Review Article

Novel Au-Based Solder Alloys: A Potential Answer for Electrical Packaging Problem

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With the development of electronical technology and the construction of the fifth-generation cellular networks, electronic devices with higher integrated level and power are widely applied. Hence, greater demands are being placed on electronic packaging materials. High-Pb solder alloys were widely used for low- and medium-temperature soldering for the past decades but have been prohibited due to toxicity. Au-based solder alloys with proper melting and mechanical properties show great potential to replace high-Pb solder alloys and are being emphasized recently. But in comparison with Pb-containing solder alloys, the investigation on novel Au-based solder alloys is quite insufficient, and their performance and reliability are still unclear. In this paper, the recent research studies on Au-based solder alloys with low temperature and medium temperature were reviewed and their microstructure, mechanical performance, and reliability were introduced and analyzed. Moreover, the novel processing technologies of Au-based solder alloys were discussed and compared.

1. Introduction

In the past decades, electronical industry is becoming more and more important for every country due to its significant effect on the development of economy and national security, and many efforts have been made for design and manufacture novel electrical devices [1–3]. Sn-based solder alloys with excellent properties are widely used in electronic packaging, and a few novel Sn-based solder alloys that are applied in the packaging of integrated circuits (IC) have been designed to meet the rising requirement of electrical devices, thanks to the researchers [4–6]. Recently, owing to the development of electronics industry, the high-density packaging technologies for integrated circuits (IC), such as BGA, CSP, IGBT, and WLP, have been applied gradually, promoting the upgrading and miniaturizing process of electrical products [7, 8]. But miniaturization of ICs with higher power also results in increasingly higher service temperature of more than 300°C, which puts much emphasis on the electrical devices as well as their packaging materials [9].

Pb-based solder alloys with excellent wettability and suitable melting temperature are widely used in electronic packaging [10–12]. Nevertheless, under the drive of environmentally friendly manufacturing, much requirement has been attached to lead-free solder alloys, among which Au-based solder alloy is seen as an excellent filler metal to replace the Pb-based solder alloy used in high-temperature conditions [13, 14]. Au-Sn [15], Au-Si [16], Au-Ge [17], Au-Sb [18], and other Au-based low-temperature solders with a melting temperature lower than 400°C have become the ideal substitute for solder alloys containing high content of lead due to their good wettability, excellent brazing performance, high joint strength, good thermal fatigue resistance, high thermal conductivity, and small dissolution for gold-plated pads [19, 20]. In recent years, to meet the temperature requirement of high integrated electronic devices, Au-based medium-temperature solder alloys with the melting temperature of 400–600°C have received more and more attention, the majority of which are Au-Ag, Au-In, and Au-Ga solder alloys [13, 21]. But in comparison with Au-based

low-temperature solder alloys, the research studies on Au-based medium-temperature solder alloys are still inadequate, which limits their application [22].

Gold-based medium- and low-temperature solders have excellent performance and high reliability, but due to the presence of brittle phases, they have poor processing properties and cannot be manufactured by conventional methods [23]. At present, although many processing methods, such as melt-casting and toughening process, laminated cold rolling process, electroplating deposition process, mechanical alloying process, and rapid solidification process, have been developed and the processing of the foil with the thickness of 0.1 mm or less has been basically realized, the process is still needed to be improved. Therefore, the development of new processing technologies will be one of the future research directions of gold-based medium- and low-temperature solders. At the same time, in order to reduce the cost of gold-based medium- and low-temperature solder alloys and meet the application requirements of gold-based solders, it is of great significance to develop a new gold-based alloy system [20, 24, 25]. This paper mainly introduced the microstructure and performances of gold-based medium- and low-temperature solders and analyzed the advantages and shortcomings of different preparation processes. Finally, the development direction of gold-based medium- and low-temperature solders was discussed and prospected.

2. Au-Based Low-Temperature Solder Alloys

The gold-based low-temperature solder mainly refers to a gold-based solder with a melting temperature less than 400°C, such as Au-Sn, Au-Si, Au-Ge, and Au-Sb [15–18]. Gold-based low-temperature solders have excellent wettability, thermomechanical properties, and high corrosion resistance, which are the main soldering materials for hermetic packaging.

2.1. Au-Sn Solder

2.1.1. Matrix Microstructure. In comparison with other Au-based solder alloys, Au-Sn solder possesses higher electrical conductivity, more excellent creep resistance, and solderability [27]. Hence, Au-Sn solder alloys, the majority of which is Au-20Sn eutectic solder, are seen as the ideal filler metal for optoelectronic packages. With the advancement of manufacturing technology of electrical devices, Au-Sn solder shows great potential for the packaging of future precise instruments and has been obtaining more attention recently. The microstructure of Au-20Sn solder consists of two brittle intermetallic compounds (IMC): Au_5Sn (ξ) and $AuSn$ (δ), which disperse evenly and form the eutectic structure [28]. The well-distributed morphology of Au_5Sn (ξ) and $AuSn$ (δ) gives a high strength of as-soldered Au-Sn joint, which would be affected by the service temperature, however. As illustrated in Figure 1, the majority of microstructure in the soldered joint was identified to be a fine eutectic structure and some ξ particles dispersed in the matrix [26]. After long-term thermal aging at 150°C, the growing behavior of ξ

particles could be observed, but the eutectic microstructure was hardly changed. However, if the aging temperature rose to be 200°C, the fine eutectic microstructure would be destroyed and only thick ξ and δ phases could be obtained. Therefore, the service temperature of Au-Sn solder should be concerned, especially for the packaging of future high-power electrical devices.

2.1.2. Interfacial Microstructure. The IMC layer that forms between solder matrix and substrate during soldering process is the foundation of reliable bonding, whose morphology and property play an important role in the solder joint [7]. After soldering process, a ξ-$(Au, Cu)_5Sn$ thick IMC layer with irregular columnar morphology and a very thin Au-Cu IMC layer formed at the interface of the Au-Sn/Cu solder joint [29, 30]. But this Au-Cu IMC layer was claimed to be sensitive to the service temperature. The atomic migration of Cu from Cu substrate to solder matrix was significantly accelerated at high temperature, and hence, Cu content at the interface was increased, giving a new interfacial layer [31]. As illustrated in Figure 2, after being aged, at 200°C, the thickness of the Cu-Au IMC layer was greatly increased with the formation of a new Cu_3Au layer, and hence, a bilayer of $CuAu/Cu_3Au$ between ξ-$(Au, Cu)_5Sn$ and Cu substrate formed, which coarsened with the progress of thermal aging [32]. The same phenomenon could be observed in the Au-Sn/Ni solder joint [33]. In the as-soldered Au-Sn/Ni solder joint, a thick δ layer and a thin $(Au, Ni)_3Sn_2$ layer formed at the interface [34]. During the aging test, the Ni atom migrated from the substrate and reacted with the δ phase, forming the $(Au, Ni)Sn$ IMC layer. But compared with Cu substrate, the migration speed of Ni from Ni substrate to interface was much lower, and hence, the growth of $(Au, Ni)_3Sn_2$ and $(Au, Ni)Sn$ IMC layer was relatively slower [35]. Moreover, the oxygen content of the Au-Sn solder matrix was also found to be an adverse factor for the morphology and strength of interfacial layer. Wang et al. [36] found that once the oxygen content exceeded 42 ppm, the oxygen would be entrapped in the Au-Sn/Cu solder joint during the soldering process and formed a number of voids, even a few cracks, which would deteriorate the property of solder joint. Therefore, it is of great significance to focus on the storage condition of Au-Sn solder alloys.

