Investigation of Adhesion Mechanism at the Metal-Organic Interface Modified by Plasma – Part I

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For the mold die sticking mechanism, the major explanation is that EMC filler of silica wears die surface roughened, which results in increase of adhesion strength. As big differences in experimental results from semiconductor manufacturers are dependent on EMC models, however, chemisorptions or acid-base interaction is apt to be also functioning as major mechanisms.
In this investigation, the plasma source ion implantation (PSII) using O_2, N_2, and CF_4 modifies sample surface to form a new dense layer and improve surface hardness, and change metal surface condition from hydrophilic to hydrophobic and vice versa. Through surface energy quantification by measuring contact angle and surface ion coupling state analysis by Auger, major governing mechanism for sticking issue was figured out to be a complex of mechanical and chemical factors.

Keywords: Molding, Sticking, Plasma implantation, Adhesion

1. Introduction

As the thickness of memory TSOP type package is getting slimmer from 1.0mm to 0.6mm, the Biphenyl and/or Multi-function system EMC has been used to prevent the popcorn crack mostly occurred during reliability test. On the other point of view, since its high adhesion strength seriously induces sticking problem between package and mol die, if the hot hardness of EMC cannot endure the sticking condition from die contamination, the chip encapsulated in the slimmer TSOP can be broken into two parts during ejection of pre-cured package component. Therefore, it is necessary to minimize the adhesion strength between the floating-out constituents from EMC molded and die surface, and to lessen the amount of the constituents accumulated on the die surface, which lengthens the cleaning period definitely.

In order to eliminate this kind of sticking problem, the waxing and cleaning operation should be done frequently, which causes cost-up for productivity and cumbersome issues for by-product disposition. The waxing mechanism can be described as follows. Resin piled-up on cavity wall adsorbs to melamine and the resin is detached from the cavity wall as melamine shrinks. The cleaning is done by physical scrub of contaminants with silica in molten resin. In general for TSOP, waxing moves in a 320 shot cycle for OCN type and in a 240 shot cycle for low molecular EMC. The cleaning moves generally in a 3 shift cycle for both OCN and low molecular EMC. However, it strongly depends upon the make.

If you look for the major governing factor for the sticking issue in real world, it can be categorized in two mechanisms. One is the mechanical adhesion concerning mechanical interlocking and large contact area. According to a manufacturer's experimental result showing that the filler content variation from 75% to 85% reveals nothing distinguishable, it cannot be a sole governing mechanism for sticking issue. The other one is the chemical adhesion concerning chemi-sorption, acid-basic interaction, inter-diffusion, electrostatic coupling, and polymer entanglement. It is well known that hydrogen bond mechanism is working on the EMC and metal oxide interface. In order to reveal the real working mechanism, surface roughness and energy are examined, which are modified by plasma.

2. Experimental procedure

The mold die sample was modified by plasma source ion implantation. The schematic diagram of the PSII apparatus is depicted in Fig.1.[1]
The size of the SUS-304 vacuum chamber is 500mmΦx560mm. The 13.56 MHz rf power supply and a matching network system was used to generate plasma by a single-turn aluminum strip antenna of 250mmΦ and 25mm wide. The antenna surface was coated with 10㎛ alumina. The chamber outside is arranged with permanent magnets and lead sheets. A magnetron source was located at the top of the chamber for ion-beam-enhanced deposition. The negative high voltage pulse generator was constructed with a tetrode as a switch tube. The maximum voltage and current ratings are 100kV and 10A. The grid swing was controlled by IGBT. The variable pulse width and repetition rate were monitored during implantation.

