

Soldering Immersion Tin

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Abstract

The stimulating impact of the automotive industry has sharpened focus on immersion tin (i-Sn) more than ever before. Immersion tin with its associated attributes, is well placed to fulfill the requirements of such a demanding application.

In an environment dominated by reliability, the automotive market not only has very stringent specifications but also demands thorough qualification protocols. Qualification is ultimately a costly exercise. The good news is that i-Sn is already qualified by many tier one OSATs.

The focus of this paper is to generate awareness of the key factors attributed to soldering i-Sn. Immersion tin is not suitable for wire bonding but ultimately suited for multiple soldering applications. The dominant topics of this paper will be IMC formations in relation to reflow cycles and the associated solderability performance.

Under contamination free conditions, i-Sn can provide a solderable finish even after multiple reflow cycles. The reflow conditions employed in this paper are typical for lead free soldering environments and the i-Sn thicknesses are approximately 1 μm .

Introduction

Immersion tin is enjoying a continued upwards trend in terms of market share and sales in the market. This is directly related to the growth in automotive electronics. The reader only needs to take a look at various reports and market synopsis to confirm these conclusions [1,2].

Safety in numbers is a significant consideration in the electronics business. A representative reference list for a process is as, or more, important than the technical capabilities touted by the chemical suppliers.

In Figure 1, it is demonstrated that i-Sn is established as the 'safety in numbers' final finish for the automotive industry. I-Sn is present in many of the top 30 automotive PCB manufacturers and in 80% of the top 10 end users.

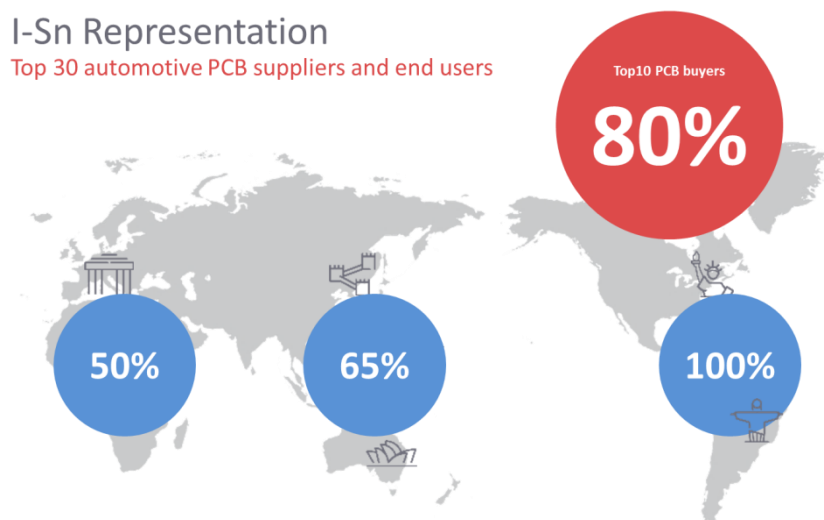


Figure 1: The presence of i-Sn in the automotive global arena [2]

Figure 2 is a representation of i-Sn at the top 5 automotive OEMs for each segment [3]. It is evident that i-Sn is utilized for high reliability automotive applications such as engine CPUs, braking and air bags.

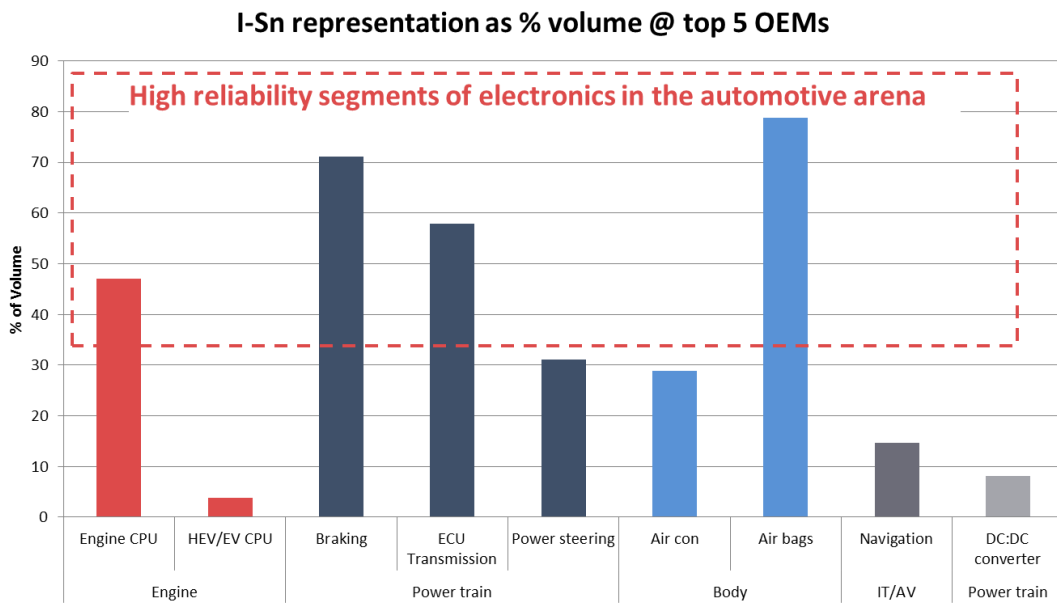


Figure 2: Representation of i-Sn according to automotive segments versus top 5 Automotive OEMs [3]

IMC formations

The formation of the intermetallic compound (IMC) is of great concern in the industry. This is because the solderability and wettability can be impacted by the IMC formation related to the remaining pure tin. The growth of the IMC is a reflection of its production viable shelf life. The primary function of a surface finish is to protect the integrity of the copper conductor and maintain utilization performance until the panel is populated.

As solderability is the key concern of this paper, multiple soldering steps must be evaluated. Only the non soldered side is considered in an evaluation of the IMC. In Figure 3, the as-received condition (ASR) is shown. Approximately 1 μm immersion tin is plated on copper. The ASR condition means directly after plating. The IMC is not yet visibly apparent and therefore solderability is of no concern. This is why results shown in this paper benchmark test conditions against ASR conditions.

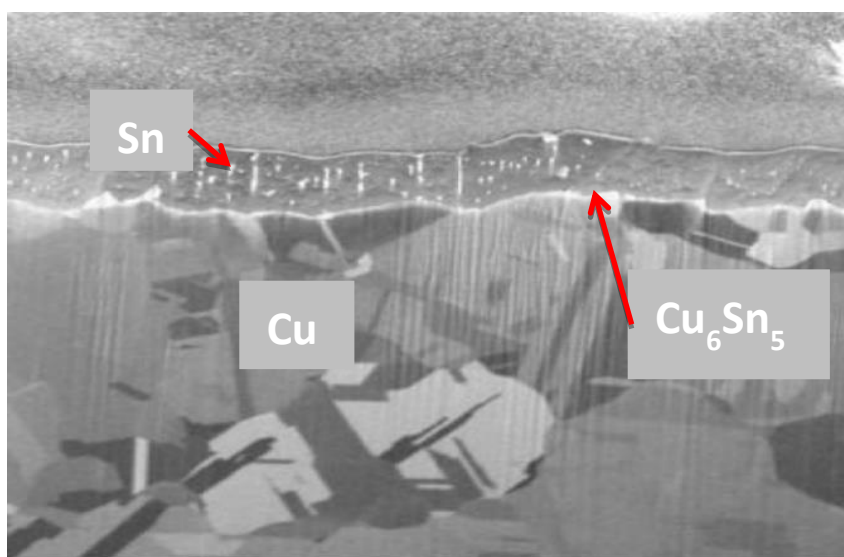


Figure 3: As received i-Sn deposit on copper (FIB)

In production, solder paste is only applied to 80% of the feature area to guarantee acceptable wetting. After the first reflow cycle two distinct IMC types are generated, (Figure 4). There is a copper rich (Cu_3Sn) IMC and a less copper saturated (Cu_6Sn_5) IMC. The ‘scallop’ formation is the Cu_6Sn_5 IMC. The growth of the Cu_6Sn_5 IMC is inhibited by the copper rich IMC which limits the copper migration. This formation is expected under normal conditions.

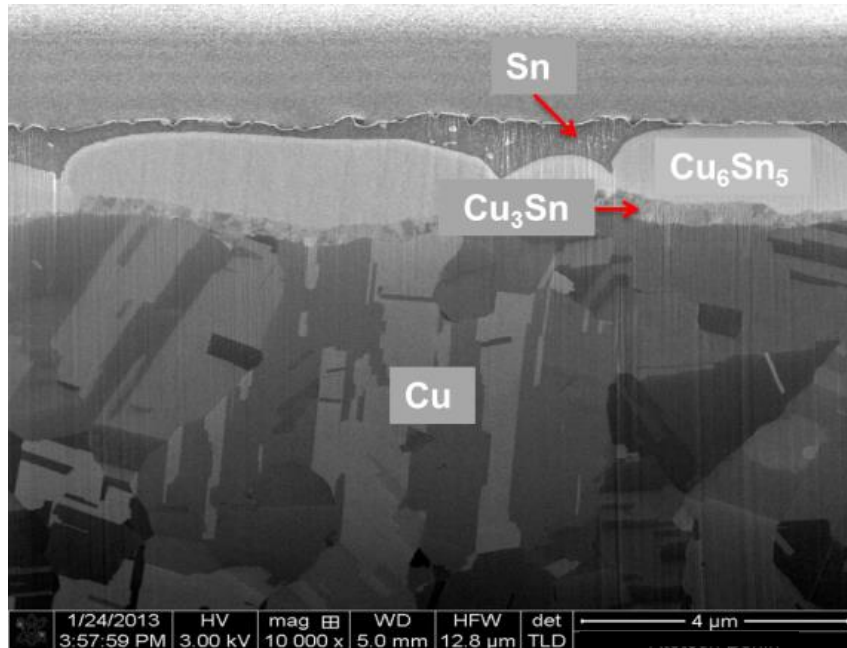


Figure 4: IMC formation after 1 x reflow at 245°C (FIB)

The most significant IMC formation occurs after the first reflow. In figure 5, it can be seen that the IMC formation does not change significantly compared to the first reflow. The key to solderability is presumed to be the presence of free tin. And as demonstrated in the figure: areas of pure tin are still available for soldering. At this stage the IMC may break the surface affecting wetting but the islands of pure tin ensure that solderability is maintained.

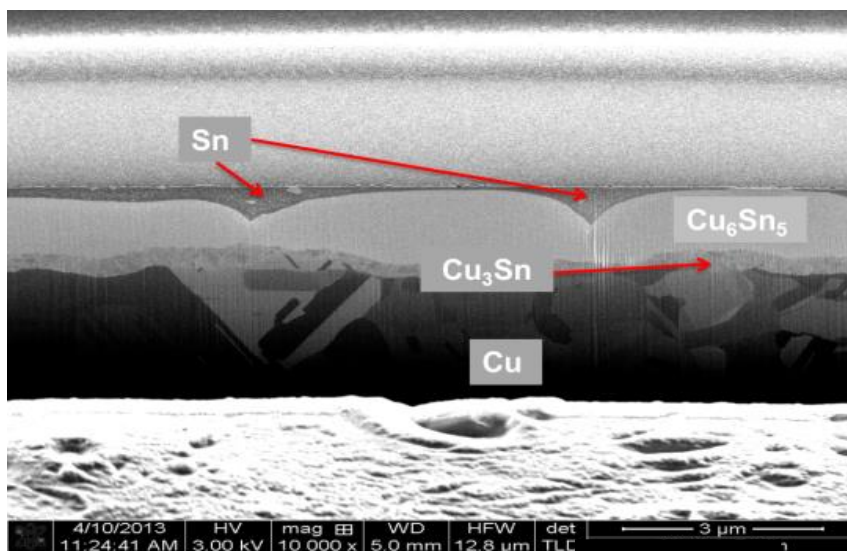


Figure 5: IMC of unpopulated side after second reflow at 245°C (FIB)

The development of the IMC under controlled storage conditions is very slow and is testament to the production viable shelf-life of i-Sn. This will be demonstrated later during the testing carried out to evaluate the practical factors that influence IMC generation. The factors considered in this test were thermal ageing by lead free reflow and holding time at room temperature (RT).

The measurements for the IMC were carried out using a combination of XRF and electrochemical measurements (e.g. coulometric stripping). The value for pure tin is a proportion of the bulk metal. The method above does not give a value for the shape of the IMC formation. This can only be assessed optically as shown in Figures 3,4 and 5.

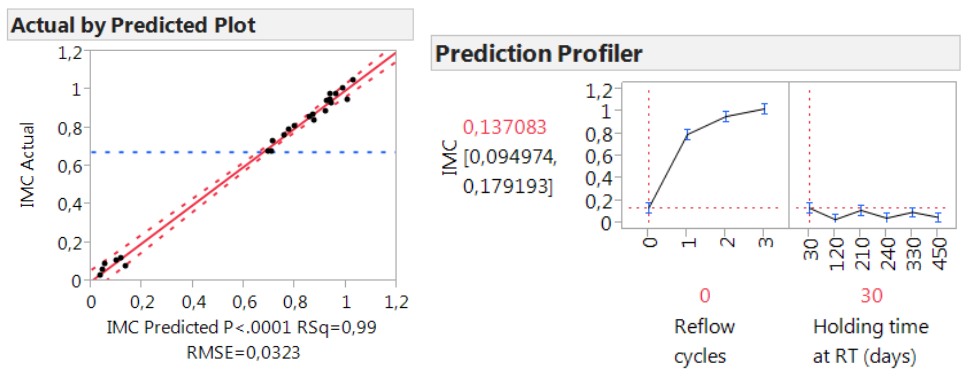


Figure 6: The statistical verification of testing

In Figure 6, it is proven that the tests are statistically significant and that the main impact on the IMC formation is thermal ageing by reflow cycles. The impact of holding time is insignificant, which is a demonstration for the good shelf life of i-Sn. For that reason, only the impact of the thermal ageing will be considered further.

A more detailed view of the impact of the lead free reflow profile, supports the notion that the copper migration into the tin is inhibited by the copper rich IMC (Figure 7). The most significant increase in the IMC is due to the first reflow cycle, whereas the increase in the IMC between cycles 2 and 3 is not statistically significant.

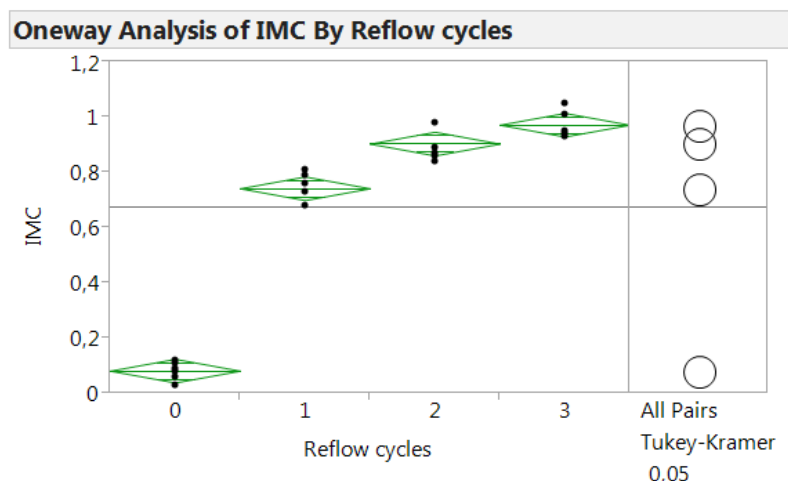


Figure 7: IMC formation by thermal ageing (Reflow profile used is shown in the Appendix)

Figure 8 on the other hand, demonstrates that pure tin is left over even after 3 lead free reflow cycles.

