

Manufacture of rapid SiC heating element and increased durability through glass frit coating

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We investigated the optimal conditions for the manufacture of a rapid SiC heating element with increased durability for a flip chip bonder. In the moulding step prior to the sintering of the SiC heating element, a pressure of either 25 or 125 MPa was applied by uniaxial pressing to control the micropores; this was aimed at improving the resistance of the ultimate specimen. The moulded specimen was sintered by using a vacuum furnace with silicon as a sintering additive. The measurement of the hot modulus of rupture (HMOR) of the resulting SiC sintered body revealed that the HMOR was high. In addition, a method for protecting the heating element from the external environment was developed. A glassy coating layer was deposited on the surface of the structure to improve the corrosion resistance of the sintered body; further, the performance of the coating layer was verified through a neutral and acidic salt spray test. Finally, we established the optimal process conditions for manufacturing a rapid SiC heating element with improved corrosion resistance.

Keywords: Heating element, Silicon carbide, Glass coating, Corrosion resistance.

Introduction

The improvement of semiconductor manufacturing technology is a driving force that facilitates the development of next-generation semiconductor equipment and the relevant components and materials. There is a necessity to increase the manufacturing speed of high-end semiconductors, such as those used in smart phones and tablet PCs, and to further reduce the percentage of manufacturing defects. This is being achieved by the rapid replacement of the wire bonder-based method with the flip chip bonder-based method [1-3]. The flip chip bonder-based method, where a printed circuit board (PCB) is connected with a chip by solder ball bumping, can be applied to precise processes. This is because its high heat radiation rate, energy efficiency, and precision enable the reduction of the amount of defects in the manufacturing process, which then increases productivity; further, the conventional wire bonding is avoided in this case due to the compactness of the device and the processing speed [4, 5].

The core of the flip chip bonder equipment is the heating element inside the bonder. A heating element that can rapidly radiate heat is employed in the semiconductor process to enable rapid processing. Silicon carbide (SiC) is used as the material for the flip-chip bonder heating element because it has excellent

physical, electrical, and thermal properties, and also demonstrates good corrosion and heat resistance [6-10]. However, due to the low electrical conductivity ($\sigma = 10^{-13} \text{ S m}^{-1}$) of SiC, it is difficult to apply SiC alone to a heating element; therefore, a method for increasing the conductivity is needed [11, 12].

Conversely, parts of the flip chip bonder heating element undergo oxidation because of the gaseous atmosphere used in the process and the rapid heating and cooling cycles. The oxidation can decrease product quality and reduce the lifetime of the heating element [13]. An effective protective layer to shield the heating element from the extreme external environment is necessary to solve the problem.

In the present study, the optimum conditions for the manufacture of rapid SiC heating element with increased durability through a simple process were investigated. We sintered SiC under vacuum using Si as a sintering additive. Further, the porosity of the heating element was controlled during the manufacturing the flip chip bonder heating element; this control was aimed at achieving a rapid heating performance. In addition, a glassy protective layer was formed by coating the surface of the manufactured heating element with a solution containing glass frit to increase the oxidation resistance.

Experimental Procedure

Preparation of specimens at different pressures

Commercially available silicon carbide (β -SiC, 99.8%

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purity, 1 μm , Alfa Aesar, USA) and silicon powder (Si, 99.9% (metals basis), Alfa Aesar, USA) were used without further processing. The SiC and Si powder were mixed at a volumetric ratio of 6:4. The SiC/Si mixture (2.5 g) was charged into a mould, and a load either 25 or 125 MPa was applied through uniaxial pressing using an oil-hydraulic press to obtain specimens with dimensions of 20 mm \times 20 mm \times 2 mm. The processed specimens were sintered using a vacuum furnace under vacuum. During sintering, the temperature was increased to 1,400 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ and kept constant for 30 min. The temperature was then increased to 1,600 $^{\circ}\text{C}$, the final sintering temperature, at a rate of 5 $^{\circ}\text{C}/\text{min}$ and kept constant for 1.5 h. The specimens were subsequently allowed to cool to room temperature at a natural, uncontrolled rate to prepare the final SiC/Si specimens.

