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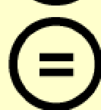

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The Thermal Stability of Alkanethiol Self-Assembled Monolayers on Copper for Fluxless Soldering Applications

Stephen Ebbens, David Hutt, *Senior Member, IEEE,* and Changqing Liu, *Senior Member, IEEE*

***Abstract*—The ability of alkanethiol monolayers deposited on copper to prevent surface oxidation has suggested their application as preservatives for fluxless soldering. However, the utility of such coatings for this purpose will critically depend on their ability to continue to preserve the substrate during exposure to elevated temperatures throughout the electronics manufacturing process. Consequently, the aim of this paper is to systematically determine the effect of storage temperature and duration on the ability of alkanethiol coated copper samples to undergo fluxless soldering. Similarly, the effect of pre-heating copper immediately prior to soldering is also investigated. The effect of reducing atmospheric oxygen concentration during storage and soldering is also considered as a potential route to improve the thermal resilience of the coatings. Parallel to ascertaining these industrially relevant performance parameters, a quantitative correlation between surface chemistry and solder wetting is established, and the temperature dependence of the kinetics of surface oxidation through an alkanethiol barrier layer is discussed.**

***Index Terms*—Copper, fluxless-soldering, oxidation, printed circuit boards, self-assembled monolayers.**

I. Introduction

Attaching electronic components to printed circuit boards (PCBs) using solder interconnections conventionally requires flux to be applied to the metal surfaces to promote the formation of strong metallurgical joints. Flux solutions typically comprise organic acids dissolved in solvents and serve to remove oxide layers and contamination from the metallic surfaces to be joined in order to enhance subsequent solder wetting. However, there are a range of disadvantages associated with the use of flux, of which the primary concern is the effect of potentially corrosive residues containing acidic and ionic species on long term device reliability. In production, these residues are typically washed from the PCB, introducing an additional process step which can be problematic, particularly with the increasing drive to reduce the size of surface mount technology components and the move toward flip-chip assembly, which makes it more difficult to clean residues from the small gaps between assembled parts. In addition, flux residues are known to degrade the function of optoelectronic devices: laser signals can be deflected or absorbed by the residues, and emitter/receiver performance can be degraded. A further concern is the environmental impact of organic fumes released during high temperature processing.

The main obstacle to fluxless soldering is the need to remove the oxide layers that impede the solder wetting of components and PCB tracks and pads. One approach is to modify the atmosphere during reflow. For example, introducing a reducing gas, such as hydrogen, has been shown to remove oxide layers, while using a vacuum/inert atmosphere to reduce the partial pressure of oxygen can drive the oxide formation equilibrium back toward bare metal and oxygen [1], [2]. Other possibilities include ultrasonic agitation to break up oxide during reflow [3] and laser beam ablation of the oxide layer [4]. In addition, methods such as plasma assisted dry soldering (PADS) address the issue of removing oxide layers from solder finishes on circuit boards or solder balls on flip-chips by using a SF_6 plasma to convert tin oxide to oxyfluorides that decompose during reflow [5]. However, many of these approaches are specialized and not appropriate in all situations.

A potentially more general and cost efficient method is to apply coatings to oxide free metal surfaces of component leads and PCB tracks, to preserve them for fluxless soldering. In principle, this approach is similar to the use of organic solderability preservatives (OSP) for conventional soldering. However, while cleaning stages prior to preservation reduce the surface oxide levels, some residual oxide remains, and consequently although OSP protected PCBs are compatible with low activity fluxes, they do not allow fluxless soldering [6], [7]. In general, this surface treatment approach relies on developing coatings possessing excellent oxygen barrier properties, which can be easily attached to the oxide free metallic surface and then be displaced by the soldering process. Previous work by the authors has demonstrated that alkanethiol self-assembled monolayer (SAM) coatings are suitable candidates for preserving oxide free copper surfaces and are thought to be spontaneously displaced or degraded by the soldering process (the mechanism is not known) such that they allow fluxless soldering under an inert atmosphere [8], [9] without

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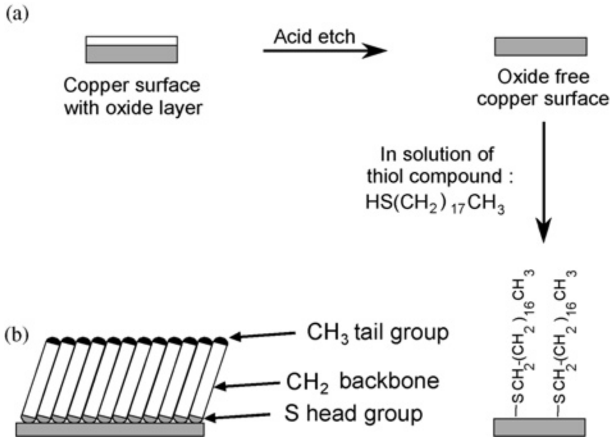


Fig. 1. Schematic diagrams. (a) SAM deposition by immersion of copper substrate in octadecanethiol. (b) Packing arrangement of the resulting monolayer.

