DISPLACEMENT (IMMERSION) TIN PLATING

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Keywords: *Electroless immersion coatings, tin coatings, printed circuit boards, etching, wet angle*

Abstract: *The metal layering on the metal surface flowing without the presence of the reducing agents or an external source of electricity is called immersion plating. The salt solution of the noble metal and less noble metal substrate are needed the process to take place. The deposition of the noble metal on the plated surface is observed due to displacement process.*

The immersion plating of Tin on Copper is too popular in the production of printed circuit boards. The displacement of copper with tin in the solution of tin salt becomes. The achieved layer is characterized with better solder wettability, corrosion and oxidation protection of the surface.

The morphology observation, hardness and elasticity measurements are carried out of the Tin and Tin-DND coatings.

ИМЕРСИОННО ОТЛАГАНЕ НА КАЛАЙ

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Ключови думи: *Безтокови имерсионни покрития, калаено покритие, печатни платки, ецване, ъгъл на омокряне*

Резюме: *Процесът на отлагане на покрития върху метална повърхност, протичащ без наличие на външен източник на ток или без химически редуктор се нарича имерсионно отлагане на покрития. За да протече процесът е необходимо наличие на разтвор на сол на благороден метал и субстрат от по-неблагороден метал. При това се наблюдава отлагане на по-благородния метал върху покриваната повърхност в резултат на обменен процес между атомите на субстрата и металните йони в разтвора.*

Имерсионното отлагане на калай върху мед е много популярен метод в производството на печатни платки, при който става заместване на мед с калай в разтвор на калаена сол. Полученото покритие се характеризира с добра спойваемост, корозионна устойчивост и висока защита на покритата повърхност от окисление.

Проведени са изпитвания за твърдост, еластичност и наблюдения на морфологията на повътхността на покритие от калай и композитно покритие калай-нанодиамант.

Introduction

Displacement (immersion) plating

The process of displacement plating, or also called immersion plating, is possible to flow on the metal surface immersed in a salt solution of more noble metal. The deposition of a more electropositive metal on a substrate of a more electronegative metal is observed. A chemical replacement between metallic ions of the coating metal and the substrate metallic atoms becomes into stoichiometric ratio (fig. 1). Displacement plating requires no reducing agents or an external source of electricity which is result in difference in both process' mechanisms and its results.

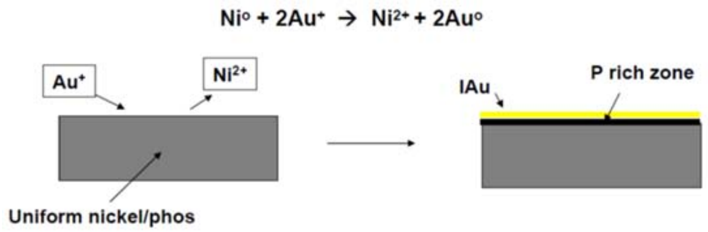


Fig. 1. The displacement reaction in which the substrate metal dissolves, as the solution metal deposits. Phosphorous does not dissolve and become concentrated at the surface [1].

The electrons are delivered to the more electropositive metal ions in solution by the metallic substrate due to its dissolution as the substrate is completely covered by the metal coating. This is a reason for the coating thickness limitation to the full covering of the substrate surface. [2]. Typical thicknesses vary from 10-200 pm.

The main advantage of the process requirements are low costs of the technological equipment and chemicals.

Immersion Deposition of Tin

Displacement reaction between copper and tin leading to a tin deposition on copper substrate is widely used in the printed circuit board technology [3-7]. According to the value of the electrode potential the tin deposition on copper is couldn't be realized. Addition of some complex agents to the solution allows the reversion to be achieved. The most used complex agent is thiourea. The produced tin coating during immersion plating characterized with a good solderability, thickness uniformity, an important property for the coatings' application in production of printed circuit boards and electronic components [8]. The spontaneous formation of tiny crystalline length growing from the surface of tin coating named whiskers are a big problem for electronic systems due to formation of short circuits leading to systems' failure. Several instances have been reported where tin whiskers have caused system failures in both earth and space-based applications. To date, there are reports of at least three tin whisker induced short circuits that resulted in complete failure of on-orbit commercial satellites. There have also been whisker-induced failures in medical devices, weapon systems, power plants, and consumer products. The mechanism of the whiskers formation is not been established. There are few suggestions regarding to the whiskers growing connected to the affection of the stress relief. Such stresses with internal compressive nature are generated due to formation of the diffusion layer (Cu_6Sn_5) between copper and tin layers and lead to the whisker growth. Some additives as metal ions could prevent this phenomena [9].

