Vol 15 No 11, November 2006
1009-1963/2006/15(11)/2746-05

Chinese Physics

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and IOP Publishing Ltd

Experimental study of surface crystallization on integrated circuit chips

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(Received 7 January 2006; revised manuscript received 27 May 2006)

A surface crystallization phenomenon on bonding pads and wires of integrated circuit chip is reported in this paper. Through a lot of experiments, an unknown failure effect caused by mixed crystalline matter is revealed, whereas non-plasma fluorine contamination cannot cause the failure of bonding pads. By experiments combined with infrared spectroscopy analysis, the surface crystallization effect is studied. The conclusion of the study can provide the guidance for IC fabrication, modelling and analysis.

Keywords: infrared spectrum technology, bonding pad, crystallization, failure
PACC: 7850G, 7340, 7340J, 8160B

1. Introduction

Surface crystallization effect on bonding pads and wires of integrated circuit (IC) chip is caused by corrosion of external materials, which is one of reasons of IC failures. Currently, bonding wire crystallization on Cu ends of IC seal package on printed-circuit board(PCB) has been reported.[1] The resulting matter of crystallization mainly is $CuCl_3$. Effect of Sn–Pb solder and flux performance on solder joint quality has also been reported,[2] but it is not addressed that these materials can cause corrosion on solder joint. In failures occurring at semiconductor (IC) circuit, of which 40% is the failure in aluminium bonding system.[3] Most of the failures are the internal corrosion on bonding pads, which is caused by insufficient cleaning of the soldering interface. It is studied that there is fluoride-bearing polymer or chemical bond of complex on semiconductor chip surface.[4] A resistance model based on the free volume in very large scale integration interconnection electromigration and a study of the change of resistance were reported in Ref.[5]. The analysis of aluminium interconnection was researched from the viewpoint of thermal stress and electrical stress in Ref.[6]. But it has not been reported that surface crystallization causes deep corrosion on wires and bonding pads as described in this paper. Through plenty of comparison experiments combined with Mangan-IR750 Fourier transform infrared spectroscopy analysis, surface crystallization effect is studied in this paper. The results show that the surface crystallization on wires and bonding pads are caused by mixed effect of materials during IC manufacture, such as solder, flux, cleaning agent and fluorocarbon oil.

2. Description of crystallization effect

Some of IC chips failed as disqualification of the electric performance test after normal processing and screening. Examined with a 40× binocular microscope, it is found that there is surface corrosion, white or faint yellow crystallization matter occurring on bonding wires and pads, as shown in Fig.1 (micrograph of corrosion chip). Occasionally a blackening effect occurs at a bonding joint, as shown in Fig.2 (micrograph of corrosion of bonding joint).

As a preliminary conclusion, it is possible that external material causes chemical reaction and results in corrosion on chips, so as to fail the electric performance of chips. External materials may be high temperature fluorocarbon oil, cleaning agent or adhesive, which can have effect separately or together. Later

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screening process, such as high temperature storage, temperature cycling and high temperature electric aging, makes the effect more serious, but the effect has no direct relation to the chip's bulk material.

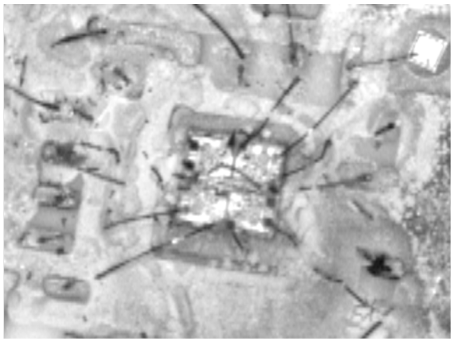


Fig.1. Photomicrograph of a corroded IC chip.

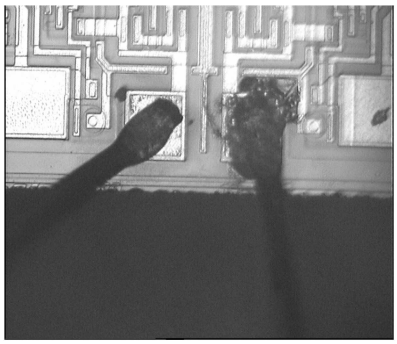


Fig.2. Photomicrograph of the bonding pad.

3. Test result and analysis

The operation principle of the Fourier transform infrared spectrum technique is a kind of frequency modulation interference with an interferometer. Using the corresponding relation of interference image and spectrum, we can obtain the spectrum by measuring interference image and by performing Fourier transform. It can simultaneously measure and record the spectrum information. By the absorbing characters of material to infrared light, it is realized to identify the structure of material and to do the qualitative and quantitative analysis.