The molding die sample is made of ASP23 whose compositions are C 1.28%, Cr 4.2%, Mo 5.0%, W 6.4%, V 3.1%, which was fine ground, matte finished and hard Cr plated of 1μm thickness. The sample dimension is 24x5.3x0.25mm.
The chamber was evacuated to the base pressure of 10^{-6} Torr and then filled with Ar back to 0.5 mTorr. Then Ar plasma was generated by rf power of 200W and target was biased at –2kV d.c. for 10 minutes for removal of oxide and contaminants. After re-vacuum the chamber down to the base pressure, the process gases, O_2, N_2, and CF_4, were introduced to the chamber. The gas pressure was set to 0.5 mTorr and the rf power was 200W during PSII. The target bias was –60kV. The pulse width and repetition rate were 20㎲ and 100Hz. The samples were implanted for 30 minutes.

The modified samples were examined for depth profile with the PHI-670 scanning Auger nano-probe, and for surface energy with the Rame-Hart 100 contact angle apparatus, and for surface roughness with SEM. The sputtering rate by 3kV Ar ion with a raster size of 2x2mm was equivalent to 100Å per minute of SiO_2.

The adhesion strength of samples was compared to the releasing force. The samples were book molded and pull-out test (Fig.2) to measure the releasing force was carried out in 6 hours. And the modified samples were compared with non-modified samples and lead frame samples.

3. Results and Discussion

As shown in Fig.3 a)-c), the Auger depth profiles indicate that sample surfaces modified by O_2 and N_2 are changed in chemical states based upon the energy shift of Cr peak. But sample surface modified by CF_4 shows no shift of Cr peak and the fluorine piled up at the bottom of the modified surface layer which was sputtered away by Ar ion, which means that the surface was etched by CF_4 instead modified.

Table 1 shows contact angles and pull-out strengths obtained from different samples. As expected, surfaces modified by O_2 and N_2 exhibit same tendency of low contact angle, ie. hydrophilic surface. But surfaces modified by CF_4 have the same high contact angles as Cr hard coated surfaces which were not modified, ie. hydrophobic surface. The facts described above are well matched with the Auger depth profile results. The chemical states of surfaces modified by O_2 and N_2 are indeed changed. A42 stands for the alloy 42 lead frame.

Table 1 Contact angle and adhesion strength

Gas	O_2	N_2	CF_4	HCr	A42
Angle(°)	7	6	76	69	-
Strength	86	116	101,107	51	56,54,52
(Kgf)	72	72	98, 64	41	50,50,48

When the pull-out strengths are correlated with the contact angles, they seem to be irrelevant. The hydrophilic samples, which were modified by O_2 and N_2, showed relatively low strength values compared to the hydrophobic sample, which was modified by CF_4. These measured strengths are, however, quite higher than the strength of non-modified sample. This result can be explained like that as the Ar plasma was applied for removal of oxide and contaminants at the initial stage just before the re-evacuation, the sample surfaces were preferentially sputtered to leave grinding marks as shown in Fig.4. Especially in the CF_4 treated sample, as described earlier, the surface was etched by CF_4 down to the bottom of the so-called modified surface layer, at which the fluorine piled up. It can be summarized that the major governing mechanism for sticking issue is mechanical adhesion if the samples are compared between modified and non-modified. If the adhesion strengths are compared between samples modified, the hydrophilic samples show lower value than the hydrophobic samples, which means that surface energy state is also taken into account as a governing factor in somewhat extent. At this point, one thing important is that it is better to use trapezoid mold instead of pull-out mold to attain the adhesion strength more reasonably. (Fig.5)

The cost issue is a huddle to make many trapezoid mold modified with different source gases. The other thing is that the package mold die are originally EDM processed not mechanically ground. EDM stands for electrical discharge machining and its dimensional tolerance within a couple of microns.

4. Conclusions

1. Sticking mechanism is a complex of mechanical and chemical.
2. Contact angle represents the surface energy states and can be correlated to the adhesion strength.
3. Pull-out test is not a good method for measuring the adhesion strength, but it can be utilized if it is compensated with the trapezoid mold test results.
4. The EDM sample should be evaluated to figure out the actual difference in adhesion strength resulted from the surface finish.

In order to confirm the governing mechanism for sticking issue, Along with the academic study and site run test on examination of sticking mechanism, information exchange between EMC manufacturers, die maker, and assembly house will be accelerated.

