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Interfacial phenomena in electric field assisted anodic bonding of Kovar/ Al film glass^①

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[Abstract] Anodic bonding of glass to Kovar alloy coated with Al film (Glass-Al film/Kovar) was performed in the temperature range of 513~ 713 K under the static electric voltage of 500 V in order to investigate the interfacial phenomena of Al-glass joint. The results reveal that Na and K ions within the glass are displaced by the applied field from the anode side surface of the glass to form depletion layers of them. The K ion depletion layer is narrow and followed by a K pile-up layer, and both the two layers are formed within the Na depletion layer. The width of the Na and K depletion layers is increased with increasing bonding temperature and time. The activation energies for the growth of both depletion layers were close to that for Na diffusion in the glass. TEM observations reveal that Al film coated at the surface of Kovar alloy is oxidized to amorphous Al₂O₃ containing a few of Fe, Ni and Co by oxygen ions from the glass drifted by high electric field during bonding. The amount of Fe ions diffusing into the glass adjacent to the anode is significantly low due to the presence of Al film between Kovar alloy and the glass. As a result, the amorphous reaction layer of Fe-Si-O in the glass near the interface is avoided which is formed in Kovar-glass joints.

[Key words] anodic bonding; aluminum anode; glass; ions drift; depletion layer; interfacial reaction

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1 INTRODUCTION

Anodic bonding is a promising technique for glass-to-metal sealing at temperature significantly lower than those used in the conventional thermal sealing^[1-3]. Low processes temperature allow bonding of the glass to low melting point materials such as aluminum. Anodic bonding has a variety of commercial applications including pressure sensors, photovoltaic as well as microelectronic device packaging. Recently, a significant amount of research has been done on the processes of anodic bonding, including mechanisms of surface contact, modeling of the current transfer, polarization of the glass and interfacial phenomena as well as chemical bond formation^[4-12]. In anodic bonding process, the metal anode and the glass are firstly brought into intimate contact (a primary requirement for a good seal) under the electrostatic force resulted from the drift of ions within the glass; then anodic oxidation of anode materials occurs which is responsible for strong bond formation. Therefore, a key mechanism of anodic bonding is the electric-field assisted activation of ions and their drift under the electric-field applied during bonding. The electrostatic force brings the parts into intimate contact so as to establish a chemical bond at the interface. So the process requires high temperatures for Na ions to migrate in the glass and high voltage to displace Na ions from the joint interface (anode side) to

the cathode. Direct evidence of anodic oxidation (formation of an amorphous reaction layer of Fe-Si-O and a crystal oxide of Fe) in anodic glass-Kovar bonding was recently published by Ikeuchi et al^[13,14].

It is known that Al is a typical blocking anode. Its characteristics are different from those of Kovar alloy anode. But there was relatively little investigation on the interfacial phenomena of Al-glass anode-bonded joint. The aim of the present work is to study the interfacial phenomena of Al-glass joint. In order to produce a sound joint for preparing the cross-section specimen that can be used for SEM and TEM observations, Al was coated at the surface of Kovar alloy to be sealed. Then, the Kovar alloy was anode-bonded to the glass. Since the expansion coefficient of bulk Kovar alloy is very close to that of the glass used, the residual stress can be decreased.

2 EXPERIMENTAL

The borosilicate glass ($d 25 \text{ mm} \times 1 \text{ mm}$) and Kovar alloy ($d 20 \text{ mm} \times 5 \text{ mm}$) were used as bonding pair. Their chemical compositions are listed in Table 1 and Table 2 respectively. After Kovar disk surface was polished, RF sputtering was used to produce an Al film about 0.1 μm thick on it.

