The reaction between ruthenium dioxide and aluminium nitride in resistor pastes

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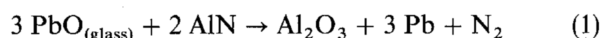
Thermodynamic considerations predict that RuO_2 used in resistor pastes for AlN as conductive phase, can be reduced by AlN. In air RuO_2 reacts with AlN only to a very small extent. In the presence of a "non-reducible" glass the reaction between RuO_2 and AlN is demonstrated by thermoanalytical, mass spectroscopical and XRD methods. The described reaction could be a reason for bubbles in resistor layers on AlN. A crystallizing glass impedes the complete reaction.

1. Introduction

Aluminium nitride represents, because of excellent physical and chemical properties, a real alternative to other substrate materials such as alumina and beryllium oxide [1–5]. These properties include high thermal conductivity, high electrical resistivity, a thermal expansion coefficient close to that of silicon and the non-toxicity of AlN. The field of application of AlN will depend on the realization of thick film conductors, resistors and dielectrics too [6–9]. Commercially available resistor pastes for alumina bubble on AlN during the firing process and so form non-functional layers.

The reason for the bubbles is seen in the use of glasses with a high lead oxide content in these pastes. The lead oxide of the glass is able to react with AlN [6, 10]; it is reduced:



$$3\,PbO_{(glass)} + 2\,AlN \rightarrow Al_2O_3 + 3\,Pb + N_2 \quad (1)$$

The oxides of bismuth, cadmium and copper are able to react with AlN similarly.

Therefore, in previous years much effort has been devoted to developing resistor pastes for AlN with "non-reducible" glasses. The known possibilities to realize thick film resistors on AlN are the use of glasses which do not contain lead oxide or contain only a small amount of lead oxide or which are crystallizing glasses of the ZnO–B_2O_3–SiO_2–glass system in connection with ruthenium dioxide as the conductive material [7, 9].

So far, commercially available resistor pastes for AlN do not as yet have such excellent properties as pastes for alumina. The most difficult problem of research is the realization of resistor pastes with sheet resistivities from $1\ k\Omega\,sq^{-1}$ to $1\ M\Omega\,sq^{-1}$, with little sensitivity of the final properties to the firing conditions and with excellent reliability of the fired resistors.

Chemical reactions between ruthenium dioxide and AlN are another reason for the bubbles and for the sensitivity of these pastes to the firing profile.

In the present study thermoanalytical (DTA and TG), mass spectroscopical and XRD tests were carried out to evaluate the reaction between RuO_2 and AlN in the presence of "non-reducible" glasses.

2. Experimental procedure

The powder compositions listed in Table I were used to investigate the reaction between ruthenium dioxide and AlN.

The surface area of the AlN powder was $10.5\ m^2\,g^{-1}$ and of the RuO_2 powder was $9.1\ m^2\,g^{-1}$. The oxygen content of AlN was 4.3%, equivalent to 9.1% alumina.

The glasses used belong to the ZnO–CaO–B_2O_3–Al_2O_3–SiO_2 system; glass A is a crystallizing glass and glass B is a non-crystallizing glass.

DTA and TG measurements were carried out in air or in nitrogen, respectively, at a heating rate of $10\ K\,min^{-1}$.

In some tests the thermoanalysis was coupled with a mass spectrometer to study the reaction products. The coupling between the sample room and the mass spectrometer with a skimmer coupling system was supplied by Netzsch GmbH with a skimmer coupling system. The gas used was helium (4.6, Linde) or a helium–oxygen mixture.

TABLE I Powder compositions

Mixture	Composition (wt %)
1	100 AlN
2	70.9 RuO_2, 29.1 AlN
3	35.4 RuO_2, 14.6 AlN, 50 glass A
4	35.4 RuO_2, 14.6 AlN, 50 glass B
5	54.7 RuO_2, 45.3 AlN
6	9.0 AlN, 91.0 glass A

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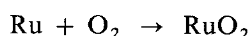
The solid products of the chemical reaction of mixtures 2 and 3 were studied by X-ray diffraction (XRD). For that, 20 μm thick films were screen printed on alumina. Then the films were dried and heated at a rate of $10\ \mathrm{K\,min^{-1}}$ up to 810 or 960 °C, respectively. The thick films had the same compositions as the powder mixtures 2 and 3.

