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Hermetic Glass Sealing of AlN Packages for High Temperature Applications

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Abstract

In this study the feasibility of glass soldering of aluminium nitride (AlN) for the package of silicon carbide semiconductors with application temperatures up to 600°C was evaluated. The components used were various commercially available solder glasses and a crystallising three-component glass. Chemical compatibility between the glass and AlN was investigated by means of both thermodynamic calculations and experimental work on solder joints. The PbO-free three-component glass was stable against AlN. Lead oxide containing glasses showed deleterious reaction with AlN, which can be inhibited by a passivating layer. Additionally the influence of the processing parameters atmosphere and mechanical pressure was investigated. Hermeticity of sealed packages could be proved for three glasses allowing high temperature application between 500 and 600°C. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Silicon carbide semiconductors can be used up to temperatures of 600°C. For the chip packaging AlN is the preferred material since, additional to good dielectrical properties and high thermal conductivity, AlN exhibits a similar coefficient of thermal expansion[3] which minimises thermomechanically induced stresses. A well established method for hermetic sealing of ceramic packages is glass soldering, usually working with leadborate glasses.[4,5] In literature deleterious reactions between thick film binder glasses and AlN substrates are reported.[6,7] These lead to the formation of bubbles and metallic lead spheres as a result of redox reactions between AlN and oxides of the glass according to the general equation

$$^{2}/_{n}\mathrm{MeO}_{n}+^{4}/_{3}\mathrm{AlN}\rightarrow^{2}/_{3}\mathrm{Al_2O_3}+^{2}/_{3}\mathrm{N_2}+^{2}/_{n}\mathrm{Me} \quad (1)$$

Me stands for a metal with the valency 2 *n*. An oxide can be reduced by AlN to metal in a spontaneous reaction if the change of Gibbs' free energy, ΔG^0, is negative. By calculating ΔG^0 for some oxides Norton[7] made predictions on the reactivity of different oxides. This consideration describes the situation of pure crystalline oxides at standard pressure. Yet in glasses, oxides are incorporated in an amorphous network, the critical oxides may be diluted by other ones. This knowledge was taken into consideration for the experiments.

2 Experimental

According to parameters found in Kubaschewski *et al.* and Kasatschkow,[8,9] ΔG^0 was calculated for zinc silicate and several oxides including zinc oxide which was omitted by Norton.[7] ZnO is an important component because with high ZnO concentrations processing temperatures of about 700°C and a coefficient of thermal expansion of about $4\times10^{-6}\,\mathrm{K}^{-1}$ can be obtained. The dilution effect in glasses can be taken into account by relating ΔG^0 and the equilibrium constant *K*:

$$\Delta G^0 = -RT\ln K \quad (2)$$

R is the universal gas constant, *T* the absolute temperature. The equilibrium constant is further on described by the equation

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$$K = \frac{a(\mathrm{Al_2O_3})^{2/3} \cdot a(\mathrm{Me})^{2/n} \cdot a(\mathrm{N_2})^{2/3}}{a(\mathrm{AlN})^{4/3} \cdot a(\mathrm{MeO}_n)^{2/n}} \qquad (3)$$

The activities a of the pure phases AlN and Me are 1 and in approximation $a(Al_2O_3)$ is set equal to 1 since Al_2O_3 is dissolved at the reaction interface into the glass very slowly. $a(MeO_n)$ and $a(N_2)$ are set equal to the molar concentration and the partial pressure respectively which consequently reduces (3) to

$$K = \frac{p(\mathrm{N_2})^{2/3}}{[\mathrm{MeO}_n]^{2/n}} \qquad (4)$$

Combining eqns (3) and (4) and transforming the equation into common logarithm leads to

$$\log p(\mathrm{N_2}) = \frac{3}{n}\log[\mathrm{MeO}_n] - \frac{3\log e \cdot \Delta G^\circ}{2RT} \qquad (5)$$

