ANODICALLY-BONDED INTERFACE OF GLASS TO ALUMINUM

by
Makoto Takahashi[1*], Satoru Nishikawa[2], Zheng Chen[3] and Kenji Ikeuchi[1]
[1]Joining and Welding Research Institute, Osaka University,
11-1 Mihogaoka, Ibaraki, Osaka, 567-0047, Japan, makotot@jwri.osaka-u.ac.jp
[2]Graduate School, Osaka University
(Present affiliation: Japan Power Engineering and Inspection,
14-1 Bentencho, Tsurumi-ku, Yokohama, Kanagawa 230-0044, Japan, nishikawa-satoru@japeic.or.jp)
[3] Joining and Welding Research Institute, Osaka University
(Present Affiliation: Department of Material Science and Engineering, East China Shipbuilding Institute,
Huancheng Rd. No. 2 Zhenjiang, Jiangsu China, chenz@public.zj.js.cn)

ABSTRACT

An Al film deposited on the Kovar alloy substrate was anodically-bonded to the borosilicate glass, and the bond interfaces was closely investigated by transmission electron microscopy. Al oxide was found to form a layer ~10 nm thick at the bond interface, and fibrous structure of the same oxide was found to grow epitaxially in the glass from the oxide layer. The fibrous structure grew with the bonding time. The mechanism of the formation of this fibrous structure is proposed on the basis of the migration of Al ions under the electric field. Penetration of Al into glass beyond the interfacial Al oxide was not detected. The comparison of the amount of excess oxygen ions generated in the alkali depletion layer with that incorporated in the Al oxide suggests that the growth of the alkali-ion depletion layer is controlled by the consumption of excess oxygen to form the interfacial Al oxide.

KEYWORDS

Anodic bonding, aluminum, borosilicate glass, interfacial reaction layer, transmission electron microscopy.

1. Introduction

Anodic bonding is a method to bond metal or semi-conductor to glass containing alkali ions by applying D.C. voltage as shown in **Fig. 1**. The application of D.C. voltage brings an electric field in the glass, which drifts the alkali ion toward the cathode side. Then an alkali ion depletion layer forms in the glass near the interface to the metal surface to be bonded. This layer has a strong negative charge, because of the presence of non-bridging oxygen anions that lose their bonds with the alkali ion. The image 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 interface[1]. In order to enhance the mobility of the alkali ion, the glass is usually heated during the anodic bonding; e.g., borosilicate glass can be anodically-bonded at temperatures about 600 K. In general, the bonding temperature necessary for anodic bonding is lower than the softening point of the glass[2]. Therefore, anodic bonding is suitable especially for precise bonding that dislikes plastic deformation and heating of materials; e.g., bonding for the assembling of micromachines or microsensors.

Thus the alkali depletion layer plays an important role in the achievement of anodic bonding, but its physical properties differ from those of the original glass. For example, the lower content of the alkali ion can change the specific volume and thermal expansion coefficient of the glass in the depletion layer. In some instances, these changes cause unacceptable distortion in the joint. With the miniaturization of joints accompanied by the advance of micromachining (expected application field of the anodic bonding), the effect of these changes in the properties of the depletion layer will be more emphasized.

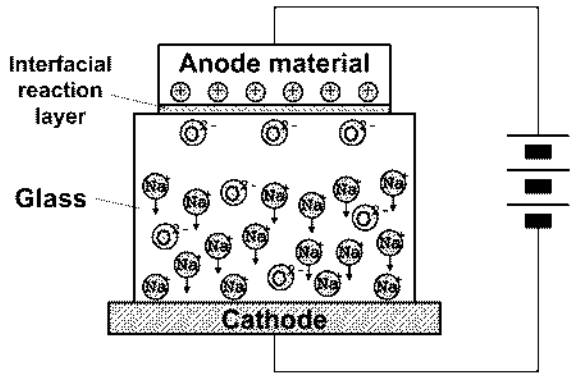
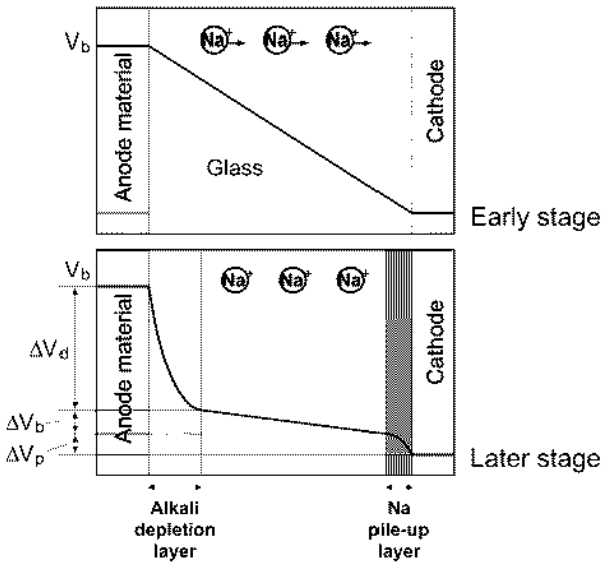


Fig. 1 The principle of anodic bonding.

