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Interfacial adhesion and microstructure of thick film metallized aluminum nitride substrates

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Abstract

The adhesive strength and fractured microstructure of aluminum nitride (AlN) substrate metallized with resistor thick-films followed by firing at 850 °C have been investigated via a pull-out rupture test loaded in tension. The AlN substrate used includes the as-received form and an oxidized form that was thermally treated at 1450 °C prior to the metallization. The thick-film paste includes both the as-received form (which is an RuO_2-based resistor) and a mixture of the paste with varying fractions of submicrometer alumina powder (5–20 wt.%) for comparison purposes. When the as-received AlN is used as the substrate, rupture strength decreases monotonically from 1.2 to ~0.1 MPa as the alumina loading (in the film) increased from 0 to 20 wt.%. The strength, however, remains relatively constant (~0.5 MPa) for the pre-oxidized AlN case, i.e. the adhesion is found insensitive to the change of alumina loading. This strength dependency has been compared with their fractured microstructure and the possible fracture mechanism that caused the failure is discussed.

Keywords: B. Interfaces; C. Fracture; D. AlN; Thick film metallization

1. Introduction

Polycrystalline aluminum nitride (AlN) has been used as a substrate material when heat dissipation is critical to the reliability and performance of microelectronic and optoelectronic devices, owning mostly to the distinguished thermal and dielectric properties the AlN possessed [1]. For the thick-film hybrids that utilize AlN as a base substrate, layers of conductor, dielectric and/or resistor are deposited onto the substrate followed by firing at elevated temperatures for improved film-substrate adhesion [2–8]. Defects such as pores and cracks are readily observable after firing at the film-substrate interface when commercial thick film pastes prepared mostly for the alumina substrates are used as the coating material for AlN [9]. Yamaguchi and Kageyama [10] have reported that chemical reactions occurred at the interface of AlN grains and the glass species of thick films were critical to the defect formation. Search of suitable glass constitutes (of the film) for improved compatibility with AlN hybrids has hence been pursued to resolve this problem [2,7]. Yet, the multifunctional role of the glass plays in the thick-film paste has often made the selection of an appropriate glass composition and its content as well a tough choice to make. An approach different from the "traditional" selection of appropriate glass chemistry has been proposed by the authors recently [11,12]. This method involves addition of "non-sintering" particles embedded within the thick-film matrix so that the densification of the film is retarded to a certain extent, allowing sufficient time long enough for dissipation of reaction gases formed at the film-substrate interface to the free surface at relatively lower temperatures. We have shown that as long as the non-sintering "inclusion" fraction does not exceed a certain critical level, the film seems to have evolved toward an adhesive bonding at the interface *microstructurally* as the firing temperature was subsequently raised to a higher level, allowing for densification of the "composite" film [11].

In this study, we intend to conduct a tensile rupture test on the fired AlN substrates that have been metallized

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with the resistor paste blended with varying fractions of alumina powder (0 to 20 wt.%) acting as the "rigid" inclusion during firing. The paste investigated is a glass-based RuO_2 thick-film resistor mainly designed for alumina substrate [11,12]. Blister has been found to occur at the resistor–AlN interface as temperature was raised above ~700 °C [13]. The adhesive strength of the film (to the AlN substrate) has been determined for polycrystalline AlN substrates of both the as-received and the pre-oxidized forms, and their fractured microstructure being examined to compare with the tensile properties attained.

