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스퍼터링법으로 증착한 주석 합금층을 중간재로 사용한 순동의 저온접합법에 대한 연구

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A Study on the Low Temperature Bonding of Cu with Sn Alloy Interlayer Coated by Sputtering

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초 록 동과 동을 저온에서 단시간내에 접합시키는 가능성을 검토하기 위해서 직류 자기 스퍼터링을 이용한 코팅한 주석 및 주석-납 합금층을 중간층으로 사용하였다. 접합은 대기중 200-350℃의 온도에서 수행되었고 접합온도에 도달직후 바로 냉각하였다. 접합 계면에는 액상의 주석과 고상의 동간의 반응에 의해 η-상(Cu_6Sn_5) 및 ε-상(Cu_3Sn)으로 구성된 금속간화합물 층이 형성되었다. 전단강도로 측정된 접합강도는 접합온도에 따라 비례적으로 증가하지만 300℃ 이상에서 감소하였다. 접합강도는 2.8-6.2MPa 범위로 나타났으며, 중간층합금 성분에 따른 접합계면에서의 금속간화합물의 생성거동과 관련지어 설명되었다. 실험결과 실용적인 접합법으로서 저온 단시간 접합의 가능성이 확인되었다.

Abstract The possibility of Cu/Cu bonding process at lower temperatures in a short time has been investigated. DC magnetron sputtering of Sn and Sn-Pb alloys on Cu substrate was provided as an interlayer for bonding. Bonding was performed at the temperature of 200-350℃ under air environment and cooled immediately when the temperature was reached. It was found that an intermetallic compound layer consisted of η-phase(Cu_6Sn_5) and/or ε-(Cu_3Sn) was formed at the joint interface by the reaction between liquid Sn and solid Cu. The bond strenght, measured as the shear strength, was increased with bonding temperature, but decreased above about 300℃. The obtained strength, appeared as 2.8-6.2MPa, was explained based on the behavior of the intermetallic compound formation depending on the compositions of the interlayer. From the experimental results, the low tmeperature bonding process was believed the be applicable as a practical bonding process.

1. Introduction

Recent advances in microelectronics have allowed the integration of termendous functionality into very small physical structures. The ideal bonding process would attach a component with a solder at lower temperature, minimizing the stress level, but would withstand higher temperature to allow higher levels of assembly or permit high temperature operation of the component itself.

Many researchers are keen to develope the new and innovative bonding processes[1~7] which shorten the bonding time and decrease the bonding temperature. As a new interfacial bonding process called low temperature transient liquid phase (LTTLP) bonding[2~3] using conventional solders offers this potential. LTTLP bonding occurs when some of the base metal dissolves into the liquid interlayer of the solder alloy and causes an isothermal solidification at the bond. The interlayer can be provided by foils, electroplate, sputter coats, or any other process that deposits a thin film on the faying surface.

Although the conventional soft soldering provides the means of joining two pieces of metals at relatively low temperatures, LTTLP bonding is more advantageous due to its ability to produce the joint consisting entirely intermetallic phases which have high melting points and high thermal stability. Hence, this LTTLP process can allow components to be solder attached in the low temperature range but not remelt until a much higher temperature. This feature is unique and not achievable by any other joining technique like welding or soldering. This type of bonding process was originally investigated in the 1960′s for die bonding at temperatures of 300℃ and higher, primarily with In and Au[8)].

Experimentally, LTTLP bond was achieved by soldering first, and then immediately transferred to the dwell apparatus and holding, called dwelling, at a temperature just above the solder melting temperature with a light fixture pressure for varying amounts of time.

The investigation of the LTTLP has uncovered many more questions than answers. A better understanding of the scientific fundamentals could allow development of solder alloys specific to the base metal which would form optimum LTTLP bonds. The challenge is to make a bond develope in a short enough time to make LTTLP bonding a commercially attractive process. The reliability of the joint has always been of concern, especially as the formation of invariably brittle intermetallic compounds between the solder and the base metal[9~11)]. Theoretically, it is not clear what effect intermetallics have on the kinetics of bonding or strength of LTTLP bond joint, and the selection and control of interlayer/intermetallic must be better understood to develope the effective bonding process for many alloy systems.

