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Physicochemical Processes at the Interface of Heterostructures Ag-Pd – Sn-Pb

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Physicochemical processes taking place at the interface of film elements (conductors) of hybrid integrated circuits, thick-film sensors and other microelectronic devices (MED) based on silver-palladium pastes and elements of standard soldering materials have been studied. Physicochemical mechanisms of processes of the material element mutual dissolution at the interface are proposed and analyzed. Conclusions are made that these processes affect the degradation of the electrophysical parameters and contact switch connections operational characteristics. It is established that the degradation main cause (partial or complete destruction of the contact connections on substrateceramics (glass) Ag-Pd – Sn-Pb) is the functional film material significant dissolution in the Sn-Pb melt.

Keywords: interface boundaries of heterostructures, physicochemical processes.

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Introduction

Reducing of the overall dimensions of electronic equipment (REA) leads to a sharp decrease in the distance between the current-carrying circuits and the contacts of the switchboards, which, in turn, necessitates accurate dosing of solders and solder pastes. In such cases, the geometric dimensions (thickness, width) of the soldered layers decrease sharply (so-called skeletal soldering) and the significant factors determining soldering reliability and quality are physicochemical processes occurring at the interface of the solder material - low temperature solder. In the study of the contact processes occurring during the soldered layer formation, there is a need to consider the processes at the interface "hard metal - liquid solder". Determining the parameters of such thermodynamic metastable systems is complicated by the presence of phase transitions of the first kind and is carried out mainly using various approximations [1]. A rather strict mathematical approach to the description of processes at the "solid metal - liquid solder" boundary leads to the problem of the "Stefan problems" [2, 3, 4].

I. Research and discussion of the results

As shown by our studies [5, 6], the main reason for the soldered connections failure in microelectronic devices (in the case of skeletal soldering) is the contact destruction due to liquation processes occurring at the interface. Therefore, studies were carried out on the interface between brazed metal – solder for the system conductive layer based on silver – solder POS-61. The studies were performed on a scanning electron microscope - X-ray microanalyzers.

Conductors based on silver pastes, which are soldered with POS-61 solder using industrial low-activity (low-corrosion) fluxes such as FKSP, were used as samples. The concentration profiles were made in the X-ray microanalysis mode with wavelength dispersion on the longitudinal section of the soldered layer.

The photomicrograph (Fig. 1) shows the degradation (oxidation) of the Sn-Pb layer as a result of physicochemical processes at the interface.

Fig. 1. Sn-Pb degradation (oxidation of the solder layer). Raster electron microscope. Mode of superimposition of secondary electrons. 1000x magnification.

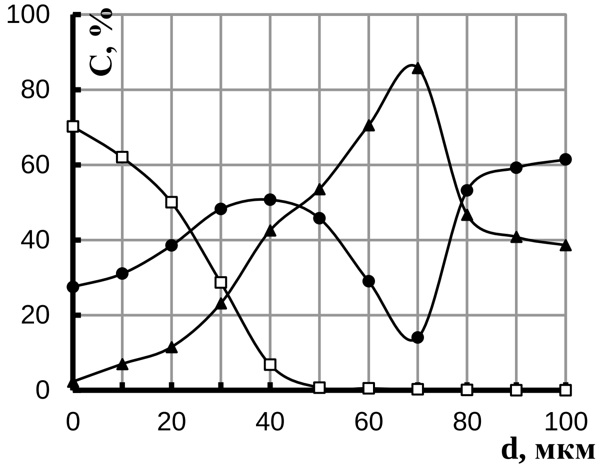

Fig. 2. Distribution of Ag, Sn, Pd concentrations at the interface between Ag-Pd and Sn-Pb. ● - Sn, ▲ - Pd, □ – Ag.

