JCS-Japan

July
vol.125

Journal of the Ceramic Society of Japan

2017

A novel method for joining aluminum and silicon nitride by polysiloxane

Ken'ichiro KITA[†] and Naoki KONDO

National Institute of Advanced Industrial Science and Technology (AIST),
2266-98 Shimo-shidami, Moriyama-ku, Nagoya 463-8560, Japan

This paper describes a novel method for joining aluminum and silicon nitride using a polysiloxane. The X-ray diffraction patterns suggested that the polysiloxane surrounded by aluminum and silicon nitride powders could be transformed into silicon, aluminum silicate, and SiAlON. Neither cracks nor exfoliation between aluminum and silicon nitride could be observed, and they were joined through the joining layer. Moreover, detailed investigation of the layer by transmission electronic microscopy, selected area electron diffraction, and point analysis energy-dispersive X-ray spectroscopy suggested that the layer consisted of amorphous and nano-sized polycrystalline particles containing aluminum, silicon, nitrogen, and oxygen. The minimum thickness of the layer was less than 10 nm. The bending strength of the joined sample was 204 MPa and the fracture point was the joining layer between aluminum and silicon nitride.

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Key-words : Silicon nitride, Aluminum, Joining, Polymer, Polysiloxane

[Received March 30, 2017; Accepted May 19, 2017]

1. Introduction

Power semiconductor devices are promising products for energy saving owing to their control of electric power, and are applied to hybrid vehicles, renewable energy power plants, high-speed railway vehicles, etc. The devices must be able to control high voltage and electric current and be durable for several years without careful maintenance. Therefore, thermal conductivity and durability are necessary properties for the device substrates. Due to the better insulation property and thermal conductivity than oxide ceramics, non-oxide ceramics are suitable for the substrate.¹⁾ It is conceivable that aluminum nitride is a desirable ceramic for the substrate owing to its high thermal conductivity.^{2),3)} However, aluminum nitride has poor flexural strength and generates ammonia because of its easy reaction with water or moisture. This reveals that we have to search for another ceramic material for the substrate.

To this end, many researchers have paid attention to silicon nitride, which is stable and has good flexural strength.⁴⁾⁻⁶⁾ Moreover, due to an interlocking microstructure composed of rod-like silicon nitride grains, the thermal conductivity of silicon nitride is 177 W/(m·K) with high fracture toughness.^{7),8)} This reveals that silicon nitride with high thermal conductivity should be a superior substrate material compared to aluminum nitride for future high power electronic devices and other new applications.

Though copper is commonly used for wires and radiators in devices due to its good thermal and electrical conductivities, there are devices in which copper is replaced with aluminum for reducing cost and device weight. Therefore, a novel joining method between aluminum and silicon nitride is promising, and there have been some studies exploring the joining.^{9),10)} Tanaka et al. tried joining aluminum alloy and silicon nitride using an Al-Cu-Si alloy whose melting point was lower than that of aluminum alloy. Suganuma et al. tried joining silicon nitride and aluminum

by joining the silicon nitride parts together. However, this joining required a chloride flux to remove the oxidized layer on aluminum or a temperature higher than the melting point of aluminum during joining.

These conditions for joining aluminum and silicon nitride have disadvantages. The use of a chloride flux presents a negative environmental impact. In addition, this joining method has been limited to use in the joining temperature above melting point of aluminum, such as the joining of bulk aluminum. Therefore, a novel method of joining aluminum and silicon nitride is required.

To join these materials, we paid attention to using polysiloxane. The Si-O-Si group in the polymer can be transformed into aluminum silicate on ceramics.^{11),12)} In addition, aluminum silicate is a kind of glass and grains of silicon nitride can be joined together by using glass.¹³⁾ Hence, there is a possibility that aluminum and silicon nitride can be joined using polysiloxane. In this study, we tried joining aluminum and silicon nitride using polymethylphenylsiloxane (PMPHS). PMPHS is a kind of polysiloxane containing phenyl groups and silicon nitride could be coated uniformly with PMPHS in the absence of solvent.

2. Experimental procedure

To analyze the thermal reactions between aluminum, silicon nitride, and polymethylphenylsiloxane (PMPHS), the mixed powder containing aluminum powder (#800F, Minalco Ltd., Japan), silicon nitride powder (SN-9, Denka Company Limited, Japan), and PMPHS (KF-54, Shin-Etsu Chemical Co., Ltd., Japan) was prepared and mixed. The mixed powder contained the equal quantity of aluminum powder, silicon nitride powder and PMPHS. This powder was analyzed by thermogravimetric differential scanning calorimetry (TG-DSC; Q600, TA Instruments—Waters LLC, USA). In addition, this powder was heated at 903 K under an inert atmosphere and studied by X-ray diffraction (XRD; RINT2500, Rigaku Corporation, Japan).

