Polarographic methods of monitoring addition agents in the electroplating of Sn–Pb solders

by J. Horkans

The electrochemical techniques typically used to monitor organic addition agents in electroplating baths work poorly in Sn–Pb solder plating baths. These electrochemical monitoring methods are based on the principle that additives act through their effects on the kinetics of the metal-deposition reaction, and thus the reaction $M^{n+} + ne^- \rightarrow M$ can be used as a probe to determine the additive concentration. The heavy metal ions in solder plating baths readily poison probe electrodes, however, and thus electrochemical methods on solid electrodes are irreproducible and unreliable in these systems. A polarographic technique, which uses a renewable Hg drop electrode, can be used for the quantitative analysis of addition agents in solder plating solutions, even though the chemical identity of these species may not be known to the user of the plating solution.

Introduction

An essential part of implementing any manufacturing process is the understanding of how to control the process within the product specifications. The dependence of the overall process on each of the operating parameters must be known, the operating window within which each parameter can vary must be established, and a procedure of process control must be set up. There are special problems in controlling electroplating processes, and the control requirements become more stringent as electroplating technology is extended in microelectronic products.

In metal plating, the material deposited from simple aqueous solutions generally does not have suitable properties for most technological purposes. Plating solutions therefore generally contain small amounts of addition agents used to control alloy composition, grain size, mechanical properties, and the distribution of mass on macro and micro scales. Users of electroplating processes very often employ plating solutions that are

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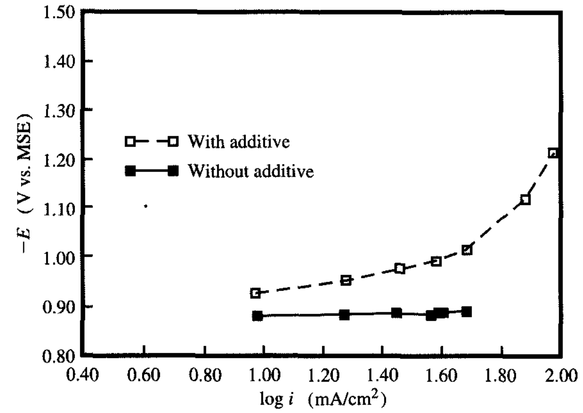

Figure 1

Effect of a commercial additive on Sn deposition from MSA. The Sn(II) concentration was 0.2 M. The MSA concentration was about 1.4 M. The steady-state polarization measurements were IR-corrected. The reference electrode was the mercury sulfate electrode (MSE) — Hg/Hg_2SO_4/sat. K_2SO_4 — which has a potential of +0.64 V versus the normal hydrogen electrode or +0.40 V vs. calomel. Rotation rate of the RDE was 350 rpm.

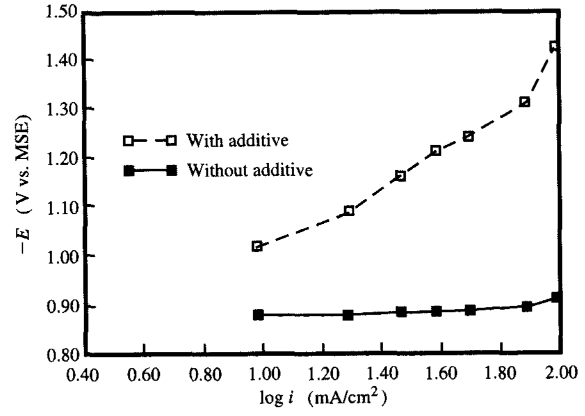

Figure 2

Effect of a commercial additive on Pb deposition from MSA. The Pb(II) concentration was 0.2 M. The MSA concentration and measurement conditions were the same as in Figure 1.

purchased from vendors who have formulated them to produce the desired deposit properties. Analysis of the inorganic components in plating solutions is straightforward and is not discussed here. On the other hand, these plating baths may contain a mixture of organic additives, with compositions proprietary to the vendor, and they present a complex problem of organic analysis.

There is an interrelationship between the effects of addition agents on the electrochemistry of metal deposition and the effects on the deposit properties. Electrochemical technologists have tried to exploit this interrelationship as a monitoring technique, with varying degrees of success. In principle, it should be possible to develop electrochemical monitors for any system in which the addition agents act by influencing electrode kinetics. In practice, however, traditional electrochemical techniques do not work well for the additives used in the deposition of Sn–Pb solders.