The purpose of this work is to investigate the possibility of the development of high speed bonding process operable in one step at lower temperatures. In order to get an understanding for the interfacial reaction, Cu substrates sputter coated with Sn and Sn/Pb were chosen to use. This study provided a description of the experimental approach, the equipment and the investigation on the microstructure and bond strength of the joint interface.

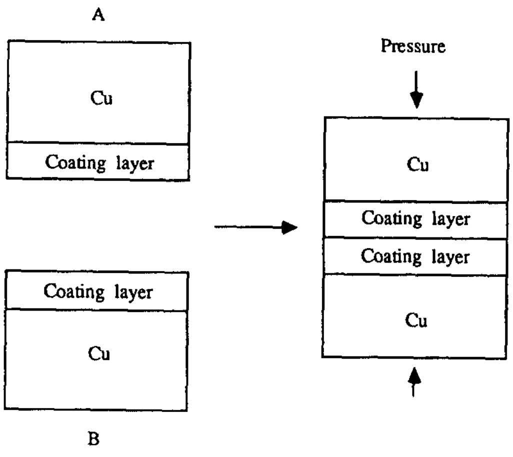
2. Experimental procedure

The base metal used, the most common base material on electronic component, was a commercially available polycrystalline copper (99.94%). The Cu substrates for microstructural examination were prepared into discs of 15mm dia. by 1.5mm in height. For the shear strength test, specimens of 15mm dia. x 1.5mm in bottom and 8x8x1.5mm square plated Cu in top were also prepared. Those substrates were ground to 600 grit, cleaned and immersed in aqua regia(3parts HCl, 1part HNO_3) for approximately 30 sec. and then dried. After these pretreatments, the Cu substrate was placed in vacuum chamber of the magnetron 3-gun, DC sputter coater (Denton 502A). Sn and Pb were coated with varied thickness of 1-6μm using 99.99% target metals. The operating condition of sputter coater was above $4x10^{-6}$ torr and 18μ Hg Ar pressure. Detailed sputtering conditions are summarized in Table 1.

After the coating was completed, two coated substrates were positioned with the coated layer in contact like a sandwitch shown in Fig. 1, which demonstrates the subsequent bonding process schematically. Bonding treatment was carried out in air using OMEGA magneflux furnace. Prior to bonding, mild chemical flux (RMA-F) was applied to all of the coated samples. The set-up was then heated up to the bonding temperature at a rate of 11℃/sec under a mechanical pressure. All samples were fixtured using Vlier screw[12)] with pressure to produce a uniform bond line and to expel flux

Table 1. Sputter coating and bonding conditions for Cu/coated layer/Cu joint

Substrate	Coating materials	Sputter coating Voltage (V)	Sputter coating Current (A)	Sputter coating Time (min)	Bonding Temperature (℃)	Bonding Time (sec)
Cu	Sn	400-500	0.1	5-60	250-350	0-1800
Cu	Sn ↓ Pb	400-500 380-420	0.1 0.07-0.08	30-40 15-20	200-300	0-60



Dimension of Specimens (unit : mm)

	A	B
Micorstructure	15ϕx1.5t	15ϕx1.5t
Shear strength	8x8x1.5t	15ϕx1.5t

Fig. 1. Schematic diagrams showing the bond joint

remnant. The bonding temperature of 200-350 ℃ was chosen to about above the temperature in which the coating materials are melted. When the bonding temperature was reached, samples are removed from the furnace and then air cooled. Detailed bonding conditions were also shown in Table 1.

The composition and microstructure of the joint was examined using optical microscope (OM) and SEM/EDX. Intermetallic phases formed at the interface were identified by XRD. To evaluate the reliability of the joint, a room temperature shear test was performed on the bonded specimens. The shear strength test was done using a custom built machine originally manufactured for testing the die bond strength on silicon chips. It was modified to measure a normal range of 0-75 lbs absolute with an over-ranging capability of approximately 50%. The motor speed and torque were independently and variably controllable. The shear force was measured by an Ametek model D75 spring force gauge accurate to ±0.5%. The shear test machine and a closed-up photo of a sample mounted in the fixture is shown in Fig. 2. All testing was performed at room temprerature with a shear loading rate of 5 lbs/sec. The primary value of this testing is to determine whether the bond joint is grossly weaker or stronger than other joints.

