Anodic Bonding of Silicon Carbide to Borosilicate Glass*

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Joinability of silicon carbide to glass by anodic bonding was evaluated. Polycrystalline silicon carbide was successfully bonded to borosilicate glass Corning 7740. No crack by the residual stress occurred in all bonding conditions adopted in the present study. Increase in the bonding temperature enhanced progress of bonding, and the joint strength increased with the bonding temperature and the voltage application time. But the shear fracture stress of the joints did not exceed 6 MPa, and all the joints broken at the joint interface. Formation of a carbon-rich amorphous layer at the bond interface was observed by transmission electron microscopy. It was suggested that this layer caused relatively low joint strength of silicon carbide/glass anodically-bonded joint.

Key Words: anodic bonding, silicon carbide, borosilicate glass, joint strength, microstructure, interfacial reaction

1. Introduction

Anodic bonding is a method for bonding metals or semiconductors to glass containing alkali ions by applying a D.C. voltage of 100-1000 V between them with the metal side anodic at a bonding temperature of 500-700 K. In this temperature range thermal diffusion of alkali ions in glass is activated, and under the influence of the electric field induced by applied voltage, these ions drift toward the cathode side, and an alkali ion depletion layer forms in the glass near the joint surface. This layer has a strong negative charge because of the presence of non-bridging oxygen (O) anions that lose their bonds with the alkali ions. A Coulomb force acting between this charge and the charge appearing on the surface of the anode conductor brings the glass and the conductor into intimate contact, and a permanent bond is achieved by the oxidation of the surface of the conductor by oxygen derived from the alkali ion depletion layer in the glass¹⁾. Anodic bonding achieves direct bonding of conductor to glass without intermediates such as solder or adhesive, and it is workable at a temperature low enough not to cause deformation of the glass²⁾. These features make anodic bonding a powerful method for precise bonding of conductors to glass. Anodic bonding is commonly used in sealing of silicon micro devices, for example, sensors for pressure or acceleration. Silicon carbide (SiC) has been used as a ceramic for structural material that has high strength, thermal shock resistance, and chemical stability, and it is a promising semiconductor that can be used in high temperature or radiation environments. Utilization of SiC can extend application of semiconductor sensor devices, and it is

desirable to establish the technique of anodic bonding of SiC. A possible problem exists in anodic bonding of SiC. In anodic bonding, the surface of conductor is oxidized by oxygen from the glass³⁾. In anodic bonding of silicon, this reaction produces SiO₂ to form a sound interfacial structure. But in anodic bonding of SiC, the oxidation of SiC may produce CO, CO₂, or free carbon besides SiO₂⁴⁾. These products can cause degradation of bond interface. In this study, anodic bonding of SiC to borosilicate glass was tried. The progress of bonding and the change in the joint strength with bonding time were observed at various bonding temperatures, and microstructure of the joint interfaces was examined to investigate its influence on the joint strength.

2. Experimental procedure

Pressureless sintered polycrystalline SiC and borosilicate glass Corning 7740 were adopted as experimental materials. The SiC used in this study contained some free carbon. Chemical composition of the Corning 7740 glass is shown in Table 1. The linear expansion coefficients of SiC and the Corning 7740 glass are 4.2×10^{-6} /K and 3.25×10^{-6} /K, respectively. The difference between them is relatively small. The glass was provided as disks of 1 mm in thickness and 25 mm in diameter. Surfaces of the glass disk were mechanically-polished and made optical-flat. SiC was cut into disks of 3 mm in thickness and 16 mm in diameter. Faying surface of the SiC disk was finished glossy by grinding and chemical-mechanical polishing. Anodic bonding was performed in an argon atmosphere. In the specimen chamber of the bonding apparatus, the glass disk was put on the negative electrode plate of copper. The surface of the glass disk which

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Table 1 Chemical composition of the glass (mass%).

SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	B ₂ O ₃
81.0	2.02	4.04	0.01	0.02	12.7

contacted the electrode plate (the surface NOT to be joined with SiC) was coated with conductive paint (colloidal graphite) in order to make the electric potential of the surface uniform. The SiC disk was put on the glass disk with its faying surface contacting the glass, and the positive electrode was connected to the SiC disk. After the displacement of the gas in the chamber, the joint pieces were heated to the bonding temperature (T_b) by the graphite resistive heaters surrounding them. Then bonding voltage of 500 V was applied to the joint pieces with the SiC side anodic for a bonding time (t_b). The T_b and the t_b were changed in a range from 523 K to 613 K and from 40 s to 1800 s, respectively. After that the heaters were turned off immediately, and the joint was cooled to the room temperature in about 2000 s. For the produced joints, the progress of bonding was evaluated by observation of appearances of the joint interfaces through the glass, and the joint strength was estimated by the shear test. In the shear test, only the joints in which intimate contact was achieved all over the joint interfaces were used. And multiple specimens bonded in the same bonding condition were examined and the results were averaged. The cross-sectional microstructures of the joint interfaces were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The metallographic specimen for SEM was finished by buffing with diamond paste. The environmental scanning electron microscope (ESEM) NIKON ESEM-2700 was used for SEM. Usually the SEM of insulating materials like glass needs some conductive deposit on the surface of the specimen in order to avoid the charge-up of the specimen that caused by electron beam. But the deposit is not required with this ESEM, because the atmosphere of observation in ESEM is not a vacuum but moisture vapor of ~ 2700 Pa, and the charge of the specimen is neutralized with the moisture vapor. This is the advantage of ESEM in the observation of insulating specimens. Thin foil specimen for TEM was prepared with HITACHI FB-2000A focused ion beam (FIB) apparatus, and TEM observation was performed with JEOL JEM-2010 transmission electron microscope operating at 200 kV. The SEM and the TEM apparatuses were both equipped with energy dispersion spectroscopy analysis (EDS) systems.

3. Result and discussion

Anodic bonding of SiC to borosilicate glass was available. Figure 1 shows the appearance of the produced joint interfaces. The bonding time of these two joints were both 40 s. Intimate contact was achieved all over the joint interface at T_b of 613 K (Fig. 1(a)). On the other hand, in the joint bonded at T_b of 523 K the intimate contact area was rather small (Fig. 1(b)). No crack by the residual stress occurred in all the bonding conditions. In Fig. 2,

Fig. 1 Appearances of the anodically-bonded SiC/glass joints with the voltage application for 40 s at 523 K (a) and 613 K (b). The intimate contacting areas are indicated by the letters 'c' in both photos.

Fig. 2 Fractional contacting area in the joint interface in anodically-bonded SiC/glass joints as functions of the voltage application time.

the fractional contacting area in the joint interface is shown as functions of the bonding time. The expansion rate of the intimate contacting area increased with T_b . At 523 K, the fractional contact area exceeded 90% with the voltage application for 1800 s, and the same fraction was achieved in 40 s at 613 K. Increase in the temperature accelerates the drift of the alkali ions in the glass, and the growth of the alkali ion depletion layer. The depletion layer is the source of the attractive Coulomb force that causes the intimate contact of the glass and the conductor, and the oxygen that works in the oxidation of the conductor surface that is required for completion of the permanent bonding. Figure 3 shows the change in the current that ran through the glass in anodic bonding at 523 K (Fig. 3(a)) and 613 K (Fig. 3(b)) with the voltage application time. A large current ran at the first, and it decreased quickly. At 523 K the peak value of the current was ~ 1.7 A/m², and the peak value at 613 K was ~ 34 A/m². The current decrease was caused by growth of the alkali ion depletion layer, and it shows that the normal anodic bonding process was operating. The alkali ion is the main current carrier in the glass, so the resistance of the depletion layer is much higher than the original glass. The amount of the charge that was transferred by the current is shown in Fig. 3 besides the current. It represents the total amount of the ions drifting in the glass and the growth of the

Fig. 3 Current that ran through the glass and the charge transferred by the current in anodic bonding of SiC to glass at 523 K (a) and 613 K (b)

alkali ion depletion layer. The amount of the charge that was transferred in 40 s from the beginning of the application of the voltage was ~ 57 C/m² at 523 K, and that at 613 K was ~ 230 C/m².