Two recent trends in Sn–Pb plating are driving the development of better monitoring techniques for solder plating systems. First, a new solder plating chemistry, based on methane sulfonic acid (MSA), has been introduced and is finding acceptance among electroplaters. Second, solder plating is being extended to the fabrication of flip-chip interconnections [1], an application that requires the most stringent controls to achieve the required composition, compositional uniformity, and thickness uniformity. The required control of the additives in these MSA plating baths has been achieved by implementing electrochemical techniques on the clean, reproducible surface of a dropping Hg electrode.

Effects of addition agents on the electrochemistry of Sn and Pb deposition

Solder plating is an old technology that has recently undergone a rapid change. The newly introduced electrolyte, MSA, is displacing the more traditionally used fluoboric acid in many applications. Solutions based on MSA are more expensive than fluoborate solutions, but they give high-quality deposits, and they are less corrosive and more amenable to waste treatment [2–4].

The electrode kinetics of both Sn and Pb deposition are extremely fast [5, 6] in acids, including MSA.
The practical result of such fast kinetics is the tendency for electrodeposits to be dendritic. Organic addition agents can greatly impede the deposition reaction [5–9]; they are universally used in Sn–Pb deposition to control the deposit properties, and they also are important in controlling the deposit composition [10]. The literature concerning additives in Sn–Pb electroplating largely predates the introduction of MSA plating systems. Examples of typical additives in MSA are given by Hurley et al. [11].

The polarization behavior of Sn and Pb deposition from MSA and the effects of a commercial plating bath additive are given in **Figures 1** and **2**, which show the dependence on potential of, respectively, the partial currents i_{Sn} and i_{Pb}. These curves were derived from steady-state measurements of potential when a constant plating current was applied to a Pt rotating disk electrode (RDE). The deposits were stripped anodically from the RDE, and the stripping charge was used to calculate the metal deposition current, as distinct from the total applied current. (Stripping analysis of a pure metal is a simpler version of the procedure described by Horkans et al. [10].) The potential measurements were IR corrected to compensate for the effect of the cell resistance. (Cell resistance and IR correction are explained in detail by Bard and Faulkner [12].)

The electrochemical characteristics of Sn(II) and of Pb(II) are similar in acid solution; their deposition potentials are separated by only a few millivolts. Both metals are deposited with nearly 100% current efficiency at lower current densities. The current efficiency of Sn deposition is less than 100% at high current densities, but Pb deposition is essentially 100% at all practical current densities because of the slow kinetics of H_2 evolution on Pb. The very fast kinetics of both Sn and Pb deposition in pure MSA are reflected in the very steep current rise with potential.

The commercial additive strongly polarizes both Sn and Pb deposition, especially at higher current densities. The effect is large for both metals, but it is larger for Pb than for Sn.

Principle of electrochemical analysis of plating bath additives

The concentrations of the organic addition agents in plating solutions can change if these species are oxidized at the anode during plating or if they are entrained in the deposited metal. Furthermore, the replenishment of other plating-bath components, the replacement of solution volume "dragged out" with parts and fixtures, and the replenishment of evaporated H_2O can all lead to changes in the plating bath composition. It is thus essential to monitor the composition of plating solutions to ensure a constant deposit quality. The monitoring of addition agents in commercial electroplating systems presents the problem of determining the concentration of species of unknown composition in a complicated solution matrix.

Hurley et al. [11] suggest the simplest of control techniques, a replenishment scheme based on the current passed through the solution. Replenishment schemes without monitors cannot provide a warning when a plating bath is outside its operating specifications.

One widely used tool, the Hull cell [13] and its variations [14], depends on an assessment of the visual appearance of the deposit in order to make adjustments in the additive levels. Since solder deposits are not shiny, a Hull cell is not a suitable monitor in Sn–Pb plating systems. Liquid chromatography has been applied to the analysis of some components of various plating systems [15] but not yet to the organic additives in MSA-based Sn–Pb systems.