the need for prior removal. Alkanethiol molecules comprise a thiol (SH) head group attached to a methylene (CH_2) chain backbone (typically with between 6 and 20 methylene groups) and end with a simple organic tail group (e.g., –CH_3, –COOH, –CH_2OH). When metallic surfaces with a face-centered cubic arrangement of atoms such as copper, are exposed to a dilute organic solution of alkanethiol, an ordered coating with single molecule thickness spontaneously forms. The mechanism of coating assembly involves the thiol head group attaching to the copper surface in a densely packed pattern, at regular positions across the underlying atomic structure [Fig. 1(a)]. This process is driven by the energetically favorable formation of a thiolate bond between the metal surface and the alkanethiol sulfur atom. The close proximity of the attached alkanethiol head groups forces the pendant alkane chains to adopt a highly ordered arrangement to maximize the van der Waals interactions between them. This optimization of intermolecular forces results in the alkane chains lining up in a common orientation pointing away from the metal surface [Fig. 1(b)].

The ability of SAM coatings to reduce the surface oxidation rate of the substrate metal has been demonstrated in earlier studies [9]–[11] and is attributed to the densely packed pseudo-crystalline arrangement of the alkanethiol chains that retards the diffusion of oxygen and other oxidizing species including water vapor, to the underlying copper substrate. It has also been shown that barrier properties improve with increasing alkanethiol chain length due to an increase in the van der Waals interactions and greater coating thickness [12]. While these observations all suggest that SAM coatings make ideal preservative coatings for fluxless soldering, changes in their structure occur at elevated temperatures, which may reduce their effectiveness. For example, the ordered alkane structure can undergo phase transitions such as melting, due to the increased disorder in the chains at higher temperatures [13], and ultimately at a sufficiently high temperature the SAM molecules will desorb and decompose [14]. In earlier work, qualitative data gathered using wetting balance testing confirmed a reduction in the efficiency of the barrier properties of SAM coatings at elevated temperatures [8], [9].

The deterioration in SAM barrier layer performance with temperature may have an impact on the potential industrial applications of these coatings. In electronics manufacturing, PCBs are likely to be subjected to several high temperature excursions, including multiple reflow processing and adhesive cure stages. In addition, pre-heating of materials prior to soldering is used in order to reduce the thermal load and thermal shock during reflow. As mentioned above, such high temperature excursions may have a deleterious effect on the SAM coated copper by encouraging oxidation. In this paper, through the use of wetting balance experiments, the effect of pre-heating regimes is considered, to establish optimum conditions for solder wetting. In addition, PCBs are often stored for many months before assembly and thermal stability studies are therefore needed. To address these issues, this paper presents a comprehensive investigation of the effect of storing SAM coated samples in air, at temperatures in the range of $-20\,°C$ to $120\,°C$, as a function of time.

One possible route to counteract the reduction in efficiency of SAM films at higher temperature is to reduce the atmospheric oxygen concentration above the sample. As many industrial soldering processes can be performed under inert atmospheres, this would provide a feasible method to extend the utility of the SAM coatings to higher/longer temperature exposures. To investigate this effect, this paper also explores the effect of oxygen concentration in the storage and processing atmosphere on the solder wetting of SAM coated samples. In addition to determining the limits of the application of SAM coatings as fluxless solder preservatives in electronics manufacturing, this paper also aims to increase understanding of the mechanism by which the coatings function and establish a firmer base for the factors that determine solderability of metallic surfaces. To this end, X-ray photoelectron spectroscopy (XPS) was used to measure surface oxidation levels after samples are subjected to thermal excursions and directly correlate these findings with solder wetability.

The particular alkanethiol considered in this paper is octadecanethiol, with a chain length of 17 methylene units and a methyl tail group. This molecule was selected due to its long chain length and commercial availability. It should be noted that at present, in comparison to other more general preservative approaches, the alkanethiol method investigated here is only relevant to components and tracks terminated with copper, however extensions to other oxidizable metals such as nickel may be possible. In addition, this approach does not address the issue of removing oxide from the solder, and may be best utilized in conjunction with solder wave joining or the PADS method described above.

II. Experimental

A. Preparation of SAM Modified Copper

Copper foil (0.25 mm thickness, purity 99.9%, Goodfellow) was immersed in a commercial aqueous microetch solution for 4 min. After rapid washing in deionized water the sample was transferred to a dilute aqueous hydrochloric acid bath (18 ml of 32% HCl in 250 ml water) for a further 10–15 min in order to remove the oxide layer. The copper was then

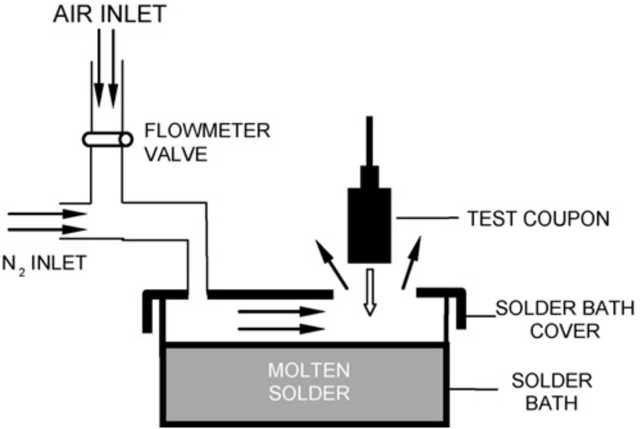


Fig. 2. Schematic view of the modified solder bath with additional covers to allow wetting balance testing in a reduced oxygen content atmosphere.