2.1.3. Mechanical Property. Due to higher brittleness of IMC phase than solder matrix, the brittle fracture of Au-Sn solder joint is always a problem for electrical packaging, especially for those applied in high-temperature conditions [37]. The formation of IMC layer is the foundation of reliable bonding between solder matrix and substrate, but the morphology of IMC layer significantly affects the property of solder joint [38]. During the service condition, the coefficient of thermal expansion (CTE) mismatch of solder matrix and substrate put much thermal stress at the interface, where the existence of thick brittle IMC layer provides the crack source and increases the fracture risk of solder joint [39]. Recently, some researchers tried to suppress the precipitation of Au_5Sn and precipitate relatively ductile phases by doping Ag or Cu. Ag
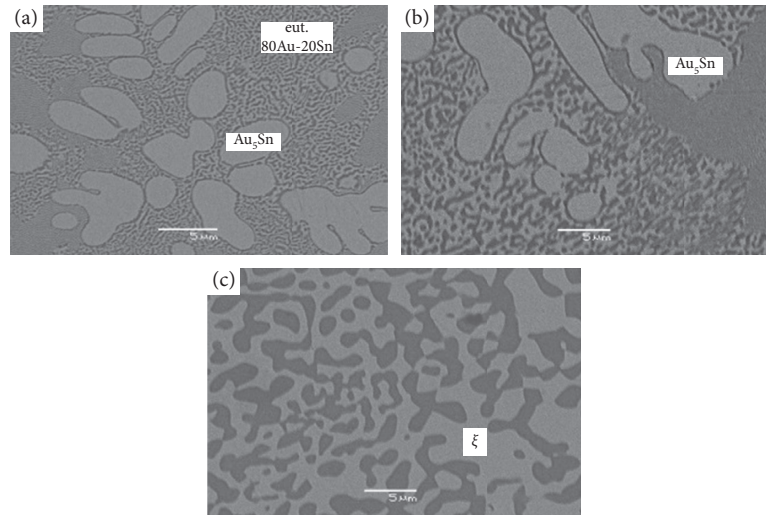
FIGURE 1: SEM-BSE micrographs of eutectic Au-Sn alloy depicting the phase transformations during thermal aging. (a) As-produced, (b) 150°C, 1 week, and (c) 200°C, 1 week [26].
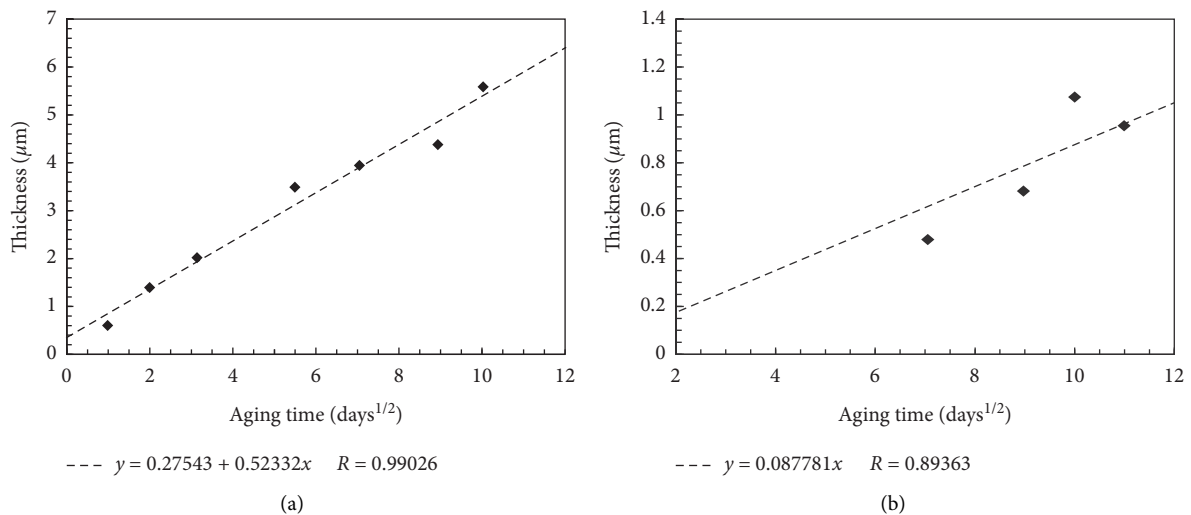

FIGURE 2: Thickness of (a) the Cu-Au layer and (b) the Cu_3Au layer in solder bumps with the square root of aging time at 200°C [32].

and Cu elements could perform as the solid solute in Au_5Sn, blocking the atomic migration and increasing glide resistance of grain boundary and hence gave a fine morphology of Au_5Sn [40]. As a result, a higher reliability of Au-Sn solder was obtained. Jung et al. [41] investigated the effect of thermal aging on the fracture behavior of the eutectic Au-Sn/Ni solder joint and found that for the soldered joint, the fracture tended to initiate and prolongate in the solder matrix, where only the solder matrix was observed on the fracture surface. But as shown in Figure 3, the fracture location was changed to be the interface of solder matrix and IMC layer after thermal aging, which was attributed to coarsening of the $(Au, Ni)_3Sn_4$ IMC layer. The voids and cracks that formed during thermal aging process hardly affected the shear force and fracture location, which indicated that the excessive growth of IMC layer was the main deteriorating factor for the solder joint. In comparison with

Cu substrate, the growth behavior of IMC layer in the Au-Sn/Ni solder joint was found to be more unobvious during thermal aging, which gave a relatively lower strength decrement. It could be seen from Figure 4 that the shear force of Au-Sn/Ni solder bump was hardly decreased after aged at 150°C for 1000 h, which indicated the solder bump had an excellent reliability [33].

