Semi-Additive Process for Variant Polyimide Substrates in Ultra-Fine Flexible Circuitry

Fei Peng, Ernest Long, Jim Watkowski, William Bowerman
MacDermid Enthone Electronics Solutions, Waterbury, CT, USA

Abstract

Ultra-fine flexible circuitry has been more and more applied in electronic devices due to their fast innovation and the increasing demand on miniaturization, light weight and flexibility in some cases. These devices range from personal electronics to medical instruments, including smart phones, tablets, ultra-thin or/and convertible laptops, wear-able electronics, flexible connecting parts and antennas in all other types.

In addition to their flexibility and light-weight advantages, flexible circuits need to incorporate ultra-fine features, maintain good signal integrity at high frequency transmission, and guarantee long-term use with good stability under heat-accumulated conditions. To meet such high requirements, polyimide (PI) has been the most widely used dielectric substrate material due to its very good electronic, physical and chemical properties. It has low D_k and D_f to support high frequency signal transmission; low CTE, high T_g and T_d to maintain good shape and size stability, thermal stability and processing ability; good chemical resistance, low moisture but good UV absorption.

However, due to the superior properties above, it is generally difficult to obtain good PI-plating adhesion on the very smooth PI substrate, which is also required for good signalintegrity in the ultra-fine circuitry. Even more challenging is to maintain the plating-PI adhesion at a certain high level after continuous exposure ina high temperature environment. To meet the demand, the company developed a semi-additive process (SAP-FLEX), which was tailored for different kinds of PI films widely used in the current market of the ultra-fineflexible circuitry. Using SAP-FLEX, the PI surface not only maintained a Ra lower than 27 nm, but also consistently achieved a uniform initial peel strength from715 to more than2055 gf/cm on variant PI substrates. After a 7-day continuous baking test at 150°C, the peel strength can be maintainedfrom465 to more than1287 gf/cm.This paper will discuss the SAP-FLEX process flow;its performance on different kinds of PI films; its processing window and the bath life of the adhesion promoter; and its process capability using Six-Sigma tools.

1. Introduction

The miniaturization trend in personal electronic devices (such as mobile phones, tablets and other hand-held devices) demands the new design of integrated circuitry (IC) to combine ultra-fine features, such as very tight pitch and very fine line and spacings. Meanwhile, the interface between the high density integrated circuitry (HDIC) and the IC substrate needs to be very smooth to support good signal integrity of high speed signal transmission at high frequency. Semi-Additive processing, or SAP, has been widely used in the manufacture of HDIC for many years.

Flexible circuitry has been proliferating rapidly to replace traditional wire harnesses due to many benefits compared to traditional cabling and rigid boards. Physically, it presents smaller size, lighter weight, better thermal stability and wider operating temperature. As to electronic properties, it provides higher wiring accuracy and circuit density, stronger signal quality, better reliability and impedance control. In addition, it shows good flexibility in circuit design and enables the elimination of mechanical connectors.

With the growing need to maintain and improve signal integrity, different dielectric materials have being evaluated as IC substrates for the ultra-fine flexible circuitry. One of them is polyimide (PI), which shows good chemical resistance, low moisture adsorption and good UV absorption. In addition, PI has excellent thermal and shape/size stability, low dielectric constant and good processing ability. For example, PI films are widely available in a variety of thicknesses ranging from 76.2 micron (3.0 mil) to as thin as 12.7 micron (0.5 mil). These unique chemical, mechanical and electronic properties make PI one of the best candidates for flexible IC substrates.

The company has developed a semi-additive process (SAP-FLEX), which was tailored for different kinds of PI films widely used in the current market of flexible circuitry. Using SAP-FLEX, 4 different kinds of PI substrates (**Figure 1**) not only maintained a Ra lower than 27 nm, but also consistently achieved a uniform initial peel strength from 715 to more than 2055 gf/cm on various PI substrates. After the 7-day baking test at 150°C, the peel strength can be maintained from465 to higher than1287 gf/cm on different PI films. This paper will discuss the SAP-FLEX process flow, its application on various PI substrates, its processing window, and the bath life of the adhesion promoting step: conditioning. Of the most interest, it will discuss the initial and heat-exposed PI-plating adhesion from 90° peel tests. The process capability would be evaluated using Six-Sigma tools.

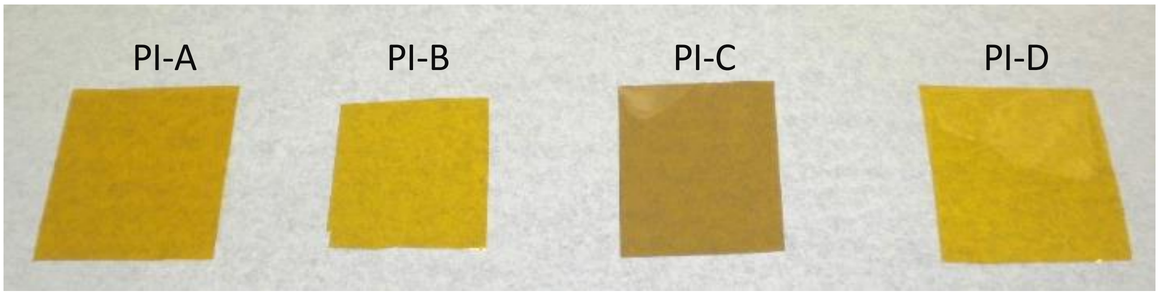


Figure 1. Pictures of 4 different kinds of PI substrates, which are widely used in the current market of ultra-fine flexible circuity, were processed using the SAP-FLEX process and investigated here.

2. SAP-FLEX Process Flow

The process flow for SAP-FLEX includes etching (desmear), conditioning, electroless and electrolytic plating techniques developed for PI-based flexible IC substrates from the company. Following a mildetching on the PI surface, an innovative conditionerwas utilized to impart the PI film with a very smooth but highly functionalized surface. Different from conventional conditioner, the SAP-FLEX conditioner not only promotes the initial adhesion between PI and plating layer, but also helps to maintain it against the accelerated heat exposure.

After the conditioning step, there are activating and reducing steps. Then a Ni plating step is used to introduce a thin Ni layer which bonds directly to PI film, which functions as a metal tie-coat to enhance PI-plating adhesion. The EDX spectrumfrom the Ni plating showedthat the phosphorus content in the Ni layer is only 2.5 wt%. Therefore, this Ni tie-coat can provide much better electrical conductivity compared to conventional high-phosphorus Ni plating. It is preferred for the upcoming plating process.After Ni tie-coat plating, a thin Cu seed layer was applied on the film surface using an electroless Cu plating process. This Cu layer provided the film surface with an increased electrical conductivity. And such a thin Cu layer helps to get a uniform Cu thickness across the filmsurface in the following Cu build-up step in the electrolytic Cu plating.

3. Results and Discussions

3.1. Surface Pre-treatment in SAP-FLEX

With the SAP-FLEX process, the surface pretreatment step, i.e. etching and conditioning of PI films, is conducted at lower caustic solution (NaOH wt% as low as 5~10) for a short time of 2~5 min. And this step happens at a lower and wider processing window regarding temperature (from room temperature to 70°C) compared to conventional etching for PI substrates. Consequently, the PI maintains an ultra-smooth surface after the SAP-FLEX pretreatment. It is well demonstrated in **Figure 2**, which shows the topographies of one kind of PI film namely PI-A before (**Figure 2-(a, b)**) and after (**Figure 2-(c, d)**) the surface pretreatment. Although the surface roughness of the transparent PI film cannot be quantified directly, a non-transparent rigid board with a surface roughness of Ra=27 is also shown in **Figure 2-(e, f)** as a reference. Apparently, the treated PI-A surface is no rougher than the reference. In other words, the treated PI-A film maintained an ultra-smooth topography with a surface roughness Ra≤ 27 nm.

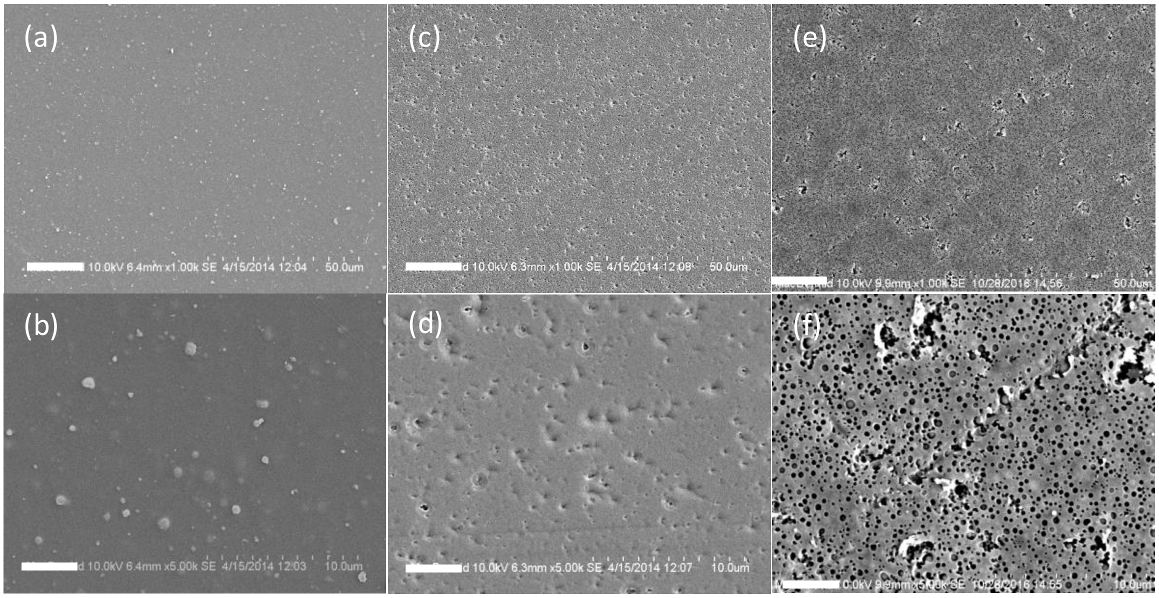


Figure 2. SEM images for PI-A(a, b) before and (c, d) after the surface pretreatment in SAP-FLEX. For comparison, (e, f) show a non-transparent resin as a reference, whose surface roughness was quantified to be Ra= 27 nm. (a, c, e) are taken at the 1000× magnification and (b, d, f) are taken at the 5000× magnification.

