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Oxide film formation on aluminium nitride substrates covered with thin aluminium layers

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The growth of oxide films on aluminium nitride substrates covered by vapour-deposited aluminium films of 1.5 and 4 μm thickness has been studied in air at atmospheric pressure as a function of temperature. Oxide films were grown by oxidation in air at temperatures between 800 and 1300 °C. The kinetics of the growth of oxide films on such substrates was observed to be complex. In particular, there are three subsequent periods of observed oxide growth: (1) an initial period of rapid oxide growth, (2) an incubation period with very slow oxide growth, and (3) a second period of relatively fast oxide growth.

1. Introduction

Aluminium nitride has recently been the subject of numerous studies because of its potential to be used as an electronic packaging material, (see, for example, [1–4]). This is primarily due to its high thermal conductivity of $320\ \mathrm{W\,m^{-1}K^{-1}}$ [5, 6] compared to alumina (20–$40\ \mathrm{W\,m^{-1}K^{-1}}$ [3, 4]) which is currently used as computer chip substrate material. Another attractive feature of aluminium nitride is that its coefficient of thermal expansion ($\sim 4.5\times10^{-6}\ ^{\circ}\mathrm{C}^{-1}$ from 20–400 °C [3]) is close to that of silicon [4]. Because of the preparation methods used to make aluminium nitride, oxygen impurities are inherent in the material and they adversely affect the thermal conductivity [5, 7].

Oxide films on aluminium nitride substrates have been shown to be beneficial for the adhesion of copper films [2]. We have previously studied the growth of oxide films on aluminium nitride substrates by direct oxidation [8]. The purpose of this study was to identify conditions under which thin, uniform oxide films can be formed on aluminium nitride substrates. In the direct oxidation experiments, it was observed that, as the oxide film thickness increased, the α-alumina product layer cracked. This cracking is caused by the difference between the coefficients of thermal expansion of oxide and substrate material, and by the stresses due to the volume change involved in the transformation of aluminium nitride into alumina. To avoid the build-up of such stresses during the formation of aluminium oxide films on aluminium nitride, we have explored an alternative approach, which was to form oxide layers by oxidizing a liquid layer of aluminium on the substrate surface. As long as a continuous, liquid aluminium layer is present between the growing oxide film and the substrate, stresses due to the occurring volume change should not be built up to a large extent. Significant stresses should begin to build up after the aluminium film is completely oxidized, and also upon cooling to room temperature.

The kinetics of oxide formation by this alternative approach is expected to be different from that by direct oxidation of aluminium nitride substrates. Initially, as long as the aluminium has not been completely converted to oxide, the kinetics should correspond to the oxidation of liquid aluminium (in a constrained geometry) to alumina. After all the aluminium is consumed, the kinetics are likely to become very similar to those of the direct oxidation of aluminium nitride substrates. A transition period between these two types of kinetics may occur.

The oxidation of liquid aluminium and related alloys has been the subject of several studies, for example [9–13]. It has been shown that impurities significantly influence the kinetics. From the point of view of the transport of matter through the reaction product, this is no surprise, because the concentration of intrinsic defects in alumina is extremely small [14]. Impurities, present even in very small concentrations, may significantly alter the defect concentrations and consequently the rate of transport of matter. Furthermore, impurities, if they segregate at surfaces and/or interfaces, may significantly change the kinetics of interfacial processes.

One impurity often present in aluminium is magnesium. The influence of magnesium on the surface tension of liquid aluminium has been investigated [12] for unoxidized and oxidized surfaces. The results very clearly show that magnesium is a surface-active element and enriches at both unoxidized and oxidized surfaces. From this observation one may conclude that the oxide formed on molten aluminium containing magnesium impurities will be an MgO-doped alumina. This conclusion is supported by experimental observations by Bergsmark *et al.* [13]. Similar statements hold for other impurities [9, 10].

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The oxidation kinetics observed for liquid aluminium of different origin and impurity level seems to be complex. Besides the influence of impurities in the starting material, it has been observed that impurities in the oxidizing gas phase, such as water [13] (and possibly others), can have a dramatic effect on the kinetics of the oxidation of liquid aluminium. Currently, there is no unified picture available of these kinetics.