Anodic bonding was conducted in a vacuum chamber of 10^{-3} Pa . A copper plate was employed as the cathode, on which the specimen couple was

Table 1 Chemical composition of borosilicate glass (mass fraction, %)

SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	K ₂ O
68.7	3.60	18.8	3.83	4.06
Li ₂ O	CaO	BaO	Sb ₂ O ₃	
0.51	0.047	0.024	0.42	

Table 2 Chemical composition of Kovar alloy (mass fraction, %)

C	Co	Fe	Mn	Ni	Si
0.003	16.2	Bal.	0.45	29.6	0.1

placed with the glass at the cathode side, as shown in Fig. 1. The bonding temperature was monitored using a chromel-alumel thermocouple percussion-welded in the vicinity of the joint interface of a dummy specimen that was placed close to the specimen to be sealed. After the glass-metal assembly was heated to a desired temperature, a DC voltage was applied across it for different time (bonding time). A 1 kΩ resistance was connected in series with the specimen to record the current response. After bonding operation, the specimens were cooled to a temperature below 423 K at a rate of 5 K/s. SEM, EPMA and TEM were used to analyze interfacial structure and concentration across the interface. TEM observations were carried out with a JEOL-2010 microscope equipped with an EDX microanalytical system at an acceleration voltage of 200 kV.

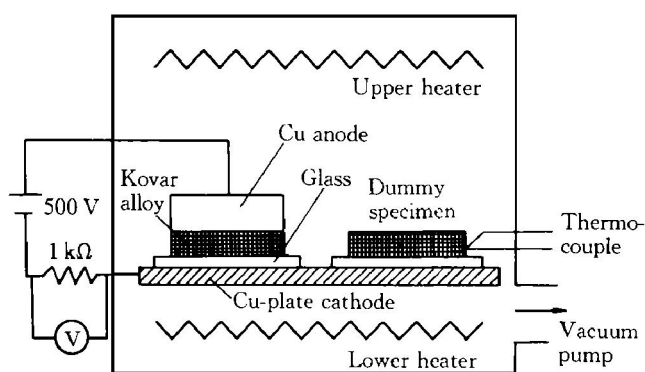


Fig. 1 Schematic diagram of assembly of anodic bonding apparatus

3 EXPERIMENTAL RESULTS

3.1 SEM observation and EDX analyses of glass-metal interface

SEM micrographs and element profiles across the Kovar/Al-glass interface after bonding at 663 K for 0.6 ks and 10.8 ks are shown in Fig. 2(a) and (b), respectively. Corresponding to the drift current in the external circuit after applying the voltage, alkali ions, Na and K within the glass are displaced adjacent to

the anode interface, leaving a depletion region of them. The K depletion layer is narrow and followed by a pile-up layer of K, and both are within the Na depletion layer. As shown in Fig. 2, the thickness of these layers involving K pile-up layer increases as bonding time is prolonged. The detailed change in the thickness of Na and K depletion layer is plotted against bonding time at different bonding temperatures, as shown in Fig. 3(a) and (b), respectively. The thickness of these layers increase with increasing both the bonding time and temperature, and always at a higher rate at the onset of the bonding.

