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Han, Young Hwan

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Bonding of silicon nitride using preceramic polymer and germanium powders for potential fuel cell applications

Y. H. Han*[1,2], N. Uekawa[3], T. Saito[3] and K. Kakegawa[3]

A new method for bonding blocks of Si_3N_4 has been developed that produces bonds whose maximum service temperature is equal to the temperature used during the bonding process. In the present paper a system consisting of blocks of Si_3N_4 coated with a preceramic film containing a fine dispersion of silicon and a thin layer of germanium powder has been investigated to determine the effect of the thickness of the germanium film. The maximum service temperature is not determined by the melting point of the germanium since the germanium forms a higher melting point solid solution with the silicon in the film. Control of the thickness of the germanium film is found to be critical as a thicker layers results in lower strength bonds owing to differences in thermal expansion, and the maximum service temperature is lower owing to the lower liquidus temperature of the leaner Ge–Si solid solution. This technique has potential applications in fuel cells as a result of the small differences in thermal expansion coefficients and firing shrinkage in fuel cell materials, thus allowing successful fabrication and joining of monolithic solid oxide fuel cells (MSOFCs) with few defects.

Introduction

As methods of bonding silicon nitride for service at high temperatures, diffusion sintering and brazing methods are proposed. Diffusion sintering involves heating materials under pressure at high temperature. Such high temperature can be a cause of deterioration in bonded materials. In brazing, heat resistance cannot be expected above the melting point of the metal used for bonding.[1–3]

Iseki et al.[4,5] investigated bonding of silicon carbide blocks using germanium powder. When heated, the germanium reacts with free silicon in the silicon carbide to form a solid solution between Si and Ge. This results in bonds which can be maintained up to 1323 K despite the fact that germanium has a melting point of only 1210 K.

Shaltz et al.[6] developed a partially transient liquid phase (PTLP) method of joining two high melting point components using a trilayer film consisting of a high melting point material sandwiched between two low melting point materials. Specifically, SiC and Si_3N_4 were joined using a number of metal films. This technique is simpler than Iseki et al.'s, but it does require the use of

the silicon dispersed phase. This demonstrates that bonding using low melting point materials need not result in a low melting point bond.

The present work embraces both Iseki et al.'s and Shaltz et al.'s approaches to obtaining high temperature bonds using relatively low melting point materials. It employs germanium powder and polyureasilazane $(Si_{1.0}N_{1.0}C_{1.4}H_{5.4})_2$, which is widely used to sinter SiC–Si_3N_4 composites, to form strong, heat resistant bonds between Si_3N_4 components.[7–9] In conventional high pressure sintering processes employing a nitrogen atmosphere, the polyureasilazane reacts to form a Si_3N_4–SiC nanocomposite that helps form the bond between the powders. In the process described below the germanium also plays a role in bonding when it reacts with free silicon in the ceramic, and silicon dispersed in the polyureasilazane provides a source of free silicon. As in previous work, this allows for higher service temperatures than were used in the bonding process. Potential applications in fuel cells include the chemical reactor/heat exchanger in a MEMS device, consisting of suspended tubes of low stress silicon nitride with integrated slabs of silicon, attached to a silicon substrate for hydrogen production, with a potential joining application of silicon nitride components.[9–11]

Experimental procedure

The experimental procedure consisted of forming the silicon dispersed polyureasilazane film on a block of Si_3N_4, evaluating the wetting of germanium on the

[1]Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA
[2]Advanced Materials, Sungkyunkwan University, Suwon, Gyeonggi-do 440-746, Korea
[3]Graduate School of Science and Technology, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