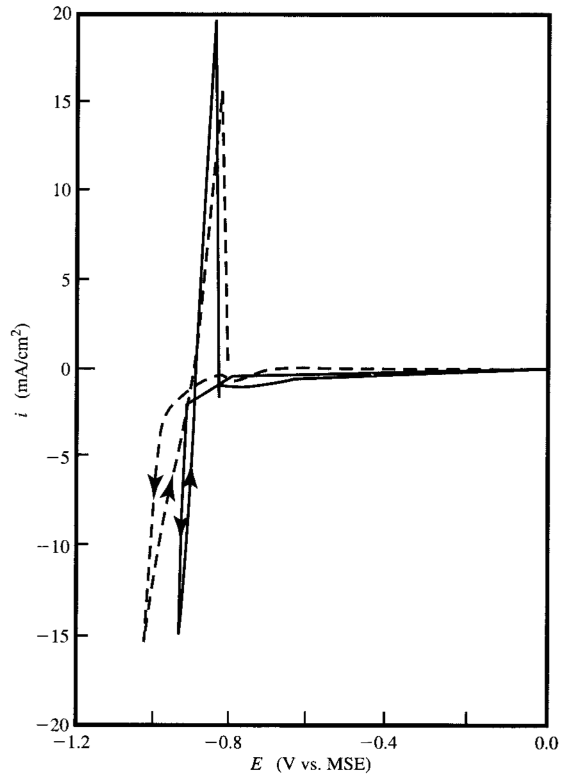

Figure 3

Cyclic voltammetry of a Pt RDE in solutions of 0.1 M Sn(II) in 1 M MSA without additives (solid curve) and with a commercial additive (dashed curve). The electrode rotation rate was 1600 rpm; the potential sweep rate was 100 mV/s. The measurement was made in an air atmosphere.

The effects of the addition agents on the electrode kinetics of metal deposition, through which they govern the deposit properties, can provide an indirect means of monitoring the solution concentrations of these species. Technologists have struggled, with mixed results, to find suitable electrochemical monitoring techniques. Many of the proposed techniques are based on cyclic voltammetry. (Cyclic voltammetry is described by Bard and Faulkner [12].) The procedures were originally developed as monitors for Cu plating solutions [16–25], and they are widely used in the printed-circuit-board industry. Automated instruments for such analyses are commercially available.

The strong polarization effect of the addition agent on the Sn and Pb reaction kinetics, shown in Figures 1 and 2, provides a path for determining the concentrations of the additives used in Sn–Pb plating solutions. The cyclic voltammetry of Sn–Pb systems and the effect of a typical addition agent are illustrated in **Figure 3**. The solid curve

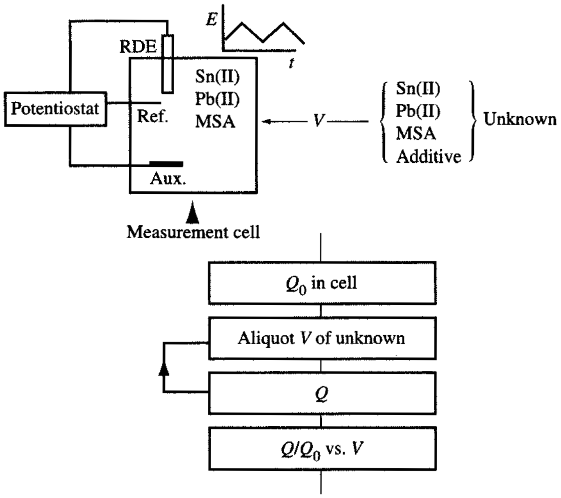

Figure 4

Schematic representation of the cyclic voltammetric analysis of the additive in a plating solution. The measurements yield a dependence of normalized charge Q/Q_0 on addition volume V, as shown in Figure 5, from which the concentration of the additive can be calculated.

is the cyclic voltammetry of a Pt RDE in a solution of Sn(II) methane sulfonate and methane sulfonic acid. [The curves are similar for solutions of Pb(II) methane sulfonate in MSA and for mixtures of Sn(II) and Pb(II) in MSA.] In this figure, reducing currents (metal deposition) are shown as negative, and oxidizing currents (metal dissolution) are shown as positive. As the potential is swept from its positive limit in the negative direction, a reducing current begins to flow at about −0.8 V. The small current between about −0.8 V and about −0.94 V results from the strong interaction between Sn(II) and the Pt electrode surface (i.e., in this region a layer of Sn with a thickness of the order of a monolayer is formed on the Pt by the phenomenon of underpotential deposition [26]). At about −0.94 V, bulk Sn deposition begins. Tin deposition continues when the direction of the potential sweep is reversed at the negative limit of the scan. The hysteresis (i.e., a larger current in the positive-going sweep) can be explained by roughness of the growing Sn layer. In the positive-going sweep, Sn dissolution starts at about −0.87 V. The charge under the dissolution peak equals the deposition charge, since Sn deposition is essentially 100% efficient under these conditions.