In this regard, we have found that the property of the anode metal had a significant influence on the growth rate of the alkali depletion layer[3]. Under bonding conditions when the thickness of the formed depletion layer is a few μm thick or more, the depletion layer in a joint of Kovar alloy to borosilicate glass is several times as thick as that observed in a joint of Al to borosilicate glass. As suggested in our previous paper[3], the growth of the depletion layer is governed by the potential drop in the layer (**Fig. 2**). The potential drop in the depletion layer that has a

strong negative charge is very steep, as derived easily from solving Poisson's equation. Therefore, with the growth of the depletion layer, the electric field in the bulk glass is rapidly reduced to a level insufficient to cause the drift of alkali ions toward the cathode, unless the negative charge accumulated in the depletion layer is not compensated. The negative charge in the depletion layer can be compensated in two ways: the penetration of the anode metal cation into the depletion layer and consumption of the non-bridging oxygen ion by the reaction with the anode metal at the joint interface. It follows from this that the capability of the anode metal to compensate the negative charge in these ways can significant influence on the thickness of the depletion layer. To our knowledge, however, there has been no report that observed the interfacial reaction layer or penetration of the anode metal into the glass in anodically-bonded joints. In this investigation, therefore, we have carried out TEM (Transmission Electron Microscopy) observations of anodically-bonded joints of borosilicate glass to Al in order to reveal the interfacial reaction layer and to analyze the distributions of elements around the joint interface.



ΔV_d : Potential drop in Alkali depletion layer
ΔV_b : Potential drop in bulk glass
ΔV_p : Potential drop in Na pile-up layer

Fig. 2 Potential distribution in the glass during anodic bonding. At first the electric field in the glass is uniform. With the growth of the alkali-ion depletion layer, the electric field in the bulk glass becomes weak because of the large potential drop in the depletion layer.

2. Experimental Details

A borosilicate glass disk was anodically-bonded to the Al layer deposited on the substrates of the Kovar alloy by RF sputtering with a 99.99% Al target. In **Table 1** are shown the chemical composition of borosilicate glass used in this study. The thermal expansion coefficients of this glass and the Kovar alloy are very close to each other in a range from room temperature to ~800 K. The Kovar alloy was shaped into disks 5 mm in thickness and 20 mm in diameter. One side of the disk was finished by grinding and polishing on metallographic papers and cloths. After that an Al layer ~1 μm thick was deposited on the polished surface. The surface of the deposited Al layer was polished with diamond paste for a short time just before bonding to improve its smoothness. The glass was supplied in the shape of disk 1 mm in thickness and 25 mm in diameter. The bonding apparatus is illustrated in **Fig. 3**. A glass disk was laid on the cathode Cu plate, and a Kovar disk was placed on the glass with the Al-deposited surface in contact with the glass. The cathode-side surface of the glass was coated with conductive carbon paint to make the electric potential on the surface uniform. The Kovar disk was connected to the anode. A couple of graphite heaters were placed above and below these specimens to be bonded. The bonding was carried out in a vacuum chamber evacuated to $< 1 \times 10^{-3}$ Pa with a diffusion pump. The bonding temperature employed was 613 K. The temperature was monitored with a thermocouple connected to a dummy specimen that was placed next the specimens for bonding. After the specimens were heated to the bonding temperature, a bonding voltage of 500 V was applied. Application times of the bonding voltage were 1.8 and 10.8 ks.

Table 1 Chemical compositions of the borosilicate glass.

