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HIGH TEMPERATURE INTERFACIAL PHENOMENA IN PROCESSING COFIRED CERAMICS FOR ELECTRONIC PACKAGING OF SEMICONDUCTOR DEVICES

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ABSTRACT

The sessile-drop wetting of tungsten by a CaO-MgO-Al₂O₃-SiO₂ glass was found to be independent of temperature but strongly dependent on the furnace atmosphere between 1300 and 1500 °C. Similar results from two gas buffer systems (CO/CO₂ and H₂/H₂O) established the oxygen partial pressure as the critical parameter. The contact angle, θ , decreased at higher pO₂ with stable contact angles existing at both ends of the pO₂ range. The equilibrium contact angles, established after 8 hours under isothermal conditions, ranged from 50-55 degrees at a pO₂ = 10^{-15.5} atm to 30 degrees, at a pO₂ = 10^{-10.9} atm. Two different drop formation techniques demonstrated that the temperature and atmospheric conditions at the time of the solid-liquid interface formation affect the magnitude of the contact angles. θ was higher when the solid-liquid interface was established at the test temperature (doser tube technique) than when the drop was formed *in situ* from a piece of glass placed on the substrate at room temperature (non-doser method). The solid-liquid interfacial energy, γ_{SL} , controlled the wetting behavior. An increase in the oxygen adsorbed at the solid-liquid interface produced a lower γ_{SL} resulting in a smaller contact angle.

Recent hydrodynamic and surface physics models fit the spreading kinetics of the liquid glass droplets on a smooth, horizontal surface. The temperature was held above 1275 °C (1548 K) to prevent devitrification of the glass and below 1400 °C (1673 K) to limit the extent of reaction with the sapphire substrate. Drops were formed both *in situ*, during the ramp, or by a doser technique which enabled a closer approach to isothermal conditions. The rate of advance of drops ranging in mass from 0.002 to 0.3 g (0.06-0.31 cm spherical radius at temperature) was monitored both through analysis of videotapes and by direct observation of the contact angles using a telegoniometer. A Tanner Law expression describes the kinetics of the drop radius or contact angle change from drop volume, liquid-vapor interfacial energy, and liquid viscosity.

INTRODUCTION

Multilayer Ceramic (MLC) packages are produced by a high temperature process involving the simultaneous densification (cofire) of multilayer structures composed of alumina-glass dielectric layers with embedded refractory metal conductive paths. The quaternary glass phase anchors the metal to the ceramic by a combination of mechanical interlocking and chemical bonding. It fills the porosity in the metal lines and is the liquid in the liquid-phase-sintering of the composite package. Two interfacial phenomena were studied to gain fundamental insight into this complex cofiring process. A well-characterized, 60 wt.% SiO₂, 20 wt.% Al₂O₃, 10 wt.% CaO, and 10 wt.% MgO glass was used in these studies. The liquidus temperature of this composition is 1282°C in the Anorthite primary phase field. Other properties, impurity details, and experimental setups are discussed elsewhere.[1,2,3] Equilibrium wetting of tungsten by the glass in controlled oxygen partial pressure atmospheres is addressed first. Second, the spreading kinetics of small sessile drops of the glass on sapphire will be discussed.

WETTING OF TUNGSTEN

Previous wetting studies of glass on tungsten have shown the effect of the dew point of the gaseous atmosphere on the contact angle but have not distinguished the surface active species responsible for the effect.[5-8] The objective of the work was to clearly identify the surface active species and to define the interface responsible for the changes in wetting. Polished polycrystalline tungsten plates provided the sessile drop substrates.

EXPERIMENTAL APPROACH

The sessile drops were formed on the substrates by two different techniques. One method was to place the glass drop on the substrate after it had already reached and equilibrated at the test temperature. This was accomplished by forcing the liquid glass through a small hole in a doser tube placed over the center of the substrate. The second method was to place a solid piece of glass on the substrate prior to heating in the controlled atmosphere. In this method the sessile drop was formed during the ramp to temperature as the glass softened to a liquid drop. Heating began in a dry hydrogen atmosphere which was replaced by a buffer gas mixture as the temperature rose above 900°C. Two different buffer gas systems, CO/CO₂ and H₂/H₂O, were used to control the pO₂ in the 10⁻¹¹ to 10⁻¹⁵ atm range. A CaO-stabilized zirconia oxygen sensor measured the oxygen partial pressure in the buffer gas stream in a separate furnace at a constant temperature of 1000°C. A fused quartz viewport permitted sample temperature measurement with an optical pyrometer as well as observation and photographing the *in situ* sessile drop.