2. Experimental procedure

Resistor paste consisting of RuO_2 as the functional phase (R-2310, sheet resistance of 1 kΩ/□, Shoei Chemical Inc., Japan) was coated onto as-received AlN substrate (TAN-170, Toshiba, Japan) by screen-printing. All the substrates have been ultrasonically cleaned in acetone prior to the printing process. Some of the bare AlN substrates were pre-oxidized at 1450 °C for 10 min before being printed with the resistor. This introduced a grown oxide layer on the AlN surface typically ~30 μm in thickness. The coated substrates were leveled at room temperature, allowed to dry at ~50 °C for 24 h followed by firing to 850 °C in air at a heating rate of 10 °C/min and with 10 min isothermal holding. The adhesive strength of the printed and fired substrates was examined under tension loading in a manner shown schematically in Fig. 1. Two pieces of the coated substrates were brought together in a way that the resistor layers were joined face-to-face before the samples as a whole were being fired to the pre-determined temperature (850 °C). A dead weight of 0.5 kg (corresponding to a nominal compression pressure of 49 kPa in given substrate dimension of 10×10 mm^2) was applied onto the stacked substrates during firing for facilitating a hermetic joining of the substrates. Tensile stress in a loading direction perpendicular to the fired substrates was applied. A gradual increment of the loading weight by slowly adding determined weight onto a weighing pan hanging in a position underneath the stacked substrates was invoked until catastrophic failure of the substrates eventually occurs. The nominal rupture strength was then determined by dividing the load at fracture by the cross-sectional area of the resistor over the substrate surface. Five to 10 samples were tested before an average strength value was determined.

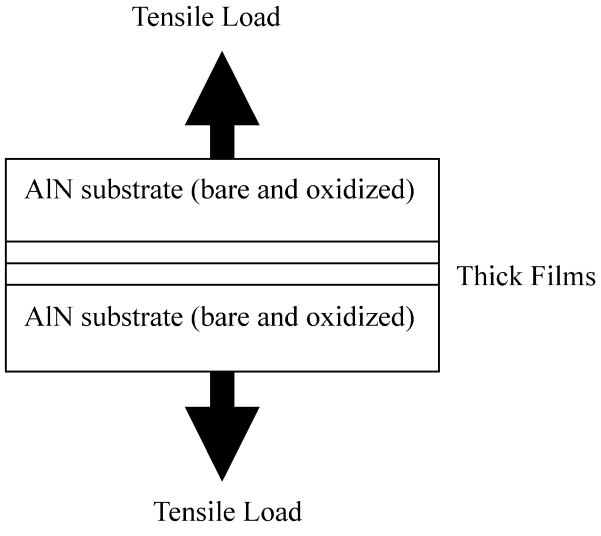

Fig. 1. A schematic showing the loading direction of the rupture test.

Submicrometer alumina powders (AKP-50, Sumitomo Co., Japan, particle size ~0.2 μm) were blended with the as-received resistor paste via a three-roll mixer (Exakt-50, Koenen, Germany) [12]. The doping level of the Al_2O_3 ranged from 5 to 20% in terms of the paste weight. Some AlN substrates (including those of the as-received and the pre-oxidized forms) were printed with the "composite" pastes, fired to 850 °C with the same compression pressure applied over the stacked structure aforementioned, and their tensile rupture strength also determined to compare with those without the alumina doping. The fractured surfaces were examined by both optical and scanning electron microscopy (S-2700, Hitachi, Japan) equipped with an energy dispersive spectrometer (EDS) for determination of possible fracture mechanisms.

3. Results and discussion

3.1. Adhesion and microstructure of resistor coated as-received AlN

Fig. 2 shows the adhesive strength of the thick-film coated AlN substrates, including both the as-received and the pre-oxidized forms. When the as-received AlN was used as the substrate, rupture strength reduces monotonously as the alumina loading in the film increases. The rupture strength reduces linearly from an average of 1.2 MPa to ~0.1 MPa as the alumina loading was increased from 0 to 15 wt.%, while the strength remains virtually unchanged as the loading further increases toward 20 wt.%. The strength also shows notable scattering, especially when the alumina loading is at lower doping levels ($\leqslant$5 wt.%). This scattering suggests that the microstructure of the coated substrates is quite inhomogeneous in character so that the rupture strength resulted is broadly distributed. In our earlier reports [11,12], we have shown that interconnected blisters of size ranging from about 5 to 30 μm were apparently observable at the film-substrate interface after

firing when pastes of the as-received and the 5 wt.%-doped were used as the coating material for the AlN. It is plausible that the uneven distribution of the blister size (and hence the inhomogeneous film structure) has led in part to the strength scattering observed at the lower alumina doping levels.

