УДК 621.791

Zhang Y. P., Yi J. L., Luo Z. Y., Dong C. L., Wang X. X.

Guangdong Welding Institute, Guangdong Provincial Key Laboratory of Advanced Welding Technology, Guangdong Academy of Sciences. China, Guangzhou

ON THE DIAMOND AND COPPER BONDING WITH ALNI MICRO/NANO MULTILAYERS FABRICATED BY MAGNETRON SPUTTERING METHOD

This paper focus on the bonding between the diamond heat sink and copper stent in the LED package in which high thermal conductivity is needed. AlNi nano/micro-multilayers were fabricated and evaluated to satisfy the need to bonding copper and diamond by self-propagation for the first time. The thermal analysis results and micro structure observation showed that the bilayer (one alternative sputtering period of aluminium and nickel layers) of the mulilayers could influence the heat releasing rate of propagation reaction and help control the bonding process with steady. The influence of the Vanadium addition and the magneto-conductivity of Nickel element on the structures of the multilyers were also discussed, which has relation with the bilayer

either. The quality of the diamond-copper joint by nano-multilayer bonding is better than that of the silver glue bonding in shearing strength and thermal conductivity

Key words: Micro/Nano-multilayers; Al-Ni; self- propagation joining; diamond; intermetallic.

Rapid development in LED lighting field requires high-power LED chips. Heat dissipation problems have been one of the bottlenecks in the development of high-power chips. To improve the heat dissipation capability of LED chip, a new approach of using diamond as the heat sink material have been explored because the diamond physically has super high thermal conductivity (138.16 W/(m·K)) and insulativity [1]. However, this improvement results joining problems between heat sink and the base which traditionally were joined by glue bonding between copper and copper. Consequently, it is necessary to bond diomand and copper base together instead of copper and copper joining. Certainly, the joint should have high thermal conductivity and required reliability. Currently the potential methods include silver glue bonding and tin alloy soldering, however glue bonding joint can't have high thermal conductivity (below 20 W/m·K), and the soldering joint has to suffer the reflow process in a furnace at 260 °C which has the potential damage to those heat sensitive zones of the package. The Al-Ni multilayers have been investigated as a micro joining material by self-propagation which could bond microstructures through an intensive heat release at several microseconds [2-3]. As a novel method, the application of nano multilayer in bonding heat sink and base copper could give a solution having both high reliability and required thermal conductivity because of the instantaneous metallic bonding process. This paper investigates the probability of joining diomand and copper with Al/Ni nano multilayer films, reveals the rules of control bonding process through the bilayer structure design and shows several critical points which are worth to be concern in future study.

1. Experiments

Nickel alloy (93 wt. % Ni and 7 wt.% V) and Aluminum (Purity: 99.95%) targets were used to fabricate the Al/Ni multilayers film on stainless steel base with high vacuum magnetron sputtering method (Type: JGP-650, ShenYang scientific instruments company, The Chinese Academy of Sciences). After being cleaned by the ultrasonic with acetone for 10 min respectively, the targets were mounted in the vaccum chamber and vaccum to 6×10^{-3} Pa. The Al and Ni were alternately sputtered to the base metal until the thickness reach different series listed in table 1. The designed atomic ratio of the nickel and aluminum is 1:1. After sputtering and being stripped from the base, the prepared samples were cut to different pieces for microstructure observation (SEM, Nova Nano 430, FEI, USA) and thermal analysis (STA409 PC, NETZSCH). The phase compositions of the AlNi multilayers at different heating temperature were analyzed by X-Ray diffraction (XRD, D/MAX-RC) method.

To join the diamond and the copper base, the prepared samples were stripped from the base and cut to 3.0 mm pieces sandwiched by SAC305 solder films as bonding material. The diamond sink and the copper base in the LED package have the same size and were coated by Ti (0.1 μm) layer and Ag (1 μm). Through a DC power source (30 V, 5 A) to initiate the self-propagation reaction of the nano multilayers, the sandwich bonding materials were melted by the reaction heat to join the diamond and copper pieces together under 5 MPa pressure.