2.1.4. Solderability. Eutectic Au-Sn solder with excellent wettability and a melting temperature (T_m) of 278°C can meet the requirements of high-end electronic components, such as military products and aerospace industry. But due to its narrow liquidus range around eutectic chemical composition, the soldering processing window is quite limited. Moreover, the inert barrier metallization, the majority of which is Ti/Pt/Au, has been applied to avoid the
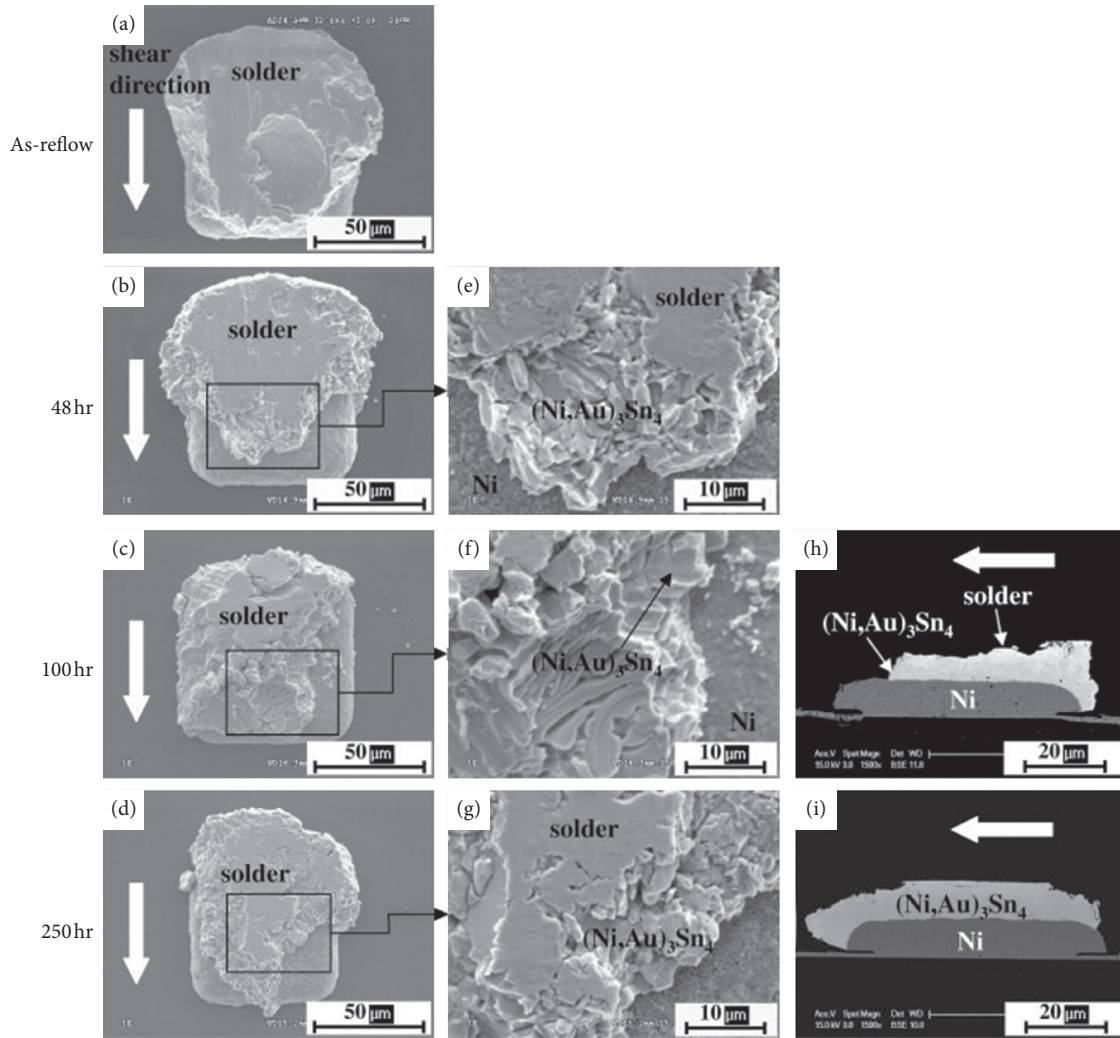
FIGURE 3: Top views and cross-sectional SEM images of the fracture surfaces of eutectic Au-Sn/Ni joints aged under various conditions [41].
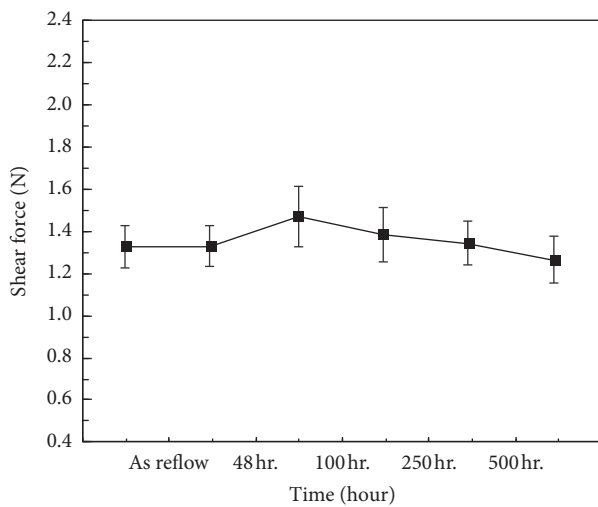

FIGURE 4: Shear force variation of Au-Sn/Ni solder bump with aging time [33].

deterioration of eutectic solder matrix [42]. However, it was found that this barrier metallization layer resulted in the consumption of Sn from solder matrix and the premature freezing of the thin solder layer, giving a decrease in strength of the solder joint. Therefore, a new barrier metallization of Ti/W/W-NiSn/NiSn showed excellent application potential for Au-Sn solder alloys at all processing temperatures because the existence of W-NiSn and NiSn provided an excellent solution to ensure a perfect adhesion of molten solder matrix and substrate [43]. What is more, it had been found that the reflow process of AuSn solder alloy should be focused [29]. Liu et al. [44] studied the effect of reflow parameter on the wetting reaction between Au-Sn solder and Au foil and found that the best wettability of molten Au-Sn solder was obtained at 390°C, giving a wetting angle of 25°. The oxidation of the Au-Sn solder matrix was greatly accelerated above 390°C, which could retard the soldering process. For the Au-Sn/Ni solder joint, a short reflow time gave an insufficient wetting of molten solder, while a long

reflow time led to the excessive growth of $(Au, Ni)_3Sn_2$ IMC, which would be spalled from the interface and embedded in the solder matrix [45]. Hence, the strength of solder joint was greatly reduced. The oxygen content of AuSn solder matrix was also claimed to affect its solderability. As it could be seen from Figure 5, the increasing oxygen content gave a lower spreading area, whether flux was applied or not [36]. The reason was that the high content of oxygen element was absorbed at the surface of the solder matrix and led to the formation of SnO and SnO_2 oxide films, which hindered the spreading process and the interfacial reaction of molten solder matrix and substrate during the soldering process.

2.2. Au-Ge Solder

2.2.1. Microstructure. Au-Ge solder alloys have many advantages, such as low vapor pressure, high stability, corrosion resistance, thermal fatigue resistance, high electrical conductivity, and thermal conductivity, which are widely used in chip soldering and packaging [46]. Figure 6 exhibited the microstructure of eutectic Au-Ge solder alloys [47]. As illustrated in Figure 6(a), the Au phase (bright phase) and Ge phase (dark phase) distributed alternately in the solder matrix. The Au phase was a soft phase, whereas the Ge phase was a hard phase, and the later one with fine morphology could help enhance the solder matrix by acting as a strengthening phase. But after thermal aging at 300°C for 100 h~500 h, it could be seen from Figures 6(b)–6(f) that the Ge phase coarsened with time and then the dissolution of Ge into the Au phase was observed. Moreover, the thermal aging also influenced the interfacial microstructure of the Au-Ge solder joint. In the soldered Au-Ge joint on Cu/Au under bump metallization (UBM), a continuous (Au, Cu) layer formed at the interface, as shown in Figure 7(a) [47]. But the subsequent thermal aging destroyed this morphology, and the continuous diffusion of Cu atoms from UBM into solder matrix led to the spalling behavior, as shown in Figure 7(b). In the eutectic Au-Ge/ENIG solder joint, the oxidation of Cu layer occurred between Ni-Ge IMC layer and Cu substrate during the thermal aging, which decreased the mechanical properties of solder joint [48].

2.2.2. Mechanical Property. As a kind of low-temperature solder alloy, the mechanical property of eutectic Au-Ge solder alloys is excellent. It has been found that the tensile strength of eutectic Au-Ge solder was more than five times higher than SnPb solder at room temperature and ten times at 120°C [49]. The substrate materials could greatly influence the mechanical property of solder joint. As listed in Table 1, the shear strength of Ni/Au-Ge/Ni solder joint was obviously higher than the others because of the formation of Cu diffusion layer and high-strength Ni_5Ge_3 IMC layer [50]. The eutectic Au-Ge solder has superior high-temperature reliability than Au-Si solder, so it is widely used in high-temperature packaging, such as oil and gas exploration and other special industrial fields that require long-term high-temperature operation [51]. But
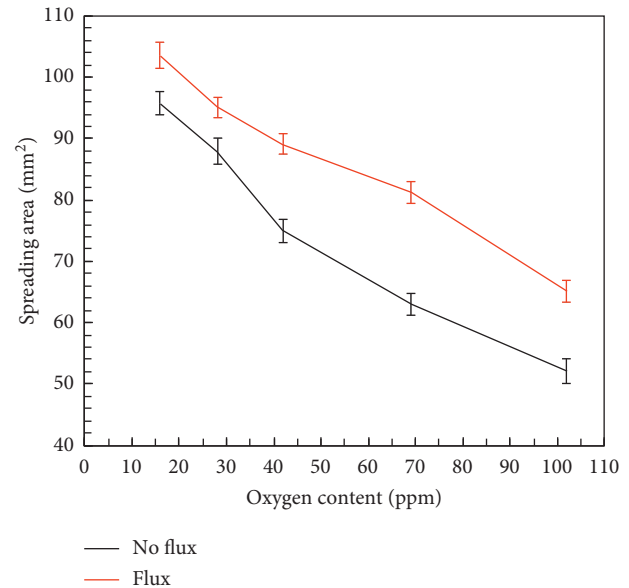