By means of formula eqn (5) the partial pressure of nitrogen can be calculated. Formation of bubbles and metallic spheres only occurs if $p(N_2)$ is greater than the atmospheric pressure. For soldering experiments six commercially available solder glasses were used, which contained PbO, ZnO, B_2O_3, and SiO_2 as main constituents. In addition a PbO free glass (ZnO–B_2O_3–SiO_2)[10] was prepared. To obtain a processable screen printing paste Elvacite® (Lehmann & Voss & Co, Germany) as an organic binder system and α-terpineol (Merck, Germany) as a solvent were added to the glass frits. Each paste was then applied on a first AlN substrate (Alunit®, CeramTec, Germany) by means of a doctor blade. Burnout of the organics and the following densification of the powder by viscous sintering occurred during the preglazing process in air. The second piece of substrate was put on the preglazed substrate and loaded using a dead weight. By heating up this arrangement for 30 min in a second process, the two AlN substrates were joined. Due to the later package sealing application this final soldering process has to be performed in an inert atmosphere. Samples were joined under neutral nitrogen in a tube furnace and under argon and vacuum atmospheres in an furnace with carbon heating elements which led to a reducing atmosphere. Temperatures for the preglazing and sealing process and properties of the glasses are given in Table 1. The applied pressure on the substrates with a size of 5 × 5 mm^2 was varied between 0·16 and 18·9 kPa during the joining process.

The long term behaviour of glasses that showed no visible reaction after the soldering process was tested by a 450 h heat treatment of the solder joints at 500 or 650°C in air. Afterwards polished samples were examined microscopically and by XRD.

Sealed AlN packages (NGK Spark Plug Co. Ltd., Japan) with a cavity of 120 mm^3 were tested on leaks according to DIN IEC 68 part 2-17 and MIL STD 883 with a bubble tester (BT 8000, Pink Vakuumtechnik, Germany) and a He-leck tester (HLT 150, BaIzer, Germany), respectively.

3 Results and Discussion

In Fig. 1 ΔG^0 is plotted versus temperature for oxides in the standard state. Oxides with negative values of ΔG^0 can react with AlN whereas oxides with positive ΔG^0 like SiO_2, B_2O_3 and the crystallisation product zinc silicate are expected to behave inert. The situation in glasses is represented in Fig. 2 where the nitrogen partial pressure is plotted vs temperature for several oxides in a fixed molar concentration. The reaction of SiO_2, for example, is suppressed by the ambient pressure whereas Cu_2O and PbO—preferably used to improve melting properties of the solder glasses—show very high nitrogen pressures. Unfortunately, if combining only thermodynamically uncritical oxides, a solder glass with the desired properties can not be composed. ZnO is of special interest as it is an intermediate oxide that could facilitate the desired glass properties. It leads to a lower nitrogen partial pressure than PbO, coming in the range of atmospheric pressure for low concentrations. In addition ZnO incorporated in glasses can be passivated by transforming into thermodynamically stable oxides like zinc silicate (see Fig. 1).

During the soldering process glasses 3, 4 and 6 which contain 39·3–66·8 wt% PbO developed gas

Table 1. Some properties of the solder glasses

Glass	*PbO (wt%)*	$T_{preglaze}$, T_{seal} (°C)	α_{25-300} (10^{-6} K^{-1})	*Type (type of filler)*	*Average grain size (μm)*	*Maximum grain size (μm)*
Glass 1	2·7	650, 700	3·6	Stable (cordierite)	2·8	12
Glass 2	21·6	610, 700	4·3	Stable (cordierite)	9·8	50
Glass 3	60·3	530, 580	6·5	Crystallising	14·6	50
Glass 4	66·8	520, 650	6·5	Crystallising	8·5	64
Glass 5	6·2	620, 700	3·3	Crystallising	5·6	30
Glass 6	39·3	465, 575	4·8	Crystallising	65·3	35
Glass ZBS	—	650, 700	4·3	Crystallising	12·9	45

