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Development of Microstructure of the Anodically-bonded Interface between Aluminum and Borosilicate Glass[†]

TAKAHASHI, Makoto* and IKEUCHI, Kenji**

Abstract

A voltage was applied to the interfaces between borosilicate glass and Al deposited layer, and changes in the microstructure around the interfaces were investigated by transmission electron microscopy. At the Al/glass interface, two types of the oxide, a layer at the bond interface and fibers growing from the layer into the glass, were observed. Both these oxide structures were γ -Al₂O₃, and they grew epitaxially from the Al layer. In the early stage of the voltage application, the oxide layer formed and grew, after that the oxide fibers began to form. After the appearance of the oxide fibers, growth of the oxide layer stopped. The mechanism of formation and growth of these oxide structures is proposed from the viewpoint of the transportation of Al ions in the glass and the γ -Al₂O₃.

KEY WORDS: (anodic bonding) (aluminum) (borosilicate glass) (interfacial reaction) (microstructure)

1. Introduction

Anodic bonding is a unique method for bonding metal or semi-conductor to glass containing alkali ions by applying D.C. voltage between them with the metal side being anode. The application of D.C. voltage produces an electric field in the glass, and the alkali ions drift toward the cathode side. Then 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 ion. The force caused by this charge brings the glass and metal surfaces into intimate contact, and the permanent bond is achieved by a chemical reaction on the glass/metal interface¹⁾. In general, the bonding temperature for anodic bonding is lower than the softening point of the glass²⁾. This is the advantage that makes anodic bonding indispensable for precise bonding that avoids plastic deformation of the materials; e.g., bonding for the assembling of micromachines or microsensors.

The thickness of the alkali ion depletion layers are 1~10 μ m in the usual anodically-bonded joints³⁾. At the bond interface, reaction products can form through reactions between excess O ions in the layer and the

anode elements. Reaction products may exert some essential role in the bonding, and they can affect the properties of the joints. But reaction products at the bond interfaces in anodically-bonded joints are too minute for observation by optical microscopy or scanning electron microscopy. Therefore, we prepared simulated anodically-bonded interfaces between Al and borosilicate glass, and observed them by transmission electron microscopy (TEM). An Al layer was deposited on the surface of a glass plate by vacuum deposition, and a DC voltage was applied between the glass and the Al layer under similar conditions to those of anodic bonding. The preparation of TEM specimens from the simulated joints is much easier than from real joints. Simulated joints are free from some of the extrinsic factors that can influence the evolution of microstructure around the bond interface, e.g. cleanliness and flatness of the surfaces of the joint pieces.

2. Experimental

In Table 1 is shown the chemical composition of the borosilicate glass used in this study. This glass contained alkali metal elements, Na, K, and Li, besides Si and B that are the basic components of the borosilicate glass.

Table 1 Chemical composition of the borosilicate glass

	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	K ₂ O	Li ₂ O	CaO	BaO	Sb ₂ O ₃
Composition (mass%)	69.0	3.64	18.6	3.60	3.86	0.50	0.042	0.024	0.50

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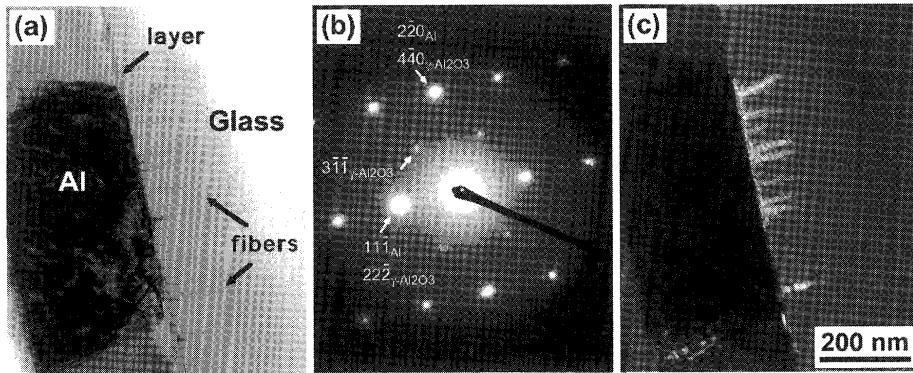


Fig. 1 Microstructure around the Al/glass interface receiving the voltage for 120 s (a), the SAD pattern from the middle area in a (b), and the dark field image taken by the $3\bar{1}1_{\gamma\text{-Al}_2\text{O}_3}$ reflection in b (c).