3.2. Initial Adhesion

The adhesion between the ultra-smooth PI surface and the plating layer was evaluated by the peel strength ata 90^o peel testwhende-adhesion happened at the PI-plating interface. Specifically, freshly plated PI sample was cut into a 0.5 in W × 2.5 in L specimen and taped down to a board (such as a rigid epoxy laminate board) using a strong double tape. The board was used as a specimen-holder, whichwas mounted at the peel test instrument as shown in **Figure 3-(a)**.The peel strengths from the freshly plated PI samples were recorded as the initial peel strength. Meanwhile, specimens of the same size were cut from the same samples and kept in an oven for a 7-day continuous baking at 150^{o}C. After the 7-day baking test, these specimens were also mounted and peeled as above, whose results were recorded as the 7-daypeel strength. In most cases, de-adhesion happened between the PI-plating interface (**Figure 3-(a)**). However, when the PI-plating adhesion was higher than 1200 gf/cm, which is around the bonding limit of the double tape, de-adhesion would happen within the double tape as shown in **Figure 3-(b)**. In the latter case, the recorded peel strength would be the bonding limit of the double tape, which may fluctuate through the tape length. Therefore, the real PI-plating peel strength would be higher than the recorded value (**Figure 4-(b, d)** and **Figure 5 (b)**).

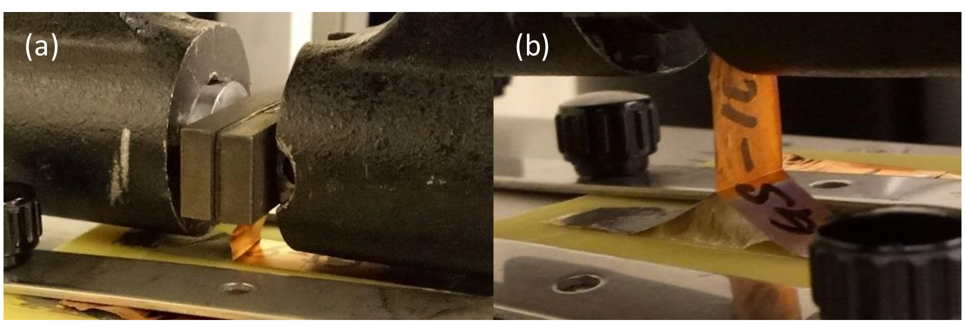


Figure 3. (a) Specimen set-up forthe 90^o peel test. (b) With very good adhesion at the PI-plating interface, de-adhesion proceeds within the double tape, which was used to glue the specimen down to the specimen-holder surface (here shown is the epoxy board underneath), and the peeling proceeds in a tape-off mode.

Figure 4 presents the representative load versus dislocation profiles from the 90^o peel tests on 4 different kinds of PI substrates, namely PI-A (**Figure 4-(a)**), PI-B (**Figure 4-(b)**), PI-C (**Figure 4-(d)**) and PI-D (**Figure 4-(d)**). On PI-A and C, de-adhesion happened at the PI-plating interface. Ignoring the edge effects at the end of peeling, their peeling profiles demonstrated that: processed with SAP-FLEX, the initial PI-plating peel strength on PI-A is as high as 1215 gf/cm. Such value is more than double than 550 gf/cm, which is the widely acceptedlower limit of the initial substrate-circuit adhesion in the flexible circuitry. For PI-C, its initial PI-plating peel strength is 715 gf/cm, which is lower than that of PI-A but still much higher than the required lower limit. As to films PI-B and D, the PI-plating adhesion on them were much better than the bonding limit of the double tape. Therefore, after their peel strength reached high enough to challenge the tape bonding, the peeling started to proceed within the tape. As a result, the tape was continuously peeled off from the specimen-holder and the recorded peel strength started to go down and fluctuate at a tape-off mode (**Figure 4-(b, d)**). In these cases, the real initial peel strength values on PI-B and D should be higher than the peak values of peelingfrom which point tape-off mode started. In other words, the initial peel strength on PI-B should be higher than 2055 gf/cm (11.5 lb/in) and that on PI-D should be higher than 1859 gf/cm (10.4 lb/in).

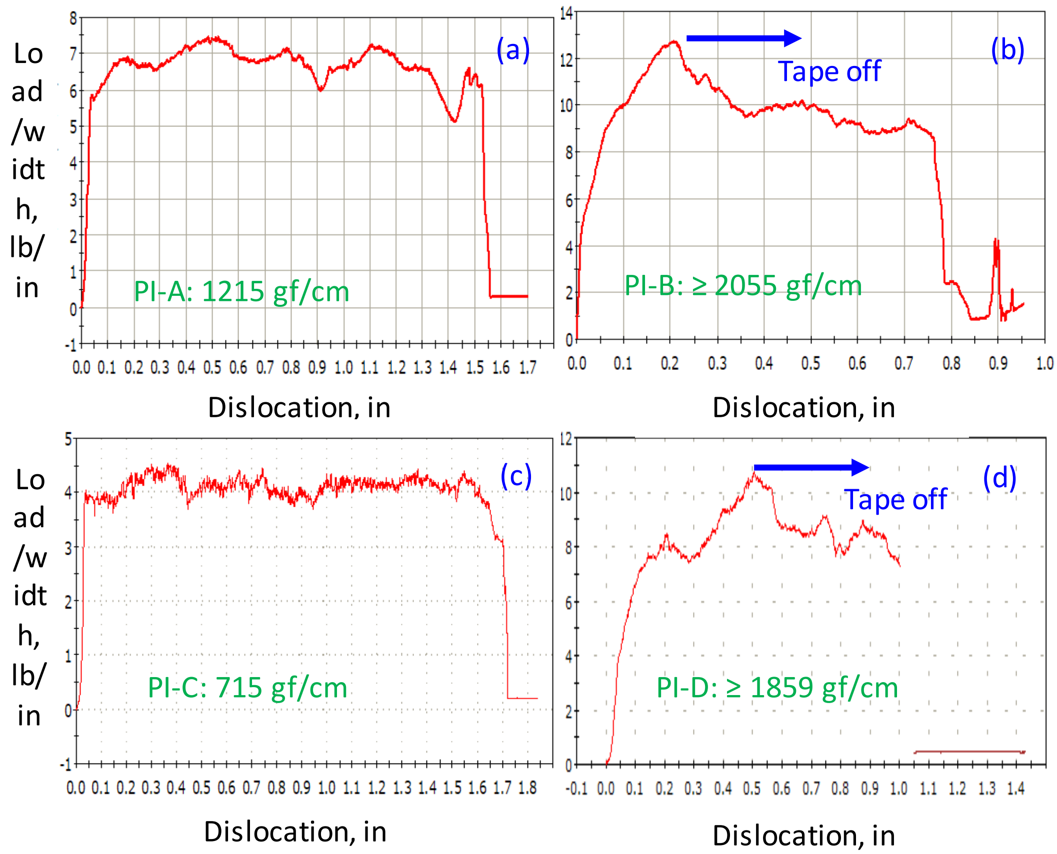


Figure 4. Representative Load versus dislocation profiles from 90° peel tests showing the initial PI-plating peel strengthson 4 different kinds of PI substrates namely (a) PI-A, (b) PI-B, (c) PI-Cand (d) PI-D. All of them were processed with SAP-FLEX. Due to very good PI-plating adhesion, peelings on films PI-B and PI-D proceeded with the tape-off mode after the peel strength exceeded the bonding limit of the double tape.

3.3. 7-Day Baked Adhesion

As an important technical criteria for flexible circuitry, the adhesion at the PI-plating interface needs to be subjected to an accelerated heat exposure test, such as the 7-day continuous baking at 150°C. **Figure 5** shows the peeling profiles of films PI-A, B and C after the 7-day baking test. Specifically, the 7-day baked peel strength on PI-A can still be as high as 806 gf/cm (**Figure 5-(a)**). And that on PI-B film is still higher than 1287 gf/cm (7.2 lb/in), because peeling proceeded with tape-off mode after reaching that value (**Figure 5-(b)**). On PI-C film, the 7-day baked peel strength drops to 465 gf/cm (**Figure 5-(b)**). Nevertheless, all these peel strength values are much higher than 350 gf/cm, which is widely accepted as the lower limit of the 7-day baked adhesion test in the flexible circuitry. These data well demonstrate that, the SAP-FLEX process can not only bring superior PI-plating adhesion at the initial stage, but also make it maintain at a very high level after the accelerated heat exposure test.

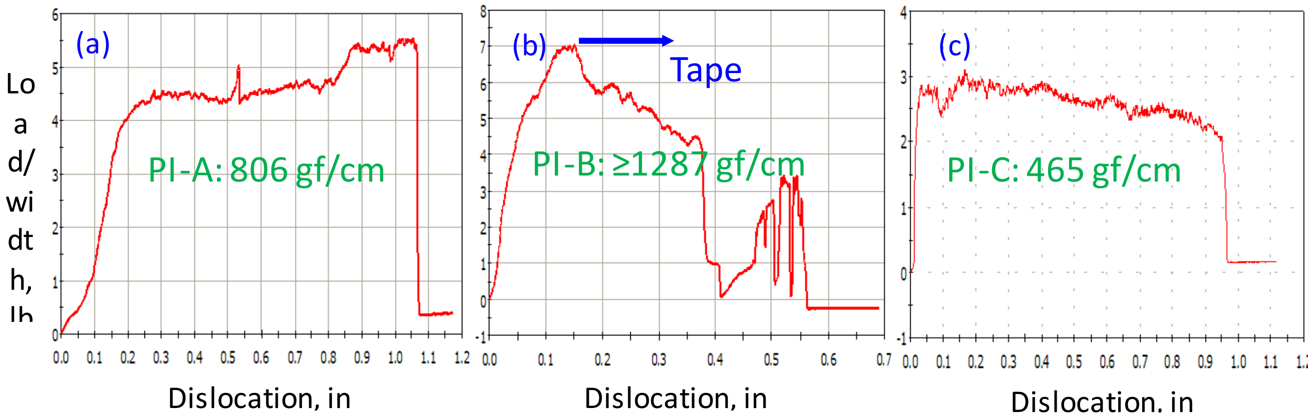


Figure 5. Representative Load versus dislocation profiles from the 90° peel tests showing the 7-day baked peel strengths on(a) PI-A, (b)PI-B, and (c) PI-C, respectively.