bubbles and lead spheres and in the case of glass 6 with its Cu_2O content of 4·7 wt%, additional copper spheres occur. Thus, the calculated behaviour for PbO and Cu_2O is confirmed. When soldering glass 5 in reducing atmospheres dewetting of the substrate and the formation of bubbles and lead spheres occurred. This was only observed at glass surfaces exposed to atmosphere. Yet no sign of reaction was found at interfaces with the AlN-substrates. The reduction was induced by the atmosphere (which was reducing due to the carbon heating elements), shifting the equilibrium of the reaction $PbO \Longleftrightarrow Pb + {}^{1}/_{2}\,O_2$ to the right. Glasses 3, 4, 5 and 6 were no further examined due to their high reduction capability.

The other solder glasses showed unvaried good joints when sealed under different atmospheres. Sealing under vacuum had no effect on the porosity of the soldered glasses. Prolonged heat treatment of solder joints at 500°C did not lead to reactions with any of the glasses 1, 2 and ZBS containing 0–21·6 wt% PbO. The lead free zinc borate glass ZBS exhibited no deterioration of the joint even after 450 h at 650°C. The crystalline phases identified by XRD analysis for the almost completely devitrified glass ZBS before and after the 650°C heat treatment are ZnB_4O_7, ZnB_2O_4, $Zn_3B_2O_6$ and Zn_2SiO_4. The zinc silicate and zinc borate phases have coefficients of thermal expansion in the range of $2.5–3{\cdot}5\times10^{-6}\,K^{-1}$[10] which ensure good thermomechanical compatibility to AlN. Additionally devitrification of the solder glasses generally leads to higher mechanical strength and allows higher application temperatures due to the increased viscosity of the glass ceramic. The remaining glassy phase of glass ZBS is expected to contain still some ZnO incorporated into the glassy network. Since no reaction was observed, ZnO seems to be stabilised by both crystallisation into thermodynamically stable mixed oxides and kinetical stabilisation in the glassy network even over long periods of time. Solder joints of glasses 1 and 2 treated at 650°C showed large voids as clear indications of corrosion at the AlN/glass interface. This deleterious reaction could be avoided by a passivating layer of Al_2O_3. This layer of 3–6 μm thickness could be formed by oxidation of the AlN substrate at 1100°C for 9 h in air prior to the soldering process. In Fig. 3 the corrosion of glass 1 (2·7 wt% PbO) at the interface with the upper AlN substrate can be seen. The lower piece of AlN has a passivating surface layer of Al_2O_3 and stays inert. Glasses 1 and 2 are originally intended to stay amorphous, they contain cordierite filler particles to accommodate thermal expansion behaviour. After the heat treatment at 650°C cordierite was dissolved into the glass and could no longer be identified by XRD analysis but—besides a remainder of glassy phase—the crystalline phases ZnB_4O_7, ZnB_2O_4, $Zn_3B_2O_6$ and Zn_2SiO_4 were detected.

Under the pressure of 18·9 kPa part of the glass was pressed out of the gap between the

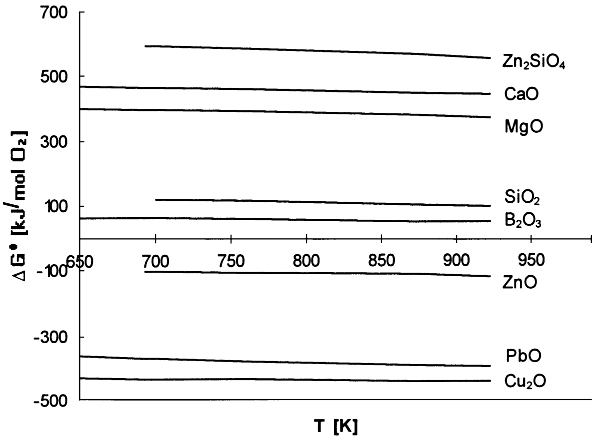

Fig. 1. Change of Gibb's free energy for the reaction between oxides and AlN. ${}^{2}/_{n}MeO_{n}\ {}^{4}/_{3}AlN \rightarrow {}^{2}/_{3}Al_2O_3 + {}^{2}/_{3}N_2 + {}^{2}/_{n}Me$.