RESULTS AND DISCUSSION

Several experiments were conducted under identical conditions of temperature and pO₂, differing only in the method of drop formation. Typical data from these experiments are shown on Fig. 1. Below a threshold value of the oxygen partial pressure, lower stable contact angles are obtained when the glass drop is formed *in situ* on the tungsten substrate, during the ramp to the hold temperature, than when a drop is placed on the substrate at temperature. Several other experiments were conducted under identical conditions of temperature and pO₂, using different buffer gas systems to fix the pO₂. Fig. 2 shows the change in the stable contact angle with pO₂ at 1400°C using the two gas buffer systems.

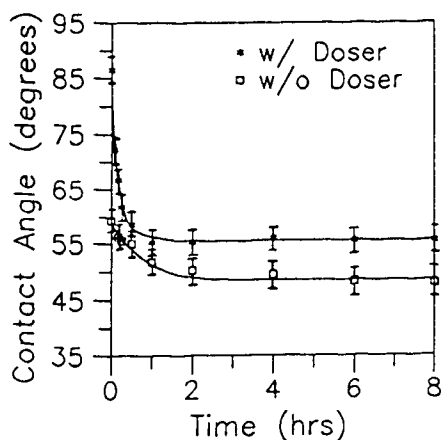


Fig. 1. Wetting of W at 1400°C, log pO₂ = -15.5

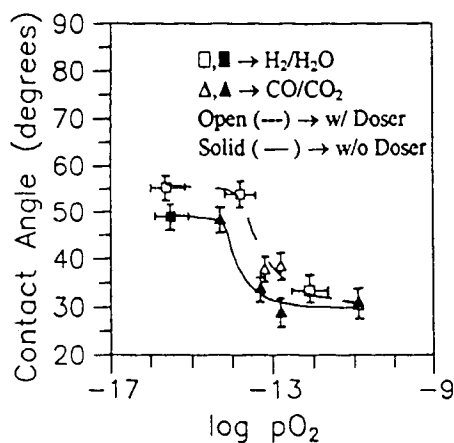


Fig. 2. θ of glass/W vs. log pO₂ at 1400°C

Results from both drop formation techniques are shown. The pO_2 dependency is independent of the gas buffer system. The drop formation method affects the magnitude of the stable contact angle, but does not alter the shape of the pO_2 dependency. The contact angle values from the two drop formation techniques converge at the highest pO_2 . These experiments also established that the contact angles are independent of temperature in the range 1300°C to 1500°C within the pO_2 range of these experiments. An example of this behavior is shown on Fig. 3. The main difference between the two drop formation techniques is the temperature at which the solid-liquid interface is formed. In the *in situ* method, the interface forms at about 1100°C when the glass has softened sufficiently to form a spheroidal cap shape. At this lower temperature, more oxygen is adsorbed on the tungsten surface below the drop than when the drop is placed at higher temperature. Therefore, the liquid glass-tungsten interfacial free energy, γ_{SL} , starts out lower for the *in situ* case making θ smaller. Similar results from both buffer systems establishes pO_2 , not the water vapor as suggested by previous investigators, to be the surface active species which determines the degree of wetting. The variation of the contact angle with pO_2 , shown on Fig. 2, exhibits three distinct stages with increasing pO_2 that are characteristic of oxygen adsorption on metals. First, at very low pO_2 , oxygen can be accommodated in the bulk glass with negligible adsorption at the interface yielding constant θ in this range. Second, the slope of the curve becomes constant as adsorption at the tungsten-glass interface proceeds. Third, monolayer adsorption is achieved, θ becomes constant again and the two curves converge. The Gibbs-Langmuir equation describes the adsorption of surface active species at interfaces. For atomic oxygen adsorption at the glass-tungsten interface,

$$d\gamma_{SL} = -RT\Gamma_o d\ln[(pO_2)^{1/2}] \quad (1)$$

Fig. 4 represents a plot of Eq.(1), where γ_{LV} is assumed to be constant at 0.400 J/m². The upper curve is based on a constant $\gamma_{SV} = 2.947$ J/m². From the slope, $\Gamma_o = 5.02 \times 10^{14}$ O²⁻ ions/cm². For a pO_2 below 10^{-14} atm, monolayer chemisorption of oxygen is expected to take > 28hr. Above 10^{-13} atm, monolayer formation could occur in 2.8hr, which is within the time of these experiments. A 7.9% reduction in γ_{SV} yields 1.66×10^{15} O²⁻ ions/cm² which is the value calculated for a close-packed layer of O²⁻ ions (lower curve).