3.4. SAP-FLEX Conditioner

The excellent performance of the SAP-FLEX process is possible not only because of the advanced plating solutions, but are also closely related to the surface pretreatment process, especially the conditioning step. **Figure 6-(a)** compares the initial and 7-day baked peel strengths from the PI-A film processed with the SAP-FLEX conditioner at different concentrations (from 0% ,i.e. no SAP-FLEX conditioner, to 100%). Without SAP-FLEX conditioner, the initial and 7-day baked PI-plating peel strengths are 500 and 393 gf/cm, respectively. Moreover, as published in a previous paper, such peel strength was not uniform through the PI surface [1]. On the contrary, treated with 100% SAP-FLEX conditioner, the initial peel strength on PI-A is 942±88 gf/cm (**Figure 7-(a)**) and the 7-day baked one is 605±63 (**Figure 7-(b)**) gf/cm. And both of them are very uniform through the film surface. Comparing the two groups of data above, it is obvious that the SAP-FLEX conditioner brings an improved adhesion-promoting effect on the PI substrate regardless of being in the initial ($p= 0.0024$) or 7-day baked ($p=0.0022$) case. Meanwhile, as also shown in **Figure 6-(a)**, when ranging the concentration of the conditioner from 10 to 100%, the initial peel strengths seem to vary from 769 to 1090 gf/cm, and the 7-day baked ones change between 554 to 804 gf/cm. However, such differences are not significant when compared to the values obtained with 100% SAP-FLEX conditioner (for initial peel strength, $p= 0.935$; for 7-day baked ones, $p= 0.525$). In other words, there is a wide processing window regarding the concentration of the SAP-FLEX conditioner.

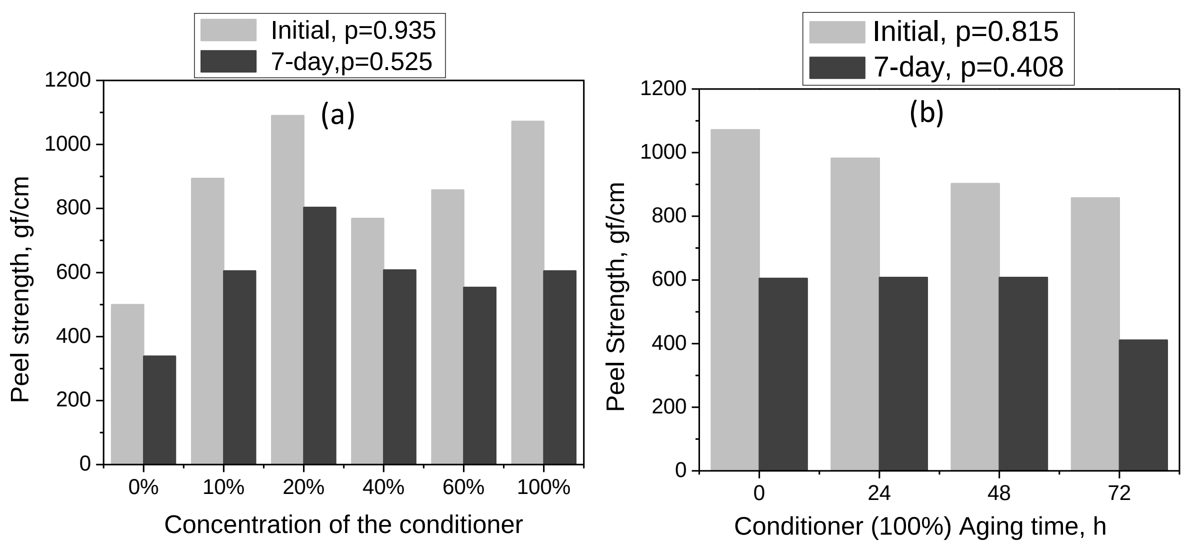
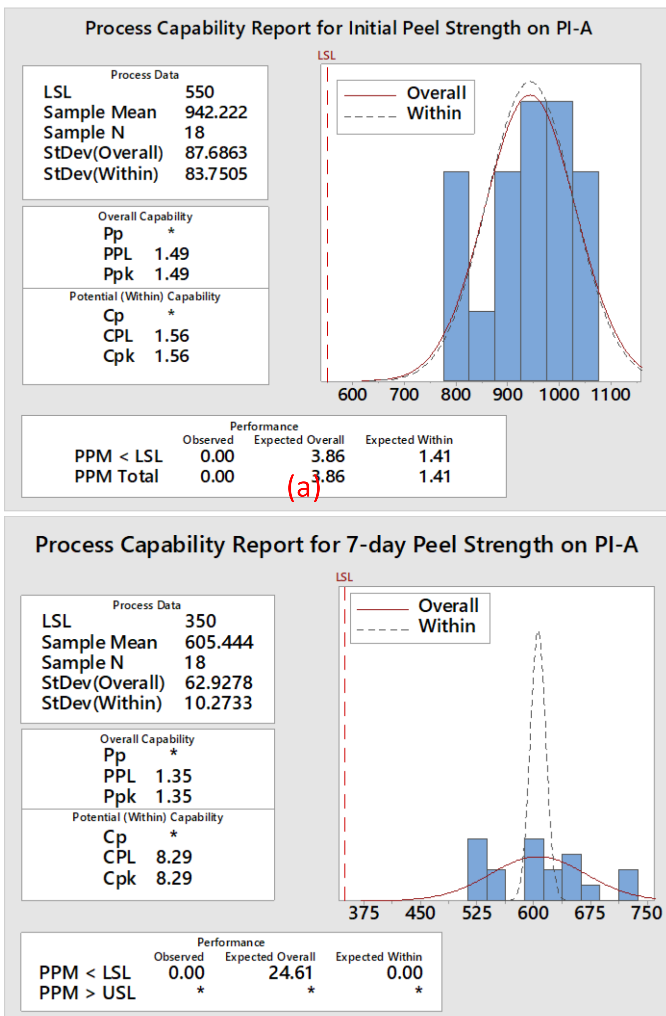


Figure 6. Initial and 7-day baked PI-plating peel strength data on PI-A processed with (a) the fresh SAP-FLEX conditioner at different concentrations; or (b) with the 100% conditioner aged for different hours.

In addition, the SAP-FLEX conditioner was also subjected to a bath-life test by aging it for different times. **Figure 6 (b)** shows the peel strengths on the PI-A substrates processed with the 100% conditioner aged for a different length of time without any replenishment. From freshly made to a 72-h continuous aging, the SAP-FLEX conditioner provided good treatment on the PI-A film, which showed an initial peel strength from 858 to 1072 gf/cm. As to the 7-day baked peel strength, it stays at 605-608 gf/cm on PI-A films treated with 0-48 h aged conditioner; while it seems to drop to 411 gf/cm when the conditionerwas aged for 72 h. Nevertheless, compared to the values obtained with fresh conditioner, the differences in the initial or 7-day baked peel strengths from the aged conditioning are not significant (for initial peel strength, $p = 0.815$; for 7-day baked ones, $p = 0.408$). In other words, without replenishment, the bath life for SAP-FLEX conditioner is longer than 72 h.

3.5. Process Capabilities

Using Six-Sigma tools, the capabilities of the SAP-FLEX process were evaluated regarding the initial and 7-day baked peel strength data from the substrate PI-A. As demonstrated in **Figure 7 (a)**, with a lower limit of 550 gf/cm for the initial peel strength, the SAP-FLEX process has a short-term capability of Cpk= 1.56, and a long-term capability of Ppk= 1.49. Therefore, over-all it is a 4.47-sigma process to get good initial PI-plating adhesion. With a lower limit of 350 gf/cm for the 7-day baked peel strength, the SAP-FLEX process has a very high short-term capability of Cpk= 8.29, and a long-term capability of Ppk= 1.35 (**Figure 7 (b)**). Therefore, over-all it is a 4.05-sigma process to get good 7-day baked PI-plating adhesion.



(b)

Figure 7. Process capability analysis regarding (a) initial and (b) 7-day baked PI-plating peel strengths on PI-A.

4. Conclusions

The new SAP-FLEX process combines gentle etching, excellent conditioning, and direct metallization techniques from our company. The processed PI surface maintained a very-smooth topography with a Ra lower than 27 nm, which is excellent to support ultra-fine circuit features in the flexible circuitry. On 4 different kinds of PI substrates widely used in the current market of flexible circuitry, the SAP-FLEX process can bring in an initial adhesion from 715 to more than 2055 gf/cm. After an accelerated heat exposure of a 7-day continuous baking test at 150^{o}C, the PI-plating peel strength can still be maintained from465 to higher than 1287 gf/cm. Moreover, the key adhesion-promoting treatment, the SAP-FLEX conditioner, has a wide processing window ranging from 10 to 100% concentration and 0-72 h aging time. The overall capability of the SAP-FLEX process showed that it is a >4-Sigma process.

5. References

[1]Peng, F.; Long, E.; Watkowski, J.; Feng, K.; Ando, N.; Inazu, K. *Adhesion to Very Smooth Substrates Utilizing an Optimized Semi-Additive Process*.Paper and oral presentation. *International Microsystems, Packaging, Assembly, Circuits Technology Conference (IMPACT)*, Taipei, Taiwan, **2014**.