FIGURE 5: Spreading areas of Au-20Sn solders of 16, 28, 42, 69, and 102 atom ppm oxygen, respectively [36].

the decrease in strength of Au-Ge solder joint during thermal aging is always a problem for electronical packaging, and many efforts have been carried out. The strength of Au-Ge/ENIG solder joint would be significantly decreased during thermal aging due to the conductive oxidation of Cu. But as shown in Figure 8, A W diffusion barrier (DB) could effectively block the atomic migration between solder matrix and substrate, which suppressed the diffusion of Cu atoms and enhanced the reliability of the eutectic Au-Ge/ENIG solder joint [48]. Yang et al. [52] prepared a 200 nm-thick Ta/TaN/Ta diffusion barrier layer on Ni substrate and found that the interfacial reaction between Au-Ge solder and Ni was greatly postponed, which gave a lower growth rate of Ni_5Ge_3 IMC layer during thermal aging. Subjected to a long-term thermal aging at 330°C, the solder joint with Ta/TaN/Ta DB still gave a shear strength of 56 MPa, which was hardly reduced compared with the soldered joint.

2.2.3. Solderability. The wettability of molten Au-Ge solder alloys on various substrates is much different. The wetting angle of eutectic Au-Ge solder was 14° for Cu and 13° for Ni substrate, showing an excellent wettability [53]. This could be attributed to the interfacial reaction between eutectic Au-Ge solder alloys and the substrates. The dissolution of Cu and Ni into the solder matrix formed the interfacial IMC layer and promoted the soldering process, exhibiting a dissolutive wetting characteristic [54]. The wettability of Au-Ge solder alloys on SiC substrate was very unsatisfactory, and the increase in the Ge content was claimed to be helpful to promote the wetting process. But the enhancing effect of Ge addition was limited, the contact angle of Au-Ge solder with 2.8 at. % of Ge was still as high as 110° [55]. Therefore, it is necessary to clarify the wettability mechanism of molten Au-Ge solder alloy and find the
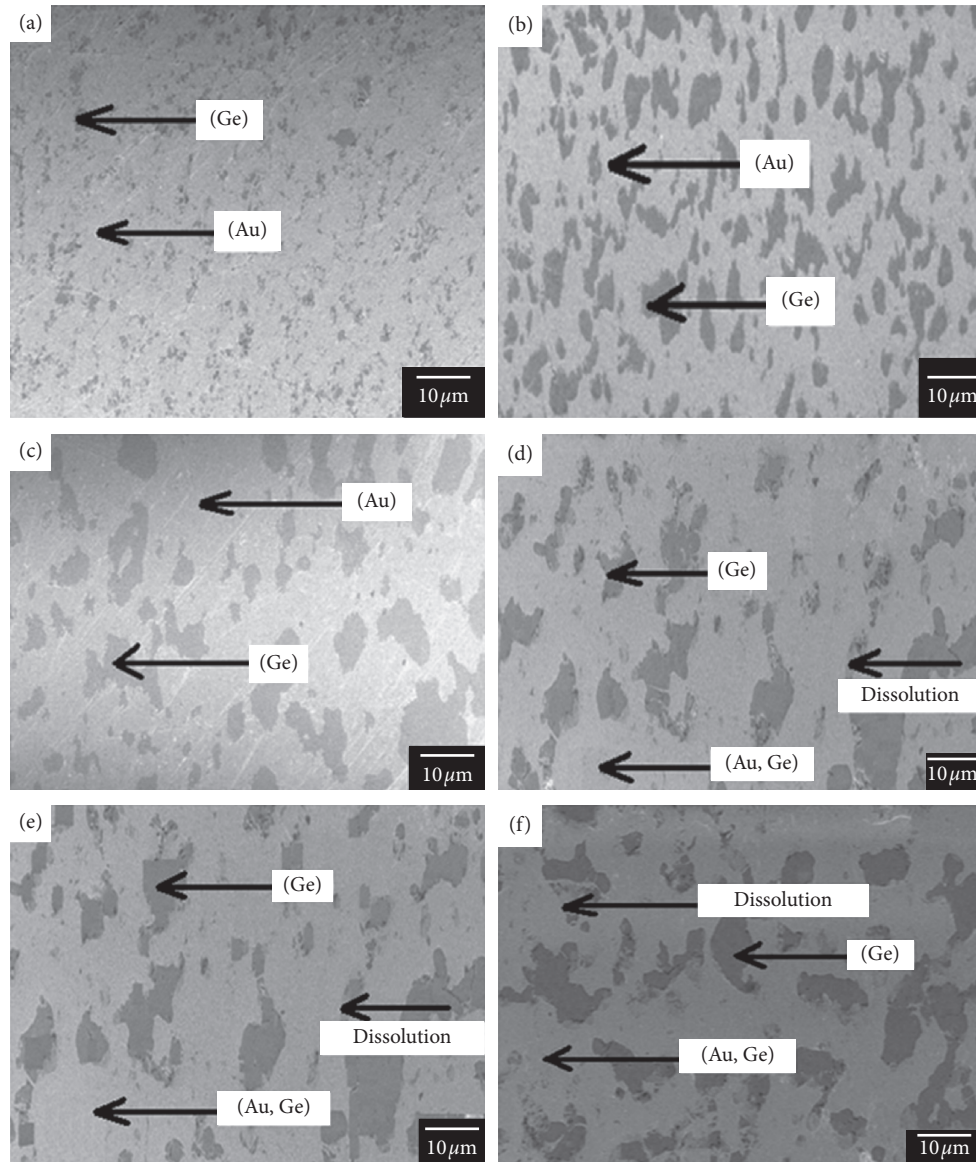
FIGURE 6: SEM secondary electron imaging (SEI) micrographs of Au-Ge eutectic alloy: (a) without thermal aging and after (b) 100 h, (c) 200 h, (d) 300 h, (e) 400 h, and (f) 500 h of thermal aging at 300°C [47].
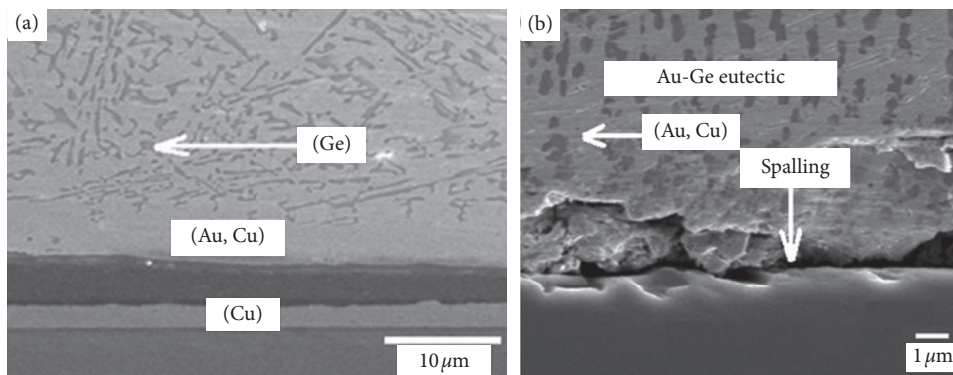
FIGURE 7: SEM-SEI micrographs of the cross section between Au-Ge eutectic solder and Cu/Au UBM: (a) without thermal aging and (b) after thermal aging for 500 h at 300°C [47].

TABLE 1: Shear strength of Au-28Ge solder joints on different substrates [50].