3. Thermodynamic considerations

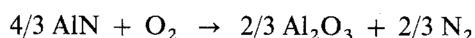
Ruthenium dioxide and other ruthenium oxide compounds such as earth alkali ruthenate (perovskite) or lead and bismuth ruthenate (pyrochlore) have been proved as electrically conductive components in air-fired thick film resistors on alumina. Resistor pastes for AlN also contain ruthenium dioxide [7, 9, 11]. Even if the paste contains a non-reducible glass and small concentrations of RuO_2 (high sheet resistivity), the resistor film on AlN also has bubbles. The reduction of RuO_2 by AlN is thermodynamically possible, because of the negative free energy change.

This is followed by the balance of the free energies of the following reactions



$$\mathrm{Ru} + \mathrm{O_2} \rightarrow \mathrm{RuO_2}$$

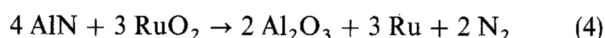
$$G_f = -116\ \mathrm{kJ\,mol^{-1}}\ [12]\ \text{at}\ 850\,^\circ\mathrm{C} \quad (2)$$



$$4/3\ \mathrm{AlN} + \mathrm{O_2} \rightarrow 2/3\ \mathrm{Al_2O_3} + 2/3\ \mathrm{N_2}$$

$$G_f = -628\ \mathrm{kJ}\ [13]\ \text{at}\ 850\,^\circ\mathrm{C} \quad (3)$$

The oxidation of AlN by RuO_2 has a free energy change of $G_f = -1536$ kJ at 850 °C



$$4\ \mathrm{AlN} + 3\ \mathrm{RuO_2} \rightarrow 2\ \mathrm{Al_2O_3} + 3\ \mathrm{Ru} + 2\ \mathrm{N_2} \quad (4)$$

This means that the ruthenium dioxide of the resistor pastes can be reduced by AlN during the firing process and elemental ruthenium and gaseous nitrogen are generated.

4. Results and discussion

By thermoanalysis the reaction between ruthenium dioxide and aluminium nitride (Equation 4) proceeding during the firing process of resistor pastes shall be demonstrated.

The AlN powder shows, in air, above 753 °C (extrapolated onset) a continuous mass gain (Fig. 1) and the DTA graph shows, corresponding to the mass gain, an exotherm peak with a maximum at 1075 °C.

In an atmosphere consisting of 20 vol % oxygen and 80 vol % helium, above 753 °C the oxidation products nitrogen and nitrogen monoxide were detected by mass spectrometer. In air AlN powder starts to oxidize between 700 and 800 °C. At 1200 °C the reaction is finished.

In the presence of glass A (mixture 6) the oxidation of AlN by atmospheric oxygen begins at 1000 °C. The glass prevents oxidation at temperatures below 1000 °C.

According to Equation 4 mixture 2 should show a reaction energy and a mass loss, but an almost steady mass gain is observed from 753 to 1200 °C on heating in air (Fig. 2). However, an obvious turning point can be seen at 960 °C connected with a reaction exotherm (maximum at 1010 °C). This is an indication of two competing reactions.

In nitrogen the same mixture reacts exothermally (maximum at 1082 °C) and a mass loss occurs above 900 °C (Fig. 3).

The two competing reactions concern the oxidation of AlN by atmospheric oxygen and the reaction between AlN and RuO_2. The first reaction is coupled with a mass gain (Equation 3), unlike the second reaction (Equation 4), which is connected with a mass loss. Table II shows the calculated and the measured mass balance of all analysed samples.