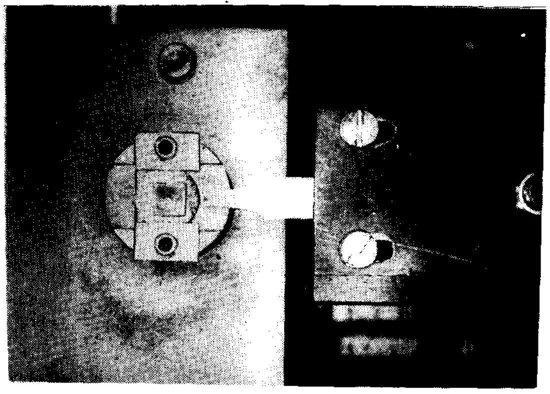


Fig. 2. Mounted sample in the fixture of shear strength testing machine.

3. Results and discussion

Microstructural analysis of joint interface

Optical micrographs of the joint interface between Cu substrates with residual Sn alloy selectively etched away are shown in Fig. 3. A thin interconnecting intermetallic layer was seen at the interface. But, it was found that the entire joining area wasn't covered uniformly by the intermetallic layer in the case of Sn coating, and this has been related with the insufficient coating thickness caused by the short coating time.

It was well known[9, 10, 13~15] that Sn formed a series of intermetallics with Cu, Sn-rich Cu_6Sn_5 (η-phase) and Cu-rich Cu_3Sn (ε-phase), and the phase formed in Fig. 3 might be one or both of the these phases.

Figs. 4 and 5 show SEM photographs of cross-section of the joint interface between Cu substrates coated with Sn and Sn/Pb. Cu-Sn

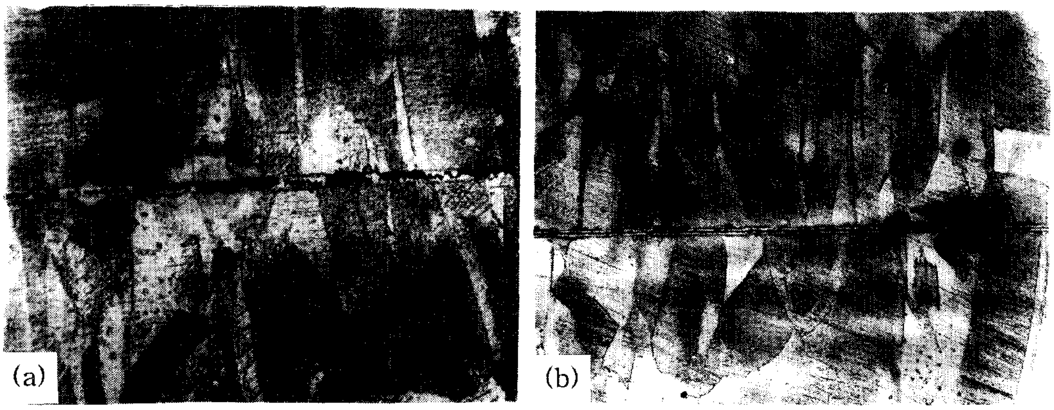
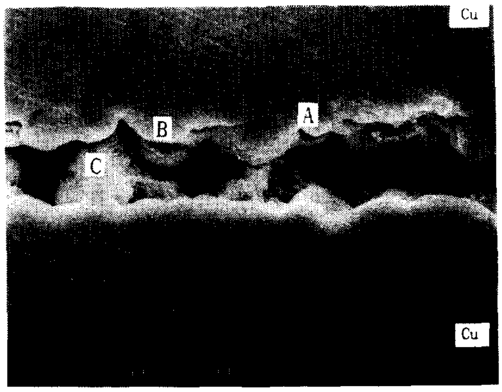
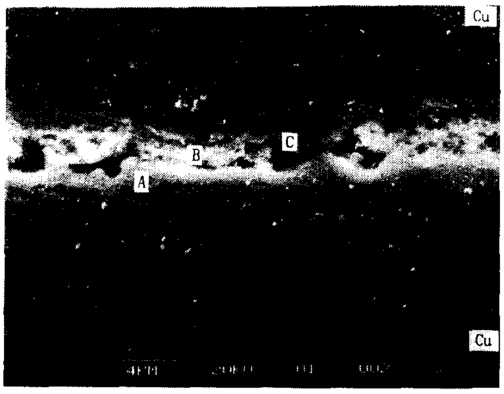