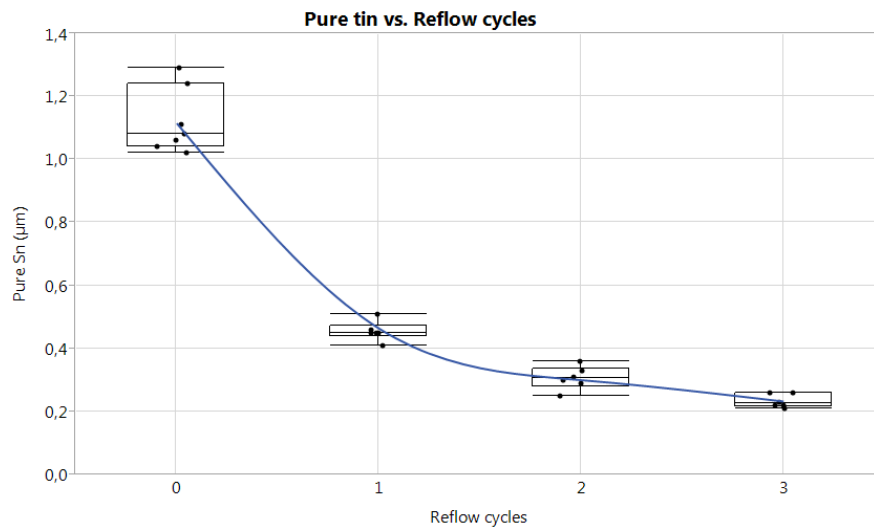


Figure 8: Remaining pure Sn versus reflow cycles

The next section will demonstrate the solderability potential for i-Sn after ageing. The testing does not directly correlate with the ageing conditions discussed in the previous section but is representative of production and includes 3 times reflow followed by selective wave soldering. This is considered as an extreme condition and will be the benchmark for the soldering performance after ageing. Typically, the automotive industry employs press fit assembly for high power lead frame components.

The conditions for this evaluation were to apply 3x reflow (see Appendix) and to selectively wave solder. The production selective wave soldering machine used Sn3Ag0.5Cu solder with a production low solids no-clean wave flux. The size of the solder nozzle was 18 mm inside, 20 mm outside. The solder pot temperature was 280°C and the soldering speed 6 mm/s. Two through hole dimensions were evaluated, these were of 0.8 mm and 1.2 mm in diameter at a board thickness of 1.5 mm.

Figure 9 is a typical result for the solder performance of the i-Sn even after multiple reflows. The PTHs are fully filled and the contact sides show excellent covered and potential filleting. With lead frame components the capillary action would further improve the performance.



Figure 9: Result for selective wave soldering after 3 x reflow

Typical external causes for failures on i-Sn finishes

The main external causes for failures on i-Sn finishes can be attributed to the following general issues:

- Contamination of the copper tin interface
- Contamination of the tin surface
- Redeposition of volatiles from solder masks and fluxes.

Copper contamination is usually down to handling. The resultant failure is typically dewetting, whereby the solder covers the feature initially only to retreat on cooling after reflow. The alternative failure is non wetting. This is normally the result of heavy organic contamination. Copper contamination can result in an abnormal IMC formation.

A chemical system is generally equipped with a pretreatment to remove contaminants on the copper surface. Generally these are adequate and non-wetting and dewetting are rarely caused by copper contamination. However tin surface contamination is common and often disregarded. The reflow equipment is in many cases a solvent derived volatile rich environment (fluxes and soldermask solvents) where re-deposition is possible. Exhaust levels depend on the reflow atmosphere (O_2 or N_2) but regardless, the environment is challenging. Additionally poor rinsing, poor soldermask applications and plugging operations can lead to surface issues.

Conclusions

Whilst i-Sn can be shown to be a reliable final finish for soldering even after multiple thermal ageing tests that could feasibly be encountered in production, uncontrolled external influences can result in poor results. These are not only problematic to i-Sn final finishes and can be eliminated by good practice.

The production environment is a complex one where controls and good practice can help to ensure high yields. This paper proves that i-Sn can provide a reliable solderable finish with a long shelf life and a compatibility to realistically challenging production environments.

References

1. Brian Swiggett, EMTC Conference, October 2014.
2. Dr. Hayao Nakahara, NTI Digest, August 2016.
3. Kiminori Miyata, Norie Matsui, et. al., Japan Marketing Survey Co., Ltd. October 2014.

Appendix

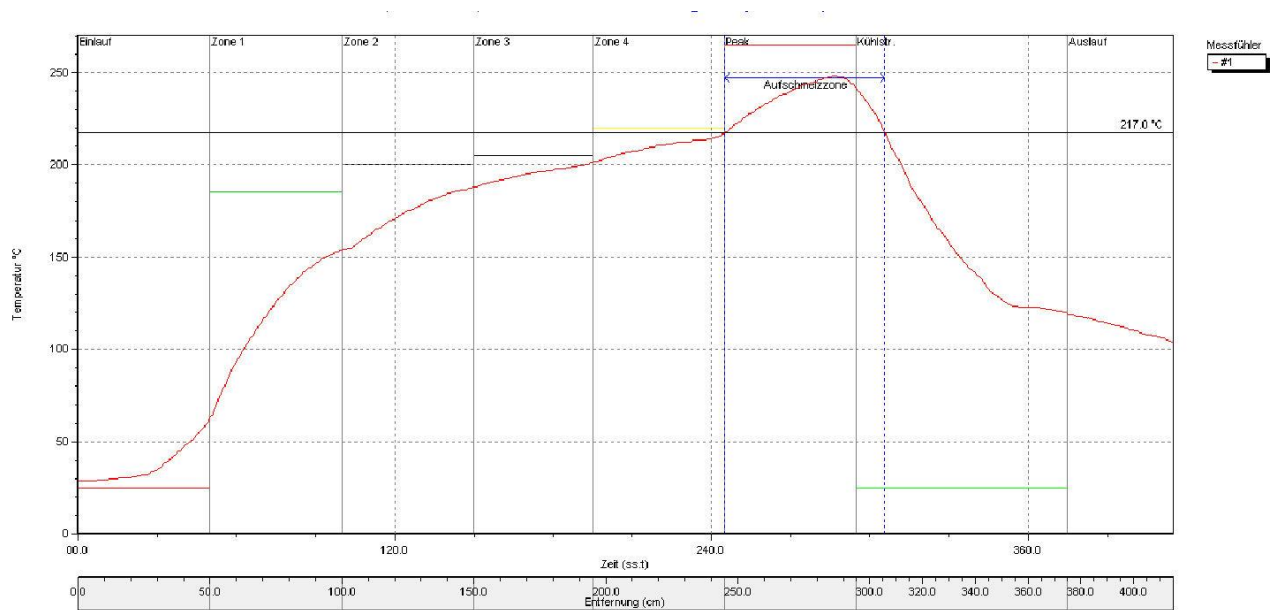
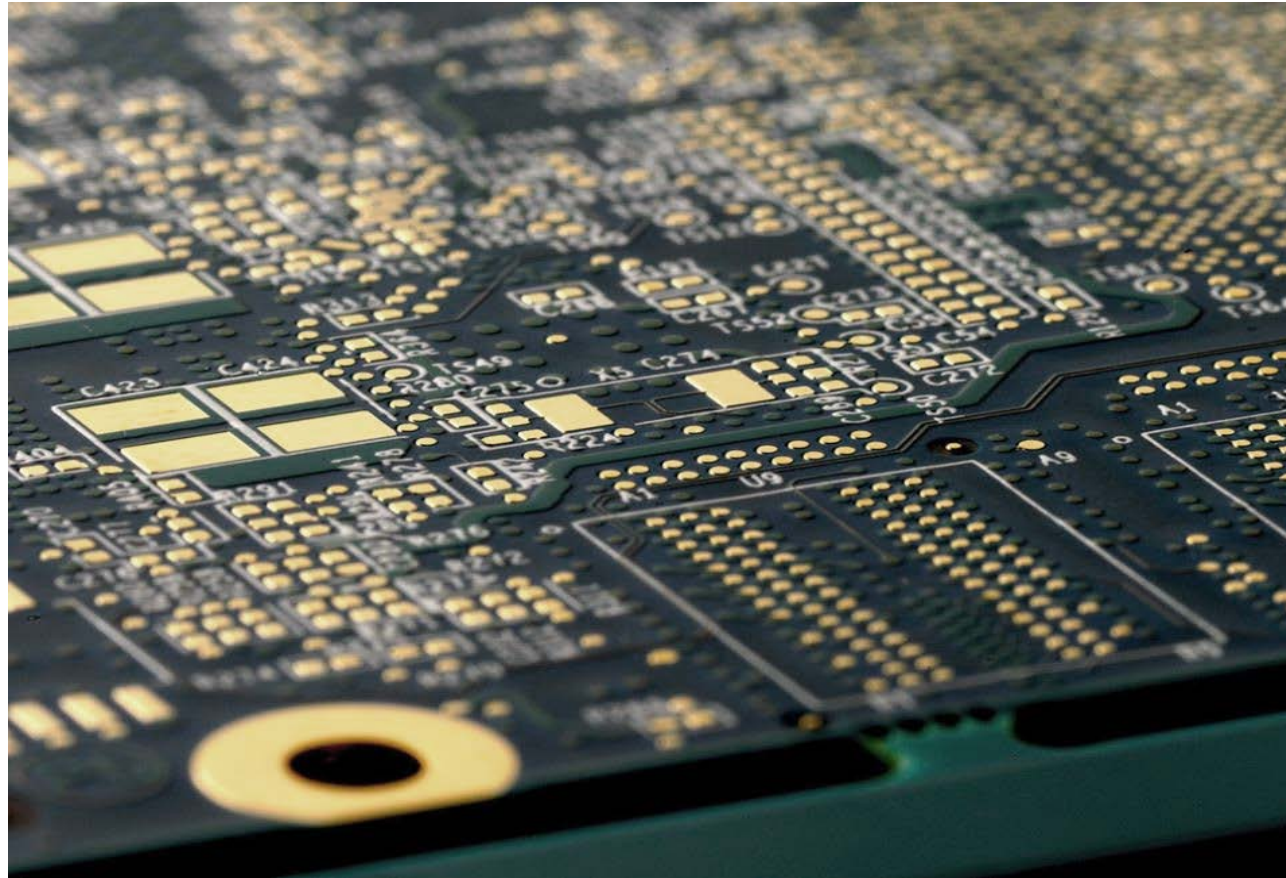


Figure 10: Reflow condition used: Peak temperature: 246°C, time over 217°C: 68 sec

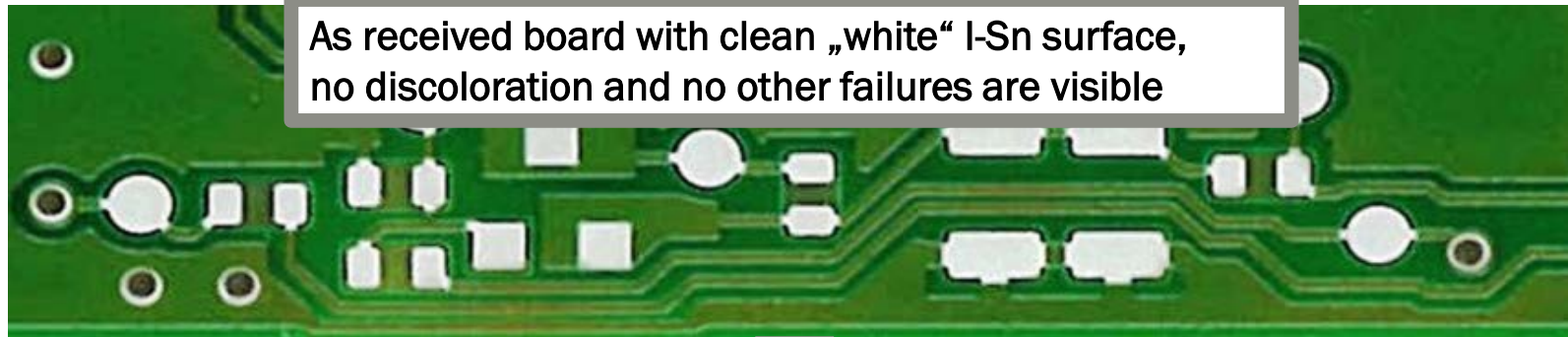
Soldering Immersion Tin



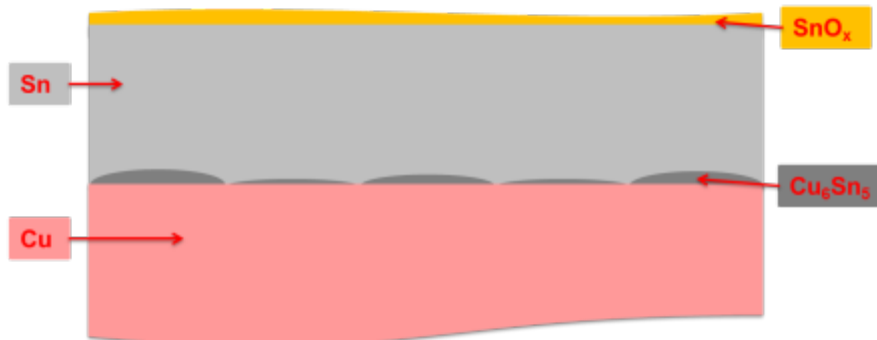
Rick Nichols, Atotech

As received – condition of **immersion tin**
before soldering

Soldering Immersion Tin As Received (asr)