The dashed curve in Figure 3 shows the effect of a commercial plating additive on Sn deposition from MSA. Tin deposition requires a stronger driving force, i.e., a considerably more negative potential, in the presence of the addition agent. The cyclic voltammetry of Pb or Sn–Pb alloys also shows this strong inhibiting effect of the addition agent.

Since the addition agent in a plating bath acts through its influence on the kinetics of metal deposition, cyclic voltammetry indirectly gives information about the concentration of the addition agent. A scheme for using cyclic voltammetry for addition agent monitoring in plating solutions is shown in **Figure 4**. The metal plating reaction is used as the probe reaction for detecting the additive.

The conditions of the cyclic voltammetry are selected such that metal is plated and stripped from the Pt RDE during the cycle. If these conditions are invariant (i.e., if the potential sweep rate, the electrode rotation rate, and the potential range are kept constant), the amount of metal deposited is an indirect measure of the electrode kinetics. The amount of metal deposited is measured by the charge under the stripping peak of the cyclic voltammetry.

Into the test cell is measured a known volume V_0 of a stock solution containing, at their target concentrations, all of the components of the plating solution except the addition agent. The metal stripping charge in cyclic voltammetry is determined; the initial charge in the stock is called Q_0. Into this additive-free stock are added known aliquots of a plating bath, either the production bath with unknown additive concentration or a standard bath with known concentration, and the charge is remeasured. The process is repeated until the value of Q/Q_0 has passed a predetermined endpoint.

The kind of data gathered is shown schematically in **Figure 5**. The Q/Q_0 vs. addition-volume curves are determined both for the standard and for the unknown and are fitted to a quadratic equation. The addition volume required to give a predetermined endpoint value of Q/Q_0 is inversely proportional to the concentration of the additive, and thus the knowledge of the unknown and standard curves allows the calculation of the concentration of the unknown, whether or not its identity is known.

The voltammetric technique outlined, which can be used to monitor additives in Cu plating, should in principle be usable in the Sn–Pb plating system with its strongly polarizing additive. Voltammetry has, however, proven ineffective for the determination of the additives in Sn–Pb plating because of the irreproducibility of the measurement. The problem is illustrated in **Figure 6**. The curves of Figure 6 show the dependence of the stripping charge Q in voltammetry on a Pt RDE in a known volume V of an MSA solution of Sn(II) and Pb(II) as a function of additions of a standard solution with the same metal-ion and acid concentrations and a known concentration of the additive (the procedure represented in Figures 4 and 5). The two curves were consecutive measurements with the same standard solution. In this case, the strong influence of the addition agents on the cyclic voltammetry could not be translated into an analytical technique because of the irreproducibility of the measurement. Consecutive measurements with the same solution routinely differed by as much 20%, which is larger than the expected day-to-day variations in working plating baths. The curves in Figure 6 have not been normalized to the initial charge Q_0; normalization does not significantly improve the reproducibility.

The reason for this irreproducibility can be surmised; the strong interaction between Sn(II) or Pb(II) ions and a Pt electrode (on which they form, by underpotential deposition, deposits on the order of monolayers in thickness) can make it difficult to control the surface condition of the Pt from cycle to cycle in voltammetry. It is not necessary to understand the reason for the irreproducibility, however, in order to surmount it. Electrochemists have available to them a highly reproducible electrode surface, the dropping Hg electrode (DME). A clean electrode surface is produced with the formation of each drop. The electrochemical analysis of additive concentration can be modified for polarography on a DME, as described below.

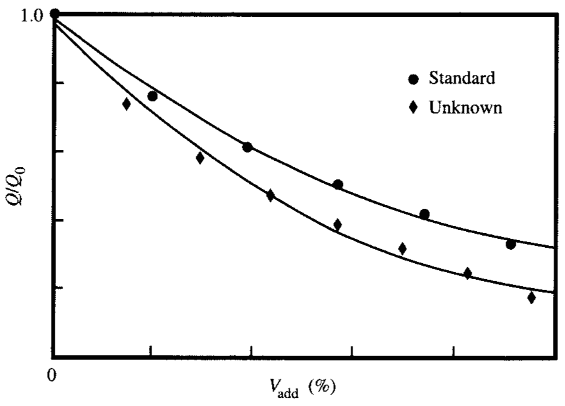

Figure 5

Schematic representation of the data gathered in the procedure of Figure 4. The normalized metal stripping charge in cyclic voltammetry, Q/Q_0, is plotted against the volume V of standard (circles) or unknown (diamonds) plating solution added to the initial volume V_0 of stock. The data are fitted to quadratic equations (solid curves).