Fig. 3. Optical micrographs of joint interface between Cu substrates. (a) Sn coated at 450V/0.1A/15min., bonded at 300℃/0sec. (b) Sn/Pb coated at 400V/0.1A/30min.-400V/0.07A/17min., bonded at 280℃/0sec. (0sec means that specimens cooled immediately after the desired temperature reached.)



Element / Point	Cu	Sn	Remark
A	73.9	26.1	Cu_3Sn
B	56.7	43.3	Cu_6Sn_5
C	64.3	35.7	–

Fig. 4. SEM photographs of joint interface and microanalysis for the joint between Cu substrates coated with Sn at 450V/0.1A/45min. and bonded at 300℃/0sec.



Element / Point	Cu	Sn	Pb	Remark
A	63.9	18.7	12.1	Cu_3Sn
B	13.4	8.6	78.0	Cu_6Sn_5
C	17.5	13.1	69.5	Cu_6Sn_5

Fig. 5. SEM photographs of joint interface and microanalysis for the joint between Cu substrates coated with Sn/Pb at 400V/0.1A/40min. -400V/0.07A/17min. and boned at 280℃/60sec.

intermetallic phases formed at the interface were clearly seen in the both specimens, but their thickness and morphology were very different. The width of the joint interface in Sn coated specimen was about two times larger than that of Sn/Pb coated.

Many previous studies[13,14,16] have looked at the reaction of Pb-Sn eutectic solder on Cu. When eutectic solder was used two layers of intermetallic phases were formed. ε-phase(Cu_3Sn) was formed adjacent to the Cu and η-phase(Cu_6Sn_5) was formed next to the solder. The solubility of Cu in Sn increased at higher temperatures and this partially account for the increased thickness of η-phase(Cu_6Sn_5), and resultantly the large growth of intermetallic phases in the Sn coated specimen[9].

From the EDX analysis of the phases at the interface shown in Fig. 4 and 5, the intermetallic layer was identified at composed of η-phase (Cu_6Sn_5) or ε-phase(Cu_3Sn). It was also recognized that Cu-rich ε-phase(Cu_3Sn) was formed adjacent to Cu, and Sn-rich η-phase (Cu_6Sn_5) was formed at the coating layer side.

The forming mechanism of such phases can be explained using other's result[11] which had shown that η-phase(Cu_6Sn_5) was grown by a liquid-solid reaction between Sn and Cu, and ε-phase(Cu_3Sn) was grown by solid-solid reaction between Cu and the already formed η-phase(Cu_6Sn_5). When the reaction rate was very high, the intermetallic phase layer was not dense, and exhibited narrow channels between isolated intermetallic grains. In the channels between the grains, liquid Sn is in contact with Cu substrate, and then Cu can be dissolved in liquid Sn and diffuse via the liquid phase to the top region of the η-grains.

In order to ascertain precisely the compositions of intermetallic phases formed at the joint interface between the Cu substrates, XRD analysis was done on the fracture surfaces of shear tested specimens. The results, shown in Fig. 6, indicated that both η-phase (Cu_6Sn_5) an ε-phase(Cu_3Sn) were formed in the samples coated with Sn or Sn/Pb. While ε-phase(Cu_3Sn) has been found as dominant phase in the Sn coated specimen, η-phase(Cu_6Sn_5) was appeared predominantly in the Sn/Pb coated specimen.

