The sonochemical surface modification of materials for electronic manufacturing. The effect of ultrasonic source to sample distance

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Structured Abstract

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Keywords: Sonochemistry, ultrasound, acoustic, surface modification, Noryl, ABS, Isola 370HR, weight loss, SEM, contact angle, roughness, electroless copper, adhesion, water.

Purpose of the paper: To build on the results detailed in the previous paper where it was shown that sonochemical surface modification could be achieved in water. This paper looks at one of the factors affecting sonochemical surface modification, namely the ultrasonic source to sample distance.

Design/methodology/approach: Ultrasound was applied through DI water for the surface modification of three materials: a high Tg laminate (Isola 370HR) a polyphenylene ester, polystyrene polymer (Noryl HM4025) and an acrylonitrile-butadiene-styrene/polycarbonate (ABS/PC – Cycolac S705).The efficacy of the treatment was determined by weight loss, SEM, contact angle, roughness and tape testing after electroless copper plating.

Findings: The study confirmed and extended the previous findings that a range of substrates could be sonochemically surface modified in water even though in this work the ultrasonic horn had a larger tip size and produced a different ultrasonic intensity. Although the results were material dependent the ultrasonic source to sample distance was found to be critical. Employing a spacing of 5 mm produced samples which generally exhibited higher weight loss, roughness and significant changes in surface morphology than when a distance of 25 mm was utilized.

Original/value of the paper: The paper demonstrates that sonochemical surface modification has the potential to be a much more sustainable surface modification process than those currently employed in the electronics industry. However to achieve this outcome acoustic cavitation and factors affecting it (such as source to sample distance) must be understood so that suitable equipment can be built.

Introduction

Ultrasound has been utilized in the electronics manufacturing industry for many years e.g. the cleaning of silicon wafers [1] and the removal of flux from soldered printed circuit boards (PCBs) [2]. In these cases no change in the substrate morphology is desired and for this reason ultrasonic frequencies of 40 kHz or higher are utilized. The desmear process has also employed ultrasound for some time and this is an essential part of the manufacturing sequence for the production of plated through holes in PCBs. Performing desmear under the influence of an ultrasonic field aids efficient movement of the chemistry through the holes and vias of the PCB and has been found to be of particular importance for horizontal processing [3].

Clearly therefore ultrasound has been employed for surface modification techniques in the past but it has often been simply 'bolted on' to an existing process with little thought being given to providing the best conditions (ultrasonic equipment, frequency, power, temperature, solution chemistry etc) to achieve optimal acoustic cavitation; the driving force for sonochemical surface modification as detailed in a previous paper in this journal [4].One such factor is the distance between the ultrasonic source (i.e. the probe tip) and the substrate.

A previous study by these authors [4] investigated the use of ultrasound in combination with a range of different surface modification chemistries and found that significant surface modification could be achieved even in water. As this project is concerned with developing a more sustainable surface modification technique it was decided that further work should concentrate on the use of water as the liquid medium and determine the factors that might enhance such a process. This paper reports the findings when three materials, which are employed in electronic manufacturing, are sonochemically surface modified again using only water in the sonication cell. The effect of ultrasonic source to sample distance is investigated and the efficacy of the process is evaluated by weight loss, contact angle, roughness measurements, adhesion after electroless copper plating (tape test) and scanning electron microscopy (SEM).

Experimental

The sample holder and basic experimental design was as described in the previous paper [4]. However in this case a Sonic Systems Ltd processor (model P100/3-20) was used with a 20 kHz ultrasonic horn (model 99892) which had been hard chrome plated. The end of the horn had a diameter of 27 mm which it was anticipated would give a more uniform surface modification over the sample area. It must be noted that this is a change from the source used in the previous study [4] which had a diameter of 12 mm. Therefore the ultrasonic intensity (Power/Area) will be reduced by a factor of 5 and the results are not directly comparable. The ultrasonic power generator was set at 50 W and delivered an 'actual' power of 33.5 W (determined calorimetrically). The sonication time was set at 30 minutes whilst the sample to source distance was 5 or 25 mm. The only liquid medium used was deionized (DI) water which was changed after each experiment and the temperature was held at a constant 40 ºC. The sonochemical surface modification process was as detailed in Table 1.

