Structure and Properties of Au–Sn Lead-Free Solders in Electronic Packaging

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The requirements for electronic devices in high-temperature environment such as avionics and automotive have promoted the development of high-temperature solders. The Au–20Sn solder, which is one of the hot topics of the current research in the field of electronic packaging, is widely used in flip-chip, light-emitting diode and hermetic package fields because of its good creep resistance, corrosion resistance and flux-free soldering. Recent research about the microstructure, wettability, interfacial intermetallic compounds, and mechanical properties of Au–20Sn solder were reviewed. This paper focuses on the interfacial reaction of Au–20Sn with different substrates and the mechanical properties of Au–20Sn solder joints. In addition, the current research shortages of Au–20Sn solders and the development directions are presented.
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1. Introduction

Conventional Sn–Pb solders have the advantages of good mechanical strength, creep resistance, and thermal stability. However, SnPb solders have been banned in many countries because lead is harmful to the ecology and human.^{1–3)} With the development of lead-free electronics, researchers have conducted a lot of research on lead-free solders, trying to find solders that can replace traditional Sn–Pb solders. Currently, Sn-based solders have the most potential to replace SnPb solders.⁴⁾ Solders that are suitable for low-temperature applications are SnBi,⁵⁾ SnAg,⁶⁾ SnAgCu,^{7,8)} and SnZn.⁹⁾ SnSb¹⁰⁾ and AuSn¹¹⁾ are suitable for high-temperature applications. With the development of the electronics industry, solders are used in high-temperature environments increasingly but there are relatively little researches about high-temperature solders in numerous references.¹²⁾ Therefore, it was necessary to find high-temperature solders that could be adapted to the automotive and avionics sectors. etc.

Au–20Sn is a eutectic solder with a eutectic temperature of 278°C. The Au–20Sn solder matrix consists of ζ -Au₅Sn and δ -AuSn phase.¹³⁾ The ζ -Au₅Sn phase has superior mechanical properties and reliability, so Au–20Sn solder is stable at high temperatures.¹⁴⁾ Au–20Sn solder, which has the advantages of good creep resistance, corrosion resistance, and flux-free welding, is one of the candidate solders to replace Pb-based solders that have a high melting point.¹⁵⁾ However, Au–Sn solders have some drawbacks and research deficiencies. The brittleness of ζ -Au₅Sn intermetallic compounds (IMC) is relatively high, and Au–20Sn solders cannot be easily prepared by conventional casting and rolling processes, so researchers have carried many research on the preparation of Au–20Sn solders.¹⁶⁾ Most of the electronic components fail because of the breakdown of the solder joints, so the evaluation of the reliability of AuSn solder joints is one of the hot topics of research in electronic packaging. In addition, Au–20Sn solder has relatively high cost because it contains 80 mass% Au elements.

According to the research results of Au–Sn solders at home and abroad in recent years, the microstructure of Au–Sn solders prepared by different preparation processes and the wetting behavior under different conditions are summarized. What's more, the interfacial reaction of Au–Sn solders with different substrates and the mechanical properties of the solder joints are highlighted in this review. Finally, the research deficiencies and development trends of Au–Sn solders are summarized in the hope of bringing valuable references for the research of Au–Sn solders in the future.

2. Microstructure

Based on the phase diagram of Au–Sn binary alloy, it is known that Au–20Sn is the binary eutectic region with a melting point of 278°C. The eutectic reaction is shown in eq. (1). Au–20Sn solder is very brittle at room temperature, mainly because the solder contains the brittle ζ' -Au₅Sn phase, so it is not easy to prepare by conventional processing.¹⁷⁾

The Au and Sn laminated process is a preparation method for preparing Au–Sn solder. The laminated composite method is to stack Au and Sn layers in the arrangement of Au/Sn/Au/...../Sn/Au and then cold roll them into shape. The stacked diffusion method is a homogenization annealing based on the stacked composite method.¹⁸⁾ It was found that AuSn, AuSn₂, and AuSn₄ IMC were formed after annealed at the Au/Sn interface. The proportion of their thicknesses throughout the annealing process was approximately 1:1:4. The link between the total thickness of the interface and the annealing time is shown in eq. (2).

$$l = k(t/t_0)^n \quad (2)$$

where l is the total thickness, t_0 is the annealing time, and k and n are 2.7×10^{-7} and 0.42, respectively. Wei *et al.*¹⁹⁾ used a stacked diffusion method to make Au/Sn combinations to form a fast diffusion system, and also found that AuSn, AuSn₂, and AuSn₄ IMC were formed during rolling. With the rapid diffusion of Au and Sn, the Au–Sn solder formed by pressing was annealed at a temperature of 453 K. It was

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Fig. 1 The relationship between thickness of each IMC layer and the storage time at (a) 298 K and (b) 333 K.

found that AuSn, AuSn₂ and AuSn₄ IMC transform into ζ and δ (AuSn) phases. In contrast, the Sn and AuSn₄ phases were melted to increase the brittleness of the solder when the solder was annealed at 543 K, so the Au–Sn solders prepared by the pressure ligation process should be applied at 543 K. The Au–Sn solders prepared by the lamination process are not sufficiently alloyed resulting in non-uniform microstructure and unstable melting point, thus making the solder poorly welded. Therefore, the laminated process is gradually replaced by other processes.