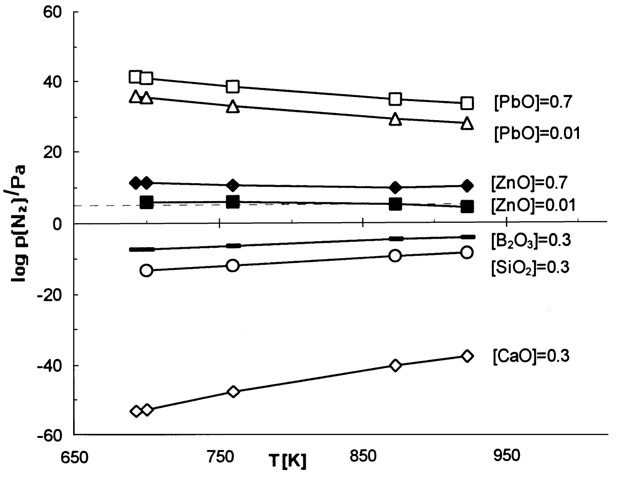

Fig. 2. Nitrogen partial pressure for the reaction with a fixed concentration of MeO_n. ${}^{2}/_{n}MeO_{n} + {}^{4}/_{3}AlN \rightarrow {}^{2}/_{3}Al_2O_3 + {}^{2}/_{3}N_2 + {}^{2}/_{n}Me$.

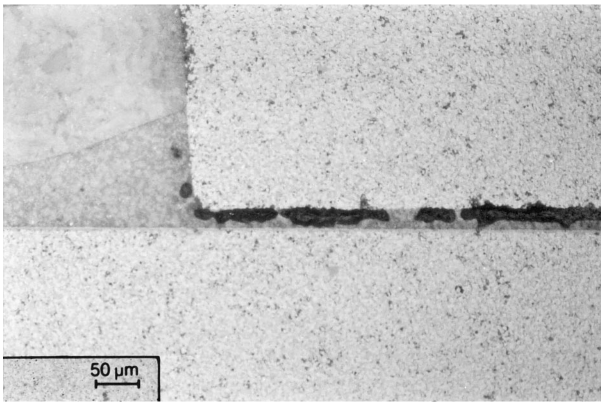

Fig. 3. AlN/glass 1 joint after 450 h at 650°C. Lower substrate passivated by an alumina layer.

two substrates. This surplus of glass that remained besides the substrate was highly porous. Glass inside the thinner gap, however, showed very little porosity which had been eliminated faster than in the samples soldered under a load of 0·16 kPa. A further advantage of applying mechanical pressure is a reduced processing time and temperature by enforced viscous flow of the glass.

Packages sealed with glasses 1, 2 and ZBS passed gross and fine leak tests with leaking rates of less than 5×10^{-3} Pa cm^3 s^{-1} and thus can be regarded as hermetic seals according to MIL STD 883.

4 Conclusion

Hermetic sealing of AlN packages for high temperature application can be performed by solder glasses of the main constituents ZnO, B_2O_3 and SiO_2. Glasses with a high PbO content already reacted during processing whereas low concentrated PbO can be tolerated for application temperatures up to 500°C. At 650°C reactions are evident but can be prevented by passivation of the AlN. No passivation is needed for the PbO free glass ZBS. Zinc oxide is kinetically stabilised or transformed into crystallisation products which are thermodynamically stable, give mechanical strength and allow higher application temperatures of the glass ceramic. Applying mechanical pressure onto the joint assembly during the joining process enhances elimination of porosity and viscous flow of the glass.

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