Formation of oxidation resistive coating layer

The SiC specimens were dip-coated. First, 100 cc of a mixed solution was prepared using isopropyl alcohol (IPA, 99.9%, DUKSAN, Korea) and ethyl cellulose (EC, $\text{C}_{23}\text{H}_{24}\text{N}_6\text{O}_4$, Sigma-Aldrich, USA) at a mixing ratio of 90:10 (vol%). To the prepared mixed solution, 50 g to 150 g of glass frit (S-4000, coefficient of thermal expansion: $75.8 \times 10^{-7}/^{\circ}\text{C}$, SHINCERAMIC Co., LTD., Korea) was added, and the resulting mixture was mechanically stirred to prepare a coating solution. The sintered specimen was dip-coated in the coating solution and dried at 70 $^{\circ}\text{C}$ for 2 h. Thermal treatment of the specimen was then performed using an electric furnace, increasing the temperature to 220 $^{\circ}\text{C}$ at a rate of 5 $^{\circ}\text{C}/\text{min}$ and keeping the temperature constant for 2.5 h, and then increasing the temperature to 650 $^{\circ}\text{C}$ and keeping it constant for 2 h. Following thermal treatment, the specimen was allowed to cool to room temperature at a natural, uncontrolled rate to prepare the final specimen with an oxidation resistive coating layer.

Analysis

The microstructure was analysed using field-emission

scanning electron microscopy (FE-SEM, JSM-7610F, JEOL, Japan) and the porosity of the moulded bodies was measured using mercury porosimetry (Model PoreSizer 9320, Micrometrics Instrument Group, Norcross, GA). The time-dependent variation of the current of the specimens prepared at different press pressures was measured using a switching type programmable DC power supply (EX30-120, 30V/120A, ODA TECHNOLOGIES, Korea). The hot modulus of rupture (HMOR) of the prepared specimens at 400 $^{\circ}\text{C}$ was measured by using HBTS 422 equipment (3-point bending test, Netzsch, Germany) at a loading speed of 0.3 mm/min. For the measurement, the specimens were processed in dimensions of 3 mm \times 4 mm \times 40 mm.

To verify the corrosion prevention performance of the coated specimens, a salt spray test was performed with either a neutral or acidic solution. The neutral salt spray test was performed by exposing the specimens to a 5% NaCl mist at pH 7.1 and keeping the spray temperature constant (Chamber ambient temperature: 35 $^{\circ}\text{C}$, Salt spray temperature: 37 $^{\circ}\text{C}$) for 96 h. The acetic acid salt spray (AASS) test was performed by spraying an acetic acid salt solution, titrated to pH 3.0, at a constant temperature (Chamber ambient temperature: 35 $^{\circ}\text{C}$, Salt spray temperature: 37 $^{\circ}\text{C}$) onto the specimens for 48 h.

Results and Discussion

Fig. 1 presents SEM images showing the surface morphology of the sintered bodies at different press pressures. In the sintered body prepared by applying 125 MPa, the particles were broken and coagulated, resulting in the collapse of the pores. The sintered body prepared by applying 25 MPa showed a more uniform particle distribution without particle destruction.

A pore characteristic analysis was performed to measure the porosity of the sintered bodies depending on the pressure. The porosity was 23.9% in the sintered body prepared under 125 MPa and 33.49% under 25 MPa. As shown by the pore characteristic analysis, the

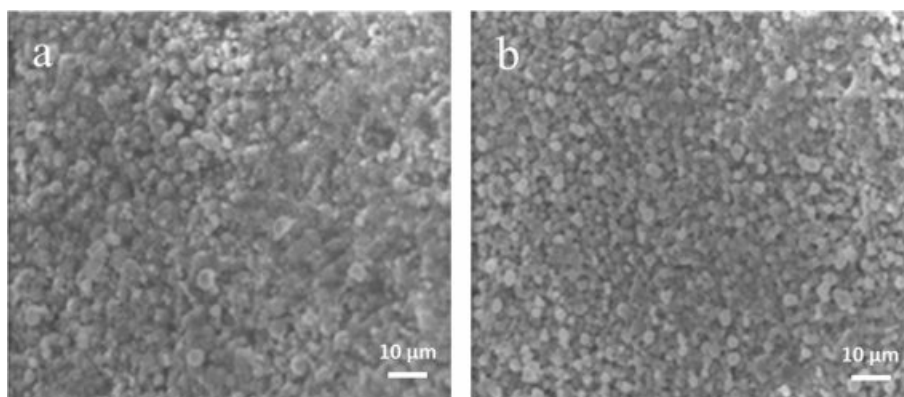


Fig. 1. Cross-sections of sintered bodies prepared at different pressures applied by the press. (a) Specimen prepared by applying 125 MPa; and (b) specimen prepared by applying 25 MPa.

porosity of the moulded bodies was significantly dependent upon the pressure load: as the press pressure increased, the porosity greatly decreased.