Illustrated presentation of an as received pad



The drawing sizes were chosen for clarity, they are not really like that

FIB of an as received pad



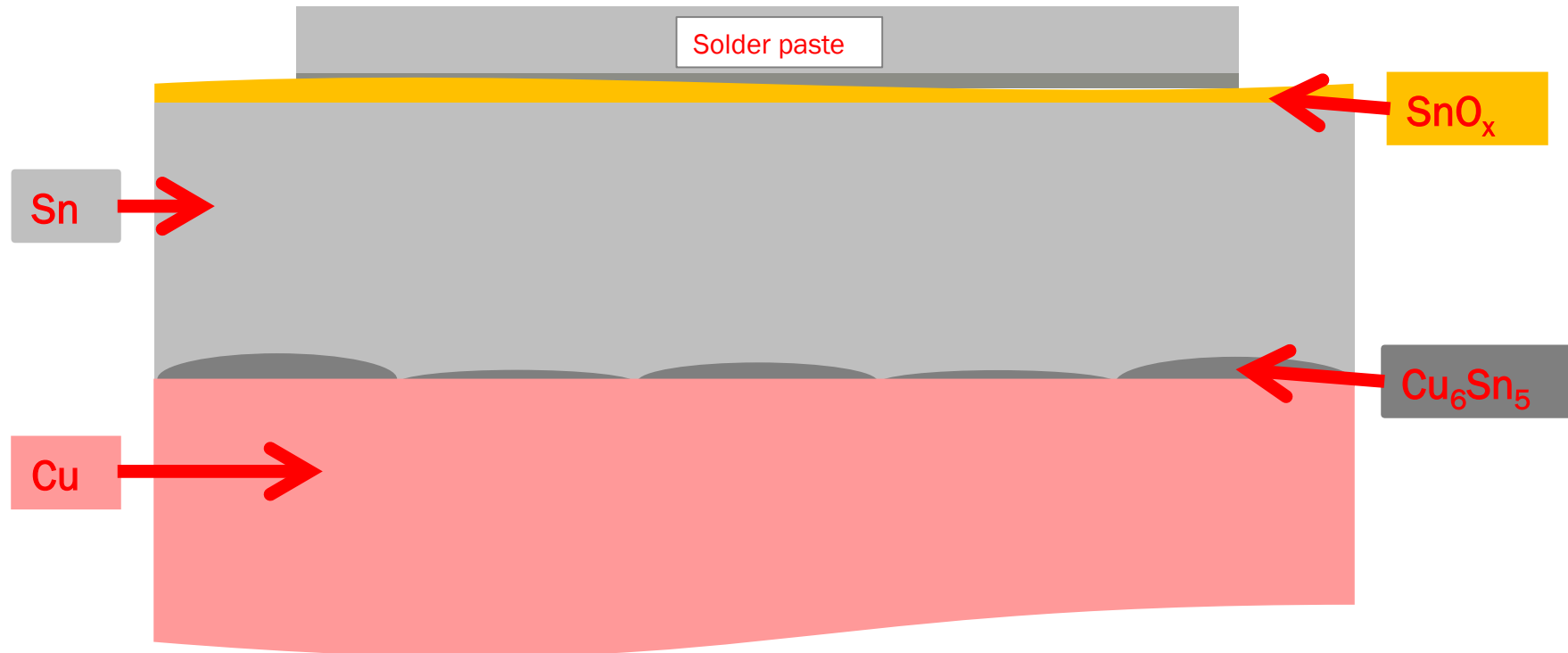
Oxide and Cu₆Sn₅ are beneficial

1st reflow – changes of I-Sn/Cu layer
on the soldered side

Soldering Immersion Tin

1st reflow – changes of I-Sn/Cu layer on the soldered side

After solder paste printing

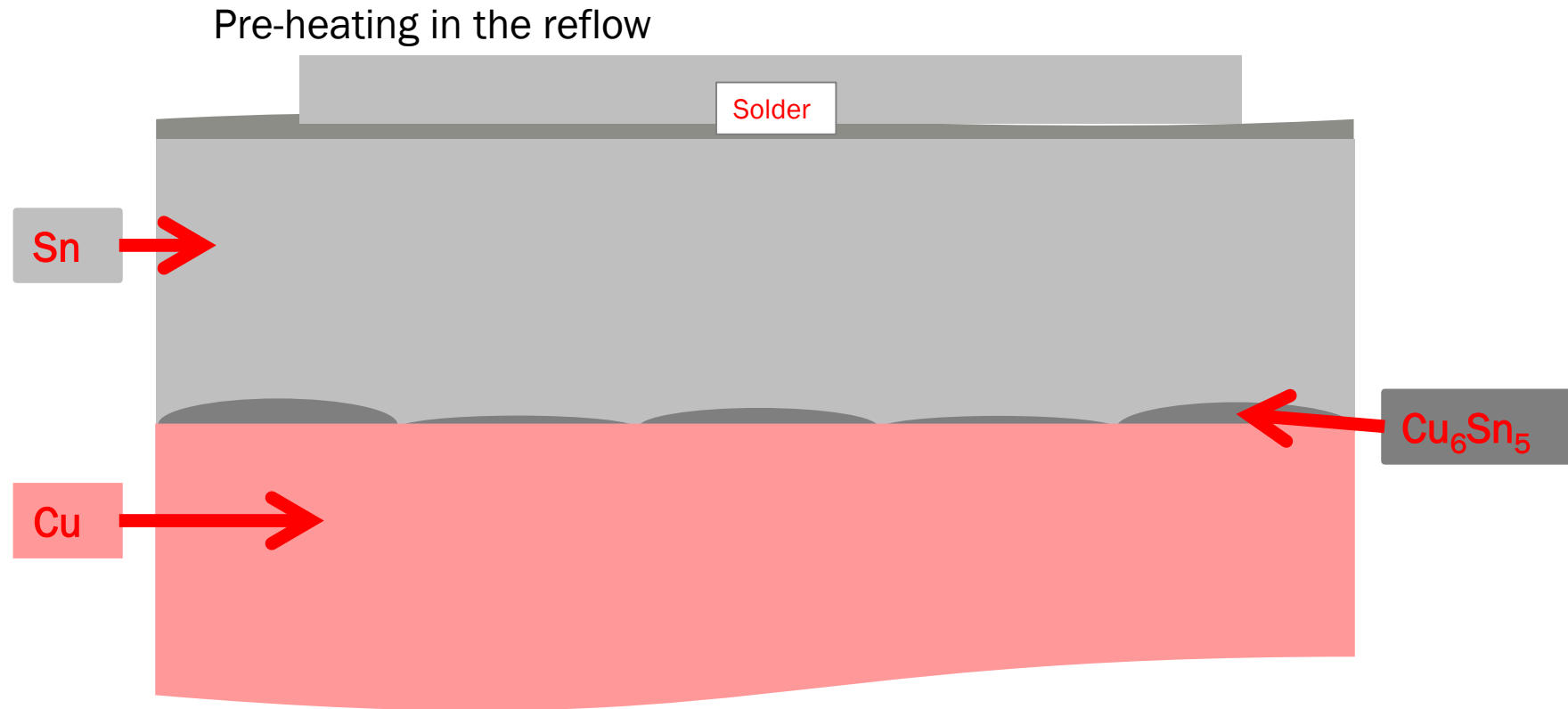


The drawing sizes were chosen for clarity, they are not really like that

Only 80% of pad surface needs to be covered with solder paste to ensure complete pad wetting during reflow (production proven)

Soldering Immersion Tin

1st reflow - changes of I-Sn/Cu layer on the soldered side



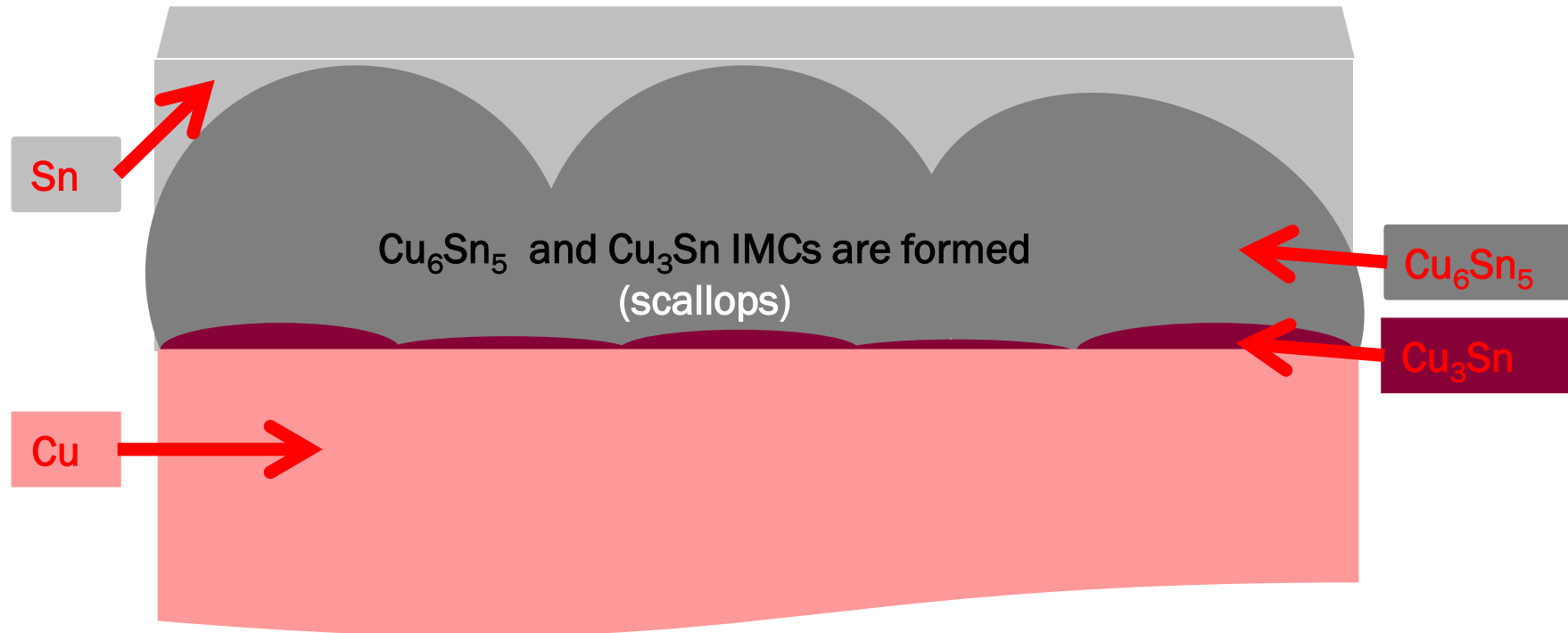
The drawing sizes were chosen for clarity, they are not really like that

Pre-heating, the flux is required to remove the oxide and "clean" the surface for good wettability

Soldering Immersion Tin

1st reflow – changes of I-Sn/Cu layer on the soldered side

During peak temperature in the reflow

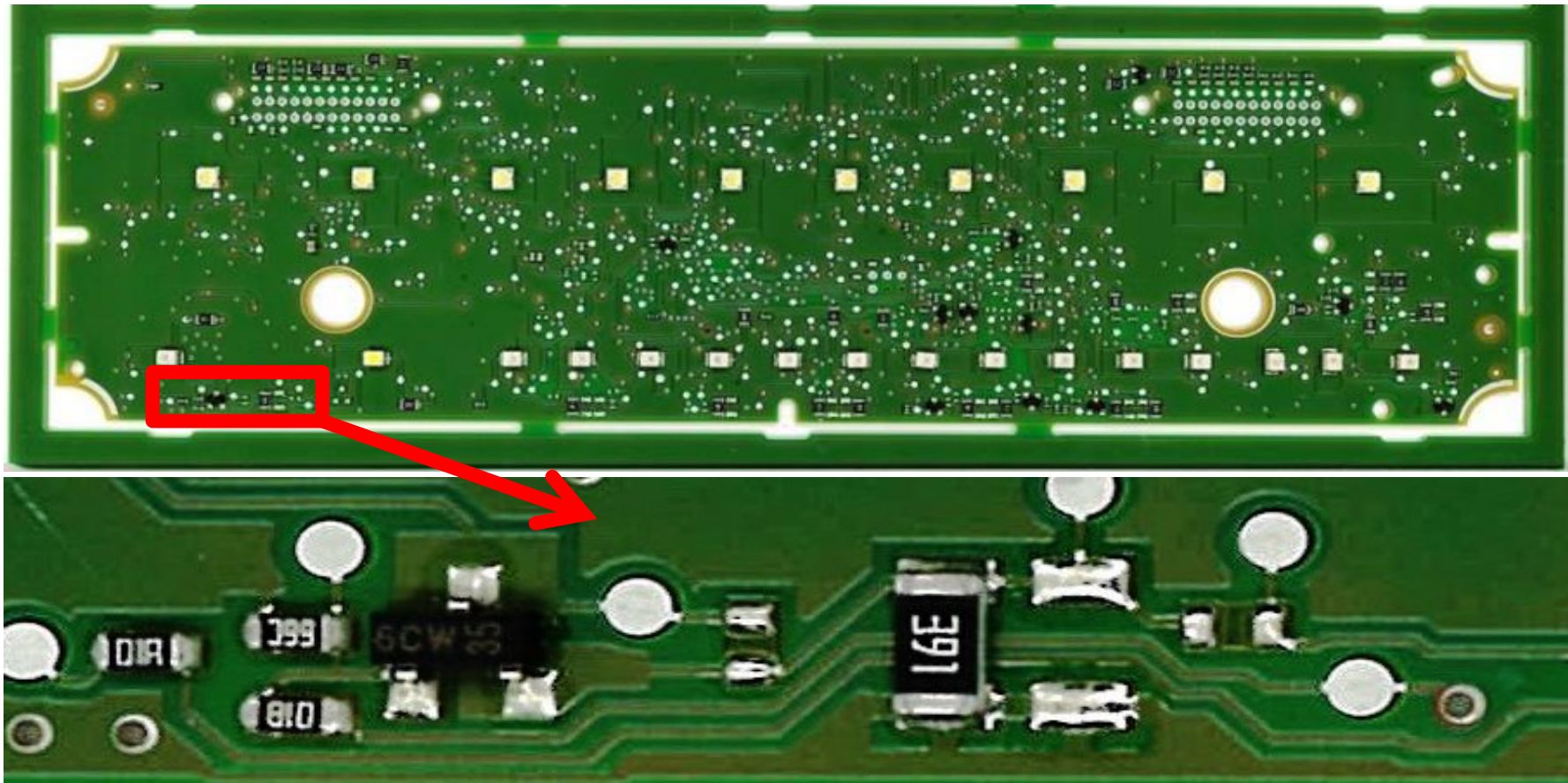


The drawing sizes were chosen for clarity, they are not really like that

When the melting point has been achieved in the reflow process, the I-Sn and solder paste melt and fuse.

Soldering Immersion Tin

1st reflow – changes of I-Sn/Cu layer on the soldered side



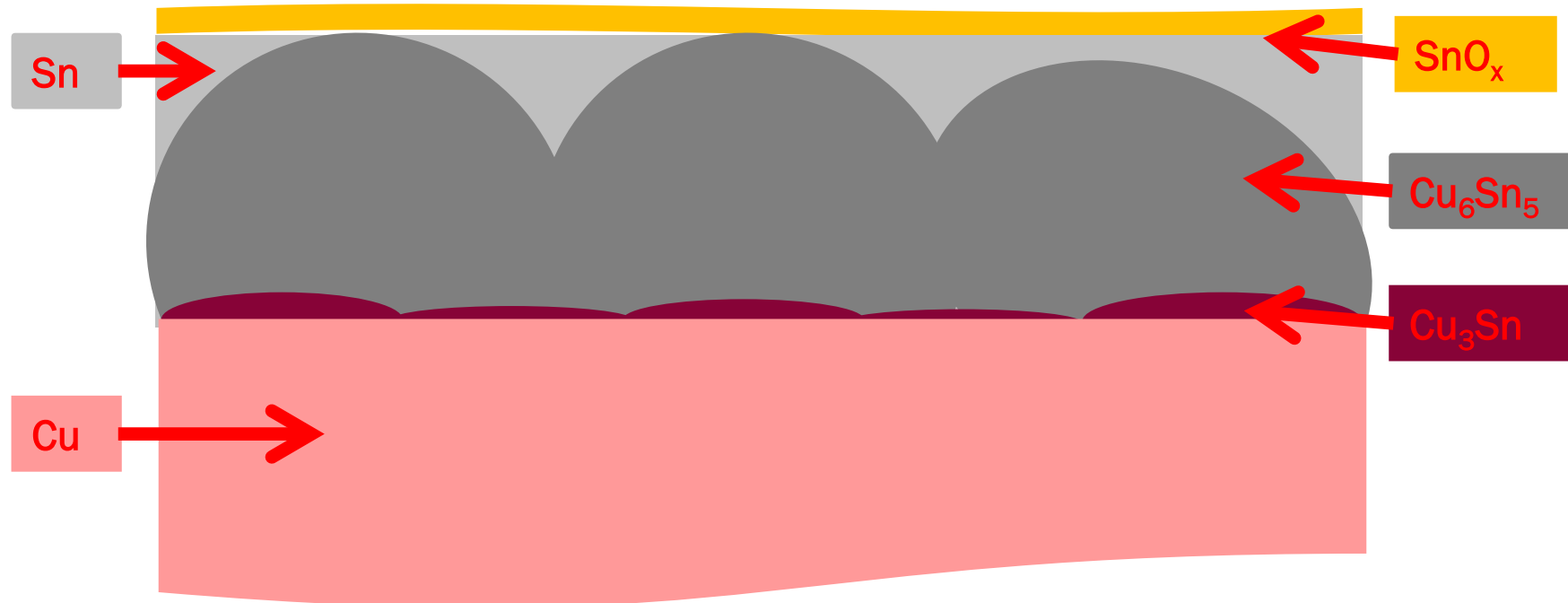
After 1st reflow soldered pads are very well covered with solder. The non-soldered pads appear clean and white with no discoloration or dewetting

