JOURNAL OF MATERIALS SCIENCE 26 (1991) 787–791

Wetting behaviour of eutectic tin/lead solder and fluxes on copper surfaces

L. J. MATIENZO*, R. R. SCHAFFER
IBM Corporation, Systems Technology Division, Endicott, New York 13760, USA

An apparatus for the measurement of reproducible dynamic contact-angle measurements is described and used to follow the interaction of a eutectic tin/lead solder on copper surfaces at various temperatures. Because activated (glutamic acid hydrochloride type) and non-activated (abietic acid type) fluxes are commonly used for surface preparation of microelectronic components prior to soldering, the wetting behaviour of these fluxes on bare copper and corrosion-inhibited surfaces with benzotriazole is also measured. The experimental results follow the Arrhenius equation; therefore, activation energies of wetting can be estimated. Surface reactions are proposed to account for the differences in wetting rates observed with the fluxes on the different copper surfaces during the joining process.

1. Introduction

The spreading of liquids over solid surfaces is an important topic in the fabrication of microelectronic components. Fabrication processes such as chemical cleaning, electroplating, corrosion inhibition, surface protection, coatings, and soldering rely on the spreading of liquids for adequate performance. The wetting of a liquid on a solid surface depends on the magnitude of the surface-free energies of the solid–vapour, solid–liquid, and liquid–vapour interface, respectively. Spreading of a liquid will occur when the interfacial energy of the solid vapour boundary is higher than that of the solid–liquid boundary.

The work of surface expansion is done against surface tension, a measure of the attraction between molecules. As the temperature is raised, the kinetic energy of the molecules increases, resulting in a decrease in surface tension. At any point in time, the contact angle at the solid–liquid interface may be regarded as an inherent property of the solid–liquid–vapour system and a measure of wettability. For a given system, wetting depends on parameters such as the chemical characteristics of the surface and the spreading liquid, temperature, time, and surface roughness. For example, in tribological systems, the rate of spreading of lubricating oils on a surface is a function of temperature and time. These factors determine lubricant wettability [1].

Another illustration of these interrelations can be found in the extensive use of solder alloys for coating and joining copper surfaces in the microelectronics industry. In this case, considerable attention is focused on the mechanical and electrical reliability of the solder connection [2]. Because the actual surfaces that are joined may contain some thin layers of oxide, the expected wetting behaviour of the pure metal is changed. Many liquid metals can displace the oxide layer from the the base metal either by diffusion or migration through defects with the formation of intermetallic compounds. When this is achieved, wetting and spreading will occur rapidly.

Some organic and inorganic materials known as fluxes are used to remove impurities and metal oxides from metal surfaces at elevated temperatures [3]. Industrial processes use either organic fluxes that are water soluble or solvent soluble. These materials induce chemical reduction of the metal oxides as evinced by recent surface studies on the reaction of abietic acid flux with CuO and Cu_2O [4]. Fluxes can be classified as non-activated and activated fluxes. This distinction is made because the two types have different oxide removal capabilities and they leave different residues after soldering. Activated fluxes form corrosive and conductive residues which need to be removed. A non-activated flux yields a non-corrosive and non-conducting residue. Non-activated fluxes are also known as rosin fluxes because they primarily consist of a mixture of isomeric diterpene acids, of which abietic acid is about 80 to 90% of the total mixture. Activated fluxes can contain acids, bases or salts to reduce oxides and they can be water soluble.

In most microelectronic applications, solder joining is done with a low melting point tin–lead solder which wets by forming a tin–copper intermetallic. Prior to joining, a flux is used, and in most cases, the joining is done in a reducing atmosphere [5]. The surface activation energy of both the flux and solder alloy will determine the temperature–time required to meet equilibrium conditions of the soldering process. Because copper surfaces oxidize during storage, it is standard practice to cover the surfaces with a thin layer of a corrosion inhibitor. Typically, azole compounds such as benzotriazole (BTA) or benzoimidazole (BI) are used for this purpose [6–8]. Because copper joining may be done after the copper surfaces have been stored for some time, potential complications on the wetting of these surfaces may develop if a corrosion inhibitor layer exists.

