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Joining mechanism of field-assisted diffusion bonding of solid electrolyte ceramic to metals①

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Abstract: Field-assisted diffusion bonding applied in the joining of solid electrolyte borosilicate glass, β″-Al_2O_3, Y_2O-ZrO_2 to monocrystal silicate and aluminum were proceeded with bonding machine in the assistance of static electric field. TEM, SEM, XRD and other means were applied to investigate and analyze microstructure of interface. It is supposed that the interfacial area is a model of metal-oxides-ceramic, and the joining mechanism is solid diffusion joining and static electric bonding. The process of ions migration and accumulation under electric field is the most essential factor for the anodic oxidation and interfacial joining. Temperature and voltage are the basic factors of the solid diffusion bonding of interfacial oxidation. And voltage, temperature, pressure and the condition of surface are the most important factors that govern the bonding process.

Key words: solid electrolyte; ceramic; metal; composite; field-assisted bonding

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1 INTRODUCTION

Field-assisted diffusion bonding(FDB), as a special method of solid-state diffusion bonding, has been investigated widely in the field of bonding of ceramics and metals. Applied in a static electric field, it can be proceeded at low temperature and pressure and in short time. FDB is suitable for assembly sealing of metal-oxide simeconductor(MOS), such as miniature instruments, sensors and so on. Now lots of physical characters during bonding have been reported[1-3], and in order to meet the requirement of micro electromechanical systems(MEMS) processing, bonding equipment and technology were investigated. In former studies, researchers paid more attention to the technological characteristics of bonding and the effect of materials and composition but less to interfacial bonding mechanism, microstructures, physical and chemical characters, especially less to the bonding of solid state ionics and solid state chemistry[4, 5].

Field-assisted diffusion bonding applied in the joining of solid electrolyte borosilicate glass, β″-Al_2O_3, Y-ZrO_2 to monocrystal silicate and aluminum are proceeded with bonding machine, and interfacial microstructure is analyzed by means of TEM, SEM and XRD in this paper.

2 EXPERIMENTAL

2.1 Materials

K4glass(Pyrex) is a kind of solid electrolyte with fast ions electric conductivity applied in vacuum instruments, meters and sensors, whose dominant chemical composition is 69% SiO_2, 8.3% Na_2O, 3.5% B_2O_3, 3% Al_2O_3, 4% K_2O; and its thermal expansion coefficient (at 20－200 ℃) $\alpha_l = 5.3 \times 10^{-6}$/℃. β″-$Al_2O_3$, which has an excellent ion conductibility and high-temperature endurance, is employed as chemical sensors, Na-S cell and so on. β″-Al_2O_3 used in the experiments is supplied by Shanghai Silicate Research Institute, whose dominant chemical composition is 85%－90% Al_2O_3, 8%－12% Na_2O, (0.3%－1.0%) Li_2O + MgO, and its $\alpha_l = 4.90 \times 10^{-6}$/℃ (100 ℃). ZrO_2, which has a high ion conductivity and high-temperature endurance, is a kind of solid electrolyte ceramic that conducts electricity through oxygen ion, and it is the best one for chemical sensor and fuel battery; flexibility of ZrO_2 can be improved by adding Y_2O_3. ZrO_2 wafer used in the experiments is sintered in vacuum, whose dominant chemical composition is 90% ZrO_2, 3%－5% Y_2O_3, 3%－5% MgO; and its $\alpha_l = 5.1 \times 10^{-6}$/℃. The thickness of aluminum and monocrystal silicon wafers are 0.03 mm and 0.5 mm, respectively.

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2.2 Experimental procedure

The wafers were cut in the size of 20 mm × 20 mm × 2 mm and ground and polished till their surface roughness is less than 1 μm, then cleaned with acetone in an ultrasonic bath.

In the experiments, the lapped wafers were fixed on a platform of a special bonding machine and the metal was positive(Fig. 1). Test temperature was about 250−400 ℃, direct voltage was 400−800 V, pressure was 0.05−1.00 MPa, and bonding time was 10−20 min. After bonding, the wafers were cooled to room temperature in the oven at a speed of 4 ℃/min.

The extending rods were glued on both sides of the bonded wafers to test their bonding strengths with WD-10 tensile test machine. Kevex Superdry SEM and EDAX, Rigaku D/MAX-250 XRD were employed to analyze the microstructure and elements distribution of the interfacial area.