Semi-Additive Process for Variant Polyimide Substrates in Ultra-Fine Flexible Circuitry

Fei Peng, Ernest Long, Jim Watkowski, William Bowerman

MacDermid Enthone Electronics Solutions

Content

- Introduction:

  Ultra-Fine and Flexible Circuitry

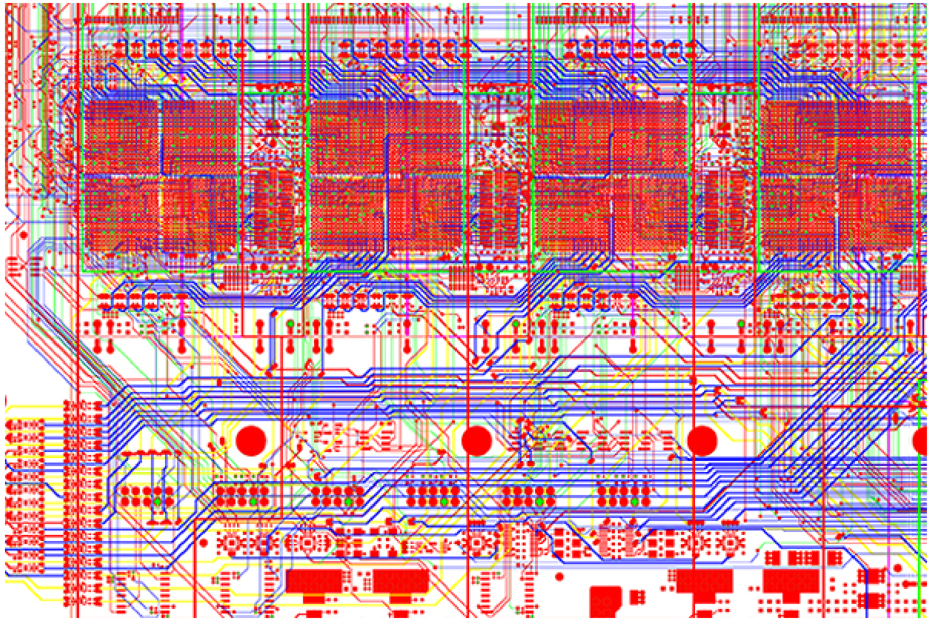
  Semi-Additive Process (**SAP**)

- **SAP-FLEX** for Ultra-Fine Flexible Circuitry

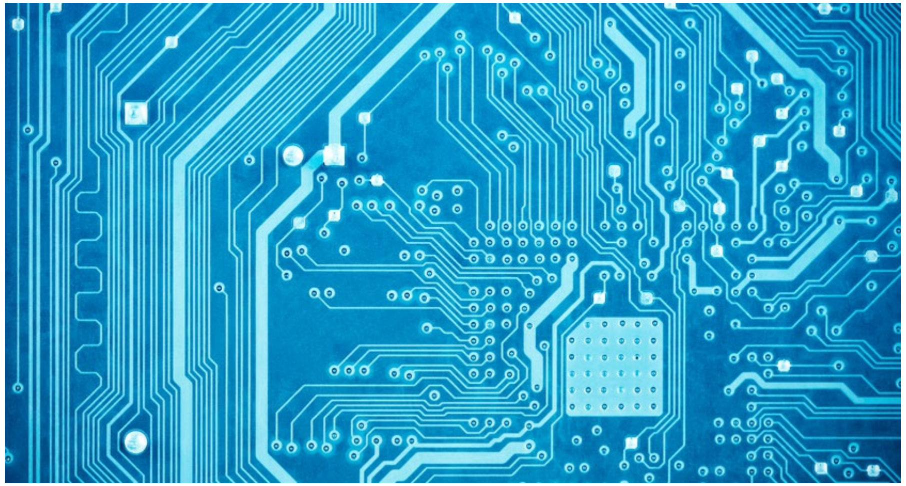
- Summary

Introduction: Ultra-Fine Circuitry

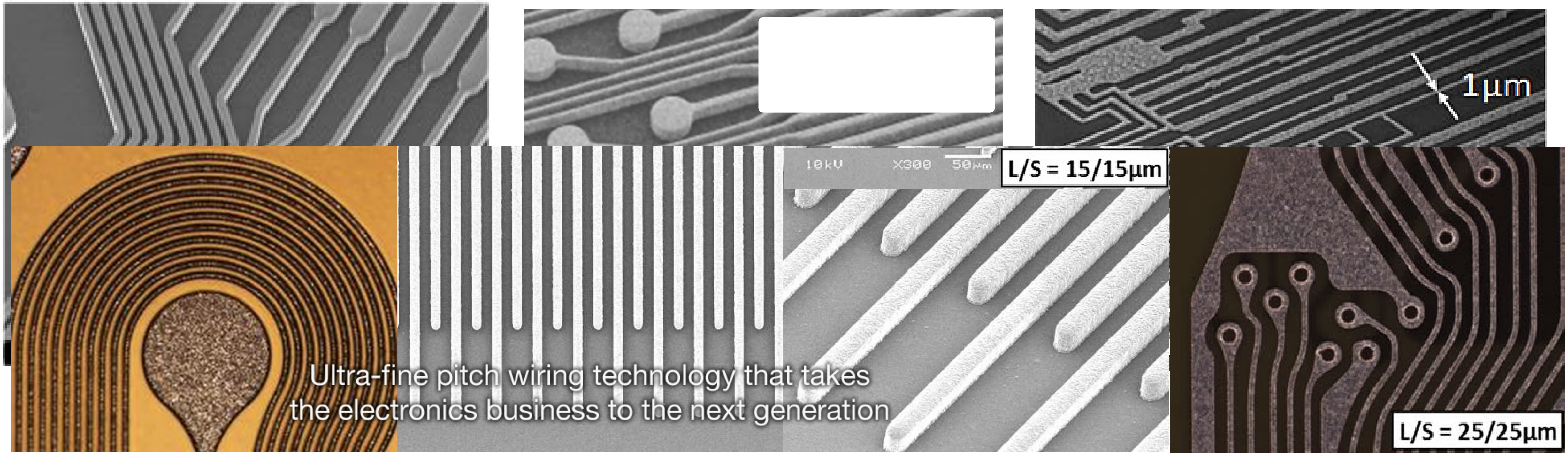
Why Ultra-Fine?



- Miniaturization
- Light weight
- Better high-speed signal



Ultra-Fine Circuitry: **How Fine?**

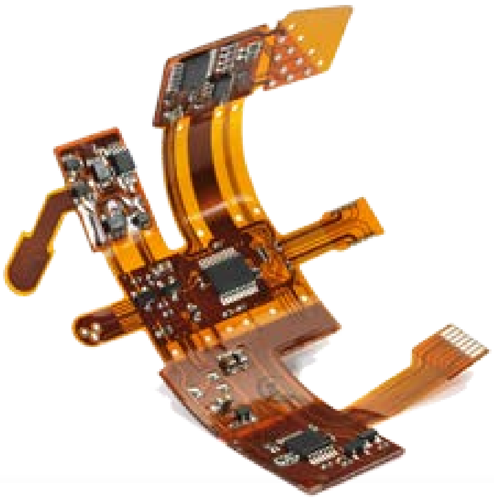


Tighter Pitch, Thinner Line/Spacing, Smaller Via

Flexible Circuitry

Adhesion in FPC

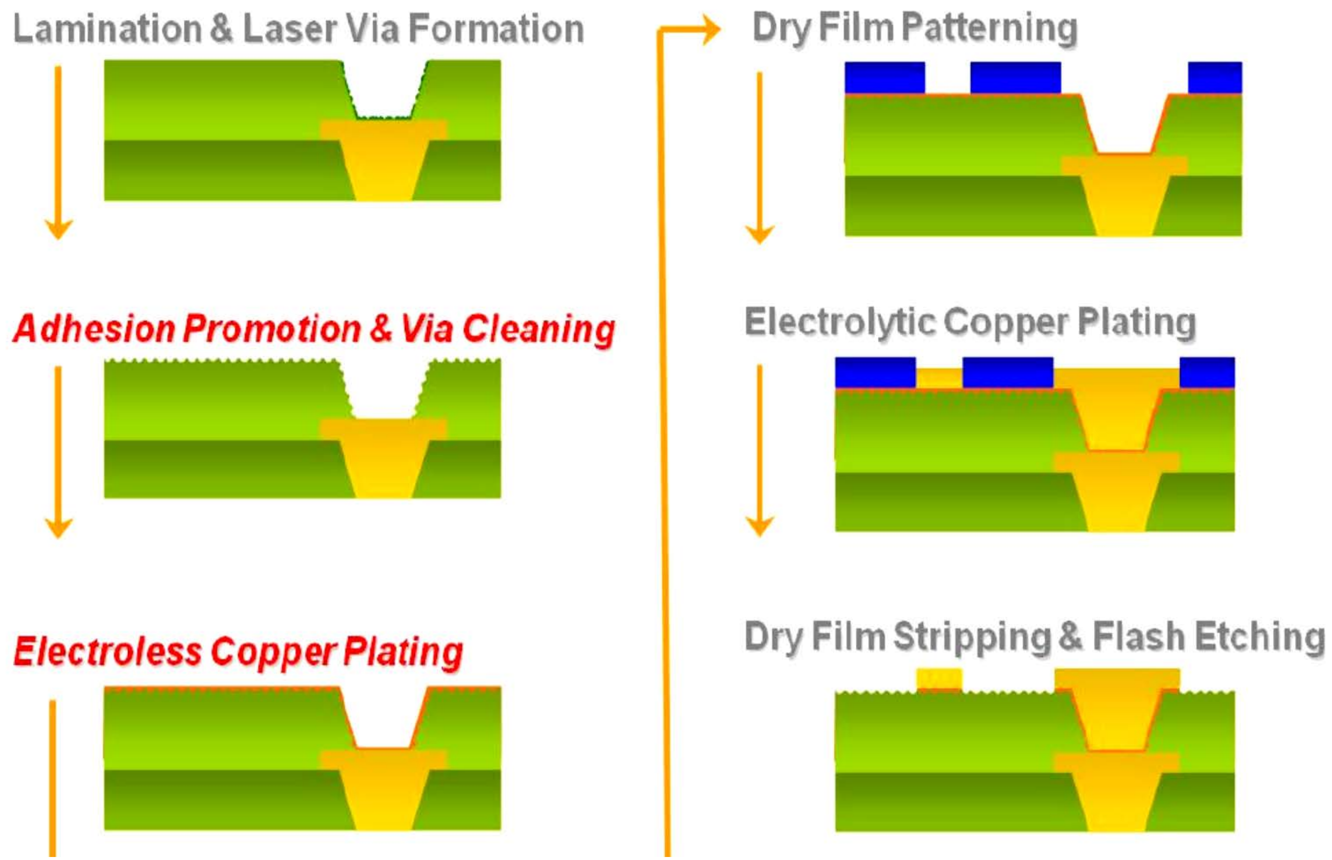
- Surface roughness: Ra ≤ 100 nm
- Initial adhesion: ≥550 gf/cm
- Baking test: after 7-day @ 150 °C, ≥ 350 gf/cm