rapidly removed from the HCl solution, washed briefly with iso-propyl alcohol (IPA) and then SAM coated by immersion in a 5–10 mM solution of octadecanethiol (CH_3–$(CH_2)_{17}$–SH) (Aldrich) in IPA for 1 h. This thiol solution also contained acetic acid (approx 0.7 M) to act as an *in-situ* etchant. Finally, the sample was washed in copious amounts of IPA and then dried in a stream of room temperature air. Samples were immediately transferred to a freezer to ensure the SAM films remained intact prior to testing. Wetting balance testing had previously shown that samples stored under these conditions would not diminish in solderability over the timescale of these experiments. This was periodically verified by testing the solderability of samples fresh from the freezer. Samples were allowed to acquire room temperature after removal from cold storage prior to testing.

B. Wetting Balance Testing

Fluxless wetting balance testing was performed using a RPS 6-Sigma Wetting Balance Tester (Robotic Process Systems) equipped with a bath comprising eutectic Sn–3.8Ag–0.7Cu lead free solder held at 245 °C. A software correction was performed to allow for the effect of sample buoyancy on the measured force, thereby providing wetting force against sample immersion time plots for each test sample. The wetting balance approach rate and dwell time in the molten solder were fixed at 25 mm/s and 25 s, respectively. In order to allow the oxygen content to be reduced above the solder bath, a continuous nitrogen purge was arranged by adding a cover to the solder bath as shown in Fig. 2. Oxygen content was determined using an oxygen analyzer (Z210 Hitec Instruments) and a probe positioned immediately above the solder surface to withdraw atmospheric samples for testing. Pure nitrogen gas from a cylinder (British Oxygen Company gases) was supplied at constant flow rate. This allowed oxygen concentrations above the solder bath to be reduced to less than 150 ppm. In order to increase the oxygen content above this level, a T-piece was used to draw in atmospheric air through a valve and mix with the nitrogen supply. Adjusting the valve allowed stable oxygen concentrations in the 150–5000 ppm range to be reproducibly achieved above the solder bath.

During the experiments where wetting balance testing was used in isolation, at least four individual 1 cm × 2 cm SAM coated copper samples were tested for each condition. Each wetting curve is summarized by extracting key parameters reflecting wetting force and speed. Where numerical values are plotted, these are the mean value of the parameters recorded for the four samples. The standard deviation of the mean of these measurements is used to represent the spread of the data, with error bars representing plus/minus one standard deviation. In order to correlate wetting balance measurements with oxidation levels determined by XPS, a separate set of experiments were conducted. In this case, for each thermal treatment condition, all samples were cut from the same 4 cm × 2 cm sample, to ensure identical preparation and thermal history. This allowed a 2 cm × 2 cm sample to be used for XPS and two corresponding 1 cm × 2 cm portions to be used for wetting balance testing. To ensure that there was no opportunity for oxidation, samples were inserted into the vacuum chamber of the XPS machine within 15 min of the corresponding wetting balance tests.

C. Thermal Treatments

Aging experiments in air (40–100 °C) were performed using a T40/25 environmental chamber (Alphagate Ltd.). A commercial fridge and freezer were used to store samples at 4 °C and −20 °C, respectively. In order to age samples under an inert atmosphere, the cover system illustrated in Fig. 2 was used with the solder bath replaced by a hotplate to allow purging with nitrogen gas. For these experiments, it was found that it was important to maintain samples in a reduced oxygen environment throughout the entire heating and cooling cycle. This was because samples heated under nitrogen and subsequently cooled in air were found to be susceptible to dramatic reductions in solder wetting. This problem was resolved by resting samples on a thin layer of foil attached below the cover, allowing them to be separated from the hotplate and cooled to ambient temperatures under a continuously purged atmosphere. An oxygen analyzer was used to show that this arrangement maintained oxygen concentrations less than 150 ppm during heating and cooling. For comparison, samples were also aged using this apparatus with no nitrogen flow.

D. X-Ray Photoelectron Spectroscopy

XPS spectra were acquired using a Vacuum Generators ESCALAB instrument. All spectra were recorded using unmonochromated Al K_α X-rays with a 90° take-off angle. Peak area and position data were extracted by fitting to raw data using XPS Peak version 4.1. For relative changes in the quantities of elements with time, peak area ratios to Cu were used based on the area under the fitted curves rather than the raw data.

III. Results

A. Effect of Preheat Duration and Atmosphere on Fluxless Solder Wetting

Fig. 3 displays a typical buoyancy corrected wetting curve obtained from a freshly alkanethiol modified copper sample.

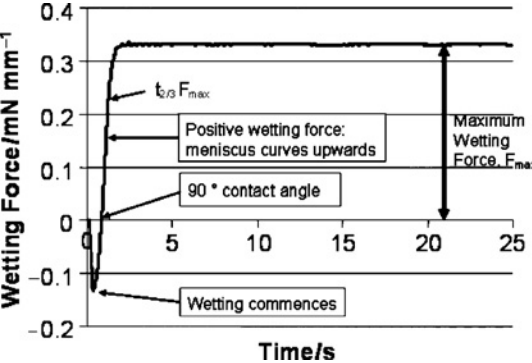


Fig. 3. Typical fluxless wetting balance curve for a freshly prepared SAM coated copper sample.