The kinetics of the oxidation of aluminium nitride to aluminium oxide were studied previously [8]; we reported experimental data for the direct oxidation of aluminium nitride substrates in different gas atmospheres at temperatures in the range 1000–1400 °C. These data could be fitted very closely to a linear rate law, indicating that an interfacial process is rate controlling. In the literature, other types of kinetics have also been reported [15–18], such as following a parabolic or more complicated rate laws, for example, composed of parabolic and linear terms.

In this paper, results from the oxidation of aluminium nitride substrates covered with liquid, vapour-deposited aluminium layers will be presented. The reaction kinetics for the oxidation process will be discussed.

2. Experimental procedure

The substrates division of Carborundum at Sanborn, supplied the experimental aluminium nitride substrates used in this study. The exact manufacturing methods of these substrates are not known to us because of their proprietary nature. The substrates were received with dimensions of 1 cm × 1 cm × 3 mm and prepared for coating with 1.5 μm aluminium by grinding them plane-parallel. The lapping procedure used has been described elsewhere [8]. After lapping the substrates, 1.5 μm aluminium was vapour-deposited on to the surface. The aluminium (Kamis, Inc., Mahopac Falls, NY) used during the vapour-deposition process was at least 99.999% pure. Later, oxidation studies were also performed on as-received aluminium nitride substrates with approximately 4 μm thick aluminium layers.

After the evaporation of aluminium onto the aluminium nitride substrate samples, they were oxidized in a muffle furnace in air between 800 and 1300 °C for up to 12 h. Samples to be oxidized in air were heated from room temperature to the desired temperature in 3 h. The time at which the furnace reached the desired temperature was taken as $t = 0$. At $t = 0$, one sample was removed from the furnace and quenched to room temperature. Thereafter, samples were removed from the furnace after regular time intervals and quenched to room temperature.

The two lowest oxidation temperatures were 800 and 1000 °C, above the melting point of aluminium metal ($T_m = 660$ °C). They were chosen because at these temperatures oxynitrides and oxides, respectively, can be formed [19]. The upper temperature limit for our investigation was set to 1300 °C. Above this temperature, the oxidation rate becomes too large to allow accurate oxide film growth control on aluminium nitride substrates in air [8].

Because the oxidation temperatures are above the melting point of aluminium, the evaporation and pooling of aluminium metal is of concern. If significant evaporation occurs, porosity can develop in the aluminium films. This becomes more of a concern as the oxidation temperature and aluminium film thickness is increased. If significant pooling occurs, uniform oxide films cannot be obtained.

The experimental techniques used for the characterization of the substrates were X-ray diffraction and electron microprobe analysis. The preparation of the samples and the sample configuration for these analyses were the same as described earlier [8].

3. Results and discussion

The characteristics of the experimental aluminium nitride substrates used have been reported elsewhere [8]. The overall yttria concentrations of the as-received substrate materials were determined to be approximately 2 vol% by energy dispersive X-ray spectroscopy with an electron microprobe (Jeol 733). The secondary phases present in the substrates were found to be $Y_4Al_2O_9$ and $Y_3Al_5O_{12}$. The aluminium film thicknesses of 1.5 and 4 μm were selected to produce oxide film thicknesses of approximately 2 and 5 μm for completely oxidized aluminium layers. The oxide thicknesses were calculated by assuming that the change in thickness corresponds to the change in density, i.e. based on the assumption of completely dense layers. A variation of ± 0.2 μm was observed by electron microprobe in the thickness of the vapour-deposited aluminium layers. This error can result in a variation of ± 0.25 μm in the corresponding oxide thickness. It was observed that the oxide layers formed by oxidizing the aluminium nitride/aluminium samples were not completely uniform. Therefore, in determining the thickness of oxide films formed by oxidizing aluminium layers, special care was taken to ensure that the oxide film whose thickness was determined had been formed by the oxidation of

