Chapter-4

Formulation and Optimization of Ternary Sn-Ag-Cu Co-deposition bath
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Formulation and Optimization of Ternary Sn-Ag-Cu Co-deposition bath

Formulation of a co-deposition bath is a formidable task. One of the most important issues in formulating a co-deposition bath is the bath stability, arising out of the compatibility of the chemical constituents with each other. The base electrolyte, the chemicals that source the metals, the chelating agents, the bath additives including surfactants and surface finishing agents, antioxidants, pH buffers etc. are the major constituents of an electroplating bath. Their compatibility with each other and their combined behaviour at a particular pH level largely determine the properties of the bath as well as the deposited film. The reported literature does help in the selection of the bath system grossly but the composition of bath constituents and the deposition parameters have to be optimized experimentally in order to obtain the desired film properties. The reason is that it is difficult to predict the microscopic behaviour of such large number of chemicals in one electrolyte beyond a point. Usually, either highly acidic or highly alkaline baths are sufficiently stable, and are not affected by minor changes in the bath or deposition conditions. For these baths, small changes in the ambient temperature or other process parameters may not produce a noticeable change in the film properties. However, as the pH of the bath approaches close to the neutral value, the baths may become sensitive to small variations in the deposition conditions which may
be amplified unpredictably in the film properties. Inspite of this, the industry would prefer a neutral or close to neutral pH bath which gives the desired film properties. This makes the selection of bath very crucial. The work for the development of Sn-Ag-Cu co-deposition bath, with a targeted pH range of 4-5, also needed to trace this path for identifying the right constituents and their combination. From the literature survey in Chapter 3, it is already identified that chelating agents such as EDTA, thiourea, pyrophosphate and tartarate may be useful as chelating agent for one or more metal ions among Sn, Ag and Cu while POELE, PEG, Tartarate, OPPE, gelatin can function as bath additives in methane sulfonic acid based Sn-Ag-Cu co-deposition baths.

The initial part of this work was devoted to identifying the right combination of the identified chelating agent(s) and additives by formulating a series of baths and studying their stability and the composition and microstructure of the deposited films. This Chapter presents the experimental details and details of the various combinations of chemicals that were used for formulating the tri-metal co-deposition bath. Thiourea and EDTA were explored as chelating agents, POELE, OPPE, sodium potassium tartarate, polyethylene glycol, gelatin, alkylbenzene sulfonate etc were examined as additives and hydroquinone was tried as antioxidant. The chemical structures of these compounds are presented in the next page. Many bath formulations were found to be extremely unstable. The results of the baths which showed acceptable stability are presented here. After various iterations on the combinations of chelating agents and additives, the best bath was optimized and some of the basic studies related to the behavior of this bath are also reported here.
4.1 Bath Selection: Approaching an Optimized Bath

Having selected methane sulfonic acid as the base electrolyte, it was decided to explore chemicals compatible with this electrolyte base. Amongst the two possible chelating agents, viz., EDTA and thiourea, EDTA was explored first and it was found to be incompatible with MSA system. Different concentrations of EDTA were tried but the bath precipitated out. Later, a combination of EDTA and thiourea were investigated but this did not help in obtaining a stable bath.

![Figure 4.1: The bath optimization process](image)

The next approach was to test Thiourea alone as a chelating agent. The results of these experiments were encouraging, and were pursued further. This chelating agent, although found to be better than EDTA in terms of bath stability, required lot of iterations in terms of thiourea concentration and chemical combinations in the bath. Finally, a particular combination of thiourea and other additives produced a bath with stability of about 8-10 days which also deposited film with desired chemical composition and acceptable microstructure. The flow chart in Figure 4.1 pictorially represents the experimental approach followed to obtain a stable ternary Sn-Ag-Cu electroplating bath.
4.2 Experimental Procedure

Whichever chemicals were to be used in any particular bath, the bath preparation procedure was common. After mixing the base electrolyte with water to form the required concentration, the Sn source was added which was followed by the addition of chelating agent. Thus, the preparation process of adding chemicals in a particular sequence in a single bath was followed. It was important to form chelates with Sn (possible in case of EDTA) or to have chelating agent for Cu/Ag present in the bath before this addition. This sequence of addition of chemicals was chosen over the preparation process wherein all the metal are first added in to the electrolyte system followed by the chelating agent and other additives so as to ensure better bath stability. Separate solutions of individual metal and its chelating agent followed by addition of each such solution to electrolyte is another approach. However, no significant difference in final bath stability was noticed when this procedure was followed. The stable and sometimes semi-stable baths were then used to electro deposit the ternary film. This generalized description of the bath formulation process is presented in the flowchart in Figure 4.2. Each bath was prepared in a quantity that made it up to 100ml.

Unless the bath became unstable immediately after preparation, the bath was divided into two parts. One part was stored for observation of bath stability and the other part (60ml) was used for film deposition experiments. In some cases the first part was also used for electrochemical and other analysis, such as, Cyclic Voltametry, optical absorption etc. Whenever the bath was used for deposition of films, a standard area of 1cm$^2$ area was delineated on the substrate. All the films were deposited on Ni coated Cu clads. Simple adhesive tape was used for masking the rest of the substrate area. The depositions were carried out using GPES module of the Potentiostat-
galvanostat (PGSTAT 100, Autolab, The Netherlands). Figure 4.3

**Figure 4.2: Flowchart depicting the bath formulation process**

- **Addition of appropriate amount of MSA into distilled water**
- **Addition of Sn metal source (Tin methane sulfonate)**
- **Addition of chelating agent (EDTA/EDTA+Thiourea/Thiourea)**
- **Addition of bath additives (POELE/OPPE/Polyethyleneglycol)**
- **Addition of Cu metal source (Copper Sulphate)**
- **Addition of Ag metal source (Silver Sulphate)**
- **Addition of surface finishing agent (Gelatin)**
- **Raising of pH (Acetate Buffers)**

presents the general flowchart of the electro deposition experiments. While the Cu clads could be used directly for the deposition of solder, adding a sandwiched Ni film helped in using EDS for the chemical analysis with more confidence and reliability. This film ensured that the characteristic X-rays detected by EDS was primarily from the solder film and the Cu clad does not interfere. The nickel films on the copper clad substrates were deposited using
commercial bath ('Bright Nickel', from M/s. Growel (I) Ltd). Following were the deposition conditions

- Current Density: 40mAcm\(^{-2}\)
- Deposition time: 7min
- Anode: Ni plate
- Cathode: Cu clad substrate

![Flowchart](image)

**Figure 4.3: Flowchart depicting the cathode substrate preparation and the electroplating process**

Basic characterization of the Ni film was done. The films were shiny and compact and showed good repeatability in terms of microstructure. Figure 4.4 presents the microstructure of a typical Ni film.
Figure 4.4: SEM Micrograph (10000X) of electrodeposited Ni on copper clad

Fine grained (sub100nm size) compact, smooth granular structure can be observed. With the above deposition condition, a thickness of about 5±1μm was repeatedly obtained. In general, it was found that the properties of the underlying Ni film on which the solder deposition was to be carried out were quite stable and repeatable.