	SiO_2	Al_2O_3	B_2O_3	Na_2O	K_2O	Li_2O	CaO	BaO	Sb_2O_3
Composition (mass%)	69.0	3.64	18.6	3.60	3.86	0.50	0.042	0.024	0.50

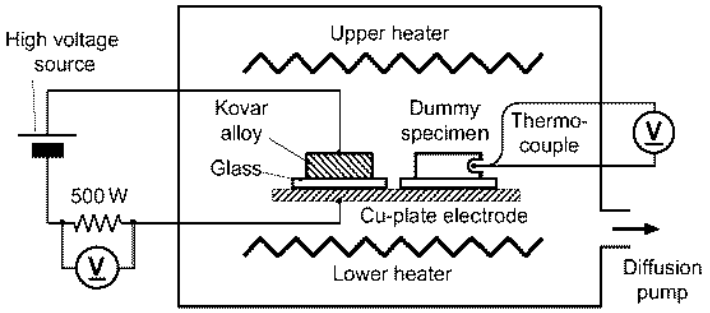


Fig. 3 The apparatus for anodic bonding.

The specimen for the TEM observation was prepared by the following process: a joint obtained was cut into slices of 1 mm thickness in a direction perpendicular to the joint interface, and the slice was thinned to about 100 μm thickness by grinding on metallographic papers. The slice was further thinned with a dimple grinder,

and finally a thin foil specimen for TEM observation was produced with an Ar atom milling. The TEM observation was performed with JEM-2010 transmission electron microscope operated at 200 kV, and the nano-scale analysis was done with a built-in EDS (Energy Dispersion X-ray Spectroscopy) system.

3. Results and Discussion

The progress of the anodic bonding of borosilicate glass to Al at a bonding temperature (T_b) of 613 K and bonding voltage (V_b) of 500 V is shown in **Fig. 4**, where the ratio of the intimate contact area to the whole joint interface is plotted against the bonding time. The intimate contact over the whole joint interface was achieved in 60 s. An increase in the bonding temperature considerably accelerates the bonding process.

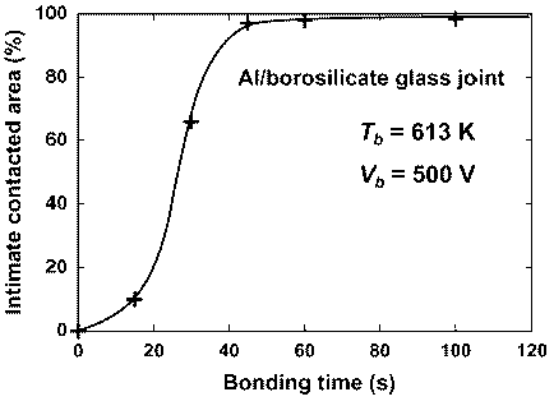


Fig. 4 The change in the intimate contact area in the anodically-bonded Al/glass joint interface with the bonding time.

In **Fig. 5** are shown a result from EPMA (electron probed microanalysis) around the bond interface in an Al/glass joint anodically-bonded at T_b = 663 K and V_b = 500V for a bonding time (t_b) of 3.6 ks. The contents of Fe and Si changed steeply at the bond interface. An area very poor in Na and K waws observed in the glass adjacent to the bond interface. It was the alkali-ion depletion layer. The K ion depletion layer was extended to a thickness of 1.5 μm in this joint, and the thickness of the Na depletion layer was 5 μm.

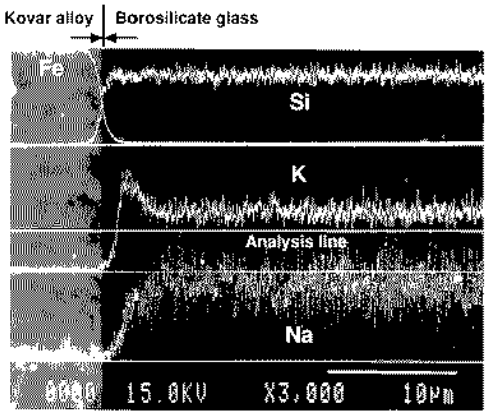


Fig. 5 Distribution of elements around the bond interface in the Al/glass joint anodically-bonded at Tb = 663 K and Vb = 500 V for tb = 3.6 ks.