---

*Author to whom all correspondence should be addressed.

0022–2461/91 $03.00 + .12

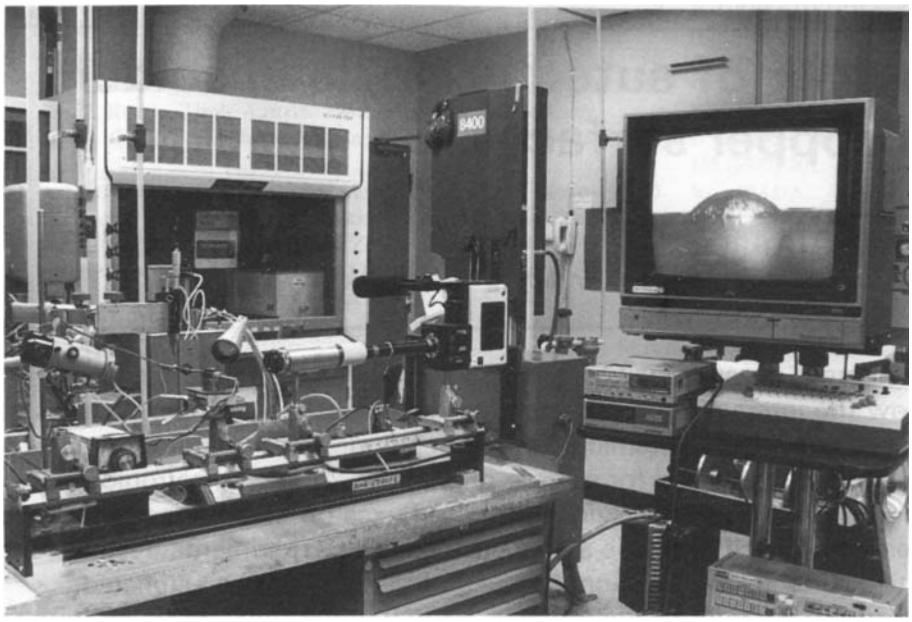

Figure 1 Apparatus for dynamic wetting measurements

In this paper, dynamic measurements of contact angle for the wetting of a low melting point tin–solder alloy are made as a function of temperature for two different types of fluxes (abietic acid and glutamic acid-based) used to treat copper surfaces prior to metal joining. The wetting of corrosion-inhibited surfaces with BTA is also studied to determine the performance and time dependence of the fluxes toward intermetallic formation. Finally, the activation energies for the two different systems are estimated and used to predict contact angle–time relationships at other temperatures.

2. Experimental procedure

2.1. Apparatus for dynamic wetting measurements

The experimental system is mounted on an optical bench and consists of a standard Rahmé–Hart goniometer coupled with a video system capable of capturing sequential images every 1/30 sec. The sample under investigation sits on a heated chamber with quartz windows. During an actual run, the video recorder stores the images and the individual frames can be back-played to determine the precise contact angles as a function of time. Data can be collected by dispensing liquid from a syringe directly on to a preheated substrate or by placing solder balls on the desired material and heating both simultaneously. This technique not only provides a comparative measurement of wetting, but it also yields dynamic information to estimate the rate of wetting (advancing contact angle) for a continuous production process. A photograph of the experimental set-up is shown in Fig. 1.

2.2. Copper substrates

Commercial 1 oz (~ 28.35 g) copper foils were used. For direct tests on copper films, the copper was cleaned in a dilute solution of HCl immediately before the test. In other cases, the foils were treated in a dilute solution of BTA to produce a corrosion-resistant layer. The thickness of the protective layer was estimated by means of argon-ion sputtering coupled with X-ray photoelectron spectroscopy (XPS).