The electroplating deposition process refers to the deposition of Au and Sn ions on a substrate after a redox reaction to form Au–Sn films. Xu *et al.*²⁰⁾ found that AuSn, AuSn₂ and AuSn₄ IMC were formed at Au/Sn layers plated on metallized Si wafers at 298 K and 333 K. Their thicknesses varied with the aging time as shown in Fig. 1. The interfacial reaction of Au–Sn films affects the ensuing solid-liquid phase diffusion linkage (SLID) during storage. Therefore, Au/Sn plating prepared by electroplating deposition should be stored at low-temperature. Yoon *et al.*²¹⁾ prepared Au–20Sn bumps with an average diameter of about 80 μm on a flip-chip using electroplating. Only (Ni,Au)₃Sn₂ IMC was formed between Au–20Sn solder and Ni under bump metallurgy (UBM) after aging at 150°C. All of (Ni,Au)₃Sn₂ IMC were transformed into (Au,Ni)Sn phase, and the (Au,Ni)Sn IMC reacted with Ni UBM to form (Ni,Au)₃Sn₂ phase after aging for 1000 h at 250°C. The electroplating deposition process is less expensive and can prepare solder layers of various shapes. The electroplating deposition process requires an electroplating solution. Although cyanide-containing electroplating solution is stable and suitable for industrial requirements, cyanide is hazardous to humans and ecological environment, so a suitable cyanide-free electroplating solution needs to be found to meet the production requirements. In addition, Au–Sn films prepared by the electroplating process should be stored at low temperatures to hinder the growth of IMC at the Au/Sn interface.

The rapid solidification process involves the formation of thin strips of liquid metal in a single pass under centrifugal force. The microstructure of Au–20Sn solder prepared by the single-roll rapid solidification technology is the same as that prepared by the cast-roll process, and both consist of eutectic

organization (ζ' -Au₅Sn+ δ -AuSn) and ζ' -Au₅Sn phase, as shown in Fig. 2.²²⁾ It was found that the grain of Au–20Sn solder prepared by single-roll rapid solidification technology is finer and more uniform, so its melting point reduce, and specific surface area and surface energy increase. Huang *et al.*¹⁷⁾ found that the ζ' -Au₅Sn phase was still present in the solder at very fast cooling rates, and the application of a magnetic field effectively suppressed the growth of ζ' -Au₅Sn phase during the rapid solidification of Au–20Sn solder. The fracture stress and the fracture strain of the solder were 1456.7 MPa and 64% under the action of the magnetic field, respectively. However, ζ' -Au₅Sn still existed at the conventional cooling rate. The crystallization process of Au–20Sn rapid solidification and conventional solidification under magnetic field induction is shown in Fig. 3. The rapid solidification process which is a simple procedure with low cost has a broad application prospect in the preparation of Au–20Sn solder.

What's more, Tabatabaei *et al.*²³⁾ successfully prepared 2–10 nm Au–Sn alloy nanoparticles (ANPs) by chemical reduction method. The ANPs can reflow at lower temperatures, thus reducing the thermal stress in electrical devices and being more suitable for electronic devices operating at high temperatures. The Au–20Sn solder prepared by planar flow casting (PFC) method consists of inhomogeneous AuSn IMC and Au₅Sn IMC, and the grains of Au–20Sn solder prepared by PFC transformed into coarse and homogeneous phases with heat-treated at 170°C.²⁴⁾ The plasticity of the heat-treated solder was increased, and the yield and tensile strengths of solder were reduced. He *et al.*²⁵⁾ made the initial thickness of 4 mm of cast Au–20Sn solder into a thickness of 48 μm of Au–20Sn film by hot rolling. During the hot rolling process, the eutectic lamellar microstructure of the Au–20Sn solder underwent plastic deformation. This process promoted the spheroidization of the microstructure. The spheroidization of the AuSn IMC was more pronounced than that of the Au₅Sn IMC because the AuSn layer had a higher strain accumulation as well as a more random strain distribution.²⁶⁾

3. Wettability

Wettability of solders defined as the ability of the liquid solder to spread on the surface of the substrate.²⁷⁾ Good

Fig. 2 The microstructure of Au–20Sn solder: (a) as-cast solder, (b) enlarged view of the marked portion of (a), (c) rapidly solidified solder, (d) enlarged view of the marked portion of (c).

Fig. 3 The schematic of Au–Sn20 crystallization process under magnetic-field-induced rapid solidification and conventional solidification.