1st reflow – changes of ImSn/Cu layer on the non-soldered side

Soldering Immersion Tin

1st reflow - changes of I-Sn/Cu layer on the non-soldered side

After 1st reflow

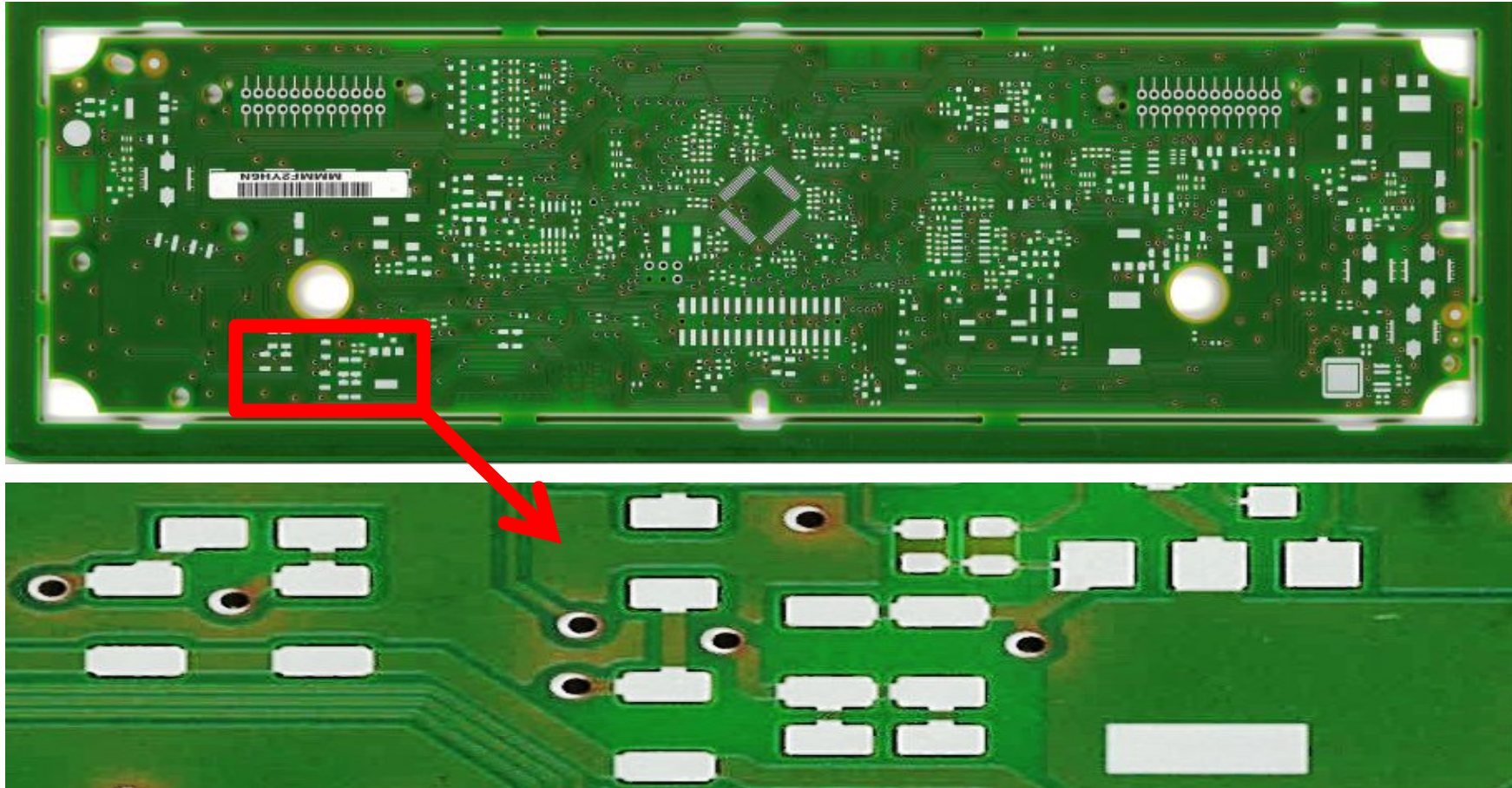


The drawing sizes were chosen for clarity, they are not really like that

The shell-shaped (Scallop) formation of the IMC (Cu_6Sn_5) can sometimes reach the surface. The oxide layer is now thicker than in as received depending on the reflow atmosphere.

Soldering Immersion Tin

1st reflow – changes of ImSn/Cu layer on the non-soldered side unsolder side

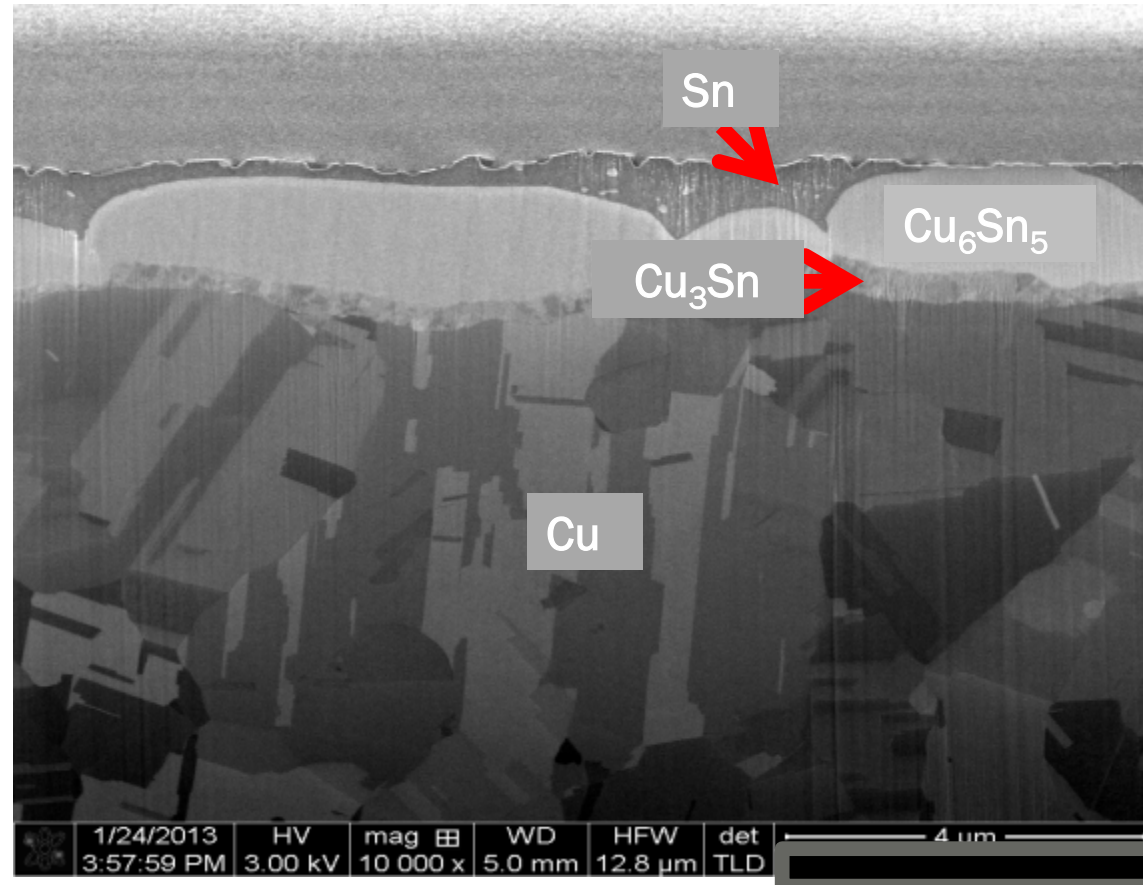


After 1st reflow the non-soldered look clean „white“, no discoloration and no other failures are visible

Soldering Immersion Tin

1st reflow – changes of ImSn/Cu layer on the non-soldered side

FIB of a non-soldered pad after 1st reflow

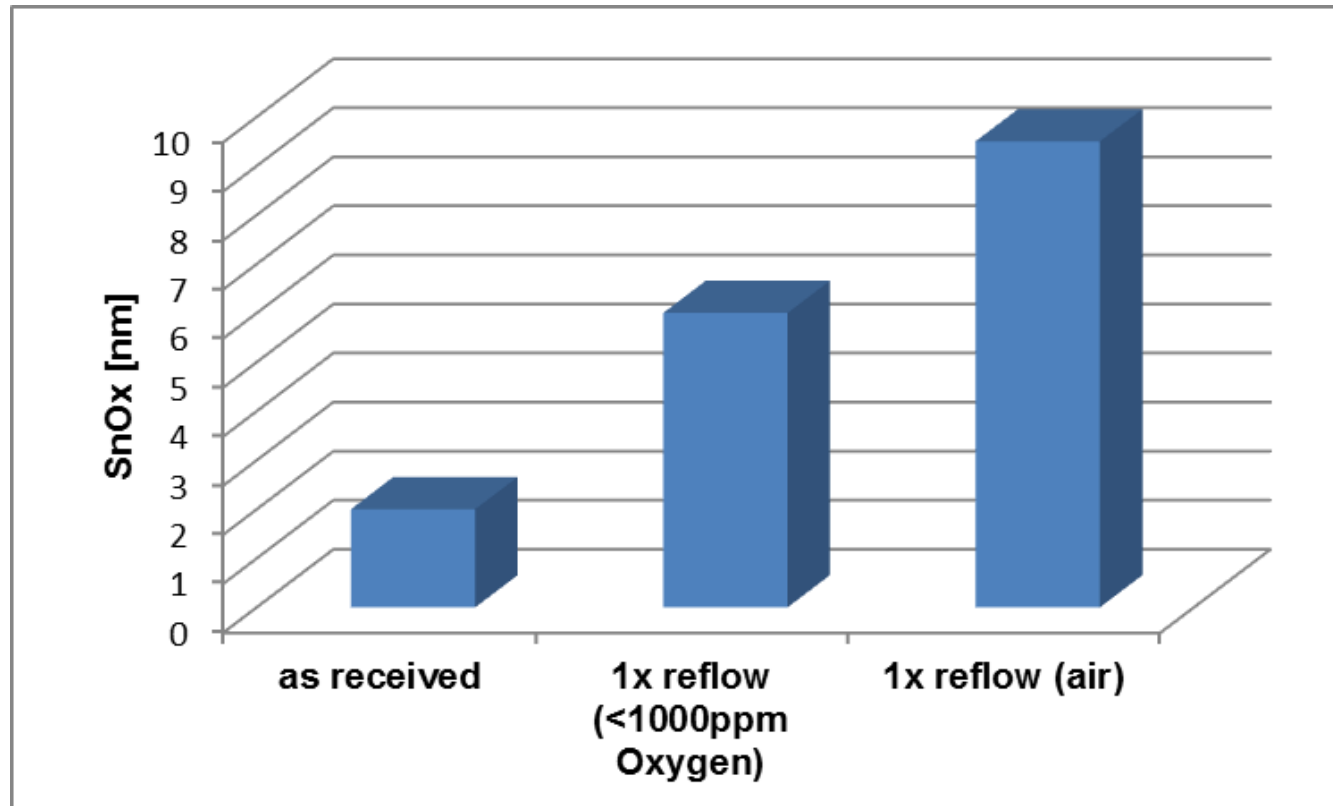


What is different after 1st reflow on non-soldered pads

Soldering Immersion Tin

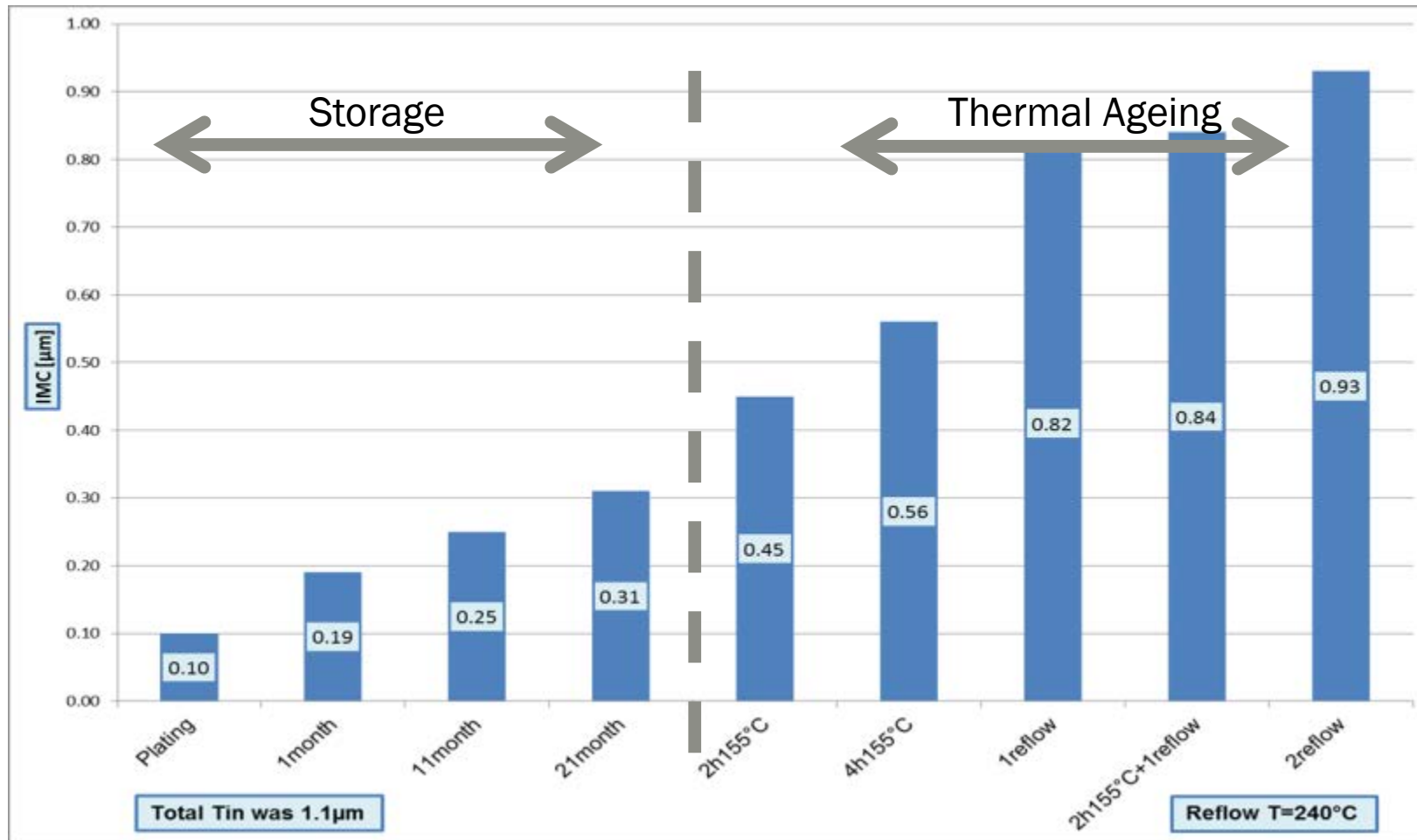
What is different after 1st reflow on non-soldered pads

Thickness of SnO_x



Soldering Immersion Tin (for 1.1 μ m thick tin finish)