2.3. Chemical fluxes

Two different organic fluxes were evaluated: (a) a standard abietic acid formulation (Alpha-Flux) in isopropanol (water-insoluble flux), and (b) a water-soluble formulation containing glutamic acid hydrochloride (Lonco 3355–11). This general type of water-soluble flux has been described in the literature by Roberts [9]. Both fluxes were diluted in isopropanol in a one-to-one proportion.

2.4. Tin–lead solder

Commercial eutectic tin–lead solder balls (67%/33%) of 0.03 in. (~ 0.076 cm) diameter were used to evaluate the dynamic wetting of copper surfaces. No additional treatments were introduced on the solder balls prior to testing.

2.5. Surface analysis

A 560 Perkin–Elmer Physical Electronics ESCA/Auger spectrometer or an SSX-100 Surface Science spectrometer were used to obtain photoelectron spectra. Mg$K\alpha$ or Al$K\alpha$ X-rays were used for excitation. High-resolution spectra were taken with a pass energy of 25 eV and the elemental binding energies were referenced to the carbon signal at 284.6 eV produced by adventitious carbon. With the addition of argon-ion sputtering, XPS depth profiles were obtained with the SSX-100 spectrometer with a sample spot size of 600 μm to estimate the thickness of the inhibitor layer. The selected sputtering rate was 2 nm min^{-1}.

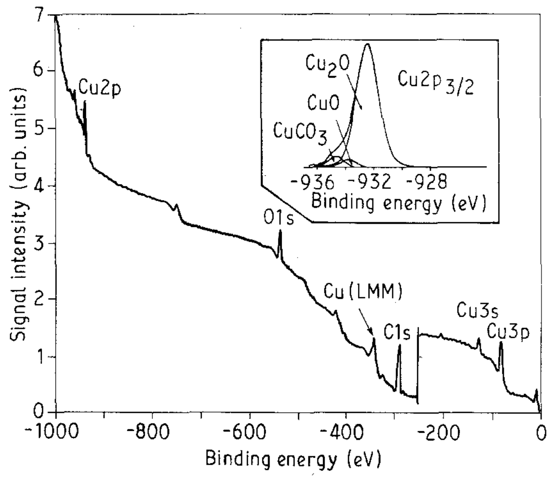

Figure 2 XPS survey spectrum of a typical surface of copper prior to any treatment. In the inset, the curve-resolved Cu $2p_{3/2}$ signal is shown to illustrate the contributions from Cu_2O, CuO, and $CuCO_3$.

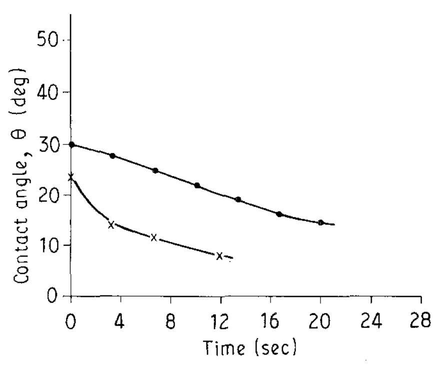

Figure 4 Contact angle (θ)–time plots for the spreading of (●) abietic acid flux and (×) glutamic acid hydrochloride flux on a clean copper substrate at 20 °C.

3. Results and discussion

The wetting of solders on copper substrates is dependent upon the removal of oxides to form an intermetallic phase. In industrial processing, the joining operations are accomplished efficiently through approaches which tend to maximize productivity [10]. Because of these reasons, actual simulations of wetting phenomena are very important to develop adequate process conditions, which depend on the state of the copper surface and the type of flux used. Flux activity is dictated by the rate of surface activation required for efficient soldering at a given production rate.