Fig. 4 The histogram on the wetting area of Sn–Au–Ag(Ni) solders on Cu and Ni substrates.

wettability which is the key to soldering welding Ag and Sn–Au–Ni solders on Ni substrates was larger than Cu substrates, as shown in Fig. 4, indicating better wetting of both solders on Ni substrates.²⁸⁾ The rapid reaction of Sn atoms with Cu forms Cu₆Sn₅ IMC in the solder because the diffusion speed of Cu atoms is greater than Ni atoms. It reduces the wettability of the solder on the Cu substrate. The Au–20Sn solder prepared by the rapid solidification method has a larger spread area of 14.48 mm² compared to as-cast Au–20Sn solder, as shown in Fig. 5. It is 1.43 mm² larger than as-cast Au–20Sn solder.²²⁾ Vianco *et al.*²⁹⁾ investigated the reasons why Au–20Sn was not incomplete wetting on the Au surface of Fe–Ni alloy on sealed ceramics and found that Fe and Ni prevented the wetting and diffusion of the solder. The presence of element C in the Au layer also affected the wettability of the solder. When the C contaminants in the Au layer are removed, there is little danger to the reliability of the solder joint.

The oxide film is mainly consist of SnO₂ and SnO on the surface of Au–20Sn solder, and the formation process is

Fig. 5 The images of two Au–20Sn eutectic solder ribbons after the spreading experiment: (a) cast-rolling, (b) rapid solidification-rolling.

shown in Fig. 6.³⁰⁾ As the oxygen content increases, the spreading area of the solder decreases. The spreading area of the solder is 96.5 mm² with the oxygen content of 16 ppm. As the oxygen content increases to 102 ppm, the spreading area decreases by 45.8%. The spreading area of Au–20Sn solder on Cu substrate decreases as the oxygen content increases.³¹⁾ As the oxygen content increased from 18 to 77 ppm, the spread area decreased from 92.8 to 49.2 mm², mainly because the oxide film on the surface of the molten

Fig. 6 The formation process of oxide films on surface of Au-20 solder.

Fig. 7 The SEM images of microstructure of Au-20Sn/Cu solder joints with high temperature storage test for 250 h to 1000 h. (a)–(c) and (d)–(f) are isothermal storage at 125°C and 150°C, respectively.

Au–Sn solder increased the surface tension. Secondly, the oxides consist of high melting point SnO and SnO₂ in the Au–20Sn. It reduces the fluidity of the solder, resulting in a reduction in the spread area of the Au–20Sn on the Cu substrate.

4. Interfacial Reactions

The interfacial IMC acts as a bond between the solder and the substrate at the interface, and it improves the mechanical properties of the solder joint, but too much IMC can cause the interface to fracture due to its brittleness.³²⁾

Cu substrate is a commonly used in the field of electronic packaging. At the beginning of reflow, irregular ζ -(Au,Cu)₅ IMC and layered AuCu IMC were formed at Au–20Sn/Cu solder joints.³³⁾ The growth of dendritic ζ -(Au,Cu)₅ IMC was discovered in the substrate because of the diffusion of Cu elements when the reflow time reached 60 min. The Au₂Cu₆Sn₂ IMC was formed in Au–20Sn/Cu solder joints prepared using the electrodeposition process, with the reaction equations shown in eq. (3) and (4).³⁴⁾ Yoon *et al.*³⁵⁾ found the evolution of the interfacial microstructure of flux-free soldered Au–20Sn/Cu joints during reflow and aging treatment. Only an irregular layer of ζ (Cu) phase was formed at the interface at the beginning of reflow, and an AuCu IMC was generated in the interface as the reflow time increased. After aging at 250°C, the ζ (Cu), AuCu, and AuCu₃ IMC layers were present at the interface of Au–20Sn solder and Cu substrate. The (Au,Cu)Sn and AuCu IMC layers in Au–20Sn/Cu solder joints thickened with the increase of aging

time.³²⁾ The thickness of IMC layer was increased because of the diffusion of Au and Sn elements. However, the diffusion of Au and Sn elements is gradually suppressed as the (Au,Cu)Sn IMC thickens, so that the AuCu₃ IMC appears underneath the AuCu IMC, as shown in Fig. 7. The (Au,Cu)₅Sn phase was generated in Au–29Sn/Cu solder joint formed by transient liquid phase bonding (TLP). As the welding time increases to 60 min, Cu/Au–Sn/Cu solder joints consist mainly of α' (Au), α (Au), and Au_{6.6}Cu_{9.6}Sn_{3.8} IMC, as shown in Fig. 8.³⁶⁾ Du *et al.*³⁷⁾ found that three IMC layers with a total thickness of about 2 μ m exist in Au–20Sn/Cu solder joints bonded by TLP. The IMC layer which is face-centered cubic with transient atomic ratios is Au–Cu solid solution adjacent to Cu layer. The other two layers have a more complex microstructure with many nanoscale IMCs. Liu *et al.*³⁸⁾ found the AuSn/AuSn₂/AuSn₄/Sn/(Cu,Au)₆Sn₅/Cu₃Sn layer at the interface of the Au–20Sn solder and (Sn)Cu substrate during reflow at 250°C, and the AuSn₄ IMC layer gradually disappeared as the reflow time increased. The AuSn₂ and (Cu,Au)₆Sn₅ IMC at the solder joint gradually disappeared and the interfacial structure was transformed into AuSn/Cu₃Sn after isothermal aging treatment.

