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Effect of localized redox equilibria on adhesion between gold and thick-film dielectrics

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The effect of processing atmospheres with decreasing partial pressure of oxygen on the stability of dielectric glass formers and on the wetting between gold and dielectrics was studied. Thermodynamic calculations, contrasted with experimental results, suggest that localized redox conditions may differ from ideal thermodynamic equilibria. As the redox equilibrium shifts towards reducing conditions, a compositional change occurs and affects the interfacial energies. Screen-printed gold combined with a lead-borosilicate glass dielectric becomes non-wetting when fired in nitrogen gas.

1. Introduction

Gold is commonly used in thick film technology where good conductivity, inertness and excellent overall reliability are required. Because gold does not react with the ceramic in the processing temperature range 800 to 1000° C, gold inks usually contain added reactive glass frit to improve adhesion. Commonly, three different types of bonding techniques are employed; fritted, reactive, and mixed. During firing, which is normally in air, the organic vehicle responsible for the ink's rheology, is burned away. The metal and glass particulates sinter to a coherent structure and adhesion between conductor and dielectric develops. Sometimes inert atmospheres (nitrogen) are required to protect hybrid metal components having high chemical affinities for oxygen (copper and palladium). As the organic vehicle decomposes, the local equilibrium may shift towards increasingly reducing conditions. In such circumstances, the oxide components of the dielectric may be reduced, causing loss of adhesion, electrical shorts or other deleterious effects. In particular, a decrease of adhesion between noble metals and ceramics (Al_2O_3, SiO_2) when oxygen pressure decreased was observed by several investigators [1–3].

In this report the stability of common dielectric constituents is examined in the context of the free energies of redox reactions and the change from wetting to non-wetting conditions between gold and the ceramic.

2. Experimental procedure

Fritted gold ink (Engelhard gold A3798) was used as a conductor. The total gold content in the powder was about 85 wt %; the remainder was glass frit. The frit had the following composition (wt %): Bi_2O_3 59, PbO 23, CaO 8, B_2O_3 3.4 and SiO_2 6.6. The Bi_2O_3 was added to improve wetting, while the remaining oxides often appear in dielectric formulations. An ink was made by adding 25 wt % organic vehicle to the powder. This was screen printed on 96% pure-alumina substrates via a steel screen, and dried at 125° C. A dielectric pattern, some 40 μm thick, with via holes was then screen printed on the gold. Dried substrates were co-fired in an electrically heated continuous furnace to a peak temperature of 850° C for a total time of 45 min, to produce dense, integrated circuits. Furnace atmosphere (oxygen potential) was varied in different experiments from air (oxygen partial pressure 0.211 atm) to nitrogen, with p_{O_2} of about 10^{-6} atm.

The quality of the lines on fired substrates and the adhesion (wetting) of gold was inspected by microscopy.

3. Analysis of thermodynamic equilibria

It is of interest to predict the stability of oxides as a function of the partial pressure of oxygen in the furnace atmosphere. For illustrative purposes, the components of a common dielectric, i.e. borosilicate glass containing CaO, PbO and Bi_2O_3, a gold conductor and an Al_2O_3 substrate, are included in the study. This glass is similar to the frit added to gold powder, although the oxide proportions usually differ in the two applications. The following redox reactions were considered:

$$Bi_2O_3 \rightarrow 2Bi + 1.5O_2 \qquad (1)$$

$$2PbO \rightarrow 2Pb + O_2 \qquad (2)$$

$$CaO \rightarrow Ca + 0.5O_2 \qquad (3)$$

$$B_2O_3 \rightarrow 2B + 1.5O_2 \qquad (4)$$

$$SiO_2 \rightarrow Si + O_2 \qquad (5)$$

To calculate the stability of metal-oxygen systems 1 to 5, standard free energy changes were taken from Barin *et al.* [4]. The activities of condensed phases are assumed to be equal to one, and the activity of oxygen to equal its partial pressure (atm). The latter was

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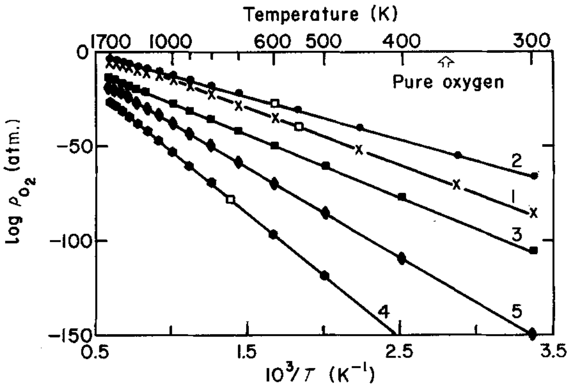

Figure 1 Plot of free energy of formation for typical dielectric components.

computed over a temperature range 298 to 1700 K while assuming equilibrium for the above reactions. The reaction constants, log K_p, were 1.5 log p_{O_2} for Reactions 1 and 4, 0.5 log p_{O_2} for Reaction 3 and log p_{O_2} for Reactions 2 and 5, respectively.