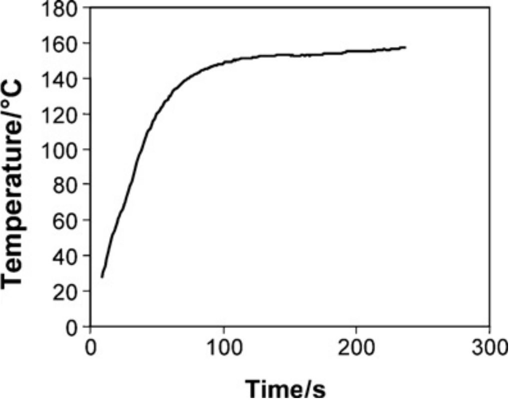


Fig. 4. Temperature of a typical copper sample as a function of time during the preheat period.

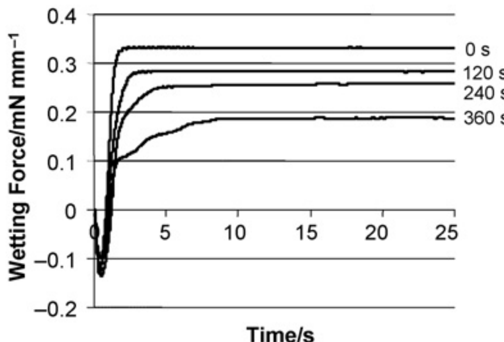


Fig. 5. Typical wetting balance curves for SAM preserved samples recorded as a function of hang-time (oxygen concentration <150 ppm).

The form of the curve reflects the balance of forces the copper sample experiences as it is immersed into the solder bath. When the sample initially contacts the solder there is a momentary delay in wetting, giving rise to a region dominated by upward (defined as negative in the wetting balance test) forces due to surface tension. Following this, solder wetting commences causing a turning point in the trace. As the solder meniscus starts to rise up the sample, a point is reached at which the contact angle is 90° and the wetting curve crosses the x-axis. Beyond this point the solder meniscus curves upward and exerts an increasing downward force on the sample giving rise to positive wetting forces. The rise in wetting force then gradually slows until an equilibrium is reached.

Both the speed of wetting and the maximum wetting force are important measures of the solderability performance [15]. There are various parameters used to summarize wetting speed, however in this paper the characteristic time taken for the wetting force to reach two-thirds of the maximum value ($t_{2/3}F_{\max}$) is used, as indicated in Fig. 3. In the example shown, the maximum wetting force was 0.33 mN/mm, and the characteristic time was 1.5 s. The form of the example curve and the numerical values of the extracted parameters correspond to excellent solderability for the test piece under consideration and are consistent with a freshly preserved sample [8], [15].

To start an investigation of the factors affecting fluxless solder wetting performance, the effect of varying the pre-heat duration was considered. In the wetting balance apparatus, pre-heat duration is controlled by the hang-time parameter, which determines the duration for which the sample is held 1 mm above the solder bath prior to immersion. During this period the sample is heated by forced convection due to the stream of nitrogen used to inert the wetting balance. A thermocouple positioned at the end of a typical copper sample was used to record the changes in temperature as a function of hang-time (Fig. 4). This profile shows that the copper sample reaches a steady temperature after 120 s and that the maximum temperature reached was 158 °C. Fig. 5 shows examples of wetting balance curves recorded for freshly SAM coated samples as a function of hang-time. A nitrogen only purge was used, ensuring that the oxygen concentration was less than 150 ppm. It is clear that an increased preheat duration produces a decrease in the maximum solder wetting force and reduces the rate at which this force is reached. This indicates that for fluxless soldering of SAM coated samples of the dimensions used here, there is no advantage gained by pre-heating the sample. To investigate the effect of oxygen concentration during pre-heat, the experiment was repeated at two additional higher oxygen levels. In each case the total purge flow rate was unchanged, to avoid altering the heating rate through forced convection. Fig. 6 displays typical wetting curves for the three different oxygen concentrations at a fixed hang-time of 30 s. It is apparent that as the oxygen concentration during pre-heat increases, the maximum wetting force decreases. However, the rate at which the maximum wetting force is reached is similar for each curve. Fig. 7 displays the entire data set by plotting the average maximum wetting force as a function of preheat duration and oxygen concentration. This reveals that the reduction in maximum wetting force with increasing pre-heat duration is more rapid at higher oxygen concentration. It should also be noted that even with 0 s hang-time the oxygen concentration exerts a significant effect over the maximum wetting force. This is most likely due to the dynamic heating of the copper sample that occurs during its approach to the solder bath.