Figure 1 shows the sample preparation process for the 4-point bending test, which is standardized as JIS R 1601:2008. Com-

[†] Corresponding author: K. Kita; E-mail: kita.kennichiro@aist.go.jp

Fig. 1. Outline of sample preparation process for the 4-point bending test.

mercialized bulk silicon nitride (SN-210, Japan Fine Ceramics Co., Ltd., Japan) was cut into pieces. Each piece was 20 mm in length, 30 mm in width, and 20 mm in height. A surface area of 600 mm² for joining was abraded using a grinder. After abrading, the area was dipped into PMPhS. Aluminum foil with a thickness of 25 μm (AL-013221, The Nilaco Corporation, Japan) was sandwiched between two silicon nitride samples, and the samples were heated at 903 K for 1 h under an Ar atmosphere for joining. This heating temperature was the highest used for joining aluminum. At the temperature near the melting point, which is approximately 933 K, the softening of aluminum is carried out during heating. These joined samples were cut into pieces having dimensions of 3 mm × 4 mm × 40 mm.

After the above-mentioned process, 4-point bending tests on these samples—in accordance with JIS R 1601:2008—were performed using a bending testing machine. Finally, the cross-section of joining layer before and after the binding test was analyzed by scanning electronic microscopy (SEM; JEM-5600, JEOL, Japan), transmitting electronic microscopy (TEM; JEM-2100, JEOL, Japan), energy dispersive X-ray spectroscopy (EDS; JEM-2300, JEOL, Japan), and selected area electron diffraction (SAED; JEM-2010, JEOL, Japan).

3. Results and discussion

Figure 2 presents the results of the TG analysis and DSC curves of the Al powder, PMPhS, and the mixed powder containing aluminum and PMPhS. These powders were heated under Ar flow. The weight of aluminum did not decrease, whereas that of PMPhS decreased until 873 K and it remained less than 10 wt %. Aluminum had a strong endothermic reaction at 923 K and this suggests the melting of aluminum powder, whereas PMPhS had a strong endothermic peak that continued until 973 K. Taking into account the weight change, it reveals that PMPhS decomposed on reaching 873 K and the phase transformation of PMPhS to a glass was carried out above 873 K.

The weight of the mixed powder continued to decrease until 773 K and kept constant over 773 K. The heat flow of the powder shows that an endothermic reaction continued between 673 and 823 K and an exothermic reaction occurred between 823 and 873 K. Keeping the temperature constant, a phase change or crystallization would occur during the exothermic reaction. Based on this result, we set the temperature for joining at 903 K and

Fig. 2. Weight change and heat flow graphs obtained by TG-DSC.

Fig. 3. XRD patterns of aluminum powder, silicon nitride powder, and the mixed powder after heating at 903 K.

expected that aluminum and silicon nitride would be joined together by PMPhS without the fusion of aluminum.

To investigate the composition of the joining layer in this method, the crystalline phase of the mixed powder heated at 903 K in Ar was examined by XRD and the pattern is shown in **Fig. 3**. The patterns of aluminum powder and silicon nitride powder are also shown in **Fig. 3** for comparison. The aluminum pattern shows no extra peaks except those of aluminum, and that of silicon nitride powder mainly shows β -silicon nitride peaks. These reveal that these powders were of high purity and contained few impurities.

The XRD pattern of the mixed powder after heating at 903 K had many prominent peaks apart from those resulting from aluminum and silicon nitride powders. Strong peaks at 2θ values of 28, 47, and 56° indicate the existence of silicon and the patterns also suggest that some PMPhS was deoxygenized. The peaks at 36, 40, and 54° indicate the existence of aluminum silicate and the peaks at 26, 33, 38, and 46° indicate the existence of SiAlON ceramics. According to some papers, polysiloxane could be transformed into glassy or nano-crystalline aluminum silicate by heating.^{14)–16)} Therefore, the presence of aluminum silicate in the powder is reasonable. In addition, SiAlON can be obtained by the substitution of oxygen with nitrogen in aluminum silicate.^{17)–19)} Therefore, SiAlON could form in the mixed powder if the nitrogen derived from silicon nitride diffused into aluminum silicate.

Figure 4 presents SEM images of the cross section of the joined sample. The image on the left is a low magnification image of the joining layer of the sample. The bright grey in the center of the image is aluminum and the grey areas that sandwich the bright grey area are bulk silicon nitride. The image on the right is the high magnification image of the image on the left. The arrows on this image show the joining layer of the joining sample. These images reveal that there were no remarkable cracks or exfoliation between the bulk aluminum and silicon nitride.