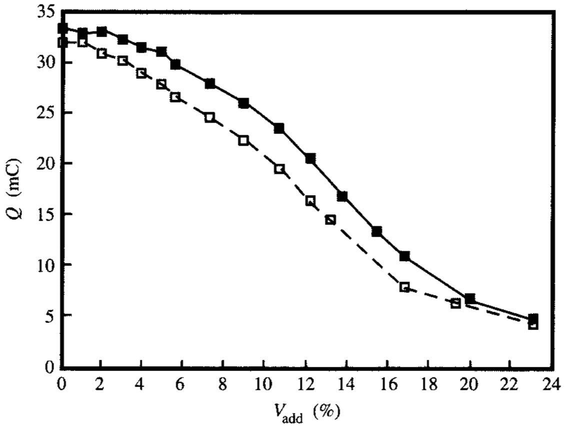

Figure 6

Dependence of the metal stripping charge, as determined by cyclic voltammetry on a Pt RDE electrode, in a stock Sn–Pb solution in MSA, without addition agent, as a function of the addition volume of a plating solution containing a known concentration of the additive. The two curves were obtained consecutively.

Polarographic analysis of additives in Sn–Pb plating

Polarography is a form of voltammetry. It is usually employed as an analytical technique for the determination of the concentrations of trace amounts of metal ions in solution. Under the well-defined mass-transport conditions of the dropping Hg electrode, when the reduction of metal ions in solution to mercury amalgam is fast, the limiting current is directly proportional to the ion concentration. In the presence of the strongly inhibiting additives used in electroplating, however, Sn and Pb deposition are kinetically limited rather than diffusion-limited. Under these conditions, polarography is completely analogous to voltammetry on an RDE; the amount of metal deposited reflects the influence of the addition agent on the electrode kinetics.

Polarography has not been commonly used for analysis of organic addition agents in plating systems. A lone example is the work of Szolnoki [27], which demonstrated a polarographic determination of surface-active components of plating solutions through their effect on the O_2-reduction reaction as measured with polarography. A pre-extraction of the surface-active species was required.

It is more relevant and simpler to use the metal-reduction reaction itself, as measured by polarography, as the probe for determining the concentration of the additive. The solution chemistry of Pb(II) is somewhat less complicated than that of Sn(II), and thus Pb(II) reduction is the better probe reaction in Sn–Pb systems.

The technique used was square-wave voltammetry (SWV), which is a form of differential pulse polarography. (See Bard and Faulker [12] for a description of