The bonded joints were polished and epoxy mounted. After being coated to have electro conductivity, they were observed and analyzed by EPMA (JEOL JXA-8100) and SEM (Nova Nano SEM 430) methods.

Table 1

The prepared AlNi nano-multilayers

Specimen No.		The bilayer (λ, nm)	Number of the bilayers (n)	Thickness of the multilayers (d,μm)
Atomic ratio design: Al:Ni=1:1	1#	125	180	22.5
	2#	195		35
	3#	250		45
	4#	350	100	35
	5#	400		40
	6#	600		60

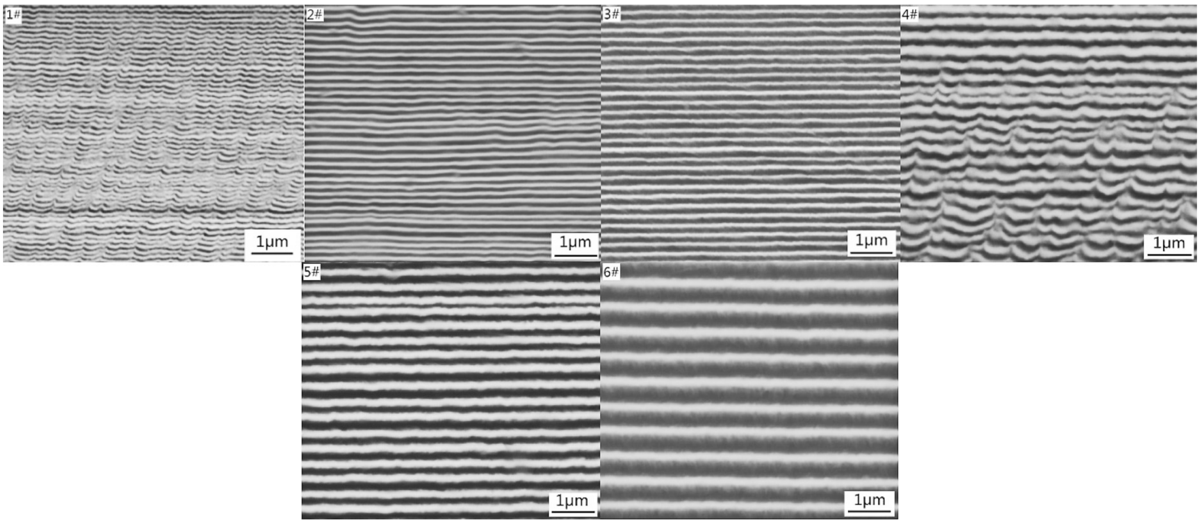

Fig. 1. Microstructure of the films

Finally, the coefficient of thermal conductivity and shearing strength of the joint were measured referring to the national standard.

2. Results and Discussion

2.1. Microstructure and phase observations

Fig.1. shows the microstructures of the prepared specimens. The bright fringes and the dark fringes represent the nickel layer and the aluminium layer respectively. The thickness of the nickel layer is 2/3 of the aluminium layer which convinced the experimental design with 1:1 atomic radio of aluminum and nickel elements. It can be seen obviously that well-defined multilayers form successfully by the magnetron sputtering method. However, the streaks inside the specimens turn to have ripple shape and change with the bilayer (λ, the thickness of the layers in one alternative sputtering period).

It has a clearly tendency that the specimen having thinner bilayers is more likely rippling when the bilayer number is constant because of the surface state of the sputtering base and the influences of the electro-magnetic effect in sputtering. This kind of ripples has a similar wave period range (300~700 nm) in spite of the change of the bilayer and bilayer number. The irregular shape of the ripples convinces the nano-effect influence of the irregular surface state, otherwise the ripples should have regular periodic shape and whose wave length will have direct proportion with the electromagnetic wave length. It is interesting that the wave period length of the ripples is almost the same as the wave-length range of the visible light (380~780 nm).