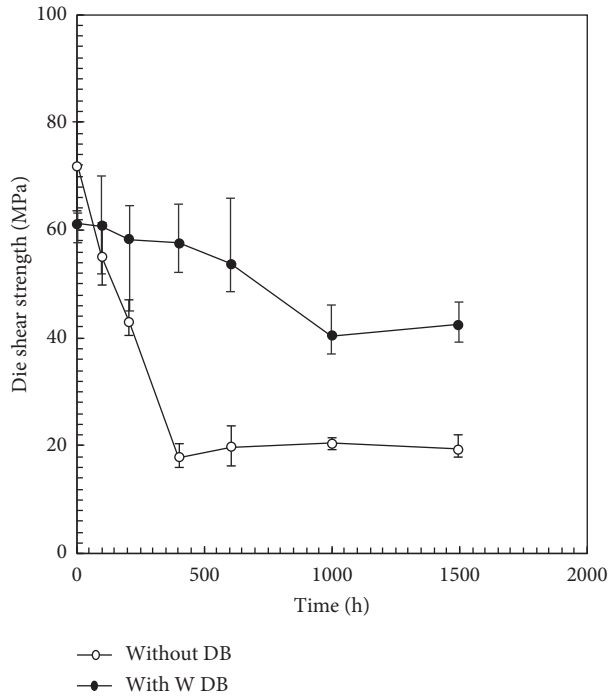| Solder	Substrate	Mean value (MPa)	Standard deviation (MPa)	Min value (MPa)	Max value (MPa)
	Cu-Ni	121	11	109	142
Au-28Ge	Cu-Ti	68	24	29	48
	Ni-Ti	38	8	23	48

FIGURE 8: Influence of aging time on the die shear strength of Au-Ge/ENIG solder joint with or without W-DB [48].

relevant enhancing method to meet the requirement of electronic packaging [56].

2.3. Au-Si Solder

2.3.1. Microstructure. Au-Si solder alloys have high-temperature oxidation resistance, satisfying thermal conductivity and electrical conductivity, and good electromigration resistance and mechanical properties, which make it quite suitable for electronic device packaging with high power and high integration. It could be seen from the binary phase diagram in Figure 9 that, although T_m of pure Au and that of Si metals are both higher than 1000°C, eutectic Au-Si solder alloys, consisting of 18 at.% of Si, possess a melting temperature as low as 363°C, which meets the requirement of low-temperature soldering [57]. The T_m and density (ρ) of eutectic Au-Si solder alloys are similar to that of eutectic Au-Ge, but eutectic Au-Si solder alloys exhibit better property than Au-Ge with higher ultimate tensile strength (σ_{UTS}) and lower CTE from room temperature (RT) to 400°C, as listed in Table 2 [58]. The solid solubility of Si in Au is small, and Au is substantially insoluble in Si. Therefore, Au-Si eutectic alloys are composed of Au-rich α solid
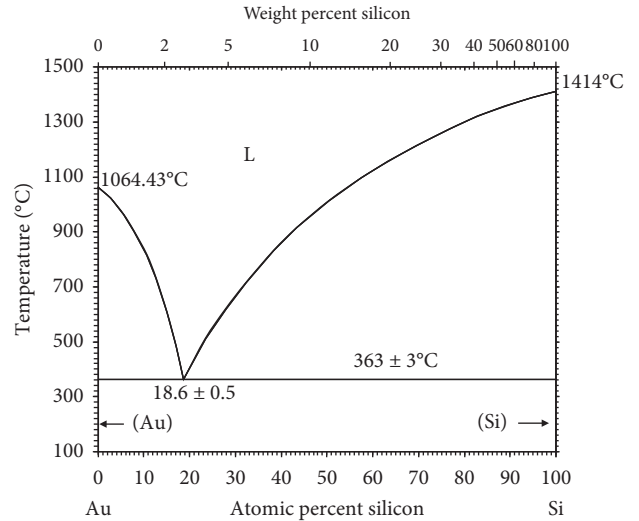

FIGURE 9: Binary phase diagram of Au-Si system [57].

TABLE 2: Properties of eutectic Au-Si and Au-Ge solder alloys [58].

Solder	Properties			
	ρ (kg·m^3)	σ_{UTS} (MPa)	T_m (°C)	CTE (RT-400°C) (10^{-6}·K^{-1})
Pb-5Sn	10.8	36	314	28.4
Au-20Sn	14.51	338.3	280	15.9
Au-3Si	15.7	255	363	12.3
Au-12Ge	14.67	185	361	13.4

solution and Si phase. The brittle Si phase would deteriorate the mechanical properties of the solder joint, which should be concerned. During thermal aging, the migration of Si particles was greatly accelerated, resulting in the formation of Au-rich zone at the joint center, and the inhomogeneity microstructure was obtained with micro defects induced by thermal stress, as illustrated in Figure 10 [47].

2.3.2. Mechanical Property. The high strength of eutectic Au-Si solder alloys makes it an excellent filler metal for the electronic system. It has been found that the three-dimensional Si-based micro-electrical system could be assembled well by eutectic Au-Si solder alloys, where a bond strength of up to 65 MPa was obtained [59]. But there are also some research studies claiming that the bonding effect of eutectic Au-Si solder on Si wafers with Cr or Ti metallization was not reliable enough, which limited its application [60, 61]. As listed in Table 3, the shear strength of eutectic Au-Si solder on two different substrates of Cu/Au and ENIG were both decreased during a thermal aging of 300°C, and the subsequent hot shear
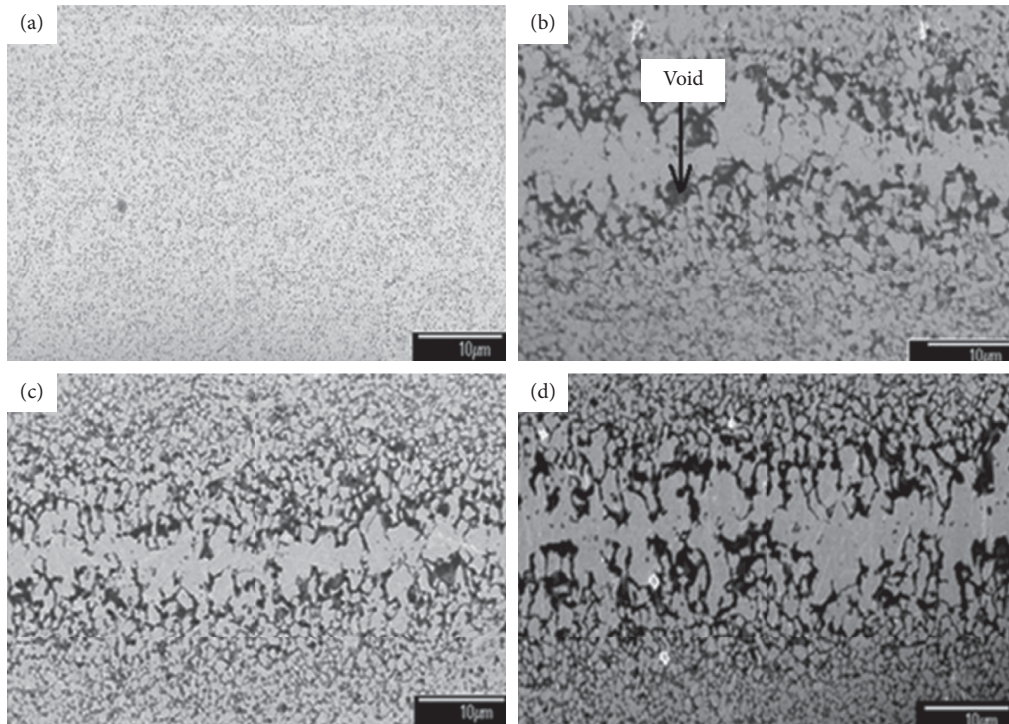
FIGURE 10: SEM images of Au-Si eutectic alloy: (a) without thermal aging and after (b) 100 h, (c) 300 h, and (d) 500 h of thermal aging at 300°C [47].

TABLE 3: Shear strength of Au-Si eutectic alloys with Cu/Au and ENIG UBM before and after thermal aging at 300°C for various durations [47].