Experimental Methods

Tin coatings are deposited on the circuit board sided glass size 1mm, Copper - foiled of 35 microns thickness in the solution for immersion tin plating.

The preliminary processing for copper surface degreasing and micro etching are performed before tin layers deposition. The deposition process is performed at ambient temperature.

Two kinds of coatings are investigated: immersion tin coating and composite tin coating. The ultra dispersed diamond powder obtained by detonation synthesis (ND) [10] is used as an additive to the immersion solution. The size of ND particles is in the range 4-6nm.In [11,12] the positive nanosized condition on the material properties is proved.

The baths composition is as follows:
Stannous chloride concentration from 0.06M to 0.02M,
Thiourea(TU)-concentration from 0.3M to 1.0M,
Sulphuric acid concentration from 0.1M to 0.5M
Additives of different divalent ions of Co, Cd, Mn, Fe, Ni, Pb
Surface to be coated per Liter: 3dm2
Tinning time - 30min.
The ND particles concentration – 5 g/l, determined in [13].

The thickness of Sn coatings is determined by Back-scattering of beta-radiation method on Betascope 2045 equipment. Sometimes the direction of beta-particles is changed when going through a substance layer. This process is the scattering. The beta-particles interact with the electrons. Since the mass of the beta-particle and the electron are the same, their collisions result in a scattering with a great angle. When the change in the direction is near to 180 °, back-scattering takes place. The degree of back-scattering depends on the atomic number and the thickness of the scattering matter [14, 15].

For solderability investigation of Sn layers the solder spread test is used by the contact angle measurement. The lead free solder wire is used. The solder of 0,036-0,038g is heated at 250°C to the melting of the wire [16].

Nanoindentation testing of the tin samples is carried out using a NanoScan measuring system. The NanoScan is a unique device for surface properties investigations and measurements of hardness, elastic modulus of materials, coatings and thin films. The main characteristic feature of NanoScan is the use of piezoceramic probe sensor with high bending stiffness of the cantilever. The system is developed by Technological Institute for Super hard and Novel Carbon Materials, Russia on the principles of Scanning Probe Microscopy (SPM) and represents a scanning force microscope (SFM) of original construction, working in a regime of a rigid contact in ambient environment.

The tin coatings characteristics are investigated after deposition and after aging (corrosion test) for 10 days in an Air Humidity Chamber above the following condition: 93±3% relative humidity and T=40°±2C, which represents storage over few months.

The coatings' topography is observed by SEM Jed 100C at magnification of 2000 the tin coatings' graininess to be determined.

Results and Discussions

The obtained coatings are of gray color, dense and uniform.

The influence of different parameters on the coatings' characteristics is investigated.

The results of coatings' thickness dependence on the tinning time and working temperature are presented in Table 1 and Figure 2.

Table 1. Influence of the tinning time on the coating thickness, received at different working temperature

Tinning time, min	Thickness (d), µm					
	Sn		Sn-Co		Sn-Cd	
	T=20°C	T=70°C	T=20°C	T=70°C	T=20°C	T=70°C
1	0,76	1,19	0,51	1,19	0,79	1,32
2	0,83	1,59	0,64	1,41	0,79	1,64
8	0,75	1,80	-	1,48	0,98	2,54
10	0,88	3,60	0,58	3,22	1,14	3,18
15	-	-	0,82	3,41	-	-
20	1,16	4,37	0,90	3,77	1,36	4,67
30	1,26	4,26	1,20	4,23	1,46	7,03

The experimental results show significant influence of the mentioned parameters on the Sn deposition rate irrespective of the type of solution. The coatings' thickness increases with the increased tinning time and it is observed rapid increase at higher temperatures.