A 250ml beaker with a jig that ensured vertical immersion of the anode and reference electrode as well as a specially prepared cathode holder was used for the deposition of solder. An Ag/AgCl electrode was used as reference electrode. The distance between the anode and the cathode was maintained at ~3cm. The reference electrode was kept at about 0.5-1cm from the cathode. The depositions were carried out using Potentiostat Galvanostat by chronopotentiometry (galvanostatic) method. The general conditions and parameters used for electro deposition experiments are presented in Table 4.1.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Current Density</td>
<td>10 mA/cm²</td>
</tr>
<tr>
<td>2</td>
<td>Plating Area</td>
<td>1cm²</td>
</tr>
<tr>
<td>3</td>
<td>Plating time</td>
<td>1 hour</td>
</tr>
<tr>
<td>4</td>
<td>Temperature</td>
<td>Room temperature</td>
</tr>
<tr>
<td>5</td>
<td>pH</td>
<td>~4</td>
</tr>
<tr>
<td>6</td>
<td>Cathode</td>
<td>Ni coated Cu clads</td>
</tr>
<tr>
<td>7</td>
<td>Anode</td>
<td>Pure Sn plate</td>
</tr>
</tbody>
</table>

Table 4.1: Range of experimental conditions for electroplating of Sn-Ag-Cu films

The deposited films were rinsed with distilled water and dried in air before characterization. The baths were characterized first by the
simple visual transparency and the deposited films were characterized for their microstructure, elemental composition, film thickness and adhesion.

4.3 Film Characterization

The characterization of the deposited films was done by visual inspection, microstructural and elemental analysis and other physical analyses, such as, thickness of the deposit, adhesion etc. In order to maintain comparability between samples, a definite procedure was adopted for sample management and characterization.

Unless the bath was found to be unstable and the films too poor, a minimum of the following tests were undertaken on each deposited film:

- Optical inspection
- Thickness measurement
- Adhesion test
- Elemental Composition and microstructural analysis

While the above tests were routinely carried out for all the deposited films, some additional depositions were done for representative structural analysis by X-ray diffraction. The following sub-section describes the sample management and the characterization procedure in detail.
4.3.1 Sample management

It may be recollected that all the solder depositions were done on Cu clads having an under lying Ni film with a pre-defined area of 1cm$^2$. After obtaining dried deposited film, about half the area of the film was used for adhesion test. The rest of the area was used for the thickness measurements, microstructure analysis and elemental analyses. Figure 4.5 presents the sample management schematically.

4.3.2 Adhesion test (90° Peel Test)

A simple qualitative ‘scotch tape’ method was used to determine the adhesion of the films on the substrate. A scotch tape was pasted over the portion of the film where the adhesion is desired to be checked and pulled out from one side. If the film is loosely adhered to the substrate, the film comes off with the tape. While a complete removal of films would indicate poor surface preparation removal of only an upper layer of the film would indicate a loosely adhered non-compact vertical growth that is usually seen for unsustainably high current density.

4.3.3 Microstructure analysis

The microstructure of the deposited film was observed using Scanning Electron Microscope (SEM-EDS, Phillips XL-30 with EDAX). This was useful in determining the uniformity of the deposited film, its grain size, microstructure, and compactness of the film and, in general, the quality of the deposition. Most of the films
were observed at 500X magnification. For films with very fine microstructure, the observations were done at 1000X magnification, which helped in observing the compactness.

4.3.4 Elemental compositions

The elemental composition of the deposited films was determined using EDAX (SEM-EDS, Phillips XL-30 with EDAX) using the standardless estimation technique. This method employs correction factors for errors due to varying atomic number, absorption of X-rays and fluorescence (ZAF) which are not very specific. This method of elemental analysis, however, provides better estimation accuracy above 5% weight content of metals, while providing indicative figures below this percentage. The exact amount of error involved would depend upon the composition of the specific element as shown in Table 4.2.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Expected composition</th>
<th>Possible error</th>
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<tbody>
<tr>
<td>1</td>
<td>0.2-1%</td>
<td>50-100%</td>
</tr>
<tr>
<td>2</td>
<td>1-5%</td>
<td>Up to 20%</td>
</tr>
<tr>
<td>3</td>
<td>5-20%</td>
<td>Up to 10%</td>
</tr>
<tr>
<td>4</td>
<td>20-100%</td>
<td>Up to 5%</td>
</tr>
</tbody>
</table>

*Table 4.2: Error involved in Elemental Analysis using EDAX (124)*

X-ray Diffraction technique was used to cross-check presence of Cu in the films, apart from the confirmation of crystallinity of the deposited films. This structural characterization of the films was done using the X-Ray Diffractometer (XRD, Brüker, AXS D5005).

4.3.5 Thickness measurement

The thickness of the deposited films was determined using the focusing method of the metallurgical measuring microscope. (Nikon MM40) having digital readout (DRO). The DRO has a least count of 1μm. Care was taken to find appropriate parts of film surface and
the substrate in the same field of view and not to move the sample during measurement. This eliminated the risk of large misreading of the thickness due to issues such as sample warpage. An appropriate magnification was thus chosen for this purpose. Usually, efforts were taken to keep the same magnification for each measurement.