The equilibrium between each metal and the corresponding oxide is shown in Fig. 1 as a function of oxygen partial pressure and temperature. An oxide is the stable phase in the T–p_{O_2} region above the log $p_{O_2} = \Delta G^0/2.3RT$ line, where ΔG^0 is the standard free energy change and R is the gas constant, while at lower p_{O_2} pressures, the metal is stable. The oxides' melting points are also marked on the lines; Bi_2O_3, PbO and B_2O_3 are liquids at the firing temperature of 850° C. They are likely to form glass with other glass formers of the frit, but the calculations are valid when an oxide is a glass constituent. The Bi_2O_3–Al_2O_3 eutectic forms at 820° C, so that at 850° C a transient liquid phase is expected to develop which assists wetting.

Note that log partial pressure of oxygen in air equals − 0.675 atm. Because the equilibrium oxygen potentials for all the reactions are below this value, the oxides considered are the stable phases in the temperature range of interest, providing equilibrium is achieved. In practice such gold–dielectric systems perform well and have widespread applications in electronics.

In the nitrogen gas commonly used in thick-film technology, traces of oxygen are present (0.0002% to 0.0005%). Although this implies a p_{O_2} decrease of the order of 10^{-6} atm, the equilibrium lines are still below this value at temperatures < 1000° C. To reduce the least stable oxides (PbO, Bi_2O_3), log p_{O_2} should drop to at least − 10 (10^{-10} atm) in the temperature range of interest, and even larger pressure drops would be required for the remaining oxides. Seemingly such conditions are unlikely to occur in the nitrogen atmosphere of the continuous BTU furnaces where air leaks may contribute to a residual oxygen pressure higher than that mentioned above. Therefore, reduction of even the least stable oxides does not appear to be plausible.

However, in the actual processing of mineral–organic systems, the equilibrium may not be attained because of the sluggish decomposition of organics and the associated kinetic retardation.

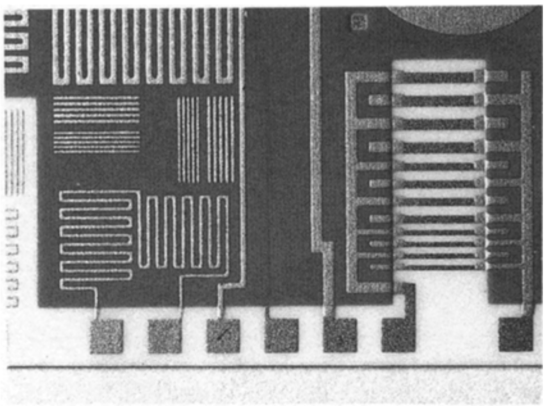

Figure 2 A screen-printed hybrid microcircuit consisting of gold conductor lines on a glass–ceramic dielectric supported on alumina. Air fired at 850° C (× 3).

4. Results

To investigate the actual behaviour of the system under consideration, comparison of the gold–dielectric hybrid after firing in air and in nitrogen was made. An example of an air-fired microcircuit is shown in Fig. 2. Printed components maintained high resolution, good wetting and adhesion between gold and ceramic and the dimensional stability of the components is thus demonstrable.

A detail of a similar hybrid microcircuit after firing in a nitrogen atmosphere is shown in Fig. 3. Here the gold is no longer evenly spread on the Al_2O_3 substrate; it has assumed the spherical shape characteristic of a nonwetting equilibrium. The liquid–solid contact angle between gold and Al_2O_3 was > 120°. The surface tension of gold was high enough to cause piercing of the metal through via holes and through the dielectric layer printed on top of the conductor. Because pure gold melts at 1063° C, a eutectic alloy must have been formed with a melting point $\leqslant 850°$ C. Reduction of an oxide component may cause alloying which lowers the melting point. Alloy formation could also alter the gold's surface tension and its interfacial energy with Al_2O_3. In such circumstances, differences between wetting and adhesion properties are understandable. The thermodynamic calculations show that PbO and