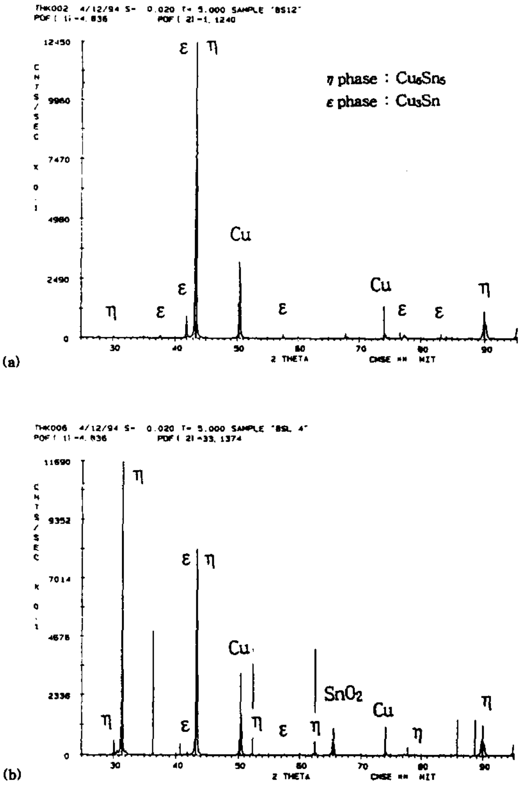


Fig. 6. X-ray diffraction patterns showing the intermetallic phases formed at the joint interface. (a) Sn coated at 400V/0.1A/30min. and bonded at 260℃/30min. (b) Sn/Pb coated at 400V/0.1A/40min. -400V/0.07A/17min. and bonded at 280℃/60sec.

But these results are considered to be available on the present coating and bonding conditions. The variation in the coating thickness and the accompanied relative content of Sn and Pb which are caused by different coating conditions may lead to the change in the compositions of intermetallic phases during the heating period of bonding process.

The relative fraction of the two phases in the intermetallic layer has been studied[17~18] as depending on the temperature and the amount of Sn. In the reaction between Cu and 95Pb-5Sn solder, only ε-phase(Cu_3Sn) was known to be formed. Apparently the smaller amount of Sn in the solder precludes the formation of Sn-rich η-phase(Cu_6Sn_5). Sn diffuses from the molten solder into the Cu and allows the ε-phase(Cu_3Sn) to form at the Cu-side interface. This hypothesis is in accord with the results in other literatures[19~20] that Sn is the fast diffusing species in the ε-phase(Cu_3Sn).

Cu_3Sn was also known[21] as the predominant intermetallic phase formed at the higher exposure temperatures. The intermetallic layer that forms on initial contact with molten solder is ordinarily η-phase(Cu_6Sn_5). However if the molten solder has a high temperature, the initial layer has more stable structure of ε-phase (Cu_3Sn).

Tu and Thompson found[22] that ε-phase(Cu_3Sn) had been formed at the expense of η-phase(Cu_6Sn_5) at temperatures above 100℃. Therefore, the ε-phase(Cu_3Sn) obtained as the dominant phase of the Sn coated specimen from XRD results can be interpreted to be formed at the expense of η-phase(Cu_6Sn_5) due to the long bonding time at high temperatures.

Fig. 7 is the SEM image of η-phase(Cu_6Sn_5) formed on the surface of the Cu substrate coated with Sn/Pb alloy, from which Sn/Pb alloy was removed by selective etching. It shows that the η-phase(Cu_6Sn_5) formed dominantly in Sn/Pb coated sample was globular structure.

Fig. 7. SEM image of the η-phase(Cu_6Sn_5) on the surface of the Cu substrate coated with Sn/Pb at 400V/0.1A/30min. -380V/0.08A/15min. and bonded at 260 ℃/0sec. (Sn/Pb alloy was removed by selective etching.)

Shear strength test

Shear strength test results with bonding temperarures were shown in Fig. 8, and indicated that the strength was greatly changed with bonding temperatures. The relatively low strength and wide scattering in bond strength can be explained in connection with the formation of brittle intermetallics. Intermetallic phases were known[23] to have a detrimental influence on the mechanical properties of the joint due to their normally high brittleness. As a general explanation, it had simply been stated that the decrease in strength are accompanied by increasing in the thickness of the intermetallic layers[24~25]. But most of the failure analysis for the intermetallic layer has been remained largely empirical and a clear understanding of the role of the intermetallics is not yet avalable.