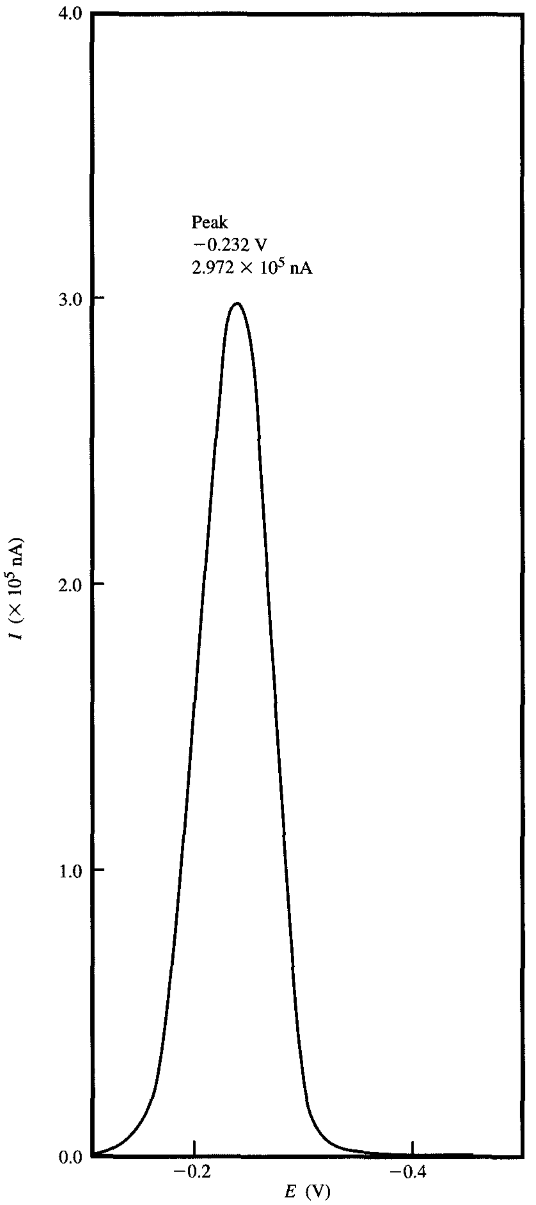

Figure 7

Output of the polarograph for square-wave voltammetry (SWV) in a 6.4-mM solution of Pb(II) in 0.1 N MSA.

polarographic methods.) The polarographic output for SWV in a 6.4-mM solution of Pb(II) in 0.1 N MSA is shown in **Figure 7**. The potential was swept between −0.1 V and −0.8 V vs. a Ag/AgCl reference electrode using the instrument's default settings for SWV (a scan increment of 2 mV, a pulse height of 20 mV, a frequency of 100 Hz, and a drop time of 1 s). In the Pb(II)-containing solution,

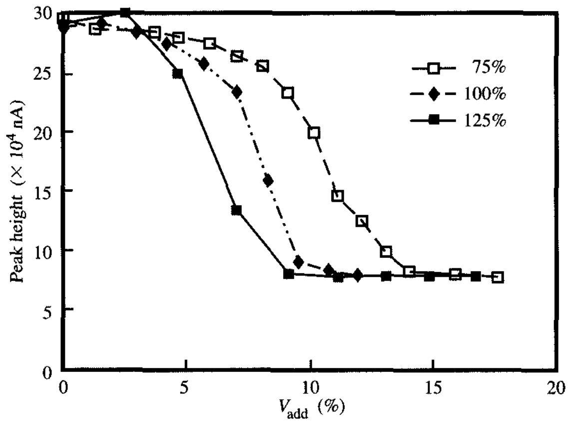

Figure 8

Dependence of the peak height for Pb(II) reduction in SWV on a DME on the addition volume of diluted Sn–Pb plating solutions with additive concentrations 75%, 100%, and 125% of the target concentration.

these conditions result in a well-defined peak from Pb(II) reduction. The polarographic procedure measures the effect of the organic additive on the height of the polarographic peak for Pb(II) reduction to determine the concentration of the additive in a Sn–Pb plating solution. The detailed procedure follows.

The test solution used was 6.4 mM Pb(II) in 0.1 N MSA. The exact concentrations are not very important, but the concentration should be the same for all of the measurements. A series of additive standards was prepared having the same metal content as the plating solution to be analyzed and varying additive levels. Each of the standards was diluted by a factor of 100 in 0.1 N MSA; the unknown plating solution was also diluted by a factor of 100 in 0.1 N MSA.

The same series of steps was followed for each standard plating solution and for each unknown plating solution. A 10-ml volume of the diluted Pb(II)/MSA stock was pipetted into the polarograph's cell, and the peak height was measured in SWV. A 0.5-ml aliquot of the diluted plating solution was added to the cell, and the peak height was measured again. The steps of addition of the diluted plating solution and SWV measurement of peak height were repeated until the peak height reached a stable, constant value.

The dependence of the peak height in SWV on the addition volume for three solutions with known additive concentration—75, 100, and 125% of the target concentration—is shown in **Figure 8**. An endpoint was arbitrarily defined for each curve as the addition volume that produces half the total change in peak height. The calibration curve is given in **Figure 9**. The concentration of additive in the plating solution is plotted against the reciprocal of the endpoint volume. The additive concentration in any unknown plating solution can be determined from this calibration curve.

The data shown in Figure 8 and those used in the concentration determinations have not been normalized to the initial charge Q_0. Because of the reproducibility inherent in the technique, normalization is not necessary. The reproducibility was examined by reanalyzing the same plating bath sample over a period of three months. No given data point differed by more than 2% from the average of all data.

The probe reaction evolves from Pb(II) reduction to a combination of Pb(II) reduction and Sn(II) reduction during the course of the titration. Since the calibration standards have essentially the same content of metal ions as the plating bath, there are no consequences to the determination of the additive concentration. It has furthermore been demonstrated that large variations of the Sn(II) concentration in the plating solution affect the analytical procedure by only a few percent.