The three materials studied were:

i) Isola 370HR – a glass woven epoxy laminate utilized for PCB assembly (Tg 180 ºC)
ii) GE Plastics, Noryl HM4025 - a glass filled polyphenylene ester, polystyrene blend employed in the manufacture of MIDs and supplied by Moulded Circuits,
iii) GE Plastics, Cycolac S705 ABS/PC blend, used for the casings of various electronic devices e.g. mobile phones.

Plaques of the material were cut to a size of approximately 2.5 cm X 3.0 cm and the following responses were recorded to determine the efficacy of the sonochemical surface modification process.

- **Weight loss**

The method shown in Table 2 was employed to determine weight loss of the substrate after surface modification.

The weight loss (mg/cm^2) was then calculated:

[Initial Weight(mg)-End Weight(mg)]/Surface area (cm^2)

- **Contact Angle**

A Kruss DSA 100 drop shape analysis system was utilized to determine contact angle.

- **Roughness**

Roughness was measured over a 1.3 cm length of the substrate using a Rank Taylor Hobson Form Talysurf 120L.

- **Adhesion**

The surface modified material was metallised using a Rohm and Haas Electronic Materials electroless copper procedure supplied by Chestech Ltd as detailed in Table 3.The metallised samples were then tape tested and assigned a subjective grading from 0 (no adhesion, i.e. all copper removed by tape) to 10 (excellent adhesion, i.e. no copper removed by tape)

- **SEM Analysis**

Samples of the various materials after surface treatment were sputter coated with palladium/gold and then examined using a Jeol JSM-6060LV SEM.

Results and Discussion

Reference to Figure 1 indicates that the effect of spacing is most significant for the Isola material such that reducing the source to sample distance caused a dramatic increase in weight loss. Under these processing conditions the weight losses recorded for the Noryl plaques were not so high but were still more than double those found with a 25 mm source to sample distance. Values for the ABS substrate were extremely low with some negative values and suggest that very little material is being lost by the action of ultrasound.

Although the Noryl material had lower weight loss than the Isola laminate, the sonicated samples of this substrate exhibited significantly higher roughness as illustrated in Figure 2, where it can be seen that, with a source to sample distance of 5 mm the roughness was more than double that achieved when the horn tip was moved further away from the surface. The results for the Isola material were also slightly higher with a short source to sample distance but overall the sonicated laminate remained relatively smooth. This is despite the fact that the weight losses observed with a 5 mm source to sample distance were the highest of the 3 materials and suggests that surface modification is occurring uniformly across the substrate. Plaques of the Cycolac ABS gave the lowest roughness readings for the materials tested although again the reduced source to sample distance produced a marginally rougher surface.

For the Noryl and, to a lesser extent, ABS substrates contact angle (Figure 3) decreased when the source was moved closer to the substrate suggesting that under these conditions a more wettable surface is being produced. Although the Isola laminate exhibited the lowest values for contact angle, the source to sample distance appeared to have little effect on this response.

Figure 4 shows the tape test results for the sonicated samples. Good adhesion was obtained on the Isola samples whichever source to sample distance was used and it is interesting to note that these samples also gave the lowest contact angle values. If SEM Photograph 2 is considered then it can be seen that the Isola sample produced with a 25 mm source to sample distance has quite a porous morphology and, indeed, this is very similar to the as received material. As long as such a surface structure was clean and debris free then it would be expected to provide anchor points for the electroless copper and result in good adhesion. The SEM shown in Photograph 1 was produced with the short source to sample distance and it can be seen that glass fibres have been exposed (indicating significant material removal) and some texturing of the epoxy. Once again the whole structure is clean and debris free and this mixture of exposed glass and textured laminate would be expected to provide a good mechanical key to any coating and result in excellent adhesion. One might conclude from this that utilizing a source to sample distance of 25 mm was as effective as using 5 mm for this laminate. However, it is important to note that if the process was being used for desmear, a certain degree of weight loss is important as smeared epoxy must be removed from the inner layers of drilled PCBs.