Examination of the fractured microstructure of the resistor-coated, as-received AlN samples reveals that substrate failure occurred exclusively in the film as the alumina doping is under 10 wt.%. As shown in Fig. 3a and b, fracture occurs within the film itself after the tensile loading; whilst, the film – AlN interface remains virtually intact after the tensile rupture. This finding suggests that the resistor film provides a relatively strong bonding to the AlN substrate, regardless of the formation of reaction gases at the interface that literally reduces the load-bearing area supposedly critical to the film–substrate adhesion. An EDS elemental analysis shows that the glass compositions of the paste, e.g. lead, has diffused into the AlN substrates, preferably the grain boundaries of the AlN, considerably with a depth greater than 10 μm from the interface (Fig. 4). We suspect the diffusion actually help the film–substrate adhesion obtained in Fig. 2.

As the alumina loading increases toward 10 wt.% (Fig. 3b), the fractured film becomes rather smooth. The alumina particles exist within the resistor matrix are considered non-sinterable at the working temperature employed, the alumina "inclusions" are hence expected to constrain the film densification, leading to insufficient densification of the film as the doping level increases and hence a weaker strength of the film is resulted. This proposition explains why the adhesive strength (of the as-received AlN case) reduces as the alumina fraction in the film increases; nonetheless, it neglects possible reactions that might occur between the alumina and the glass species of the film at the given temperature involved. Even if some reactions did have occurred between the alumina and the glass (of the film) during firing, addition of alumina powders would still inevitably result in a reduced densification rate and a minimized end-point density of the composite film [14–17], resulting in a reduced film strength due to the increased porosity in the film.