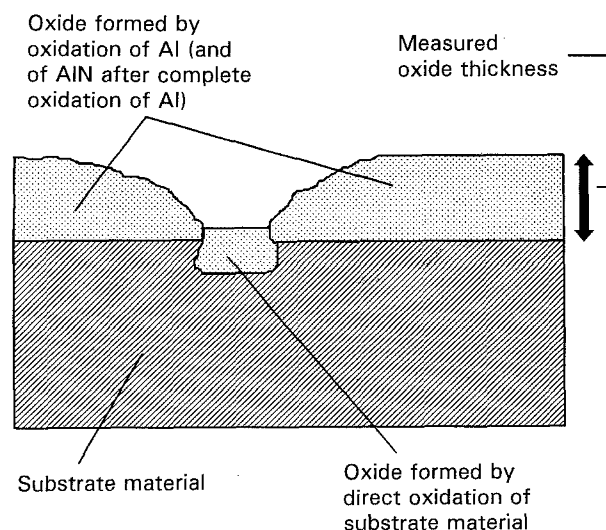


Figure 1 Schematic representation of the near-surface morphology of an AlN substrate covered with an aluminium film and oxidized at high temperature.

aluminium (and subsequently of AlN after completion of the oxidation of aluminium). As shown in the schematic representation of an oxidized sample in Fig. 1, the oxide layer attributed to the aluminium film is easily distinguishable from that formed by oxidation of only substrate material. Referring to Fig. 1, the oxide film thickness was determined perpendicular to the original sample surface, as the distance from the alumina/gas interface to the alumina/AlN interface at locations where the oxide must have at least initially been formed by the oxidation of aluminium. Some porosity was visible in the oxide films obtained by oxidizing aluminium films of 1.5 μm thickness. As discussed above, the error in the oxide film thickness is of the order of $\pm$ 0.25 μm. Significantly more porosity was observed in the oxidized 4 μm aluminium films than in the 1.5 μm films.

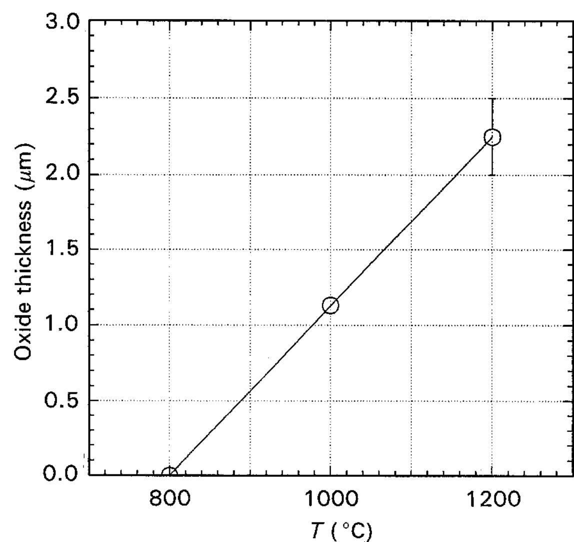


Figure 3 Comparison of observed oxide thicknesses as a function of temperature for aluminium nitride substrates with a 1.5 μm Al layer oxidized for 3 h in air.

3.1. Oxide film formation

A preliminary study was first performed to identify appropriate oxidation temperatures. For this purpose, aluminium nitride substrate samples coated with 1.5 μm aluminium layers were oxidized in air at 800, 1000 and 1200 °C for 3 h, and at 1100, 1200, 1250 and 1300 °C for 1 h. A comparison of the oxide thicknesses observed after 1 h as function of the oxidation temperature is shown in Fig. 2. The observed oxide film thicknesses were all about 2 μm for samples oxidized between 1100 and 1250 °C. At 1300 °C, an oxide film thickness of 12.5 μm was observed, which is much larger than can result from the oxidation of only the aluminium layer. A comparison of oxide thicknesses observed for samples oxidized for 3 h at temperatures between 800 and 1200 °C is shown in Fig. 3 as a function of temperature. Analysis of these data reveals that the growth of oxide and/or oxynitride films is very slow at 800 and slow at 1000 °C. At 1200 °C, the aluminium film has been completely oxidized to alumina after 1 h. Based on the above results, further