*Corresponding author, email yhhan@ucdavis.edu
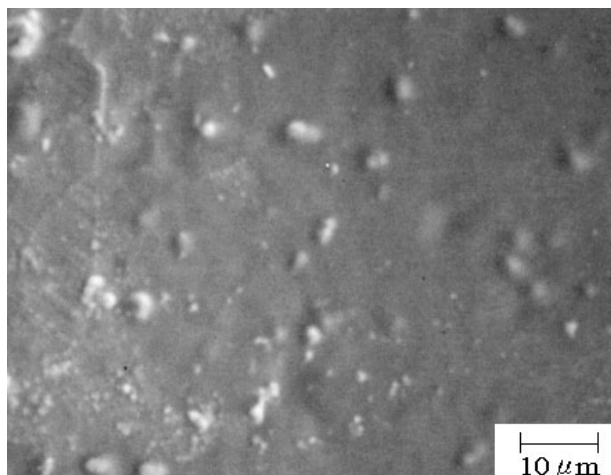
1 Secondary electron scanning electron micrograph of film applied to Si$_3$N$_4$ blocks: film produced by curing mixture of silicon particles dispersed in polyureasilazane; particles shown are silicon particles smaller than 5 μm

2 Contact angles of three Ge–Si solid solutions on uncoated silicon nitride as function of time at 1150°C: ○ 3 wt-%Si, ■ 5 wt-%Si, ◇ 10 wt-%Si

Si$_3$N$_4$, then bonding two blocks of Si$_3$N$_4$. Four point bend testing and examination of the surfaces and cross-sections of the film followed.

Film formation

The silicon dispersion was produced using an agate mortar and pestle. It was put into a 10 cm high cylinder with acetone for sedimentation. After 25 min, silicon particles less than 5 μm in size were still dispersed (as per Stokes's Law) while particles larger than 5 μm settled to the bottom. The top clear layer was then warmed and stirred to evaporate part of the acetone in order to adjust the concentration to 0·05 g Si per millilitre of suspension. After letting the suspension set again for approximately 25 min, particles larger than 25 μm settled to the bottom. This was confirmed using SEM, as shown in Fig. 1. The sediment at the bottom of the cylinder was discarded and the liquid kept. The liquid contained a suspension of fine silicon particles smaller than 25 μm.

Polyureasilazane (Tonen, Tokyo, Japan) was dissolved in the acetone–silicon mixture (1·0 g acetone–silicon, 2·0 g polyureasilazane). One face of a 10 mm cube of Si$_3$N$_4$ (Nippon Fine Ceramics, Japan) was briefly dipped in the solution, and then spun at 8000 rev min^{-1} for 1 min to remove excess solution. It was then heated at 210°C for 5 min to remove the residual acetone, with insignificant Si–O bond incorporation from the intake of oxygen in the air, and then fired at 1200°C in a purified nitrogen atmosphere (oxygen and water were removed using a copper catalyst, silica gel and phosphor pentoxide) for 60 min. X-ray diffraction confirmed that the resulting film was amorphous. Only silicon peaks were observed.

Measurement of wetting

A small particle of germanium (approximately 1 mm^3) was put on the film side of a Si$_3$N$_4$ block and heated to 1150°C under a vacuum of 0·6 Pa. A microscope equipped with a measuring reticule was used to measure the contact angle.
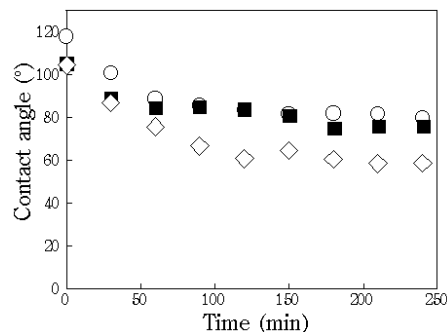
To investigate the effect of dissolved silicon in the germanium on the wetting angle, samples of germanium–silicon solid solutions were prepared by putting a piece of silicon on a germanium block and slowly heating it. At approximately 950°C the germanium melted and the silicon dissolved into the germanium. This was done three times to provide germanium pieces with silicon concentrations of 3, 5 and 10 wt-%. The contact angles of these alloys on the coated surface of the Si$_3$N$_4$ blocks were measured using the same method as above.