Polyimide (PI)

- Thin
- Flexible
- Light weight
- Good dielectrics properties
- Excellent chemical & thermal stability

Introduction: Semi-Additive Process (**SAP**)



Additive vs. Subtractive

- Pattern plating on dielectric top
- Etching on Cu for Pattern

Semi-Additive vs. Full-Additive

- Cu thickness= E-less + E-lytic
- Cu thickness= E-less only

SAP-FLEX for Ultra-Fine FPC

Surface Treatment

Etch
Conditioner

Activation

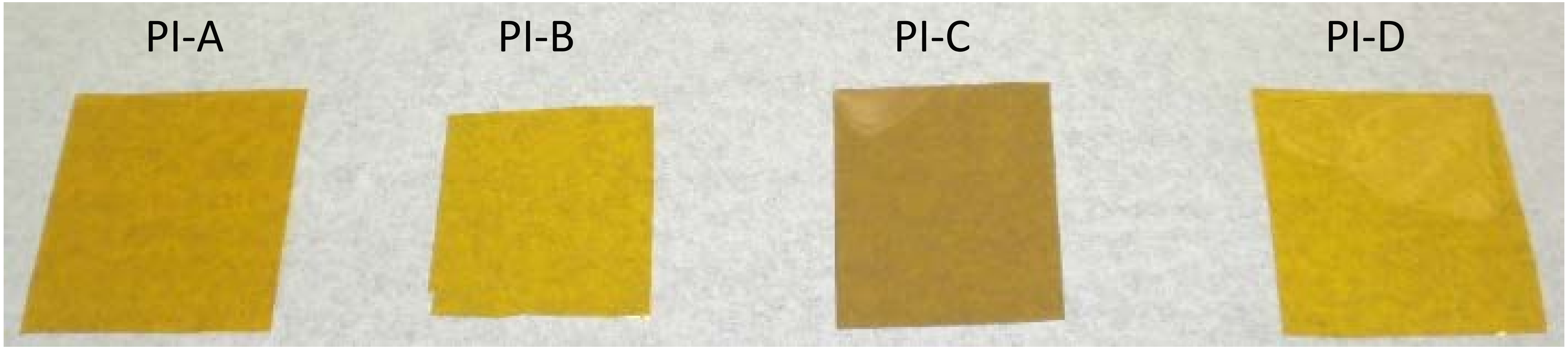
Activator
Accelerator

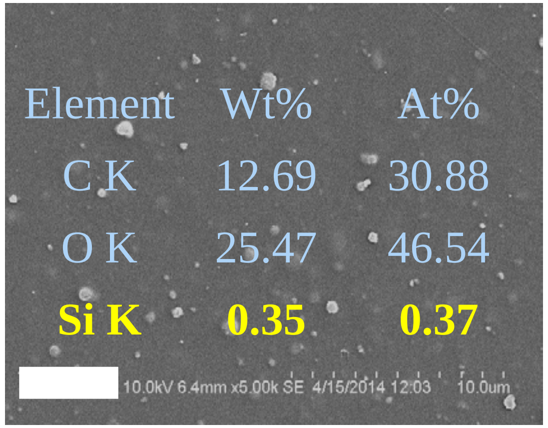
Electroless Ni

Electroless Cu

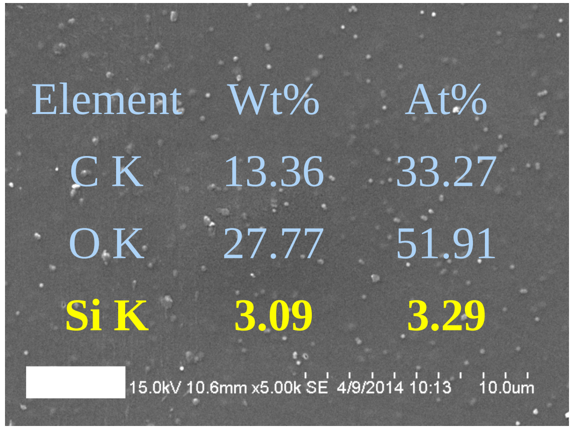
Electrolytic Cu

SAP-FLEX: 4 PI Substrates

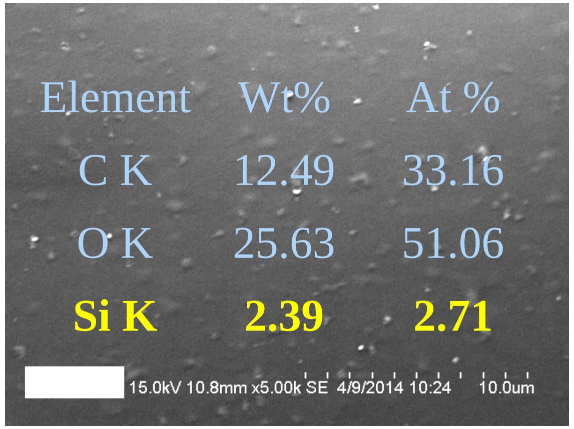




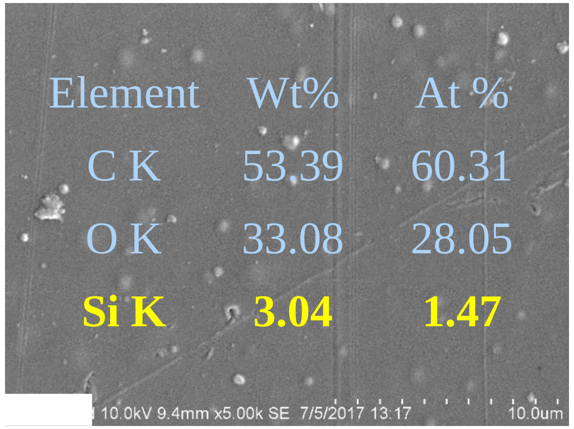
Element	Wt%	At%
C K	12.69	30.88
O K	25.47	46.54
Si K	0.35	0.37