4.4 Experiments for Formulation of the Bath

The literature survey presented in the previous Chapter helped in short-listing a few chelating agents and additives that would be useful in formulating a co-deposition bath. Different chemical combinations were tried out to obtain a co-deposition bath. Initially, EDTA as chelating agent was chosen as it forms complexes with more than one metal ion out of Sn, Cu, and Ag. It is known that EDTA chelates Sn and Cu in the acidic range and with Ag it forms indirect complexes. Later thiourea, which chelates Ag and Cu in the acidic range, was used. The experiments with various additives followed. The following Sections provide details of the various experimental results obtained by using the different chemical combinations tried.

4.4.1 Experiments with EDTA as chelating agent

The composition of EDTA required for chelating the metal ions was evaluated based upon their coordination numbers (111). Accordingly 0.24M EDTA was added to the bath mentioned in Table 4.3 but the entire amount of EDTA could not be dissolved into the MSA electrolyte and the solution turned whitish even before the copper and silver salts could be added. EDTA seems to be having limited solubility in MSA electrolyte. Slight changes in the bath preparation procedure, with EDTA being dissolved in water, followed by addition of MSA also did not help. The procedure for bath preparation as described in Figure 4.2 was then followed. The addition of the additives also did not help in reducing the turbidity of the bath.
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Chemicals</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methane Sulfonic acid</td>
<td>1.54M</td>
</tr>
<tr>
<td>2</td>
<td>Tin Methane Sulfonate</td>
<td>0.34M</td>
</tr>
<tr>
<td>3</td>
<td>Copper Sulphate</td>
<td>0.08mM</td>
</tr>
<tr>
<td>4</td>
<td>Silver Sulphate</td>
<td>0.64mM</td>
</tr>
<tr>
<td>5</td>
<td>EDTA</td>
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</tr>
<tr>
<td>6</td>
<td>Gelatin</td>
<td>2g.lit⁻¹</td>
</tr>
<tr>
<td>7</td>
<td>OPPE</td>
<td>12ml.lit⁻¹</td>
</tr>
</tbody>
</table>

*Table 4.3: Bath composition of EDTA based electrolytes*

Bath formulations with reduced EDTA concentration such as 0.026 and 0.04M did not have any solubility problems but both the baths precipitated out just as soon as the silver salt was added. Clearly, this amount of EDTA was not sufficient. For all the above experiments, the pH of this solution was less than 1.

### 4.4.2 Addition of thiourea along with EDTA

A new electrolyte containing both thiourea and EDTA as chelating agents was formulated. While all the constituents had the same composition as mentioned in Table 4.3, additionally, 0.2M thiourea was added to the bath. Table 4.4 presents the bath composition used for these experiments. It was found that the as-prepared bath (pH<1) is stable. Having obtained a stable bath, though highly acidic, the depositions were carried out.
Table 4.4: Bath composition of electrolytes containing thiourea and EDTA

<table>
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</tr>
<tr>
<td>6</td>
<td>Thiourea</td>
<td>0.2M</td>
</tr>
<tr>
<td>7</td>
<td>Gelatin</td>
<td>2g.lit⁻¹</td>
</tr>
<tr>
<td>8</td>
<td>OPPE</td>
<td>12ml.lit⁻¹</td>
</tr>
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</table>

Figure 4.6 shows the SEM micrograph of the deposited ternary film. The film had compact microstructure with a composition of 95.1Sn-3.34Ag-1.6Cu.

Due to the encouraging result at low pH, another few experiments were carried out wherein the pH was attempted to be raised using acetate buffers, while keeping the rest bath compositions same as Table 4.4. However, these baths became unstable ever before the pH was raised to 2. Deposition could not be carried out due to the precipitation of the bath. Even though the Sn-Ag-Cu films deposited

Figure 4.6: SEM micrograph of Sn-Ag-Cu film deposited using EDTA based as prepared bath
at low pH was having composition close to the expected eutectic. This bath was not found to be desirable due to very low pH value.

### 4.4.3 Experiments with thiourea as chelating agent

The function of thiourea as a chelating agent for Ag and Cu is widely reported (100,125-131). However, its effectiveness in MSA based baths is yet to be explored. It would be ideal to have a chelating agent that holds both the electropositive metals in chelation thereby controlling the precipitation. The series of experiments carried out using this chelating agent, are discussed in this Section.

This set of experiments had the metal sources along with 0.04M of thiourea in the electrolyte. No additives were used for these experiments. This bath is later referred to as 'OP' bath. Table 4.5 details the chemical composition of the bath. It may be noted that this as prepared bath had a very low pH (<1). This bath precipitated as the pH was raised to about 4-5. Since this low pH bath was stable, it was used to deposit the Sn-Ag-Cu films, and the films were characterized for their elemental composition and microstructure. Figure 4.7 presents the SEM micrograph of a film deposited using this acidic bath at a current density of 10mAcm⁻². The microstructure showed highly granular growth with very large granules in the range of 50-70µm. The surface, therefore, was not smooth. This film had a composition of 92Sn-6.5Ag-1.5Cu. The large concentration of silver prompted the next experiments with reduction in Ag salt content in the bath.

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<td>1.2mM</td>
</tr>
<tr>
<td>5</td>
<td>Thiourea</td>
<td>0.04M</td>
</tr>
</tbody>
</table>

*Table 4.5: Bath composition of thiourea based electrolytes without additives*
i. **Reduction of Silver content:** Based upon the previous result, it was decided to reduce the silver content in the plating bath at low pH and without additives. This bath was found having better stability. Therefore, it was decided to increase the pH. Accordingly, the pH was maintained to about ~3. The composition of other chemicals remained the same as mentioned in Table 4.5. The silver content was reduced to 0.64 mM. As the pH was raised to 3, the solution remained stable and some precipitate could be seen settled overnight. When the pH was raised to a 3-4, the precipitation could be seen within 2 hours.