Fig. 2 shows the time-dependent variation of the current of the SiC sintered body at different press pressures. When the specimen was prepared with a press pressure of 125 MPa, the average current of the SiC sintered body was approximately 65 A at 12 V. Although this sintered body satisfies the required performance for a rapid heating element, the instantaneous heating may not be controlled when it is applied for the flip chip bonder equipment. The specimen prepared by applying a lower press pressure of 25 MPa showed an average current of approximately 34 A at 12 V, indicating that a resistance range suitable for a heating element was obtained. Specimens prepared by applying a press pressure lower than 25 MPa showed either a lack of moldability or a severe decrease of strength after sintering, making the specimens unsuitable. The relatively high porosity of the specimen prepared by applying 25 MPa may have increased its electrical resistance. Therefore, moulding the specimens at a low pressure before the sintering allows the formation of abundant pores, although the density of the structure may become relatively low. The pores decrease the electric conductivity of the specimens and increase the resistance, and the specimens thereby could successfully serve as rapid heating elements.

Considering that the prepared specimens are to be used as a heating element for a flip chip bonder, the strength in a high-temperature environment is a critical property. The HMOR of the specimens prepared under different press pressures was measured to verify their physical properties in a high-temperature environment, and the results are shown in Fig. 3. The error bars shown in the measurement data represent the range of the measurement values obtained from five samples prepared under identical conditions in order to ensure

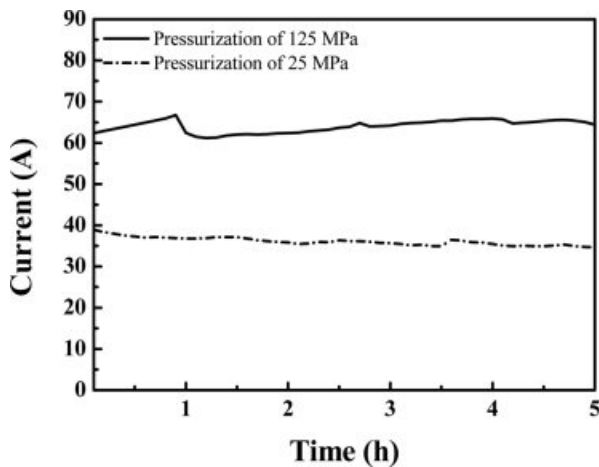


Fig. 2. Time-dependent variation of current through the SiC sintered bodies formed under press pressures of 125 MPa and 25 MPa at equal voltages.

reliability. The three-point HMOR values at 400 °C of the specimens prepared by applying press pressures of 125 MPa and 25 MPa were approximately 502 MPa and 448 MPa, respectively, indicating that both specimens had sufficiently high HMOR values. The data shows that an initial moulded body prepared under a higher load gives a higher HMOR after being prepared as a sintered body. However, considering the porosity and previously measured current values, the specimen prepared by applying 25 MPa may be more appropriate for application as a rapid heating element. Therefore, further experiments were performed using only the specimens prepared at this pressure.