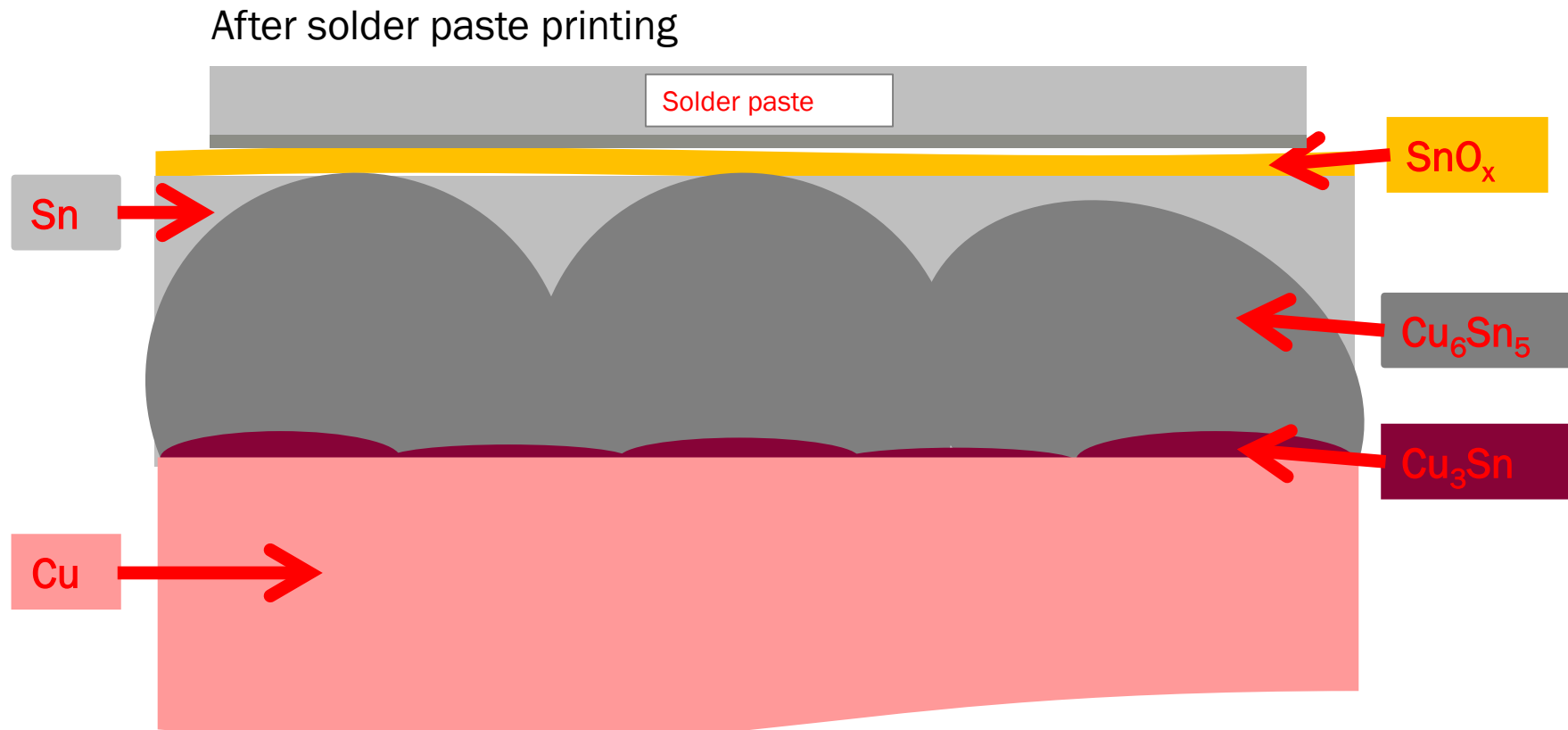
What is different after 1st reflow on non-soldered pads



2nd reflow

Soldering Immersion Tin

2nd reflow



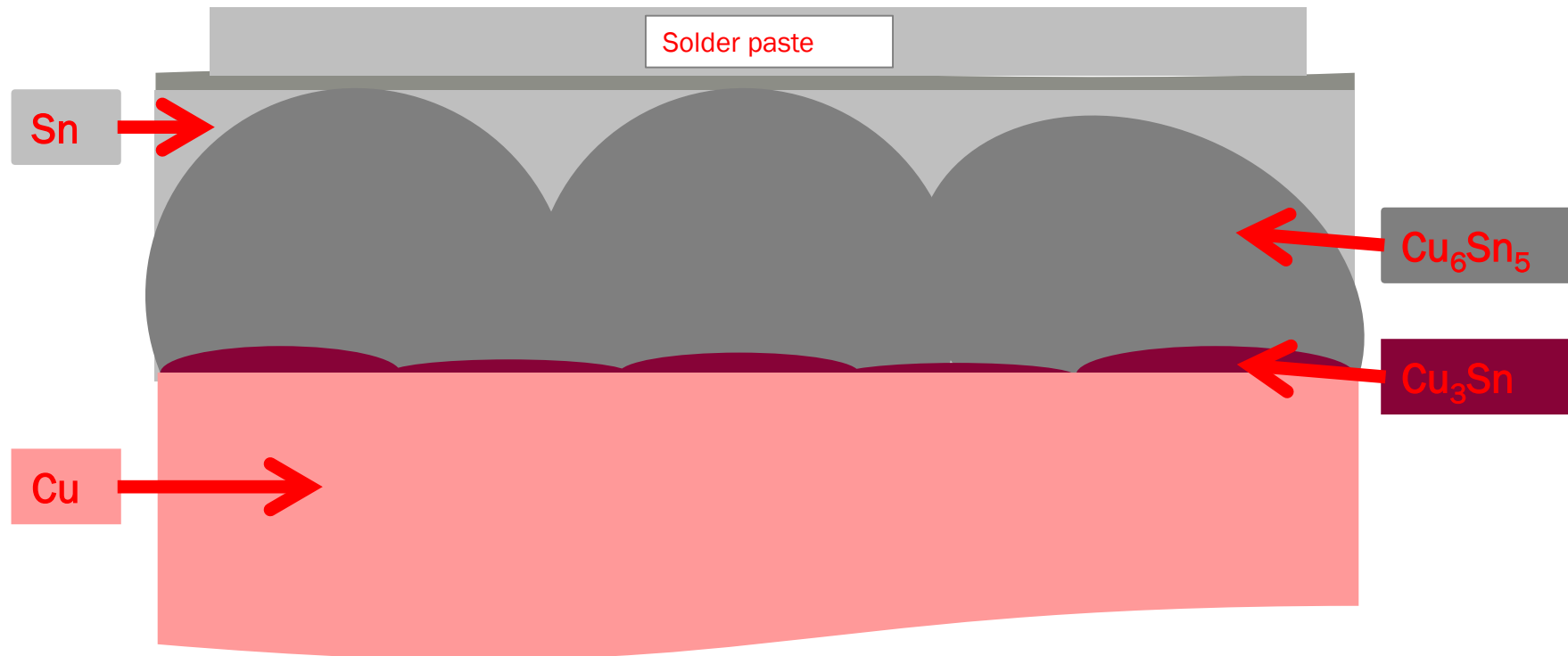
The drawing sizes were chosen for clarity, they are not really like that

2nd reflow solder spreading will be lower, therefore it is recommended to cover 90-100% of the pad with solder paste

Soldering Immersion Tin

2nd reflow

During the pre-heating in the reflow



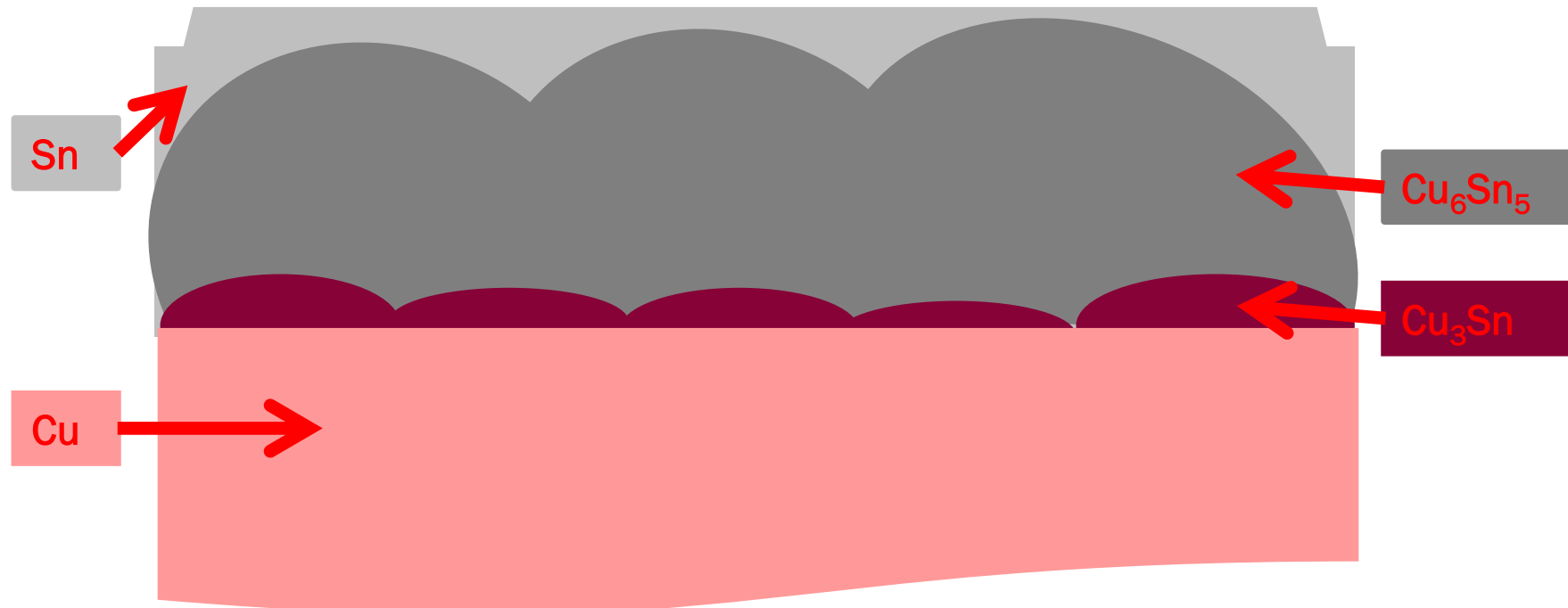
The drawing sizes were chosen for clarity, they are not really like that

During pre-heating,
flux has to remove the oxide and “clean” the surface for good wettability

Soldering Immersion Tin

2nd reflow

During peak temperature in the reflow

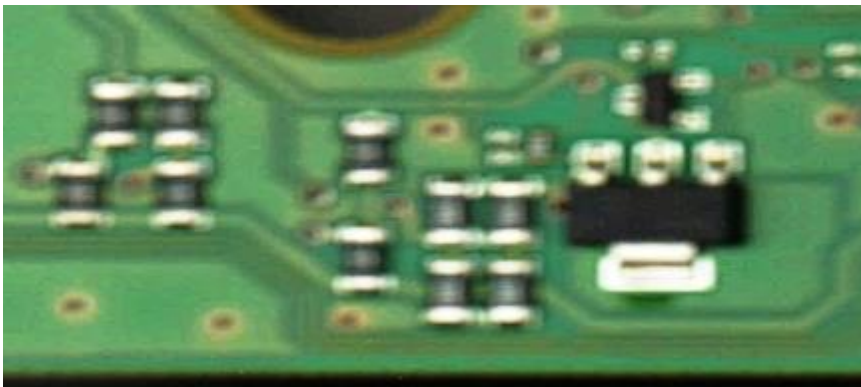


The drawing sizes were chosen for clarity, they are not really like that

The Cu_6Sn_5 and Cu_3Sn IMCs will

Soldering Immersion Tin

2nd reflow

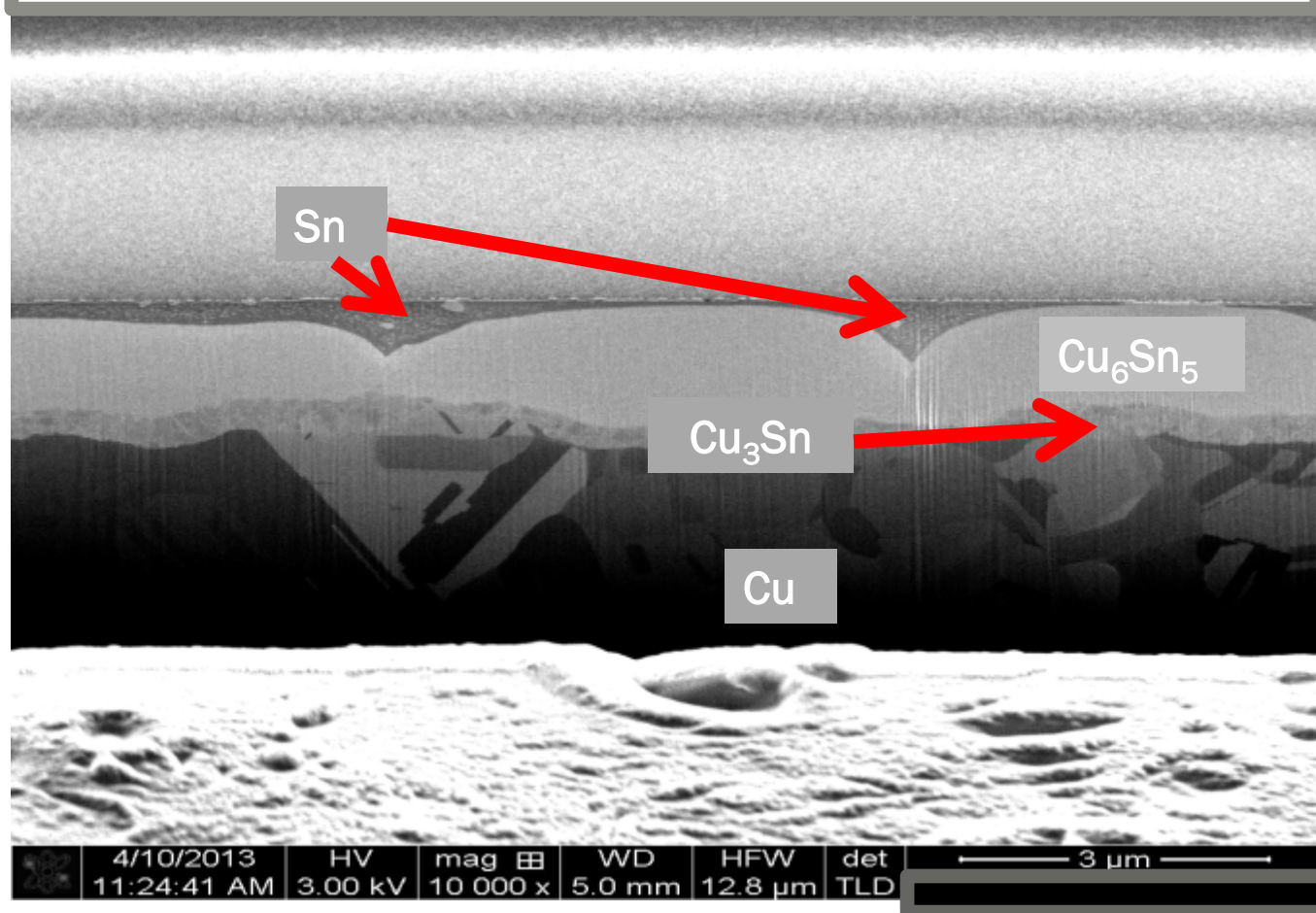


After 2nd reflow the non-soldered pads are visually clean, a little more gray, no discoloration or any other failures are visible

Soldering Immersion Tin

2nd reflow- un populated

FIB of a non-soldered pad after 2nd reflow



*e.g. the IMC can differ in shape and size depending on reflow, storage, copper crystal structure etc.