This bath with pH ~3 and one with pH above 3 was used to deposit films at 10 mA cm\(^2\) current density. These films were found to be different from each other in appearance. The film deposited at pH 3 had bright granular appearance while the one deposited at pH >3 (3 – 4) had dull appearance Figure 4.8 and 4.9 present the SEM micrographs of the two films deposited using the above baths.
Figure 4.8: SEM micrograph of ternary film at pH 3

The SEM pictures show non uniform microstructure with large grains at pH 3 while highly porous, loose deposits at higher pH. The film composition was 81.1Sn-17.5Ag-1.28Cu for the bath at pH 3 and 95.5n-3.2Ag-1.3Cu at the slightly higher pH value. These experiments indicated the possibility of influence of pH on bath composition. However, due to poor bath stability (though much improved as compared to EDTA and EDTA with thiourea baths) it was decided to modify bath composition further, and introduce the additives in the bath.
4.4.4 Experiments with additives for thiourea containing bath

Experiments with additives in the thiourea bath were carried out with various ways. Different additives and their combinations were tried, and concentrations were varied.

i. **POELE as additive:** Polyoxyethylene lauryl ether (POELE) as found from the literature is an additive that helps to improve the microstructure of the deposited film. It gets adsorbed on the deposited film and controls further growth, which helps in microstructure refinement (109-110). Accordingly, about 4mM POELE was introduced into the bath containing thiourea, while the rest of the composition remained same as mentioned in Table 4.5. The current density used for the experiment was 10mAcm⁻².

As POELE was introduced in the bath, the bath solution appeared to be stable for a day and overnight some precipitation could be seen. This solution at pH~3 deposited compact film with an average composition of 90Sn-9Ag-0.2Cu. The microstructure for these films is shown in Figure 4.10.
As the pH of the solution was raised to about ‘5’, it became slightly turbid almost immediately and after two days, little precipitate could be seen settled down. Nevertheless, the deposition was carried out using this bath. It was found that these films were porous having a composition of 91.3Sn-5.4Ag-3.3Cu. Fig 4.11 presents the SEM micrograph of the deposited film.

It was observed that the films obtained using POELE based electrolytes were far away from the desired composition. While the microstructure of the film obtained using low pH (~3) bath was compact, the film contained almost three times silver than the expected one and the film deposited at higher pitch was porous and had comparatively lower silver content but copper content was higher. In general, these baths did not produce desired results in terms of composition, and stability and film properties at high pH.
Increase in thiourea concentration: It may be recalled that the desired pH range for the bath was close to neutral. The results with thiourea as chelating agent and POELE as surfactant were encouraging as compared to those without POELE. However, better stability at pH higher than 3 was expected. In order to achieve this goal, one possible way was to increase thiourea content and ensure that there is excess thiourea in the bath. Accordingly, in this set of experiments, thiourea concentration was then increased to 0.2M while continuing with POELE concentration which was kept constant at 4mM. All the other constituents remained the same as detailed in Table 4.5.

The bath was stable for a day at pH~3 and with further increase in pH, the bath precipitated within 2 hours. The SEM micrograph at pH ~3 and pH~5 are shown in Figure 4.12 and Figure 4.13 respectively. As found earlier, the bath at higher pH produced porous films while shiny, faceted and crystalline films were obtained at a pH of ~3.
The average film composition was found to be 95.3Sn-2.6Ag-2Cu at pH ~3 and 80.6Sn-18Ag-1.4Cu at higher pH. Thus, the composition was found to be far away from the unexpected at higher pH and it also produced poor microstructure compared to the film with lower pH (~3), which had compact microstructure with large faceted grains, which was far better. These results, though better, had two problems. One, the pH was limited to about 3-4, and second the large granular depositions are not desirable. In order to improve these results, another additive *viz.* OPPE was used in place of POELE.
iii. *Plating bath containing thiourea and OPPE*: OPPE is a widely known surfactant and is also reported to be used in wide application including biomedical, auto catalytic and electroplating of metal (132-135). Even in Sn-Pb baths, this chemical helps Pb in controlling the whisker formation tendency of Sn (136). As a surfactant it improves the microstructure of the deposited film. Based upon these expectations OPPE was used in the thiourea containing plating bath. Table 4.6 presents the composition of bath used for deposition:

<table>
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<tr>
<td>4</td>
<td>Silver Sulphate</td>
<td>1.2mM</td>
</tr>
<tr>
<td>5</td>
<td>Thiourea</td>
<td>0.04M</td>
</tr>
<tr>
<td>6</td>
<td>OPPE</td>
<td>6mM</td>
</tr>
</tbody>
</table>

*Table 4.6: Bath composition of thiourea and OPPE based electrolytes (OP1)*

This series of experiments having OPPE in the bath, showed much improved bath stability in comparison to stability. The bath remained clear for 4-5 days after which some precipitation could be seen. The pH of the bath was maintained close to 4. The film deposited at current density of $10\text{mAcm}^{-2}$ had a microstructure as shown in Figure 4.14. The film had a silvery white appearance and the microstructure was found to be compact, faceted and crystalline. The deposited film had a composition of 96.05Sn-3.05Ag-0.9Cu. The film had a thickness of ~20$\mu$m at the end of one hour of deposition.
It is seen that this bath, containing thiourea and OPPE produced best results thus far, and needed further investigations.

4.4.5 Conclusions

This Section previously presented the different experiments carried out to identify the right combination of chelating agents and other bath additives in order to obtain a co-deposition bath that deposits the ternary Sn-Ag-Cu film in the desired composition range. The chelating property of EDTA towards Sn and Bi has been studied earlier (111) for sulfuric acid based systems but that does not hold true for MSA based electrolytes. EDTA seems to be having limited solubility in this electrolyte system and the dissolved amount of EDTA was not sufficient to chelate the metal ions. The bath, therefore, precipitated out as the pH was raised. The EDTA based the bath is stable at highly acidic condition, which is not favorable for its use in electronic applications. Thiourea is reported to have produced good results with POELE in sulfuric acid based bath. However, it did not produce favorable results for MSA baths with POELE as additive. Trials with many other additives, such as, Sodium Potasssium
tartarate, alkylbenzene sulphonate, polyethylene glycol along with thiourea were also unsuccessful.

It is seen that baths containing thiourea with OPPE produced results that were amongst the best in the series of experiments carried out to identify the basic bath composition. Without the use of OPPE the bath precipitated overnight but in the presence of OPPE, the bath showed better stability, which remained for 4-5 days and slight precipitation could be seen thereafter. The film microstructure was also compact and uniform. Coordination bonding between thiourea and mostly Ag and Cu ions was probably one of the important reasons. However, this needed to be confirmed.

