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Thermophysical Properties of Microelectronic Substrates Finished with Organic Solderability Preservatives

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Various surface treatments have been used for microelectronic substrates in order to help optimize the microelectronic packages required for finer pitch and higher reliability in mobile applications such as cellular phones and portable networks, etc. Organic solderability preservatives (OSP) have been considered as a particularly effective lower-cost method for enhancing the interface properties of microelectronic packages. However, discoloration of the OSP layer on Cu pads has remained an issue during the assembly process, limiting the applications of OSP in advanced packages such as the Multi-Chip Package (MCP), Fine-Pitch BGA (FBGA) and Flip Chip BGA (FCBGA) for mobile applications. The reason for discoloration of the OSP layer during the assembly process must be understood in order to apply this surface treatment in package production. Microelectronic substrates with a solder resist open (SRO) size of 280 um and a solder mask defined (SMD) pad were selectively finished with organic solderability preservative chemicals and characterized by optical microscope, SEM, XPS and FTIR. It was determined that the discoloration was caused by cuprous oxide, Cu_2O at the surface of the OSP layer. The discoloration did not influence the ball shear strengths of substrates finished with organic solderability preservatives, which were statistically similar to those of Ni-Au-finished substrates.

Keywords: organic solderability preservatives, surface treatment, discoloration, solder joint

1. INTRODUCTION

Various surface treatments such as organic solderability preservative (OSP), electrolytic Ni/Au, hot-air-leveling (HAL), electroless Ni & immersion gold (ENIG), direct immersion gold (DIG), electroless Ni & electroless palladium & immersion gold (ENEPIG), etc., have been applied to microelectronic substrates in order to help optimize the microelectronic packages which are required for finer pitch and higher reliability in mobile applications such as cellular phones and portable networks, etc. Use of such surface treatments must take into account interface properties, high-volume mass production capability and industrial costs [1-4]. Organic solderability preservatives, which are organic finish materials substituted for inorganic Ni/Au or HAL on a Cu pad, have been known to enhance the mechanical properties of the Cu pad/solder interface, and at lower cost [5]. Over the past year, OSP have been mainly applied in motherboards using surface mounting technology (SMT)[6]. However, the application of OSP is being expanded for various products such as Fine-Pitch BGA (FBGA) and Flip Chip BGA (FCBGA) for mobile applications because the higher solder joint strength and lower cost they offer is highly desirable in microelectronic packages [7]. Organic solderability preservative finishes offer the additional advantage of being environmentally-friendly materials, as they do not contain toxic compositions such as Pb, Cd, Hg, polybromobiphenyl (PBB), or PolyBrominated Diphenyl Ether (PBDE), all of which are prohibited by most advanced countries. The smaller size and higher performance of end products like cellular phones, PDAs and DVDs, etc., have increased the possibility of accidental impacts or drops resulting in solder ball joint cracks and poor final quality. The weakness of conventional Ni/Au finish can be attributed to Au brittleness at solder ball joints when subjected to impact load [8-13], prompting users to seek other choices for surface treatment.

Most substrates finished by OSP are currently applied to chip scale packages or ball grid arrays with wire-bonding type packages, where the Cu pad is coated selectively as shown in Fig. 1. The solder side is coated with OSP and the comp side is coated with Ni and Au. Thermal damage to microelectronic packages is more severe than that to motherboards during the assembly process due to a longer period of time under thermal conditions. The OSP layer on a Cu pad is thereby inevitably discolored during assembly because OSP are very sensitive to temperature. In addition to reducing solder ball joint strength, this causes assembly difficulties such

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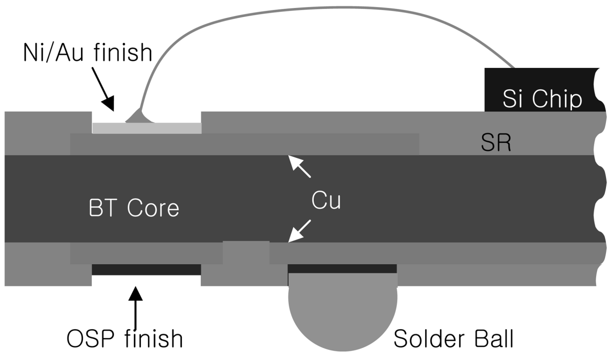


Fig. 1. Microelectronic substrates finished by organic solderability preservative.

as solder ball missing, solder ball misalignment, and other equipment trouble when automatically attaching solder balls to Cu pads.