Because copper surfaces are normally coated with a corrosion inhibitor for safe storage, it is important to know the role the coating plays on wetting phenomena. Surface analysis shows that the typical components on a copper foil are oxides and copper carbonate, where the major component of the coating is Cu_2O. Fig. 2 shows the survey XPS spectrum for a typical copper surface prior to any processing. The high-resolution XPS spectrum of the Cu $2p_{3/2}$ signal after deconvolution is shown in the inset. Following the application of a corrosion inhibitor such as BTA, the additional element detected is nitrogen. Thickness estimation for the inhibitor layer can be obtained by depth profiling. In this study, the approximate thickness of the organic layer is about 2 nm as shown in Fig. 3. The presence of this inhibiting layer, consisting of Cu(I)BTA complex and some free BTA, could conceivably modify the interaction of the metal with a flux; therefore, dynamic contact-angle measurements are expected to reflect some change relative to uncoated metal. In addition, depending on the activity of the flux, the relative rates of wetting can be markedly different.

In Fig. 4, the contact angle changes at room temperature, as a function of time for the two different fluxes spreading on a copper surface treated with BTA are plotted. The glutamic acid flux spreads more rapidly than the abietic acid. Temperature also plays an important role in the wetting of copper surfaces by the eutectic solder. Fig. 5 shows the results obtained for copper surfaces cleaned with dilute HCl solution and surfaces coated with BTA as they are exposed to the two types of flux with the eutectic solder at 249 °C. When abietic acid is used, the surface coated with the BTA complex has a slightly better wetting than the metal coated with the oxide layer. For the glutamic acid flux, this difference is almost non-existent. These results can be interpreted as three different reaction processes which may occur when the metal surface interacts with a flux.

1. Regardless of flux activity, the role of the organic acid (in this study, either abietic or glutamic acid) is to remove the surface oxide and yield a metal carboxylate complex prior to the solder reaction with the metal surface. The removal of the surface oxide, for example

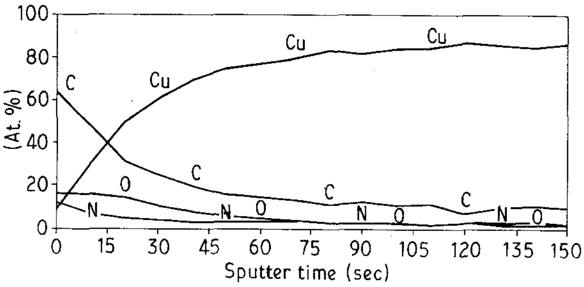

Figure 3 XPS depth profile of a typical copper surface coated with a BTA layer. The approximate thickness of the organic layer is about 2 nm.

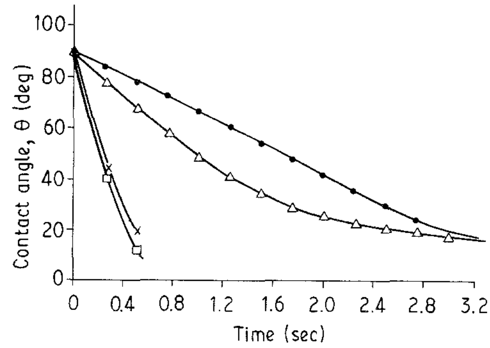

Figure 5 Contact angle (θ)–time plots for lead–tin solder wetting of copper surfaces coated and uncoated with BTA. The experimental temperature is 249 °C. (●) Clean copper and abietic acid, (△) BTA-treated copper surface and abietic acid, (×) clean copper and glutamic acid hydrochloride flux, (□) BTA-treated copper surface and glutamic acid hydrochloride flux.

Cu_2O, proceeds according to

$$Cu_2O + 2RCOOH = 2Cu(RCOO) + H_2O \quad (1)$$

2. When the metal surface is coated by an inhibitor, the spreading rate at a given temperature also depends on the type of flux used. If a non-activated flux, such as abietic acid is used, the formation of the metal carboxylate complex depends on the decomposition of the Cu(I)BTA layer. This can be accomplished thermally or hydrolytically. Thermal stabilities for free BTA and the Cu(I)BTA complex are very different.