This bath, named OP1, may not be an ideal bath for the desired ternary deposition, but the stability, film microstructure and composition is close to the desired properties. It became necessary at this point to understand the bath chemistry and reasons for the improved properties and then proceed toward further refinement of bath. The effect of thiourea in the presence and absence of OPPE and the effect of OPPE on the metals deposition process are worth investigating. The function of the surfactant OPPE also needed to be understood.

In order to understand and confirm the observation of improved bath stability and improved film properties, a detailed plan was prepared to study these aspects with the help of two bath analysis techniques viz. UV-Visible absorption spectrometry and cyclic voltametry. Simultaneously, the deposited films were characterized for the microstructure and composition SEM-EDS. In the following Section first the plan of experiments is presented, which is followed by the results of bath and film analysis.
4.5 Study of Thiourea and OPPE Containing Bath (OP1)

Having identified a reasonably stable bath that produces films with composition in the acceptable range and similarly acceptable microstructure, the further task was two-fold. First was to undertake a study that determines the effect of the chelating agent and its additives, and to enumerate their role in the given bath. Second was to determine their limits with respect to parameters such as pH, current density based upon the properties of the deposited films. Thiourea is a known chelating agent and its effect could be greatly noticed by the reduction in precipitation and improvement in bath stability. The chelating effect of thiourea in presence of multiple metal ions, however, needed to be understood. Additionally, the contribution of OPPE, a surfactant, in improving the bath stability required investigation. The effect of these chemicals on the film properties also needed to be understood. All these experiments, formed the basis of the in-depth analysis of the ternary Sn-Ag-Cu electrolyte.

4.5.1 Experimental plan for electrolyte and film analysis

Two types of experiments were undertaken. First was the bath analysis part, which involved CV and UV-Visible absorption spectroscopy of the ternary bath, followed by similar analysis of separate baths prepared using single metal elements. Such analysis was found necessary due to due to the complexity of the bath containing three metal ions. The second part was the behavioral analysis of the bath, determined from properties of the film microstructure refinement and elemental content followed by its response to current density. The flowchart in Figure 4.15 presents the experimental path followed for the said investigation.
4.5.2 Bath characterization: Uv-Visible absorption studies

UV-Visible spectrometry is one of the best techniques to study the chelating effect of a ligand (137). The absorption of the free metal ions can be recorded and the chelating effect can be understood. Once the metal ion gets engaged with the chelate molecule, the concentration of free metal ion reduces, causing reduction in UV and optical absorption.

UV-Visible studies were undertaken for individual baths as well as ternary baths to understand the effect of thiourea as well as OPPE on the individual metal ions and in turn on the ternary bath. For all the three metal ions i.e. Sn, Cu and Ag, three sets of solutions were prepared. Set I was prepared with just MSA solution, Set II with MSA and thiourea, and, Set III with MSA, thiourea and OPPE. The change in absorption in the visible range was recorded.

The absorbance curves for Copper system are presented in Figure 4.16.
As can be seen from the figure, there is substantial reduction in the absorption of the bath after the introduction of thiourea in the MSA electrolyte containing Cu$^{2+}$ (Set II). This suggests chelation of copper by thiourea, thereby reducing the concentration of free metal ion and hence its absorption. After OPPE was added into the system containing MSA and Thiourea, a slight reduction in the absorption could be seen indicating a minor positive effect of OPPE on the bath.

Figure 4.17 presents the UV-visible absorption spectra for the Ag system, wherein Set I, II and III of the Ag bath were subjected to UV-Vis absorption studies. Similar to copper, there is a considerable reduction in the absorption of Ag$^{+}$ ions after introducing thiourea into the bath containing only MSA. However, unlike copper, there is slight increase in the absorption with the addition of OPPE. The chelating effect of thiourea is clear from this study but the effect of OPPE cannot be concluded precisely.
Figure 4.17: UV-visible absorption spectra for bath containing MSA, MSA+ thiourea and MSA+ thiourea+ OPPE, for Ag+ ions

Similar experiments were conducted on Sn ion containing baths. Figure 4.18 presents the UV-visible graphs for Sn ions. It is seen that in this case, there is no clear trend in the behaviour of the baths due to thiourea as well as OPPE. Although the average absorbance of the Sn ions decreases in both the cases, the absorbance curves show
a wavelength dependent spectral response. Further analysis of the bath system was required to understand their bonding.

4.5.3 Bath characterization: Voltametric studies

The cyclic voltametric analysis helps in identifying the oxidation and the reduction peak positions with respect to the applied voltage. When the metal ion is in chelated form, there would normally be a considerable shift in the reduction position helping in identifying chelate formation.

Cyclic voltametry studies were carried out on all the sets of electrolytes containing individual metal ions with different additives (set I, II and III) as well as for the ternary system using the potentiostat-galvanostat. These measurements were carried out using carbon as counter electrode and Ag/AgCl electrode as reference electrode. A standard platinum electrode was used as working electrode. The cyclic voltametry curves were recorded for the range −0.6V to +0.6V depending upon the metal ion being studied. Figure 4.19 presents the cyclic voltametric curves for copper based

Figure 4.19: Cyclic voltamogram of Cu²⁺ ions with additives. (a) Cu²⁺ in MSA and (b) Cu²⁺ in MSA+thiourea and MSA+thiourea+OPPE
solutions in MSA electrolyte with and without thiourea and OPPE. The chelating effect of thiourea on Cu\(^{2+}\) in MSA based baths is clearly visible in the CV curves presented here. It can be observed that the reduction potential of Cu\(^{2+}\) in MSA alone is about 0.1V. This is found to have changed substantially to -0.47V after thiourea was introduced into the system. Substantial shift in reduction potential is a characteristic signal of chelate formation. It is clear that Thiourea chelates Cu\(^{2+}\) ions and alters its deposition potential. When OPPE was added to the bath containing MSA and thiourea, there was no apparent change in the reduction potential but there was reduction in cathodic current as can be observed from Figure 4.19 (b). The cyclic voltametric curves for silver system in solutions similar to the ones prepared for copper baths are presented in Figure 4.20. The deposition potential of Ag\(^+\) in MSA electrolyte was found to be +0.329V, which shifted to -0.05V when thiourea was added to the bath containing Ag ions and MSA. This confirms the chelating effect of thiourea. Introduction of OPPE imparts a positive shift of 0.027V

![Cyclic voltametry for Ag\(^+\) in MSA bath with and without thiourea and OPPE (OPPE)](image)

*Figure 4.20: Cyclic voltametry for Ag\(^+\) in MSA bath with and without thiourea and OPPE (OPPE)*
in the deposition potential and reduction in the cathodic current. An additional bath was prepared without thiourea, which contained Ag ions in MSA, and OPPE alone. A similar small shift of (0.05V) was observed in this bath as it can be seen in Figure 4.20. Effect of OPPE on the bath is noticed, however, small change in the reduction potential does not indicate any chelation. It can also be observed from the figure, that there is a marked reduction in the cathodic current after the introduction of thiourea and OPPE in the silver containing electrolytes. Change in cathodic current is an indication of electrode coverage by a non-conducting film.