In this study, the discoloration of the OSP layer on Cu pads was investigated qualitatively during the assembly process and the mechanical properties were characterized for degree of discoloration.

2. EXPERIMENTAL PROCEDURE

The experimental flow, shown in Fig. 2, included degreasing, soft etching and organic solderability preservative finishing, as well as the assembly process, which consisted of prebaking, die attachment, wire bonding, post mold curing (PMC), and soldering. Alkylbenzimidazole, the most popular organic solderability preservative, was used in this study. The microelectronic substrates were fabricated with 2 layers, a solder resist open (SRO) size of 280 um and a solder mask defined (SMD) pad, on which 4 chips are generally stacked. Microelectronic substrates with electrolytic Ni/Au finish on the comp side and with bare Cu pad on the solder side were aligned in order to coat only the bare Cu pad.

Macrocontamination such as grease and other foreign particles was removed by degreasing with 3 wt% H_2SO_4, followed by a sprayed water rinse. Oxidation of the Cu pad during storage was eliminated by a soft etching process with H_2SO_4-H_2O_2, whereby the roughness of the Cu pad was homogenized to a range of 300 - 400 nm in order to provide the best conditions for an OSP finish. The pad was then dried at 80°C for 15sec. to remove water droplets from the microelectronic substrates on the Cu pad. The organic layer was then coated on Cu pad by dipping the samples into a reservoir with a pH of 3 at 40°C for 60 sec.

Residual organic solderability preservative on the Cu pad was removed with an air knife. Failure to remove the residual organic layer after the coating process may result in an inhomogeneous layer thickness or formation of a water stain on the Cu pad during the drying process. The organic layer

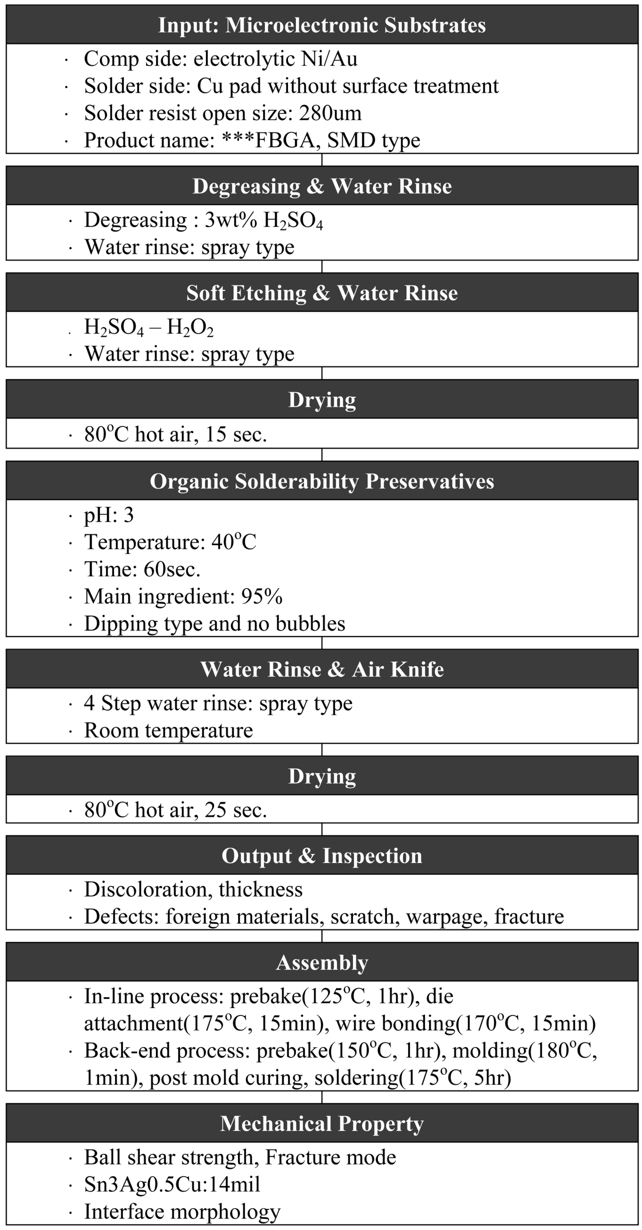


Fig. 2. Experimental flow of organic solderability preservatives finished products.

