



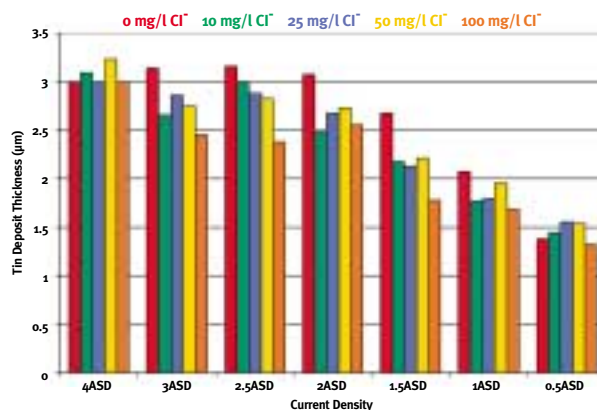
Influence of Chloride in Acid Tin Methanesulfonate Plating Solutions

In the development of E-PURE MSA® Arkema studied the effects of various impurities on the electroplating of tin in Methane Sulfonic Acid based plating solutions. The following article summarizes our research on the effect of chloride in acid tin methanesulfonate plating solutions.

The influence of trace amounts of chloride ion (< 500 mg/l) in stannous methanesulfonate solutions has been the subject of debate over the past few years. Methanesulfonic acid is produced by the chemical oxidation of methyl mercaptan CH_3SH , using a variety of oxidants such as chlorine gas, nitric acid or ozone. Intermediate methanesulfonyl chloride, $\text{CH}_3\text{SO}_2\text{Cl}$, is then hydrolyzed to produce methanesulfonic acid, $\text{CH}_3\text{SO}_3\text{H}$ (MSA). During the manufacturing process, excess chlorine and hydrochloric acid are removed from the MSA to produce a highly purified product. However, even under the best possible manufacturing conditions, it may be impossible to remove trace amounts (< 2 mg/l) of residual chloride ion in 70% MSA.

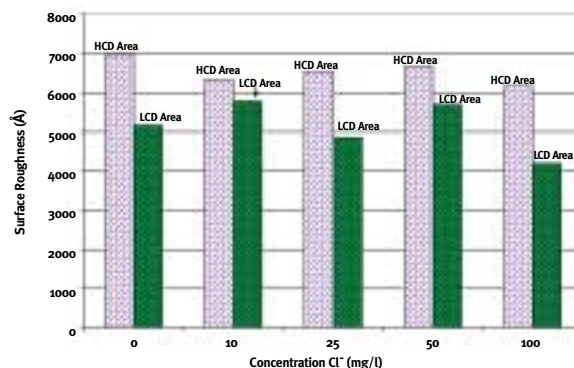
To address questions regarding the impact of Cl^- in Pb-free tin plating solutions, Arkema scientists studied the role of chloride ion and its impact during the plating of tin and changes in the composition and morphology of the deposits. Thermodynamic and electrochemical studies were performed to follow the electrochemical deposition processes with and without Cl^- and any concomitant changes in the pure tin coatings' composition, morphologies and structures.

Effects of Cl^- on Tin Electrodeposition: Thermodynamic calculations performed at Arkema's laboratories show complete solubility of any stannous-chloro species. Thus Sn^{+2} is reduced from a hydrated cation with no residual covalent Sn-Cl_x species. Electrochemical techniques including linear sweep and cyclic voltammetry, mass transport methods, potential step and impedance spectroscopy were used to study the deposition of tin and the role of Cl^- in the MSA electrolytes. It was found that Cl^- does not affect the reduction of stannous under conditions normally used to deposit a layer of matte tin. Some inhibition of tin deposition was observed at very low current densities (< $1\text{mA}/\text{cm}^2$), which are not normally used during the plating of electronic components and only when the Cl^- concentration was < 50 mg/l in the Sn-MSA solution.

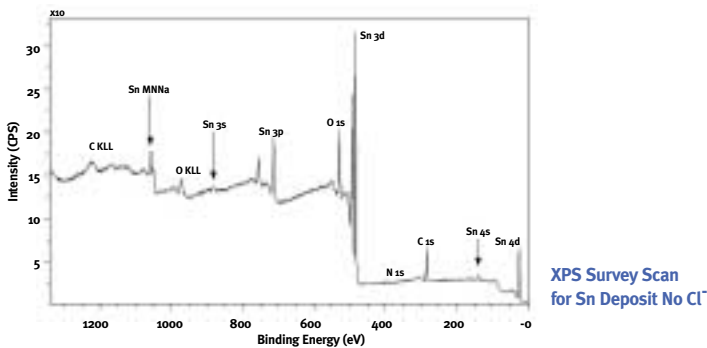


Effects of Cl^- on Sn Thickness vs. Current Density: Studies were conducted to monitor the changes in tin deposit thickness with increasing Cl^- concentration. The following graph shows that even up to 100 mg/l Cl^- in the acid tin methanesulfonate solution, the anion had little impact on the tin thickness at a given current density. The 100 mg/l Cl^- in the actual Sn electrolyte equates to about 500 mg/l Cl^- in 70% MSA (dilution of 70% MSA to ~15% MSA), a level that is never seen in a modern MSA manufacturing process.

