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## Residual Stress Mechanisms in Aluminium Oxide Films Grown by MOCVD

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Residual stresses in amorphous aluminium oxide films were investigated with *in situ* wafer curvature measurements. The films were deposited from aluminium tri-isopropoxide, on sapphire substrates. Large tensile stresses of 1-2 GPa occurred during growth. These values are well above the fracture stress in bulk materials, but they are sustainable in thin film form. Subsequent heat treatment of these films produced additional tensile stress, even at low temperatures prior to crystallization. The mechanisms responsible for all of these stress contributions are discussed. The variety of operative mechanisms at low to moderate temperatures in these amorphous films suggests that different processing routes can be used to engineer significant differences in the final stress state of these materials.

### Introduction

Aluminium oxide is a material of high technological interest for a wide range of applications. With numerous crystallized allotropic forms ( $\alpha$ ,  $\gamma$ ,  $\kappa$ ,  $\delta$ ,  $\theta$ ,  $\chi$ ,  $\eta$ ,  $\epsilon$ ) and the amorphous form, aluminium oxides are widely used as protective coatings in the metal cutting tools industry, for optical and microelectronic components, catalyst supports, and for protection against corrosion and high temperature oxidation. Metal-Organic Chemical Vapor Deposition (MOCVD) is an appropriate interesting technique for producing these coatings, especially on complex-shape materials and temperature-sensitive materials. The composition, allotropic form, microstructure and crystallinity of films can be adjusted by varying the MOCVD experimental conditions. Knowing the correlation between processing conditions and the composition of such films should help optimize the process with regards to any required property of use.

### Experiments

#### Film Growth

Sapphire substrates were used for this work, to prevent the large thermal stresses that can occur when other substrates are used. This also removed any uncertainties about possible stress contributions from interface reactions between the film and substrate.

The alumina films were processed by MOCVD from aluminium tri-isopropoxide (ATI) in a horizontal hot wall reactor. ATI is a convenient precursor for the processing of aluminium oxide coatings. In a previous contribution to this conference, its shelf-life and thermal stability have been investigated in detail [1]. It will be recalled here that despite its instability and trend to ageing, it can be used easily if it is stored in a glove box and if

it stays only a few hours in the bubbler. 10 mm \* 27 mm sapphire plates were used as the substrate material. The curvature of these substrates was measured prior to deposition, using the MOSS technique. This provided a reference curvature value, for the subsequent stress measurements of the films.

The MOCVD apparatus was described in previous papers [2]. The precursor was melted in a bubbler at 413K and was kept at 373K during deposition. Deposition was investigated using nitrogen as a carrier gas, at a pressure of 0.67 kPa. The processing conditions are detailed in Table I.

**TABLE I:** Processing conditions for the aluminum oxy-hydroxide and amorphous alumina coatings

Sample number	T <sub>deposition</sub> (K)	P (torr)	Q <sub>total</sub> (sccm)	Q <sub>N<sub>2</sub>, ATI</sub> (sccm)	Q <sub>N<sub>2</sub>, dil</sub> (sccm)	Q <sub>ATI</sub> (sccm)	T <sub>ATI</sub> (K)	P <sub>ATI</sub> (kPa)
08-0107-24	623	5	653	20	631.5	1.54	373	0.67
08-1612-26	623	5	653	20	631.5	1.54	373	0.67
08-0207-25	823	5	653	20	631.5	1.54	373	0.67
08-1712-27	823	5	653	20	631.5	1.54	373	0.67

### Multibeam Optical Stress Sensor (MOSS)

During temperature controlled heating, the curvature of the film-substrate system was systematically measured using *in situ* MOSS [5,6]. The schematic ray diagram shown in Fig 1, describes the working principle of this system. In this apparatus an etalon splits a He-Ne laser beam into an array of parallel beams, which are further directed on a polished surface of the substrate through a flat mirror assembly. These incident parallel beams reflect off the polished substrate, and these reflected signals are captured on a charge-coupled device (CCD camera). The spots spacing were further tracked through KSAMOS software provided by K Space Associates.

Stoney's equation was used to relate the stress to the measured curvature [5]. In the most basic form the Stoney's equation relates the curvature of the substrate to the stress in a thin film undergoing very small deformations as

$$\kappa = \frac{6\sigma_f h_{film}}{E_s h_s^2} \quad (1)$$

where  $\kappa$  is the curvature of the substrate,  $E_s$  is the elastic modulus of the substrate,  $h_s$  and  $h_f$  are the heights of the substrate and film respectively, and  $\sigma_f$  is the average stress in the film. The formula does not involve the properties of the film material, nor does it presume any particular through thickness distribution of the film stress. Thicker films typically require a corrected form of Eq. (1) [8], however, this is not necessary for the thin films studied here.