Bonding

Spreading germanium powder on the silicon dispersed polyureasilazane film of one block and placing a second coated Si$_3$N$_4$ block on top with the film coated sides in contact with each other bonded two film coated blocks of Si$_3$N$_4$. The assembly was heated at 1150°C for 240 min under a vacuum of 0·6 Pa and a clamping pressure of 13 MPa.

Four point bend testing

The four point bend samples were bars 2 mm high by 2 mm wide by 20 mm long and were obtained from the centre sections of the bonded block assemblies. The bond was located at mid length and was oriented parallel to the direction of loading. Two samples were tested, one having been processed using a 1 mm thick layer of germanium powder and the other using a 0·5 mm thick layer. In one set of tests a load of 75 kPa was applied to both samples while they were heated and the temperature at which they failed was noted. In the second set of tests both samples were tested at room temperature and the fracture strengths recorded.

Results and discussion

Wetting measurements

Wetting between silicon nitride and germanium is essential for good bonding.[12] Figure 2 shows the results of wetting measurements of the Ge–Si solid solution conducted on uncoated Si$_3$N$_4$ at 1150°C, where increasing the concentration of silicon lowers the contact angle. This effect is pronounced at 10 wt-%Si. Figure 3 shows the results of similar measurements made for the case where the Ge–Si solid solution is placed on the film coated Si$_3$N$_4$. As before, the contact angle decreased over time, but this time the decrease was a greater. The film, which contains amorphous silicon carbide and amorphous silicon nitride, is effective at increasing the
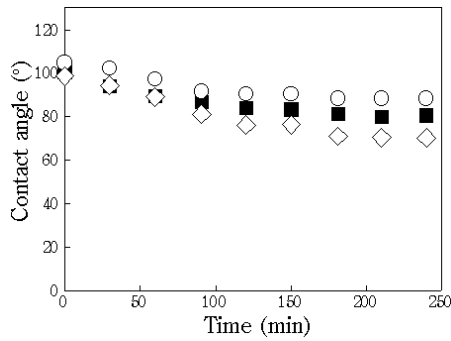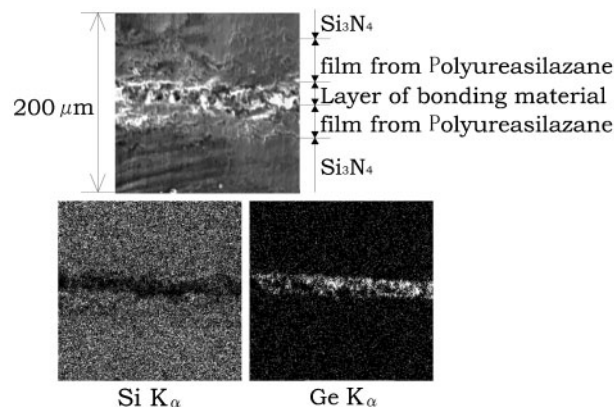
3 Contact angles of three Ge–Si solid solutions on coated silicon nitride as function of time at 1150°C: ○ 3 wt-%Si, ■ 5 wt-%Si, ◇ 10 wt-%Si

5 Backscatter electron image and X-ray dot maps of cross-section of bond formed using 0·5 mm thick layer of Ge powder

wettability. In both cases, however, the contact angle decreased to less than 90°, so conditions for good bonding can be met with and without the film. However, the film improved wettability and should therefore result in better bonds.
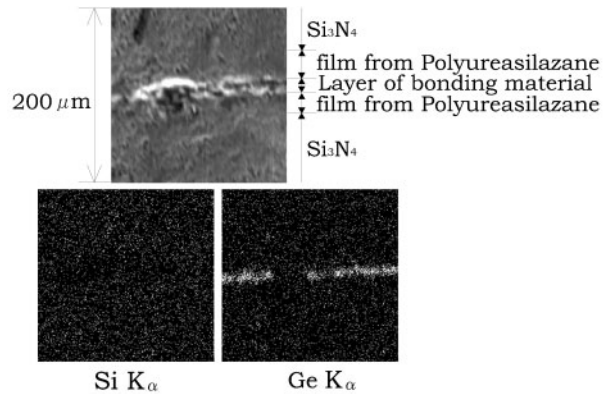
SEM imaging of bond regions