Figure 4.21 presents the cyclic voltametric curve for Sn$^{2+}$ ions in MSA bath with and without thiourea and OPPE. In the case on Sn electrolytes, a marginal shift in the position of the reduction peak after the introduction of both thiourea as well as OPPE was observed. The reduction peak at -0.439V shifted to -0.447V after the addition of thiourea and with the introduction of OPPE, the peak position shifted to -0.429V. Usually, such small shift in reduction potential

![Cyclic voltametry for Sn$^{2+}$ in MSA bath with and without thiourea and OPPE (OPPE)](image)
does not indicate any chelation. Thiourea is a well known brightener and leveler (138, 139), is reported to cover the deposited film and improve the film properties. The small shift in potential probably points towards such an effect. Again, the positive shift in potential and reduction in cathodic current with the addition of OPPE in the case of Sn electrolyte also indicates the possibility of surface coverage and reduction in effective area, due to adsorption.

Figure 4.22 presents the cyclic voltametry of Sn-Ag-Cu bath. As can be observed from the graph, there is one reduction peak at -0.541V. The presence of a single peak indicates that all the three metal ions deposit together in a narrow range of potential. This is an indication of effective chelation of thiourea, which is able to modify the deposition potentials of the noble metals silver and copper and bring them closer to the reduction potential of Sn.

![Cyclic voltametry for ternary Sn-Ag-Cu bath](OP1)

**Figure 4.22: Cyclic voltametry for ternary Sn-Ag-Cu bath(OP1)**

### 4.5.4 Bath characterization: Microstructure refinement

In order to study the effect of OPPE on the microstructure and composition of the films, the electrolyte OP1 that contains thiourea
as well as OPPE and the bath containing only thiourea and metal ions in MSA electrolyte (that is, without OPPE) were prepared and the ternary film was deposited. The bath was maintained at a pH of ~4 and the films were deposited at a current density of 10mAcm⁻². The SEM micrographs of the two films are presented in Figure 4.23.

![Microstructure of the Sn–Ag–Cu films deposited at 10 mAcm⁻² using an electrolyte with MSA and thiourea (a) without OPPE and (b) with OPPE.](image)

It is seen from the micrographs that OPPE brings about refinement in microstructure of the electrodeposited films. Surfactants are known to have a positive effect on the microstructure of the deposited films by way of refining the grain structure. The refinement in microstructure is usually brought about by the adsorbed organic species. Adsorption of POELE on cathode has been shown earlier.
(109,110). This view is also supported by the reduced current seen in CV curves of all the baths containing OPPE.

4.5.5 Bath characterization: Effect of current density
In the case of multi-element systems, usually at lower current densities the noble metals get deposited first and then as the current density is increased the less noble metals also start getting deposited. The chelating agents in the bath modify the deposition potential and the effect of current density on such a system, therefore, needs investigations. This study would help in identifying an appropriate process window which would help in getting consistent properties of the deposited film. A bath which is sensitive to minor variations in operating parameters is undesirable.

The OP1 bath was used to deposit films with varying current density from 2mAcm\(^{-2}\) to 25mAcm\(^{-2}\). The films were characterized mainly for their elemental composition and microstructure using SEM-EDS. Figure 4.24 presents the dependence of the film composition on

![Graph showing the effect of current density on film composition](image)

**Figure 4.24: Effect of current Density on the film composition**
current density. As expected, at lower current density, the noble metals have higher concentration in the deposited film, which gets suppressed as current density increases up to 5mA cm$^{-2}$. Beyond 5mA cm$^{-2}$, the composition of the three metals in the film does not change appreciably with increase in current density. As the current density reaches 5mA cm$^{-2}$ the three metals may have reached their limiting current density and their individual deposition rates get saturated. Similar observations have been obtained in Sn-Au depositions (132). Under this condition the depositions are said to be controlled by the kinetics happening at the electrode surface.

The SEM micrographs of the films deposited at different current density are presented in Figure 4.25.
Continued...
It is seen that all the films have compact microstructure. Most films have grain size in the range of 6–8μm for current density up to 10 mAcm⁻². The film deposited at 25 mAcm⁻², though compact, showed larger grains with sharp pyramid like structures. This could be due to the formation of preferred sites caused by local non-uniformity owing to the faster generation of cations. The deposited films were visibly uniform and bright. The films showed good uniformity in thickness across the deposited area. The average thickness of the films varied between 20μm for depositions carried out at 5 mAcm⁻² to 96μm for the films deposited at 25 mAcm⁻². Looking at the trend, the microstructure of the films is expected to deteriorate further with increasing current density beyond 25mAcm⁻². For the intended solder bumping application which requires bumps of sizes lower than 100μm, preferably lower than 50μm, finer microstructure
(<5μm) is desired. These studies were therefore not continued for current densities higher than 25mAcm⁻².

4.5.6 Bath characterization: Confirmation of Cu content

The X-ray diffraction studies of the deposited films was conducted to find structural information as well as to confirm, if possible, the Cu content in the films. The copper content in the films is of the order of 1% for the desired eutectic range, the EDS results are suspect. Figure 4.26 presents the X-Ray diffraction spectrum obtained for the ternary film deposited using OP1 bath at 10mAcm⁻² for the film deposited at 10mAcm⁻². The XRD analysis confirmed the microcrystalline nature of the deposited film and the presence of Sn, Ag and Cu in their metallic form. Similar XRD patterns were obtained for films deposited at lower and higher current density.