It should be noted that in the study of soldered layer diffusion zones in the area of significant quantitative differences in chemical composition there occur distortions associated with the X-ray passage through the studied microvolume and then through the region of another composition. To reduce these distortions, the test samples were positioned so that the detected X-ray beam was parallel to the diffusion front (interface). In this case, the compositions of the excited area and the X-ray output area is approximately the same. Accurate adjustment of the spectrometer to the peak line was achieved by stepwise scanning of the crystal-analyzer at angles in the peak region and measuring of the peak intensity at each angular position. Estimation of silver, tin and lead concentration was performed by scanning the electronic probe perpendicular to the interface by measuring the maximum intensities of the X-ray spectra characteristic lines, followed by recalculation in the values of the element concentrations. The error of these values was determined by the hardware error when measuring the line intensity, because the recalculation in the concentration was carried out using constant coefficients. The hardware error obtained on the standard samples was not more than 1 %. The distribution of the concentration of the main element of the solder and the soldered material on depth of the soldered seam diffusion zone *d* (Fig. 2) has been received.

The starting point for the calculation of the concentration distribution in the junction zone was the point $d = 0$, in which the silver concentration did not exceed 70%, because in the area with its higher content the calculation of the ternary system concentrations would lead to a large error due to low intensity of the lead characteristic X-ray signal. The lower limit of the boundary region studies was the point at which the value of the silver signal intensity approached the background level.

Figure 2 shows that the interaction of the solder melt with the soldered material leads to a strong redistribution of the solder main components (liquation) with the release of tin in contact with the silver conductor and the lead predominant crystallization in a more remote area (60 - 70 μm).

Distribution of the of Ag, Sn and Pb element concentration obtained in the region of the interface is characterized by a sharp increase in the CSn / CAg (n = 12 - 2.3) concentration ratio in the range of high silver (70.2 - 27.7 %) concentrations compared with solder PIC-61, where n = 1.6 - 1.7. This fact indicates the tin predominant content in the area of contact with the silver conductor. When the silver concentration decreases, there is an equalization of the tin and lead concentrations, then there is an increase in lead concentration to 85.8 %. In the soldered layer boundary region at a distance of 90 - 100 μm from the interface, the solder main component concentrations are equalized and its composition approaches the eutectic (n = 1.45 - 1.7).

Thus, the interaction of solid metal and liquid solder at a temperature of 250 °C together with the redistribution of the solder components leads to the low gradient of the silver concentration at the interface. This soldered metal distribution in the region of silver low concentrations can be explained by the presence of the dissolution process, which occurs by several mechanisms. Using the approach [4] it is possible to determine the process parameters by kinetic and diffusion mechanisms.

1. Kinetic mechanism (diffusion through the interfacial boundary). For the dissolution rate it is true:

$$dN / dt = \omega_T \rho\, S - \omega n S\,, \tag{1}$$

where N is the number of atoms remaining in the liquid solution; t - time; ω_T - the probability of the solid metal transition to liquid; ρ - solid metal surface density; S - the contact region area; $\omega_T \rho S$ - the number of atoms leaving the site; ω - crystallization rate; n - the liquid metal solution concentration.

By the saturation time, the dissolution rate becomes zero:

$$\omega_T \rho - \omega n_\infty = 0\,, \tag{2}$$

where n_∞ is the saturation concentration determined by the liquidus of the state diagram.

Using (2) and replacing N with nV_l (V_l - volume of liquid solder), we obtain the dependence for the dissolution rate in the form:

$$dn / dt = \omega_T\rho\ (S / V_l)\ (1 - n / n_\infty)\ , \qquad (3)$$

where n_∞ is the saturation concentration determined by the liquidus of the state diagram.

Integrating expression (3) over time and assuming that at the initial moment the concentration of the solution is zero, we find the final form of the equation describing the kinetics of dissolution:

$$n = n_\infty \{1 - \exp [- (\omega_T\rho / n_\infty)\ (S / V_l)\ t]\}. \qquad (4)$$

2. Diffusion mechanism (heterodiffusion of dissolved metal in liquid solder, which leads to a change in chemical composition).

The dissolution rate is determined by the diffusion rate. The number of atoms transferred to the solution per unit time is equal to the product of their diffusion coefficient in the liquid metal on the concentration gradient of the dissolved metal and the area S. The concentration gradient is defined as $(n_\infty - n)\ \delta$, where δ is the thickness of the boundary layer.