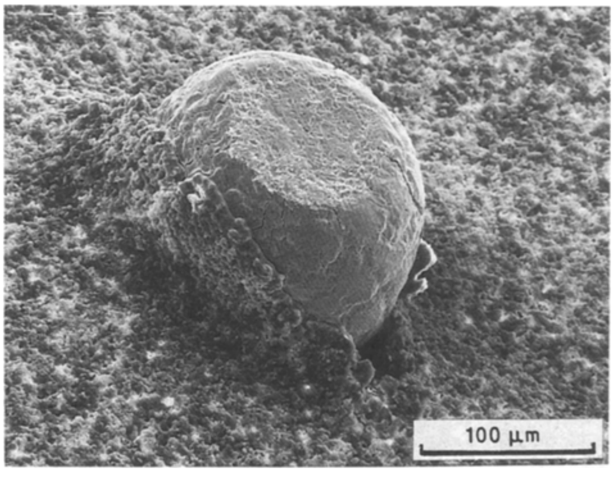

Figure 3 Non-wetting gold alloy after firing in nitrogen at 850° C. Note porosity and rough appearance of the dielectric.

Bi_2O_3 are the most likely candidates for reduction in the present system. PbO-rich glasses heated in a Bunssen burner readily assume a metallic lustre due to precipitation of lead (Fig. 1).

To verify this supposition, an optical microscope and EMX were employed. A silver colouration of the gold was visible after nitrogen-firing, while the measured distribution of the X-ray characteristic radiation confirmed the presence of lead on the gold surface. Thus, at least a portion of the PbO must have been reduced during firing. Randomly distributed black specks within the dielectric were also found, probably of carbon from pyrolysis of the organic vehicle. No carbon residue was found in the air-fired specimens.

5. Discussion

5.1. Non-equilibrium condition

The lack of wetting by gold demonstrated in Fig. 3 shows that during firing in nitrogen, interfacial properties have changed from those prevalent during air firing, and a shift towards reducing conditions may be the cause. The reasons for strongly reducing conditions are numerous. Transport of volatile decomposition products from the solid, and counterflow of oxygen into the pores are often responsible for producing actual thermodynamic conditions at the interface. As the temperature is gradually increased, the organic components evaporate, decompose and oxidize, while the solid particles sinter together. Trapping and pyrolysis of organics may occur in closing pores. The actual porous structure of the dielectric is shown in Fig. 4. Both surface-connected and closed pores are present and the porosity is higher than in the air-fired dielectric, Fig. 5. Thus, in the dielectric with closed pores, a local consumption of oxygen may occur, causing a change into more reducing conditions. This problem is well known in thick-film copper technology, where removal of carbon traces during firing in nitrogen is difficult even with organic vehicles formulated so that they decompose relatively easily. Organics containing C–O, C–S, C–N or C–H bonds may give products of scission (free radicals) which are active reducing agents. In addition, the nature of the organic response to temperature is often changed in the presence of the added ceramic powder; adsorption and capillarity phenomena retard the evaporation processes [5]. Trapping of decomposition products extends the temperature range during which the organics are removed. As a consequence the removal of carbon traces from sintered ceramic bodies is a persistent problem and isolated carbon precipitates are invariably found in dielectrics fired in nitrogen [6].

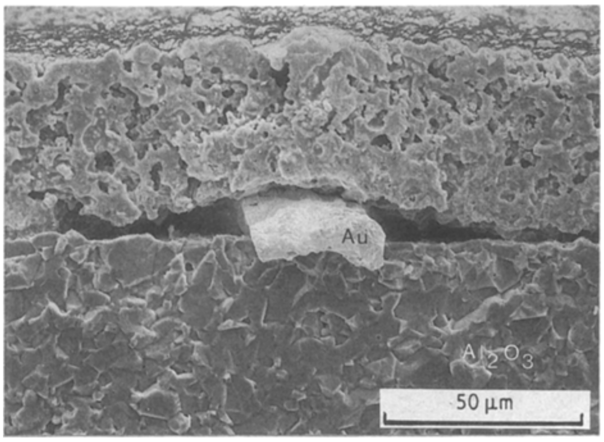

Figure 4 Transverse fracture surface of a hybrid microcircuit showing porosity in the dielectric and delamination of a gold line. Nitrogen fired.