3 RESULTS AND DISCUSSION

3.1 Microstructures and joining mechanism of interface

The microstructures and elements profile at the interfaces are shown in Fig. 2. It is indicated that joining interface of K4 glass or ceramics to metals consists of ceramic-oxidation compounds (including SiO_2, Na_2O, Al_2O_3, ZrO_2)-silicon (aluminum). In the area about 10−20 μm width, Si, O, Na, Al distribute in the pattern of density gradient. The microstructures are pillar crystal grains grown from glass to metal anodes, the width of the grains is 0.5−1.0 μm. The result of XRD indicates that the grains are $Na_2O·SiO_2$, Al_2SiO_5, Na_5AlO_8 and $Al_2O_3·ZrO_2·3H_2O$.

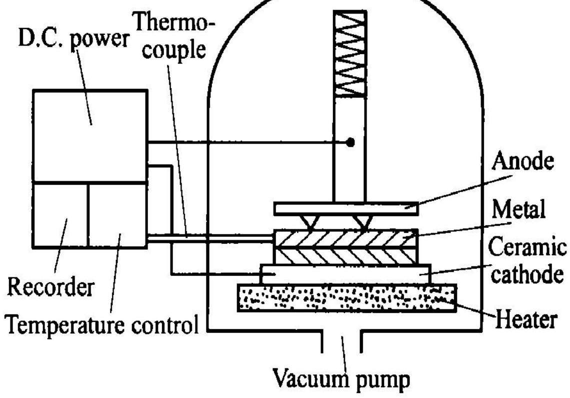

Fig. 1 Schematic drawing of FDB test

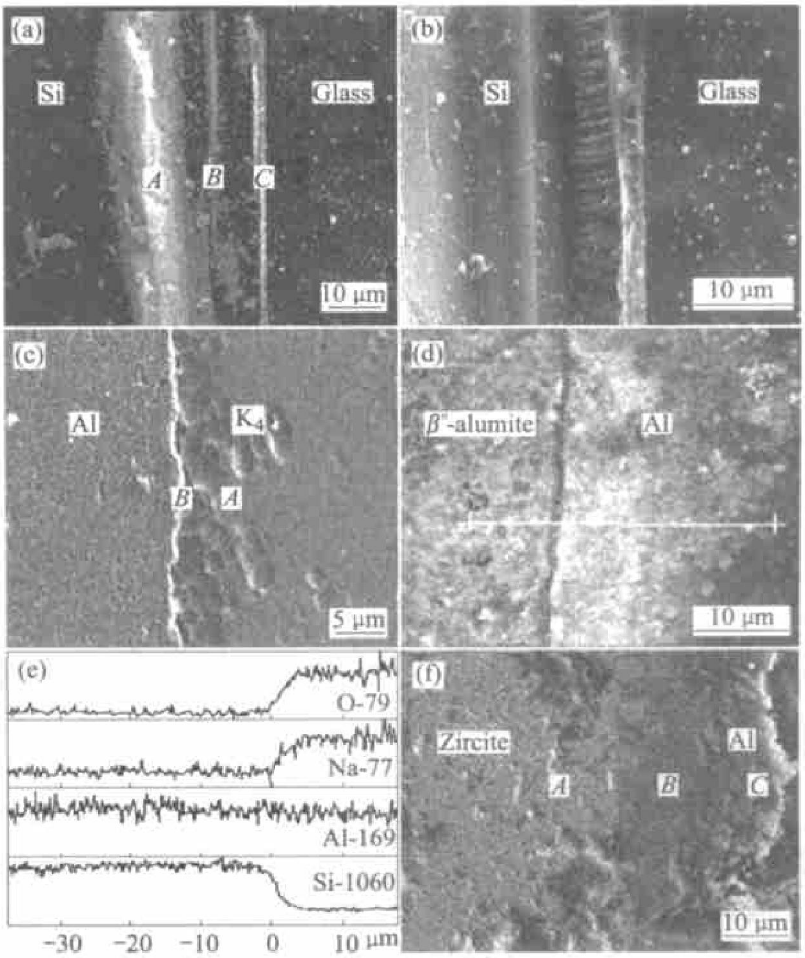

Fig. 2 Microstructures and element profiles at interface

(a) —Microstructure at K4/Si interface; (b) —Details of K4/Si interface; (c) —Microstructure of K4/Al; (d) —Microstructure of β''-Al_2O_3/Al; (e) —Element profiles at K4/Si interface; (f) —Microstructure of ZrO_2/Al interface