In **Fig. 6** is shown the microstructure of the bond interface of an Al/glass joint anodically-bonded at T_b = 613 K and V_b = 500 V for t_b = 1.8 ks. A layer of 5~10 nm thickness showing a greyish tone can be observed at the interface (indicated by the arrow with letter '**a**' in Fig. 6). From this layer, fibrous structures ~200 nm long grew toward the glass side (indicated by the arrows with the letter '**b**'). Chemical compositions of these structures analyzed with EDS are shown in **Fig. 7**. EDS spectra observed from points '**b**', '**c**', '**d**', and '**e**' in the bright-field image (Fig. 7(a)) are shown in Fig. 7(b), (c), (d), and (e), respectively. In the fibrous structure, major components were O and Al as shown in Fig. 7(b), and the Si content was very low, although this structure was formed within the glass. In the greyish layer at the joint interface, much higher contents of O and Al were detected (Fig. 7(d)). Therefore, the layer at the interface and the fibrous structures can be thought to consist of Al oxide that formed through the reaction between the excess oxygen ions in the alkali ion depletion layer and the Al atoms supplied from the Al layer. An EDS spectrum from the glass matrix adjacent to a fibrous structure is shown in Fig. 7(c) for comparison. Major components at this point were O and Si, and the content of Al was not more than that of the as-received glass (Table 1), although this point was only 30 nm away from the joint interface. In other words, no penetration of Al into the glass was observed except the Al oxide layer at the interface and the Al oxide fibres.

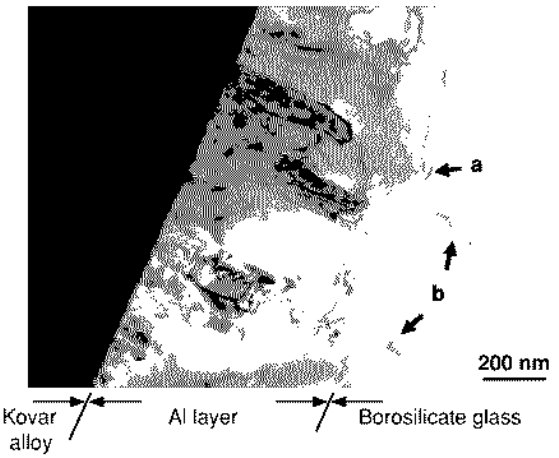


Fig. 6 The microstructure around the joint interface in the Al/glass joint anodically-bonded at 613 K for 1.8 ks.

The Al oxide layer and fibrous structure grew with an increase in bonding time. As shown in **Figs. 8**(a) and 8(d) (T_b = 10.8 ks), the thickness of the oxide layer was ~15 nm and the length of the fibrous oxide was 400~500 nm, as compared with 5~10 and 200 nm after anodic-bonding for 1.8 ks. The SAD pattern taken from the area in Fig. 8(a) is shown in Fig. 8(b). Several spots in this SAD pattern could be indexed as reflections in a 332 pole figure from γ-Al_2O_3 crystal, and the oxide layer at the interface appeared as a bright layer in the dark-field image

taken from the 440 reflection in the figure (Fig. 8(c)). In Fig. 8(e) is shown the SAD pattern taken from the area in Fig. 8(d). This pattern can also be interpreted as a 001 pole figure from γ-Al_2O_3 crystal, and in the dark-field image taken by the 400 reflection (Fig. 8(f)), the fibrous oxide appeared as bright figures. Therefore, both the Al oxide layer and the fibrous oxide structure were identified as γ-Al_2O_3. This aluminum oxide takes the spinel structure with structural vacancies at Al sites. Since this phase is stable at temperatures under 1273 K, the formation of this phase at 613 K is reasonable.

Thus oxides of Al formed at the interfaces of Al/glass joints. They were the layer and fibrous structure of crystalline γ-Al_2O_3. Evidently, the fibrous crystal in the Al/glass joint grew toward the glass side. It can be thought that the strong electric field in the alkali ion depletion layer caused the migration of Al^{3+} ions, and the growth of the oxides progressed through the reaction of these ions with the excess oxygen ions in the depletion layer. The peculiar morphology of the fibrous oxide in the Al/glass may be explained as follows: It has been said that only limited amount of aluminum ions can enter into the glass during anodic bonding. In contrast, the γ-Al_2O_3