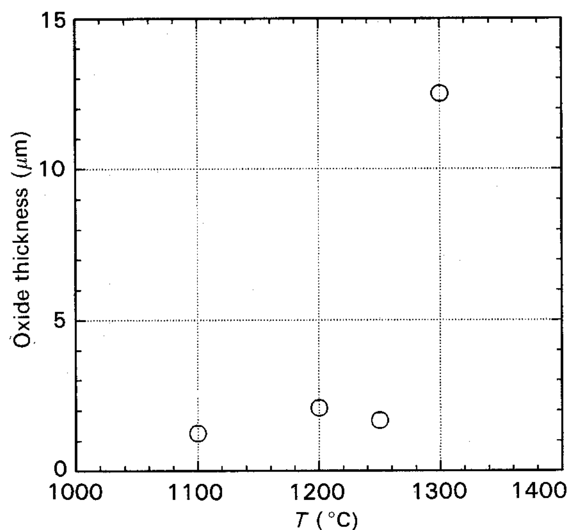


Figure 2 Comparison of observed oxide thicknesses as a function of temperature for aluminium nitride substrates with 1.5 μm Al layers oxidized for 1 h in air.

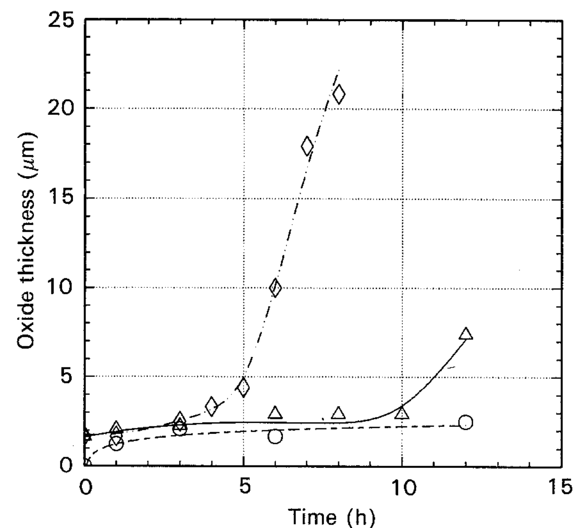


Figure 4 Comparison of observed oxide layer thicknesses as a function of time for the oxidation of aluminium nitride substrates with a 1.5 μm Al layer for temperatures (○) 1100, (△) 1200 and (◇) 1250 °C.

oxidation studies were limited to 1100, 1200 and 1250 °C.

Fig. 4 shows a comparison of oxide film thicknesses that have been observed as a function of time on aluminium nitride substrate samples originally coated with 1.5 μm aluminium after oxidation at 1100, 1200 and 1250 °C in air. The corresponding data for an initial aluminium layer thickness of 4 μm are displayed in Fig. 5.

It is found that the scatter in the observed oxide film thicknesses for samples with an initial 4 μm aluminium thickness is larger than in the case of samples with an original aluminium thickness of 1.5 μm. At temperatures above its melting temperature, the aluminium on the samples with a 4 μm layer is less constrained to the substrate surface by surface tension than in the case of 1.5 μm aluminium layers. This may

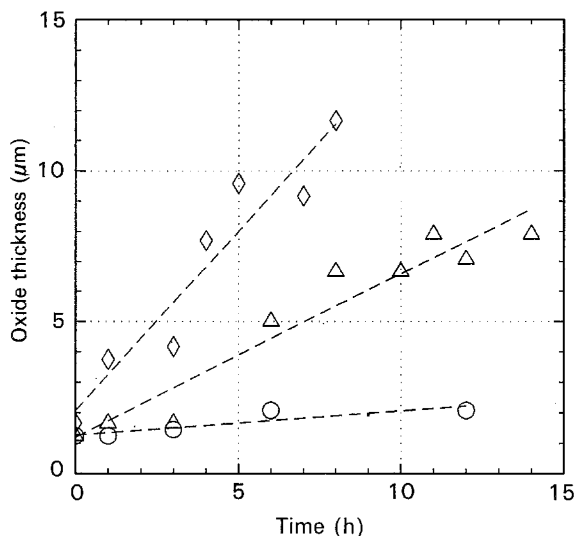


Figure 5 Comparison of observed oxide layer thicknesses as a function of time for the oxidation of aluminium nitride substrates with a 4 μm Al layer for temperatures (○) 1100, (△) 1200 and (◇) 1250 °C.

lead to the formation of aluminium islands on the substrate surface upon heating. During the oxidation of a sample with aluminium islands, the aluminium is constrained further by the connection of the oxide layer to the substrate, leading to stresses in the oxide layer, and possibly to occasional crack formation in the oxide layer during the oxidation process. As stated earlier, it was desirable to minimize the stresses in the growing oxide layer. In the case of the high-temperature oxidation of aluminium nitride substrates initially covered with 4 μm aluminium, island formation occurs to such a significant extent that stress minimization cannot be completely achieved. Furthermore, increased aluminium evaporation occurs. In view of these problems, it is no surprise that the data for oxide film thicknesses show more scatter for samples initially covered with 4 μm aluminium than with 1.5 μm.