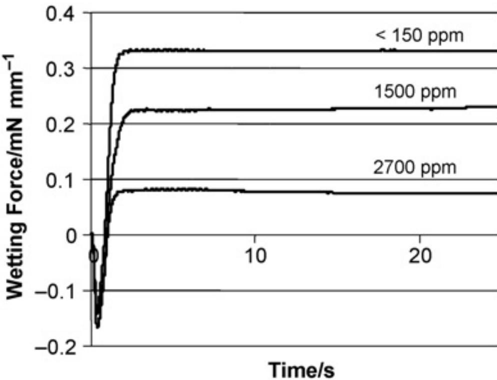


Fig. 6. Typical wetting balance curves for SAM preserved samples recorded in varying oxygen concentrations (all with 30 s hang-time).

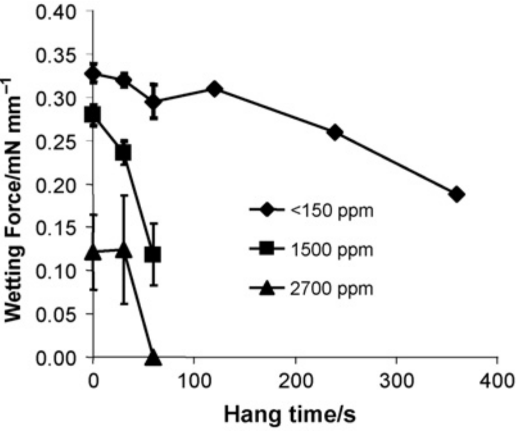
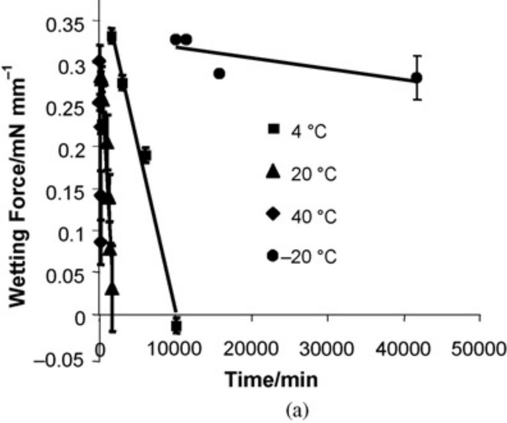


Fig. 7. Effect of hang-time on average maximum wetting force at three reduced oxygen concentrations.

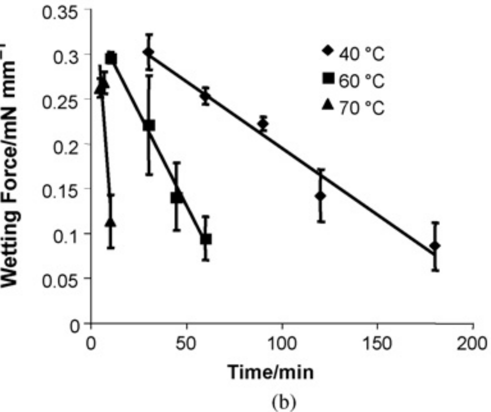
B. Effect of Storage/Processing Temperature on Fluxless Soldering Performance

In this section, the effect of storing samples in air at constant temperatures for a range of time periods prior to fluxless soldering is reported. The final solderability of these thermally treated samples was determined using wetting balance testing with the hang-time fixed at 30 s and oxygen concentrations less than 150 ppm. These conditions have been shown above to promote good solder wetting of fresh, SAM coated samples. Fig. 8 displays average maximum wetting force as a function of storage time for the temperature range −20 °C to +70 °C. At each storage temperature the reduction in wetting force with storage time occurs at an approximately constant rate. At higher temperature the rate of reduction in wetting force is more rapid. For example, during storage at 4 °C, positive wetting persisted for a week, at room temperature (20 °C) this storage time reduced to just over a day and at 60 °C positive solder wetting was lost within an hour of storage.

The speed of solder wetting is also an important parameter, and for comparison the characteristic solder wetting time was also calculated for the above data set. Fig. 9 plots the variation of characteristic solder wetting time ($t_{2/3}F_{\max}$) for samples stored at constant temperature as a function of storage time. At each storage temperature the wetting time is observed to increase with increased storage duration in an approximately linear fashion. This indicates that the rate of solder wetting reduces with increasing storage duration at a given temperature. Furthermore, this reduction in wetting speed occurs more rapidly at higher temperatures. This trend is not as well defined as the relationship found between maximum wetting force and temperature. It is interesting to note that there is little difference between the wetting rate behavior of samples stored at 40 °C and 20 °C, despite their maximum wetting force plots being separated (Fig. 8).



(a)



(b)

Fig. 8. Reduction of maximum wetting force during storage in air as a function of storage temperature. (a) Lower temperature storage. (b) Higher temperature storage (note change in x-axis range).

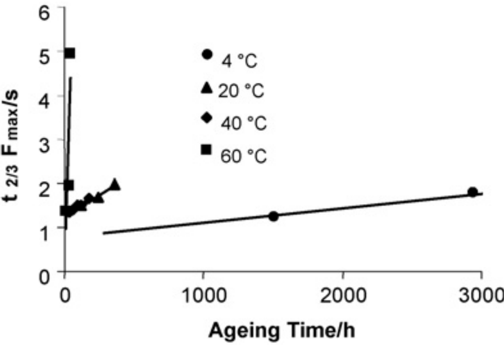


Fig. 9. Plot of characteristic time, reflecting speed of solder wetting as a function of storage time and temperature for the range 4 to 60 °C.