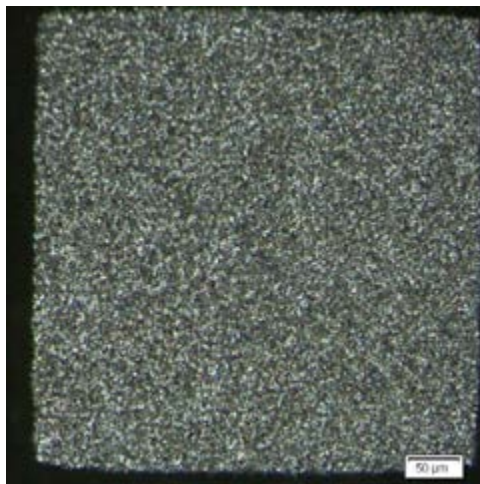
Solder defects

Soldering Immersion Tin

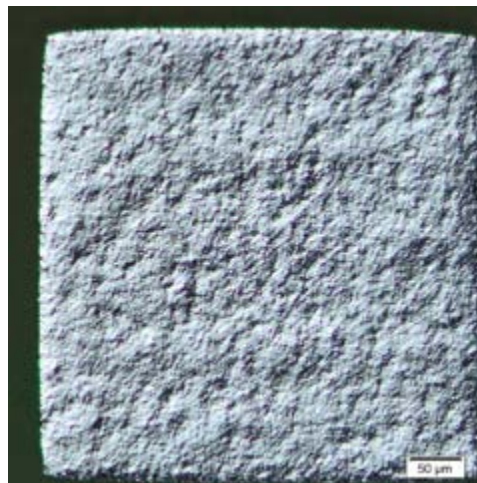
Solder defects

Self - Dewetting

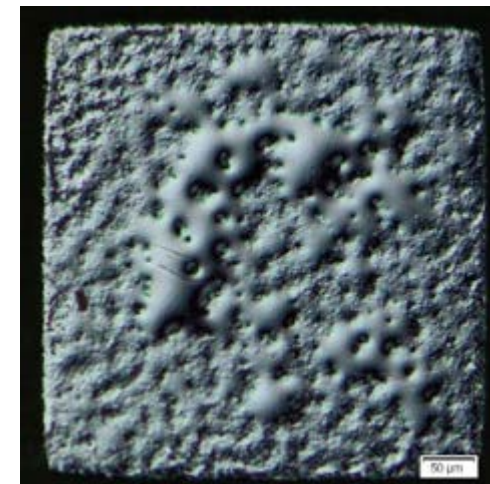
A condition that occurs when during the 1st reflow where the oxide layer of non-soldered ImSn layer has been broken. Due the high temperature in reflow (over melting point of ImSn) it always melts the ImSn layer. The oxide layer prevents agglomerate of Tin. When the oxide layer is damaged during reflow it will cause self-dewetting of the ImSn layer. ImSn surfaces with this phenomenon can cause in dewetting in 2nd reflow.



before reflow



after reflow / no self-dewetting



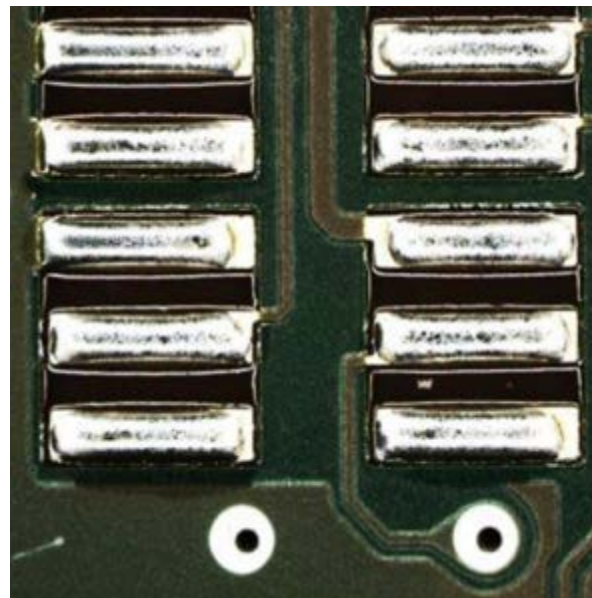
after reflow / self-dewetting

Soldering Immersion Tin

Solder defects

Dewetting

A condition that occurs when molten solder has coated a surface and then recedes (flows back), leaving irregularly shaped mounds of solder separated by areas covered with a thin solder film. Dewetting is difficult to identify since solder may be wetted at some locations and base metal exposed at others. Depending on the location, may be caused by excessive heating, inadequate cleaning or inhomogeneous oxidation of the attachment area.



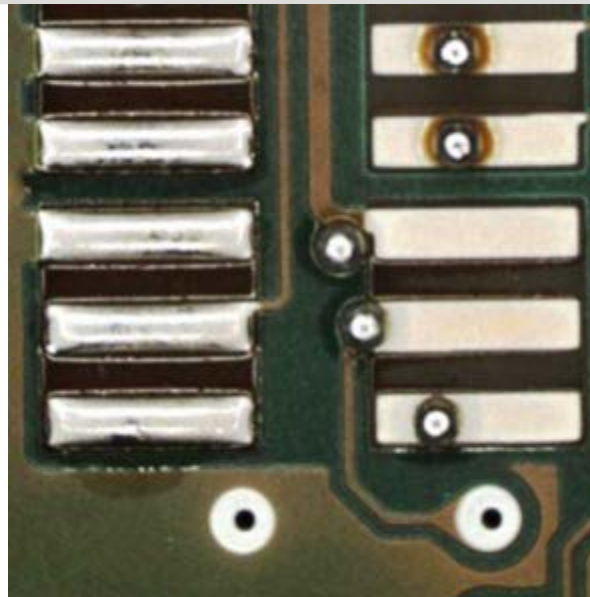
Soldering Immersion Tin

Solder defects

Non-wetting

A condition where a surface has contact to the melted solder, but the solder has not adhered to all of the surface, so that some base metal remains exposed.

Non-wetting is caused by a physical barrier (contamination or additional oxides) between the surfaces to be joined so that the wetting forces are insufficient to overcome the surface tension of the solder, resulting in the solder balling up rather than flowing out over and attaching to the metal surface. Usually caused by contamination, additional oxides of the surface and/or solder overheating.



Dewetting
Main reason

Soldering Immersion Tin

Dewetting – Main reason

After the 1st reflow there is no reliability problem with the assembled components . After 2nd reflow the second side shows a dewetting of the Tin surface.

Up to now there are 3 main reasons for dewetting identified

Residues on copper surface

Contamination on Tin surface

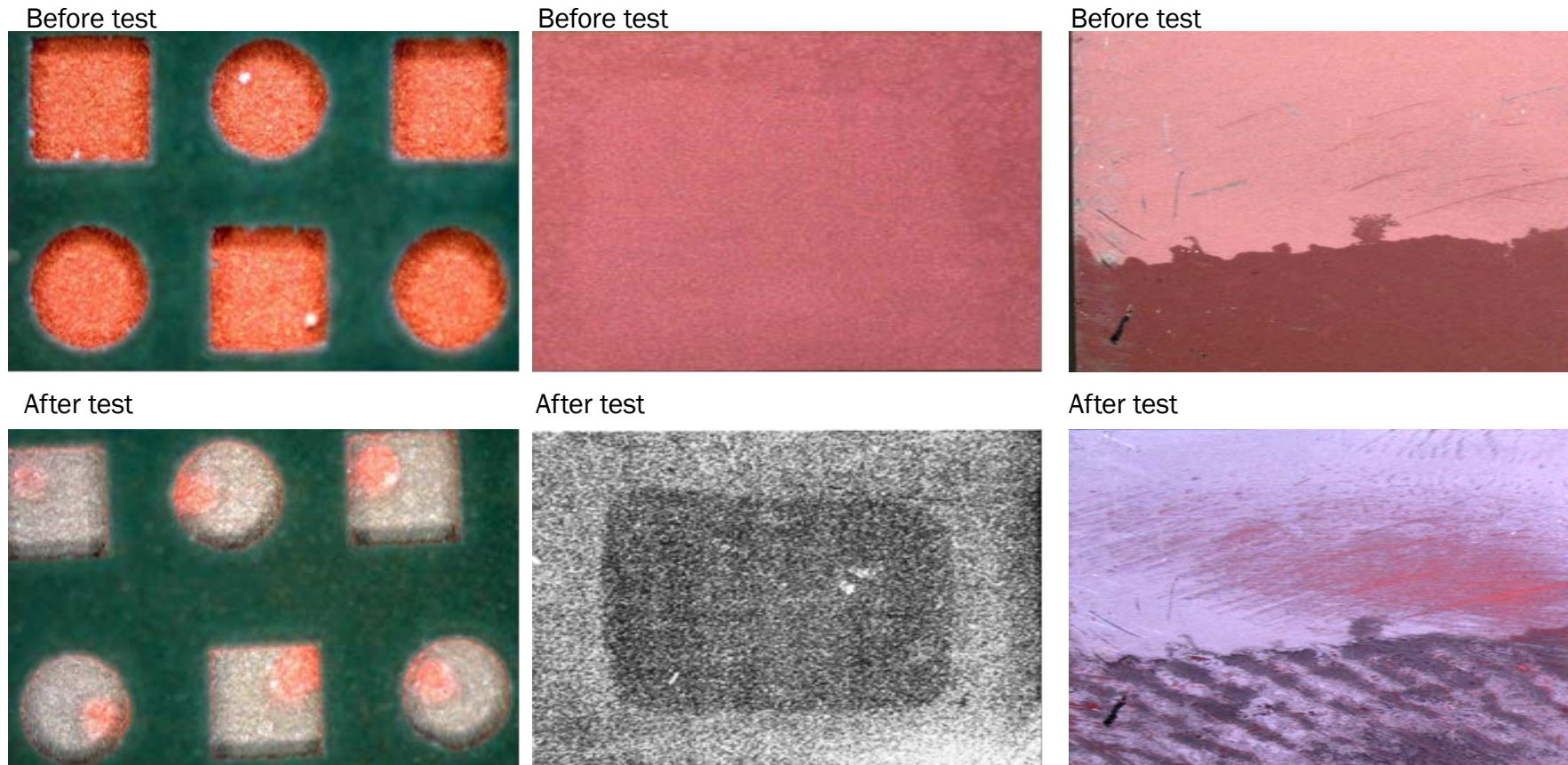
Evaporation of volatiles of solder mask in the 1st reflow

Residues on copper surface

Soldering Immersion Tin

Residues on copper surface

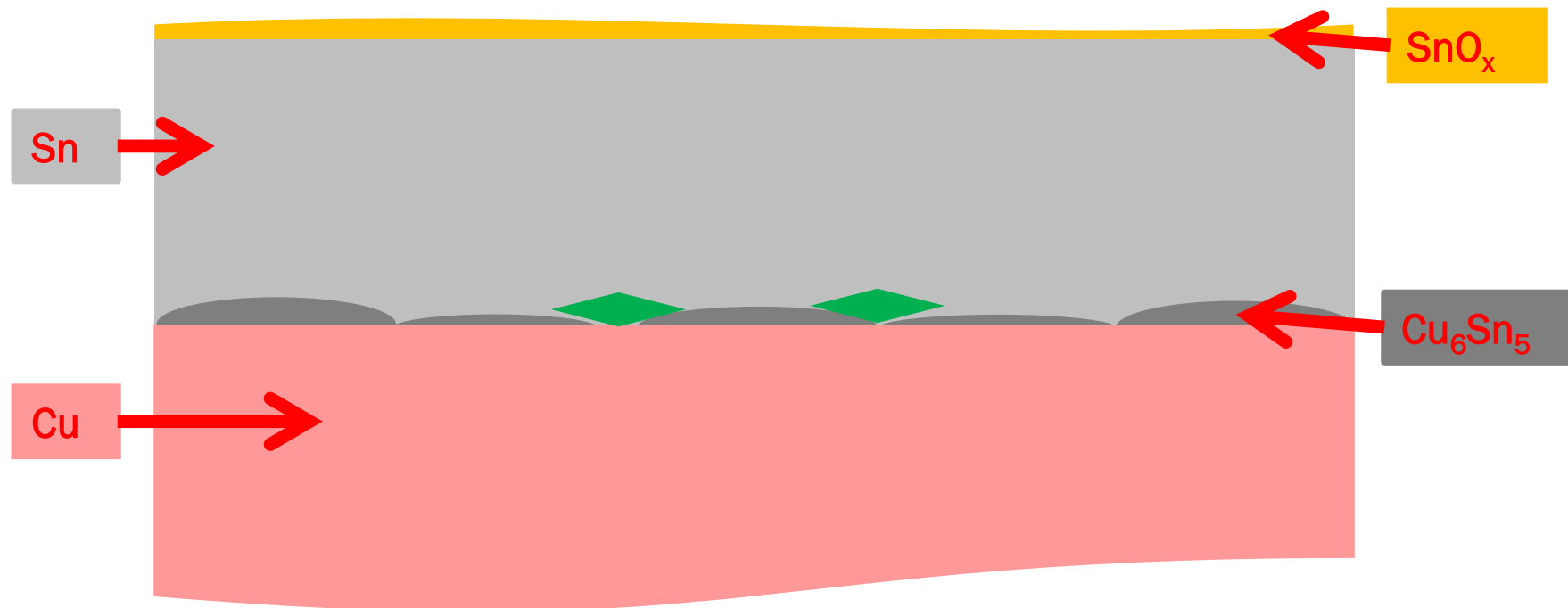
The cold Immersion tin test helps to identify residues (organic or inorganic) on the copper surface, which could disturb the Immersion Tin reaction.



Soldering Immersion Tin

Dewetting by residues on copper – 3 assumptions

Illustrated presentation



The drawing sizes were chosen for clarity, they are not really like that



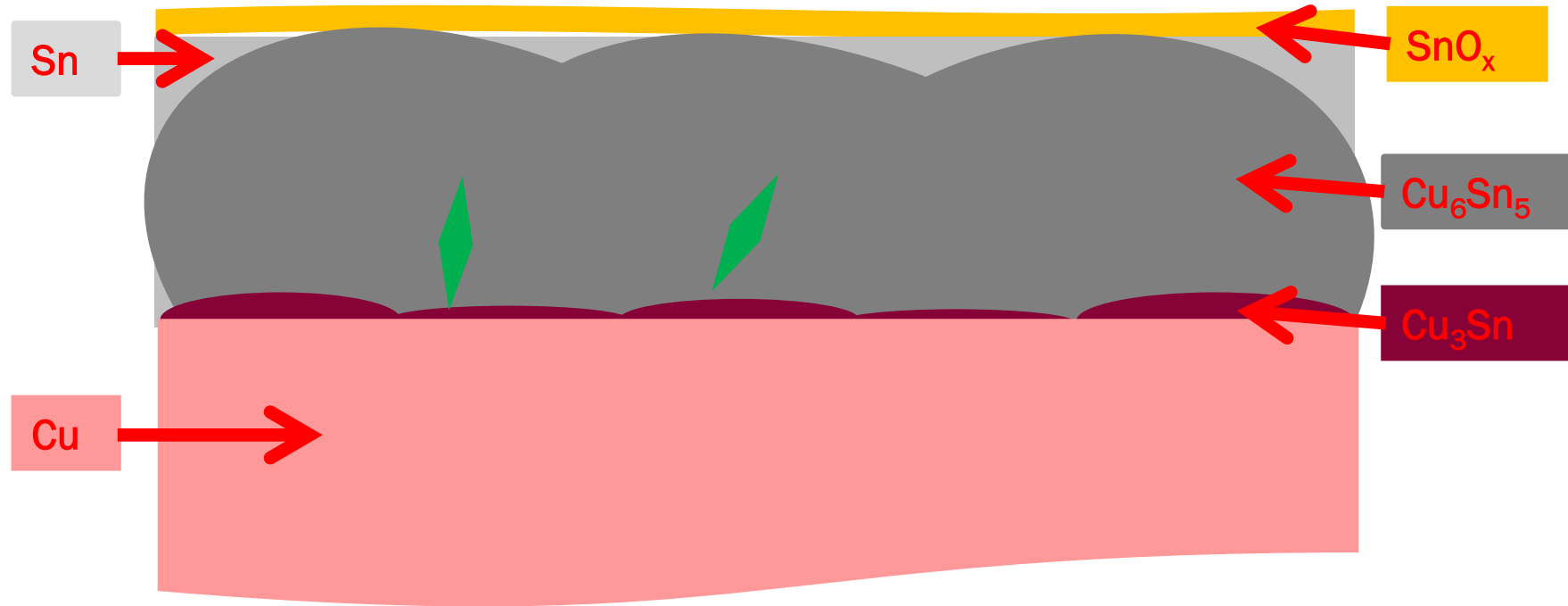
All previously mentioned residues can have the same effect.