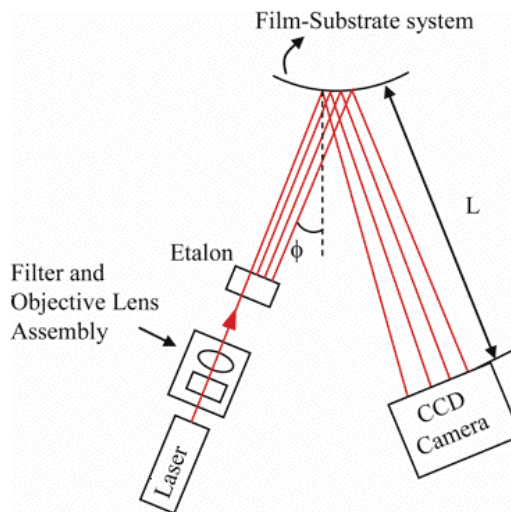


Figure 1 Multi beam Optical Stress Sensor (MOSS) [5,7].

## Results

### Film characteristics

Previous work reports the composition of these coatings (prepared by pyrolytic decomposition with ATI vapor and nitrogen as carrier and dilution gas, and in the temperature range 623 - 973 K) [1-3]. It was shown that the aluminium oxide composition depends on the processing temperature. Films prepared at 623 K are composed of amorphous aluminium oxy-hydroxide, AlO(OH). Deposition temperatures between 688K and 973K produced stoichiometric, amorphous and compact Al<sub>2</sub>O<sub>3</sub> films. A cross-sectional image of such a film grown on silicon at 723K is shown in Fig.2.

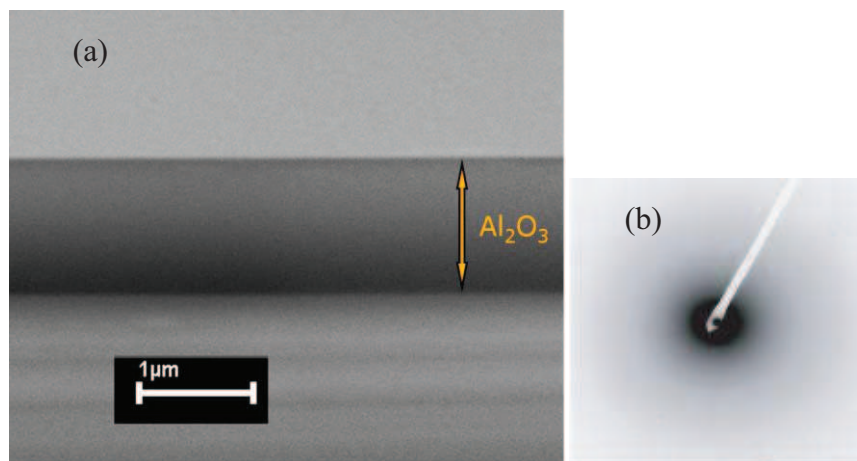
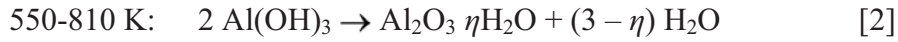


Figure 2 (a) cross-sectional transmission electron microscopy (TEM) image of alumina film deposited on Si at 450 °C. (b) electron diffraction shows that the films are amorphous.

Between 623K and 688K, the films are hydroxylated. In this range, the film composition changes gradually from AlO(OH) to Al<sub>2</sub>O<sub>3</sub> with increasing temperature. These results

were confirmed by TGA-DTA analysis and Fourier transform infrared (FTIR) spectroscopy. This characterization has led to a better understanding of the reaction mechanisms that operate when hydroxylated deposits are heated. If the films are not stored in a dry atmosphere, the AlO(OH) films absorb water from the atmosphere. On heating, these hydrated AlO(OH) films first transform into tri-hydroxide Al(OH)<sub>3</sub>, which subsequently transforms to alumina. These reaction steps can be described as follows:



where  $x > 1$  and  $\eta < 3$ . Films that were deposited at 983K showed wide diffraction peaks attributed to partially crystallized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. After annealing these films for one hour, x-ray diffraction showed improved crystallization of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [3].

