Pressureless and low-temperature sinter-joining on bare Si, SiC and GaN by a Ag flake paste

Zheng Zhang*, Chuantong Chen, Aiji Suetake, Ming-Chun Hsieh, Aya Iwaki, Katsuaki Suganuma

Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

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ABSTRACT

In this work, we applied a Ag flake formed paste for sinter-joining on bare Si, SiC, and GaN surfaces. The sintered joints possess a high shear strength of over 40 MPa under a pressureless sintering condition at 250°C. The high bonding strength of the joints is achieved by a tight adhesion between Ag and bare surfaces, which attributed to an excellent sinter-joining ability of the Ag flake. The flakes, acquired by mechanical milling, can be rapidly sintered into a homogenous porous structure at a pleasureless and low-temperature sintering condition due to its dislocation-rich nano grain structure. During sintering, a drastic morphology reconstruction of Ag flake, from a flattened flake to a drop-like particle, can introduce robust interfacial connection structures, which is important for the robust bonding. This Ag flake paste can be regarded as a promising sinter-joining material for the connection of bare surfaces in high-temperature applications.

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In the last decade, Silver (Ag) sinter-joining has attracted increasing interest in high-temperature applications in face of massive heat dissipation caused by wide bandgap (WBG) semiconductors [1–3]. Ag particles can be sintered into a homogeneous porous structure under low temperature (below 250°C). After sintering, the Ag structure owns a high melting point (over 900°C), which is capable of withstanding high junction temperature of WBG semiconductors. Meanwhile, the superior chemical stability of Ag ensures good reliability of the sintering joint structure even under harsh environments. These merits make Ag sinter-joining an ideal alternative in place of solder joining or adhesive bonding in interconnections for high-temperature applications.

Currently, massive efforts have been made on Ag sinter-joining on Ag and Au surface metallization. Shear strength of Ag sinter-joining on either surface can be over 30 MPa under a mild sintering condition due to a rapid diffusion bonding between Ag and surface metallizations. [4–6]. However, surface metallization process will unavoidably incur manufacturing costs and add some uncertain factors such as defects or detachment during reliability tests [7,8]. To cut down costs and increase reliability, more attention is shifting to Ag sinter-joining on a bare surface of material. Recently, it has been reported that Ag sinter-joining was conducted on a bare surface AlN, Al₂O₃, and silicon-based materials [9–11]. However, decent bonding quality of Ag sinter-joining on such surfaces is at the cost of severe sintering conditions (high sintering temperature; high sintering pressure) or an assistant of Ag nanoparticles since an interdiffusion bonding is unlikely to happen under a mild sintering condition on such surfaces. The harsh sintering condition dramatically limits a widespread application of Ag sinter-joining for interconnections. In this work, we realized a robust sinter-joining on three bare semiconductor material surface-Si, SiC, and GaN, by using a Ag flake paste. The sintering was conducted under a pressureless condition at 250°C. Sintering behavior of the Ag flake paste and bonding structure of the joints are comprehensively discussed to understand the formation of decent bonding quality on the bare surfaces.

Ag flake paste, consisting of mechanical milling processed Ag flakes (AgC-239, Fukuda Metal Foil and Powder Co. Ltd) and organic solvent (CELTO-1A, Daicel Corporation) was uniformly mixed at a weight ratio of 12 to 1. Si, SiC, and GaN wafers with a thickness of 0.8 mm were diced into 3 × 3 mm dummy chips and 6 × 6 mm substrates for preparation of joints. The mixed Ag flake paste was firstly printed on substrates via a stencil mask with a mask size of 3 × 3 mm and then mounted with the dummy chips. After mounting, the samples were heated on a hotplate from room temperature to 250°C in the ambient atmosphere with a holding time of 60 min at 250°C and then naturally cooled down to room temperature.

* Corresponding author.
E-mail address: zhangzheng@anken.osaka-u.ac.jp (Z. Zhang).