Soldering Immersion Tin

Dewetting by residues on copper – 3 assumptions

1st assumption – after reflow



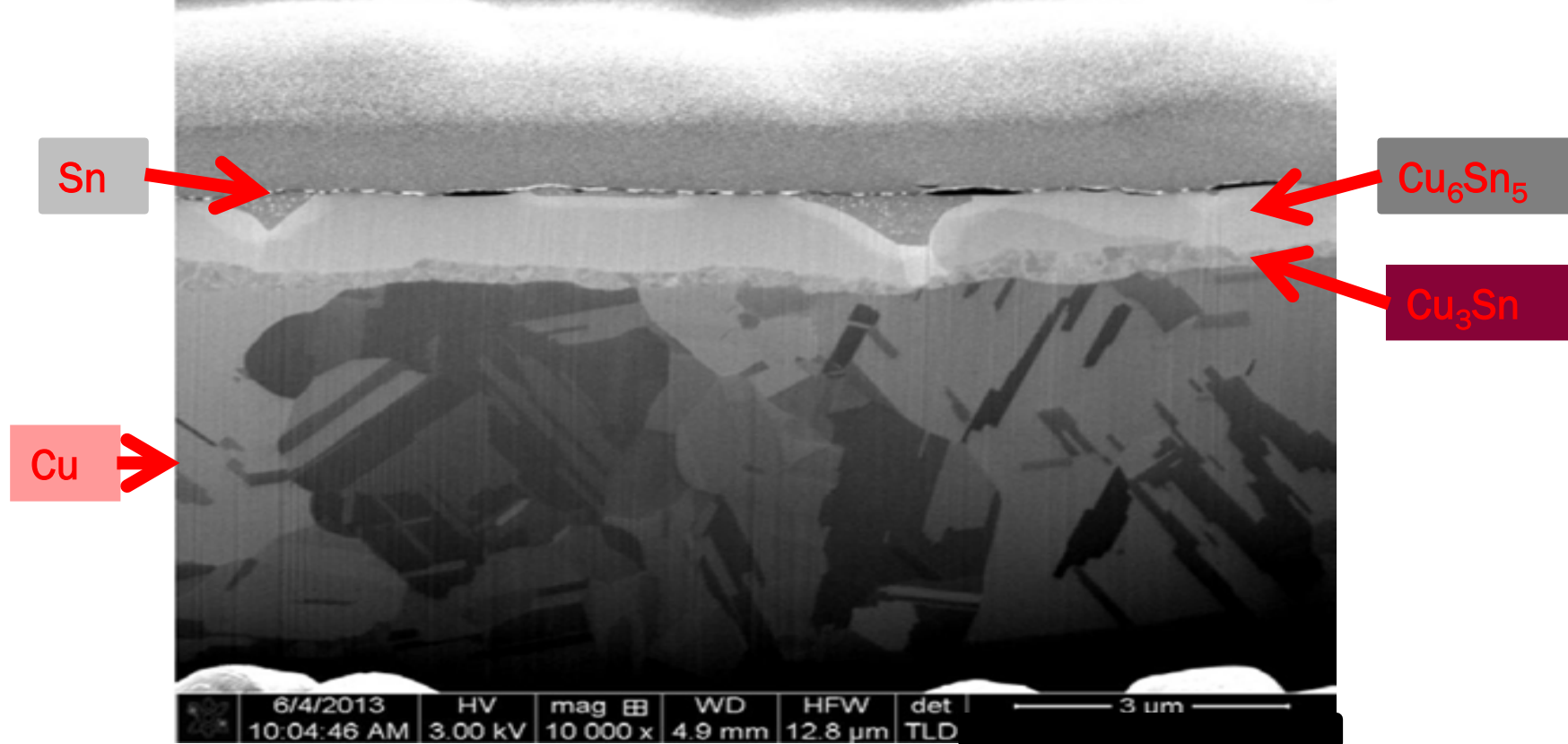
The drawing sizes were chosen for clarity, they are not really like that

The IMC growth is accelerated/modified and much more IMC can be found at the surface, which can lead to dewetting in the next reflow process.

Soldering Immersion Tin

Dewetting by residues on copper – 3 assumptions

FIB of a non-soldered pad after 1st reflow. copper surface was contaminated

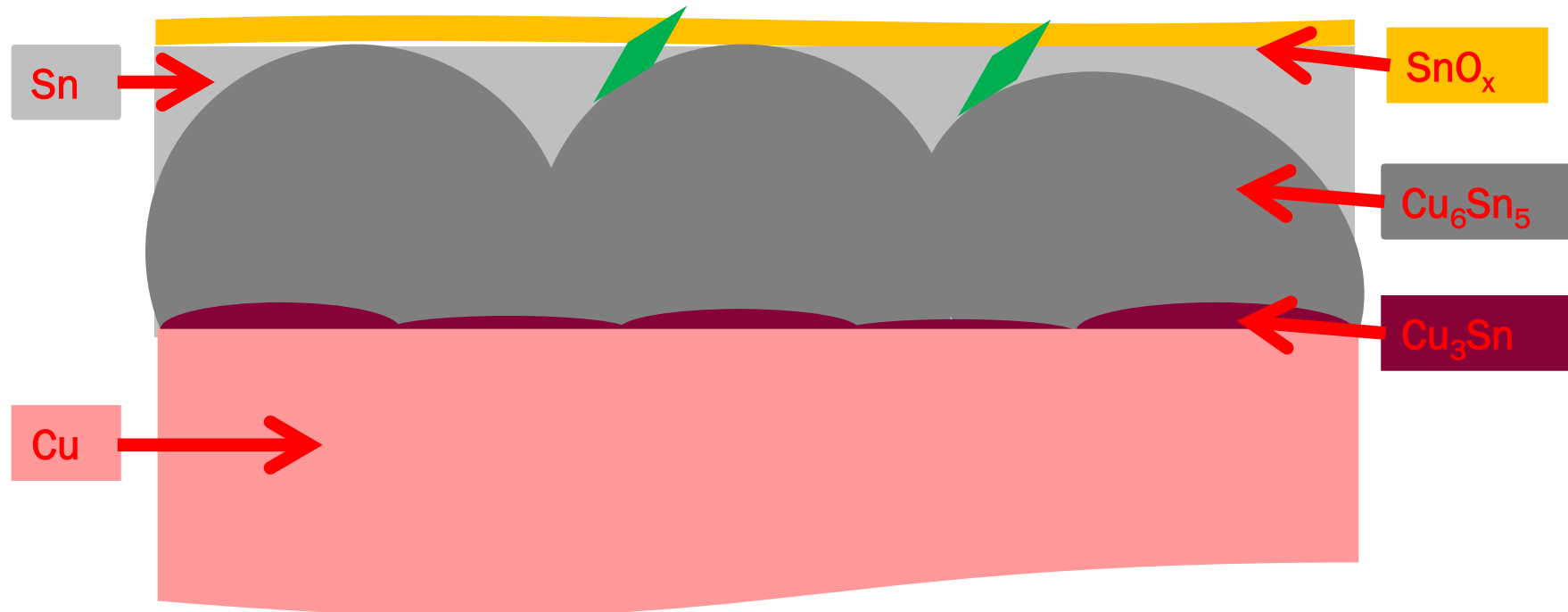


*e.g. the IMC can differ in shape and size depending on reflow, storage, copper crystal structure etc.

Soldering Immersion Tin

Dewetting by residues on copper – 3 assumptions

2nd assumptions – after reflow



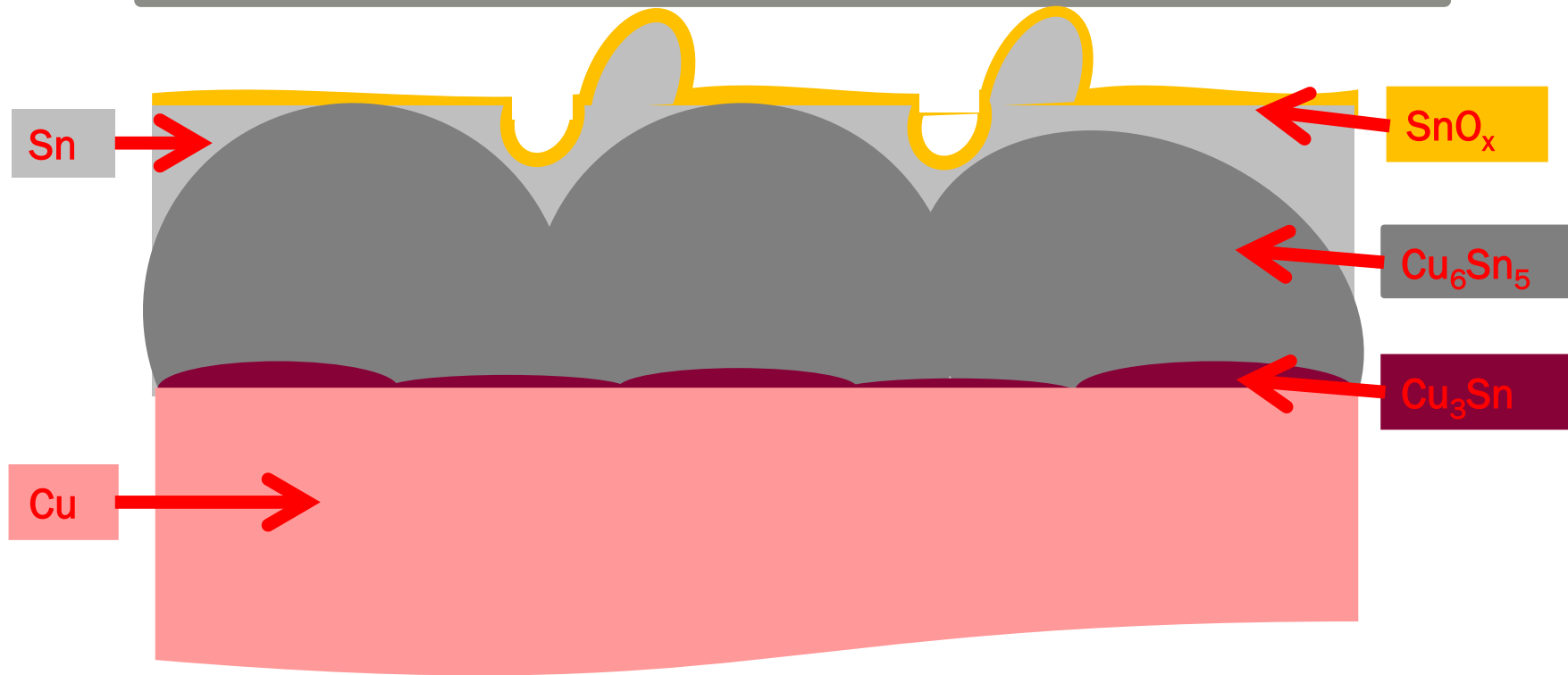
The drawing sizes were chosen for clarity, they are not really like that

The residues float to the surface during 1st reflow and damage the oxide layer.

Soldering Immersion Tin

Dewetting by residues on copper – 3 assumptions

2nd assumption – after reflow



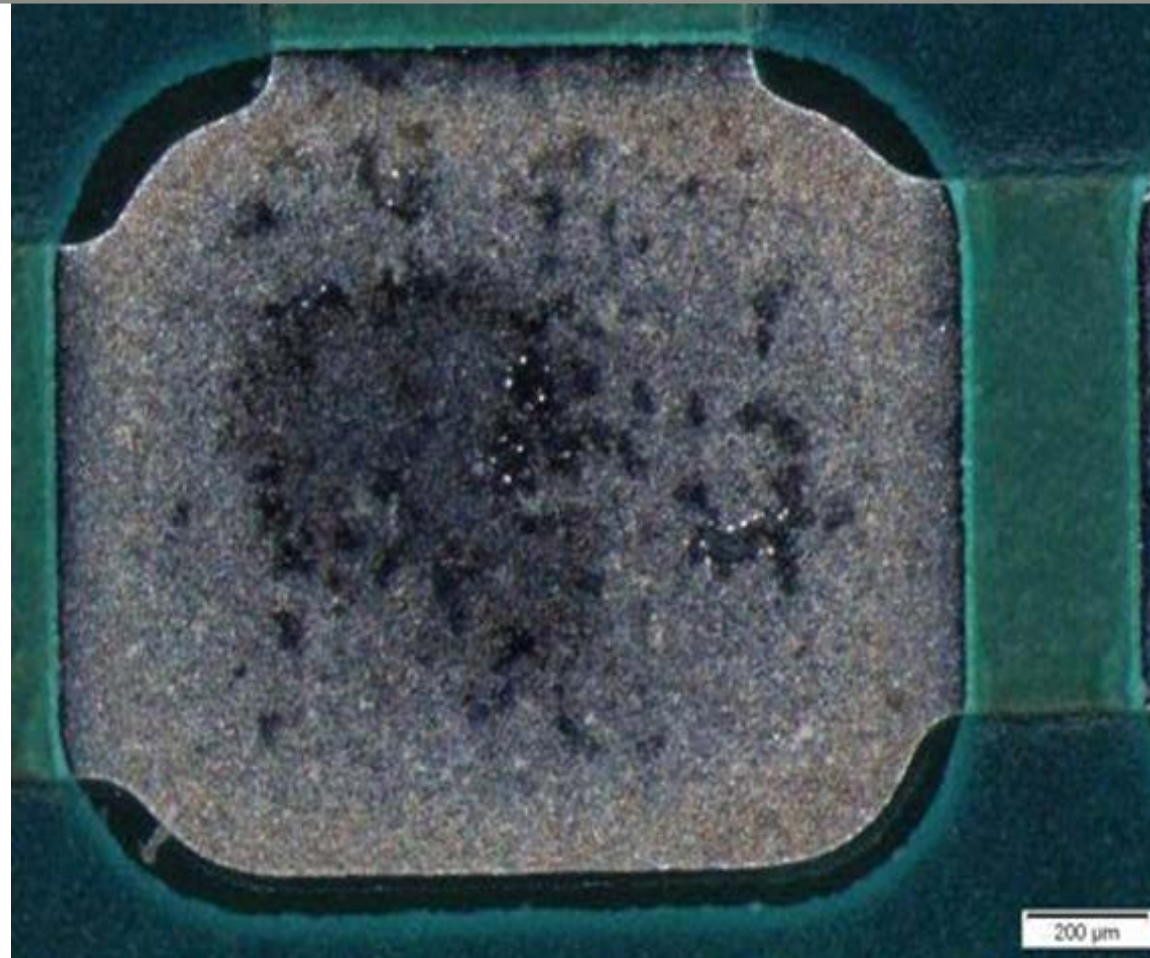
The drawing sizes were chosen for clarity, they are not really like that

Self-dewetting due to damaged oxide layer, represented by undulations in the I-Sn surface which can lead to dewetting in next reflow process.