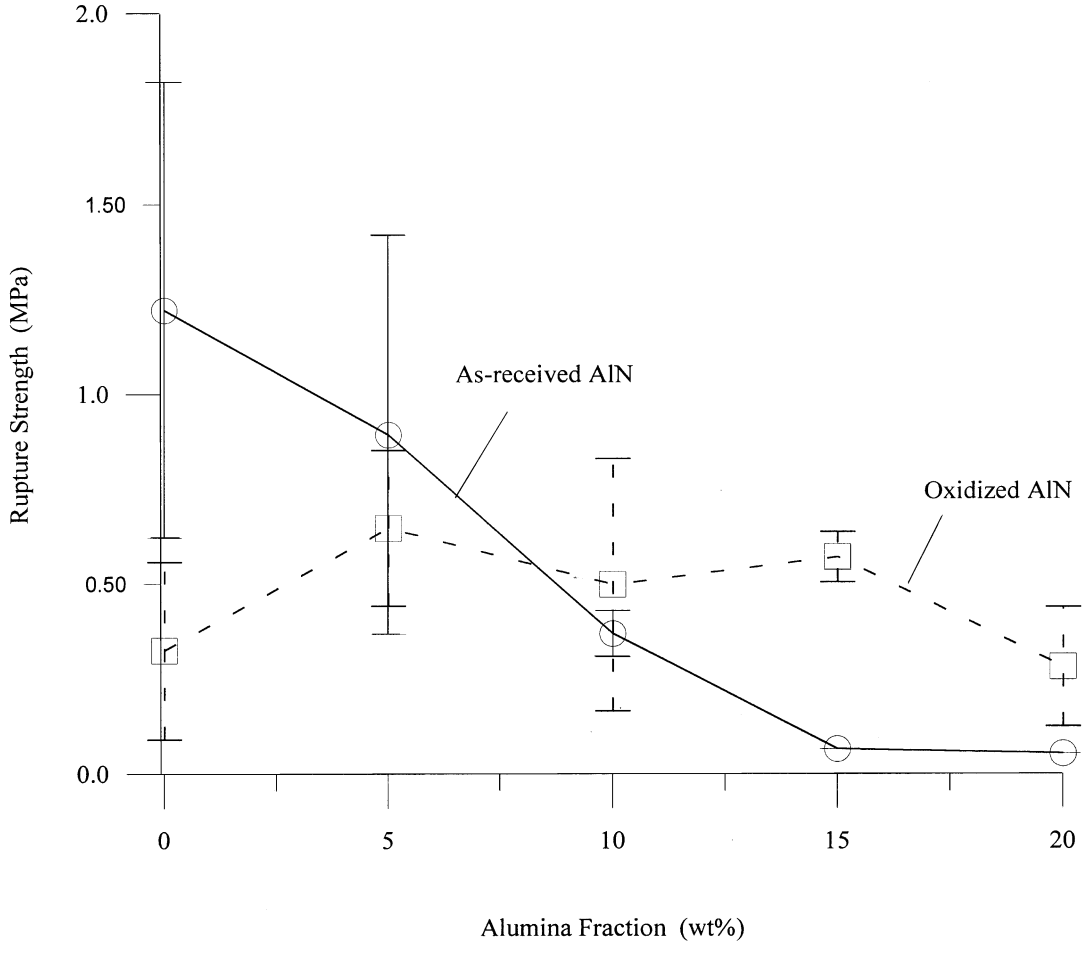

Fig. 2. The rupture strength of the fired AlN substrates metallized with the resistor pastes at 850 °C.

As the alumina fraction was further raised beyond 15 wt.% for the as-received AlN case (Fig. 3c), the film appears to become porous after firing. Notice that the failure now occurs predominately at the film-to-film interface, different from what have been observed in Fig. 3a and b. The film-to-film interface appears to be only loosely joined together by the compression loading involved in the preparation of strength-testing samples. At least two reasons may be possible for the film-to-film microstructure observed. First, the inclusion particles may have in fact formed a continuous network in the thick-film matrix as the alumina fraction exceeds a certain critical level, so that adhesion/densification of the composite film at the joining surface is prohibited even with the presence of compression load during firing. At the temperature involved in the study, there should be no sintering expected to occur between contacting "inclusions"; therefore, the continuous inclusion network would restrain the film densification and hence prohibit the film-to-film adhesion [16,17]. In Fig. 3c, the porosity found *in* the film partially substantiates this proposition. Nonetheless, in the figure, we fail to provide a direct evidence in pinpointing the exact locations of the alumina particles in the resistor matrix to support the continuous network proclaimed. This, yet, does not necessarily mean that the continuous inclusion network does not exist in the film. Second, the reaction gas formed at elevated temperatures may eventually develop a "back" pressure against the compression load that was applied onto the stacked substrates during firing. The "back" pressure may offset the applied load to a significant extent, leading to the reduced film-to-film adhesion resulted. This model appears likely when compares the strength and microstructure of the thick-film coated, as-received AlN to that of the pre-oxidized one, and will be discussed in the section follows.