Figure 5 presents the TEM image of the cross section and EDS patterns of the joining layer between aluminum and silicon nitride. The top left image is the TEM image. There is a crack on the sample, which was generated during the focused ion beam process for preparing the sample for TEM. The bottom left image is the map of the materials in the TEM image and the circle numbers on the TEM image indicate the points of the EDS analysis. The patterns of EDS analysis are on the right of Fig. 5. Peaks of gallium and molybdenum in these patterns are background peaks.

The EDS analysis of circle number 1 presents strong peaks of silicon and nitrogen. Therefore, this reveals that grains on the top area of the TEM image were silicon nitride. The bottom of the image was aluminum because the EDS analysis of circle number 3 only presents strong peaks of aluminum. The EDS analysis of circle number 2 confirms that there were strong peaks of aluminum, silicon, oxygen, and nitrogen in the joining layer. Based on the result of the XRD patterns, SiAlON was supposed to form a part of the joining layer along with the surface of silicon nitride grains.

Figure 6 presents the high magnification TEM image of the

Fig. 4. SEM image of the cross-sectional joining layer of the joined samples.

Fig. 5. The cross-sectional TEM image (top left) and the map of the image (bottom left) of the joining layer of the joined sample, and EDS point analysis (right).

joining layer. The left image of Fig. 6 is the TEM image and the right image is the map of materials in the TEM image. The top right area is silicon nitride, the bottom left area is aluminum, and the area sandwiched between silicon nitride and aluminum is the joining layer. The narrowest gap between aluminum and silicon nitride was less than 10 nm and sometimes the grains with the diameter of about 3 nm were observed in the joining layer.

Figure 7 presents the SAED pattern obtained from the joining layer in Fig. 6, including the nano-sized grains. The diffraction ring together with the halo pattern shown in the SAED suggests that the joining layer consisted of both the amorphous region and the crystalline region. However, identification of the crystals in the joining layer was very difficult.

A 4-point bending test was carried out and the average bending strength of 4 measurements was approximately 204 MPa.

Figure 8 presents the side view of the fracture surface of the joined sample after the bending test. The arrows on this image show the joining layer of the joining sample. The grinding mark, which was introduced during the machining, was traced with the dotted lines on this figure. Aluminum hardly remained on the silicon nitride on the left side of this image, whereas it remained as a layer on the silicon nitride on the right side. Therefore, the fracture point of this sample was at the joining layer between silicon nitride and aluminum. In addition, the dotted lines were deflected at the interface between aluminum and silicon nitride and this indicates that the stress applied in the direction parallel to the interface resulted to deform the aluminum layer.

Figure 9 presents a pair of the SEM images and EDS mappings of the fracture surface of the sample. The top images in the figure are SEM images, the center image is the EDS mapping of Al, and the bottom image is the EDS mapping of Si. The left and right have the mirror image correspondence.

In the case of the images on the right, the bright grey area in the SEM image corresponds to the bright colored area in the EDS mapping of Al and the dark colored area in the EDS mapping of Si; the dark grey area in the SEM image corresponds to the dark colored area in the EDS mapping of Al and the bright colored area in the EDS mapping of Si. In addition, the bright colored areas in the left images are almost consistent with the dark colored areas in the right images. These results reveal that the joined sample fractured at the joining layer between aluminum and silicon nitride, and this result is consistent with Fig. 8.

Fig. 6. The cross-sectional TEM image with high magnification (left) and the map of the image (right).

Fig. 7. SAED pattern of the cross-sectional joining layer of the joined sample.

Fig. 8. SEM image of the side view of the fracture surface of the joined sample after the bending test.

4. Conclusions

We succeeded in joining aluminum and silicon nitride using polysiloxane. XRD patterns suggested that the polysiloxane was transformed into silicon, aluminum silicate, and SiAlON by heating at 903 K. No cracks and no exfoliation between aluminum and silicon nitride was observed in the micrograph of the joining layer. Based on the selected area electron diffraction pattern and EDS mappings, the joining layer included both amorphous and polycrystalline regions with the composition consisting of aluminum, silicon, nitrogen, and oxygen atoms. In addition, the observed minimum thickness of the joining layer was less than

Fig. 9. SEM images and EDS mappings of the joining layer of the joined samples after the 4-point bending test.

10 nm, and the grains whose diameter was approximately 3 nm were observed in the joining layer. The joined sample fractured at the joining layer between aluminum and silicon nitride and the average bending strength of the joined sample was 204 MPa.

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