As known, the preparation of the AlNi multilayers is so heavily influenced by the magnetic permeability of nickel element that it's hardly to get the multilayers with pure Nickel target. The V doping Nickel target could limit the electromagnetic effect by forming nickel and vanadium solid solutions with low ferromagnetism [4]. The study indicates that the bilayer could also influence the electromagnetic effect in sputtering. It's necessary to design thicker bilayer in the case that vanadium element should be limited. Regular layer structures of AlNi multilayers can only be get with relatively higher bilayer (λ) and vanadium doping.

The XRD patterns of the AlNi multilayers with higher bilayer (λ=400 nm) can be seen in Fig. 2. The Fig. 2a represents the result get from the as prepared specimen. The Fig. 2b pattern is the result from the specimen after being heated to 500 . The Fig. 2c is the pattern of the specimen after 550 heating. The Fig. 2d pattern shows the specimen phase compositions at 600 . As known that the self-propagation reaction of Al-Ni system usually happens in three stages, where firstly Al_3Ni will be got, and hence got Al_3Ni_2, as well as the AlNi. It can be seen in Fig. 2 that after the reaction, AlNi becomes the dominating phase, however Al_3Ni_2 still exist as residual phase. Therefore sufficient reaction can only be got after a long time holding over 600 .

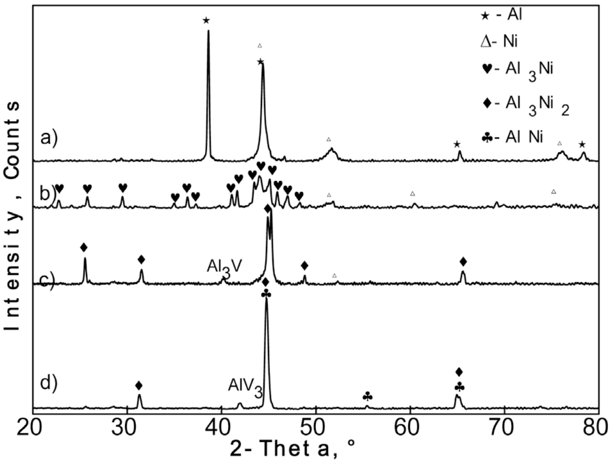

Fig. 2. XRD patterns of the layers in the reaction process when heating

If using Al-Ni multilayers as filling material to melt the solders, at least the holding temperature should be over 600 , though the ignition temperature of the self-propagation reaction could be lower to below 500 .

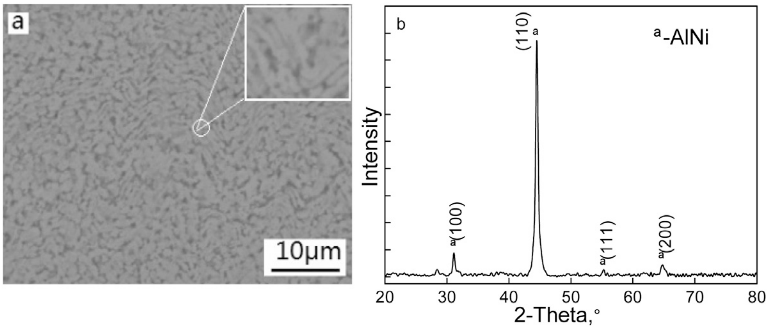

Fig.4. Morphologies micrograph (fig.4a) and composition XRD pattern (fig.4b) of a reacted sample from the specimens

2.2. Thermal analysis and reaction heat

Fig. 3 shows the thermal analysis results by the differential scanning calorimeter (DSC). Four series of heat release peaks (Series of P_1, P_2, P_3 and P_4) appear in the curves, which indicate that self-propagation reaction happens in heating process. The morphologies of the reacted specimens are the same as shown in Fig. 4a. From Fig. 4b, it could be note that the main reaction product is intermetallic of AlNi phase after sufficient reacting, see Fig. 2d. The reaction product has fine microstructure and forms typical stable self-propagation characteristic. The dark areas are voids formed in the reaction. In a sandwich bonding process, the void could facilitate the wetting of the liquid solder by the capillarity phenomenon, however the excessive closed voids inside will become defects which cannot be completely resolved.