Element	Wt%	At%
C K	13.36	33.27
O K	27.77	51.91
Si K	3.09	3.29



Element	Wt%	At %
C K	12.49	33.16
O K	25.63	51.06
Si K	2.39	2.71

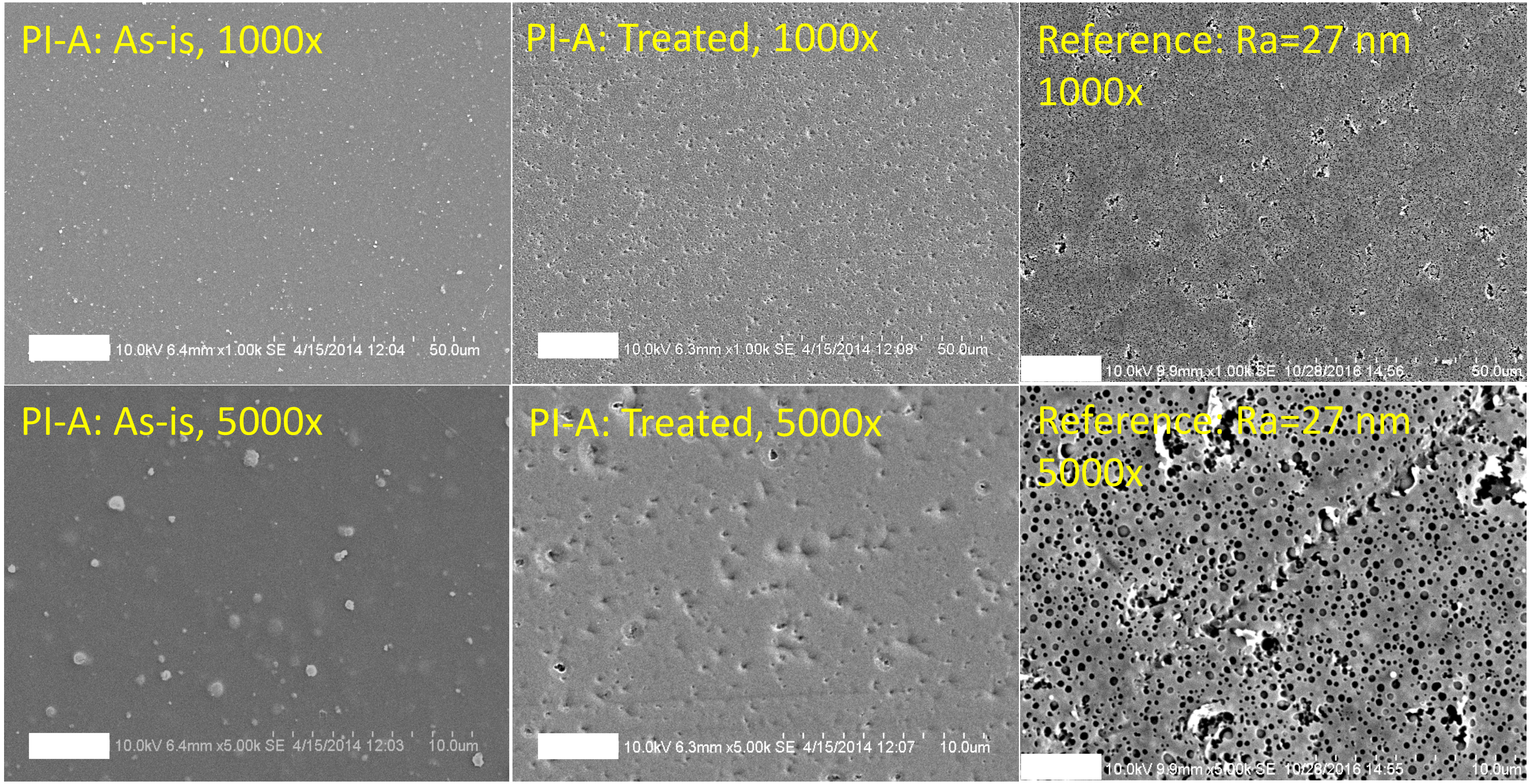


Element	Wt%	At %
C K	53.39	60.31
O K	33.08	28.05
Si K	3.04	1.47

Surface Treatment

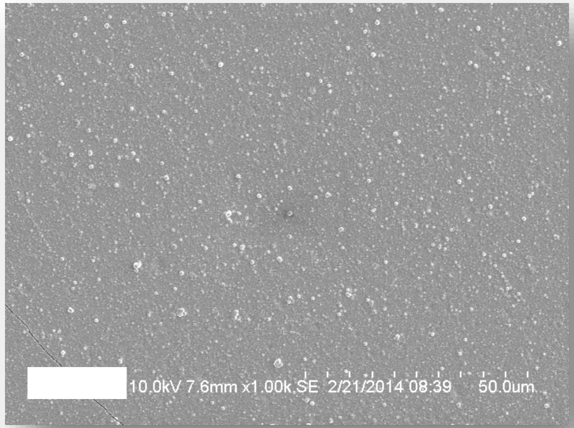
SAP-FLEX Surface Pretreatment

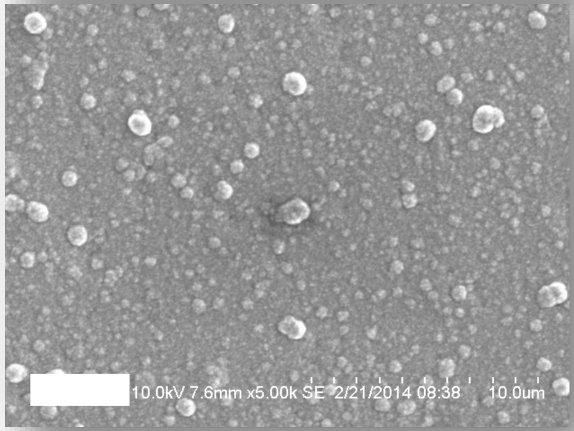
Etch Conditioner



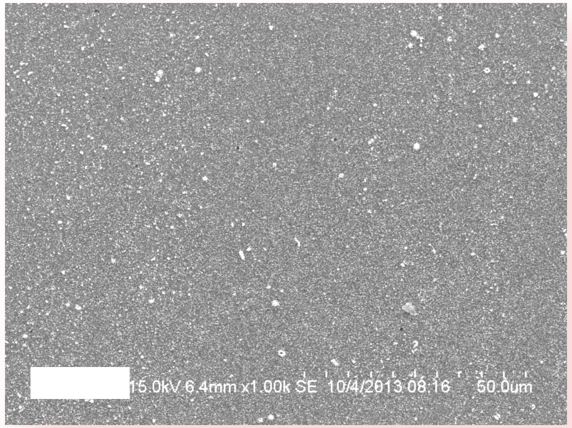
SAP-FLEX: Plating

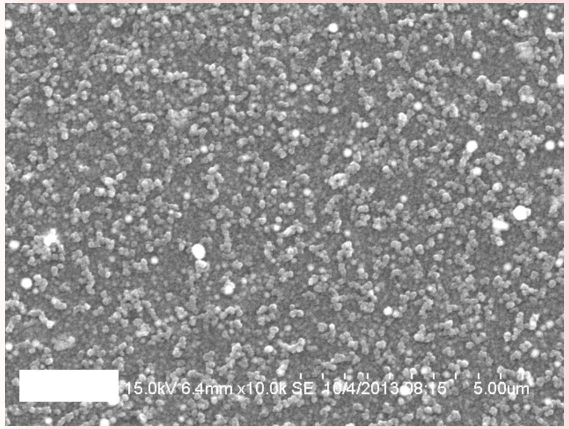
Electroless Ni



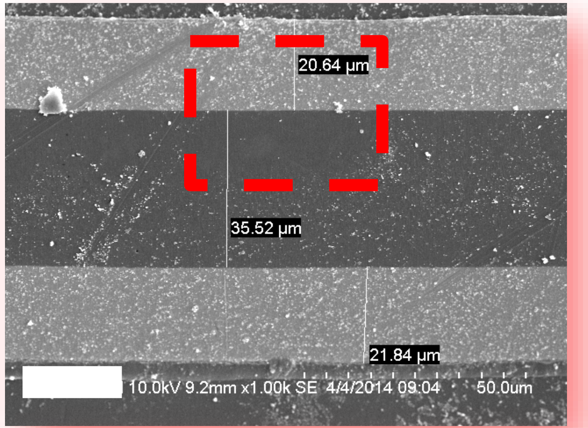