Figure 4 shows SEM (SEI) and X-ray dot map images of cross-sections of bonded Si_3N_4 blocks where a 1 mm thick layer of germanium powder was spread on the polyureasilazane coated blocks. These images show that the bond region is about 50 µm thick, that the concentration of silicon in this region is relatively low and that the concentration of germanium is high. The bond region itself consists of three layers where the germanium rich layer in the centre is from the original powder and the top and bottom layers are from the polyureasilazane film. The top film layer is difficult to see in the SEI image while the bottom layer is barely visible in the silicon dot map (Fig. 4).

Figure 5 shows similar images for the case where only a 0·5 mm thick layer of germanium powder was used. The bond region is thinner, the layer of germanium is thinner and the polyureasilazane film cannot be seen in either the SEI image or the X-ray dot maps. In addition, the concentration of silicon is nearly uniform. The silicon poor region seen in Fig. 4 is almost undetectable in Fig. 5.

Four point bend testing

The four point bend tests were conducted at constant load while the temperature was steadily increased. The temperature at which the bonds failed was noted and is shown in Fig. 6a. The results show that the bond created using the thinner (0·5 mm) layer of germanium held to a higher temperature. The sample with the thicker germanium layer (1 mm) failed at about the melting point of germanium (bond failed at 950°C, germanium melts at 937°C). Apparently melting occurred in the thicker layer of germanium seen in Fig. 4, consisting probably of germanium that did not enter solution with the silicon. The phase diagram in Fig. 7 illustrates the problem. During the bonding process, which took place at 1150°C, both liquid and solid phases would exist unless sufficient time was allowed for the germanium to diffuse away from the bond surface and into the Si_3N_4. As it cooled, the concentration of germanium in the
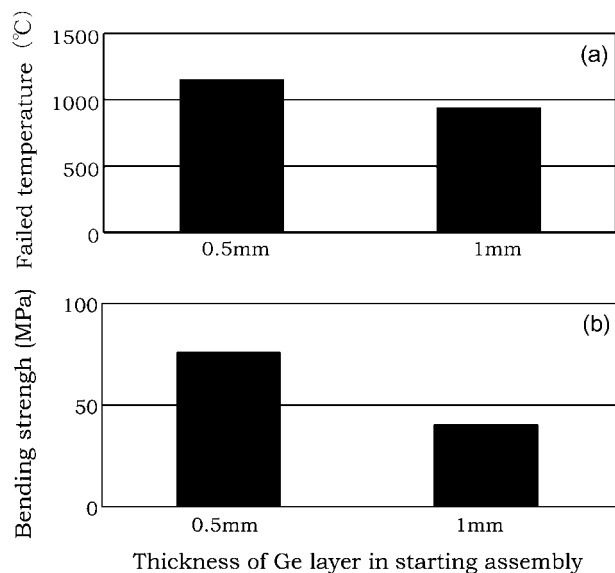
6 *a* stresses at which samples with different Ge powder layer thickness failed when tested at room temperature: sample with thicker layer failed at lower stress owing to residual stress in Ge–Si layer; *b* temperatures at which samples using different Ge powder layer thickness failed: sample with thicker layer failed near melting point of Ge while sample with thinner layer failed at bonding temperature

4 Backscatter electron image and X-ray dot maps of cross-section of bond formed using 1 mm thick layer of Ge powder

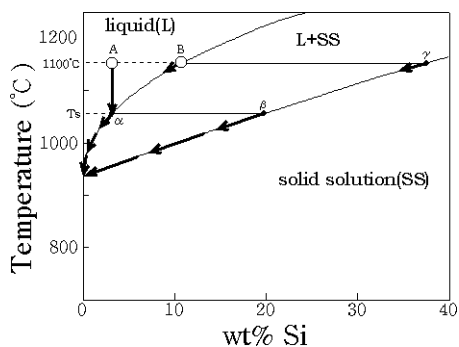**7 Illustration of paths followed during cooling of two Ge–Si compositions: when completely solidified composition A consists of large amount of low melting point Ge phase while composition B begins to precipitate at T_s**

liquid phase would increase, as indicated by the arrows. When reheated during four point bend testing it is this germanium rich phase that melted and caused the bond to fail.