The shape of the curves in Figure 8 is determined by the chemical nature of the additive and by its effect on the Pb(II) reduction reaction. The procedure does not fundamentally depend on the shape on the curves, however; it requires only the ability to define an endpoint with a value inversely dependent on the additive concentration. Cyclic voltammetry procedures frequently define the endpoint as some fraction of the normalized initial charge; this procedure is a viable alternative to the endpoint definition used here.

Summary

Voltammetric techniques can, in principle, be used to measure the concentrations of organic species that act as inhibitors in metal plating baths, even when these are proprietary chemicals. The metal deposition reaction on an inert electrode can be used as a probe reaction. Since the organic addition agent affects the metal deposition kinetics, the amount of metal deposited during a potential scan is a measure of the concentration of the inhibitor species.

When performed on solid electrodes, however, voltammetric monitors of the inhibiting addition agents in Sn–Pb solder plating baths are not reliable. The irreproducibility of the measurements is greater than the expected concentration variations in working plating baths. The irreproducibility is apparently caused by an inability to reproduce the surface condition of the inert sensing electrode.

A dropping mercury electrode is a clean and reproducible surface for electrochemical measurements. In contrast to cyclic voltammetry on a solid electrode, square-wave voltammetry on a dropping Hg electrode has given reproducible and reliable determinations of the polarizing addition agent in Sn–Pb plating solutions. The reduction of Pb(II) on the DME is used as the sensing reaction. Because Pb(II) reduction to the Hg amalgam is activation-controlled in the presence of the strongly inhibiting addition agent, the size of the Pb peak in SWV is indicative of the inhibitor's concentration. A peak-height vs. addition-volume relationship is determined in SWV when a Pb(II) stock solution is titrated with a plating solution. The endpoint of the titration is inversely proportional to the concentration of the additive in the plating bath. Since the measurement can be calibrated with known solutions, it is a quantitative measure of the additive concentration.

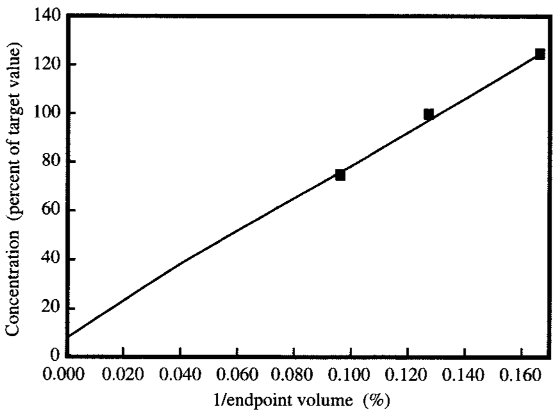

Figure 9

Calibration curve produced from Figure 8. The endpoint was taken as the volume at which half the overall change in peak height was reached. The additive concentration is a linear function of the reciprocal of the endpoint volume.

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References

1. M. Datta, R. V. Shenoy, C. Jahnes, P. C. Andricacos, J. Horkans, J. O. Dukovic, L. T. Romankiw, J. Roeder, H. Deligianni, H. Nye, B. Agarwala, H. M. Tong, and P. Totta, "Electrochemical Fabrication of Mechanically Robust C4s," *J. Electrochem. Soc.* **142,** 3779 (1995).
2. J. L. Martin and M. P. Toben, "Sn and Sn–Pb Alloy Electroplating in the Electronics Industry," *Met. Finish.* **86,** No. 1, 39–41 (January 1988).
3. W. J. Tuszynski, "MSA—Ideal Electrolyte for Electroplating," *Special. Chem.* **9,** 409–410 (1989).