The glass was supplied in a shape of disk 1 mm in thickness and 25 mm in diameter. One surface of the disk was coated with a Pure Al layer by vacuum deposition using a tantalum boat heater in a vacuum of $\sim 1 \times 10^{-3}$ Pa.

The anode terminal of the D.C. high voltage power source was connected to the Al layer, and the cathode terminal was connected to the glass surface without the Al layer. A voltage of 500 V was applied to the specimen at 613 K. The atmosphere was a vacuum of $\sim 1 \times 10^{-3}$ Pa. The time to apply the voltage was changed with each specimen from 15 s to 600 s.

Thin foil specimens for TEM were prepared by argon atom milling. For specimens receiving the voltage for short times (0~60 s), focused ion beam apparatus (FIB) was employed.

The TEM observation was performed with a JEOL JEM-2010 transmission electron microscope at an acceleration voltage of 160 kV. Distributions of elements around the Al/glass interface were measured by the built-in energy dispersion X-ray spectroscopy (EDS) system of the microscope.

3. Results and Discussion

In Fig. 1 is shown the microstructure around the Al/glass interface receiving the voltage for 120 s. There was a layer ~ 10 nm thick at the Al/glass interface, and the fibrous structures ~ 100 nm long grew into the glass from the layer. The selected area diffraction (SAD) pattern in Fig. 1(b) was taken from the Al grain that appeared dark in Fig. 3(a) and the adjacent glass that contained the fibrous structure. An 112 pole figure of Al from the Al grain was observed in the SAD pattern, and there were some extra spots. These extra spots formed a pattern similar to the pattern from the Al grain. This pattern could be indexed as a 112 pole figure of $\gamma\text{-Al}_2\text{O}_3$. The orientations of these pole figures were identical. In the dark-field image taken by the 311 reflection of $\gamma\text{-Al}_2\text{O}_3$ (Fig. 3(c)), both the layer at the interface and the fibrous structures appeared bright. The EDS analysis showed that the content of Al in these structures was very high. From these results, it was concluded that the layer at the interface and the fibrous structures consisted of $\gamma\text{-Al}_2\text{O}_3$.

growing epitaxially from the Al layer. Similar oxide structures were observed in the real Al/glass anodically-bonded interface⁴.

The growth of the fibers and the layer of $\gamma\text{-Al}_2\text{O}_3$ with the time to apply the voltage were investigated.

In Fig. 2(a)~(c) are shown the changes in the microstructure around the Al/glass interface when the times to apply the voltage increased from 120 s to 600 s. The $\gamma\text{-Al}_2\text{O}_3$ fibers and the K depletion layer were observed in both specimens. The length of the fibers and the thickness of the K depletion layer increased with the time of applying the voltage to the specimens. In Fig. 2(d)~(f) are shown the more magnified images of the interfacial areas. Even though the time to apply the voltage increased from 120 s (Fig. 2(d)) to 600 s (Fig. 2(f)), the thickness of the $\gamma\text{-Al}_2\text{O}_3$ layers remained at ~ 10 nm and the change was not obvious.

With the time to apply the voltage increased, the lengths of the Al oxide fibers also increased, but the thickness of the Al oxide layer did not increase with the time to apply the voltage longer than 120 s. These characteristic of growth of the oxide may be explained as follows:

During application of the voltage, the excess O ions in the alkali ion depletion layer drift toward the Al/glass interface and oxidize Al. In the early stage, a layer of $\gamma\text{-Al}_2\text{O}_3$ forms at the interface. It has been said that only limited amount of Al ions can enter into the glass during anodic bonding⁵. In contrast, $\gamma\text{-Al}_2\text{O}_3$ has the spinel structure and there are structural vacancies at Al sites with in it. Existence of structural vacancy enhances the mobility of Al ions in this material. Therefore, $\gamma\text{-Al}_2\text{O}_3$ forming at the joint interface acts as a fast diffusion path for Al ions. The Al ions that are provided from the Al layer are dragged toward the inside of the glass by the electric field. If there is some unevenness of the $\gamma\text{-Al}_2\text{O}_3$ layer, the Al ions will migrate to the end of the protrusions of the layer to the glass side, and react with O ions from the depletion layer there. More $\gamma\text{-Al}_2\text{O}_3$ forms with this reaction and the protrusions grow longer. After the formation of fibers with the growth of the protrusions, the density of excess O ions in the area near the joint interface becomes low, because O ions are exhausted by

