Area-selective Interfacial Bonding in Cu/Si Composites and Its Effect on Thermal Diffusivity

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ABSTRACT

Unlike using diffusion barriers to control the severe Cu-Si reactions at elevated temperature, the area-selective interfacial reaction was achieved by a simple sol dipping pretreatment of Si powders to preserve the as-received components during the hot pressing of Cu/Si composites. The results indicate that the Cu and Si components are well preserved after hot pressing at 700 °C for 30 min in vacuum. In the prepared composites, the Si particle and Cu matrix bond together via Cu-Si compounds (e.g. Cu3Si) in some areas at Cu/Si interface, but separate in the other interfacial areas due to the presence of microcracks, suggesting the area-selective interfacial bonding. Furthermore, the composites possess an enhanced thermal diffusivity of 25.7 mm²/s.

INTRODUCTION

The interfacial reaction between Cu matrix and ceramic reinforcement is like a double-edged sword during the preparation of Cu matrix composites (CMCs) at elevated temperature. For example, the reaction in the infiltration process of Cu/SiC composites is commonly controlled, since it remarkably consumes the as-received components and generates the intermetallic compound like Cu3Si [1]. On the contrary, the reaction is slightly needed during the sintering of Cu/Al2O3 composites, so as to enhance the interfacial bonding because of the high stability as well as the lack of wetting between both components [2,3]. Therefore, how to achieve proper interfacial reaction is crucial to the fabrication of CMCs.

The similar issue also appears during the sintering of Cu/Si composites, which may be a promising electronic packaging material according to the theoretically ideal thermal conductivity as well as the coefficient of thermal expansion from the Cu and Si components [4]. As indicated by the Cu-Si diffusion couples [5,6], the reaction produce a great variety of copper silicides, so that the Cu and Si components are heavily consumed. In fact, diffusion barriers such as TaSiC, (AlMoNbSiTaTiVZr)50N50 and Al2O3 films have been used to control the reaction in Cu-Si interconnects [7-9]. Accordingly, the reaction for the micro-couples...
composed of Si particle and Cu matrix in composites can be controlled by the barrier as well. In a previous study [10], Al$_2$O$_3$ films, introduced at Cu/Si interface by the repeated sol-gel and pre-sintering treatment of Si powders, could retard Cu/Si interfacial reaction, so that the Cu and Si components were preserved in the hot-pressed composites.

Being different from controlling Cu-Si reaction by diffusion barrier, in the present work, the area-selective interfacial reaction, achieved by a simple dipping pretreatment of Si powders in Al$_2$O$_3$ sol, was used to control the severe Cu-Si reaction during the hot pressing of Cu/Si composites. The microstructure and thermal diffusivity of the prepared composites were investigated. Furthermore, the formation mechanism for area-selective bonding at Cu/Si interface in composites was discussed.

**EXPERIMENTAL**

Al$_2$O$_3$ sol synthesized from aluminum isopropoxide (Al(C$_3$H$_7$O)$_3$), and the detailed procedure was shown in Ref. [10]. Si powders (<45 μm) were dipped in the sol for 30 min and dried at 80 °C, obtaining the pretreated Si powders. The pretreatment is simpler than the coating procedure as shown in Ref. [10]. Next, the pretreated Si powders were blended homogeneously with Cu powders (<45 μm). The mixed powders with Si content of 40 vol.% were sintered at 700 °C for 80 min in vacuum and subsequently hot pressed under a pressure of 100 MPa for 30 min, being identical with the fabrication conditions as shown in Ref. [10].

The phases for the pretreated Si powders were determined by an XRD-7000S X-ray diffractometer. A JSM-7000F field-emission scanning electron microscope (FESEM) was applied to observe the microstructure and interfacial characteristics of the composites, and an energy dispersive spectroscope (EDS) attachment (Oxford INCA) was used to investigate elemental distribution. The thermal diffusivity of the composite was tested from 25 to 300 °C, respectively, by use of a Netzsch LFA 447 Nanoflash thermal constant measuring equipment.

**RESULTS AND DISCUSSION**

**Phase of Si Powders After Sol Dipping**

Fig. 1 shows the XRD pattern of Si powders after sol dipping. The intense peaks at 2θ=28.5,
47.4, 56.2, 69.2, 76.6 and 88.2° correspond to (111), (220), (311), (400), (331) and (422) reflections of Si (Fig. 1(a)), respectively, indicating a weak influence of the sol dipping on the composition of Si powders. Furthermore, Fig. 1(b) shows the enlarged view of the pattern, demonstrating the diffraction peaks at 2θ=28.2, 38.3, 49.3 and 64.1°, which are attributed to (120), (031), (200) and (231) reflections of AlO(OH), respectively. It suggests the formation of boehmite phase on Si particles after dipping in Al₂O₃ sol, which is different from the formation of γ-Al₂O₃ phase on Si powders as shown in Ref. [10], due to the absence of pre-sintering process after sol dipping.