Fig. 4 shows the mass increase of the specimens after dip coating as a function of the glass frit content of the coating solution. Even when the amount glass frit in the solution was increased, the weight of the coated specimens did not change significantly. However, as the glass frit content of the coating solution increased to 100 g or more, the mass of the sample after curing also increased. In the cases where the glass frit content was 90 g or less, a primary glass frit coating layer formed between the pores of the sintered body, and the coating on top of the primary coating layer was not

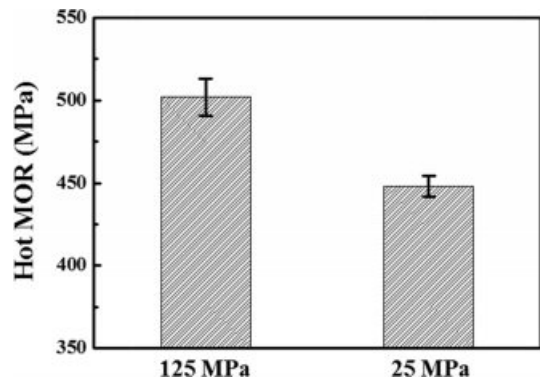


Fig. 3. Three-point HMOR (400 °C) of the specimens prepared under different pressures.

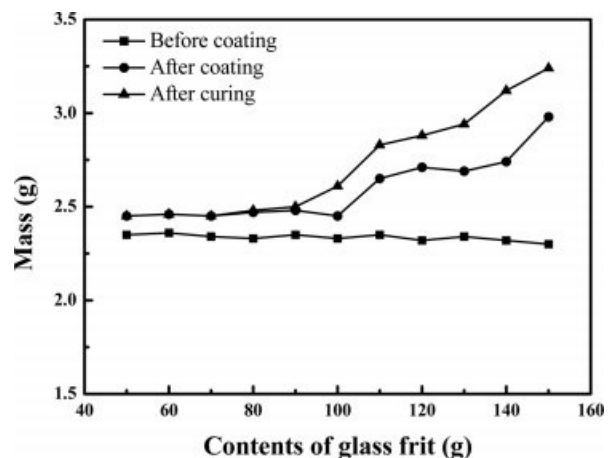


Fig. 4. Mass of coating depending on glass frit content in coating solution.

Table 1. Remaining weight ratio before and after oxidation resistive coating in corrosion resistance test.

	Remaining weight ratio after neutral salt spray (after 96 h)	Remaining weight ratio after acetic acid salt spray (after 48 h)
Before coating	98.1%	83%
After coating	99.54%	99.97%

thick. However, when the coating solution contained a glass frit content of 100 g or more, a thick glass coating layer was formed through curing. The excessive addition of the glass frit may have increased the viscosity of the coating solution, resulting in an increase of the coating solution remaining on the specimen surface during the dip coating process.

The glassy layer formed on the surface should be capable of protecting the heating element from the external environment when used in a flip chip bonder, and at the same time, should not have a negative effect on the heat radiation performance during rapid heating. Therefore, the acquired experimental data suggests that an oxidation resistance coating layer may be formed in a stable manner by performing the dip coating process using a coating solution containing 80 g of glass frit.

A salt spray test was performed to evaluate the corrosion resistivity of the specimens on which a glassy coating layer was formed by using a coating solution containing 80 g of glass frit. Table 1 shows the remaining weight ratio before and after the coating. In the neutral salt spray test, the specimens did not show a significant difference with or without the oxidation resistive coating. On the contrary, in the acetic acid salt spray test, the specimen showed a mass loss of approximately 17% without the oxidation resistive coating. The mass loss may have been due to the reactions between the metal components contained in the specimens and the acidic solution. After the formation of the oxidation resistive coating layer, the mass loss was only 0.03%, indicating that there was almost no change in the remaining mass. The low mass loss may be because both the strong resistance of the glassy oxidation resistive layer to acidic environments and the uniform formation of the coating layer on the surface of the SiC heating element samples protected the specimen.

Conclusions

In the present study, we fabricated SiC heating elements with a rapid heating performance; this was achieved by controlling the porosity of the specimens through the application of a pressing load of either 25 or 125 MPa. The SiC was sintered with Si in a furnace under vacuum at a relatively low temperature. In addition, the sintered specimens were dip-coated with a coating solution prepared with different quantities of glass frit

in the solution; further, the mass change before and after the coating and after curing was analysed to derive the optimal coating conditions. The neutral and acidic salt spray tests revealed that the glassy coating layer formed on the heating element could sufficiently protect the SiC heating element. The results showed that the optimal process conditions include a load of 25 MPa applied to the sintered body for providing a high porosity of 33.49% to increase the resistance; further, a coating solution with a glass frit content of 80 g was applied, which forms an effective oxidation resistive coating layer on the surface.

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