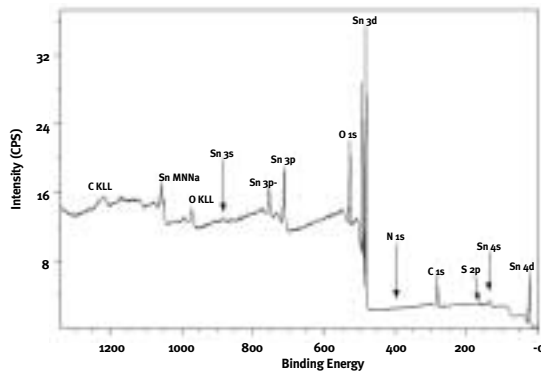
Effects of Cl^- on Surface Roughness: Surface profilometry measurements on samples plated with increasing amounts of Cl^- in the tin electrolytes showed little variation in surface roughness. The high current density (HCD) regions (~ $3.5\text{A}/\text{dm}^2$) were slightly rougher than the low current density (LCD) areas (~ $1.0\text{A}/\text{dm}^2$). The influence of chloride ion in the plating solutions on the overall roughness is insignificant even up to 250 mg/l.



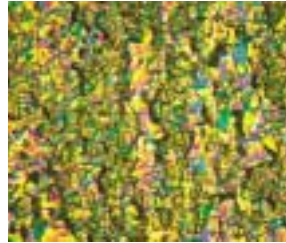
Effects of Cl⁻ on Sn Composition: Experiments were performed to monitor the changes in the purity of the tin deposit with increasing amounts of Cl⁻ in the MSA electrolytes. X-ray photoelectron spectroscopy (XPS) is a highly sensitive technique that not only identifies the elements on the tin surface but also allows one to determine the oxidation states. For example, XPS was used to determine if Cl⁻ has any effects on the surface oxidation state of tin (e.g., Sn⁰ vs. SnO vs. SnO₂) and if there is any residual Cl⁻ remaining on the surface of the tin coating, both of which may affect whisker formation, reflow or solderability. The XPS survey scan of the tin deposit plated from the solution containing 250 mg/l Cl⁻ is identical to the Cl⁻ - free deposit indicating that even with the most seriously contaminated tin electrolyte, Cl⁻ does not adhere to the tin surface:



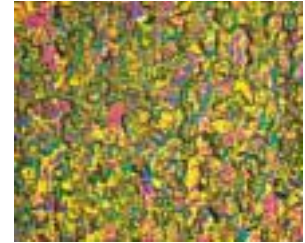
XPS Survey Scan for Sn Deposit (Plated with 250 mg/l Cl⁻)



Surface Morphology Studies: Optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques were employed to study possible changes in the surface topography of the tin coatings with Cl⁻ concentration. The optical images produced using interference contrast techniques show a slightly smoother tin surface plated with 50 mg/l Cl⁻.

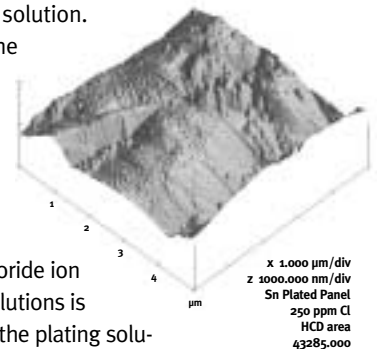


Sn Deposit No Cl⁻



Sn Deposit, 50 mg/l Cl⁻

AFM measurements confirmed a slightly smoother tin surface due to chloride ion in solution. The surface roughness (Ra) for the Cl⁻ - free deposit was 408 nm and that plated with 25 mg/l Cl⁻ was only 225 nm.



AFM Image of Tin deposit Plated with Cl⁻

Conclusions: The influence of chloride ion in stannous methanesulfonate solutions is negligible even up to 100 mg/l in the plating solution (~500 mg/l in 70% MSA). The Cl⁻ remains soluble in the tin electrolytes and is not co-deposited nor does it adhere to the matte tin coatings. It has little influence, if any, on the electrochemical reduction or mass transport processes, the roughness, composition, or morphology of the matte tin coatings.

The statements, technical information and recommendations contained herein are believed to be accurate as of the date hereof. Since the conditions and methods of use of the product and of the information referred to herein are beyond our control, Arkema Inc. expressly disclaims any and all liability as to any results obtained or arising from any use of the product or reliance on such information; NO WARRANTY OF FITNESS FOR ANY PARTICULAR PURPOSE, WARRANTY OF MERCHANTABILITY OR ANY OTHER WARRANTY EXPRESS OR IMPLIED, IS MADE CONCERNING THE GOODS DESCRIBED OR THE INFORMATION PROVIDED HEREIN. The information provided herein relates only to the specific product designated and may not be applicable when such product is used in combination with other materials or in any process. The user should thoroughly test any application before commercialization. Nothing contained herein constitutes a license to practice under any patent and it should not be construed as an inducement to infringe any patent and the user is advised to take appropriate steps to be sure that any proposed use of the product will not result in patent infringement.

BEFORE HANDLING THIS MATERIAL, READ AND UNDERSTAND THE MSDS (MATERIAL SAFETY DATA SHEET) FOR ADDITIONAL INFORMATION ON PERSONAL PROTECTIVE EQUIPMENT AND FOR SAFETY, HEALTH AND ENVIRONMENT INFORMATION.

Read more about Arkema Inc. at www.arkemagroup.com