Analyses of the data shown in Fig. 4 reveal that three distinct types of oxidation behaviour are observed for an initial aluminium thickness of 1.5 μm: (1) an initial region of very rapid oxide growth, followed by (2) a region of slow, almost non-observable oxide growth, and (3) a second region of rapid oxide growth. The first region of fast oxide growth corresponds to the oxidation of the aluminium layer. The second region corresponds to an incubation period during which the oxide film thickness is equal to that of the completely oxidized aluminium layer. The final region corresponds to the oxidation of the underlying aluminium nitride.

For samples originally coated with 1.5 μm aluminium, the oxide layer thickness of approximately 2 μm in the plateau region is expected, as explained earlier.

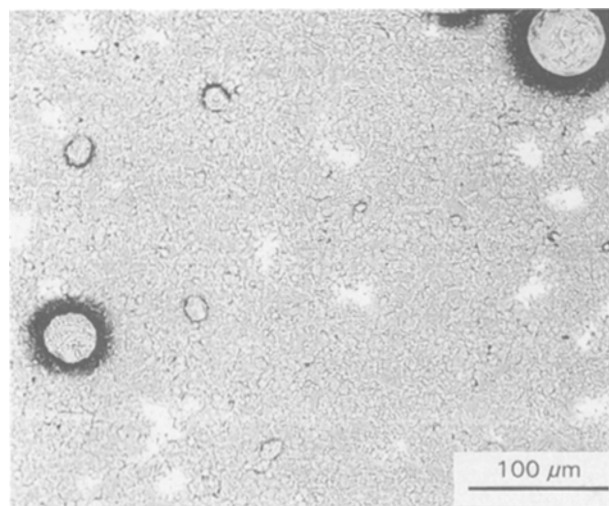
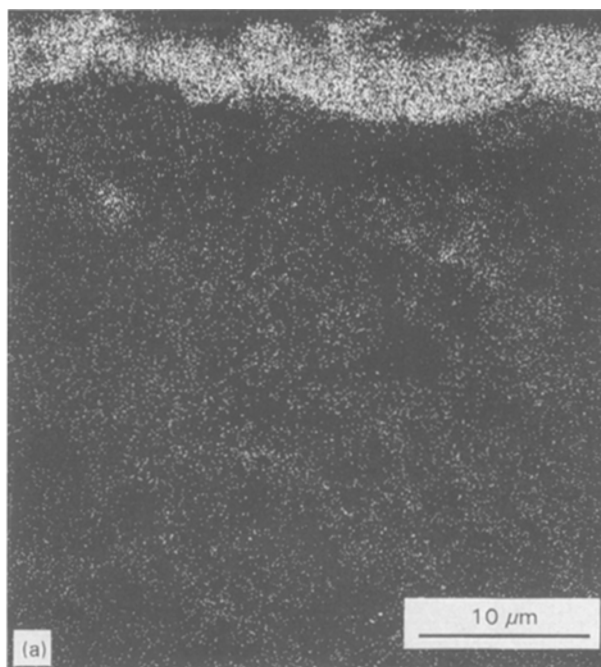


Figure 6 Backscattered electron image of an oxidized surface of an aluminium nitride sample covered with 4 μm Al. The sample was oxidized in air at 1250 °C for 4 h.