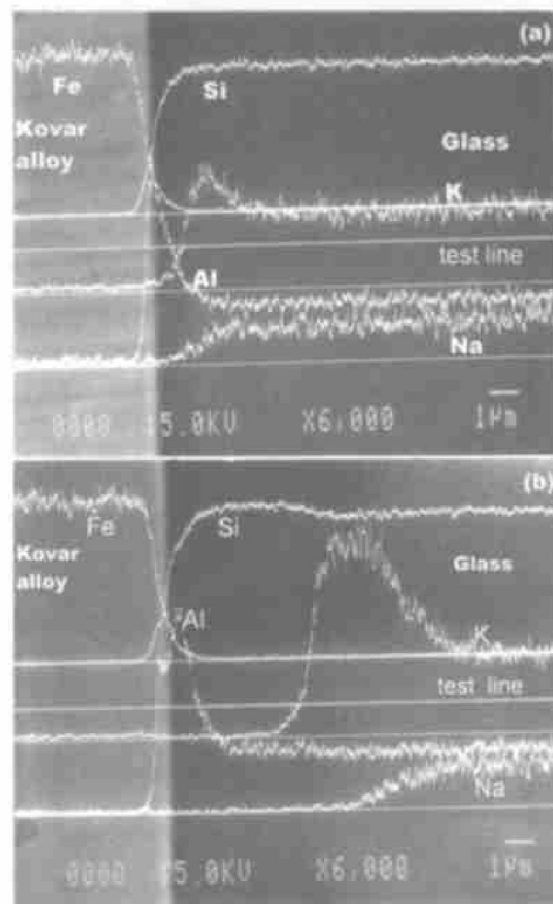


Fig. 2 SEM micrographs and EDX line analyses across Kovar/Al-glass joints interface after anodic bonding at 663 K for 600 s (a) and 10.8 ks (b)

In order to estimate the activation energies for the growth of the alkali-depletion layers, bonding time ($\ln t$) required to produce depletion layers with thickness of 0.5 μm and 1 μm, is plotted against bonding temperature ($1/T$), as shown in Fig. 4. The activation energy for the growth of the Na depletion layer is estimated to be about 64 kJ/mol from the slopes of the lines, which is nearly equal to the activation energy of 65 kJ/mol for the Na diffusion in the glass. Similarly, the activation energy for the growth of K depletion layer is about 60 kJ/mol, although the activation energy for the K diffusion in the glass was reported to be almost double that of the Na diffusion^[15].

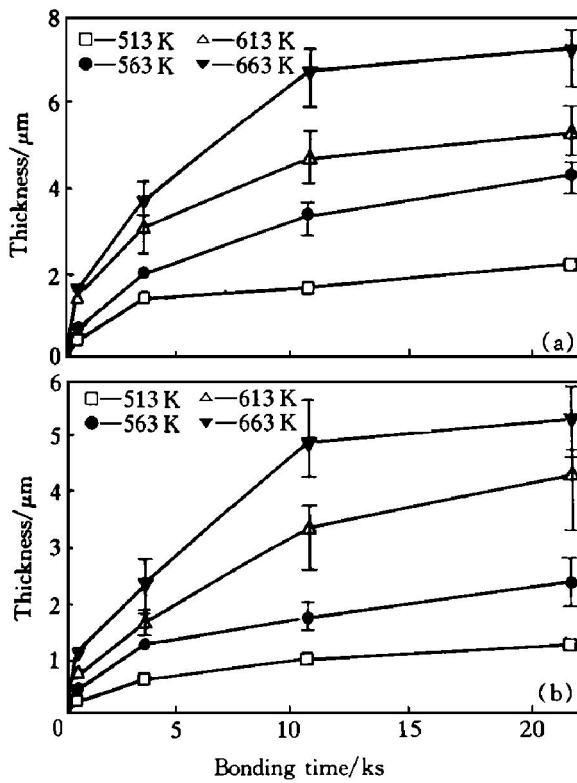


Fig. 3 Effect of bonding time on widths of Na and K depletion layers at various bonding temperature
(a) —Na depletion layer; (b) —K depletion layer

3.2 TEM observations of interfaces

The interfacial region of Kovar/Al-glass joint bonded at 613 K for 10.8 ks is shown in Fig. 5(a). Between Kovar alloy and the glass, a layer of about 70 nm thick is observed by TEM which is not found in SEM observations. EDX analyses show that this layer consists of Al and O as well as a few of Fe, Ni and Co (Fig. 5(b)). It is reasonable to believe that Al film initially coated at the surface of Kovar disk changes to oxide after anodic bonding. This oxide layer is amorphous phase since SAD patterns from