3.2 Influence of technological parameters on bonding

3.2.1 Polarized current and ions diffusion

The interface is polarized by direct current after the static electric field is built for a few seconds, then the conductivity of solid electrolyte increases and ions current is produced in the interfacial area under the action of electric field. It can be inferred that the surge current formed in the process of the current polarization, reveals the movement state of conductive ions in the bonding area, ions diffusing from instantaneous high density to low density (Fig. 3). Moving toward each other of positive and negative charged ions is fundamental to the formation of bonding interface. According to electrochemistry, under the effect of electric field, alkali metal oxides (Na_2O, K_2O) are discomposed

$$M_2O \rightarrow 2M^+ + O^{2-} \quad (1)$$

as the cation M^+ moves to the cathode, negative ions accumulate at the interface and combines with metal ions to form new oxides.

$$XM^+ + YO^{2-} \rightarrow M_XO_Y + 2Ye \quad (2)$$

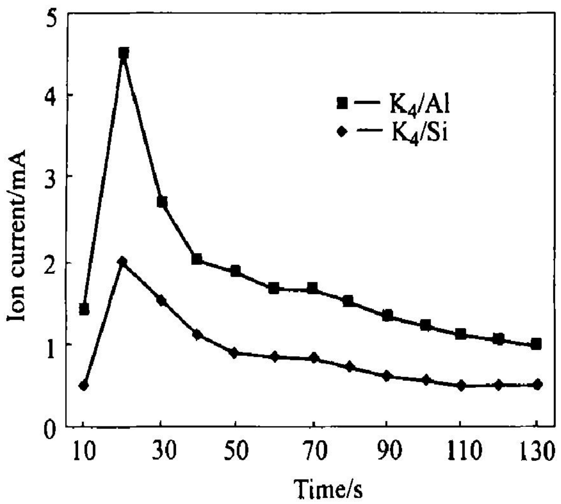

Fig. 3 Polarized current pattern at interface

O^{2-} begins to diffuse in the electric field, then oxide is formed at the interface, which makes the deposited layer extend to the anode. The deposition and diffusion of interface will be ended when the electric field is removed, at the same time, polarized current becomes to zero and bonding is finished (atom diffusion will continue at high temperature). It is indicated that the microstructure of transitional area formed during ions diffusion and chemical combination is pillar crystal vertical to the bonded interface. New oxides Al_2O_3 and SiO_2 deposit on the surface of silicon anode or Al anode and get bonded with SiO_2, Al_2O_3 crystals of glass, ceramic, then transitional area is formed. Under the effect of the electric field (E) and temperature (T), O^{2-} begins to move to the anode throughout the oxides area and oxidizes the anode, which makes the thickness and width of deposited layers increase, so the transitional area is formed. It can be inferred from Eqn. (2) that diffusion density of M^+ and O^{2-} current is in close relation to the polarized electric current density, which has been verified by Wallis[6]. All of reactions will not end until the static electric field is removed. The experimental results indicate that the width of transitional area is in direct proportion to the experiment time[7]. Under the condition of our experiments, tensile strength of joints is 8-30 MPa, and the fracture is in ceramic (glass) near the bonded interface.

3.2.2 Effects of temperature and pressure

According to Arrhenius laws, the conductivity of solid electrolyte is

$$\sigma = \sigma_0 \exp(-E_a/KT) \quad (3)$$

where σ_0 is electric conductivity at room temperature, E_a is activation energy of ions, K is Boltzmann constant, T is temperature. σ increases with the increase of temperature because the energy of moving along the certain direction of atoms increases, leading to an increment of diffusion density in the same direction as temperature increases[8]. It is indicated that when the voltage is given, the maximum of polarized current as well as the bonding ratio increases as the temperature increases. When T and E are given, outer pressure becomes the main factor to bonding ratio. It is concluded that if the pressure is less than 0.5 Pa or the roughness can not meet the requirement, it tends to come into crave or false bonding at the interface, all of which will destroy the bonding strength dramatically. An elastic deformation occurs on the surface of the wafers to be bonded due to a given pressure, which makes the electric attraction and the number of contact point increased, so that it is easy for the interface to be polarized and the ions to diffuse[9-11].

4 CONCLUSIONS

1) Solid electrolyte ceramic (glass) and metal are joinable under the condition of FDB. The bonded area is composed of metal-composite transitional area-ceramic. The microstructure of transitional area, which is formed by ions migration and bonding and oxides combination, is pillar crystal vertical to interface. The width of transitional area is in direct proportion to bonding time in the electric field.

2) Ions conduction and diffusion in electric field are essential to the formation of transitional layers that is primarily owed to the mechanism of the formation of the oxides and the combination of the compounds. Voltage, temperature and ions conductivity

of solid electrolyte are the main factors of affecting the bonding process.

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