In air RuO_2 reacts with AlN to 1200 °C only to a small extent. Only a turning point of the thermogravimetric curve at 960 °C (Fig. 2) points out that this reaction is a competing reaction to the AlN oxidation by atmospheric oxygen. Ruthenium is not proved by XRD.

If the last reaction is excluded by a non-oxidizing atmosphere, then above 900 °C a large mass loss should be observed (Fig. 3). This corresponds to an almost complete oxidation of AlN by RuO_2. Concerning the possible reactivity of thick film resistors on an AlN substrate, further impressions may be obtained by thermal analytical tests in the presence of glass.

The following experiments were carried out, in air, with a crystallizing glass A as additive to mixture 2 (= mixture 3). In the presence of this glass an exotherm reaction between RuO_2 and AlN connected

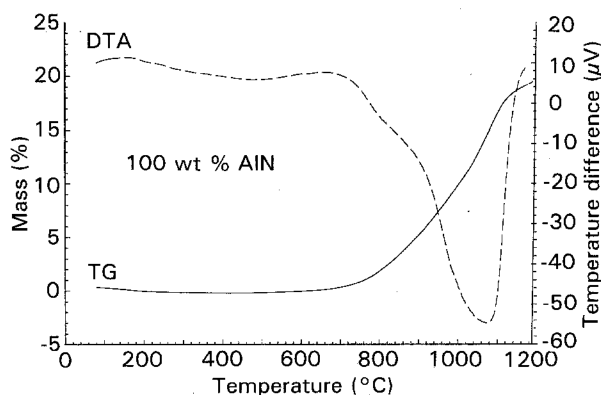


Figure 1 TG and DTA graphs of AlN powder in air versus temperature.

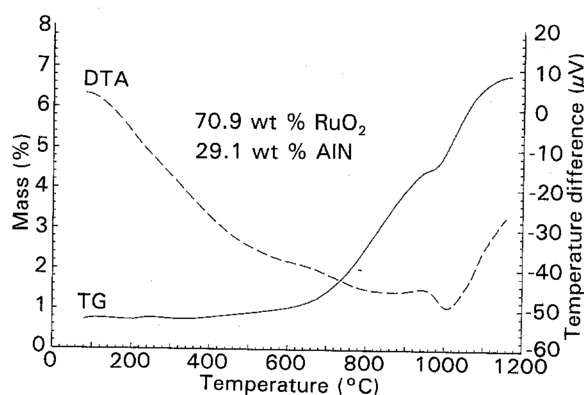


Figure 2 TG and DTA graphs of mixture 2 in air versus temperature.

TABLE II Mass balance

Mixture	Reactions	m^* (wt %)	m (measured) (wt %)
1	$AlN + 3/4\,O_2 \rightarrow 1/2\,Al_2O_3 + 1/2\,N_2$	+ 22.2	18.1 (753–1160 °C)
2	$AlN + 3/4\,O_2 \rightarrow 1/2\,Al_2O_3 + 1/2\,N_2$	+ 6.5	5.9 (753–1160 °C) in air
	$4\,AlN + 3\,RuO_2 \rightarrow 3\,Ru + 2\,N_2 + 2\,Al_2O_3$	− 9.1	− 8.6 (900–1200 °C) in nitrogen
3	$AlN + 3/4\,O_2 \rightarrow 1/2\,Al_2O_3 + 1/2\,N_2$	+ 3.3	− 1.1 (780–880 °C)
	$4\,AlN + 3\,RuO_2 \rightarrow 3\,Ru + 2\,N_2 + 2\,Al_2O_3$	− 4.5	2.8 (880–1200 °C)
4	$AlN + 3/4\,O_2 \rightarrow 1/2\,Al_2O_3 + 1/2\,N_2$	+ 3.3	− 3.6 (720–1120 °C)
	$4\,AlN + 3\,RuO_2 \rightarrow 3\,Ru + 2\,N_2 + 2\,Al_2O_3$	− 4.5	
5	No reaction up to 1100 °C	0	0
6	$AlN + 3/4\,O_2 \rightarrow 1/2\,Al_2O_3 + 1/2\,N_2$	+ 2.0	+ 1.9 (1000–1080 °C)

* Calculated value; the oxygen content of AlN is included.