In order to block the diffusion of Cu and prolong the service life of electronic devices, Ni is often plated on the Cu substrate as a barrier layer. Ni/Au–Sn/Ni solder joint form Ni₃Sn₂ IMC in the course of welding. The Ni₃Sn₂ IMC

Fig. 8 Cu/Au-29Sn/Cu solder joint after welded at 300°C for 60 min (with pressure): (a) cross-sectional micrograph; (b) XRD (diffraction of X-rays) patterns; (c) EBSD (Electron Backscattered Diffraction) OIM (imaging microscopy)+IQ (image quality) micrograph.

Fig. 9 The EBSD of the Ni/Au-Sn/Ni solder joint after exposed at 450°C for 400 h. (a) The backscattered electron (BSE) image. (b) The phase distribution (PD) image. (c) The inverse pole figure (IPF). Corresponding EDX maps of (d) Au, (e) Sn, and (f) Ni.

transforms into $\text{Au}_5\text{Sn} + \alpha(\text{Au})$ IMC after 60 min of treatment at 350°C.³⁹⁾ After 400 h of treatment at 450°C, it was observed that a Ni_3Sn IMC layer was formed at the interface of the Ni substrate and the Ni_3Sn_2 IMC layer, and Au_5Sn IMC was completely reacted, as shown in Fig. 9. No voids were found in the Ni/Au-Sn/Ni solder joints after the thermal cycling treatment because the Ni substrate was able to hinder the diffusion of Au elements. The $(\text{Au},\text{Ni})_5\text{Sn}$ IMC and $(\text{Au},\text{Ni})\text{Sn}$ IMC were formed at Au-20Sn and Ni substrate after 2 min of reflow at 290°C, and $(\text{Au},\text{Cu})_5\text{Sn}$ IMC and $(\text{Au},\text{Ni})\text{Sn}$ IMC were formed in Au-20Sn and Cu substrate. In addition, Au-20Sn/Ni solder joint has more

thermally stable than Au-20Sn/Cu solder joints at 240°C, therefore, Ni layer was more suitable than Cu as a diffusion barrier layer.⁴⁰⁾ The matrix of Au-20Sn solder consists of Au_5Sn and AuSn phases. A layered $(\text{Au},\text{Ni})\text{Sn}$ IMC and a scalloped $(\text{Au},\text{Ni})_5\text{Sn}$ IMC layer were formed at Au-20Sn/Ni solder joint.⁴¹⁾ Initially, the microstructure of Au-20Sn/Ni solder joint consists of $(\text{Au},\text{Ni})\text{Sn}$ and $(\text{Au},\text{Ni})_5\text{Sn}/\text{Ni}$ layer, and the microstructure eventually changed to $(\text{Au},\text{Ni})_5\text{Sn}$ and $(\text{Au},\text{Ni})\text{Sn}/\text{Ni}$ layer with the increase of reflow time because of the diffusion of Sn elements through Au_5Sn .⁴²⁾ The cross-sections of microstructure and elemental concentrations of Au-20Sn/Ni solder joints reflowed at 350°C for 15 min and

Fig. 10 Electron Probe Micro Analysis (EPMA) element mapping of the Au–20Sn/Ni solder joint after reflowing at 350°C for: (a) 15 min; (b) 40 min.

40 min are shown in Fig. 10, where points A–L correspond to Au₅Sn, AuSn, AuSn, (Au,Ni)Sn, (Ni,Au)₃Sn₂, AuSn, Au₅Sn, (Au,Ni)Sn, and (Ni,Au)₃Sn₂ phases, respectively.⁴³⁾ The main interfacial IMCs are (Au,Ni)Sn and (Ni,Au)₃Sn₂ in solder joints. When the content of Ni exceeds the maximum solubility in AuSn, the (Au,Ni)Sn IMC is first formed with the diffusion of Ni atoms during the welding, and (Au,Ni)Sn IMC gradually transform into (Ni,Au)₃Sn₂ IMC. Two types of intermetallic compounds (Au,Ni)₃Sn₂ and (Au,Ni)₃Sn can be observed in Au–20Sn/Ni joints at a reflow temperature of 300°C. As the temperature increases, the (Au,Ni)₃Sn₂ IMC generally changes from elongated rods to short and thick.⁴⁴⁾ The average diameter of Au–20Sn solder joints prepared by the sequential electroplating method was 80 μm, and the solder matrix consisted mainly of β-Sn phase and AuSn₄ IMC.⁴⁵⁾ The (Ni,Au)₃Sn₄ IMC was formed at Au–20Sn/Ni solder joint. The microstructure of the solder matrix was significantly coarsened after aging treatment at 150°C for 48 h, but the solder matrix was completely transformed into AuSn₄ phase after 250 h. The matrix of the solder consisted of two relatively large AuSn₂ and AuSn₄ phases after 1000 h, as shown in Fig. 11. Microstructural changes are generated by the depletion of Sn atoms in the solder matrix. The matrix