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Morphology of Ag flake was firstly studied via a scanning transmission electron microscope (STEM, brightfield; ARM200F, JOEL) and shown in Fig. 1. The Ag flake shows a nanocrystalline structure with irregular morphologies (Fig. 1a). A magnified view of the red mark is given in Fig. 1b. Grain boundaries and dislocations can be identified in the Ag flakes, which ascribe to a mechanical milling process that can introduce enormous nanograins and dislocations to metal materials [12]. This unique structure conceivably plays a critical role in the sintering of the Ag flake paste. On the one hand, Ag nanograins own a low melting point, providing a precondition for low-temperature sintering. On the other hand, dislocations in the Ag flakes contain massive energy, which can facilitate recovery and recrystallization of the Ag flake during sintering [13].

The sinter-ability of Ag flake paste is verified via thermal behaviors and SEM observations. Fig. 2a shows the TG-DTA curves of the Ag flake paste. The weight of the Ag flake paste is drastically...
reduced from room temperature to 125°C and then remains stable with a further increase of temperature. This significant weight loss at the initial stage is due to evaporation and decomposition of the organic solvent in the paste, suggesting that the organic solvent can be easily removed. The DTA curve shows a minor exothermic peak at 125°C and a huge exothermic peak at 260°C, corresponding to the decomposition of the organic solvent and recrystallization of Ag flake, respectively [14]. Cross section of the printed paste (after drying) is shown in Fig. 2b. The printed Ag flakes appear a compact structure in which Ag flakes stack layer upon layer. After sintering, the cross section of Ag flakes is completely restructured, revealing a continuous porous structure interconnected via thick bonding necks (Fig. 2c). No flake-shape particles are observed in the cross section, suggesting complete sintering of the paste. The TG-DTA curves and SEM observations illustrate that the Ag flake paste owns a superior sinter-ability and a homogenous sintered structure at a low-temperature sintering condition, which provides a precondition for a robust joint.

Fig. 3a presents a demonstration of a sintered Ag-Si joint—the Si dummy chip bonds with the Si substrate via a layer of sintered Ag. Bonding strength of sintered joints was measured by a shear tester (Nordson DAGE 4000) at a shear speed of 50 μm/s. All joints exhibit an outstanding shear strength, which is 47.3 MPa (Ag-Si joint), 48.8 MPa (Ag-SiC joint), and 41.7 MPa (Ag-GaN joint), respectively (Fig. 3b). Cross sections of different joints were polished by an ion-milling (IM-4000; Hitachi) before SEM observation. Fig. 3c–e show overall views of cross sections of different joints. The cross sections exhibit a similar sandwich-like structure, in which the bare chip and the substrate are bonded through the sintered Ag layer. Magnified views of bonding interfaces are shown in Fig. 3f–h. All the bonding interfaces present an identical structure as well. The Ag has been entirely sintered and intimately attaches to the bare surfaces via some connection structures. Average interfacial contact length of every connection structure and interfacial contact ratio of sintered Ag to the surface are listed in Table 1 by calculating three SEM images with a scanning width of 50 μm. All joints own a thick interfacial connection structure with an average contact length of over 1 μm and a considerable contact ratio. On account of the intimate attachment and the considerable connection structures at the bonding interface, all joints exhibit a decent shear strength of over 40 MPa, which is even superior to bonding quality achieved on the Ag or Au surface [15,16].