Solder joint	Aging time (h)	Shear strength at RT (g·mil^{-2})	Shear strength at 250°C (g·mil^{-2})
Au-Si/Au/Cu	0	6.5	5.2
	100	4.7	3.3
	300	2.2	1.7
	500	1.8	1.3
Au-Si/ENIG	0	6.9	5.9
	100	6	5
	300	5.8	4.6
	500	5	4

gave a further decrement [47]. This phenomenon was ascribed to the coarsening behavior of grains in Au-Si solder joint, which indicated that eutectic AuSi might not be a proper choice for high-temperature application.

2.3.3. Solderability. At present, there are two main bonding process types of Au-Si eutectic alloys. One is to place Au-Si eutectic solder between the silicon chip and the substrate, and then heat and melt to form a eutectic solder joint; the second is to put an Au film on the substrate by vapor deposition or electroplating and then place the silicon chip on the substrate to achieve a eutectic solder joint under pressure with heating, and so on. The solderability of molten Au-Si solder alloy on SiO_2 and SiC substrates was very excellent, and the wetting angle of 0~30° could be obtained [62, 63]. This indicated that Au-Si solder alloys possessed potential for the micro-packaging with SiO_2 and SiC substrates. But the wettability of Au-Si solder on Si substrate was claimed to be quite unsatisfactory, and the wetting angle of up to 165°

could be observed, which rose with the increasing temperature, as shown in Figure 11 [64].

2.4. Au-Sb Solder. Au-Sb eutectic solder has an Sb content of 25% (mass fraction) and a melting temperature of 360°C. The Au-Sb solder is mainly used for soldering semiconductor devices whose joints require good electrical conductivity and corrosion resistance. However, Sb is considered to be a potentially toxic element [21] and hence affects the application of the solder alloy.

3. Au-Based Medium-Temperature Solder Alloys

In order to meet the higher requirements for the melting temperature and thermal performance of solders due to the miniaturization, intelligence, and high power of electronic products, the research and development of gold-based medium-temperature solders have received increasing
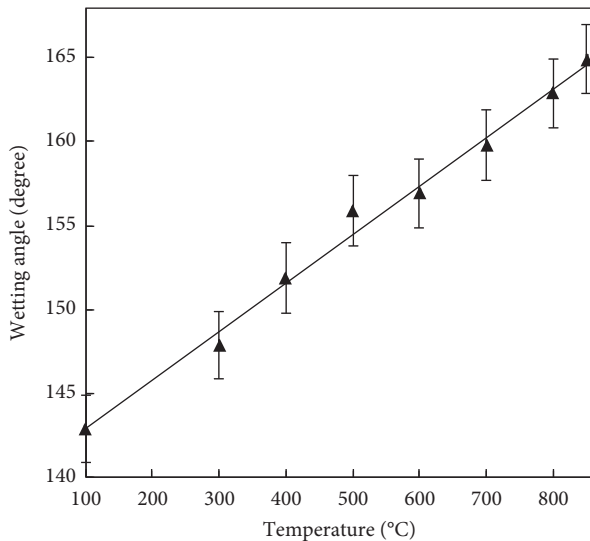
FIGURE 11: Variation of contact angle (measured in the gas phase) as a function of temperature on Si [64].

attention. Solder systems such as Au-Ag, Au-In, and Au-Ga have good solderability and great application potential.

3.1. Au-Ag Solder.
Au-Ag solder is seen an excellent filler metal to replace high-Pb solder alloys in the electronic packaging of electrical devices and the interconnection of their casings, the majority of which are Au-Ag-Si and Au-Ag-Ge solder alloys.

3.1.1. Microstructure.
Au-Ag-Si solder is mainly composed of Au element and contains a small amount of Ag and Si elements. The Au-Ag-Si solder is mainly composed of an α-Au (Ag) phase and β-Si phase. Because a large number of β phases exist in the solder matrix and are network-like distribution, the solder alloy has high brittleness and cannot be processed by traditional cold rolling processing methods [65]. The interfacial microstructure of Au-Ag-Si/Ni solder joint at different soldering temperatures is shown in Figure 12 [66]. During the soldering process, Si atoms in the molten Au-Ag-Si solder matrix migrated into Ni substrate, while the Ni element dissolved into the solder matrix, forming the Ni_3Si IMC layer. This IMC layer coarsened with the increasing temperature due to the accelerated atomic migration, giving a hill-like morphology, as illustrated in Figures 12(b) and 12(c). The Au-Ag-Ge solder consists of a primary α phase and a β phase containing a large amount of Ge element [21, 67]. Since the β phase is a brittle phase, it is difficult for the alloy to be rolled into a ribbon or pulled into a wire by general methods [68]. The microstructure of Au-Ag-Ge/Ni solder joint was found to be quite similar to that of Au-Ag-Si/Ni solder joint. A Ge_3Ni_5 IMC layer formed at the interface, and its excessive growth would be obtained if the soldering temperature was improved, as showed in Figure 13 [69]. The thick Ge_3Ni_5 IMC layer with high brittleness deteriorated the mechanical property of solder joint, and

hence the soldering parameters of Au-Ag-Ge solder alloys should be greatly concerned.

3.1.2. Solderability.
Table 4 lists melting properties of various Au-Ag solder alloys [70]. The Au-Ag-Si solder has good wettability on nickel plates, nickel-plated copper plates, and copper plates but could not wet silver. After the solder alloy was melted on the Ni plate, a wetting ring phenomenon occurred, which was mainly composed of Au elements. The interfacial microstructure analysis showed that Ni_3Si intermetallic compound formed at the interface between the solder and the Ni substrate. Compared with the Au-Ag-Si solder, Au-19.25Ag-12.80Ge solder has excellent wetting and spreading properties, and the wetting on Ni substrate is dominated by the reactive wetting mechanism, and the wetting ring is also produced. Due to the coupling enhancement of adding Si and Ge, Au-20.1Ag-2.5Si-2.5Ge quaternary solder performed better than Au-Ag-Si solder and Au-Ag-Ge solders in the wettability test, giving higher spreading properties.

3.2. Au-In Solder.
The In content of Au-In medium-temperature solder is usually between 18% and 27% (mass fraction). The microstructure of Au-In solder consists of two intermetallic compounds: a cubic structure of Au_7In_3 (γ' phase) and a three-oblique structure of AuIn (β phase) [71]. The airtightness and shear strength of the joint can meet the technical requirements of electronic device packaging, and thus the solder has a promotion and application prospect in the field of high-temperature packaging of microelectronic devices [72]. Figure 14 shows the interfacial microstructure of Au-In solder on the Cu substrate [73]. Cu dissolved into the molten solder matrix and reacted with In and Au elements during the wetting process. A thick interfacial layer, which was identified to be Cu-20In-14Au IMC, formed at the interface. But the Au content of Au-In solder alloy should not exceed a certain extent; otherwise the reliability of solder joint would be greatly decreased due to its brittleness. It has been found that the joint resistivity of Au-In solder with high Au content was significantly increased during thermal cycling owing to the formation of defects [74]. The liquidus temperature of Au-In solder alloys is from 450 to 500°C, and the spacing between the solidus and liquidus state is narrow, which means that the Au-In alloy is a suitable medium-temperature solder alloy. Besides, the solder has excellent wettability and gap filling properties for various base metals such as gold-plated Kovar, oxygen-free copper, pure nickel, and pure silver. A uniform and dense weld structure can be obtained by soldering gold-plated Kovar alloy and pure nickel base material.