of the solder consisted of AuSn IMC and Au₅Sn IMC when Au–30Sn bumps were prepared on flip-chip using alloy co-electroplating process.⁴⁶⁾ Au–30Sn/Ni UBM solder joints first formed (Au,Ni)₃Sn₂ IMC at a reflow temperature of 400°C. The (Au,Ni)₃Sn₂ began to react with the Ni substrate to form (Au,Ni)₃Sn IMC as the solder matrix was consumed. Lee *et al.*⁴⁷⁾ explored the interfacial reaction of Au–20Sn with a direct-bond-copper (DBC) ceramic substrate, and found that (Au,Ni)Sn and (Ni,Au)₃Sn₂ IMC were formed in Au–20Sn/DBC solder joints, and no significant growth existed in the IMC layer of the solder joints after heat treatment of 2000 h at 200°C.

The addition of Ni to Cu substrates can enhance the reliability of Au–20Sn solder joints, so some researchers have studied the interfacial reaction about Au–20Sn/Ni–Cu solder joints. Au–20Sn/Ni–20Cu and Au–20Sn/Ni–40Cu solder joints form Au–Cu phase and Ni₃Sn₂ phase, but discontinuous layered structures of Ni₃Sn₂ IMC appear in the solder joints when the content of Cu elements reaches 60 at% and 80 at%, as shown in Fig. 12.⁴⁸⁾ At 350°C, Au–20Sn/Ni–Cu solder joints by transient TLP consisted of AuCu, Ni₃Sn₂, and α(Au) phases, and the AuCu phase was gradually transformed into (Au,Cu) phase after 400 or 450°C. A new

Fig. 11 The cross-sectional SEM images of the Sn-rich Au–Sn/Ni solder joint aged at 150°C for (a) as-reflowed, (b) 48 h, (c) 250 h, (d) 500 h, and (e) 1000 h.

Ni_3Sn phase was generated between Ni_3Sn_2 and $\alpha(\text{Au})$ phases, as shown in Fig. 13.⁴⁹⁾ The interfacial IMC of the Ni(Si chip)/Au–20Sn/Ni–Cu solder joint consists of $(\text{Au},\text{Ni})\text{Sn}$ and $(\text{Ni},\text{Au})_3\text{Sn}_2$ IMC, as shown in Fig. 14.⁵⁰⁾ After aging the solder joints at 150–200°C for 2000 h, only

Fig. 12 The cross-section SEM images of Au–Sn/Ni–xCu solder joints for 540 min soldering: (a) $x = 20$ at%; (b) $x = 40$ at%; (c) $x = 60$ at%; (d) $x = 80$ at%.

the $(\text{Au},\text{Ni})\text{Sn}$ IMC remained at the interface, and no significant growth in the interfacial IMC of the solder joints was observed with increasing aging time. Therefore, the Au–20Sn solder has good interfacial stability at high temperatures. The Au, Sn, AuSn, AuSn₂, and AuSn₄ IMC are present in the solder matrix of Au/Sn/Au, and the solder reacts with Kovar alloy to form a new $(\text{Ni},\text{Au})_3\text{Sn}_2$ IMC. A thicker $(\text{Au},\text{Ni})\text{Sn}$ IMC layer was formed at the interface after 24 h of aging treatment of the solder joint at 250°C. As the Ni layer is consumed, the reliability is weakened, therefore, thickening the Ni layer or surface treatment of the Ni layer can better improve the reliability of the solder joint at high temperatures.⁵¹⁾

Fig. 13 TLP bonded Au–Sn/Ni–30Cu joint: (a) cross-section image; (b) XRD image of the etched interface and fracture surface; The TLP bonded Au–Sn/Ni–30Cu solder joints after exposed at 450°C for 24 h: (c) cross-section image; (d) XRD image.

Fig. 14 (a)–(e) The cross-sectional SEM images of Ni(Si chip)/Au-20Sn/Ni(substrate) interfaces aged at 150°C.

Fig. 15 The CuNiAg/Au-Sn/CuNiAg solder joint after reflowing for 20 min at 350°C. (a) XRD image of fractured surface. (b) EBSD phase distribution map. (c) BSE image. (d) IQ map. (e) Energy Dispersive Spectrometer (EDS) maps of Au, Sn, Ni, Cu, and Ag.