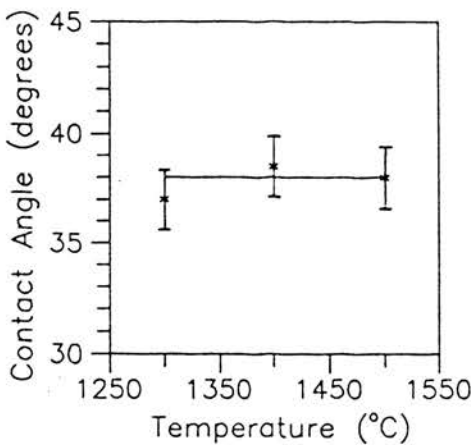


Fig.3. θ vs. T for glass/W at $\log pO_2 = -12.9$

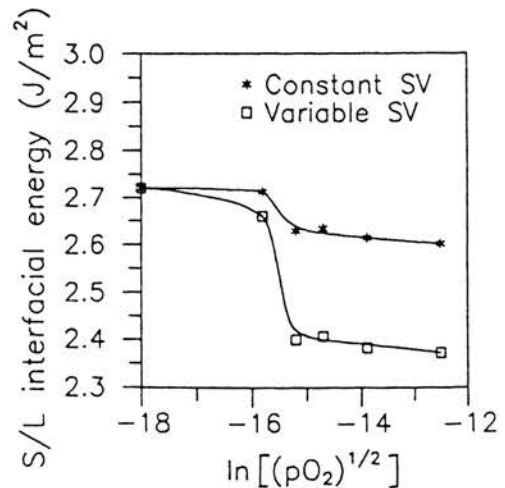


Fig.4. γ_{SL} vs. $\ln[(pO_2)^{1/2}]$ at 1400°C

SPREADING KINETICS ON SAPPHIRE

Initial experiments were conducted to determine the advancing contact angles of drops formed *in situ* on sapphire during a "ramp and hold" thermal cycle chosen to approximate that used to sinter a 94% alumina packaging body. The mass of the smaller sessile drops strongly influences the observed contact angles as shown in Fig. 5. The data from Figure 5 are replotted in Fig. 6 to show the dependency of the contact angle more clearly.

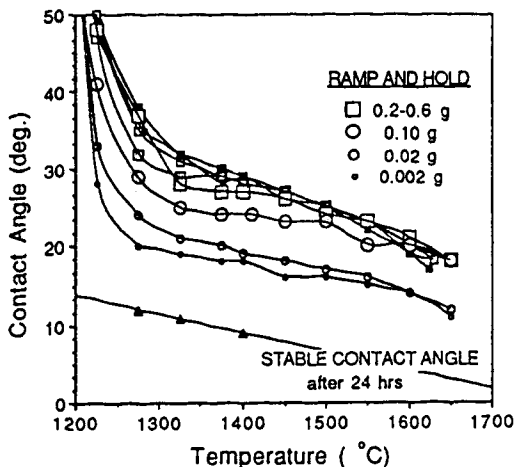


Fig.5. Glass/sapphire θ vs. T (drop mass effect.)

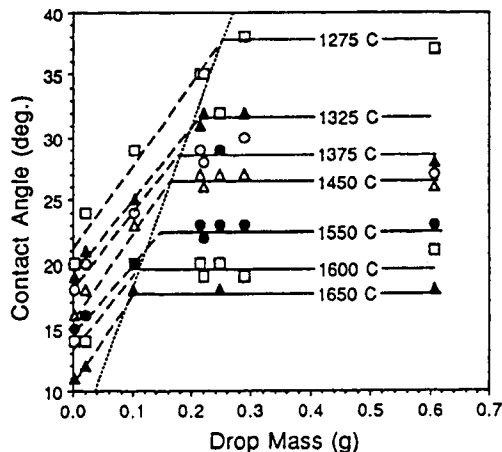


Fig.6. Glass/sapphire θ vs. Drop Mass

The effect of drop mass vanishes at a critical mass and diminishes with increasing temperature. Both *in situ* drop formation and drop placement techniques were used to study the spreading kinetics. The results of *in situ* drop formation spreading experiments at two isotherms are shown on Fig. 7. The drops formed at about 1100°C and an additional 42 min. was required to reach 1275°C or 54 min. to reach 1325°C. Therefore, the first 2520-3300 seconds of Fig. 7 occurred during the ramp to temperature. The drop basal radii were calculated from measured contact angles using the following equation for spherical caps.[9]