Under the 10 °C/min heating ramp rate, exothermic peaks appear in a window range (ΔT) of 300 °C no matter what temperature the reaction of the specimen starts. The representation reactions of the peaks have been studied by variety publications [5-7]. And it has been found in Fig. 2 that the AlNi multilayers react to form phases including Al_3Ni, Al_3Ni_2, AlNi and $AlNi_3$ etc and eventually get intermetallic AlNi. From the patterns, it can be seen that the four stage reactions shift to higher temperature range with the increment of the bilayer (λ). This means that a higher ignition temperature will be required when using multilayer with higher bilayer to do bonding because the initiation points between the nickel and the aluminium layers decrease explicitly. Another problem can be seen from Fig. 3 is that the specimens having high flatness (see. Fig. 1 specimen no.3#, 5# and 6#) likely react more sufficiently and release more heat under the same condition (see Fig. 3), while specimen 4# is restrained by the ripples mainly due to the electro-magnetic effect. Higher bilayer specimens have more severe heat explosion in the propagation process. It can be attribute to the decrement of the total contracting area between aluminum and nickel inside the specimens. This will harm the stability of the joining process, however good for diffusion bonding when joining tough high temperature materials. Thus by controlling the bilayer, the stability and thermal input of the process could be controlled.

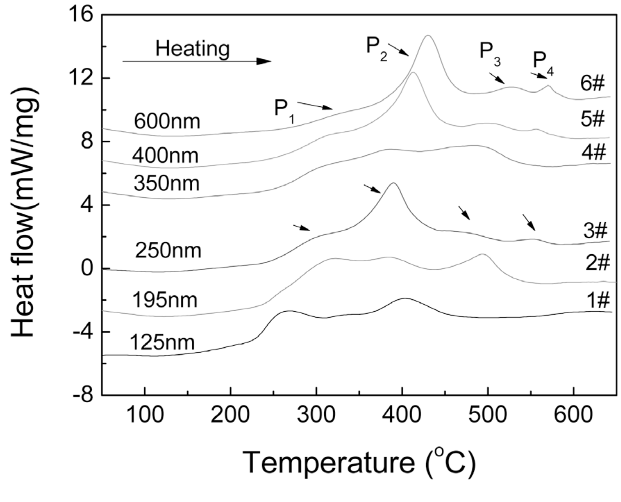

Fig. 3. The DSC curves of the specimens with different bilayers

The former study [8] of us amended a formula based on J. Wang's creative work [9] to solve nickel or aluminium rich problems which is descripted as:

$$\Delta H = \Delta H_0 \left(1 - \frac{2w + t}{\lambda}\right) \qquad (1)$$

The ΔH_0 is the maximum possible amount of heat *t*hat can be released, λ is the bilayer period, *w* represent the thickness of the intermixed layers and t is the influence factor of excessive Ni or Al.

From this study, the "*t*"could be redefined as the influence factor of V doping and magnetic permeability of nickel. The heat release of the multilayer with V element will be cost to form Ni_2V, NiV_3 and Al_xV_y ($x = 3/8/21/23/45$, $y = 1/2/4/5/7$). The electromagnetic effect on nickel will bring unsteady in the reaction. If taking the two factors into account, the heat release of the multilayers could be designed and controlled by a new formula (2).

$$\Delta H = \Delta H_0 \left(1 - \frac{2w + k\left(m - n.r\%\right)}{\lambda}\right) \qquad (2)$$

Here the *k* is a constant value determined by the mole amount of the multilayer and the input power of sputtering, the *m* is the magnetic torque of multilayer elements, *n* represents the reverse magnetic torque of the doping element and *r*% is the proportion of doping element in the multilayer.