Plating the Au layer on the surface of the Ni layer can effectively inhibit the oxidation of the Ni layer and enhance the effect of solder wettability.⁵²⁾ The interfacial microstructure of Au-29Sn bumps on Cu/chemically plated Ni/Au composed of (Au,Ni)Sn and (Au,Ni)₃Sn₂ IMC after aging at 200°C for 365 days. Discontinuous interfacial IMC were formed during Au-Sn solder react with the Pt substrate, and there are localized Pt elements that dissolve into the molten solder during reflow.⁵³⁾ The reaction behavior of Ni and Pt is similar, but the Au-Sn/Co solder joint forms continuous reaction products at a slower reaction rate, making Co more suitable than Pt and Ni as a blocking material for Au-Sn eutectic solder in optoelectronic packages.

In addition to studying the interfacial reaction of solder on Cu, Ni, and Au substrates, Peng *et al.*⁴⁴⁾ explored the interfacial reaction of Au-20Sn/UBM (Al/Ni(V)Au) solder joint at 300°C for 5 min. The Au and Al in the UBM react to form Au₈Al₃ compounds, causing the (Au,Ni)₃Sn₂ IMC to

be too high and the solder joint to fracture at the weak point of the (Au,Ni)₃Sn₂ IMC. The CuNiAg/Au-Sn/CuNiAg solder joint formed Ni₃Sn₂ IMC after heating at 350°C for 5 min, as shown in Fig. 15.⁵⁴⁾ The AuSn matrix gradually decreased in the solder after 20 min, while more IMC, consisting of the multi-principal-element alloys (MPEA) phase, Au₅Sn and Ni₃Sn₂, was formed at the joints. The reaction process is shown in eq. (5). The components of MPEA are roughly 55Au-6Sn-23Cu-2Ni-14Ag (at%). It was found that the matrix of the solder was completely transformed to the MPEA and Ni₃Sn₂ after 60 min, as shown in eq. (6). Wen *et al.*⁵⁵⁾ probed the influence of γ -ray irradiation on Au-20Sn/Ni solder joints and found that γ -ray irradiation accelerated the reaction between Ni substrate and Au-Sn solder, producing (Au,Ni)Sn IMC and (Ni,Au)₃Sn₂ IMC, as shown in Fig. 16. After 1000 h of irradiation, the weldability of MoCu20/Au-20Sn/Cu solder joints decreased from 94.7% to 88.6%, and the size of the

Fig. 16 SEM of MoCu20/Cu solder joints for (a) 0 h, (b) 300 h, (c) 600 h, (d) 1000 h.

holes in the solder joints increased with increasing irradiation time.

5. Mechanical Properties

Au–Sn solders have the advantages of good creep and mechanical properties, flux-free soldering, and excellent wettability.¹⁶⁾ The hardness of Au–20Sn solder decreases with the increase of temperature in the temperature range of 25–200°C. The rate of creep reaction increases and the stress index decreases with the increase of temperature. The main reason for the reduction of solder hardness is the high-temperature creep behavior during the heating process.⁵⁶⁾ Chu *et al.*¹³⁾ explored the mechanical properties of Au–Sn IMC using the nanoindentation method and found that the hardness of Au₅Sn and AuSn IMC was greater than ordinary soft solders, thus Au–Sn solders consisting of these two IMCs had higher creep resistance than ordinary solders. The good mechanical strength of Au–20Sn solder provides higher stability of solder joints in laser diode packages.⁵⁷⁾ However, the cost of the solder is high because of the 80% Au content of Au–20Sn solder. In addition, its relatively high microhardness leads to poor machinability, mismatch of thermal expansion coefficient, and a tendency for solder joints to break.⁵⁸⁾ Namazu *et al.*⁵⁹⁾ used microelectromechanical system method (MEMS) to assess the mechanical properties of Au–Sn solders. The Young's modulus and Poisson's ratio of Au–20Sn solders were 51.3 GPa and 0.288 at room temperature. Young's modulus decreases with the increase of temperature, but Poisson's ratio is not affected by temperature.

The microstructure of the solders differed with different preparation processes, which led to variations in their mechanical properties. The shear strength of Au–20Sn solder prepared by the rapid solidification method reached 39.17 ± 0.70 MPa, which is 19.02% higher than ordinary Au–20Sn solder because of the finer and more uniform grains of the solder.²²⁾ The strength of the Au–20Sn solder prepared by PFC was reduced but plasticity was enhanced after heat treatment. The tensile strength decreased from 338.3 MPa to 310 MPa and the yield strength decreased from 338.3 MPa to 180.5 MPa, while the plastic strain increased from 0 to 1.6%.²⁴⁾ Flux-free Au/Sn solder in laser diodes was heat-treated at 150°C for 64 days, and the stress concentration resulted in a larger number and area of cavities voids in the solder joints as the aging time increased, reducing the strength of solder joint.⁶⁰⁾ The shear strength of Au–20Sn solder joints prepared by the sequential electroplating method remained almost unchanged after 1000 h of aging at about 0.4–0.5 N. The fracture surfaces of all solder joints were mainly concentrated at the interface of the solder joints, indicating that the fracture at the interface was related to the brittle (Ni,Au)₃Sn₄ IMC.⁴⁵⁾ Chu *et al.*⁶¹⁾ explored the influence of the continuous flip-chip soldering process on the reliability of Au–Sn solder joints. It was observed that the reason for the decrease of mechanical strength in solder joints is the transformation of the eutectic phase to the ζ phase in the solder after several reflows.