There are two cells at the tinning surface according to the Authors in [17], namely the immersion cell in which tin is cathode and is depositing on the copper surface (fig. 3a) and the corrosion cell in which the same part of tin coating is getting anode and is desolating in an acid environment (fig. 3).

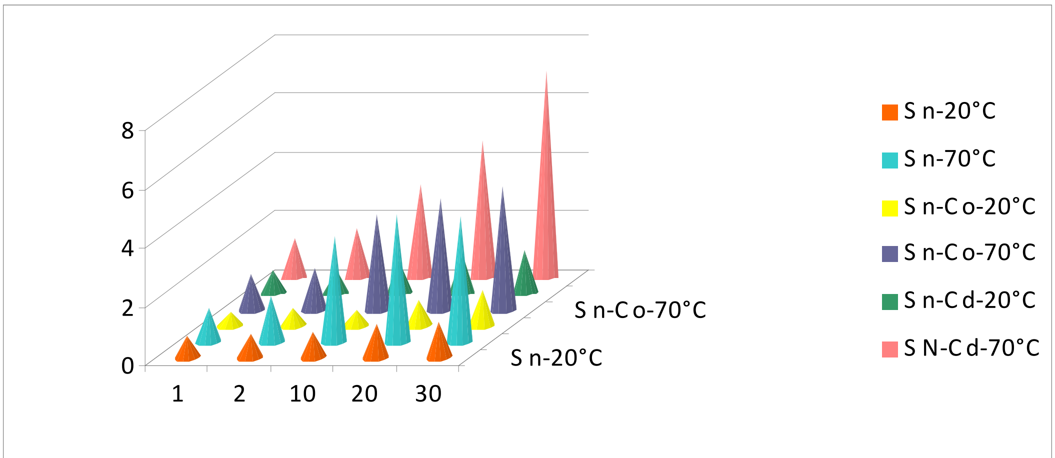


Fig. 2. Influence of the tinning time and temperature on the coatings thickness

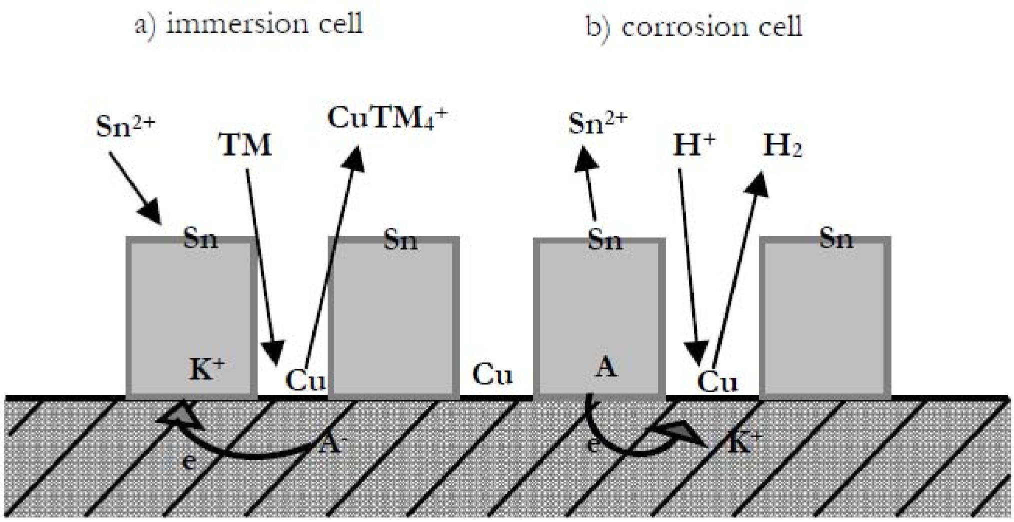


Fig. 3. The schema of galvanic cells on the surface of samples in an acid environment:
a) immersion cell, b) corrosion cell.

Given this, one could assume the greater coatings' thickness at higher temperature is due to the priority and speeding up the tin deposition process towards to the tin dissolution. This phenomenon is observed because of intensification of the chemical polarization to the cathode area through rapid chemisorption and complexation processes.

The solderability measurements are carried out for the Sn, Sn-Co and Sn-Mn layers at temperature range between 20÷80°C. The results are shown in Figure 4.