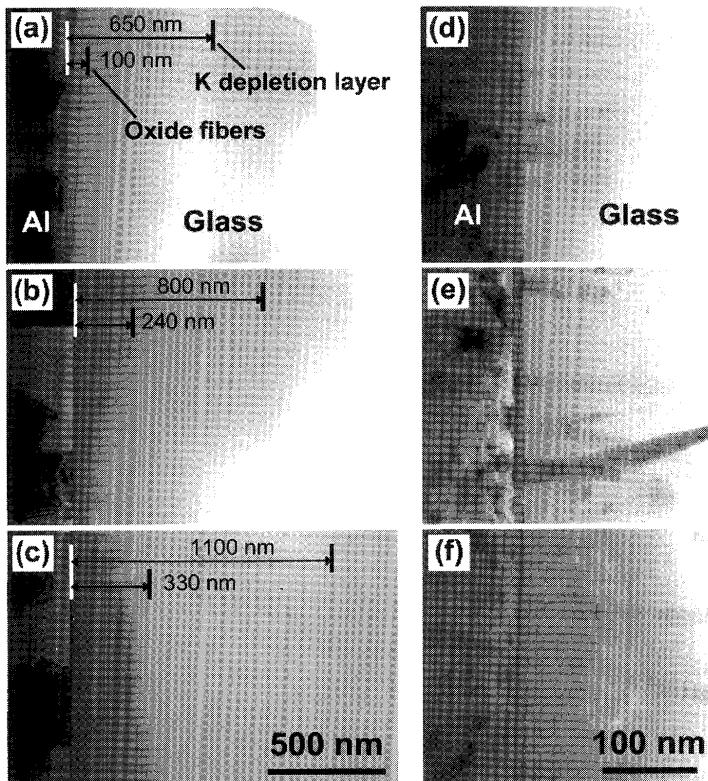


Fig. 2 Changes in the microstructure around the Al/glass interface with the application of the voltage. The microstructure after the application of the voltage for 120 s (a and d), that after 300 s (b and e), and that after 600 s (c and f).

the reaction at the ends of the fibers with Al ions that are transported from the Al layer through the fibers. Therefore, the fibers grow only in the longitudinal direction and their diameters do not increase. The thickness of the γ -Al₂O₃ layer does not increase for the same reason.

In order to verify this hypothesis, the microstructure of the Al/glass interface in the early stages of the application of the voltage was observed. The results are shown in Fig. 3. Before the application of the voltage (Fig. 3(a)), there is no Al oxide at the interface. After the application of the voltage for 15 s (Fig. 3(b)), an oxide layer \sim 7 nm thick was observed at the interface, but the oxide fiber did not form. In the specimen receiving the voltage for 60 s, the thickness of the oxide layer increased \sim 10 nm. This thickness is almost same as those in the specimens receiving longer application of the voltage. The oxide fibers appeared in this specimen. After the formation of the oxide fibers, the oxide layer did not grow. These results are consistent with the hypothesis above.

4. Conclusion

A voltage was applied to the interface between the borosilicate glass and the Al deposited layer, and changes in the microstructure around the interface were investigated by TEM. Results are summarized as follows:

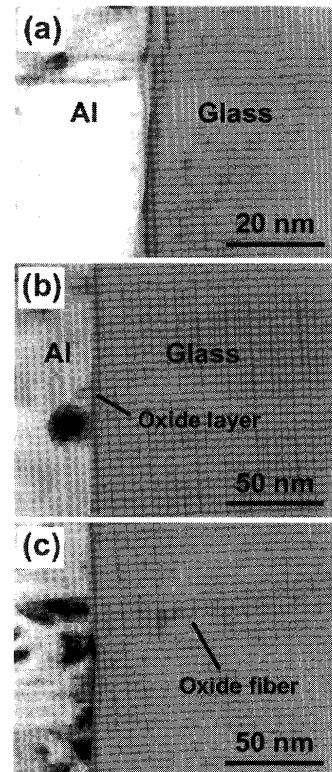


Fig. 3 Microstructure around the Al/glass interfaces as deposited (a), receiving the voltage for 15 s (b), and receiving the voltage for 60 s (c).

- (1) Two types of the oxide, the layer at the Al/glass interface and the fibers growing from the layer into the glass, were observed at the Al/glass interface receiving the voltage. These oxides were both γ -Al₂O₃, and they grew epitaxially from the Al layer.
- (2) In the early stage of the voltage application, the γ -Al₂O₃ layer formed and grew. After that the γ -Al₂O₃ fibers began to form. After the appearance of the fibers growth of the γ -Al₂O₃ layer stopped.
- (3) The mechanism of formation of the γ -Al₂O₃ layer and fibers can be explained from the difference in mobility of Al ions in γ -Al₂O₃ and glass.

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