on the substrates were inspected for discoloration, thickness and any visual defects such as foreign materials, scratches, warpage, or fractures, etc. The thickness of the organic layer was analyzed visually via FIB (focused ion beam) and with a UV spectrometer. The 20 samples were measured for thickness and the results were approached statistically using normality testing and process capability testing within a 95% confidence interval. Discoloration of the organic layer was analyzed with an Ass'y process of bare PCB, die attachment, wire bonding, and post-mold curing ranging from 150 - 200°C for 0 - 5 hr using optical microscope, XPS (x-ray photoelectron spectroscopy) and FTIR (fourier transform infrared spectroscopy). The OSP-finished substrates were assembled by an in-line process of prebaking (125°C, 1 hr), die attachment (DA, 175°C, 15 min) and wire bonding (WB, 170°C, 15 min), then a back-end process of prebaking (150°C, 1 hr), molding (180°C, 1 min), post mold curing (PMC, 175°C, 5 hr), and soldering.

The mechanical properties of 20 samples with some degree of discoloration were characterized by ball shear testing using Sn3Ag0.5Cu lead-free solder balls. The 20 samples were heated identically with process conditions of bare substrate (BS), DA, WB and PMC, which were also compared to the ball shear strength of Ni/Au-finished products. These results were analyzed statistically using analysis of variance (ANOVA) and a 2-sample test, where the significant difference of samples was also analyzed within a 95% confidence interval. The fracture mode and interface morphology were characterized by SEM.

3. RESULTS AND DISCUSSION

3.1. Thermophysical properties of organic layer on Cu pad in substrates

An OSP consists of an organic ingredient, a solvent, a pH solution and additives. The organic ingredient used here was alkylbenzimidazole, which is also popularly applied in industry. The schematic mechanism of the organic layer on the Cu pad is presented in Fig. 3 and Fig. 4, where the main ingredient is weakly linked with the Cu pad[14]. The organic layer conformed to the texture of the Cu pad, and the thickness was measured visually as 0.2 - 0.4 um. The molecular structure of most organics contains amine groups as main ingredients, which interact easily with the Cu ion on a Cu pad.

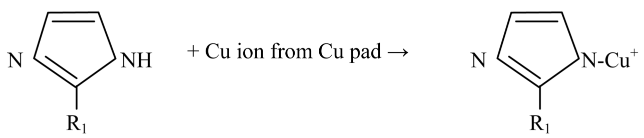


Fig. 3. Molecular structure of organic solderability preservatives.