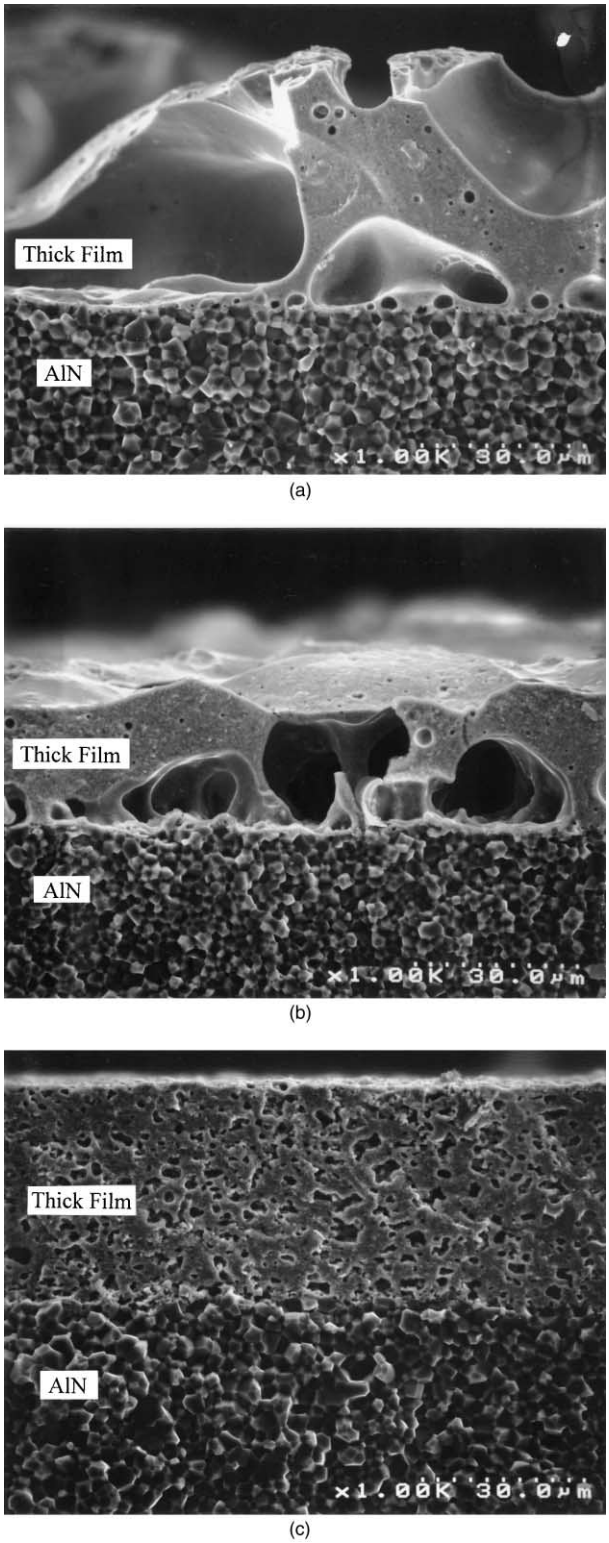

Fig. 3. Fracture surface of fired AlN substrate with alumina concentrations of (a) 0 wt.%; (b) 10 wt.% and (c) 20 wt.%.

3.2. Adhesion and microstructure of resistor coated oxidized-AlN

When the pre-oxidized AlN was used as the substrate, the rupture strength is found relatively insensitive to the alumina loading in the film (Fig. 2). The strength remains at about 0.5 MPa throughout the alumina concentrations investigated, with only a slight gain in strength as the alumina loading is in the range of 5 to 15 wt.%; but, the change is modest. This strength dependence is markedly different from that obtained in the as-received AlN case. Fig. 5 shows a typical fracture surface of the pre-oxidized AlN sample with 10% alumina doping in the resistor. Large cracks are found in a direction across the film and the oxide scale, as well as over the interface of the oxide scale and the underlying AlN grains. We suspect that the cracks might have already existed in the oxide scale before the metallization process is invoked and a separate experiment by examining the fractured surface of thermally oxidized AlN (without any thick-film coating) confirms the hypothesis. In Fig. 6, cracks appear at the interface of the oxide layer and the AlN, together with some minute

