on the deposition rate is given in Table 2. In general, additives get adsorbed over the catalysed surface and inhibit the oxidation/reduction processes, thereby altering the deposit crystal sizes and orientation, which leads to bright or semibright or dull or coloured deposits. If the additives are added in higher concentration levels, there may be a deleterious result such as total inhibition of the oxidation/reduction process or total poisoning of the catalytic activity leading to poor coverage or no deposit on the substrate. In the present study, 100 mg L<sup>-1</sup> gelatin produced a quality coating with regard to finish and coverage with a slight reduction in deposition rate.

Analysis using SEM

Photographs (SEM) of the electroless Ag coated on ABS plastic under different conditions are presented in Figs. 6–11. Figures 6 and 7 show the increasing trend of grain size with deposition time. A slight increase in grain size with improved lustre is seen in the deposit produced at a higher temperature (Fig. 8). A high temperature normally produces a high deposition rate due to the movement/orientation of the ions/molecules differing from the room temperature bath. Figures 6–8 indicate that even if the initial deposition is fine grained,



6 Image (SEM) of electroless Ag deposited for 5 min, at pH 10.8 and temperature of 30°C



7 Image (SEM) of electroless Ag deposited for 30 min at pH 10.8 and temperature of 30°C

upon metal growth into higher thicknesses, either through a higher temperature or longer plating time, the grain size becomes larger than the initial one.

Addition of gelatin improved the texture of the coating (Fig. 9). Gelatin greatly inhibits the deposit growth leading to a fine grained deposit with grain sizes in the range between 1 and 2 μm. The adsorption of gelatin at the catalytic point is the cause for this fine grained coating. It also reflects on the low deposition rate when compared with the additive free solution.

Saccharin is a brightening/stress relieving agent in nickel plating baths. One can reasonably expect such behaviour in the present system. However, little improvement is seen in the deposit produced from the present bath containing saccharin. Slightly better grain refinement (Fig. 10) is observed than in the deposit produced from the present bath without any additive.

Neither grain refinement nor compactness of the coating (Fig. 11) is seen in the deposit produced from

Table 2 Effect of additives on deposition rate

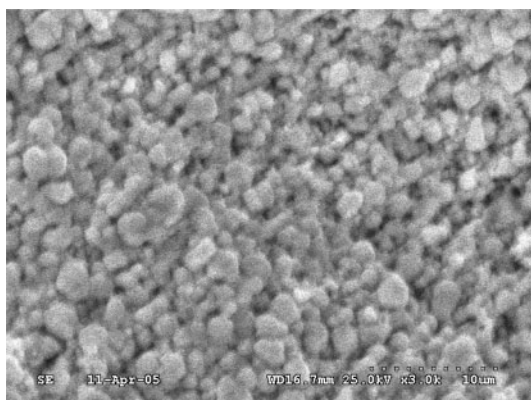
Additive	Deposition rate/μm h <sup>-1</sup>						
	10 mg L <sup>-1</sup>	50 mg L <sup>-1</sup>	100 mg L <sup>-1</sup>	200 mg L <sup>-1</sup>	400 mg L <sup>-1</sup>	600 mg L <sup>-1</sup>	1000 mg L <sup>-1</sup>
Saccharin	...	7.8	7.2	6.8	6.4	...	5
Gelatin	7.6	6.5	5.4	4.8	...	3.8	4
Naphthalene-2-sulphonate	4.3	4	3.4	...	...	...	...



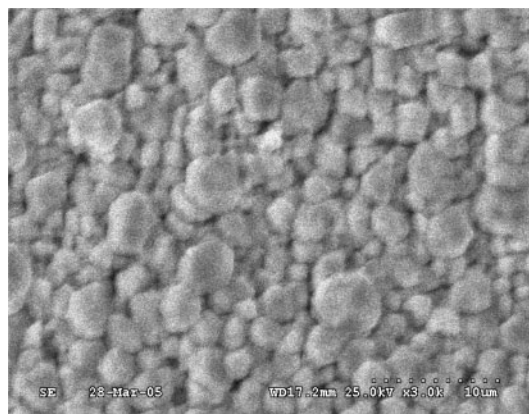
**8 Image (SEM) of electroless Ag deposited at 60°C and pH 10.8 for 30 min**

the present bath containing naphthalene-2-sulphonate. It produces a slightly porous type of coating, i.e. there is a loss of microcompactness of the crystals.

Deposition of metals on metals behaves in a different way to deposition on non-conductors. The nucleation points or centres are of a very high order when deposition takes place on another metal, whereas, the nucleation centres are much less on a catalysed surface of plastics/non-conductors where the adsorption of reacting species, the reducer and metal ion to be reduced/deposited, take place only on the available catalytic points. The catalytic points of Ag particles are formed during activation treatment with ammoniacal Ag nitrate. Thus, formed Ag particle distribution is not continuous. At initial stages there is a discontinuity of the deposit. Deposition growth takes place in both directions, perpendicular to the plane of the substrate as well as laterally. Only the lateral growth makes the connectivity of two nucleation centres, leading to continuity of the deposit. The supporting or complexing agents, and very small concentrations of additive play a major role in the growth of the deposit. Addition of a very small concentration of organic compounds, such as gelatin, thiourea, saccharin, etc., allows adsorption of these over the catalytic surfaces as well as on the deposited metal allowing the deposits to grow in a particular way, leading to different crystal sizes depending on the additives used. This depends on the deposition rate, which in turn depends on the concentration and nature of reacting species, pH, temperature



**9 Electroless Ag deposited in presence of gelatin at pH 10.8 and temperature of 30°C for 30 min**



**10 Electroless Ag deposited in presence of saccharin at pH 10.8 and temperature of 30°C for 30 min**

and stabilisers; the growth of the metal deposit also differs.