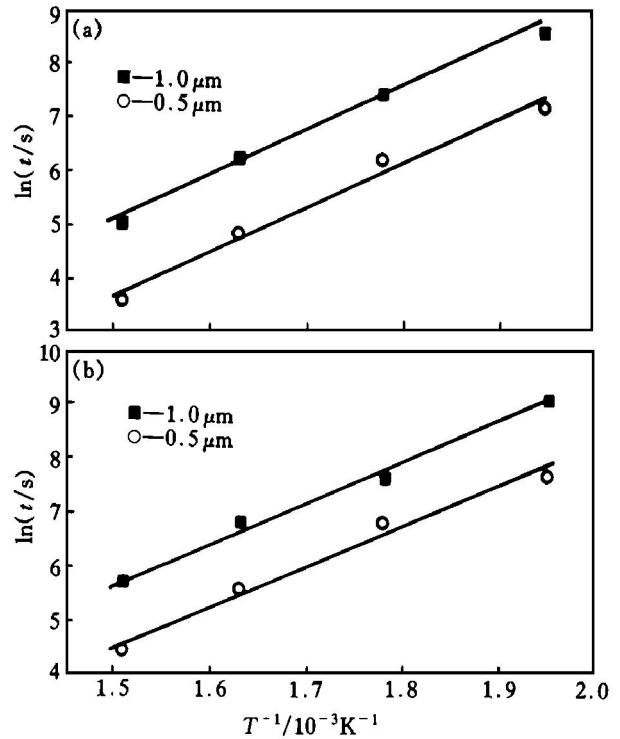


Fig. 4 Logarithm bonding time required to form Na and K depletion layers of 0.5 μm and 1 μm thick as function of reciprocal bonding temperature
(a) —Na depletion layer; (b) —K depletion layer

this layer shows the diffused halo, as shown in Fig. 5(c). The elemental distributions in the glass away from the interface about 30 nm are listed in Table 3. It is found that the diffusion of Fe ions into the glass is easier than that of Ni and Co ions. The amorphous Fe-Si-O reaction layer, which is formed in Kovar-glass anode-bonded joint^[13,14], can't be found in Kovar/Al-glass joint. Fe content in the glass near the interface is significantly lower than that in the amorphous Fe-Si-O reaction layer formed in Kovar-glass joint. In addition, Al content in the glass near the interface after anodic bonding is found to be

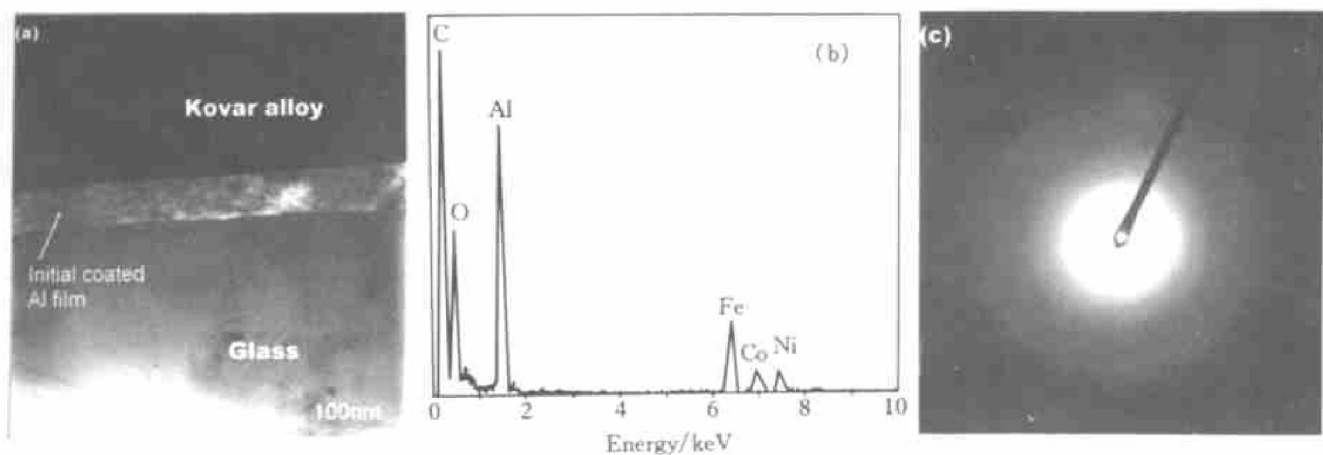


Fig. 5 TEM micrograph of Kovar/Al-glass joint interface (a), EDX spectrum (b) obtained from the interfacial reaction layer and SAD patterns (c) obtained from the amorphous alumina layer