$$V = \pi r^3/6 [(\tan \theta/2)^3 + 3 \tan \theta/2] \quad (2)$$

where V is the drop volume, and r is the basal radius of the drop. The solid curves were fit to the data by the expression, [10]

$$r^{10} = C' t V^3 \gamma_{LV}/\eta \quad (3)$$

where the constant $C' = 0.48$ in Fig. 7, t is the time, γ_{LV} is the glass surface tension, and η is the viscosity of the glass. The general form of the "Tanner Law" rate expression for spreading spherical caps is

$$A = \pi r^2 = C'' t^{2n} V^p \quad (4)$$

where A is the drop-substrate interfacial contact area. The exponents n and p , according to Eq.(3) are 0.10 and 0.60, respectively, verified by many organic [10-13] and metal [14] systems. The log A - log V plot of the *in situ* drop formation experiments is shown in Fig. 8.

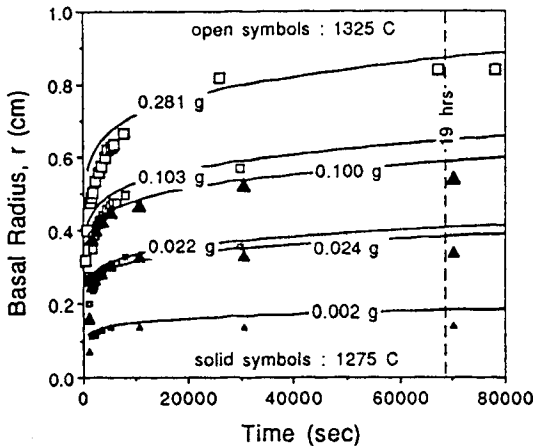


Fig. 7. Glass/sapphire Basal Radius vs. T

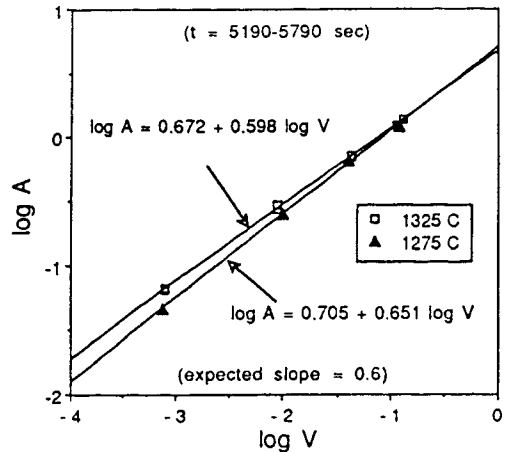


Fig. 8 Demonstration of the Tanner Law

The values of $p = 0.598$ at 1325°C and 0.651 at 1275°C are in good with the literature. As a further test of the validity of Eq.(3), a drop placement technique was used to generate data which is closer to isothermal conditions than those possible using the *in situ* technique. 0.3 g drops were placed on sapphire at 1265°C through a hole in a graphite platform. Log r -log t plots yielded slopes of 0.115 at 1275°C , 0.091 at 1325°C , and 0.048 at 1400°C against the expected value of 0.10. These results provide additional confirmation of the applicability of the rate expression, Eq.(3), at the lower temperatures of this study. The departure at 1400°C from the expected slope of 0.10 suggests that chemical reaction between the glass and the alumina substrate is significant. In summary, the rate of advance of the liquid silicate on sapphire at temperatures near 1300°C can be considered as a physical competition between the viscous stresses within the drop and the capillarity, without significant chemical interactions. The effect of drop mass can be modeled using a Tanner-Law expression, given a knowledge of the liquid viscosity, surface tension, and specific volume. Stable contact angles of 12, 11, and 9 were reached after 24 hr holds at 1275°C , 1325°C , and 1400°C , respectively, and are plotted in Fig. 5, representing the end of spreading. Care must be exercised when interpreting contact angle data for highly viscous liquids.

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