By contrast the Noryl material had quite poor adhesion which tended to be worse when the source to sample to distance was 5 mm. The as received Noryl surface was seen to be very variable in appearance with some areas glass fibre rich and others resin rich. The SEMs in Photographs 3 and 4 clearly demonstrate that many more glass fibres are exposed on the surface when the source to sample distance is short and it is possible that as sonication time is increased resin is removed and these fibres are ‘undermined’ and will become loosely adherent (indeed Photograph 3 clearly shows where glass fibres have been completely removed). After plating, therefore, these fibres will easily come away with tape testing producing poor adhesion of the coating. Such a substrate may therefore benefit from a more ‘gentle’ surface modification which simply cleans up the already rough surface and this might explain why adhesion results were somewhat better when the source to sample distance was increased.

The tape test grades for the ABS substrate were quite poor and this is perhaps not surprising considering the low weight loss and roughness findings. Reference to Photographs 6 indicates that with a source to sample distance of 25 mm the surface of the sample shows very little texturing and appears very smooth. Reducing this distance to 5 mm can produce a quite rough surface as seen in Photograph 5 but is should be stressed that this was extremely localised and was not representative of the surface as a whole.

Although some of the results vary according to the material type this work has generally indicated that a short source to sample distance produces more significant surface modification than when this distance is extended. The explanation for the differences observed in terms of source/sample spacing lie within the basic physics of sound. The ultrasonic power delivered into a fluid by an acoustic horn is not emitted in a uniform pattern with respect to distance from a surface. This is because ultrasound, like any sound, passes through water in the form of a wave and the wave will have positions of maximum amplitude at multiples of the half wavelength of sound (λ) in the medium. These distances may be calculated using the simple equation (1).

$$\nu = f\lambda \qquad (1)$$

The velocity of sound (ν) through water is approximately 1480 ms^{-1} so that for a transducer operating at a frequency (*f*) of 20,000 cycles per second (20 kHz) the wavelength of the ultrasound in water will be about 7.4 cm. We may expect the maximum effect to occur at vertical intervals of 3.7 cm from the source tip. This analysis applies to a horn operating into an open water system at low intensity

This changes somewhat in a region close to the horn itself when it is operated at higher intensities. In this situation the region of maximum cavitation bubble activity is close to the horn surface [5]. This region is referred to as the near field and has been utilized in a number of industrial mixing applications [6]

Thus the distance from the surface at which significant surface modification occurs in the samples will be at a distance which maximizes sonochemical activity. Essentially this means that the source should be as close as possible to the material surface while maintaining a liquid contact between the two in order that acoustic cavitation can be produced on the surface and therefore a 5 mm gap will be more effective than 25 mm. For convenience of operation we did not consider reducing the gap to less than 5 mm for these experiments although it may be possible to refine the conditions to allow for more aggressive surface erosion.

Conclusions

i) This study has confirmed the earlier work that a range of materials, useful in electronic manufacturing can be surface modified by applying ultrasound through DI water.

ii) A source to sample distance of 5 mm generally produced greater surface modification effects in terms of weight loss and roughness than when this was increased to 25 mm.

iii) Contact angle results showed that sonication produced a more wettable surface both the Noryl and ABS substrates but had little effect on the Isola laminate

iv) SEM analysis of the surface of the materials indicated a dramatic change in surface morphology for both the Isola and Noryl materials when the source to sample spacing was 5 mm. This was also the case for the ABS but the effect was much more localised.

v) Material type clearly played a significant role in the efficacy of sonochemical surface modification. The Isola laminate exhibited high weight loss, low roughness and low contact angles but good adhesion whilst the sonicated Noryl samples showed lower weight loss, high roughness, higher contact angles and poor tape test results. The Cycolac ABS substrate was least affected by the application of ultrasound although some localised effects were observed.

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