The shear strength of Au–20Sn/(Sn) Cu solder joint increases and then decreases with the increase of reflux times. Their fracture surfaces shifted from the Sn/(Cu,Au)₆Sn₅ layer to the AuSn₄/(Cu,Au)₆Sn₅ layer and eventually to the AuSn₂/(Cu,Au)₆Sn₅ layer.³⁸⁾ The shear strength of the solder joint reduces continuously and the fracture surface shifts from the AuSn₂/(Cu,Au)₆Sn₅ layer to the AuSn layer and

eventually to the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface as the aging time increases. With the increase of aging time, the shear strength of solder joints reduces, and the fracture surface gradually shifts from the $(\text{Au,Cu})_5\text{Sn}/\text{Cu}$ layer to the $\text{Au}-20\text{Sn}$ solder matrix. The $(\text{Ni,Au})_3\text{Sn}_2$ IMC, which is formed in the interface of $\text{Au}-\text{Sn}/\text{Ni}$ flip-chip solder joints, is gradually transformed into $(\text{Au,Ni})\text{Sn}$ IMC during aging at 150°C because the diffusion of Ni atoms is suppressed.²¹⁾ In addition, it was found that the brittle IMC layer at the interface cause the brittle failure of the solder joint by bump shear tests. The microstructure of $\text{Au}-\text{Sn}/\text{Ni}/\text{Kovar}$ solder joints was relatively reliable at 180°C . At 250°C , the solder joints fractured at the interface, indicating that the brittle IMC layer causes brittle fracture of the solder joints at the interface.⁶²⁾ In addition, the consumption of the Ni layer decreases the reliability of the solder joint during aging at 250°C in the solder joint. Therefore, the thickness of the Ni layer needs to be increased if we want the solder joint to have relatively good reliability at 250°C . In summary, it can be seen that the reason for the decrease of the reliability of the solder joint is the presence of brittle interfacial IMC in the solder joint.

Enhancing the reliability of solder joints is the focus of current research at high-temperature. $\text{Au}-\text{Sn}$ solder joints prepared by TLP usually have relatively high solder joint reliability. Peng *et al.*⁴⁹⁾ found that the shear strength of $\text{Au}-20\text{Sn}/\text{Ni}-30\text{Cu}$ solder joints prepared by TLP reached 87 MPa and 97 MPa from 75 MPa after exposure to 400°C and 450°C for 24 h, respectively, indicating that higher temperature can advance the shear strength of TLP solder joints. The $\text{Cu}/\text{Au}-29\text{Sn}/\text{Cu}$ solder joints bonded by TLP also have good reliability.³⁶⁾ The shear strength was able to remain stable at about 40 MPa after 400 thermal cycles between 25 and 350°C , as shown in Fig. 17. Moreover, the

fracture of the shear deformation of the solder joint occurs mainly in the $\text{Au}_{6.6}\text{Cu}_{9.6}\text{Sn}_{3.8}$ phase. The TLP-bonded $\text{Ni}/\text{Au}-\text{Sn}/\text{Ni}$ solder joints have good thermal stability.³⁹⁾ The shear strength was 32 MPa and 48 MPa at 450°C and room temperature, respectively. It still reached 45 MPa after 400 h of treatment at 450°C , and it decreased to only 42 MPa after 300 thermal cycles. The $\text{Au}-20\text{Sn}/\text{DBC}$ solder joints maintained stability and good mechanical strength at high temperatures.⁴⁷⁾ Among the $\text{Au}-20\text{Sn}/\text{Ni}-x\text{Cu}$ ($x = 20, 40, 60, 80 \text{ at}\%$) solder joints, the $\text{Au}-20\text{Sn}/\text{Ni}-40\text{Cu}$ solder joints have a relatively high shear strength (62 MPa) and good reliability. The AuCu layer in the solder joint was able to bond the solder and the substrate well, and the high Ni-containing $\alpha(\text{Au})$ and uniformly continuous Ni_3Sn_2 IMC layers were able to inhibit the evolution of porosity, which increased the reliability of the solder joint.⁴⁸⁾ The $55\text{Au}-6\text{Sn}-23\text{Cu}-2\text{Ni}-14\text{Ag}$ IMC was formed in $\text{CuNiAg}/\text{Au}-\text{Sn}/\text{CuNiAg}$ solder joints with yield strength of 190 MPa, Young's modulus of 100 GPa, and strain hardening rate of 0.4535. The shear strength of $\text{CuNiAg}/\text{Au}-\text{Sn}/\text{CuNiAg}$ solder joints reached 81 MPa after bonding for 20 min. It is 68% higher than $\text{Ni}/\text{Au}-\text{Sn}/\text{Ni}$ solder joints because the interfacial IMC of $\text{CuNiAg}/\text{Au}-\text{Sn}/\text{CuNiAg}$ solder joints is ductile and reduces the local stress concentration.⁵⁴⁾ This makes it difficult to weld to Al electrodes due to the natural formation of alumina on the Al electrode. Lang *et al.*⁶³⁾ studied an efficient way for welding the Al electrode by fabricating an Au-stud bump in the Al electrode with $\text{Au}-20\text{Sn}$ solder. The $\text{Au}-20\text{Sn}$ solder reacted with Al electrode to form AuAl_4 IMC. The shear strength reached 90 MPa and the activation energy of the solder joint was 159 kJ/mol. In addition, the addition of Ni and Pd increased the shear modulus and Young's modulus of AuSn_4 IMC, but the Poisson's ratio reduced.⁶⁴⁾ The shear strength of $\text{Au}-30\text{Sn}$,