Table 3 EDX analysis results of interfacial regions in Kovar/Al-glass joint (%)

Position	x (Al)	x (Fe)	x (Ni)	x (Co)	x (O)	x (Si)
Amorphous oxide	28.90	3.43	1.14	0.97	65.56	
Glass near interface	1.56	1.87	0.51	0.54	71.13	24.39

about the same as that in the glass before bonding. Those results imply that during anodic bonding uncombined non-bridging oxygen ions are drifted towards the anode surface from the depletion layer of the glass under high electric field; Al film coated is oxidized by the uncombined non-bridging oxygen ions, and the initial coated Al film and subsequently formed oxide layer act as a barrier layer to decrease the amount of Fe ions diffusing into the glass.

4 DISCUSSION

4.1 Growth of Na and K depletion layers

During anodic bonding, DC voltage is applied at sufficiently high temperature for Na ions to migrate from the anode towards the cathode. This results in the formation of Na depletion layer where a negative space charge is accumulated due to the uncombined non-bridging oxygen ions. Thus, the glass has three distinct regions: the region near the anode, the bulk glass, and the region near the cathode. The bulk glass acts as a resistor and does not undergo compositional change during bonding; but a flux of sodium ions passes through the bulk glass that is responsible for the formation of depletion layer. After an initial charge transient, most of the applied voltage occurs over the depletion layer. The Na ion flux under an external electric field can be approximated by the following transport equation:

$$J = -D \frac{\partial c}{\partial x} - \frac{D}{RT} Zec \frac{\partial V}{\partial x} \quad (1)$$

where c is the number of ions in unit volume; Z is the valence of the ion; e the electronic charge; D the diffusion coefficient, $D = D_0 \exp(-Q/kT)$ and V is the electrical potential.

Thus the potential gradients as well as the concentration gradient gives rise to the ion flux, and those terms are responsible for the formation of the Na depletion layer. Since the applied voltage drops mostly in the alkali-depletion layer as suggested by Carlson^[3], the potential gradient across the bulk glass is relatively small. The activation energy of the Na depletion layer growth is estimated to be about 64 kJ/mol (Fig. 4), which corresponds well to the activation energy of sodium diffusion in the investigated glass^[10], suggesting that the growth of the Na depletion layer is controlled mainly by the Na diffusivity. The activation energy of the K depletion layer growth is also about 63 kJ/mol, which is lower than the reported activation energy of K ions diffusion in

the glass^[15], but much close to that of Na depletion layer. Since the K ion in the glass is much less mobile than Na ion, and both the K depletion and pile-up layers are observed only within the Na depletion layer, it is suggested that these layers are formed owing to the migration of K ions drifted by the very high electric field set up in the Na depletion layer.

4.2 Interfacial phenomena in Kovar/Al-glass anodic bonding

The voltage across the alkali-depletion layer, V_A , can be approximately expressed by^[3]

$$V_A = \frac{n_- e X_p^2}{2 \epsilon_A} \quad (2)$$

where n_- is the concentration of uncombined non-bridging oxygen ions, X_p is the width of the polarized alkali-depleted layer, and ϵ_A is the permittivity of the layer. The electric field at the anode surface can be expressed in terms of the voltage across this layer:

$$E_A = \frac{2 V_A}{X_p} = \sqrt{\frac{2 n_- e V_A}{\epsilon_A}} = \frac{n_- e X_p}{\epsilon_A} \quad (3)$$