This is the experienced rule to choose and evaluate NiAl (V doping) nano-multilayers using in this joining process.

2.3. Bonding process and joining zone analysis

Fig. 5 shows the sandwich bonding setup (Fig. 5a) and the result of the copper base and diamond sink (Fig. 5b) joining by AlNi multilayers with 250 nm bilayer and SAC305 solder.

Fig. 6 reveals the cross section state of the diamond and copper. It can be seen from the Fig. 6a that both copper and diamond sides join together by the self-propagation process though a few defects still are obvious. The defects include voids formed in joining, micro-cracks and Kirkendall pores. The dark areas inside the solder are hereditary defects and crushed local zone under bonding pressure. These imperfect problems show the process still need to be improved. By measuring the area near the interface of the diamond side (see the EDS Fig. 6b), it is known that titanium coating are melt and functions in the bonding progress, which is necessary for joining diamond [10]. This also estimates that the joining reaction temperature could reach more than 1000 °C in a few milliseconds, which is one of the advantages of this bonding process, namely supply high temperature without damaging heat spreading.

The average coefficient of the thermal conductivity of the joint is 37.7 W/K·m. This value is higher than the silver glue connection which is 10-25 W/K·m. Higher thermal transport property will allow us to develop the higher power LED components although the reliability still need more studies.

The shearing strength of the diamond and copper joint reaches 18 MPa. The value is also higher than that of the silver glue joining (6 MPa), however the shearing strength need to be further improved to convince the joint has enough reliability. The possible methods should be considered including better solder alloy (such as SnAg, SnAu and SnZn series etc.), more neat and clean contact surface, as well as thinner multilayer with proper bilayer. More works need to do for copper and diamond joining.

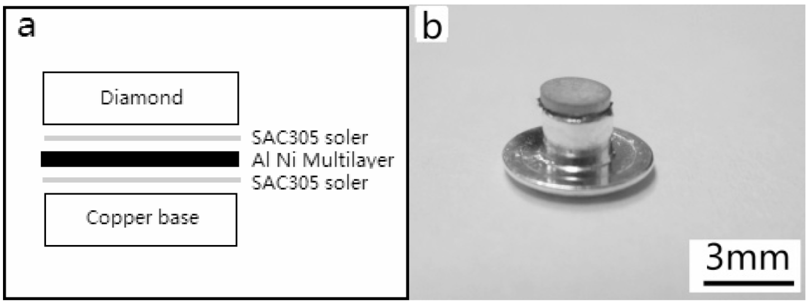

Fig. 5. Bonding method show, (a) Sandwich joining method setup (b) the joined parts