The fact that the wide scattering in the bond strength is the consequence of the interme-

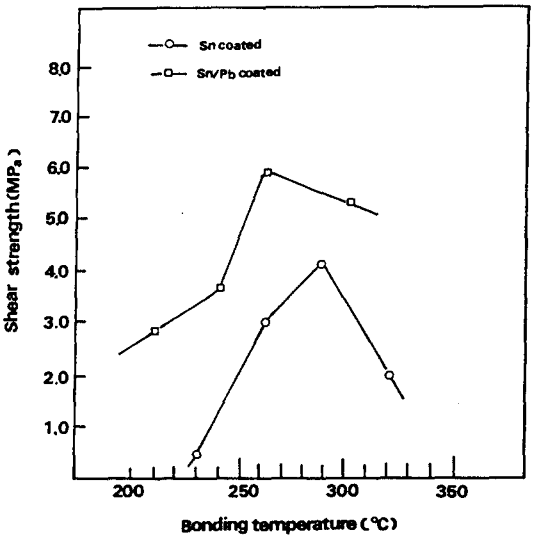


Fig. 8. Effect of bonding temperature on the shear strength of the joint for the bonding time of 0sec. The joint was coated at 400V/0.1A/30min for Sn, and at 400V/0.1A/30min -420V/0.08A/15min for Sn/Pb alloy.

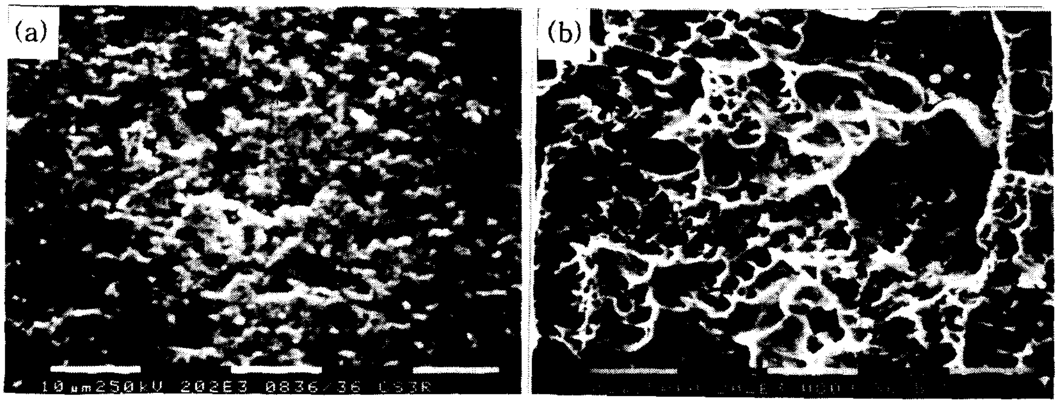


Fig. 9. Fracture surfaces of high strenth joints. (a) Intergranular fracture for the joint coated with Sn at 400V/0.1A/30min. and bonded at 290℃/0sec. (b) Ductile fracture for the joint coated with Sn/Pb at 400V/0.1A/30min. -420V/0.08A/15min. and bonded at 260℃/0sec.

tallics has also been reported[12], in which the solidification reaction was resulted from the intermetallic formation. Consequently, it has been known to be difficult to control the extent of bonding in such a process.

The fractured surface, as shown in Fig. 9, taken from the higher strength joint showed different morphologies of intermetallics. A planar shaped intermetallic phase of Cu_3Sn was seen in the fracture surface coated with Sn, and the failure was considered as intergranular fracture proceeded through this Cu_3Sn intermetallic phases. But a dimple type ductile fracture mode was seen in Sn/Pb coated joint, and failure was considered to be originated from the soft Pb-rich solder film. This fracture furface reflects that sufficient LTTLP bonds were not fully developed for this Sn/Pb alloy under those bonding conditions.

As discussed in section 3.1, detailed coating conditions may have influence on the forming of intermetallic phases. Since the failure mode and the resultant bond strength depend on the intermetallic phases at the interface, the present failure mode is interpreted as available for the present coatng conditions. Hence, in order to elucidate the formation of LTTLP bonds more clearly, more systematic investigation on the experimental parameters including coating conditions(or thickness) are proposed to be carried out.

4. Conclusions

1) This study has shown that low temperature transient liquid phase(LTTLP) bonding of Cu sputter coated Sn and Sn/Pb alloy occurred in air environment. The bonding was achieved by production of high melting intermetallics at a short bonding time of 0sec which means the specimen is immediately cooled after arriving to the temperature of 200-350℃.