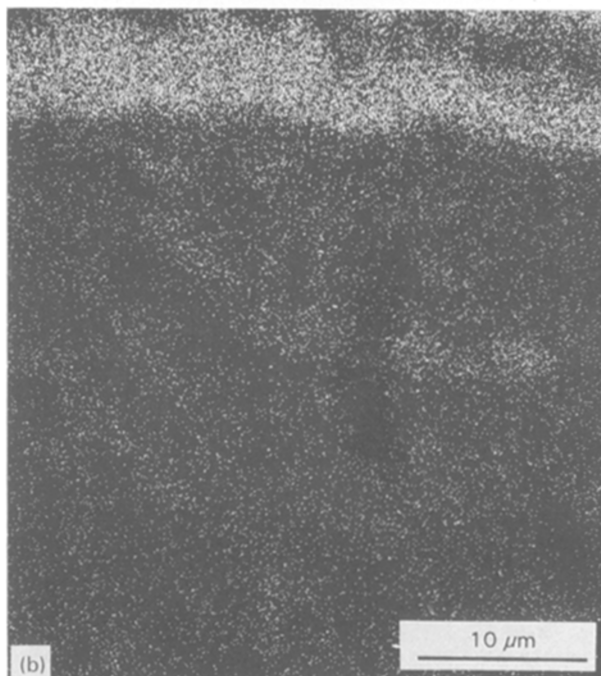


Figure 7 Oxygen concentration maps of aluminium nitride samples covered with 1.5 μm Al that were oxidized in air at atmospheric pressure: (a) 1200 °C for 6 h, and (b) 1250 °C for 5 h.

The initial region of rapid oxidation cannot be observed at higher temperatures, i.e. at 1200 and 1250 °C, because the aluminium film is already completely oxidized when the sample has reached the oxidation temperature.

For samples originally coated with 4 μm aluminium, the oxidation behaviour just discussed is not as clearly visible from Fig. 5. Inspection of the oxidized samples reveals that the uniformity of the oxide layer is much less than in the case of oxide layers formed by oxidation of 1.5 μm thick aluminium films. In the case of 4 μm aluminium films, indications of a significant pooling of liquid aluminium are visible. For 1200 °C, a plateau region could tentatively be assigned to a thickness of about 7 μm instead of the predicted 5 μm. It has been observed that a thin, compact Al_2O_3 forms adjacent to the metal and a thicker porous layer of oxide forms on the top of this dense layer [13]. The porosity may account for some of the increased thickness of the oxide layer.

For 1250 °C, a plateau cannot be easily defined. With increased initial metal thickness, evaporation of aluminium and pooling of aluminium on the aluminium nitride substrates are expected to complicate the growth of oxide films. As is shown in Fig. 6, there is a high degree of porosity in the oxide film and the growth of the oxide film is not uniform.

For samples oxidized at 1100 °C, with an initial aluminium thickness of 4 μm, a plateau region is not observed for oxidation times less than 12 h. The reason for this is that the aluminium film has not been completely oxidized over the time frame studied.

Typical oxygen maps of samples oxidized in air are shown in Fig. 7. It should be noted that the oxide films were not always continuous. This was most prevalent in oxidized samples originally covered with 4 μm aluminium. The films formed by the oxidation of aluminium layers were investigated by X-ray diffraction. After oxidation of the aluminium layer, the oxide layer was found to be predominantly α-alumina by X-ray diffraction, see Fig .8.

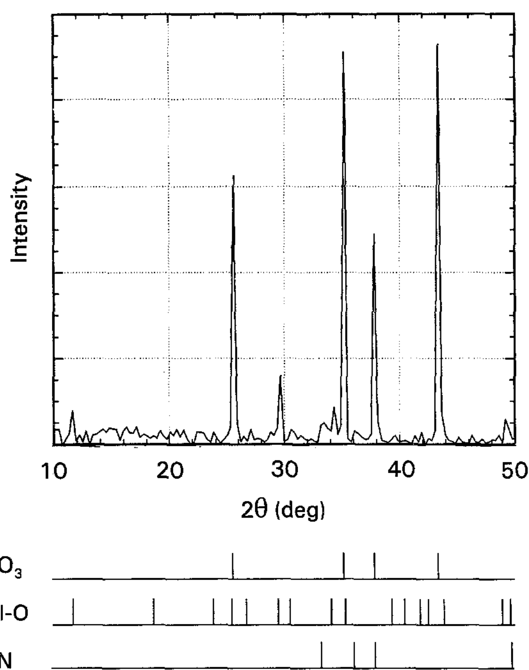
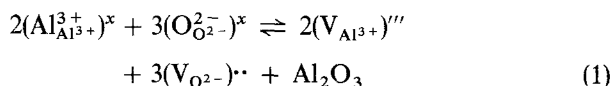


Figure 8 Thin-film X-ray diffraction patterns of aluminium nitride samples covered with an oxide film formed by the oxidation of an aluminium layer. The patterns were obtained with a fixed omega angle of 2°.