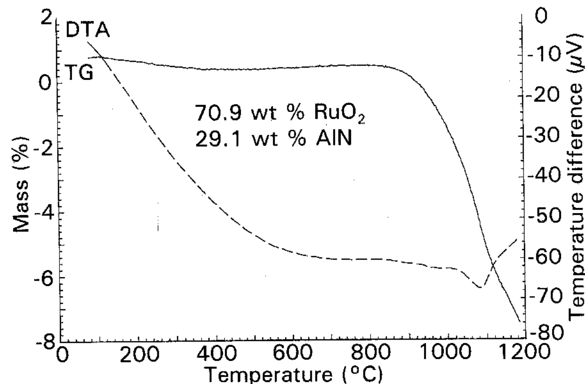


Figure 3 TG and DTA graphs of mixture 2 in nitrogen versus temperature.

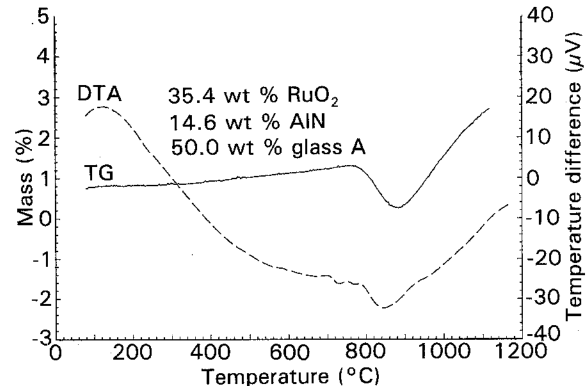


Figure 4 TG and DTA graphs of mixture 3 in air versus temperature.

with a substantial mass loss occurred from 780 to 840 °C (Fig. 4). Mixtures consisting of glass A and RuO_2 (mixture 5) as well as glass A and AlN (mixture 6) do not show mass loss and reaction heat in this temperature range.

The exotherm effects in the DTA thermogram (Fig. 4) from 710 to 790 °C are connected with the crystallization of the glass. In helium gas mixture 3 was tested to 900 °C. In the mass loss temperature range atomic and molecular nitrogen as well as nitrogen monoxide were found. The temperature dependence of this chemical reaction (thermogravimetry and mass intensity) is shown in Fig. 5.

XRD profiles of the dried and fired layer consisting of mixture 3 were measured (Fig. 6). As expected, diffraction peaks for AlN and RuO_2 were detected in the dried layer. However, in the fired layer diffraction reflexes of Ru were found, corresponding to Equation 4. The peak of a crystallized phase of the glass (zinc silicate) is also evident. However, alumina as a further reaction product was not measured. It is probably dissolved in the glass under these firing conditions.

Thus the crystallizing glass A leads to the postulated reaction (Equation 4) happening up to only 30% of the calculated amount. The crystallization increases the glass viscosity and impedes the complete reaction. The remainder of the AlN is oxidized by atmospheric oxygen (Table II).

A non-crystallizing glass B in mixture 4 causes an earlier start of the chemical reaction (about 60 K) with a large mass loss to above 1100 °C (Fig. 7).

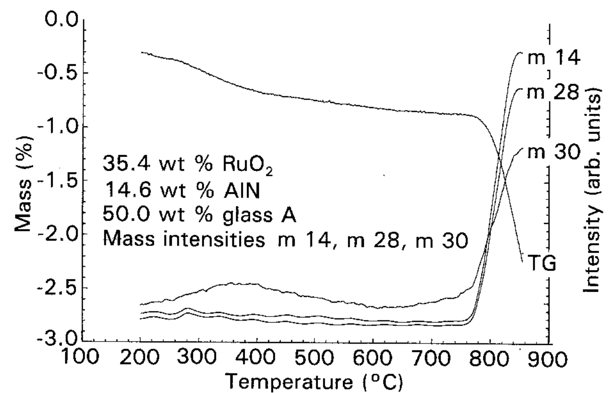


Figure 5 TG graph and mass intensities of mixture 3 in helium versus temperature.