For the corrosion effect on chip surface, samples are analysed with the Fourier transform infrared spectrum technique in order to identify the external materials and components. Figure 3 is the electron energy spectrum graph these matter. It is shown from the graph that in the corrosion area at the centre of chip there contain fairly large amount elements of Na, F, Cl, Sn, Pb, O, C etc. From left to right in Fig.3, each peak represents Pb4f, Cl2p, C1s, Sn3d, O1s, F1s, Okll, Ckll, they are denoted by a, b, c, d, e, f, g and h respectively. It is necessary to explain why there are not silicon and aluminium in the analysis result, because it is difficult to select sampling from crystallization materials at the bonding wires or pads, so we select it from chip surface. The components of the mixed materials are shown in the Table 1.

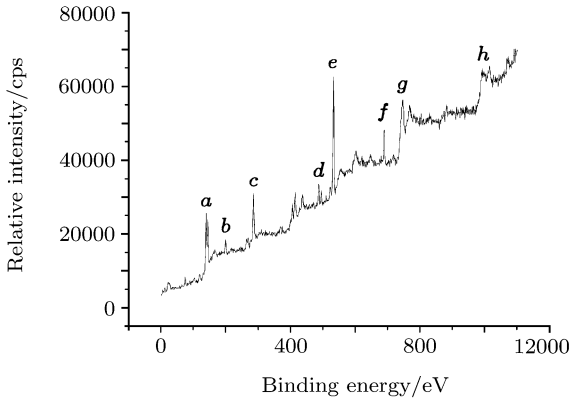


Fig.3. Fourier transform infrared spectrum analysis for the mixed materials.

Table 1. The composition of mixed materials.

peak ID	at%	centre	FWHM	area	normal	sensitivity factor	stoic
Sn3d5(metal state)	1.44	485.30	1.70	393	91	4.30	1.000
Sn3d5(SnO_2 state)	6.51	486.68	1.80	1778	413	4.30	4.521
Na1s	7.29	1072.30	3.05	1065	463	2.30	5.066
Pb4f	16.07	138.80	1.70	6844	1022	6.70	11.170
Cl2p	26.83	198.30	2.60	1245	1705	0.73	18.648
F1s	41.86	688.75	2.60	2661	2661	1.00	29.096

When the energy spectrum is analysed, spectrum of Sn and Pb are found unexpectedly, and they indicate that there contain the two materials in the crystallization. Because only solder contains Sn and Pb, so solder can be a starting part for further study.

By testing and analysing, the results show that the above supposition is correct, that is, high temperature fluorocarbon oil and cleaning agent are external materials for occurring crystallization phenomenon. The adhesive was not directly measured in crystallization materials, but the solder of Sn and Pb existing in crystallization materials were ignored. The solder of Sn and Pb, cleaning agent and fluorocarbon oil mix together, then this mixture undergoes a long process of high temperature, and the corrosion occurs. We shall prove this conclusion via experiments.

4. Experiment

In Tables 2, 3 and 4, all tested IC samples undergo the experimental processes as follows: high temperature storage at 150°C for 24 h, temperature cycling at –65°C–150°C for 10 times, consistent acceleration 5000g, Y_1 direction, 1min, electric aging at 85°C for 72h and leak test at 20kPa for 4h. The testing conditions are as follows, temperature from –55°C to +85°C, supply voltage is 24V, load resistance is 20kΩ.

The IC's functions is as follows, the low-frequency signal was obtained after the high-frequency signal was detected, by amplify, differential, gate and compare, produced one electrical pulse output to executive stage.

The IC's typical parameters are as follows, the supply voltage is 24V, the static current is no more than 5mA, the differential output voltage is 12V, the trigger amplitude is 22 V.

Commonly it is believed that high temperature fluorocarbon oil under the pressure may leak in the cavity of an IC device through the package crack due to imperfect seal when the device is undergoing mass leak test, so corrosion occurs on the chip surface and the bonding wires. To testify the effect of non-plasma high temperature fluorocarbon oil on bonding wire and chip surface, Experiment 1 and Experiment 2 are taken, as shown in Table 2.

Table 2. The effect of fluorocarbon oil on the chip surface.

Exp.	Samples /piece	Environment	Sample treat	Storage	Visual observation	Microscope examination
Exp.1	6	normal temperature	drip a drop of high temperature fluorocarbon oil on chip surface and seal the device with two of them imperfect. curing at 150°C for 45min,	humidity:80% time: 240hr	normal on surface	no corrosion on chip surface and bonding wire
Exp.2	9		after Exp.1, add high temperature storage, temperature cycling, consistent acceleration, electric aging and leak test	no		

From the results of Experiment 1 and Experiment 2, non-plasma high temperature fluorocarbon oil has no effect on chip surface, either under normal conditions, humidity environment or a series of high temperature environments. It is excluded that high temperature fluorocarbon oil may cause corrosion.