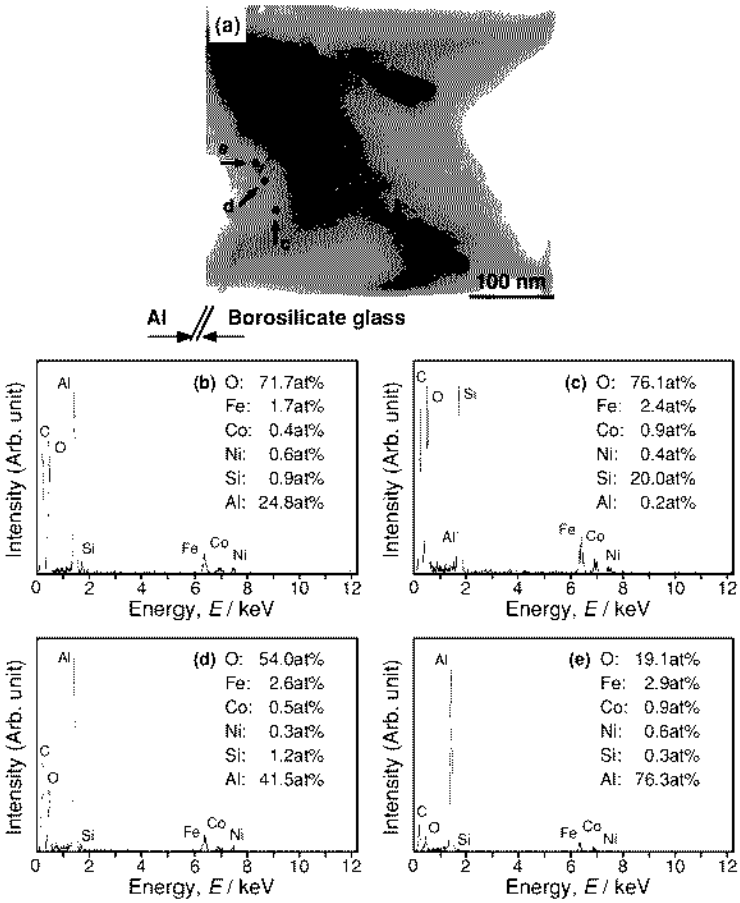


Fig. 7 Distribution of elements around the joint interface in the Al/glass joint anodically-bonded at 613 K for 1.8 ks. (a) The TEM image of the interfacial area, and (b)~(e) the results from the EDS analyses at the points indicated in (a) by the spots with coresponding letters.

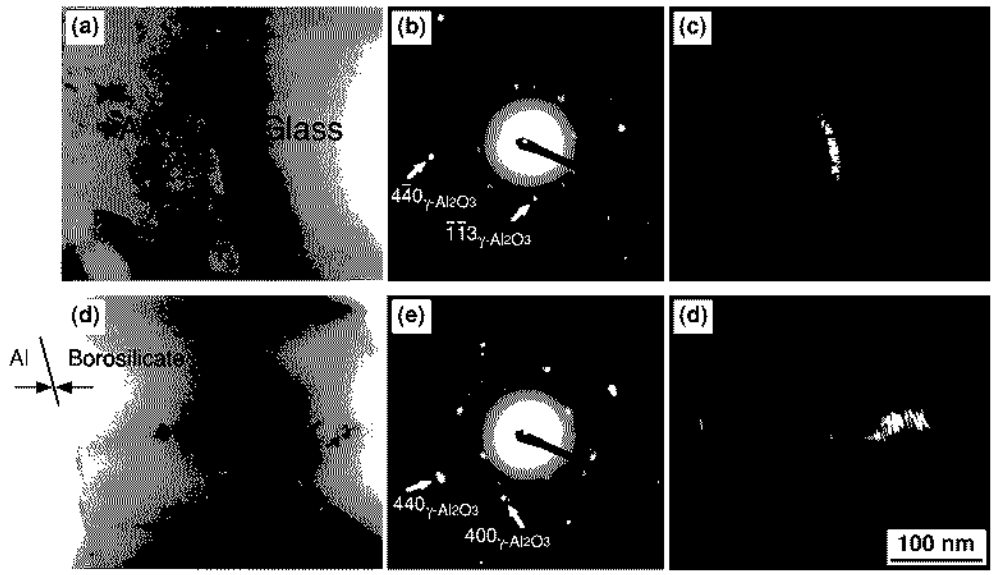


Fig. 8 Microstructure around the joint interface in the Al/glass joint anodically-bonded at 613 K for 10.8 ks. (a) The bright-field image of the interfacial reaction layer, (b) the SAD pattern taken from the central area in (a), (c) the dark-field image taken by the $440_{\gamma\text{-}Al2O3}$ reflection indicated in (b), (d) The bright-field image of the fibrous structure growing from the interface, (e) the SAD pattern from the structure, and (f) the dark-field image taken by the $400_{\gamma\text{-}Al2O3}$ reflection indicated in (e).

