



Solderless bonding with nanoporous copper as interlayer for high-temperature applications

Siyu Sun^a, Qiang Guo^a, Hongtao Chen^{a,*}, Mingyu Li^{a,*}, Chunqing Wang^b

^a Department of Materials Science and Engineering, Shenzhen Graduate School, Harbin Institute of Technology, Shenzhen, 518055, China

^b State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin, 150001, China

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ABSTRACT

The Cu₄₀Al₆₀ alloy has been developed as the precursor alloy to fabricate nanoporous copper (NPC) sheets through chemical dealloying in 1.6 mol/L dilute hydrochloric acid solution at various temperatures. A nanoporous structure with uniform pore distribution and size formed after the bath temperature exceeded 80 °C. The Cu–Cu interconnection was achieved by inserting the NPC sheet as an interlayer and reflowing without solder under a pressure of 10 MPa. After bonding, the thickness of NPC layer was greatly reduced and the porous structure was densified. The average shear strength of the bondlines was measured to be 22.10 MPa, and the bondlines exhibit a low electrical resistivity of 9.65 μΩ·cm. The Vickers hardness and shear strength of the bondline increased after aging at 150 °C for different time due to the densified porous structure. This work demonstrated that the NPC sheets can be used to achieve the Cu–Cu interconnection, which is a potential bonding technology for power devices operating at high temperature.

1. Introduction

As microelectronic devices are developing toward miniaturization and multi-functionalization and the service environments become more demanding, traditional silicon-based electronic devices are getting incompetent since the intrinsic physical property of Si semiconductor limits its application at temperature over 175 °C. Silicon carbide (SiC) and gallium nitride (GaN), known as wide band gap semiconductors can operate stably at temperature up to 400 °C and in other harsh environments [1]. In addition, they show much better performances than Si in other aspects such as switching losses, break-down voltage, power dissipation, etc. Nowadays, power devices based on wide band gap semiconductors find applications in many high temperature fields, such as automotive (623 K–873 K), underground oil logging (523 K–873 K), aircraft (218 K–498 K), and space exploration (733 K–753 K on Venus) [2–5]. However, no appropriate high temperature die attach material can make the most of the excellent properties of the wide band gap semiconductors, so there is an urgent demand for an appropriate die attach material in the field of power device packaging. The bonding materials need to meet the following requirements: (1) withstand higher operating temperature. (2) close to the current reflow technology parameters. (3) have better electrical conductivities, electromigration resistance and mechanical properties.

Traditional Pb-based solders are able to withstand higher

temperatures than other currently used solders. However, Pb-based solders had been prohibited by legislations in electronic devices in most countries because they are harmful to human health as well as the environment [6,7]. Other high-melting-point solders, such as Au-based, Bi-based and Zn-based alloys, have their own drawbacks including high cost, poor thermal conductivity, and poor corrosion resistance, respectively [8–13].

Currently, two technologies are getting increasing attentions for their ability to increase the melting point after bonding, i.e., nano-silver sintering [14–17] and transient liquid phase bonding [18,19]. Nano-silver particles can be sintered at a much lower temperature compared with bulk metal Ag, owing to the size effect [20]. The sintering temperature of nano-silver particles can be reduced down to 200 °C, and yet after sintering, the interconnection has a melting point of 961 °C [21]. Nano-silver paste has been used in high power devices for its high thermal conductivity, low electrical resistivity and high melting point after sintering, etc. [22,23]. However, voids are inherent parts of bondlines due to partial densification and evaporation of organic volatiles during sintering, which may lead to potential reliability issues or even premature failure [24]. Moreover, high cost and electro-migration problems are still serious concerns for mass production. Interconnection based on copper-nanoparticles solder paste has a low cost and good resistance to ion migration, but the strength of this solder joints is low due to the oxidation susceptibility of Cu, especially for nanoparticles

* Corresponding authors.

E-mail addresses: chenht@hit.edu.cn (H. Chen), myli@hit.edu.cn (M. Li).

[25]. Furthermore, at present, the preparation of nanomaterial involving a large number of organic reactions is still complex and costly. Transient liquid phase (TLP) bonding is another promising technology for die attachment in power devices [26–28]. It is achieved by the complete consumption of low-melting-point material, i.e. Sn [29,30] or In [31,32] and the formation of intermetallic compounds (IMCs) with the high-melting-point material, i.e. Cu [33], Ag [34] or Au [35]. However, this process is highly time-consuming (> 100 min), which is undesirable in industrial production. In addition, multiple hours of heating at high temperature (260–300 °C) would introduce extra thermal stress and reduce the reliability of microelectronic devices [36].

Lately, nanoporous metals are getting increasing attentions due to the larger specific surface area and other unique properties [37–39]. Dealloying, a procedure of selective dissolution of one or more components out of an alloy, has been explored to fabricate nanoporous metals. This process is simpler than the preparation of nanoparticles [40]. Kim and Nishikawa found that nanoporous silver prepared by dealloying can be used to fabricate an interconnection with Cu by thermo-compression [41]. The shear strength exhibited by nanoporous bonding under a high temperature of 300 °C was approximately 14.4–27.0 MPa, which is similar with that of conventional Pb–5Sn solder alloy. However, the bonding process still requires a high pressure of 20 MPa and a long bonding time of 30 min.

Other methods for achieving Cu–Cu bonding under relatively low temperature are shown in Table 1. According to the bonding parameters, it can be seen that the copper-copper bonding methods at low temperature have many drawbacks, such as complicated preparation process and high requirements of the surface quality and the bonding environment.