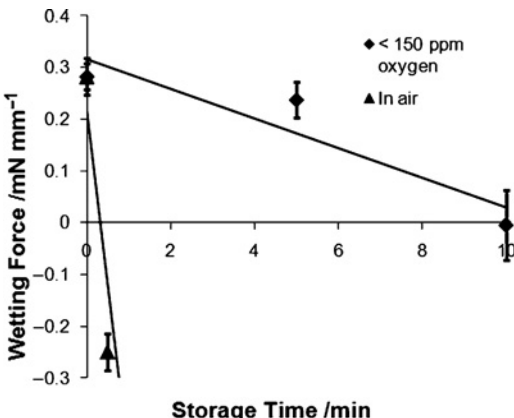


Fig. 10. Reduction of wetting force for samples stored at 150 °C under ambient conditions and in a low oxygen atmosphere.

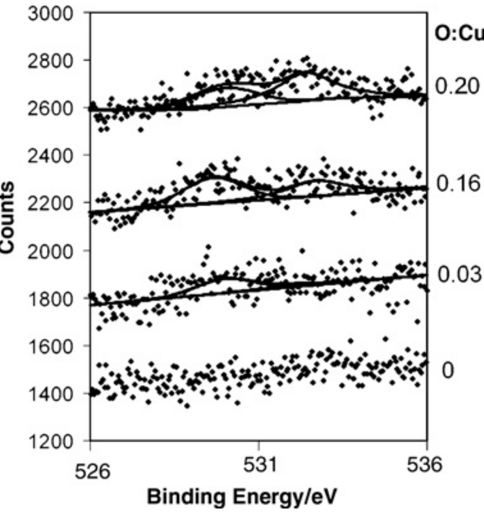


Fig. 11. Core line XPS oxygen spectra for samples stored at 60 °C for increasing time periods (from bottom to top 0, 30, 40, and 45 min).

C. Effect of Reducing Oxygen Concentration on Fluxless Solderability During Storage/Processing at High Temperatures

Fig. 10 displays a comparison between the reduction in wetting force for a sample stored at 150 °C in air and a sample stored at 150 °C in a low oxygen environment (150 ppm). This temperature was chosen as it is close to the maximum temperature obtained by a sample during the pre-heating stage of wetting balance testing. It is apparent that reducing the oxygen content significantly reduces the rate of loss of solderability. The rate of reduction of solderability observed at 150 °C with oxygen concentrations less than 150 ppm is equivalent to that seen at 70 °C in air.

D. Relationship Between Solder Wetting and Surface Oxide Levels

The above section has demonstrated a strong relationship between storage temperature and duration and maximum solder wetting force. As described in the introduction, one hypothesis for the reduction in solder wetting during storage at elevated temperatures is degradation in the SAM barrier properties allowing surface oxidation to occur. The observation that decreasing oxygen concentration in the storage (and soldering) atmosphere improves solder wetting also supports this theory. Consequently, surface chemical analysis is used here to attempt to directly establish a link between solderability and surface oxide concentration. In order to produce a set of samples with decreasing solderability, fresh SAM coated samples, were stored at 60 °C in air for increasing time periods and subsequently analyzed using XPS and wetting balance testing.

In all cases XPS analysis indicated the presence of C, S and Cu core line features that were consistent with SAM adsorption as reported previously [9]. However, the surface oxygen content of the samples varied, showing increasing oxygen levels with increasing storage time at 60 °C. The core oxygen spectra are displayed in Fig. 11, together with the corresponding O:Cu peak area ratio (Note: this ratio is an empirical measure of relative oxygen and copper concentration and does not correspond to the atomic ratio). For longer time exposures it is clear that the oxygen envelope contains two peaks separated by approximately 1.5 eV. The relative intensity of the higher binding energy peak increased with increasing surface oxide content, which was reflected in the O:Cu peak ratio. Fig. 12 plots the overall O:Cu ratio against the mean maximum solder wetting force. The data reveal that there is a very strong correlation between increasing amounts of surface oxidation and the reduction in maximum wetting force, with a R^2 value of 0.99 obtained using regression analysis. It should be noted that there was no significant correlation between S:Cu and C:Cu ratios and wetting force when analyzed in the same manner.

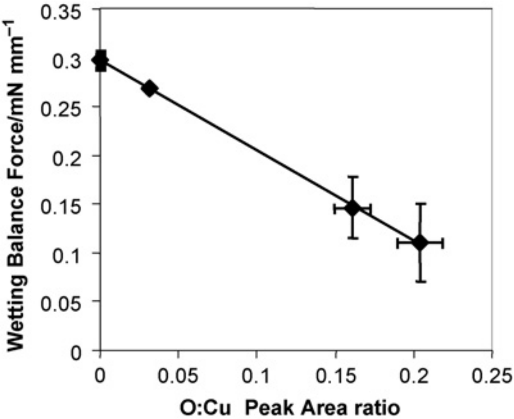


Fig. 12. Correlation plot between O:Cu XPS peak area ratio and maximum fluxless solder wetting force.