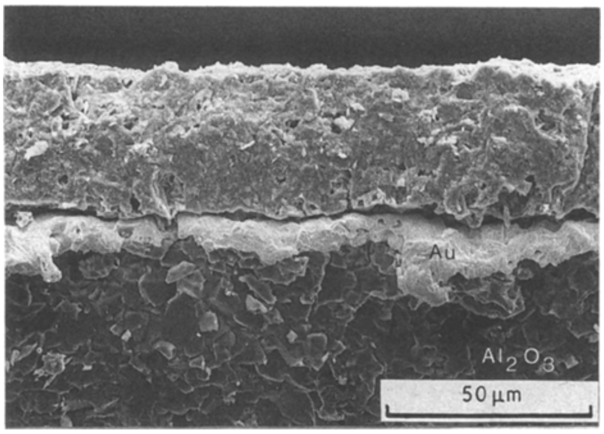

Figure 5 Fracture surface of a microcircuit similar to that in Fig. 4 after firing in air.

5.2. Wetting and adhesion

The theory of chemical bonding between ionic and metallic solids suggests that maximum adherence of glass to metals occurs when the interface is saturated with the oxide of the lowest valence cation of the metal [7]. In particular, it is claimed that gold adheres strongly to silicate glass in air because the interface is saturated with AuO. In vacuum, the adherence is poor, apparently because oxygen adsorbed on the metal is completely dissolved in the glass [8]. When this happens, the surface of the latter comes into direct contact with the metal atoms and, because the surface oxygens of the glass are already bonded, electron transfer from the metal to glass is minimized. This implies that adhesion is primarily controlled by the physical state of the metal surface, because oxide glasses are capable of dissolving a large amount of oxides.

In a nitrogen atmosphere, traces of any available oxygen are consumed by oxidation of the organics, and by dissolution in the glass. The energy of the gold–oxide system cannot be lowered by formation of an interfacial bond. Instead, the interface tension of the gold alloy tends to reduce its surface area to a minimum, and a non-wetting droplet forms on the solid. In other words, consumption of oxygen by organics is followed by reduction of PbO and subsequent alloying of gold with lead. Such alloys form low-temperature eutectics. Depletion of Pb^0 by dissolution in gold drives Reaction 2 to the right.

Because no metallic lead precipitate was observed in the dielectric, it would seem that the gold must play a role in creating locally reducing conditions which decompose PbO. Partitition of oxygen may occur at gold and glass interfaces which leads to faster depletion of available free oxygen. Evidence for this is to be found in the work of Moore and Thornton [1] who observed gas occlusion at the Au/SiO_2 interface. According to Smithells [9], oxygen is strongly adsorbed by gold.

6. Conclusions

Stability predictions based on thermodynamic equilibria require recognition of reaction rates and specific conditions which may cause unexpected shifts of redox reactions. At elevated temperatures in the system oxide glass–Au–organics, a competition for oxygen exists between the glass components of the dielectric and the decomposing organics. The resulting shift to more reducing conditions involves the appearance of Pb^{o} and an increase in the wetting angle between gold and ceramic. The available oxygen was completely consumed by those species with the highest oxygen affinity (organics) so that the least stable glass components reduced and non-wetting conditions prevailed.

For adequate process control it is important to understand the equilibria, the kinetic factors controlling the decomposition processes, the time required for burning out the organic residue, and the amount of carbon permissible in the product. Especially formulated gold and dielectric inks are necessary if firing in nitrogen is intended.

Acknowledgements

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References

1. D. G. MOORE and H. R. THORNTON, *J. Res. Nat. Bur. Stand.* **62**(3) (1959) 127.
2. P. F. BECHER, *J. Mater. Sci.* **13** (1978) 457.
3. P. J. MARTIN, W. G. SAINTY, R. P. NETTERFIELD and A. N. BUCKLEY, Vacuum, Special series on Irradiation Enhanced Adhesion **35** (1985) 621.
4. I. BARIN, O. KNACKE and O. KUBASCHEWSKI, "Thermomechanical Properties of Inorganic Substances" (Springer-Verlag, Berlin, 1977).
5. W. A. ZDANIEWSKI and W. McSHARRY, unpublished results.
6. ROGER E. LUND, "Circuit Shortening Mechanisms in Copper Multilayer System", Proceedings of the International Symposium on Microelectronics, Anaheim, California, 1985, (International Society for Hybrid Microelectronics, Virginia, 1985) pp. 463–471.
7. J. J. BRENNAN and J. A. PASK, *J. Amer. Ceram. Soc.* **56** (1973) 58.
8. J. A. PASK and R. M. FULRATH, *ibid.* **45** (1962) 592.
9. C. J. SMITHELS, "Gases and Metals" (Chapman and Hall London, 1938) p. 67.

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