It is observed that the solderability of the coatings decrease with the temperature of the process. The presence of divalent ions (Co^{2+} and Mn^{2+}) in tin solution leads to better soldering characteristics, i.e. the contact angle decreases.

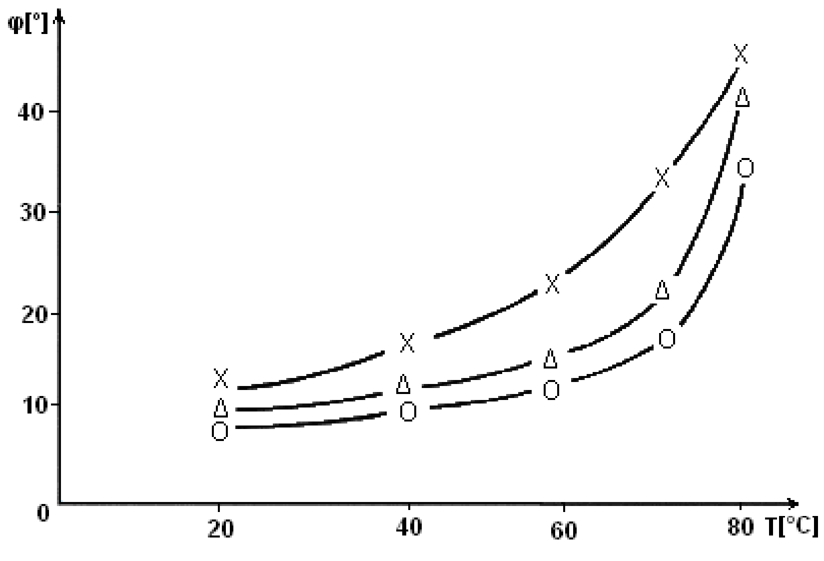
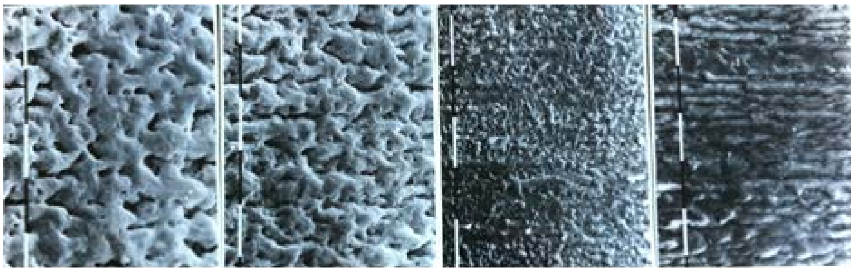


Fig. 4. The influence of the working temperature on the contact angle
(x-Sn; Δ-Sn-Mn; o-Sn-Co).

The investigation of the coatings morphology by SEM analysis at magnification of 2000 represents finer graininess for the coatings, obtained at lower temperature. The addition of the divalent ions also influences the coatings graininess. Influence of these two parameters is shown in Figure 5 and 6.



80°C 60°C 40°C 20°C

Fig. 5. SEM analysis of the morphology of tin coatings, observed at different temperatures at magnification of 2000

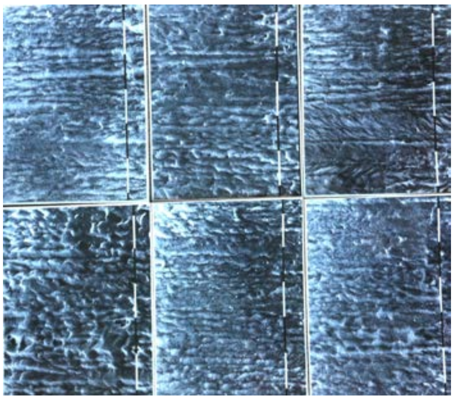
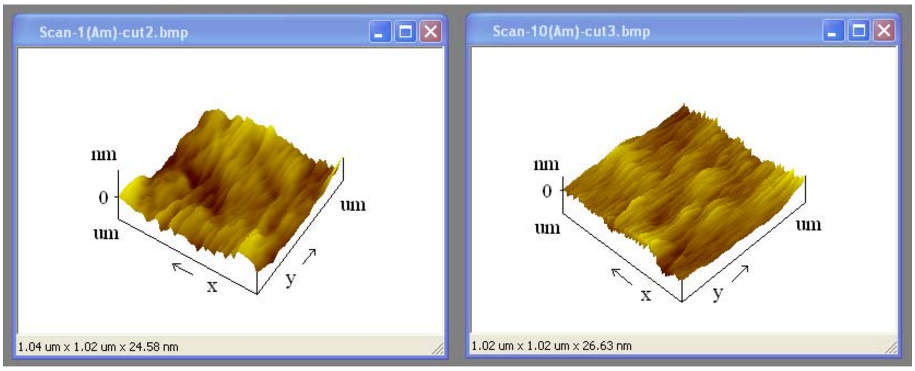