![XRD pattern](image)

*Figure 4.26: XRD pattern for Sn-Ag-Cu films deposited at 10mAcm⁻²*

4.5.7 Bath characterization: Summary and discussion on OP1 bath

The limited bath analysis using UV-Visible absorption studies and cyclic voltametry presented here were aimed at studying the effect of additives on the ternary bath. In order to gain more clarity about the
nature of interaction of these additives and chelating agent with individual metal ions, separate bath with individual ions were studied. This characterization as well as film characterization using SEM-EDS has helped in understanding the function of thiourea and OPPE in controlling the bath stability and the microstructure of the deposited ternary film. UV-Visible and CV studies clearly indicates the chelating effect of thiourea on Ag$^+$ and Cu$^{2+}$ ions. In the case of Sn$^{2+}$, the decrease in absorption and the shift in peak position are marginal indicating absence of any chelation of either thiourea or OPPE with Sn$^{2+}$ ions. Thiourea, as shown in Figure 4.27 exists in three canonical forms (Figure 4.27b).

![Figure 4.27: Molecular structure of a) Thiourea b) its three canonical forms](image)

The chelate linkages with thiourea can be formed either with the ‘S’ atom or with ‘N’ atoms. Reports on IR studies indicate the possibility of Ag and Cu chelate formation through metal-S bond formation (100,128). At the same time, in acidic medium, experiments have
shown formation of metal-N bonds since thiourea gets protonated and the H⁺ gets attached to S atom [140]. Additionally, there are reports which mention that the stability constants of Thiourea-Cu chelate being only slightly higher than thiourea-Ag chelate (127). Thus, we have an electrolyte system wherein thiourea may be forming equally stable chelates with two out of the three metal ions present in the system. From the CV studies of the ternary bath reported here it may be noted that the reduction peak for ternary system is at a different position as compared to reduction potential of the individual metal ions containing MSA, thiourea and OPPE. It is likely that a single thiourea molecule is associated with both Ag and Cu ions, causing their simultaneous delivery at the cathode and a reduction potential that is quite different from that for individual ions with thiourea. The overall effect is that the reduction potential gets modified and we find all three metal ions getting co-deposited at range of about -0.541 V and shows that the behavior of thiourea is different in single metal and tri-metal system. The exact nature of the chelate is difficult to predict due to the presence of multiple metal ions which creates chances of competitive chelation and the complexities caused by the existence of the three forms of thiourea.

With the addition of OPPE, there was a marginal shift of the reduction peaks of individual ions. The magnitude of shift indicates a possibility of physical adsorption or some loose bonding. It is known that OPPE has a hydrophilic polyethylene oxide group and a hydrocarbon lipophilic or hydrophobic group. It has a chemical structure as shown in Figure 4.28.
The linking oxygen in oxyethylene chain of this molecule provides a lone-pair of electrons that interacts with other molecules through hydrogen bonding. This helps in forming a protective coating around the suspended material, in-turn prohibiting their mutual interaction in liquid phase (133, 134). In the present case, the minor shifts in reduction potentials and improvement in the bath stability due to OPPE points towards such a phenomena occurring in the electrolyte. The overall effect of this behaviour of OPPE shows up in the refinement of microstructure due to OPPE. The increased absorbance in visible range after addition of OPPE in case of Ag⁺ bath could be due to concentration of OPPE being close to the critical micelle concentration (CMC) at which the solubility of the surfactant reaches its limit.

These studies have definitely helped in understanding the functions of thiourea and OPPE in the ternary bath. Further investigations will help in developing a deeper understanding of the deposition process. Meanwhile there should be efforts to further improve the bath stability and microstructure keeping the commercial application in view.

4.6 Improvements in OP1 bath and its characterization

The intended application of the electrodeposited solder film is for high-density interconnections. For such an application, it would be ideal to get a film with very fine and smooth microstructure. Gelatin is a very well known surface finishing agent and is expected to bring about microstructure refinement. The gel formation tendency of its
polypeptide chains might be useful in improving the bath stability. In order to study the effect of gelatin on MSA based bath system, it was decided to add about 2g.lit\(^{-1}\) of gelatin to the OP1 bath mentioned in Table 4.6. The composition of this new bath, now called OP2, is presented in Table 4.7.

Addition of gelatin to OP1 bath did help in improving the bath stability. The OPPE containing baths showed a stability of 4-5 days and slight precipitation thereafter. Whereas the gelatin containing baths showed stability reaching up to 8-10 days. The bath just turns yellowish thereafter but the transparency remained for about two weeks and a slight precipitation after that could be observed.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Chemicals</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methane Sulfonic acid</td>
<td>1.54M</td>
</tr>
<tr>
<td>2</td>
<td>Tin Methane Sulfonate</td>
<td>0.34M</td>
</tr>
<tr>
<td>3</td>
<td>Copper Sulphate</td>
<td>0.08mM</td>
</tr>
<tr>
<td>4</td>
<td>Silver Sulphate</td>
<td>1.2mM</td>
</tr>
<tr>
<td>5</td>
<td>Thiourea</td>
<td>0.04M</td>
</tr>
<tr>
<td>6</td>
<td>OPPE</td>
<td>6mM</td>
</tr>
<tr>
<td>7</td>
<td>Gelatin</td>
<td>2g.lit(^{-1})</td>
</tr>
</tbody>
</table>

*Table 4.7: Bath composition of gelatin based electrolytes (OP2)*

Table 4.8 presents a comparison of stability of OP1 and OP2 baths. The bath presented in Table 4.5 containing only thiourea (Section 4.4.3) along with the metal ions, now called as OP bath, is also compared.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Bath</th>
<th>Stability</th>
<th>Composition reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OP</td>
<td>Two hours. Later the bath became turbid and precipitated overnight</td>
<td>Table 4.5</td>
</tr>
<tr>
<td>2</td>
<td>OP1</td>
<td>4-5 days. After that some precipitate sold be seen settled down</td>
<td>Table 4.6</td>
</tr>
<tr>
<td>3</td>
<td>OP2</td>
<td>8-10 days. Later the solution turned yellowish but transparency remained for two weeks.</td>
<td>Table 4.7</td>
</tr>
</tbody>
</table>