The expression for the rate of change of the number of atoms in solution is written in the form:

$$dN / dt = DS\ (n_\infty - n)\ \delta \qquad (5)$$

For the rate of change of solution concentration we obtain the equation:

$$dn / dt = DS\ (n_\infty / \delta)\ (S / V_l)\ (1 - n / n_\infty). \qquad (6)$$

Integrating (6) under the same initial conditions as (3), we obtain:

$$n = n_\infty \{1 - \exp [- (D / \delta)\ (S / V_l)\ t]\}. \qquad (7)$$

In our case, when the dissolution rate depends on the transition of atoms into solution and the diffusion rate (both mechanisms operate), the dissolution process leads to the following distribution of dissolved metal concentrations obtained in the same way as (4) and (7):

$$n = n\infty \{1 - \exp [- (\omega T\rho / n\infty)\ (D / \delta)/(\omega T\rho / n\infty)\ + \\ + (S / Vl)\ t]\}. \qquad (8)$$

Denote by α the quantity $(\omega_T\rho / n_\infty)\ (D / \delta) / (\omega_T\rho / n_\infty) + (D / \delta)$ and call it the dissolution rate constant. Then:

$$n = n\infty \{1 - \exp [- \alpha\ (S / Vp)\ t]\}. \qquad (9)$$

Converting this dependency to a form:

$$\exp [\alpha\ (S / V_l)\ t] = n_\infty / (n_\infty - n) \qquad (10)$$

after logarithmization we get:

$$\alpha = (V_l / S)\ \ln [n_\infty / (n_\infty - n)]. \qquad (11)$$

The dissolution rate constant α can be determined by the tangent of the angle of inclination:

$$\alpha = (V_l / S)\ tg\ \varphi$$

from the graph constructed in the coordinates $\ln\ [n_\infty\ /\ (n_\infty\ -\ nt)]$ where nt is the value of silver concentrations, taking into account (11).

Conclusions

Based on the research, the following conclusions can be drawn:

1. Physicochemical processes that take place in the interaction of film heterostructures based on Ag-Pd - Sn-Pb lead to a strong separation of the main components of PIC-61 (segregation). At the interface of the soldered joint, a two-layer zone is formed - an area that is enriched with tin (tin content - 2.3 - 22.1 %), and which is prone to allotropic transformations, and an area with a high lead content (45.5 - 85,8 %), corrosion unstable and mechanically weak.

2. The negative effect of the liquidation of tin-lead alloy is most pronounced in skeletal soldering with a limited dosage of solder, especially if the geometric dimensions of the soldered seam (thickness) do not exceed 100 μm.

3. The formation in the initial glass matrix of intermetallic compounds Ag_xPd_y and solvate systems of complex spatial structure of the $Me(OH_2)$ type blocks the diffusion of tin into the matrix and prevents the dissolution of its other components (Ag, Pd) in the tin-lead melt.

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Фізико-хімічні процеси на границі розділу гетероструктур Ag-Pd – Sn-Pb

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Досліджено фізико-хімічні процеси, що мають місце на границі розділу плівкових елементів (провідників) гібридних інтегральних схем, товстоплівкових сенсорів та інших мікроелектронних пристроїв (МЕП) на основі срібно-паладієвих паст і елементів стандартних припійних матеріалів. Запропоновано і аналізуються фізико-хімічні механізми процесів взаєморозчинення елементів матеріалів на межі розподілу. Робляться висновки щодо впливу зазначених процесів на деградацію електрофізичних параметрів і експлуатаційні характеристики контактних з’єднань. Встановлено, що основною причиною деградації (часткова або повна руйнація контактних з'єднань на підкладці кераміка(скло) Ag-Pd – Sn-Pb є значне розчинення функціонального матеріалу плівки в розплаві Sn-Pb.

Ключові слова: границі розділу гетероструктур, фізико-хімічні процеси.