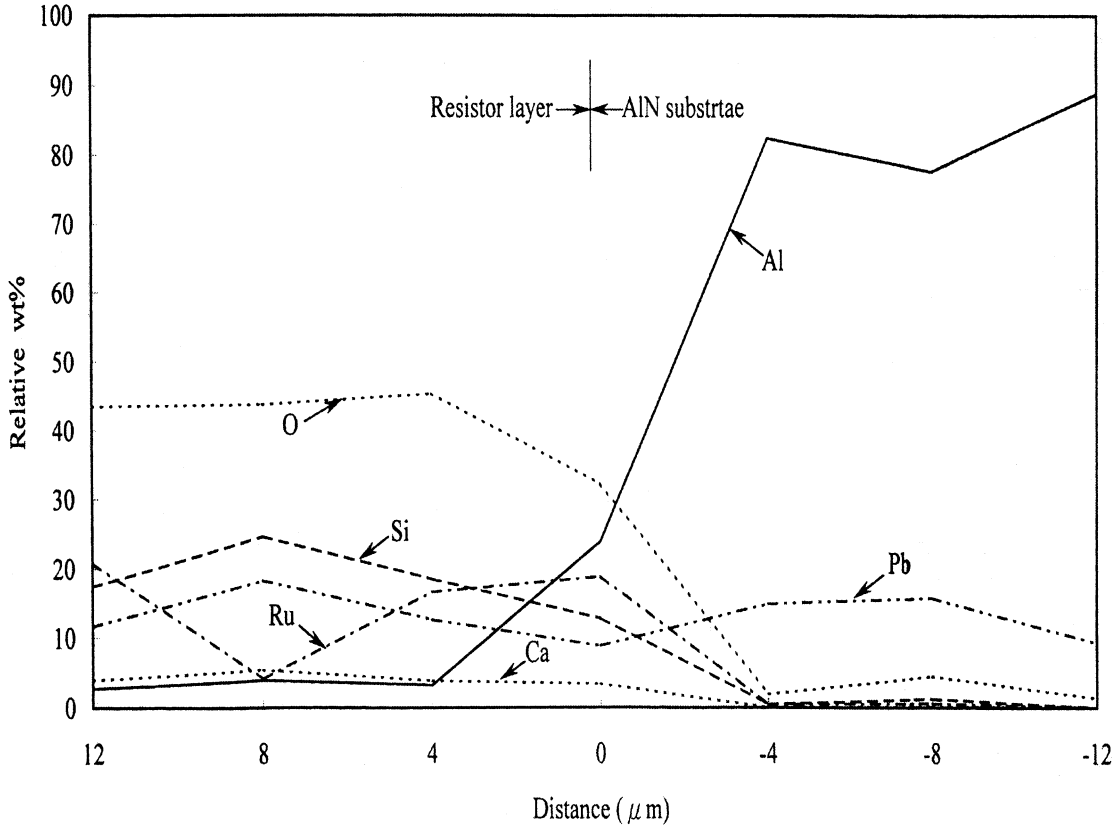

Fig. 4. An EDS result at locations near the interface of as-received resistor thick-film And AlN substrate.

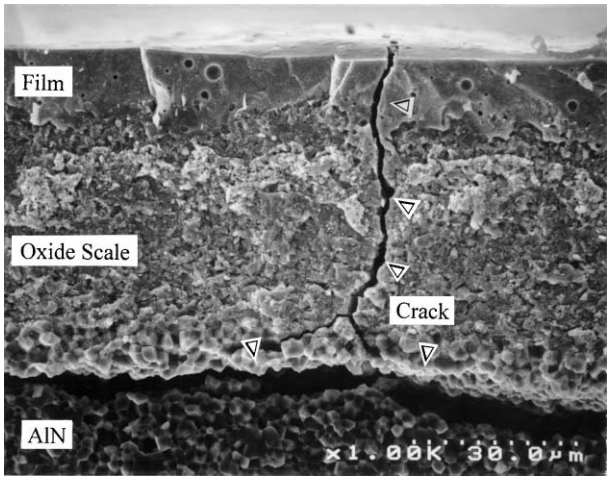

Fig. 5. A typical fracture surface of pre-oxidized AlN substrate that was coated with the resistor thick-film containing 10 wt.% of the alumina concentration.