IV. DISCUSSION

The primary focus of this paper was to determine the potential of SAM coatings to preserve copper for fluxless soldering during electronics manufacturing processes carried out at elevated temperatures. The investigation has been conducted using two approaches; the first was to consider the effect of pre-heat and oxygen concentration during wetting balance

testing and the second, to age samples under constant temperature and atmospheric conditions. When comparing these data sets, it is important to be aware of the dynamic temperature changes that occur during the wetting balance testing procedure, and the competing effects they can exert on the solderability of alkanethiol coated samples.

A. Factors Influencing Fluxless Solderability of SAM Coated Samples

The two key issues influencing the fluxless solderability of SAM coated copper are the need to pre-heat the sample to reduce thermal load and the conflicting possibility of a reduction in efficiency of the SAM preservation coatings during this period. Considering thermal load, it is clear that cold samples will be difficult to solder efficiently; as solder contacts a cold sample, it will cool rapidly and may temporarily solidify rather than continuing to wet the sample. One example is the observation of stepped wetting balance profiles when solder wetting is stopped until the thermal conduction between the contacting solder bath and sample raises its temperature sufficiently to allow the solder wetting to proceed [15].

However, due to the nature of the SAM coating, there is a competing effect: the potential for elevated temperatures to promote an increased rate of oxidation of the underlying copper surface and so reduce solderability. The SAMs ability to preserve the freshly etched, oxide free, highly solderable surface relies on the alkane chains and tail groups forming a tightly packed steric barrier. As thermal energy increases, the motion of the chains may increase. This will disrupt the ordered arrangement and reduce the steric barrier allowing oxygen and water vapor to penetrate.

Under the conditions found in these wetting balance tests, for relatively small copper samples, the reduction in SAM steric barrier efficiency during pre-heating outweighs the advantage of reduced thermal load. In the simplest case, when no pre-heat duration is chosen the sample is only briefly heated as it approaches and is immersed into the solder bath. The temperatures generated during this procedure are unknown, however it is apparent that they are sufficient to reduce the thermal load between solder and sample to result in a high wetting force and rapid solder wetting for the given thickness of test coupons.

As longer hang-times are used, the sample will reach a higher temperature before immersion into the solder bath occurs (Fig. 4), although this situation is further complicated by the existence of a temperature gradient along the test piece. While the increases in sample temperature reduce thermal loading, no further increase in maximum wetting force is observed. In fact, extending the pre-heat duration beyond 30 s causes both the wetting force to reduce and the rate of wetting to decrease. This is firm evidence for a reduction in efficiency of the steric barrier properties of the SAM during the pre-heat period enabling even low levels of oxygen (<150 ppm) in the atmosphere to penetrate to the Cu. This observation was confirmed in the simpler case where a sample was aged on a hotplate at a constant 150 °C under the same oxygen concentration (Fig. 10). The reduction in wetting force in both these cases proceeds at a similar rate.

The other trend apparent from the solder wetting data is that increasing oxygen concentration reduces the maximum wetting force at a given hang-time (Fig. 7). In the model of the SAM functioning as a steric barrier to surface oxidation, it is apparent that a higher concentration of oxygen above the coating will increase the proportion of oxidizing species that can potentially diffuse through to the copper, increasing the oxidation rate and so reducing solder wetting.

B. Effect of Storage/Processing Temperature and Duration on Fluxless Solderability

Ideally, the fluxless solder coatings would be stable to high temperatures in air. However, the data shown here suggest that while exposures to temperatures up to 60 °C can be tolerated in ambient conditions, processing stages that involve higher temperatures would need to be performed under reduced oxygen atmospheres to avoid a rapid reduction in solderability. Encouragingly, both the wetting balance testing results, and the aging studies show that positive wetting forces can be preserved after exposures of up to 150 °C, in an atmosphere with oxygen content reduced to less than 150 ppm. As many industrial processes are routinely carried out in inert atmospheres, these results suggest sufficient thermal stability for SAM coatings to be of significant utility. The data also indicate that long-term storage of coated samples prior to use is also possible. Fluxless solderability can be sustained for a week under refrigeration, and for months if placed in a freezer. The speed of solder wetting was also investigated and shown to broadly follow maximum solder wetting force for the samples aged at constant temperature. However, it was observed that altering the oxygen concentration during wetting balance testing resulted in a drop in maximum wetting force, without changing the speed of wetting. This result requires further investigation, but highlights the complexity of the solder wetting process.

Beyond these qualitative conclusions, a quantitative analysis of the thermal aging data was attempted. By using the linear relationship between the reduction in wetting force and storage time for a given temperature shown in Fig. 8, it was possible to extract quantitative values for the rate of reduction of maximum wetting force. To do this, each data set was fitted to a linear function, with the gradient of this regression line indicating wetting force reduction per unit time. To convert this rate data into numerical rate constants, it was necessary to assume that the reaction responsible for the reduction in wetting force was the formation of copper oxide underneath the SAM layer, an assumption strongly supported by the XPS data. In addition, it was assumed that the rate of oxidation would be related to the amount of oxygen above the SAM coating, leading to a basic rate equation of the form

$$-\mathrm{d}(F_{\max})/\mathrm{d}t \propto \mathrm{d}(\mathrm{Oxide})/\mathrm{d}t = k[\mathrm{O}]^{x}. \qquad (1)$$