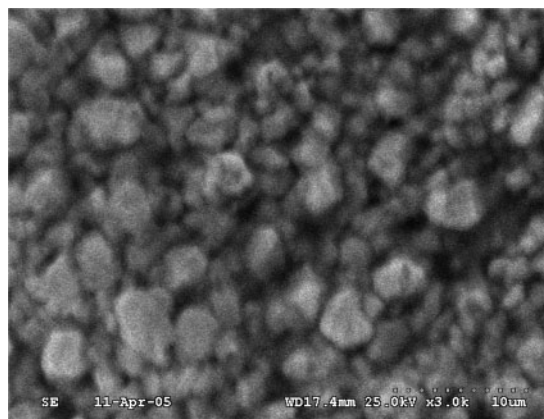
In the above SEM photographs, the topography of the electroless Ag deposited from the present bath with and without additives show that gelatin produces a fine grained nature of the deposit. Quality electroless Ag could be deposited on the plastic/non-conductors from the present bath with addition of gelatin.

### Analysis using XRD

The crystalline or amorphous nature of the Ag, deposited electrolessly from the present cyanide free solution, was determined from the XRD data which is presented in Fig. 12. X-ray diffraction data of electroless Ag deposited from the cyanide as well as from the present electrolyte are crystalline in nature and comparable. There is no peak for the presence of Co in the deposit since the ammonia complex of Co was used as the reducer. Here, Co(II) is highly complexed by the ammonia complex and cannot reduce to Co metal in competition to its oxidation while acting as a reducing agent for Ag reduction.

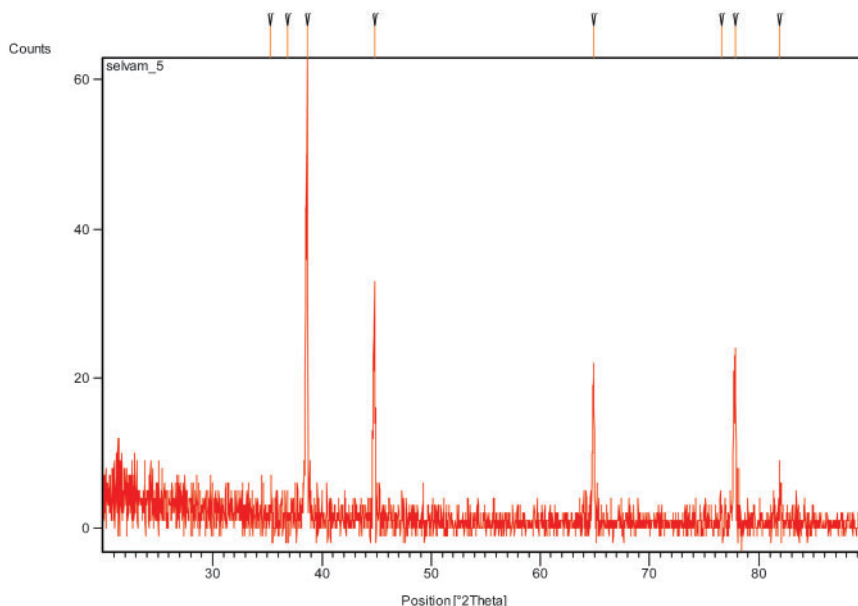
### Conclusions

Based on data from the literature, the oxidation of Co(II) to Co(III) process in the presence of ammonia was chosen as the reducing agent to reduce Ag ion to metallic Ag in electroless deposition. Studies have been



**11 Electroless Ag deposited in presence of naphthalene-2-sulphonate at pH 10.8 and temperature of 30°C for 30 min**





12 X-ray diffraction data of electroless Ag from present bath

carried out to determine a suitable bath formulation and its optimum operating conditions to plate Ag electrolessly, on ABS plastic substrate. The optimum metal ion concentration was fixed based on the study of the effect of metal ion concentration on the deposition rate. Similarly, optimum pH, temperature, area to be plated in a known volume of the bath, were also fixed based on the present studies to obtain a high deposition rate with bath stability without decomposition and the formation of Ag powder in the bath. Furthermore, the effects of three different types of additives were studied in the bath, among which the presence of gelatin in the present bath produces a quality deposit of fine grained nature.

Based on the experiments described above, the optimum preconditioning solutions such as etching, sensitisation, activation and bath compositions are recommended. Based on the detailed studies on electroless Ag deposition from non-cyanide solution using the Co non-conventional reducing agent, the following bath compositions are recommended to yield quality Ag deposit produced by electroless means on plastic/non-conductors:

- etching solution: potassium dichromate, 100 g L<sup>-1</sup>; concentrated sulphuric acid, 900 mL L<sup>-1</sup>
- sensitisation solution: stannous chloride, 10 g L<sup>-1</sup>; hydrochloric acid, 40 mL L<sup>-1</sup>
- activation solution: Ag nitrate (ammoniacal), 5 g L<sup>-1</sup>
- electroless Ag plating solution: Co<sup>2+</sup>, 0.1M; Ag<sup>+</sup>, 0.06M; NH<sub>4</sub>Cl, 0.5M; ammonia, to pH 10.8; gelatin, 0.1 g L<sup>-1</sup>; temperature, 30°C; area, 240 cm<sup>2</sup> L<sup>-1</sup>; deposition rate, 5.4 μm h<sup>-1</sup>.

## Acknowledgement

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