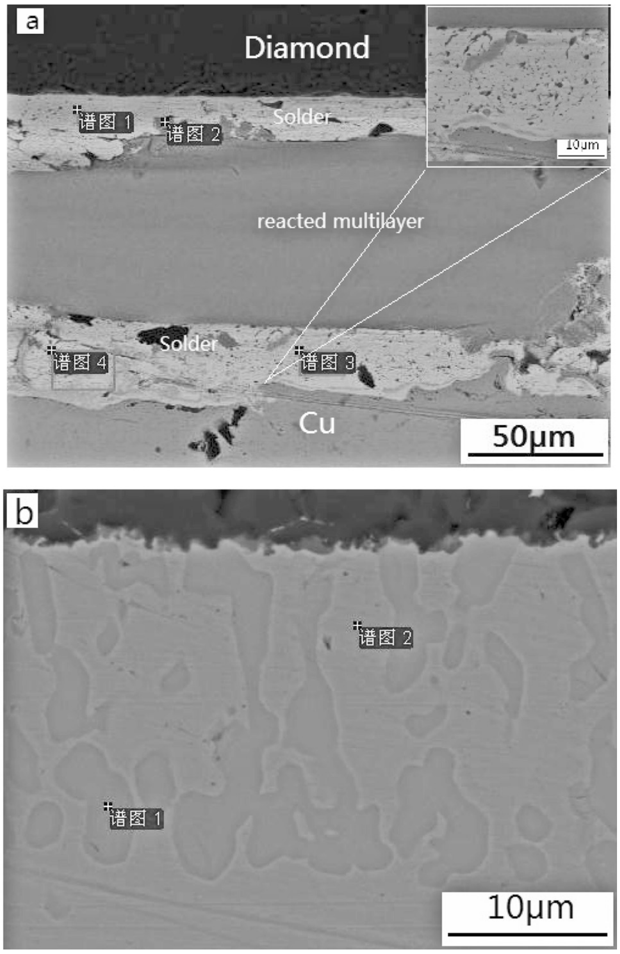

Fig. 6. Micrographs by SEM: (a) Fusion zone; (b) zone near the diamond side interface

3. Conclusions

(1) Al-Ni nano multilayer (doped by 7%V) can join the copper-diamond type LED components by the sandwich bonding method through the self-propagation reaction under initiated by a pulsed current.

(2) Though the multilayer fabrication is influenced by the electro-magnetic effect because of the ferromagnetism of nickel element, it could be controlled by the sputtering process and designing different bilayers of the nano-multilayers. The wave-period range of the rippled AlNi multilayers has relation with the wave length of the electromagnetic wave inside the sputtering furnace.

(3) The self-propagation reaction forms different intermetallics including NiAl, Ni_3Al and Ni_3Al_2. And the reaction becomes harder to be imitated with the increase of the bilayer of the specimen. Correspondingly there will be more heat release since the reaction happens at higher temperature. The ripples inside the specimens will restrain the reaction and reduce heat release.

(4) If taking the electromagnetic effect and doping process into account, the reaction heat calculation formula in our former study could be amended to a new formula which has the potential to be used to design the thermal input in bonding process, although, the work need to be estimated by experiment.

(5) The bonded components have higher coefficient of thermal conductivity and shearing strength than those of the silver glue do, however there are still defects inside the fusion zone and the reliability of the joint need further study to reveal and improve.

Acknowledgement

This work is Supported by National Natural Science Foundation of China (No.51405092)

References

[1] Zhao Qi, Dai Mingjiang, Wei Chunbei, Qiu Wanqi. Hot Working Technology[J], 2013,14: 97(in Chinese).

[2] Edward L.Dreizin. Progress in Energy and Combustion Science [J], 2009, 35: 141.

[3] Lin Tiesong, Gao Lijiao, He Peng, Gu Xiaolong, Huang Yudong, Materials Review[J], 2011, 21: 60 (in Chinese).

[4] Okamoto H. Journal of phase equilibria [J], 1993, 3:14.

[5] Edelstein A S, Everett R K., Richardson G Y, Qadri S B, Altman E I, Foley J C, et al. Journal of Applied Physics[J], 1994, 76(12): 7850.

[6] Guen K Le, Gamblin G, Jonnard P, Salou M, Youssef J Ben, Rioual S, Rouvellou B. The European Physical Journal Apply Physics[J], 2009, 45: 20502.

[7] Zalar A, Jagielski J, Mozetic M, Pracek B, Panjan P. Journal of Apply Physics[J], 2001, 61(2): 291.

[8] Zhang Yupeng, Yang Yongqiang, Yi Jianglong, Hu Haichun Materials Transactions[J], 2013, 54(6): 931.

[9] Kim H Y, Chung D S and Hong S H. Scripta Materialia[J], 2006, 54: 1715.

[10] Duckham A, Spey S J, Wang J, Reiss M E et.al. Journal of Apply Physics[J], 2004, 96: 2336.