*Table 4.8: Stability of Sn-Ag-Cu Electrolytes for the bath system under investigation*
The OP2 bath (pH 4) was used for the deposition of Sn-Ag-Cu films at a current density of 10mAcm$^{-2}$. The microstructure of the films showed good improvement in the OP2 bath. A comparison of the SEM micrographs of the films deposited using the three baths viz. the bath with no additive, referred as OP bath, the bath containing thiourea and OPPE referred as OP1 bath and the bath containing thiourea, OPPE and gelatin, referred as OP2 bath is presented in Figure 4.29. The films containing only thiourea but no additives present a compact microstructure, but have granular faceted grains and comparatively rough surface. The grain size of these films varied from about 8μm to few 10's of μm. The film composition, as measured by SEM-EDS, was found to be Sn-3.2Ag-1.3Cu. A definite improvement in the microstructure with addition of OPPE can be observed. Reduction in grain size, improvement in uniformity and compactness can be noticed from the figure. The average composition of the films was found to be Sn2.7Ag0.9Cu. The introduction of gelatin into the bath containing thiourea and OPPE brought further refinement in the film microstructure. The films were found to be smoother and fine grained, with a grain size of about 3-4μm. The microstructure showed much better uniformity and the films were far more compact. The film had a composition of Sn-4.1Ag-3.8Cu. The composition of copper was found to be higher than expected in these films. A check on compositional uniformity across the film surface yielded similar results. It is seen that this deviation from the targeted composition is one of the drawbacks of the gelatin containing OP2 bath. However, on the other hand, the dramatic improvement in the bath stability and microstructure are seen as major advantages of the OP2 bath. It may be noted here that the bath properties are not fully investigated at this stage and process parameter dependent studies may yield better results.
Continued...
The OP2 bath was further subjected to cyclic voltametric analysis. Figure 4.30 presents the CV curves of OP, OP1, OP2 baths; the other two are reproduced for comparison. It is seen that the CV curves of all the baths have a single but broad reduction peaks. Presence of a single peak in all the baths confirms co-deposition in case of OP2 bath as well.

The position of reduction peak for the electrolyte without any additives but containing only thiourea along with metal ions (OP) was found to be at $-0.546\text{V}$. This peak shifts slightly to the right when the additives \textit{i.e.} OPPE and gelatin, are introduced into the system. The reduction peak was obtained at $-0.519\text{V}$ when only OPPE (OP1) was present as additive and at $-0.529\text{V}$ when both OPPE and gelatin (OP2) were present. The total maximum shift in reduction potential is seen to be $0.027\text{V}$ which is relatively insignificant. For the electrolyte
containing gelatin and OPPE, the reduction peak was found to be much broader as compared to the bath containing only OPPE. It is also known that gelatin as a surface finishing agent alters the viscosity of the bath through gel formation and hence the ion mobility. The broadening of the reduction peak with the addition of gelatin, therefore, may have been caused by either the loose bonding of chelated ions with additives or the modified viscosity. Reduction in the current values when additives are present can be noticed from the CV curves, which confirms adsorption of additives on cathode.

![Cyclic voltametry curves for OP, OP1 and OP2 baths](image)

**Figure 4.30: Cyclic voltametry curves for OP, OP1 and OP2 baths**

### 4.7 Conclusions

This chapter details the development of a ternary Sn-Ag-Cu electrolyte using MSA system. A set of chelating agents and additives was identified earlier for use in the chosen MSA electrolyte. Without adequate chelation, precipitation of such bath is common. EDTA
and thiourea were explored as chelating agents for the electrolyte system. It is found that EDTA is not compatible with this electrolyte base and the bath remained stable only in high acidic condition. Addition of thiourea along with EDTA also did not help in improving the bath stability. It is found that EDTA has low solubility in MSA bath, which may have allowed its inadequate quantity for chelation. Additionally, it is known that EDTA requires a 'conducive' electrolyte that aids its protonation and thereby its chelation. These issues probably affect the EDTA containing bath in MSA and cause poor stability.

Thiourea is known chelating agent for silver and coppers ions which is also confirmed here through UV-visible absorbance and CV studies. It is also confirmed that thiourea does not chelate Sn in this bath. Various additives were investigated in the thiourea containing bath, such as sodium potassium tartarate, alkyl benzene sulfonate etc. However, these additives produced bath with very poor stability. It was found that bath comprising of thiourea as chelating agent, OPPE as surfactant and gelatin as surface finishing agent together helped in obtaining a bath that remained stable up to pH 4. This bath showed good stability 8-10 days, after which slight discoloration could be observed although there was no visual change in transparency. After about two weeks, some precipitate could be seen settled down. CV measurements on thiourea baths confirmed co-deposition or deposition in a close potential range. This is a very significant property especially for applications like solder bumping where consistency and high reliability is of profound importance. Thiourea does not seem to modify deposition potential on Sn, which is expected as it doe not chelate Sn ions. Slight modifications in the deposition potential may be caused due to adsorption or weak linkages.
Apart from their contributions in improving the bath stability, the addition of OPPE and gelatin also helped in obtaining a smooth and uniform film with fine-grained (3-4μm) microstructure. It is felt that OPPE forms loose bonding with all the three metal ions or their chelates through its oxygen atom and helps in the refinement of the film microstructure. This bonding can be correlated to the marginal shift in the reduction peak positions of the three metal ions and also to the film refinement. Gelatin, a proteinous material, on the other hand alters the viscosity of the bath aided by the linking of its polypeptide chains. A broadened reduction peak for gelatin containing bath may be either due to its linkage with the ion containing chelate or the slower delivery of metal ions caused by gelatin addition and the consequent linkages. The SEM micrograph reveals the remarkable improvement in the film microstructure, which became finer and smoother with the introduction of gelatin into the bath containing OPPE and thiourea. This bath produced an off-eutectic composition of the films with higher Ag and Cu. It is seen that this bath (OP2) provides best results mainly due to the improved bath stability and film microstructure. It may be possible to optimize the concentration of Cu and Ag in these films through optimization of process parameters, especially while working with the patterned films during bumping.

Such multi-element systems are quite complex and require a thorough study of the bath to find the optimum composition and process window. In view of this, it was decided to carry out further investigations as well as the solder bumping experiments using OP2 bath.