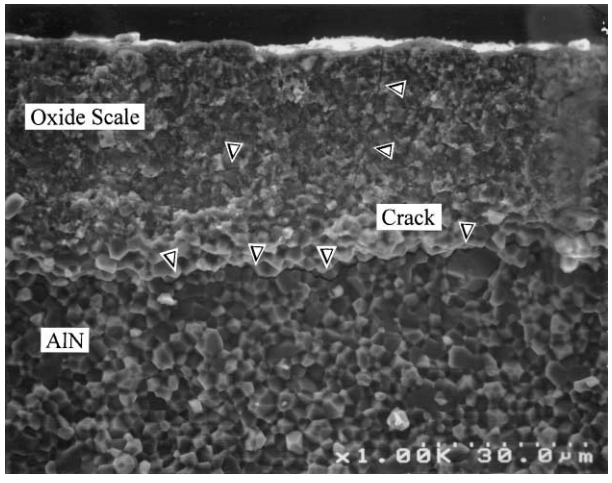

Fig. 6. A typical fractured surface of thermally grown oxide scale on AlN substrate. Minute cracks are observable at the scale–AlN interface and within the oxide as well.

cracks also observable within the film. This suggests that the cracks resulted from the thermal treatment (of the substrate) play a role in determination of the rupture strength of the coated substrates, contributing to the rather insensitivity in strength as varying alumina fractions in the film were used (Fig. 2). It is believed that the cracks have existed in all alumina-loading cases after the oxidation cycle applied; therefore, all the pre-oxidized samples fail at similar strength levels.

According to Kim and Morehead [18], the interfacial cracks that have been found spanning underneath the oxide scale are believed to result from the thermal expansion mismatch between the oxide scale and the AlN; whilst the cracks within the oxide scale is probably

due to the residual tension stresses when the oxide scale grows over a certain critical thickness. Estimation of the residual stress indicates that a tensile stress over 2 GPa is resulted as the oxide scale exceeds 10 μm in thickness [18], which is a value well above the typical tensile strength of sintered, dense alumina. It is nonetheless interesting to note that the strength of the oxidized AlN case is significantly higher than that of the bare AlN case at the alumina concentration >15 wt.%. Observation of the fractured surface reveals that some of the 15 wt.% samples (of the pre-oxidized substrates) present hermetic joining at the film-to-film interface after fracture, in contrast to the weak interface shown representatively in Fig. 3c. This suggests that the reaction gas formed at the bare-AlN case probably have imposed a "back" pressure with directions opposite to the applied compression stress during firing, so that the compression load is less effective in aiding film adhesion for the as-received AlN case. This "back" pressure may be significant enough to prohibit the film-to-film adhesion in the as-received AlN case, contributing in part to the failure occurred at the resistor-film interface.

4. Conclusions

The adhesion strength of resistor thick-film metallized AlN substrates has been determined through a pull-out rupture test that loaded the substrates with a tensile loading across the film-substrate interface. The rupture strength decreases monotonously as the alumina concentration in the film increases for the as-received AlN case. Observation of the fractured surface reveals that failure is mostly found within the film, over which, mechanisms such as the reduced cross-sectional area of the bulged film, densification retardation of the film due to the "non-sintering" alumina inclusions as well as the non-hermetic film-to-film joining at the film interface play significant roles of different significance over the varying alumina concentrations investigated. For the pre-oxidized AlN case, strength is found rather insensitive to the alumina concentrations, presumably due to the cracks already existed at the oxide scale–AlN interface when preparing the pre-oxidized samples for comparative strength evaluations. A "back" pressure arising from the reaction gases formed between the glass (of the film) and the AlN at elevated temperatures is suspected to offset the compressive load applied during firing of the stacked substrates that is aimed to facilitate resistor-film adhesion and this contributes in part to the poor film-to-film adhesion found in the as-received AlN case, resulting in a reduced adhesive strength as the alumina loading exceeds over 15 wt.%.

Acknowledgements

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