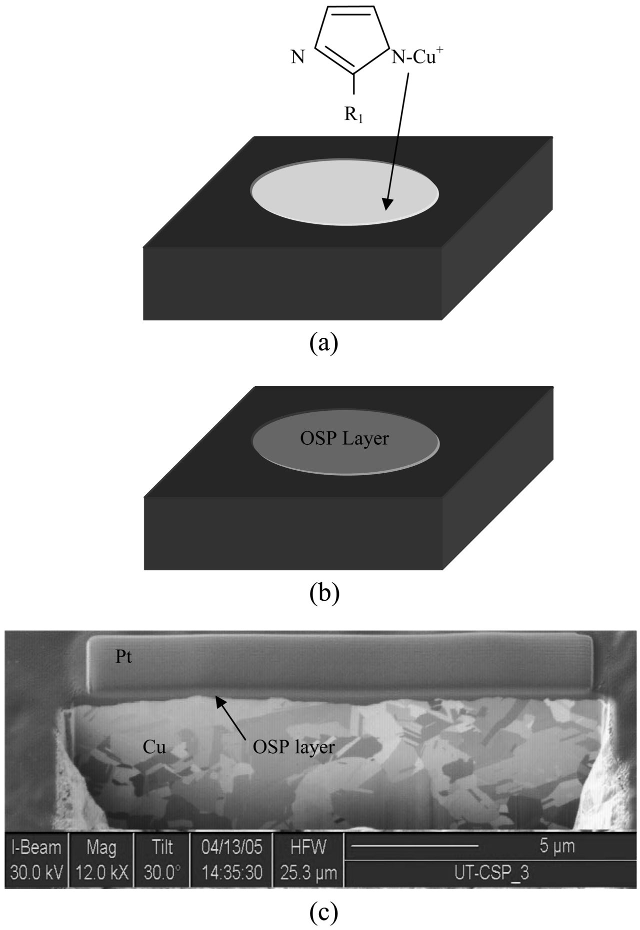


Fig. 4. Chemically bonding between organic layer and Cu pad. (a) Formation of organic layer on Cu pad by amine group bonding, (b) organic layer on Cu pad, (c) depth profile by FIB analysis.

The results of XPS analysis in Fig. 5 show that the peak of N = Cu bonding increased and the peak of amine groups bonding decreased as the OSP finish progressed, and that this phenomenon was more conspicuous with increasing temperature. These results suggest that a chemical reaction occurred between the main ingredients of the organic chemical and the Cu ion from the Cu pad. When an organic-finished substrate is applied in microelectronic package processing, thermal damage is more severe during package processes like the in-line process of prebaking, die attachment, and wire bonding, as well as in the back-end process of prebaking, molding, and post-mold curing than it is in motherboard processing. The discoloration of the organic layer is therefore generated inevitably because the organic layer is a very thermally sensitive material. The discoloration of the organic layer on the Cu pad in the in-line process and back-end process is shown in Fig. 6. It was observed that the color of the organic layer changed from yellow to red-brown with increasing temperature and time, which ranged from 150 - 200 for 0 - 5 hr. Discoloration of the organic layer can be particularly severe at the PMC stage of the assembly process due to the higher temperature and longer time involved, which can be troublesome in microelectronic package processing because the next stage of PMC is solder ball attachment. The solder ball attachment machine visually detects the solder ball point in order to align the Cu pad and solder ball. If there is a discoloration on a Cu pad, product yield decreases critically because the solder ball attachment machine comes to an abrupt stop. Discoloration of the organic layer also causes trouble in post-flux cleaning of the Cu pad prior to soldering, as it results in poor interface properties due to inadequate removal of organic fragments. It was reported previously that the discoloration of the organic layer is independent of mechanical properties because the discolored organic layer is removed post-flux during the solder ball attachment process[15]. However, in order to remove the discolored organic layer perfectly, many Design of Experiment (DOE) tests or trial and error were needed to determine appropriate post-flux materials. It can be expected that the best post-flux cleaning conditions will be determined only with an understanding of the discoloration of the organic layer on a Cu pad.

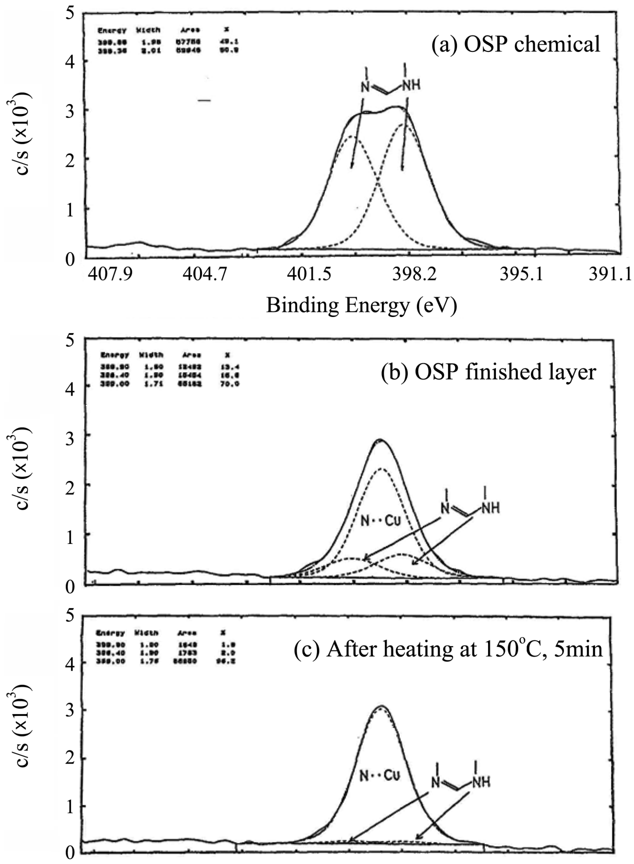


Fig. 5. Variation of N-H, N-C, N··Cu bonding with thermal conditions by XPS analysis.