Microstructure of Cu/Si Composites

Fig. 2(a) shows the SEM-BSE image of the microstructure of Cu/Si composites prepared with the sol-dipped Si powders, revealing Cu matrix, Si particle and the interfacial area between both. Fig. 2(b)-(f) show the EDS spectra at position 1-5 as denoted in Fig. 2(a), while the elemental composition is listed in Table 1. It can be seen that position 1 attributes to Si particle and position 5 to Cu matrix for nearly pure Si and Cu components. Moreover, position 3 contains 24.6 at.% Si and 75.4 at.% Cu, whose atomic ratio of Cu to Si is in accordance with that of Cu₃Si compound [6]. It is therefore inferred that position 3 is the interfacial reaction area composed of copper silicides. Position 2 and 4 correspond to the diffusional area of Cu into Si and the area of Si into Cu, respectively. In contrast, Cu₃Si compound dominates the composites prepared with the as-received Si powders [10].
Figure 2. SEM-BSE image (a) of the microstructure of Cu/Si composites and EDS spectra (b-f) for the position 1-5 shown in Fig. 2(a), respectively.

Table 1. Chemical composition at position 1-5 obtained from EDS spectra as shown in Fig. 2(b)-(f).

<table>
<thead>
<tr>
<th>Position</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si / at.%</td>
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<td>95.4</td>
<td>24.6</td>
<td>3.7</td>
<td>0</td>
</tr>
<tr>
<td>Cu / at.%</td>
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<td>4.6</td>
<td>75.4</td>
<td>96.3</td>
<td>100.0</td>
</tr>
</tbody>
</table>

**Cu/Si Interface in Composites**

Fig. 3(a) shows the high-magnification SEM-BSE image of the Cu/Si interface in composites, exhibiting an apparent boundary between Cu and Si. Whereas, the trace for the films derived from sol dipping pretreatment is not observed at the interface, being different from an obvious Al2O3 film as barrier at Cu/Si interface as shown in Ref. [10]. Noticeably, Si particle and Cu matrix bond together in some interfacial areas, but separate each other by microcracks in the other areas. Fig. 3(b) and (c) show the EDS spectra of Si and Cu distribution in the direction from A to B, suggesting that the bonded area corresponds to the interfacial reaction area due to the gradient change of the content of both elements at Cu/Si interface.

After dipping pretreatment of Si powder in Al2O3 sol, AlO(OH) gel forms on Si particles. The gel transforms to γ-Al2O3 phase in the case of sintering at 700 ℃ and simultaneously generates defects such as pores [11]. The defects also involving the uncoated areas on Si particles supply channels to interfacial reaction, by which Cu and Si atoms interdiffuse and produce Cu3Si compound. Moreover, some Cu atoms continuously diffuse into Si particles with a high mobility and may not be
incorporated in Cu₃Si compound during diffusion [12], so that two diffusional areas
of Cu into Si particle and Si into Cu matrix are formed at both sides of the
interfacial reaction area. Cu-Si diffusion and reaction preferentially occur in the
defect areas, while the micro-cracking areas are generated in the other areas owing
to the poor wetting and large thermal mismatch between Al₂O₃ and Cu [3,4]. As a
result, the severe interfacial reaction is confined in certain areas, which leads to the
weakening of the reaction for preserving Cu and Si components in composites; and
at the same time, area-selective bonding forms at Cu/Si interface for enhanced
interfacial bonding.

**Thermal Diffusivity of Cu/Si Composites**

Fig. 4 presents the variation of thermal diffusivity versus testing temperature for
Cu/Si composites. At 25 ℃, the thermal diffusivity reaches 25.7 mm²/s, much
higher than that for the composites fabricated by use of the as-received Si powders,
only 2.7 mm²/s, as reported in Ref. [10]. In addition, the testing temperature affects
the thermal diffusivity. From 25 to 300 ℃, the diffusivity decreases about 4.8
mm²/s. Generally, the thermal conduction in metals is mainly dependent on the
directional movement of free electrons. An elevation of

temperature can intensify the collision among electrons, resulting in a decrease of
thermal conductivity. It is thus supposed that the thermal conduction of the
preserved Cu component dominates the overall thermal conduction of the
composites.

**CONCLUSIONS**

In summary, the sol dipping pretreatment of Si powders can realize area-
selective interfacial reaction, so as to effectively control Cu/Si reaction during hot
pressing for the preserved Cu and Si components in composites. Si particle and Cu
matrix bond together by copper silicides such as Cu₃Si in some areas, and separate
each other in the other interfacial area, thus for area-selective interfacial bonding.
The thermal diffusivity of the Cu/Si composites at room temperature can reach 25.7
mm²/s, remarkably higher than the value for those prepared with the as-received Si
powders.

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