Thermogravimetric analysis (TGA) reveals that pure BTA decomposes in the range 97 to 99 °C. In contrast, the Cu(I)BTA complex has a higher decomposition in air with sequential weight losses starting at 280 °C. According to the wetting experiments described above, in the range 221 to 277 °C, acid hydrolysis will be the relevant reaction for fluxing

$$RCOOH = H^+ + RCOO^- \quad (2)$$

$$Cu(BTA) + H^+ = Cu^+ + BTAH \quad (3)$$

$$Cu^+ + RCOOH = Cu(RCOO) + H^+ \quad (4)$$

3. If the selected flux is activated and water soluble, a more rapid rate of wetting is expected. For glutamic acid flux, the actual component is an organic acid hydrochloride. Upon release of HCl, BTA protonation is favoured over complexation because two different sources of protons are available

$$HOOCRCOOH \cdot HCl = HCl + HOOCRCOOH \quad (5)$$

where

$$R = \text{-}(CH_2)_2CH(NH_2)\text{-} \quad (6)$$

After the initial reaction, the process is similar to the reaction for the non-activated flux and the Cu(I)BTA layer.

Thermal effects on the wetting of eutectic solder and the flux were examined by measuring the change in contact angle with time at different temperatures. The results for two of these temperatures in which abietic acid flux was used are shown in Fig. 6. These results indicate that the decay in contact angle or wetting is a logarithmic function of time. In addition, solder wetting is also a function of temperature. This relationship can be expressed mathematically as

$$\begin{aligned} \theta &= -k\log t + b \\ &= -k\log Ct \end{aligned} \quad (7)$$

where

$$C = 10^{-b/k} \quad (8)$$

The value of the slope k can be determined from the relationship given in Fig. 6. b and C are obtained from the line drawn for each specific temperature.

The Arrhenius equation provides a means for determining the response of systems that involve a rate process, such as diffusion, corrosion, stress relaxation or creep [1]. In the case of thermal effects of wetting, the surface activation energy of the process can be estimated from the equation

$$C = Ae^{-E/RT} \quad (9)$$

where A is the Arrhenius constant, E the surface activation energy (cal mol^{-1}; 1 cal = 4.18 J), R the universal ideal gas constant in (cal K^{-1} mol^{-1}), and T the absolute temperature (K). The estimated activation energy for the wetting of copper protected by BTA with the eutectic solder in the presence of abietic acid is 25.8 kcal mol^{-1} at 277 °C as calculated from the data plotted in Fig. 7. With the present model, a comparison can be made between the theoretical predictions and the experimentally measured values ($k = 65.1$) for the same system in the range 221 to 277 °C as shown in Fig. 8. For the glutamic acid flux subjected to this temperature range, little difference was obtained for the contact angle–time data as shown in Fig. 9. Here, the constants k and b are 135 and − 55, respectively. In this temperature range, the thermal energy effect is small and the activation energy for the flux reaction is very low.

4. Conclusions

The results presented in this paper have shown that the fluxing of copper films protected by BTA is dependent upon the chemical composition of the organic

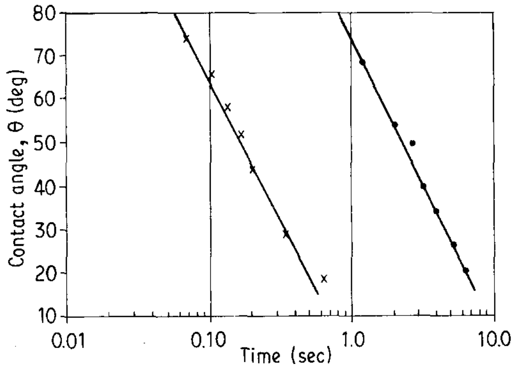

Figure 6 Contact angle (θ)–time plots for the wetting of tin–lead eutectic solder with abietic acid flux on BTA-treated copper surfaces at (●) 221 °C and (×) 277 °C.

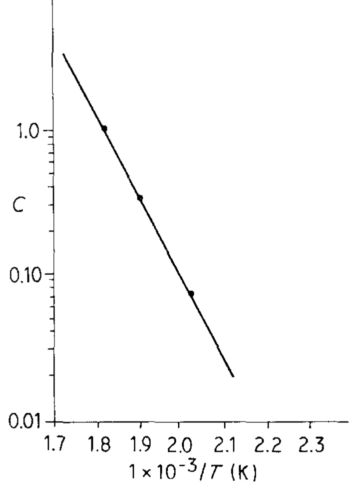

Figure 7 Arrhenius plot for the wetting of eutectic tin–lead solder with abietic acid on a BTA-treated copper surface.