In order to address the issues mentioned above, a new method was proposed. In this work, copper-copper solderless interconnection was achieved by inserting the NPC fabricated by chemical dealloying sheet as an interlayer and heating at 260 °C for a short time without any gas or vacuum protection. Compared with these technologies, the method used in this paper has the following advantages: (1) preparation process of NPC is comparatively simple. (2) no strict requirement for the roughness of the copper surface. (3) gas protection is not required. In this work, the morphologies of NPC sheets and the interfaces of NPC/Cu-substrate were analyzed in detail. Mechanical properties and electrical performance of the interconnections were characterized as well. Moreover, the microstructure and mechanical properties of the bondlines after aging were investigated.

2. Experimental

The precursor Cu₄₀Al₆₀ alloy used in this study is prepared by levitation melting of Cu (purity, 99.99%) and Al (purity, 99.99%) at an atomic ratio of 2:3 under argon atmosphere. The resulting alloy block was sectioned into sheets with a size of 10 mm × 10 mm × 0.7 mm by wire cutting. The dealloying process was performed in 1.6 mol/L dilute hydrochloric acid solution under water bath at room temperature, 65 °C, 80 °C and 90 °C, respectively, until no obvious bubbles emerged. The aim of the dealloying process is to completely remove Al in the precursor alloy and form nanoporous copper with uniform pore sizes. The

as-dealloyed NPCs were rinsed with deionized water and anhydrous alcohol, then dried in vacuum drying chamber. The NPCs were kept in an inert atmosphere glove box to avoid oxidation.

After applying flux, the NPC sheet was sandwiched between two pieces of 10 mm × 10 mm × 3 mm Cu substrates which had been ground and ultrasonic cleaned by acetone. The Cu/NPC/Cu sandwiched samples were then bonded at 260 °C for 5 min under a pressure of 10 MPa. All the processes are schematically shown in Fig. 1.

The cross-sections of samples were ground with SiC papers and polished with Al₂O₃ polishing suspension down to 0.05 μm. In order to remove smearing between ductile interlayers, the cross-sections were subsequently treated by argon ion beam flat milling (Leica EM RES102). Focused ion beam (FIB, FEI HELIOS 600) was adopted to characterize the bonding interface. The morphologies and microstructures of the precursor Cu₄₀Al₆₀ alloy, the as-dealloyed NPCs and the interfaces of the interconnections were characterized by optical microscope (MVC1000-D23) and scanning electron microscope (SEM, Hitachi S-4700) attached with energy dispersive spectrometer (EDS, EDAX XM4). Vickers hardness (HM-200A) was employed to characterize the hardness of the bondlines in the as-soldered joints and the joints aged at 150 °C for 1–15 days. The shear strength was measured by a universal tension and compression testing machine (East/WDN-100) at a strain rate of 0.2 mm/min. The reported shear strength was obtained by averaging the values of at least five samples. Fracture surfaces of some typical joints were characterized by SEM with an acceleration voltage of 15 kV. Moreover, the resistance of the samples was measured by the four-point-probe procedure (KEITHLEY 6221).

3. Results and discussion

3.1. Characterization and formation mechanism of nanoporous copper

Fig. 2(a) shows a typical microstructure of as-fabricated Cu₄₀Al₆₀ alloy. Two distinct phases, CuAl and CuAl₂, constitute the Cu₄₀Al₆₀ alloy, as confirmed by EDX results shown in Fig. 2(b) and (c), respectively. Morphologies of NPC sheets formed by dealloying of Cu₄₀Al₆₀ alloy at various temperatures are shown in Fig. 3.

The NPC sheets dealloyed at room temperature show heterogeneous pore distribution and ligament size due to the incomplete reaction, as shown in Fig. 3(a). In addition, the NPC sheets dealloyed at room temperature are fragile due to the long etching time (120 h). The porous structure of the NPC sheets formed at 65 °C is not obvious and the morphology does not exhibit a typical ligament-channel structure, as shown in Fig. 3(b). Not until the bath temperature exceeded 80 °C was a nanoporous structure with uniform pore distribution and size formed, as shown in Fig. 3(c). The average ligament width and channel size are 380 nm and 240 nm, respectively. As the bath temperature was increased to 90 °C, as shown in Fig. 3(d), the nanoporous structure still remains and the average channel size and ligament width are 560 nm and 230 nm, respectively. It is interesting to note that some nanoparticles formed among the porous structures.

In order to determine the remaining amount of Al element, the quality of the alloy sheets before and after corrosion were weighed, and the remaining amount of the Al elements in the NPC sheets were calculated as shown in Table 2. In addition, the EDS analysis was also been

Table 1
Cu–Cu bonding technology under low temperature.

Technology	Bonding(Annealing) temperature/time	Bonding environment	Pressure	Ref.
Thermo-compression using self-assembled monolayer (SAM)	350 °C/1 h (350 °C/1 h)	vacuum	0.01 Pa	[42]
Copper nanoparticles sintering	260 °C/10 min	N ₂ + H ₂	–	[43]
Diffusion bonding (Ar-FAB bombardment)	150 °C/3600 s	dry O ₂ (8 × 10 ⁴ Pa)	–	[44]
Cone bump bonding	RT/20 s	ambient air	1.25 gf/bump	[45]
Surface activated bonding (SAB)	RT/60 s	high vacuum (3.5 × 10 ^{−3} Pa)	11 MPa	[46]

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