2) From the XRD analysis on the fracture surface, it was found that two kinds of intermetallic phases, η-phase(Cu_6Sn_5) and ε-phase(Cu_3Sn), were formed at the joint interface. ε-phase(Cu_3Sn) was formed as a dominant phase at the interface coated with Sn, while η-phase(Cu_6Sn_5) was formed dominanatly at the joint interface coated with Sn/Pb alloy.

3) The shear strength of the joint was not so high as expected, and it was due to the formation of brittle intermetallic phases at the joint interface. And failure was occured in the ε-phase(Cu_3Sn) intermetallic layer for Sn coated joint, or in the Pb-rich solder film layer remained at the joint for Sn/Pb coated specimens.

4) In order to get more understanding of LTTLP bonding, fundamental information on diffusion rates between Cu and solder components at very low temperatures, and more elaborate analyzing technique for interface are required. Further developement of valuable LTTLP bonding process could be possible through the more systematic studies on the parameters of sputter coating conditions, bonding conditions, and on the control of intermetallics etc.

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References

1. W. D. MacDonald and T. W. Eagar, Annu. Review Mater. Sciences, **22**, 23(1992)
2. M. M. Hou and T. W. Eagar, J. of Electronic Package, **114**(12), 443(1992)
3. J. W. Roman and T. W. Eagar, International Soc. Hybrid Microelectronics Symp. Proceedings, Oct., 1992
4. Zhang, Y. C., Nakagawa, H. and Matsuda, F., Trans. Japan Weld. Res. Inst., **16**(1), 17(1981)
5. H. Takeda, M. Nakahashi and M. Shirokane, Proc. Japan Weld. Soc., spring meeting (1990)
6. Y. Nakao, K. Nishimoto, K. Shinozaki and C. Y. Kang, Proc. Int. Symp. Japan Weld. Soc. 5th Tokyo, p.133(1990)
7. S. Seto, K. Ohwaki, T. Koguchi and T. Irisawa, J. of Japan Weld. Soc., **10**(2), 246 (1992)
8. L. Bernstein and H. Bartholomew, Trans. AIME, **236**, 406(1966)
9. J. O. G. Parent, D. D. L. Chung and I. M. Bernstein, J. of Materials Science, **23**, 2564 (1988)
10. S. J. Muckett, M. E. Warwick and P. E. Davis, Plating Surface and Finishing, **79**, 44(1986)
11. Bartels, F., Gust, W. and Muschik, T., Mater. Res. Soc. Symposium Proceeding, **311**, (1993)
12. Roman, J. W., S. M. thesis, MIT, Dept. Mater. Sci. Engrg., 1991
13. W. G. Bader, Welding Research Supplement, Weld. J. **43**, 551-s(1969)
14. P. E. Davis, M. E. Warwick and P. J. Kay, Plating and Surface Finishing, **70**, 49 (1983)
15. P. J. Kay and C. A. Mackay, Trans. Inst. Metal Finishing. **54**, 68(1976)
16. K. N. Tu, Acta Met. **21**, 347(1973)
17. Z. Mei, A. J. Sunwoo, and J. W. Morris, Jr., Metall. Trans. A, **23A**(3), 82(1992)
18. V. C. marcotte and K. Schroder, Mater. Res. Symp. Proc., **19**, 403(1983)
19. I. Kawakatsu, T. Osawa and H. Yamaguchi, Trans. JIM **13**, 436(1972)
20. L. Dasilva and R. Mehl, Trans. AIME **191** , 155(1959)
21. D. Grivas, D. Frear, L. Quan and J. W. Morris, Jr., J. of Electronic Materials, **15** (6), 355(1986)
22. K. N. Tu and R. D. Thompson, Acta Metall., **30**, 947(1982)
23. D. Frear, D. Griva and J. W. Morris, J. Elec. Mater., **16**, 191(1987)
24. W. J. Tomlinson and N. J. Bryan, J. Mater. Sci., **21**, 103(1986)
25. K. R. Stone, R. Duckett, S. Muckett and M. Warwick, Brazing and Soldering, **4**, 20 (1983)