References

[1] S. Han et al., Surface and Coatings Technology 82, 270-276 (1996)

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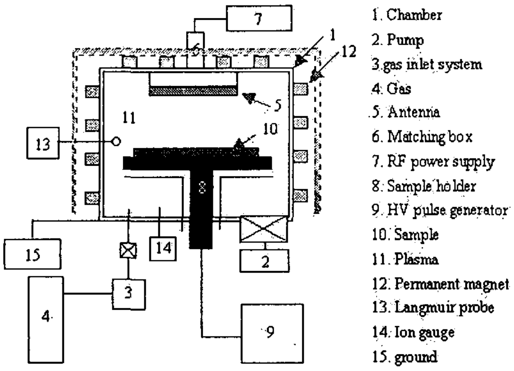


Fig.1 Schematic diagram of PSII system. [1]

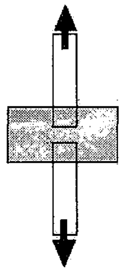
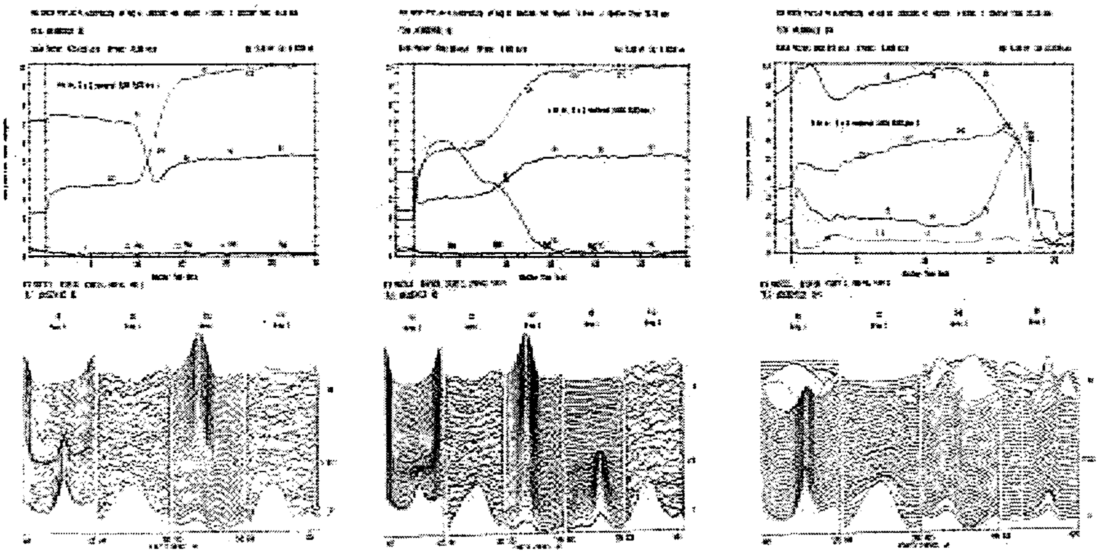


Fig.2 Schematic diagram of Pull-out mold (dark area).
The white rectangles are samples molded to be pulled against each other. The arrows show the pulling direction.



a) O_2 plasma modified b) N_2 plasma modified c) CF_4 plasma modified

Fig.3 Auger depth profiles

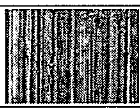
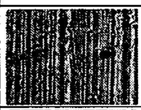
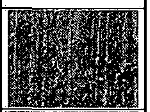
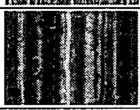
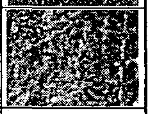
Gas	O_2	N_2	CF_4
x1500			
x5000			
Angle (degree)	7	6	76
Strength (Kgf)	86 72	116 72	101, 107 98, 64

Fig.4 the sample surfaces were preferentially sputtered to leave grinding marks.

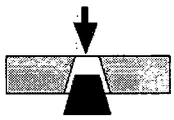


Fig.5 Schematic diagram of Trapezoid mold test.