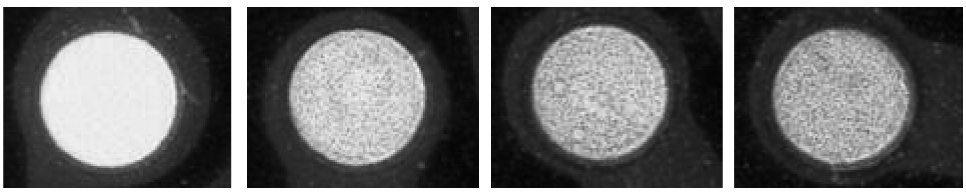
As shown in Fig. 7(a)-7(d), the depth profile of the organic layer on the Cu pad was analyzed using XPS. The left side of Fig. 7(a) and 7(c) represents the organic surface exposed to air and the right side represents the Cu pad. Fig. 7(b) and 7(d) are depth profiles of Fig. 7(a) and 7(c), respectively. The peaks of O and Cu varied significantly according to temperature. It was noted that after 6 h at 175°C, as shown in Fig. 7(c), the Cu ion was diffused from the Cu pad into the organic layer, and that the oxygen peak was detected mostly at the surface of the organic layer where it was in contact with environmental air. It is deduced from this observation that the oxidation materials of Cu such as Cu_2O and CuO, known as red color and black color respectively[16], are formed at the surface of the organic layer rather than on the Cu pad. Therefore, if the best flux materials for removing Cu_2O or CuO in the organic layer can be determined, then excellent solder joint strengths may be consistently obtained. The heated organic layer was analyzed using FTIR in order to find out which Cu compound was formed in the organic layer. Fig. 8 shows that cuprous oxide, Cu_2O in the organic layer on the Cu pad was detected at wavelength 640cm^{-1} with heating at 175°C for 0-6 h. Peak Cu_2O increased with increasing the tack time at 175°C.

It can be therefore concluded that the discoloration of the organic layer is caused by Cu_2O formed on the surface of the organic layer, which is removable by optimum post flux conditions during the Ass'y process, and that the discoloration of the organic layer may be expected not to influence the mechanical properties of microelectronic packages if the discolored organic layer can be eliminated entirely.

3.2. Mechanical properties of organic solderability preservative finished packages with discoloration.

The mechanical properties of OSP-finished products were

Ass'y Process			
Bare PCB	D/A cure	W/B	PMC



Package Process	In-Line Process				Back-End Process			
	1st Prebake	D/A Cure	Plasma	W/B	2nd Prebake	Plasma	Mold	PMC
	125'C / 1hr	175'C / 15min.	Yes	170'C / 15min.	150'C / 1hr	Yes	180'C / 1min.	175~200'C / 5hrs

Fig. 6. Variation of color of organic layer on Cu pad with Ass'y process.