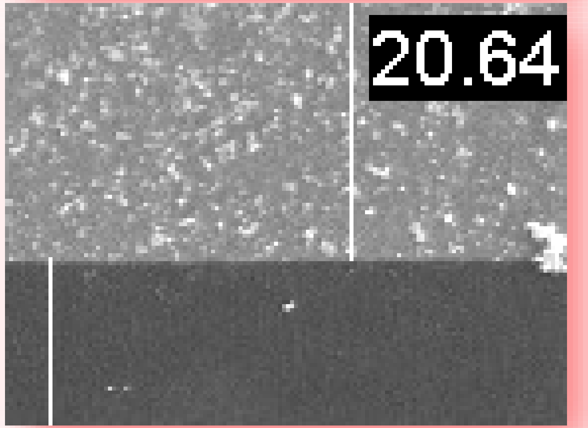
Electroless Cu



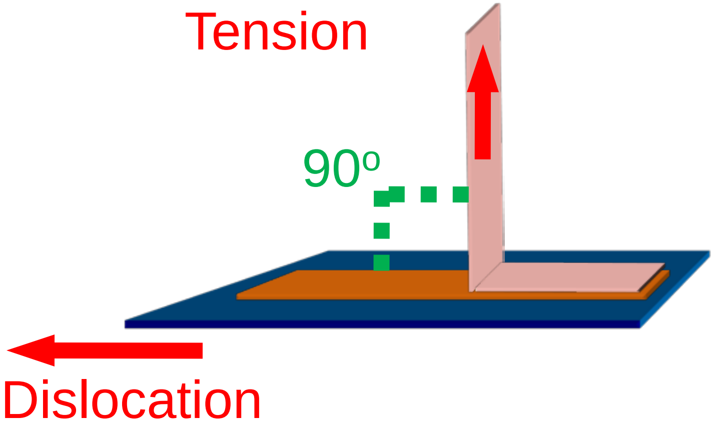


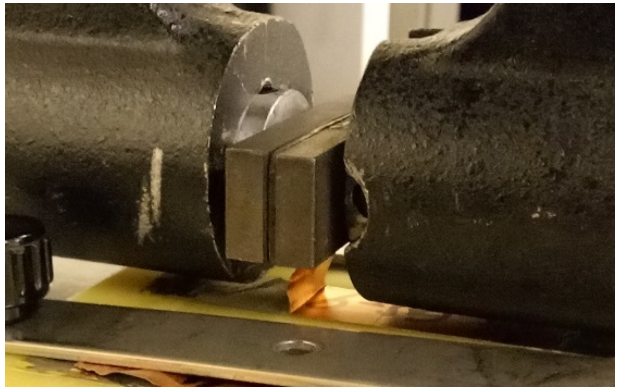
Electrolytic Cu

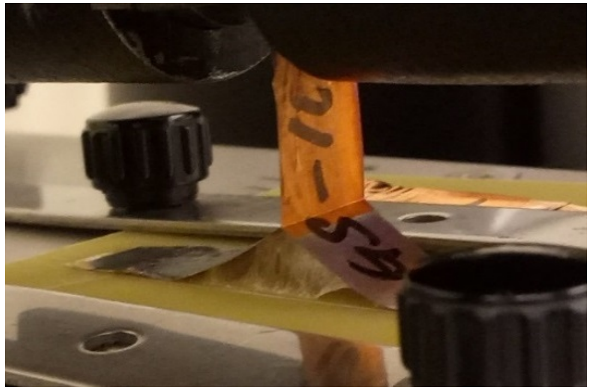


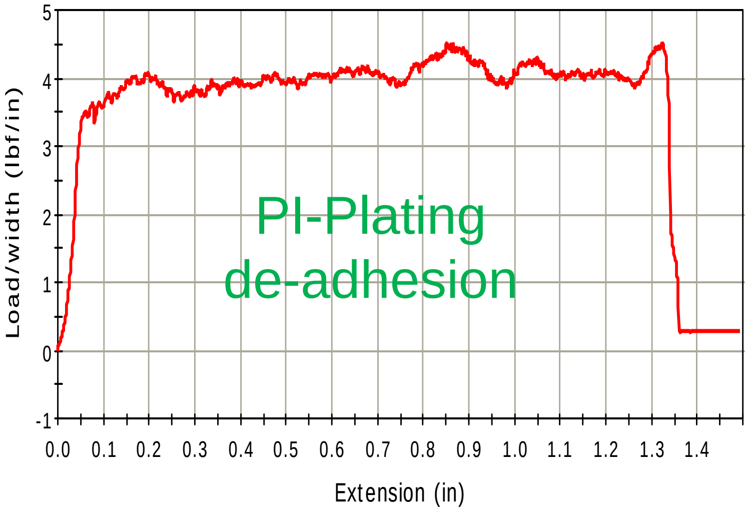


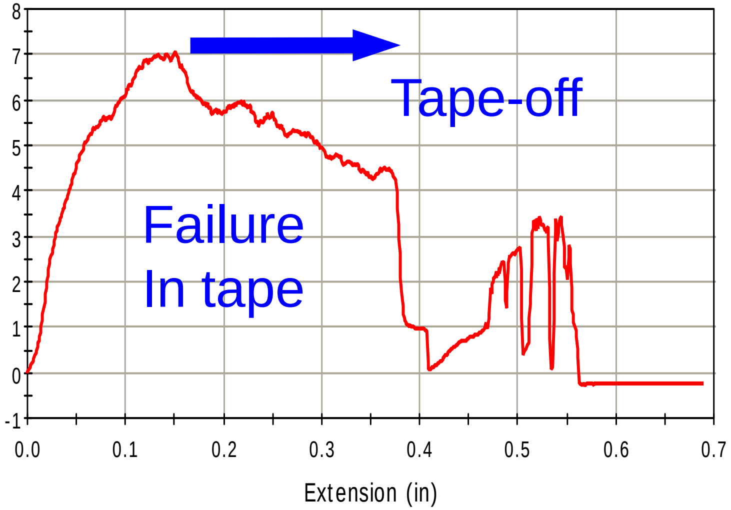
SAP-FLEX: PI-Plating Adhesion







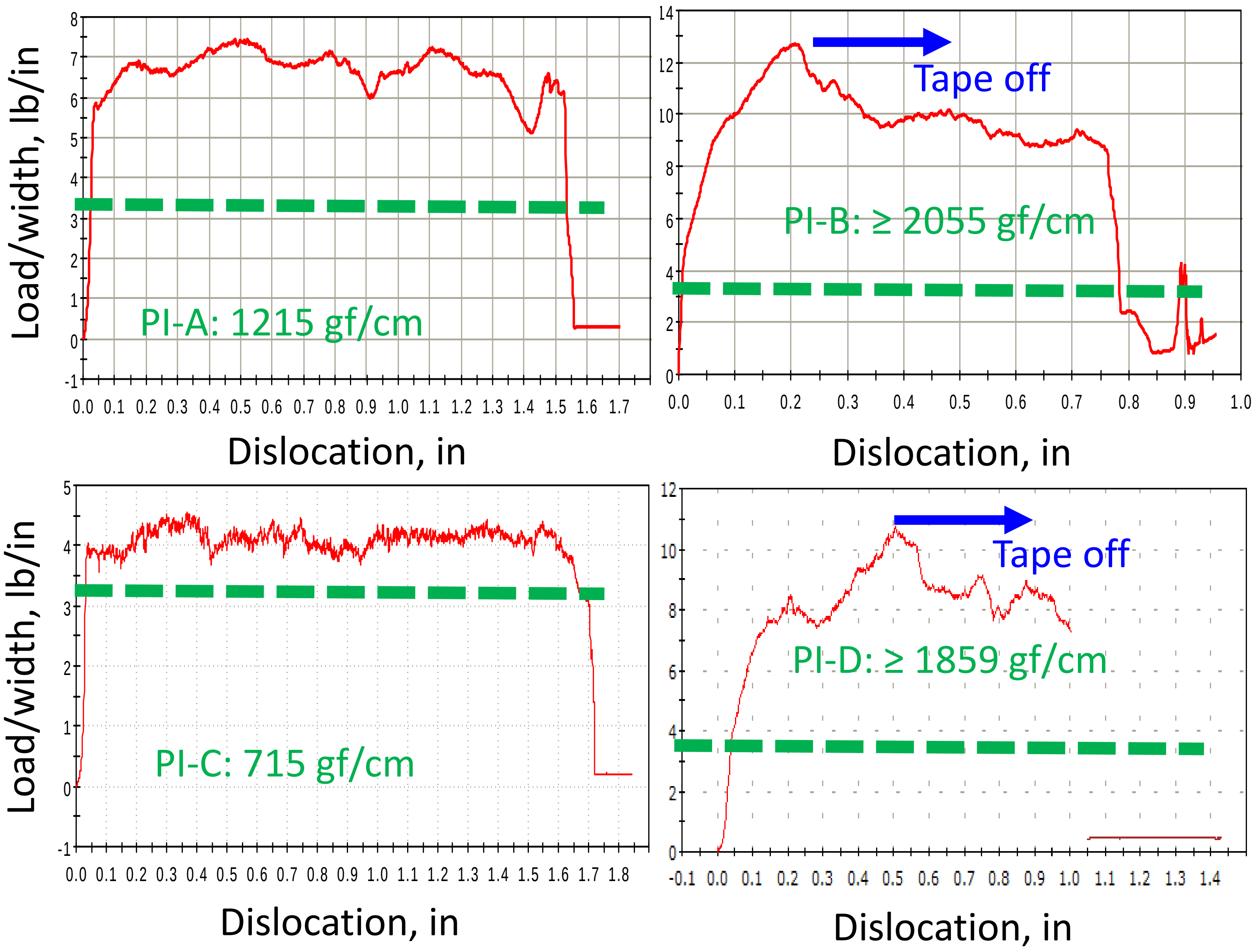




SAP-FLEX:

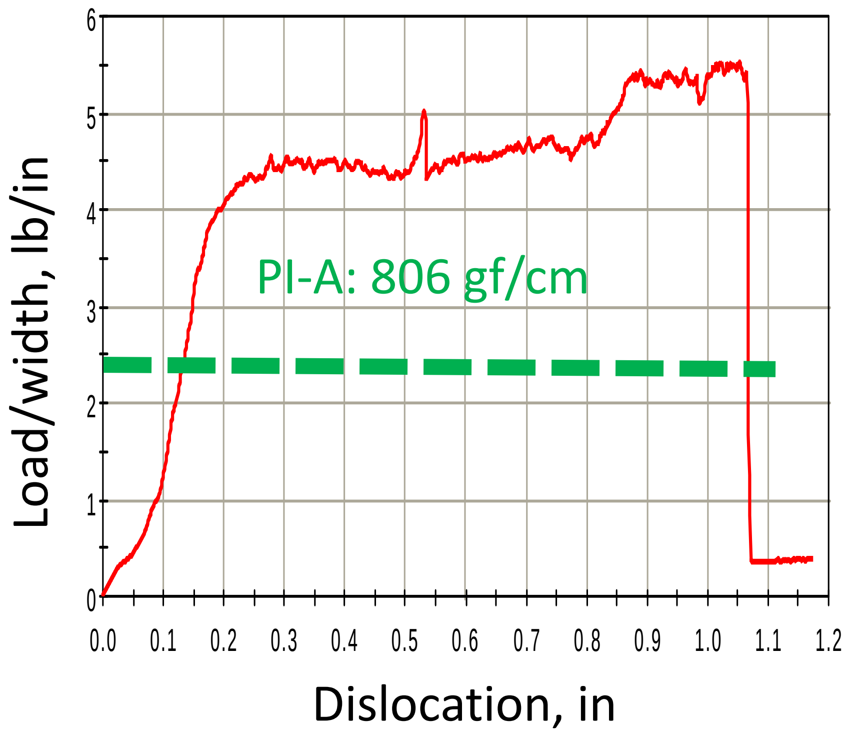
Initial Adhesion,

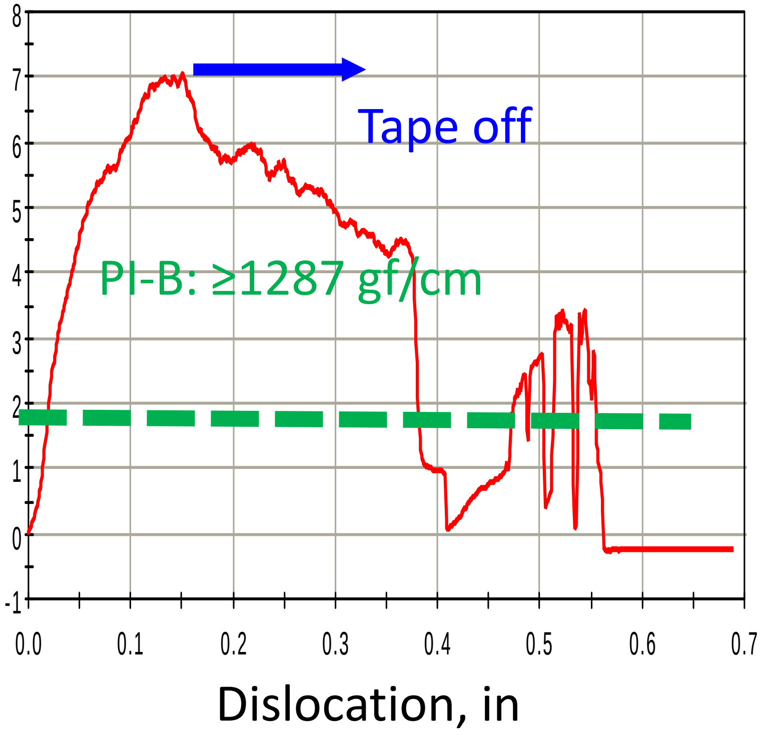
≥550 gf/cm (3.08 lb/in)

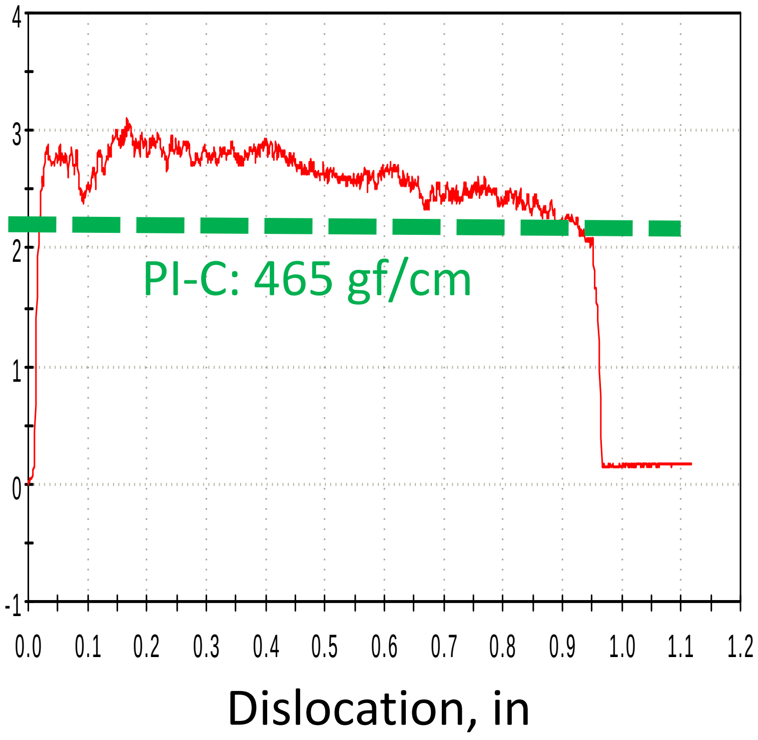


SAP-FLEX:

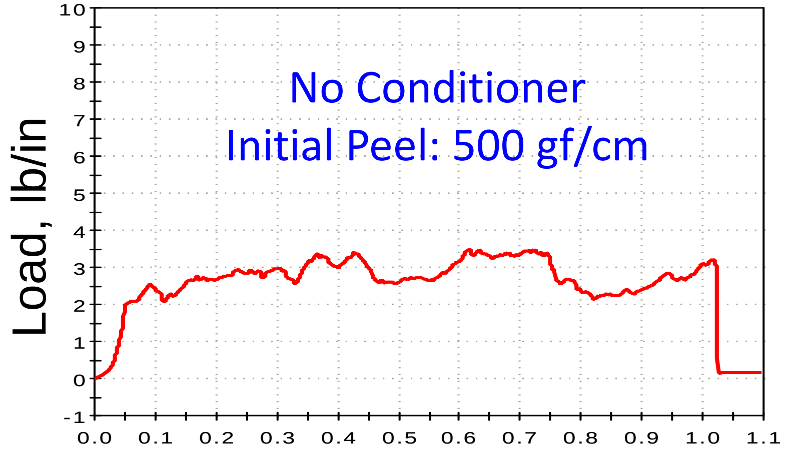
7-Day Baked Adhesion, ≥350 gf/cm (1.96 lb/in)

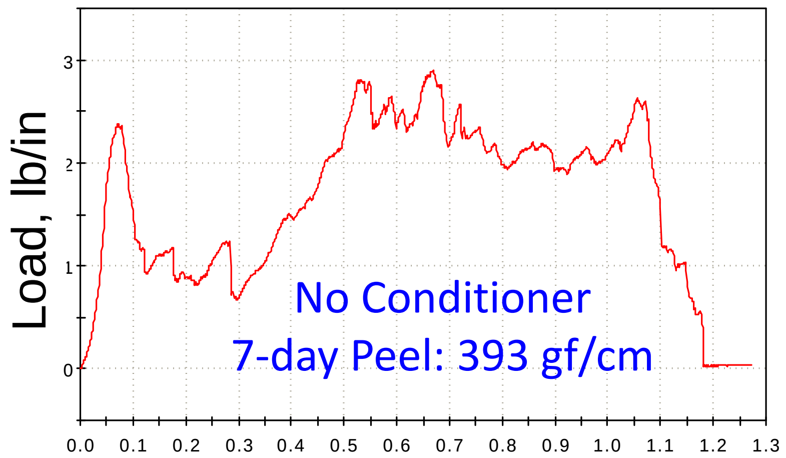




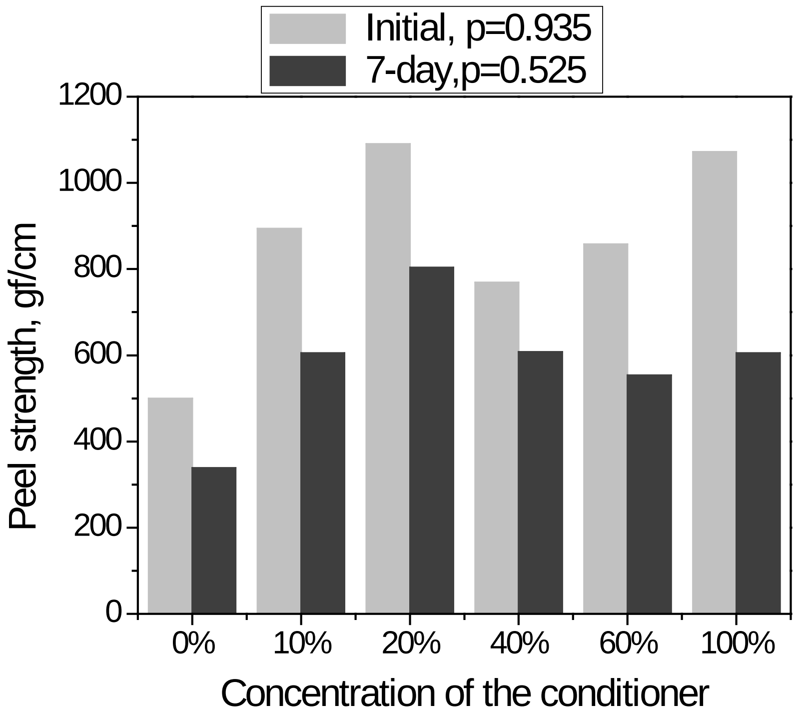


SAP-FLEX: Adhesion Promoter, SAP-FLEX Conditioner

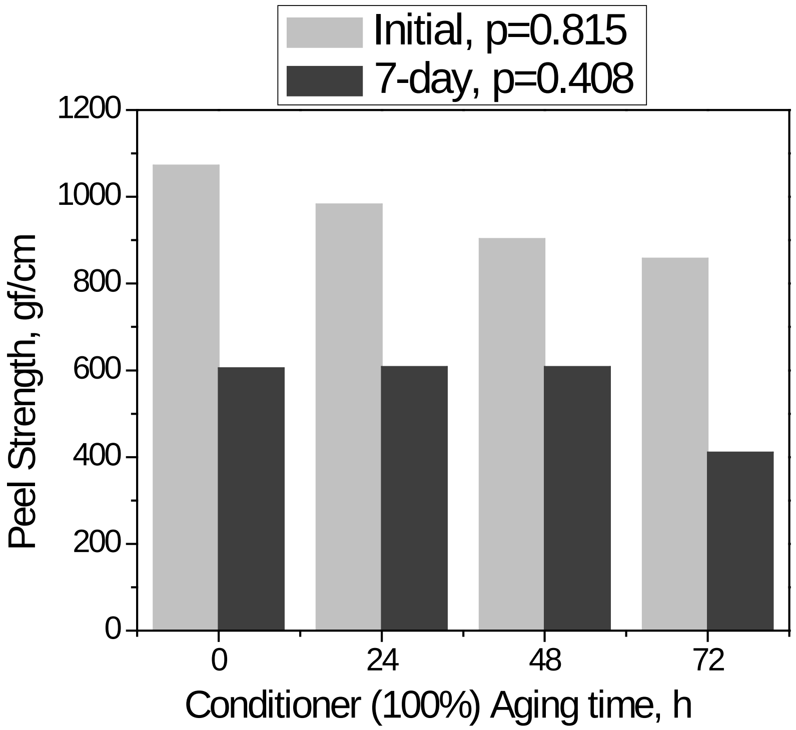




Processing Window



Bath Life



SAP-FLEX: Process Capability

Initial Peel

Process Capability Report for Initial Peel Strength on PI-A

Process Data

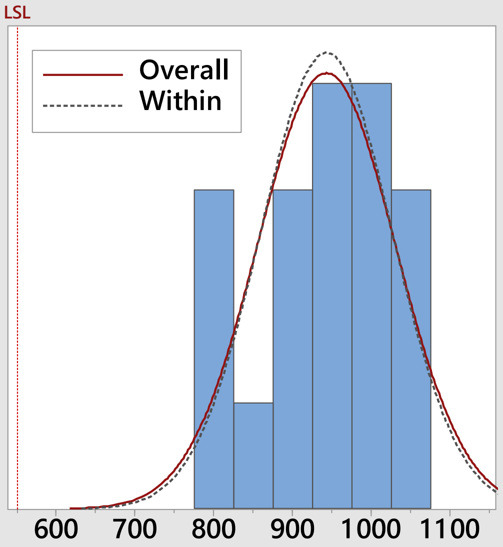
LSL	550
Sample Mean	942.222
Sample N	18
StDev(Overall)	87.6863
StDev(Within)	83.7505

Overall Capability

Pp	*
PPL	1.49
Ppk	1.49

Potential (Within) Capability

Cp	*
CPL	1.56
Cpk	1.56



Performance

	Observed	Expected Overall	Expected Within
PPM < LSL	0.00	3.86	1.41
PPM Total	0.00	3.86	1.41

7-Day Peel

Process Capability Report for 7-day Peel Strength on PI-A

Process Data

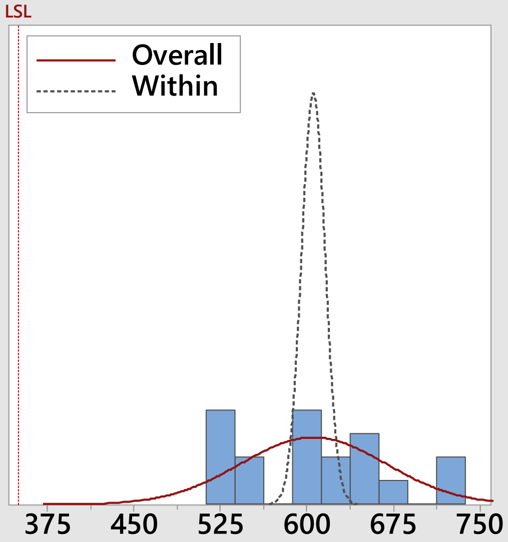
LSL	350
Sample Mean	605.444
Sample N	18
StDev(Overall)	62.9278
StDev(Within)	10.2733

Overall Capability

Pp	*
PPL	1.35
Ppk	1.35

Potential (Within) Capability

Cp	*
CPL	8.29
Cpk	8.29



Performance

	Observed	Expected Overall	Expected Within
PPM < LSL	0.00	24.61	0.00
PPM > USL	*	*	*

SAP-FLEX for Ultra-Fine Flexible Circuitry

- Ultra smooth PI-Plating Interface
- Excellent Chemical Bonding
- Excellent on Different PI Substrates
- Applies to Rigid and Flexible circuitry

Thank you!