3.3. Au-Ga Solder.
The Au-Ga-In solder alloy has a melting point between 282°C and 462°C, which is in the melting temperature range of the gold-based medium- and low-temperature solder alloys. By adjusting the composition of
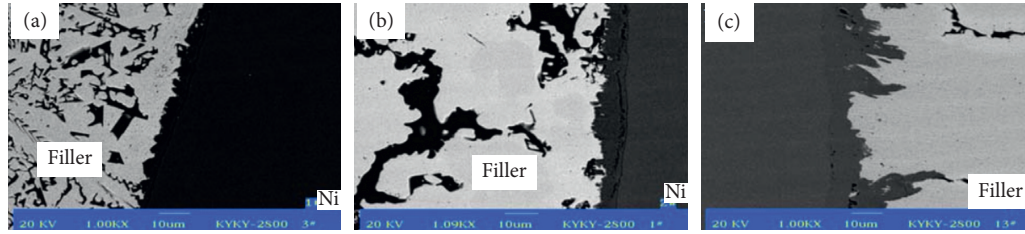
FIGURE 12: Cross-sectional electron images of Au-Ag-Si/Ni solder joint at different soldering temperatures: (a) 472°C, (b) 492°C, and (c) 512°C [66].
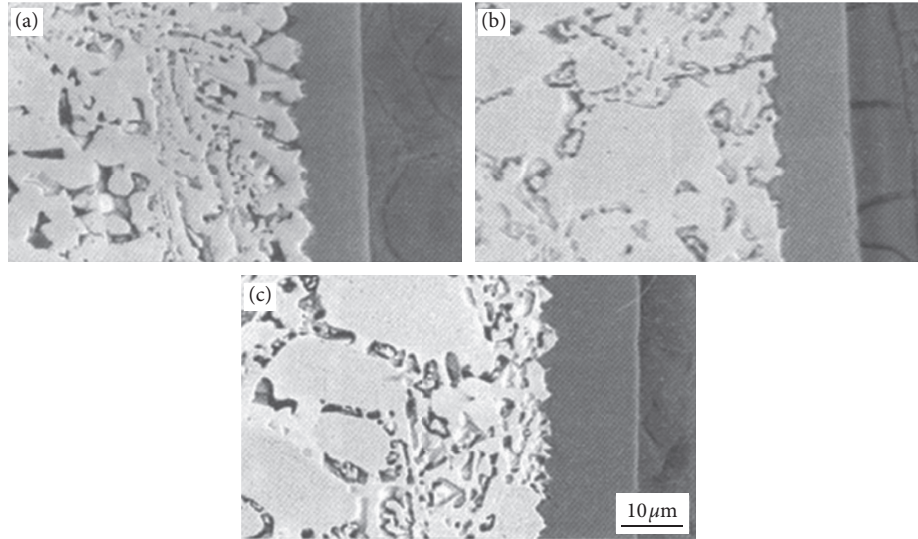

FIGURE 13: Cross-sectional electron images of Au-Ag-Si/Ni solder joint at different soldering temperatures: (a) 510°C, (b) 530°C, and (c) 550°C [69].

TABLE 4: Au-Ag-based medium-temperature solders [70].

Alloy	Composition (at.%)				Solidus (°C)	Liquidus (°C)	ΔT (°C)
	Au	Ag	Si	Ge			
Au-Ag-Si	86.72	10.02	3.26	—	409	450	41
	86.63	10.12	3.25	—	411	451	40
	82.70	14.02	3.28	—	421	457	36
	78.25	18.47	3.27	—	448	499	51
	78.30	18.50	3.20	—	449	478	29
	78.22	18.55	3.13	—	448	481	33
Au-Ag-Ge	58.5	19.5	—	22.0	410	449.8	39.8
	60.0	15.0	—	25.0	401.1	441	39.9
	67.95	19.25	—	12.80	446.76	494.4	47.64
	77.32	12.62	—	10.06	405	431	26
Au-Ag-Si-Ge	74.9	20.1	2.5	2.5	451.36	506.49	55.13

the Au-Ga-In alloy, the gold-based medium-temperature solder and the gold-based low-temperature solder alloys with different melting temperatures can be obtained. The patent [22] proposed an Au-Ga-In ternary alloy. By adjusting the addition amounts of Ga and In elements in the alloy, a series of solder alloys with different melting points can be obtained, as shown in Table 5, and can meet the requirements of different products for the melting temperature of the solder.

4. Preparation Methods of Au-Based Solder Alloys

Although Au-based medium-low temperature solder alloys have excellent performance, their high brittleness makes them difficult to be processed by conventional manufacturing methods, which seriously restricts the application of these solders. In particular, the Au-Sn eutectic solder is most widely
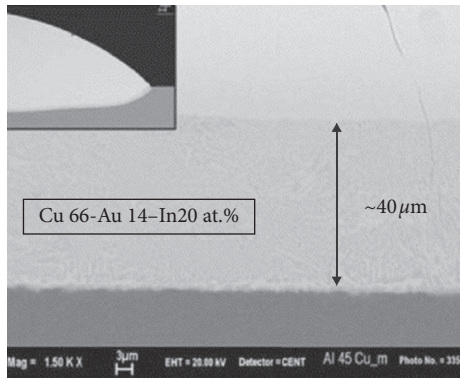
FIGURE 14: SEM micrographs of the cross section of the Au-In solder alloy on a pure Cu substrate [73].

used in electronic packaging and has the highest processing difficulty. In this regard, the researchers studied a number of special processing techniques to solve the manufacturing problem. At present, there are a few novel processing technologies, such as melt-casting and toughening process, laminated cold rolling process, electroplating deposition process, mechanical alloying process, and rapid solidification process.

4.1. Melt-Casting and Toughening Process. The melt-casting and toughening process is based on the traditional metal-casting process and introduces a hot calendaring process to refine the dendritic primary phase and the coarsening eutectic structure. Through the toughening annealing process, the alloy undergoes dynamic recrystallization to form evenly distributed small tissue. The fine structure improves the toughness of the alloy and thereby enhances the processing properties. The welding piece, foil material, and wire material are then prepared by mechanical blanking.

The melt-casting and toughening method can effectively promote the uniform alloying of the solder, improve the toughness of the solder through toughening annealing process, and provide favorable conditions for the subsequent mechanical blanking and other processes. However, the whole process uses multiple thermal processing and the operation process is cumbersome, which easily leads to the formation of some defects such as surface oxidation and introduction of impurities, affecting the performance of the solder joint.

4.2. Laminated Cold Rolling Process. The laminated cold rolling process, which is initially used for the processing of Au-Sn eutectic solder alloys, can be divided into lamination composite process and lamination diffusion process. Due to the good ductility of gold and tin, gold strip and tin strip are layered together (at least 5 layers), precompressed into a composite billet by a lamination process, and then cold-rolled into a foil of a desired specification, as shown in Figure 15. The lamination diffusion process is performed by homogenizing annealing treatment on the basis of the lamination composite process to realize alloying of Au-20Sn solder.

The Au-Sn eutectic solder prepared by the lamination cold rolling process is not easily oxidized and is easy to form, but the Au tape and the Sn tape are easily deformed during the rolling process, resulting in uneven solder component and insufficient alloying of the solder. In the soldering process, it is easy to cause segregation of chemical components, which results in an increasing melting temperature and affects the wettability of the solder, resulting in the weak formability of the solder alloy. Moreover, the uniform annealing temperature range of the composite strip after cold rolling is not easy to select. If the annealing temperature is too high, the Sn band will be melted. If the annealing temperature is too low, the atomic diffusion rate of the Au/Sn interface is slow, the production efficiency is low, and the solder cannot be prepared well.

4.3. Electroplating Deposition Process. The electroplating deposition process is mainly used for the preparation of Au-Sn eutectic solder. The method is to redox the ions containing Au and Sn to form elemental Au and elemental Sn and then deposit on the substrate. The operation process is as follows: First, a mask model of a certain shape is prepared on the substrate, and then the Au-Sn alloy plating solution is plated on the exposed surface of the substrate to form an Au/Sn film. After the plating is completed, the Au-Sn alloy foil is peeled off from the substrate. Using this process, Au-Sn bumps can be prepared on a flip chip by continuous plating [33], or Au-20Sn eutectic alloy plating can be prepared by codeposition, and the prepared solder plating layer has good bonding performance and good solderability on the Cu and Ni substrate.