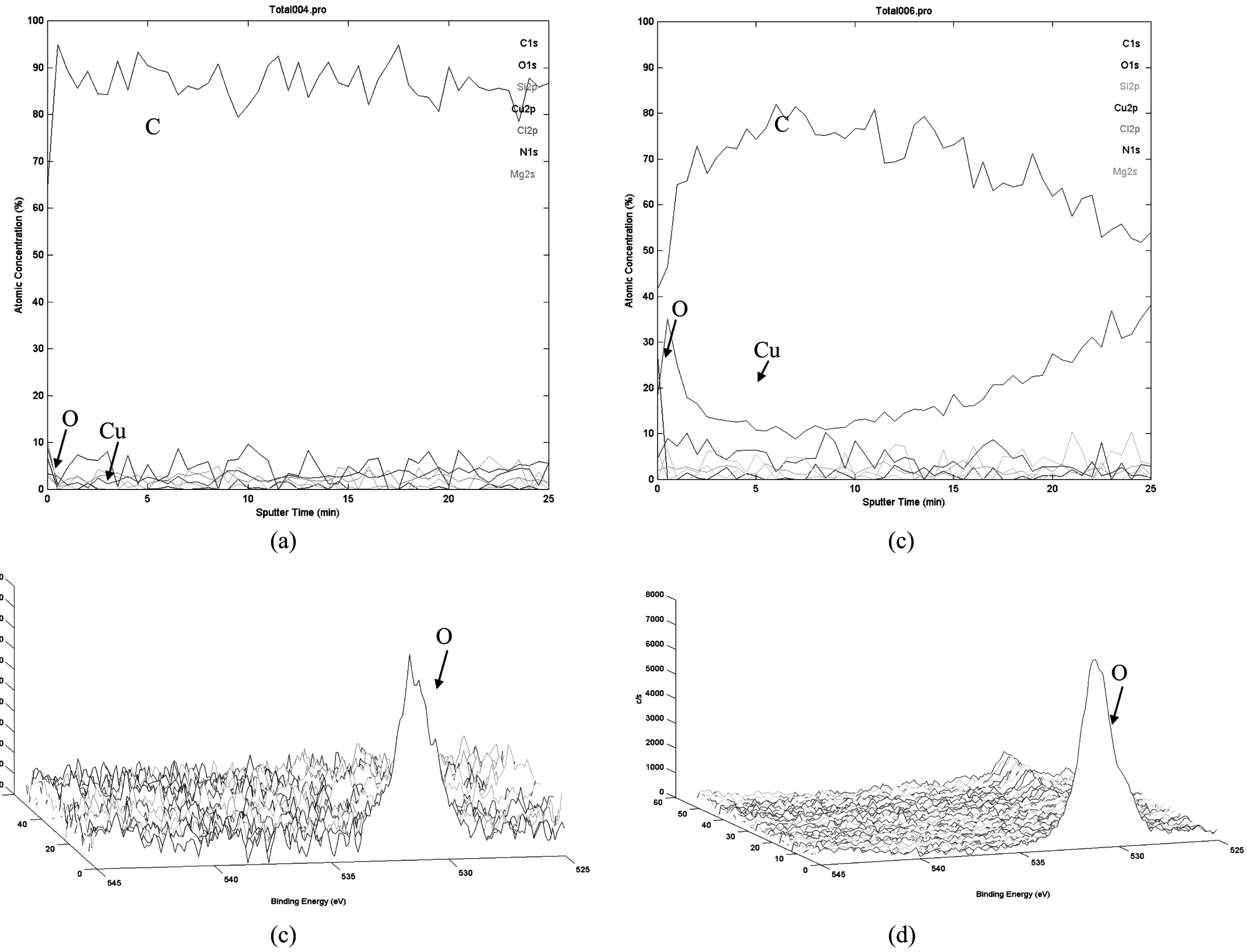


Fig. 7. XPS analysis of organic layer on Cu pad before and after heating at 175°C for 6h. (a) Before heating, (b) depth profile of (a), (c) after heating at 175°C for 6h, (d) depth profile of (c).

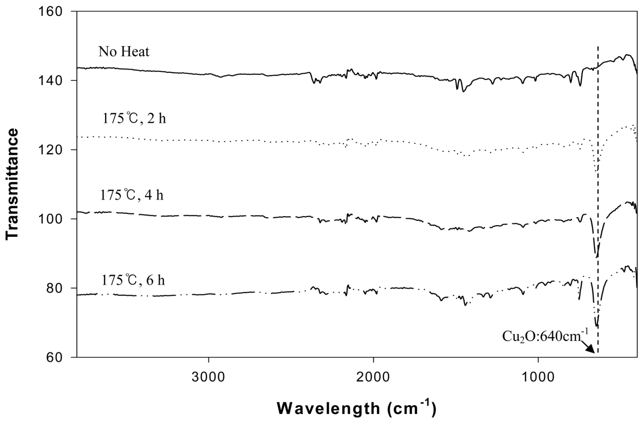
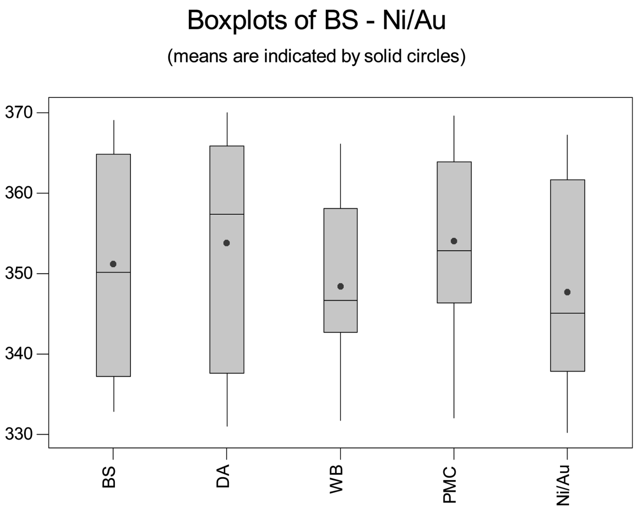