To testify the effect of cleaning agent and fluorocarbon oil on chip surface, Experiment 3 and Experiment 4 are taken, as shown in Table 3.

Table 3. The effect of cleaning agent and fluorocarbon oil on the chip surface.

Exp.	Samples /piece	Environ -ment	Sample treat	Storage	Microscope examination
Exp.3	4	normal temperature	drip mixed rosin and cleaning agent on chip surface and seal with three of them imperfect, curing at 150°C for 45min, perform high temperature storage, temperature cycling, consistent acceleration, and leak test	no	wires normal, there is corrosion, two imperfect seal sample occur white crystallization, but not serious
Exp.4	2		drip cleaning agent imperfect seal, curing at 150°C for 45 min	normal temperature for 240 h	there is crystallization on bonding wires and pads, but not clear, intensifying after 240 h high temperature storage, temperature cycling
	2		drip cleaning agent on chip surface, no curing		
	2		drip cleaning agent and fluorocarbon oil on chip surface, no curing		there is more crystallization on bonding wires and pads, intensifying further after 240 h high temperature storage, temperature cycling

From the results of Experiment 3 and Experiment 4, cleaning agent has corrosion effect on chip bonding joint, and there crystallization occurs. Cleaning agent mixed with fluorocarbon oil may intensify the effect. In the high temperature process may intensify the effect too.

To testify the effect of Sn–Pb solder, cleaning agent and fluorocarbon oil on chip surface, simulating actual manufacturing of IC, Experiment 5 and Experiment 6 are taken, as shown in Table 4.

Table 4. The effect of the mixture materials on the chip surface.

Exp.	Samples /piece	States	Sample treat	Storage	Microscope examination
Exp.5	2	unqualified testing and unqualified seal	dip in Sn and in cleaning agent to take off rosin, perform high temperature storage, temperature cycling, consistent acceleration, electric aging and leak test	no storage	there is more serious crystallization than that observed in Exp.3 and Exp.4 on bonding wires and pads
	2	qualified testing and unqualified seal			there is much serious crystallization on bonding wires and pads, electric performance testing qualified yet
	2	qualified testing and seal			there is no crystallization on bonding wires and pads, electric performance testing qualified yet
	2	unqualified testing, qualified seal			there is no crystallization on bonding wires and pads
Exp.6	8	status as in Exp.5		storage for 500h	there is no intensifying for the corrosion in Exp.5

From Experiment 5 and Experiment 6, the mixture materials of Sn–Pb solder, cleaning agent and fluorocarbon oil have a corrosion effect on the chip bonding joint, and in the high temperature process intensifies the effect. From Experiment 5, sealing an unqualified chip is more likely the cause of the occurring crystallization corrosion, while some chips are testing-qualified, but still there exists crystallization

corrosion, to which we should pay attention. From Experiment 6, corrosion is not intensified, probably because the acting mixture has produced a complete reaction at the corrosion area.

5. Conclusion

Though the comparison experiments about the effects of fluorocarbon oil, or cleaning agent and fluorocarbon oil, as well as mixture materials (Sn–Pb solder, flux and fluorocarbon oil) on chip surface, it is testified that transparent white or faint yellow crystallization occurs on bonding wires and joints, after the chips undergo Sn-dipping, cleaning agent dipping for removing rosin, and undergo high-temperature storage, temperature cycling, consistent acceleration, electric aging and leak test. This crystallization further causes corrosion on chip surface and bonding wires.

From the study, there is no evidence that non-plasma fluorine contamination will cause the failure of bonding joint, but it is revealed that an unreported failure effect exists and is caused by a mixture of materials. By experimental examination, the corrosion is due to imperfect seals of ICs. In the manufacturing process, chips contact with this mixture of materials, reacting and causing the corrosion on bonding wires and pads of chips. By analyses, this mixture includes solder, flux, cleaning agent and fluorocarbon oil. Though the acting mechanism of the mixture materials is not clear, an unreported failure mode exists. It is concluded that the seal qualified ICs will not have corrosion effect. By adjusting the process sequence, this corrosion can be avoided. Before delivery, the ICs with corrosion may qualify the electric testing, so more serious potential problem during application exists. Advanced mechanical method such as higher consistent acceleration may clean them out. The technology of soldering first and then spicing are selected especially for manufacturing hybrid integrated circuit, whether or not it will affect ICs long-term reliability which depends on the rosin taken off after soldering. If the rosin is not dislodged in process, the corrosion crystallization will occur at chip surface, this problem must be solved when we select soldering technology in hybrid ICs manufacture.

This conclusion can guide the set up of a failure mode and the active prevention of the effect occurring, who offered the guidance.

Acknowledgments

The analysis with Fourier transform infrared spectrum was performed under the management of the Physics and Chemistry Centre of University of Science and Technology of China. The authors wish to thank the teachers.

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