The electroplating deposition process can precisely control the proportion of Au and Sn components, and various shapes of Au-20Sn solder layers can be prepared according to actual needs. The solder foil prepared by this method has the thinnest thickness, and a plurality of solder bumps on the same substrate can be completed by one plating, which greatly improves the efficiency and reduces the cost. However, this method is complicated in process and lacks flexibility, resulting in high electroplating technology and high maintenance cost, which limits its application. In addition, the need of a nontoxic and environmentally friendly alloy plating solution with good stability and long service life for plating is also an urgent problem to be solved [75, 76].

4.4. Mechanical Alloying Process. In the mechanical alloying process, Au powder and Sn powder are mixed in a mass ratio of 4 : 1 and then put them into a high-energy ball mill to achieve full alloying by ball milling. With the increase of ball milling time, the elemental Au decreases gradually, the proportion of IMCs increases, and the alloying degree of Au-20Sn increases. The alloy structure gradually changes from (ξ-AuSn$_2$ + δ-AuSn) phase to (ξ-Au$_5$Sn + δ-AuSn) phase, and the hardness of the alloy increases. During the ball milling process, the Au-Sn powder is repeatedly deformed, broken, and welded by the intense collision of the ball, which causes the Au powder and the Sn powder to overcome the

TABLE 5: Au-Ga-In solders [22].

No.	Composition (at.%)				Hardness (HV)	Processability	Solidus (°C)	Liquidus (°C)	ΔT (°C)
	Au	Ga	In	Sn					
1	84	13	3	—	242	Good	304	317	13
2	82	10	8	—	267	Good	306	322	16
3	83	10	7	—	290	Good	306	321	15
4	81	10	9	—	292	Good	306	323	17
5	82	11	7	—	300	Good	306	324	18
6	83	9	8	—	301	Good	306	323	17
7	81.95	10	8	0.05	292	Good	306	320	14
8	81.19	9.9	7.92	0.99	300	Good	282	302	20
9	67	25	8	—	180	Good	390	462	72
10	65	18	17	—	224	Good	380	418	38
11	62	13	25	—	257	Good	383	408	25
12	84.8	15.2	0	—	210	Good	339	358	19

FIGURE 15: Gold-tin laminated soldering diagram.

reaction barrier and interdiffuse. Thereby, the mechanically alloyed Au-20Sn powder could be obtained.

The Au-20Sn powder prepared by mechanical alloying may be further processed by adding an additive to prepare Au-20Sn solder paste or by pressing and low-temperature sintering process to prepare solder piece in a specific shape. The Au-Sn powder prepared by high-energy ball milling does not achieve complete alloying, and at the same time, due to the large plastic deformation caused by ball milling, the dislocation density of the alloy powder increases, resulting in work hardening.

4.5. Rapid Solidification Process. The rapid solidification process is to spray the molten alloy from the nozzle, form a strip under the action of a roller having a high thermal conductivity (usually a copper roller), and control the foil thickness by controlling the surface speed of the roller. Under appropriate conditions, the foil strip is heat treated and finally formed. The rapid solidification method could be further divided into the single roll method and the double roll method, and the single roll method has a faster cooling rate and a wider application. Since rapid solidification can refine grains, reduce tissue segregation, and expand the solid solution limit of alloying elements, the strip solder prepared by this method generally has uniform composition and excellent soldering performance.

This method is costly but effective for the Au-based solder alloy, especially for these with high Au content, such as Au-20Sn and Au-12Ge solder alloys. Due to high brittleness, these solder alloys are very difficult to be processed by the conventional method to prepare solder foils and hence could be achieved by the rapid solidification process. According to this method, gold-based medium- and low-temperature solders such as Au-Sn and Au-Ag-Ge can be prepared into a thin strip having a thickness of 0.1 mm or less [77]. What is more, compared with other methods, the process technology of rapid solidification is simple and hence gives a lower fabrication cost. In the field of novel electrical packaging where Au-based solder alloys are applied, the property of solder alloys is more emphasized than the cost. It has been clarified that Au-20Sn solder foil prepared by the rapid solidification process possesses higher wettability and mechanical property than melt-casting process [77]. Therefore, the rapid solidification process shows great potential for the manufacture of Au-based solder alloys.

Although the rapid solidification process has many advantages mentioned above, there are still many disadvantages for this method, which limit its industrial application. To ensure the uniform microstructure of alloy film, it puts much emphasis on the reliability of equipment, where the accurate design of spray nozzle and spraying voltage of row solder alloy are necessary. Moreover, the velocity stability of roller is very important for the suitable thickness and chemical component of solder foil. To apply the rapid solidification process in the industry, these relevant technology parameters and methods should be obtained and hence more investigations are necessary to meet the increasing requirement of electrical packaging.

5. Investigation Prospect of Au-Based Solder Alloys

Although with high price, Au-based solder alloys possess great thermal/electrical conductivity, wettability, oxidation resistance, and reliability, which make them the excellent electronic packaging materials for the novel electrical

devices. At present, there are still some shortcomings for gold-based medium-low temperature solder alloys to limit their application and development, the majority of which are difficult processing of solder foils, easy segregation of chemical components, and high cost of use. The development of electrical industry and aerospace industry put higher property requirement of Au-based solder alloys. In this regard, the development trend of gold-based medium- and low-temperature solders mainly has the following aspects:

(1) Explore new preparation processes: Although the present preparing technologies have a positive effect on the manufacture of gold-based brittle solder alloys, the application and promotion of some fabrication technologies are limited due to low efficiency, high cost, and complicated operation. Many factors could affect the performance of the prepared solder alloy, and further investigations to enhance them are needed. Therefore, it is necessary to further optimize the present processing technologies and actively explore new preparation methods, reduce production costs, improve production efficiency, and avoid segregation and oxidation of solder components.

(2) Find methods to enhance the performance of present Au-based solder alloys: Adding new components is claimed to be able to improve the microstructure and performance of the solder alloys, giving a lower brittleness and cost. And the risk of chemical segregation could be reduced as well. The alloy elements and the particulate reinforcing phase can be added to the existing gold-based solder alloys as the new component either individually or in combination.

(3) Develop new alloy systems: On the one hand, in view of the shortcomings caused by the high gold content in the present Au-based low-temperature solder, it is of great significance to design alloy composition from a diversified perspective to reduce the Au content. At the same time of reducing the cost, the solder should have good solderability and formability. Only in this situation, the new solder alloy could be considered to replace the present Au-based low-temperature solder alloys. On the other hand, to meet the increasing requirements of packaging materials due to the trend of high integration and high power of electronic devices, a gold-based medium-temperature solder alloy system with a high thermal conductivity, low expansion coefficient, and a melting temperature of 400–600°C should be actively developed.

(4) New soldering process: Because gold-based solders are commonly used in high-end packaging, their packaging environment and requirements are generally demanding, so it is necessary to develop new soldering processes to achieve reliable packaging in nonvacuum and flux-free environments. In addition, the present soldering processes cannot meet the research and application of new Au-based medium-temperature solder alloys. The development of new soldering processes is an indispensable part of the promotion and application of Au-based medium-temperature solders.

6. Conclusion

With the rapid development of the electronics industry, lead-free, miniaturized, and high-powered electronic products have placed higher demands on solder alloys. Au-Sn, Au-Si, Au-Ge, and other gold-based low-temperature solders will have wider application fields due to their excellent comprehensive properties. At the same time, the demand for gold-based medium-temperature solders will gradually increase. Low cost, easy preparation, high performance, etc. will become the main features of Au-based medium- and low-temperature solders. Therefore, reducing the gold content in the solder, solving the processing problems, and developing new gold-based alloy systems will become the investigation focus of Au-based solders in the future.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

Acknowledgments

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