Fig. 8. FTIR analysis of organic layer on Cu pad after heating at 175°C for 0~6 h.

determined using Sn3Ag0.5Cu lead-free ball and a ball shear test. Figure 9 showed statistically the relationship of ball shear strengths with degree of discoloration during the assembly process of bare substrate, DA, WB and PMC using ANOVA analysis. Results were also compared with those of Ni/Au finished products. The ball shear strengths of all samples were measured higher than 300 gf which was considered as a general specification accepted in the industrial field. The differences of measured data can be negligible when the P-value is higher than 0.05 at 95% confidence interval in ANOVA analysis. The resultant P-value of 0.335 showed that the ball shear strengths did not differ significantly according to degree of discoloration, and were nearly the same as the ball shear strengths of Ni/Au-finished products. This indicates that the mechanical properties of organic finished products were not significantly different regardless of the discoloration of the organic layer, and that they were similar to the mechanical properties of Ni/Au-finished products.

Figure 10 shows the process capability analysis of the ball shear strengths of organic finished products passed by the PMC process. Considering the general specification for 300 gf of ball shear strength from the process capability index, Cpk was 1.8, which contributes a good solder ball joint strength applicable to the industrial field.

Figure 11 shows the interface morphology between



Analysis of Variance

Source	DF	SS	MS	F	P
Factor	4	693	173	1.16	0.335
Error	95	14234	150		
Total	99	14927			

Fig. 9. Statistic comparison of ball shear strengths of organic solderability preservative finished packages with the Ass'y process of bare substrate(BS), die attachment(DA), wire bonding(WB) and post mold curing(PMC) and Ni/Au finished package.

Sn3Ag0.5Cu lead-free solder balls and the Cu pad finished with an OSP, where the organic layer was previously removed by the post-flux process. Intermetallic compounds such as Cu_6Sn_5 and Cu_3Sn were definitely observed, with the Cu_6Sn_5 formed at the interfaces in a bumpy layer and the Cu_3Sn formed below the Cu_6Sn_5 in a thin layer.

4. CONCLUSION

OSP finishes have become one of the promising alternatives to Ni/Au finishes in microelectronic packages due to higher solder joint strength, environmentally-friendly material, and lower cost.

Discoloration of the organic layer causes process failures such as solder attachment machine trouble, inadequate post-flux cleaning and poor interface properties. It was observed that the color of the organic layer changed from yellow to red-brown with increasing temperature and time, ranging from 150-200^{o}C and 0-5 hr, respectively. It was noted that the discoloration of the organic layer was more distinct during the post-mold curing process due to the higher temperature and longer time involved. The cause of the discoloration is that cuprous oxide, Cu_2O is formed on the surface of the organic finish layer of the Cu pad. This discoloration is expected not to influence the mechanical property of microelectronic packages if it can be eliminated by optimum post-flux materials and conditions. The mechanical properties of