The order of the reaction, x, with respect to oxygen concentration is unknown, however as all the storage experiments were performed at constant oxygen concentration (ambient), the reaction order does not affect the relative values of

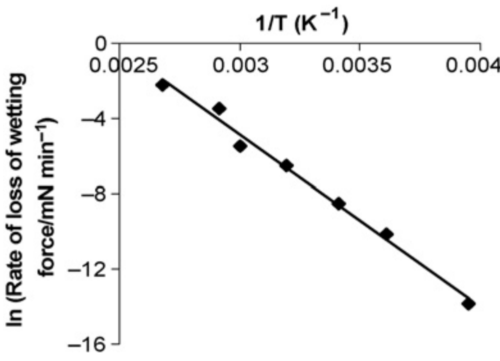


Fig. 13. Arrhenius-type plot for the relationship between rate of loss of solderability and storage temperature in air. Data shown ranges from −20 to + 100 °C.

derived rate constants. Based on this, rate constants were obtained from the gradients of the plots in Fig. 8. Analysis of this set of derived rate constants shows that they obeyed an Arrhenius-type relationship, i.e., the natural logarithm of the rate constants was inversely proportional to temperature. Fig. 13 displays the resulting Arrhenius plot over the range −20 °C to 100 °C, and regression analysis confirms a strong positive correlation for this model ($R^2 = 0.99$). Consequently, within this temperature range the model can be used to predict the storage lifetime of a SAM protected sample.

C. The Effect of Surface Oxidation on Solder Wetability

Comparing XPS and wetting balance measurements for samples thermally aged to have differing levels of solder wetting has established a quantitative relationship between maximum solder wetting force and the level of surface oxidation. Until now, solder wetting force has been viewed as a qualitative measure of an industrially relevant property, however this finding proves that wetting balance testing also reveals detailed information about changes in chemistry at the outermost layer of metal surfaces. This proves the utility of wetability testing as a surface analysis tool. It should be noted that the proportionality established here was for a set of samples with very similar surface morphology, it would be expected that variations in surface roughness would contribute to solder wetting force, in addition to surface chemistry differences.

The XPS data also reveal that two different oxygenated chemical species are formed during the oxidation process. This is in agreement to previous XPS analysis of samples with higher oxide levels [9], and also agrees with observations made by Laibinis and Whitesides [10]. In the latter paper, the lower binding energy oxygen species was assigned to Cu_2O and the higher energy peak to $Cu(OH)_2$. In this paper, no Auger peaks indicating Cu(I) or XPS signals at 942 eV characteristic of Cu(II) species were detectable. The failure to distinguish changes in copper oxidation is most likely due to the very low levels of surface oxide. The XPS data also confirm that signals due to sulphur remain present at the surface after thermal treatment for 1 h at 60 °C, in agreement with previous experiments indicating that desorption requires significantly higher temperatures [14]. Another issue of interest is whether any phase transitions or melting events occur in the SAM layer during heating. For the particular thiol used, the bulk melting point is 31–35 °C, however it is known that melting of a SAM layer can occur at significantly higher temperatures due to the intermolecular interactions in the 2-D layer [13]. It is likely changes in the state of the barrier layer would alter the rate of loss of solderability. However, the uniformity of the Arrhenius relationship over the temperature range considered here does not indicate that this is the case.

V. Conclusion

This paper has illustrated the potential utility of employing alkanethiol self-assembled monolayer coatings to preserve copper surfaces for fluxless soldering. An investigation of the factors affecting fluxless solder wetting has found that only a short pre-heat period is needed to ensure good solder wetting, longer pre-heat durations may reduce the solder wetting performance. Furthermore, fluxless soldering is best performed in reduced oxygen atmospheres. In addition, a study of the thermal stability of SAM coated samples during storage has been undertaken to ascertain their resilience to processing stages and long term storage. These data reveal that during processing stages, short exposures to temperatures up to 60 °C in air can be tolerated, at higher temperatures it is necessary to operate in a reduced oxygen atmosphere to maintain fluxless solderability. However, by adopting this approach, excursions up to 150 °C can be withstood, suggesting possible reflow applications. In addition, long term storage of samples is possible in a freezer. Further work is required to determine methods to improve the barrier properties of the SAM coating by, for example, using longer chain molecules to thicken the barrier layer, or through the use of molecules that can be "linked" together, thereby providing a less easily disrupted and less permeable barrier. However, the balance between the ability of the SAM to protect the substrate and yet be displaced by the soldering process needs to be considered. There may be potential for these materials to act as conventional solderability preservatives in normal fluxed assembly processes, for which additional studies are needed to compare their performance with standard OSPs. Finally, this paper makes some more fundamental conclusions regarding the function of SAM coatings as fluxless soldering preservatives. Using a simple kinetic model, a quantitative link between temperature and rate of loss of solder wetting force is established, with mechanistic implications. In addition, a strong correlation between the observed levels of solder wetting and the underlying copper oxide concentration is established, confirming the belief that these molecular surface coatings function as temperature dependant barrier layers to oxygen diffusion, and showing that wetting balance forces qualitatively correlate to subtle changes in surface chemistry.

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