The Ag-Si joint was thinned by polishing for a further transmission electron microscope (TEM, ARM200F, JOEL) observation. Fig. 4a shows a TEM image of the Ag-Si bonding structure in which the Ag is tightly adhering to the Si. Compared to the morphology of the original Ag flake, the sintered Ag shows a defect-free crystalline structure due to recovery and recrystallization during sin-
tering. A high-resolution TEM (HRTEM) image of the bonding interface is presented in Fig. 4b. There is an apparent amorphous layer with a thickness of around 2 nm between Ag and Si, which stems from a native oxide layer on the Si surface [17]. Finite Fourier transform (FFT) diffraction patterns of region 1-3 are shown in Fig. 4c–e, respectively. The FFT diffraction pattern of region 1 perfectly fits the Ag facet of [110]. The FFT pattern of Region 2 appears as a clouding spot dominated diffraction pattern due to the existence of the amorphous Si oxide. Region 3 exhibits a typical FFT pattern of Si with a zone axis of [110]. There are no alloys identified in the TEM observation. EDS mappings of the cross section are revealed in Fig. 4f. Three different layers can be obtained based on the contrast of STEM image, corresponding to Ag, amorphous silicon oxide, and Si, separately. According to the mapping images, elemental distribution of Ag, Si, and O are visibly differentiated, in which Si and Ag are adjacent to each other with a distinct O concentrated layer in-between. A trace amount of Si is identified in the Ag layer because of EDS measurement artifacts since it is unlikely to happen interdiffusion process or alloy generation between Ag and Si under such low sintering temperature and a short sintering duration [18]. A Ag-GaN joint was also observed through TEM (Fig. SI), which also reveals an intimate adhesion between Ag and GaN. The TEM analysis illustrates that the bonding of the joints is achieved via a tight adhesion between sintered Ag and different surfaces.

To understand Ag sinter-joining process on bare surfaces, the Ag flake paste was scattered on a bare Si surface and sintered in different heating durations. Fig. 5a shows the original morphologies of Ag flake paste (after drying). The Ag flakes present flat surfaces with irregular and shape edges due to a mechanical process. After 5 min sintering at 250°C, the Ag flake shows a bump-like surface texture and smooth edges (Fig. 5b), demonstrating recrystallization and recovery in the Ag flake. The Ag flakes are dramatically reshaped and shrink into a micron-sized droplet-like structure after 60 min sintering (Fig. 5c). The sintering process confirms an excellent sinter-ability of the Ag flake paste, which also plays a crucial role in joining Ag on different surfaces. Despite the micron-sized matrix, the Ag flakes can be rapidly sintered in a low-temperature and pressureless sintering condition due to nanograins and massless dislocations. During sintering, a significant morphology reconstruction process of Ag flake, from flattened flakes to micron droplet-like particles, occurs, which can induce substantial connections in the porous sintered Ag as well as the bonding interface. In addition, fresh Ag surfaces are generated during sintering and morphology reconstruction, allowing spreading and adhesion of Ag on bare surfaces without any influences of organic contaminations or

<table>
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<th>Table 1</th>
<th>Average interfacial contact length of connection structure and interfacial contact ratio of sintered Ag to bare surfaces.</th>
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<tr>
<td></td>
<td>Ag-Si joint</td>
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<td>Average interfacial contact length (µm)</td>
<td>1.18</td>
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<td>Interfacial contact ratio (%)</td>
<td>46.7</td>
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Fig. 4. TEM (a) and HRTEM (b) of cross section of Ag-Si joint; (c–e) corresponding FFT diffraction patterns from range 1-3; (f) STEM image and EDS mappings of the bonding interface of Ag-Si joint.
solvents. The robust connection structures and imitate adhesions provide a decent bonding quality for Ag sinter-joining on the bare semiconductor materials.

In summary, robust Ag sinter-joining is achieved on bare surfaces of Si, SiC and GaN under a pressureless sintering condition at 250°C. The sintered joints have a high shear strength of over 40 MPa. According to the SEM and TEM analysis, it is found that the bonding is realized by an adhesion between the sintered Ag and Si, SiC and GaN. The robust bonding is attributed to the excellent sinter-joining ability of the mechanically milled Ag flake. On the one hand, the Ag flake can be rapidly sintered into a continuous porous structure due to the nanograin and dislocations formed structure. On the other hand, the sintered Ag flake paste can form thick bonding structures and tight adhesions on the bare surfaces. This Ag flake paste shows versatility in bare surface bonding under a low temperature and pressureless sinter-joining, which may open a new avenue for interconnection and fixture on a bare surface in high-temperature electronics.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Fig. 5. SEM images of original Ag flakes (a); 5 min sintered Ag flakes (b); 60 min sintered Ag flakes.

Supplementary materials


References