The result of the shear test is shown in Fig. 4. The shear fracture stress of the joints is shown as functions of the voltage application time. The results were scattered because of the brittle nature of the materials and the bond interface, but it was obvious that the joint strength increased with the voltage application time. The increase was accelerated with the temperature. In all the joints the fracture occurred at the joint interface, and the shear fracture stress did not exceed 6 MPa in the bonding conditions used in this study.

In order to find the cause of the rather low joint strength of the SiC/glass anodically-bonded joints that was observed by the shear test, microstructure around the bond interface was observed. Figure 5 shows the cross-sectional microstructure of the region around the interface anodically-bonded at 613 K with application of the bonding voltage for 1800 s observed by SEM. The SiC and the glass contacted intimately and no separation of the bond interface was observed. The distributions of sodium and carbon observed by EDS are shown on the micrograph. Accumulation of carbon at the joint interface was found. Existence of the sodium ion depletion layer was not clear. Generally speaking, detection of sodium in glass by EDS is difficult, since sodium has a tendency to escape from the area that is irradiated with the

Fig. 4 Shear fracture stress of anodically-bonded SiC/glass joints as functions of the voltage application time.

Fig. 5 SEM micrograph of the macrostructure around the SiC/glass interface anodically-bonded at 613 K with the voltage application for 1800 s. Distribution of Na and C derived by EDS is superimposed on the micrograph.

electron beam⁵⁾. And the thickness of the sodium depletion layer in the glass Corning 7740 does not grow over 1 μ m thick with application of the bonding voltage of 500 V in anodic bonding of the glass to silicon or aluminum^{3,6)}. The depletion layer in the joint of SiC might be as thin as those in joints of silicon or aluminum, and detection of the layer by EDS in SEM might be difficult.

The microstructure around the bond interface was observed more closely by TEM (Fig. 6). In the bright field image (Fig. 6(a)), a layer about 200 nm thick was found between the SiC and the glass. In the selected diffraction pattern taken from the layer (Fig. 6(c)) only halo ring appeared and no sharp reflection was found. This result showed that the layer was amorphous. And the result of EDS taken from the layer (inset table in Fig. 6) showed high carbon density. It was thought that this carbon-rich layer was formed with the preferential oxidation of silicon in SiC during bonding, and it may cause the low bond strength. And a portion of carbon in this layer might originate from the free carbon content of the SiC used in this study.

It is desirable to control the growth of the carbon-rich layer in order to improve the joint strength of the anodically-bonded SiC/glass joints. The simplest measure for it is use of SiC without free carbon content. Another possible measure is reduction of the

Fig. 6 Microstructure around the SiC/glass interface anodically-bonded at 613 K with the voltage application for 1800 s. TEM bright-field image (a) and selected-area electron diffraction patterns taken from the positions indicated in the image (a) by corresponding letters (b)-(d), and results of EDS taken from the position c in the image (a).

Fig. 7 Faying surface of the SiC joint piece.

voltage application time. Though the joint strength was found to increase with the voltage application time, a long application of the voltage promotes oxidation of SiC, and the growth the carbon-rich layer. Anodic bonding is a solid state bonding, and its performance is sensitive to the condition of the faying surfaces. In this study, the faying surfaces of the SiC joint pieces were finished in a roughness of ~ 10 nm. But as seen in Fig. 7, they have many craters originating from the pores that existed in the SiC sintered block intrinsically. The voltage application time necessary to achieve a sufficient joint strength may be reduced by improvement of the flatness and roughness of the faying surface of the SiC joint piece.

4. Conclusions

The conclusions of this study are summarized as follows.

- (1) SiC has joinability to the glass by anodic bonding. In bonding of SiC to borosilicate glass Corning 7740, no cracks

by the residual stress were observed.

- (2) High bonding temperature enhanced the progress of anodic bonding of SiC to the glass, and the joint strength increased with the bonding temperature and the voltage application time. But the shear fracture stress of the joints did not exceed 6 MPa, and the fracture occurred at the joint interface in all the produced joints.
- (3) At the anodically-bonded interface between SiC and the glass an amorphous carbon-rich layer was formed. It was suggested that this layer caused low joint strength of anodically-bonded SiC/glass joints.

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