In the case of the second sample, which used a 0·5 mm thick layer of germanium, failure occurred at 1150°C, the same temperature used in the bonding process (Fig. 6*a*). The reason why the test temperature is higher in this case is that by using less germanium while using the same bonding time and temperature more of the germanium powder is able to melt and incorporate silicon from the polyureasilazane film. The result is a Ge–Si solid solution with higher silicon content than in the previous case, and thus a higher liquidus temperature. This would explain why this bond fractured when the bonding temperature was reached.

The results from these tests at room temperature are shown in Fig. 6*b*. The sample having the 1 mm layer of germanium powder fractured at 40 MPa while the sample with the 0·5 mm layer fractured at 75 MPa. In both cases fracture occurred at Ge–Si/(Si$_3$N$_4$ from preceramic polymer), (Si$_3$N$_4$ from preceramic polymer)/(Si$_3$N$_4$ block), inside the Ge–Si layer, and inside the Si$_3$N$_4$ from preceramic polymer. Iseki *et al.*[4,5] found that the strength in the bonds in reaction bonded Si$_3$N$_4$ containing germanium and free silicon decreased as the thickness of the Ge–Si solid solution layer increased. This was attributed to stresses caused by differences in thermal expansion. The results in the present work, where the bond with the thinner Ge–Si layer was stronger, are consistent with Iseki *et al.*'s findings.

Conclusions

A new method for bonding blocks of Si$_3$N$_4$ has been developed. The process involves coating these blocks with a polyureasilazane film containing a fine dispersion of silicon. This film is coated with a thin layer of pure germanium powder and then the blocks are pressed together and held at a temperature of 1150°C for 1 h. Bonding is achieved by melting the germanium and dissolving the free silicon in the polyureasilazane film to form a Ge–Si solid solution whose maximum silicon concentration is determined by the processing temperature. This Ge–Si film wets the Si$_3$N$_4$ better than pure germanium and results in a stronger bond. Afterwards, the bond is good up to temperatures as high as the bonding temperature. Control of the thickness of the

germanium film is critical as it has been shown that thicker layers result in lower strength bonds owing to differences in thermal expansion, and the maximum service temperature is lower as a result of the lower liquidus temperature of the leaner Ge–Si solid solution.

The attraction of solid oxide fuel cells (SOFCs) is based on a number of aspects including the clean conversion of chemical energy to electricity, low levels of noise pollution and the ability to cope with different fuels, but most of all on their high efficiency. The enhanced efficiency of SOFCs in comparison with other energy conversion systems is a result of the high operating temperature, which in some designs may exceed 1000°C. In these cases the potential exists, by extracting the energy present in the high temperature exhaust gases (e.g. by using gas or steam turbines), to boost the overall efficiency of the SOFC system to around 70%.

The feasibility of the monolithic solid oxide fuel cell (MSOFC) concept has been proven, and performance has been dramatically improved. The differences in thermal expansion coefficients and firing shrinkage among the fuel cell materials have been minimised, thus allowing successful fabrication and joining processes for MSOFCs with few defects. The MSOFC shows excellent promise for development into a practical power source for many fuel cell applications, from stationary power sources, to automobile propulsion, to space pulsed power.

The bonding technique described in the present paper can be effectively used in such systems. The bonds are intact to temperatures above 1000°C, and the small mismatch in coefficients of thermal expansion reduces the likelihood of failure due to internally generated stresses and should tolerate many heating and cooling cycles, thereby extending the service life of the components.

Acknowledgments

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