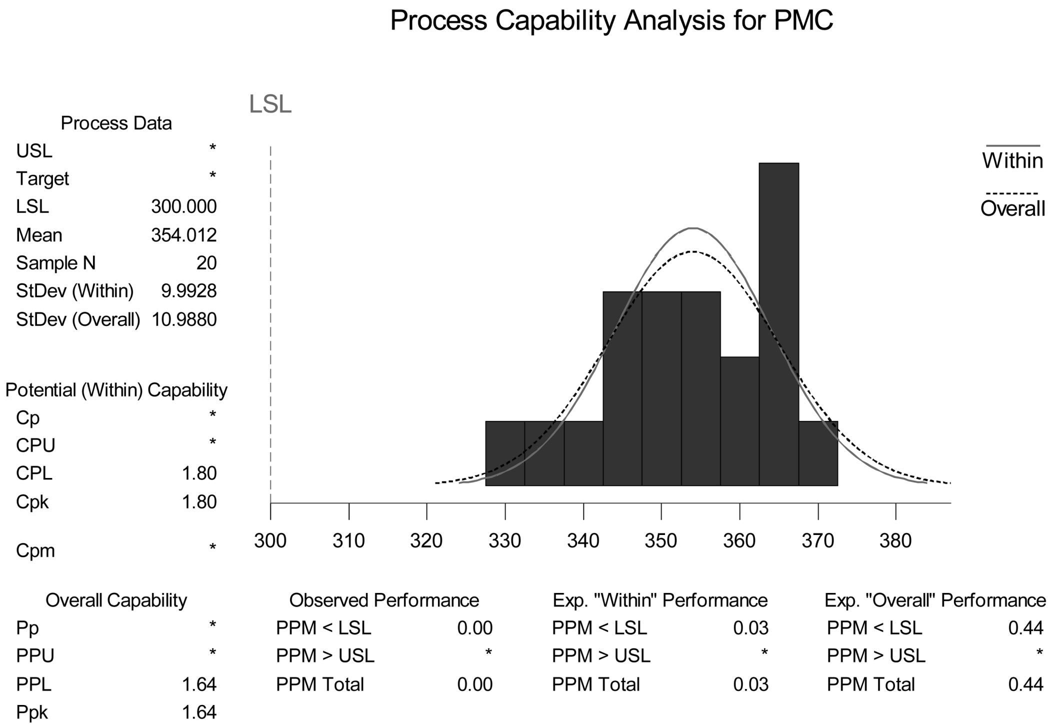


Fig. 10. Process capability analysis of ball shear strengths of organic solderability preservative finished packages passed by post mold curing process.

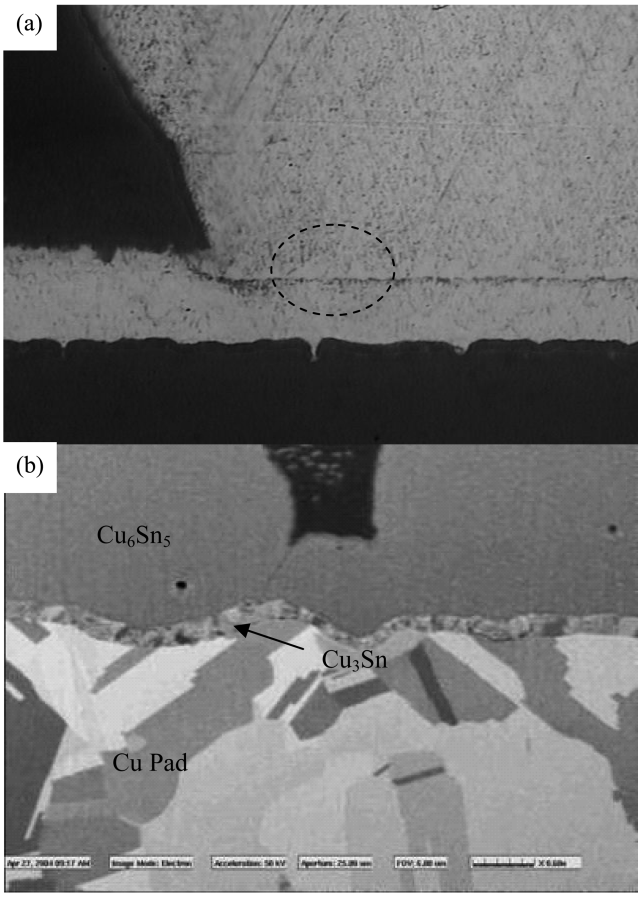


Fig. 11. Morphology of interface between Sn3Ag0.5Cu solder and Cu pad. (a) Image of interface by optical microscope, (b) Cu_6Sn_5 and Cu_3Sn intermetallic compound between leadfree solder and Cu pad from FIB analysis.

organically-finished packages were nearly the same regardless of degree of discoloration and were comparable to those of Ni/Au-finished packages.

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