5 Soldering Immersion Tin

Dewetting by residues on copper – 3 assumptions

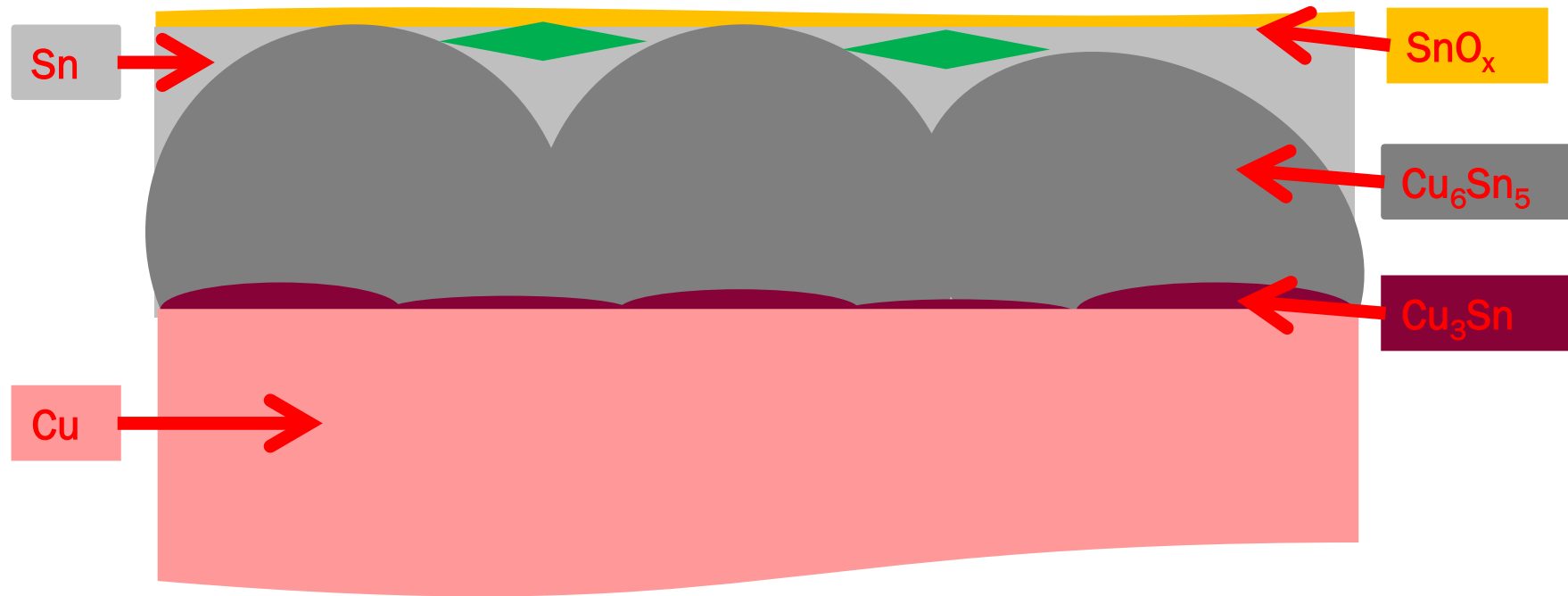
Self-dewetting after 1st reflow



Soldering Immersion Tin

Dewetting by residues on copper – 3 assumptions

3rd assumption



The drawing sizes were chosen for clarity, they are not really like that

The residues float to the surface during 1st reflow, but they don't damage the oxide layer. These residues can lead to dewetting in next reflow process.

Contamination on Tin surface

Soldering Immersion Tin

Contamination on Tin surface

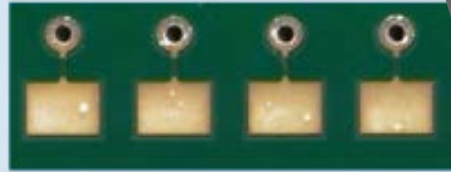
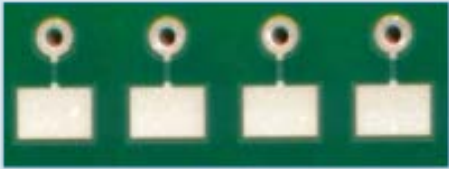


Poor PTH rinsing

As received

After 2h 155°C

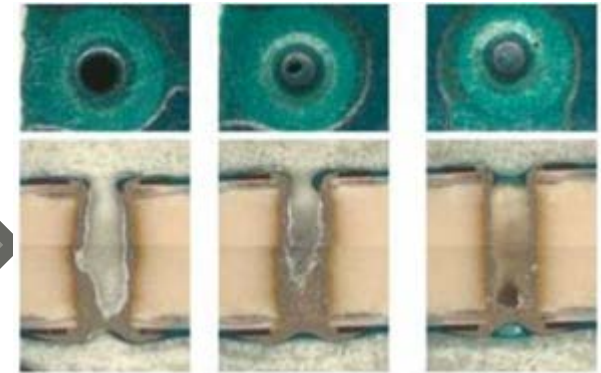
Detail 1



Detail 2



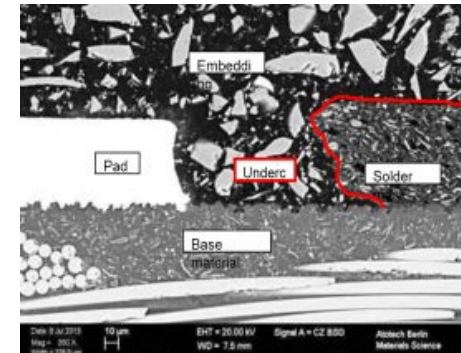
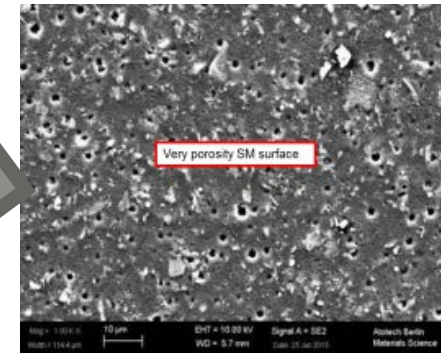
Semi plugged vias



Slightly discoloration were observed in condition "as received" which comes darker "after 2h 155°C"

SM related

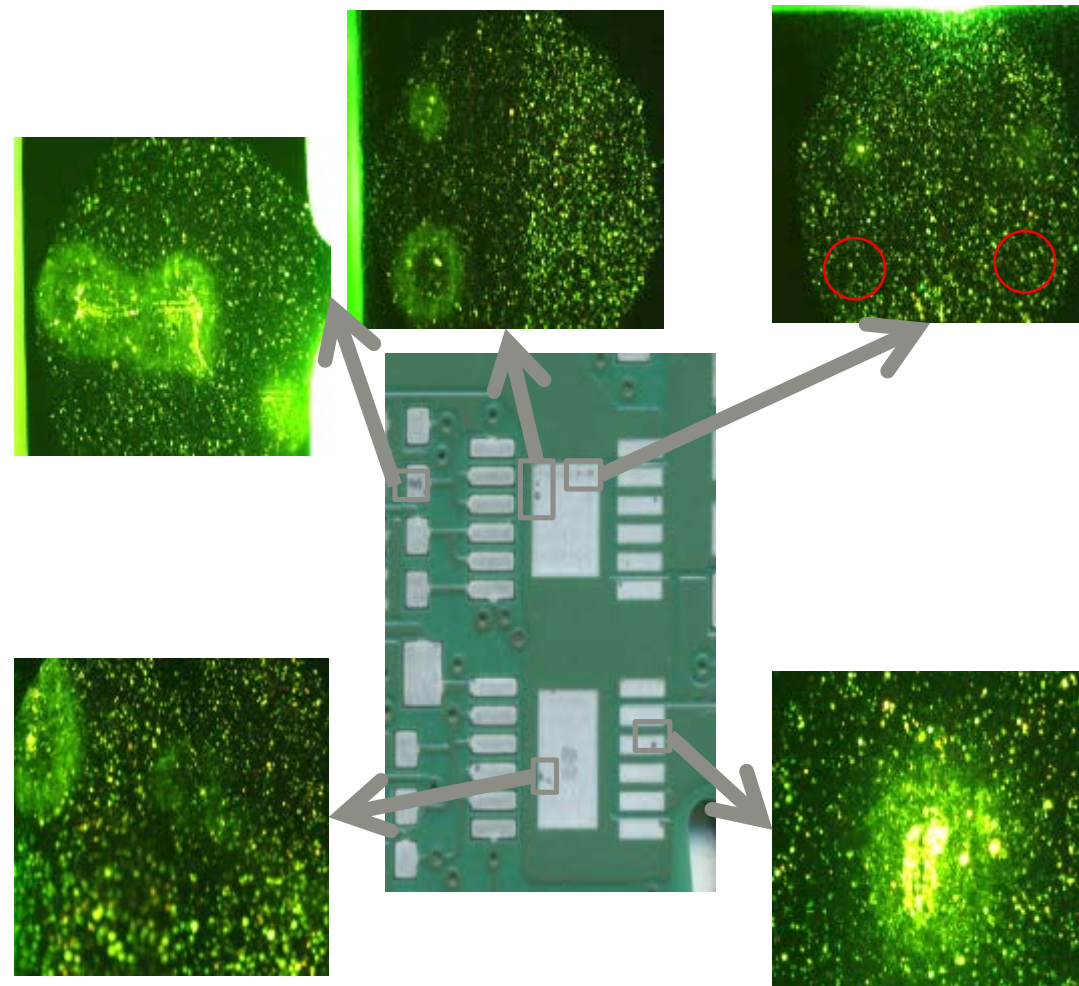
Contamination on the Tin surface may be caused by poor rinsing or by impossible rinsing or by incorrect handling or improper storage in an aggressive atmosphere.



Soldering Immersion Tin

Contamination on Tin

- Molten areas shows high fluorescence
- Clear correlation between shape of melting and fluorescence residues



Evaporation of volatiles of solder mask
during 1st reflow



Soldering Immersion Tin

Evaporation of volatiles of solder mask during 1st reflow

Solder mask systems consist of up to 30% volatiles

Many volatile substances are released during application, but there is still a significant amount of volatiles left which can evaporate (lower boiling point than 240°C) during the high reflow temperature.



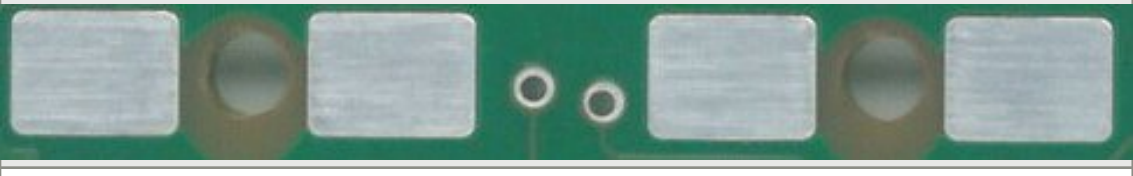

All volatile substances can condensate on the Tin surface and create a dewetting in 2nd reflow.

UV bump is strongly recommended. UV bumping gives additional reliability and prevents solder mask leaching as well as reduce the volatiles.

Soldering Immersion Tin

Evaporation of volatiles of solder mask during 1st reflow

Investigation to demonstrate the importance of UV bump

UV bump	Reflow atmosphere	Appearance on the Tin surface after reflow	Description
No	Air		Uneven partial self-dewetting (matte tin color)
No	N ₂		Self-dewetting (shiny tin color)
Yes	Air		No self-dewetting (matte tin color)
Yes	N ₂		No self-dewetting (shiny tin color)

Soldering Immersion Tin

Evaporation of volatiles of solder mask during 1st reflow

Investigation to demonstrate the importance of UV bump



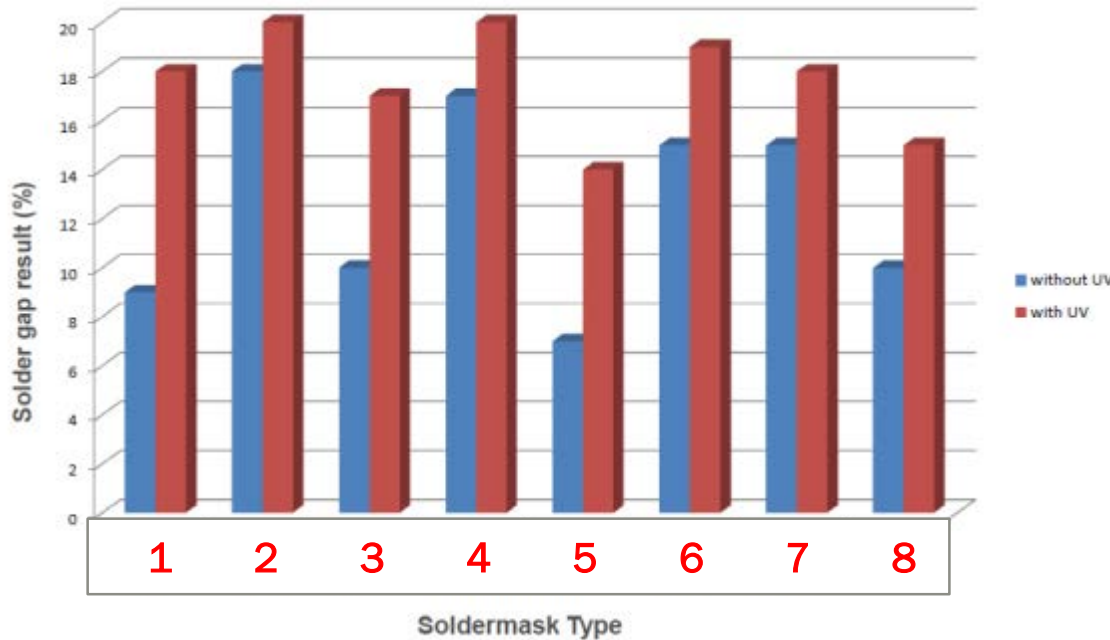
Solder mask						
Depth (Å)	C-C	C-O	C=O/CO3	O	N	Sn
0	67.9	11.9	1.7	11.8	0.8	3.1
10	58.0	17.0	0.7	11.7	3.2	4.5
50	65.9	23.6	0.0	5.4	1.6	1.0
Depth (Å)	Cu	Ag	Si	Pb	Na	Total
0	0.8	0.1	1.9	0.0	0.0	100.0
10	2.1	0.0	2.8	0.0	0.0	100.0
50	0.4	0.0	2.1	0.0	0.0	100.0

Self-dewetting area												
Depth (Å)	C-C	C-O	C=O/CO3	O	N	Sn	Cu	Ag	Si	Pb	Na	Total
0	46.7	1.9	4.1	25.1	1.5	7.3	4.4	0.3	0.4	0.2	5.4	100.0
10	28.7	4.3	4.1	28.9	1.3	12.5	8.0	0.5	0.9	0.2	7.9	100.0
50	12.6	2.4	2.8	39.5	1.0	21.1	7.5	0.5	0.6	0.5	9.4	100.0

Soldering Immersion Tin

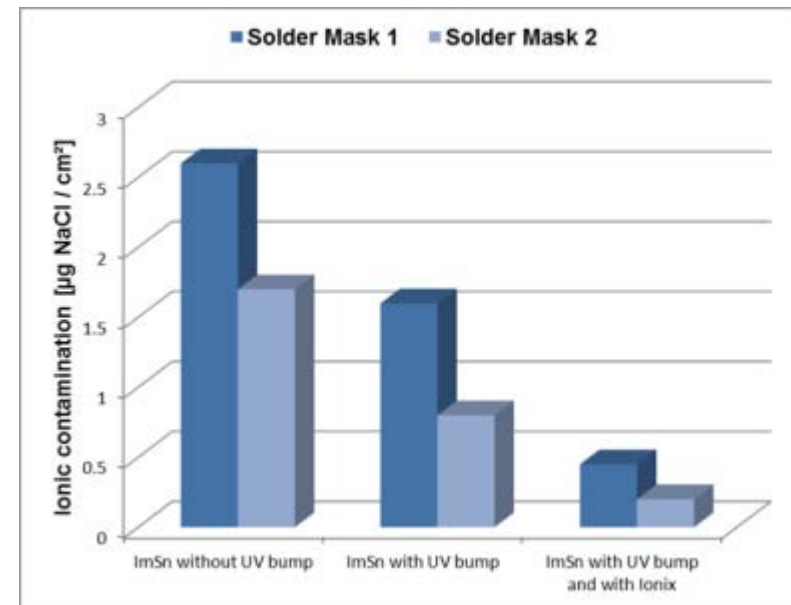
Evaporation of volatiles of solder mask during 1st reflow

Investigation to demonstrate the importance of UV bump



Therefore strongly recommend a UV bump before I-Sn.

UV Bump of the solder mask has a high impact on solderability and ionic contamination of Immersion Tin!



Immersion tin combines good solder performance at a reasonable price
Horizontal and vertical application
Gaining market share primarily due to the confidence of automotive OEMs.

Thank you!

References

1. Bosch, "Wettability Effects of Immersion Tin Final Finishes with Lead Free Solder"