4. C. Rosenstein, "Methane Sulfonic Acid as an Electrolyte for Sn, Pb, and Sn–Pb Plating for Electronics," *Met. Finish.* **88,** No. 1, 17–21 (January 1990).
5. S. H. Glarum and J. H. Marshall, "Admittance Study of the Sn Electrode," *J. Electrochem. Soc.* **130,** 1088–1096 (1983).
6. S. H. Glarum and J. H. Marshall, "Admittance Study of the Pb Electrode," *J. Electrochem. Soc.* **131,** 691–701 (1984).
7. S. Meibuhr, E. Yeager, A. Kozawa, and F. Hovorka, "The Electrochemistry of Sn. Effects of Nonionic Addition Agents on Electrodeposition from Stannous Sulfate Solutions," *J. Electrochem. Soc.* **110,** 190–202 (1963).
8. M. A. F. Samel, D. R. Gabe, and D. R. Eastham, "Electrodeposition of Pb–Sn Alloys from a Sulphamate Solution," *Trans. Inst. Met. Finish.* **65,** 116–119 (1987).
9. M. Goodenough and K. J. Whitlaw, "The Suppression of Sn, Pb, and Sn–Pb Electrodeposition by Organic Compounds," *Trans. Inst. Met. Finish.* **67,** 44–48 (1987).
10. J. Horkans, I.-C. Hsu Chang, and P. C. Andricacos, "A Rotating Ring-Disk Stripping Technique Used to Study Electroplating of Sn–Pb from Methane Sulfonic Acid Solutions," *IBM J. Res. Develop.* **37,** 97–106 (1993).
11. M. Hurley, J. Lovie, and K. Miscioscio, "Process Control in Sn and Sn–Pb Plating," *Electron. Mfg.* **36,** No. 1, 12–15 (1990).
12. A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, John Wiley & Sons, Inc., New York, 1980.
13. M. Matlosz, C. Crilon, C. Clerc, and D. Landolt, "Secondary Current Density Distribution in a Hull Cell," *J. Electrochem. Soc.* **134,** 3015–3021 (1987).
14. C. Madore, D. Landolt, C. Hassenpflug, and J. A. Hermann, "Application of the Rotating Cylinder Hull Cell to the Measurement of Throwing Power and the Monitoring of Cu Plating Baths," *Plating* **82,** No. 8, 36–41 (August 1995).
15. R. E. Smith, *Ion Chromatrography Applications*, CRC Press, Boca Raton, 1988.
16. R. Haak, C. Ogden, and D. Tench, "Cyclic Voltammetric Stripping Analysis of Acid Cu Sulfate Plating Baths, I. Polyether-Sulfide Based Additives," *Plating* **64,** No. 4, 52–55 (April 1981).
17. R. Haak, C. Ogden, and D. Tench, "Cyclic Voltammetric Stripping Analysis of Acid Cu Sulfate Plating Baths, I. Polyether-Sulfide Based Additives, II. Sulfoniumalkanesulfonate Based Additives," *Plating* **65,** No. 3, 62–66 (March 1982).
18. W. O. Freitag, C. Ogden, D. Tench, and J. White, "Determination of the Individual Additive Components in Acid Cu Plating Baths," *Plating* **70,** No. 10, 55–60 (October 1983).
19. B. Lowry, C. Ogden, D. Tench, and R. Young, "Production Implementation of Controls for Cu Pyrophosphate Circuit Board Plating Baths," *Plating* **70,** No. 9, 70–74 (September 1983).
20. D. Tench and J. White, "Cyclic Pulse Voltammetric Stripping Analysis of Acid Cu Plating Baths," *J. Electrochem. Soc.* **132,** 831–834 (1985).
21. J.-Cl. Puippe, "Anwendung der Zyklishen Voltametrie zur Überwachung eines Kupferpyrophosphatbades," *Oberfläche* **8,** 40–45 (1984).
22. W. Bauer, M. Butz, and Ch. J. Raub, "Zyklische Voltametrie als Automatisierbare Prüfmethode für die Galvanotechnik," *Metalloberfläche* **38,** 515–554 (1984).
23. W. Dahms, "Kontinuierliche Überwachung saurer Kupferelektrolyte durch Cyclische Voltammetrie," *Metalloberfläche* **43,** 345–350 (1989).
24. M. Grall, G. Durand, and J. M. Couret, "Cyclic Voltammetric Determination of Brightener Concentrations in Acid Cu Sulfate Plating Baths," *Plating* **72–75,** No. 12, 72 (1985).
25. S. Yamato and T. Tadakoshi, "Control of Additives in Acid Cu Plating," *Met. Finish.* **85,** No. 10, 67–70 (October 1987).
26. E. Budevski, G. Staikov, and W. J. Lorenz, *Electrochemical Phase Formation and Growth*, VCH, Weinheim, 1996.
27. G. Szolnoki, "Polarographische Bestimmung von Netzmitteln in Galvanischen Bädern," *Galvanotech.* **76,** 985–989 (1985).

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