As well as crystallizing glass, non-crystallizing glass leads to a mass loss connected with a reaction exotherm. The resulting reaction products (Equation 4) were identified by XRD and mass spectroscopy. They prove reaction between RuO_2 and AlN in the presence of glass by the formation of Ru and gaseous nitrogen. The glass dissolves the alumina film on the AlN particles, therefore a direct contact is enabled between RuO_2 and AlN.

It is clear that the temperature of this reaction depends on the specific glass properties, in particular the crystallization and the viscosity.

The viscosity of the non-crystallizing glass decreases with increasing temperature, causing a total reaction between AlN and RuO_2. At the temperature of the

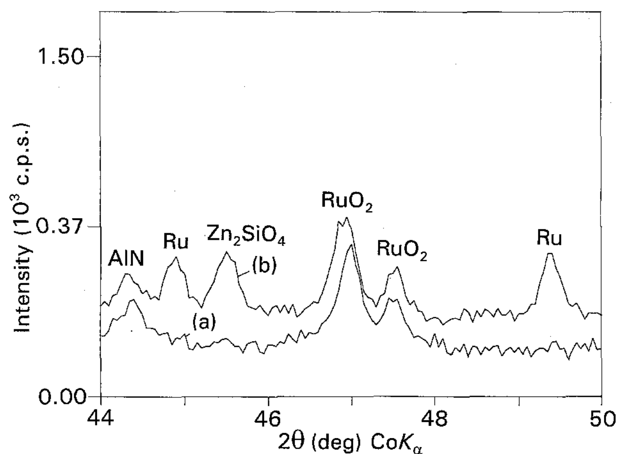


Figure 6 XRD profiles of a dried (a) and a fired (b) (at 810 °C) layer of mixture 3.

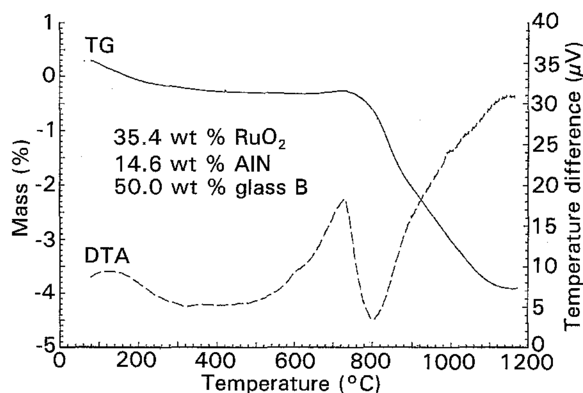


Figure 7 TG and DTA graphs of mixture 4 in air versus temperature.

thick film firing the glasses used promote the reaction between RuO_2 and AlN, but the influence of non-crystallizing glass is more intensive.

These tests show that in resistor layers on an AlN substrate not only glass but also RuO_2 is a cause of bubbles.

When RuO_2 is applied as the conductive component in resistor pastes on an AlN ceramic, then other paste components must intensively impede disturbing reactions. This was shown by the use of a crystallizing glass. Simultaneously this glass also enables the escape of gaseous reaction products.

5. Conclusion

In the presence of glass RuO_2 is able to react with AlN under the firing conditions for thick film pastes. This reaction is also a ɩeason for bubbling layers on the AlN substrate. The reaction rate depends on the specific glass properties, such as the crystallization and the viscosity. The influence of a non-crystallizing glass on this reaction is more intensive than the influence of a crystallizing glass. Furthermore, it is necessary that gaseous products can escape the resistor layer. This can be realized by using a crystallizing glass.

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