Fig. 6. SEM investigation of the Sn-Mn, Sn-Pb, Sn-Fe, Sn-Co, Sn-Cd, Sn-Ni coatings' morphology at magnification of 2000

The Nanoindentation study is carried out for two kinds of coatings: Sn and Sn-ND. The results achieved for the coatings' morphology and hardness and elastic modulus of the coatings are presented in Fig. 7 and Table 2.



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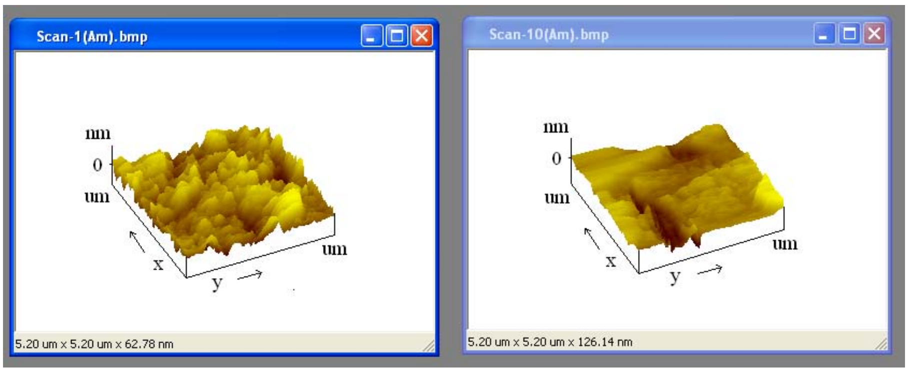

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Fig. 7. Nanoscan observation of Sn (1) and Sn-ND (2) coatings

Table 2. Elastic modulus and hardness of Sn and Sn-ND coatings

Sample	E1, GPa	E2, GPa	E3, GPa	H, GPa
Sn	90,6±8,6	42,8±4,1	14,8±1,4	6,59±0,48
Sn-ND	149,3±14,2	69,1±6,6	35,4±3,4	7,37±0,64

The addition of nanodiamond particles to the solution for tin plating leads to formation of a finer morphology of the obtained coatings' surface, characterized with enhanced elasticity and increased hardness.

Corrosion after aging at above mentioned conditions of the coatings without divalent ions additives is to a greater extent in comparison to this one of the tin coatings with divalent ions additives, despite getting on a fine structure. The presence of divalent ions in the immersion solution also leads to formation of uniform, equal tin layers with grains characterized with a fine structure which is one of the reasons of good corrosion resistance. It is found no influence of the corrosion aggressive environment on the contact angle for all of the tested coatings.

The coatings' solderability is retained after a stay 45 days, no change of the contact angle value also is observed for all of the tested coatings.

Conclusions

Analysis of the results achieved leads to the conclusion:

It is observed that the addition of divalent ions in a working solution causes a different rate of the crystalline nucleus formation and their growth, leading to finer crystalline structure.

It is found the higher temperature of the working solution is a reason for a coatings' crystal grain enlargement.

It is determined the more fine coatings are, the wettability (accordingly solderability) thereof is better.

The aasumption is made the better solderability of the coatings produced at ambient temperature in a solution with additives of divalent ions could be explain with their finer structure.

It is concluded the contact angle value, respectively solderability is kept the same after aging in corrosion aggressive environment as well as after a 45 days stay for all of the tested coatings.

It is observed that the influence of the divalent ions is weaker than that of the working temperature.

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