contains structural vacancies in Al sites, which suggests that the aluminum ion has high mobility in this phase. Possible mechanism of formation of fibrous oxide in Al/glass joints is illustrated in **Fig. 9**. During anodic bonding of Al to glass, once γ-Al_2O_3 forms at the joint interface, this works as a fast diffusion path of aluminum ions. If the thickness of γ-Al_2O_3 layer is not uniform, the electric potential at the end of the protrusion is lower than at its root. This potential difference drags aluminum ions toward the glass side, and aluminum ions penetrate into the glass through the protruding parts of the layer and react with excess oxygen ions at the ends of the protrusions. The excess oxygen ions are depleted by the reaction at the ends of the protrusions, and their density near the joint interface becomes low. Therefore, the protrusions grow only in the longitudinal direction and their diameters do not increase. Probably in this way, the fibrous oxide forms

As shown in Fig. 7(c), the penetration of Al into the glass in the alkali depletion layer was insignificant. This implies that excess oxygen ions generated in the alkali depletion layer are compensated mainly through the reaction to form the γ-Al_2O_3 layer and fibres. The amount of the excess oxygen ion can be estimated from the thickness of the alkali depletion layer and initial content of alkali elements in the glass. According to the results from EPMA analysis, the alkali depletion layer in the Al/glass joint anodically-bonded at T_b = 613 K and V_b = 500 V for t_b = 10.8 ks was 3 μm thick. If all the excess oxygen ions in this layer were consumed by the formation of the γ-Al_2O_3 layer, the thickness of the layer would be about 90 nm. The thickness of the γ-Al_2O_3 layer observed was less than 20 nm. In this joint, however, the fibrous oxide more than a few 100 nm long formed besides the oxide layer. Although it is rather difficult to estimate the volume of the fibrous Al oxide, it seems sufficient to compensate the excess oxygen ion in the depletion layer.

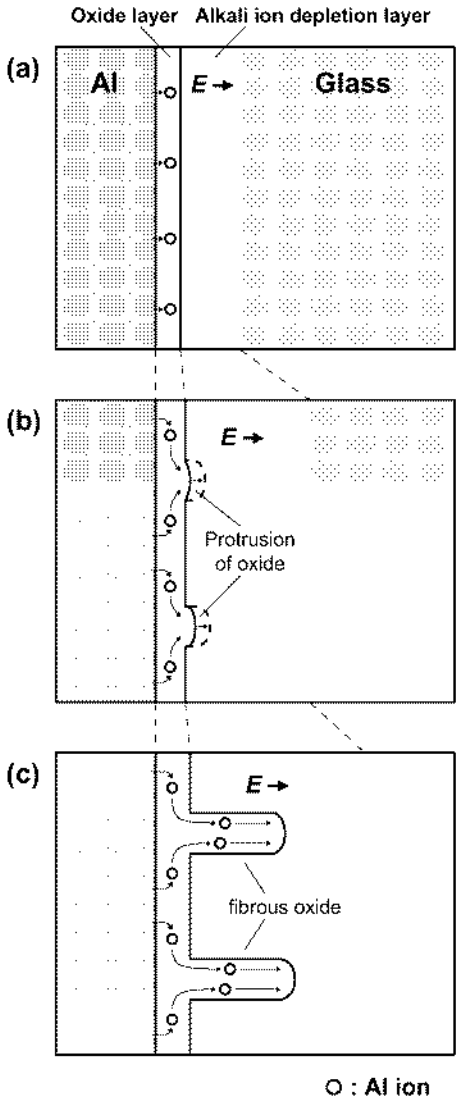


Fig. 9 Mechanism of growth of the fibrous oxide in the interfacial area in the anodically-bonded Al/glass joints. At first the oxide layer forms at the joint interface (a). Next the aluminum ions penetrates into the glass through the protrusions of the layer and react with the excess oxygen ions in the alkali ion depletion layer at the ends of the protrusions (b), in this way the fibrous oxide grows (c).

4. Conclusion

The microstructure and element distribution around the bond interface of Al/glass anodically-bonded joints were investigated by TEM observations. Results obtained are summarized as follows:

1. Aluminum oxide was formed at the joint interfaces. It formed a layer ~10 nm thick and fibrous structures a few hundred nm long growing in the glass from the joint. Both of them consisted of γ-Al_2O_3. The fibrous oxide grew evidently with the bonding time.

2. Aluminum ions were not observed to penetrate into the glass beyond the Al oxides mentioned in 1.

3. The total volume of the γ-Al_2O_3 layer and fibres was estimated to be sufficient to compensate the excess oxygen ions generated in the alkali depletion layer. It was suggested that the growth of the alkali-ion depletion layer may be explained from the consumption of excess oxygen in the depletion layer by the formation of Al oxide at the bond interface.

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