Fig. 17 (a) The relationship between shear strength of TLP-bonded joint and different thermal cycles; (b) cross-sectional image and (c) the fracture surface of TLP-bonded $\text{Cu}/\text{Au}-\text{Sn}/\text{Cu}$ solder joint after 400 cycles.

Cu/(Sn₁₁Au_{0.5}Ag_{1.5})Sn₃/Ni and Cu/(Sn₁₁Au_{0.5}Ni_{1.5})Sn₃/Ni solder joints were 24.5 MPa, 50.59 MPa and 36.38 MPa, respectively. The shear strength of Au–30Sn solder joints is higher than all three of the above.²⁸⁾

The microstructure of a solder joint deteriorates significantly when the oxygen content is too high in the joint.⁶⁵⁾ The formation of oxides on the solder surface will be promoted by the high oxygen content in Au–20Sn solder, leading to porosity and cracks that can occur during reflow, thereby the reliability of the solder joint is decreased.³⁰⁾ The Au–20Sn solder joints had good microstructure with the oxygen content level of 16 ppm. Cracks and holes appeared in the joints with the oxygen content of 55 ppm. The shear strength of Au–20Sn/Cu solder joints decreased by 44% from 56 MPa to 31.7 MPa as the oxygen content increased from 18 ppm to 77 ppm. Some tiny pores were present at the fracture surface with the oxygen content of 18 ppm.³¹⁾ The pores gradually increase as the oxygen content increases.

The γ -irradiation also has an effect on the mechanical properties of the solder joint. The fracture mode of Au–20Sn/Ni joints that was not irradiated with γ -rays was ductile fracture.⁵⁵⁾ After 300 h of irradiation, the fracture pattern includes ductile fracture of the Au–Sn IMC and granular fracture of the Ni layer. The fracture mode of the solder joints was completely changed from ductile fracture to brittle fracture after 600 h of irradiation. After 1000 h of irradiation, the shear strength of MoCu20/Au–20Sn/Cu welded joints reduced from 51.87 MPa to 32.56 MPa, and the fracture images under different aging are shown in Fig. 18. The main reason for the reduction of shear strength was the brittle IMC in the solder joints and the defects generated by irradiation.

6. Conclusions

Overall, Au–20Sn solder is the most suitable of several eutectic solders in the Au–Sn system to use in high-temperature environments, because it has good creep resistance, corrosion resistance, fatigue resistance, and the advantages of high strength, high electrical conductivity, high thermal conductivity and flux-free soldering. However, the

development of Au–20Sn solder is constrained by several issues:

- (1) Au–20Sn solder contains high content of Au elements, resulting in expensive costs.
- (2) It is impossible to prepare Au–20Sn using the conventional casting and rolling process, because the Au–20Sn matrix contains the brittle ζ -Au₅Sn phase.
- (3) Most of the current research focuses on the interfacial IMC growth of Au–20Sn solder joints and the effect of aging treatment on solder joints, lacking a systematic research of the reliability of solder joints.
- (4) Most of the research on Au–20Sn solder is conducted at the experimental stage and cannot be fully applied to the electronics industry.

The research direction of Au–20Sn solder can be started from the following points:

- (1) The effects of different preparation processes on the microstructure and material properties of Au–20Sn solders are the focus of the study. Au–20Sn solder with more excellent properties can be produced by optimizing the process parameters, refining the grain size, and finding new processing processes.
- (2) It can better reflect the failure behavior of solder joints in service and provide better theoretical support for the study of reliability by establishing the constitutive model and fatigue life prediction model of solder joints.
- (3) Research on Au–20Sn solder should be combined with practical devices, which will have a higher application value in the future.

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Fig. 18 The SEM images of fracture at Cu side of joint samples (a) 0 h, (b) 300 h, (c) 600 h, (d) 1000 h.

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