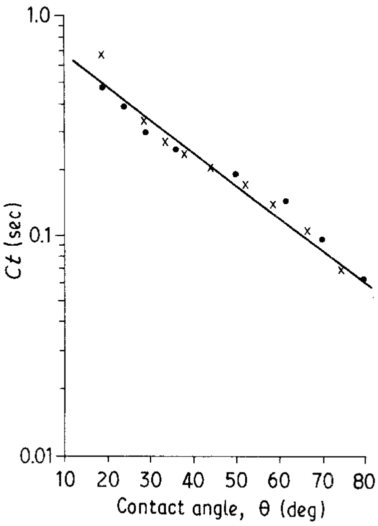

Figure 8 Comparison between (———) calculated and measured contact angles (θ) at (●) 221 °C and (×) 277 °C with wetting times multiplied by the constant *C* for eutectic tin–lead solder on a BTA-treated copper surface with abietic acid flux.

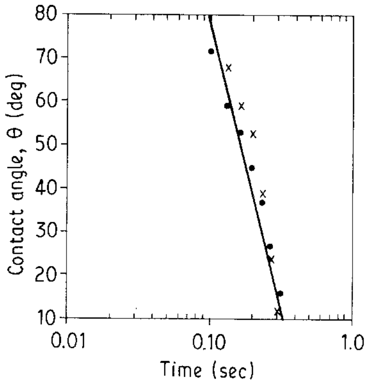

Figure 9 Comparison between (———) calculated and measured angles (θ) at (●) 221 °C and (×) 277 °C with wetting times for eutectic tin–lead on a BTA-treated copper surface with glutamic acid hydrochloride flux.

flux selected. An activated flux based on an acid–hydrochloride will react faster than a rosin flux such as abietic acid. Dynamic contact-angle measurements obtained with the apparatus described here, allow for reproducible and simple data collection. The results obtained at various temperatures can be used to estimate activation energies for a particular type of flux. The agreement between experimental and calculated values using a generic Arrhenius function is excellent and it can be used to predict the wetting behaviour of a flux at a given temperature. On a practical note, the principles described here can be applied to the selection of fluxes for specific soldering processes which have particular time and temperature requirements.

Acknowledgement

The authors thank D. Titus, IBM Corporation, for his valuable assistance with the contact-angle measurements.

References

1. F. G. ARRIETA and D. T. GAWNE, *J. Mater. Sci.* **21** (1986) 1793.
2. L. S. GOLDMAN, *IBM J. Res. Develop.* **13** (1969) 251.
3. C. G. WOYCHIK and R. C. SANGER, in "Principles of Electronic Packaging", edited by D. P. Seraphim, R. Lasky and C. Y. Li (McGraw Hill, New York, 1989) p. 591.
4. L. J. MATIENZO and R. W. SNYDER, unpublished results (1988).
5. H. H. MANKO, in "Solders and Soldering" (McGraw Hill, New York, 1979) p. 199.
6. P. G. FOX, G. LEWIS and P. J. BODEN, *Corrosion Sci.* **19** (1979) 457.
7. H. ISHIDA and R. JOHNSON, *ibid.* **26** (1986) 657.
8. M. BAKSZT, in "Printed Circuit World Convention III", Proceedings, WCIII-4, Washington D.C., 22 to 25 May (1984) (Institute of Interconnecting and Packaging Electronic Circuits, Evanston, Illinois, 1984) p. 2.
9. R. F. ROBERTS, *Surf. Interface Anal.* **7** (1985) 88.
10. R. W. WOODGATE, "Handbook of Machine Soldering" (Wiley, New York, 1983) p. 3.

Received 19 October 1989
and accepted 1 February 1990