Since the applied voltage drops mostly in the alkali-depletion layer as suggested by Carlson et al^[3], V_A can be taken as about 500 V. Substitution in Eqn. (3) of $V_A = 500$ V and $X_p \approx 2 \mu\text{m}$ (as shown in Fig. 3) gives $E_A = 5 \times 10^8$ V/m. Thus, a very high electric field can be expected at the anode surface. The electric field within the bulk glass is quite small. The flux of ions drifted by the electric field can be approximated by the following equation^[3, 16-18]:

$$J \approx 4acv \exp\left[-\frac{Q}{kT}\right] \sinh\left[\frac{|qaE|}{kT}\right] \quad (4)$$

where c is the concentration of ions, a is the half barrier width (half the average jump distance), v is the vibration frequency of ion, Q is the activation energy required for a jump, k is Boltzmann's constant, T is absolute temperature, q is the charge of the ion, and E is the electric field ($= \partial V / \partial x$). In the depletion layer, the electric fields are expected to be quite large, and a high field approximation can be applied and Eqn. (4) can be rewritten as:

$$J \approx 4acv \exp\left[-\frac{Q - |qaE|}{kT}\right] \quad (5)$$

This implies that the electric field reduces the height of the energy barrier from Q to $(Q - qaE)$. Therefore, the very high electric field set up in the Na and K depletion layers drifts uncombined non-bridging oxygen ions towards the metal anode and pulls the metal ions into the glass. Thus, oxidation reaction of anode metal occurs, as confirmed by TEM observations.

In contrast to the interfacial phenomena in anodic bonding of Kovar-glass joint which was discussed in the previous papers^[13, 14], Al film coated at the surface of the Kovar alloy decreases the amount of Fe ions diffusing into the glass since Al film acts as a bar-

rier layer in Kovar/Al-glass joint. As a result, Fe-Si-O amorphous reaction oxide layer formed in Kovar-glass joint can not be found in Kovar/Al-glass joint. Accordingly, oxygen space charge can be suggested to migrate under the high electric field towards the Al film anode forming a layer of aluminum oxide and Al ions may also be drifted into the glass by the high electric field. Based on the TEM and EDX results, however, the amount of Al ions penetrated the glass in the region adjacent to the anode is significant low due to the strong blocking characteristic of Al anode.

The interface shows a yellow color, which is generally associated with ferric ions (Fe^{+3}) when bonding time is prolonged to 10.8ks or 21.6ks at temperature higher than 613K. These results suggest that a few Fe ions are diffused into the glass across the Al film during bonding. This is consistence with the TEM results. Thus, Fe ions being diffused within the Al film towards the interface may also be oxidized by the oxygen ions towards the Kovar side drifted by high electric field to form FeO. Al film initially coated at the Kovar surface is eventually oxidized to form Al_2O_3 . It is thought that Fe^{2+} ions entered into the glass become Fe^{3+} by subsequent oxidation combining with oxygen ions supplied from the depletion layers^[13,14].

5 CONCLUSIONS

1) SEM observation of Kovar/Al-glass interface reveals that a Na depletion layer, and K depletion and pile-up layers within the Na depletion layer are formed in the glass adjacent to the anode surface.

2) The thickness of the Na and K depletion layers in Kovar/Al-glass joint is increased with increasing bonding temperature and time. The activation energies for the growth of the Na and K depletion layers are estimated to be about 64 kJ/mol and 60 kJ/mol respectively, suggesting that their growth is controlled by Na diffusivity in the glass.

3) TEM observation of the joint interface reveals that Al film coated at the surface of Kovar alloy is oxidized to form amorphous oxide of Al containing a few of oxide of Fe by uncombined non-bridging oxygen ions from the glass which results from the high electric field.

4) Compared with Kovar-glass joint, due to the presence of Al film between the Kovar alloy and glass in Kovar/Al-glass joint, the amount of Fe ions diffusing into the glass adjacent to the anode materials decreases; and the formation of Fe-Si-O amorphous reaction layer which is found in Kovar/glass joint is avoided.

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