3.2. Kinetics

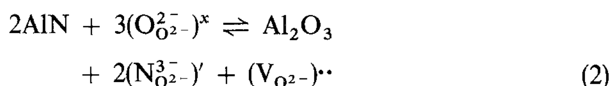
In this study of the oxidation of aluminium nitride samples covered with a thin film of aluminium, the kinetics involve a series of steps: (1) an initial rapid oxide formation due to the oxidation of the aluminium layer, (2) an incubation period, and (3) a second region of oxide growth. In the first region, oxidation occurs very fast. The driving force for this reaction is determined by the chemical potentials of oxygen at the Al/Al_2O_3 and the Al_2O_3/gas interfaces. After complete oxidation of the aluminium layer, the driving force for the continued growth of the oxide film becomes different and is finally given by the chemical potentials of oxygen and nitrogen established in the AlN substrate at the AlN/Al_2O_3 interface and in the gas near the Al_2O_3/gas interface. The values of the chemical potentials in AlN at the AlN/Al_2O_3 interface are determined by the rates of the nitrogen and oxygen transport through the oxide layer and across the AlN/Al_2O_3 and the alumina/gas interfaces. Thus, it may be expected that these chemical potentials will change with time. Only if the overall kinetics are controlled by ion transport through the product layer, will a steady state develop resulting in constant chemical potentials.

In addition to the changing driving force, the ion diffusivities in the oxide product layer will also change after the complete oxidation of the initial aluminium layer. The further growth of the oxide layer requires that nitrogen is transported across the alumina layer, most likely via oxygen vacancies (and also along grain boundaries). In sufficiently pure alumina, the concentration of oxygen vacancies is determined by the Schottky equilibrium



$$2(Al^{3+}_{Al^{3+}})^x + 3(O^{2-}_{O^{2-}})^x \rightleftharpoons 2(V_{Al^{3+}})''' + 3(V_{O^{2-}})^{\cdot\cdot} + Al_2O_3 \quad (1)$$

If the initial aluminium layer contains impurities, they may become incorporated into the oxide and control the concentrations point defects, i.e. cation and anion vacancies. At the AlN/Al_2O_3 interface, nitrogen ions have to become incorporated into the oxide layer to allow them to diffuse through this layer to the gas phase. This leads to the creation of oxygen vacancies according to the doping reaction.



$$2AlN + 3(O^{2-}_{O^{2-}})^x \rightleftharpoons Al_2O_3 + 2(N^{3-}_{O^{2-}})' + (V_{O^{2-}})^{\cdot\cdot} \quad (2)$$

Owing to this doping with nitrogen, the anion diffusion in the oxide layer is enhanced. This doping reaction cannot occur before the aluminium layer is completely transformed to alumina. The incubation period can then be attributed to the period between the time at which the first doping of alumina with

nitrogen takes place and the time at which the entire alumina layer has become significantly doped with nitrogen ions. After that, the overall kinetics become the same as those observed in the direct oxidation of AlN.

4. Conclusions

Oxide films formed by the high-temperature oxidation of vapour-deposited aluminium layers on aluminium nitride substrates in air at atmospheric pressure consist of α-alumina. In the oxidation process, the kinetics were complex and involved three different regions of oxidation in the case of thin aluminium films. The second region, an incubation period, demonstrates that a thin alumina layer formed by the oxidation of an aluminium film may be used as a protective layer against the oxidation of aluminium nitride substrates at high temperatures. A lack of oxide film continuity is at least partially caused by pooling and evaporation of aluminium during the oxidation process. This quality problem could be solved by doping the aluminium layer with metal impurities (which has also been shown to affect the overall oxidation kinetics [9, 10], and/or by altering the heat treatment including the environment present during heating.

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