The characteristic of the films as described above, clearly show that alumina microstructure varies with temperature. Based on these results, the two temperatures, 623K and 823K, corresponding to aluminium oxy-hydroxide and amorphous alumina respectively, were selected to initiate investigations of the stress in the films with the MOSS technique. The objective was to correlate the growth stress with the growth temperatures. The present work is complementary to the one by Huntz *et al* [4], where a deflexion technique was used along with X-ray diffraction to evaluate stresses due: (i) to the difference between the coefficients of the thermal expansion of the MOCVD alumina films and the metal substrates, and (ii) to the phase transformation of alumina, from the amorphous to the crystalline state.

**TABLE II:** Stress measurements of alumina coatings, after heating to different temperatures.

Sample number	T <sub>growth</sub> (K)	h <sub>film</sub> (μm)	(Stress) <sub>298 K</sub> GPa	(Stress) <sub>623 K</sub> GPa	(Stress) <sub>873 K</sub> GPa	(Stress) <sub>1048 K</sub> GPa	(Stress) <sub>1123 K</sub> GPa
08-0107-24	623	0.50	1.86	1.82	1.89	1.88	1.94
08-1612-26	623	0.52	1.75	1.74	1.75	1.73	1.75
08-0207-25	823	0.40	2.10	2.11	2.34	2.31	2.41
08-1712-27	823	0.38	2.44	2.45	2.42	2.47	2.49

### Stress measurement

Residual stresses in the alumina coatings were investigated using MOSS at different heating cycles in a controlled atmosphere. The as grown films exhibited very large growth stresses (~1-2GPa). A typical stress thickness profile of one of the above mentioned alumina coating is shown in Fig. 3.

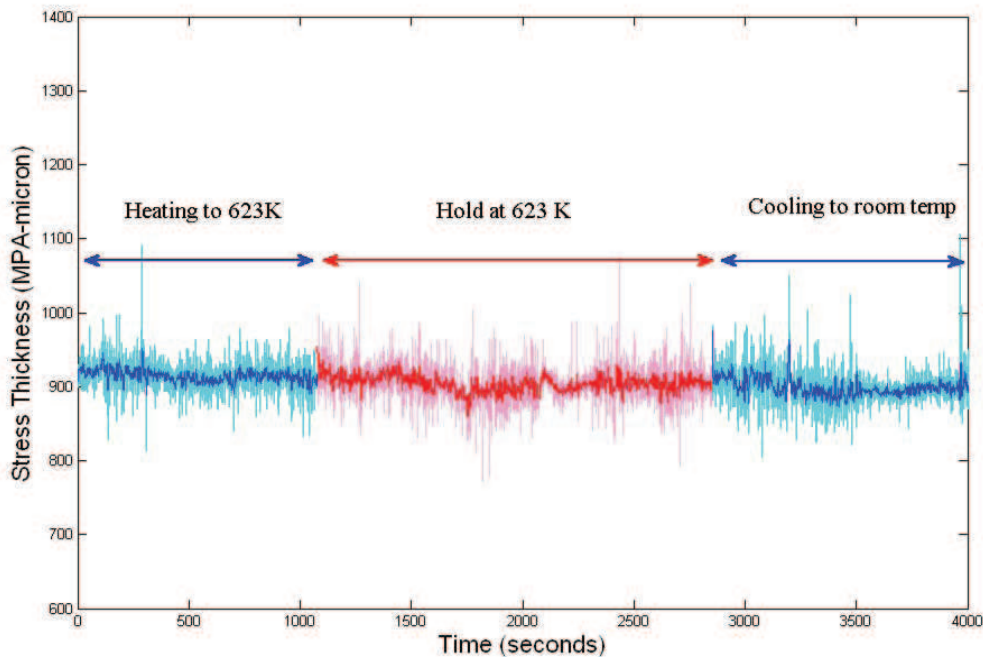


Figure 3 Typical stress thickness response of Alumina coating at 623K

Stresses were recorded during heating, holding, and then cooling of these specimens. All films demonstrated the same large tensile stresses at the room temperature. The measured stress values after different heating cycles (to 298, 623, 873, 1048 and 1123 K) are also reported in Table II. In many cases, heating and cooling of these specimens led to little or not change in the room temperature stress (see Fig. 3). Heating to higher temperatures produced some additional stresses, but these were usually less than 0.1 GPa, and thus they did not significantly alter the large growth stress. Note also that the maximum temperature exceeded the point where crystallization begins (~1050 K).

Compositional stresses due to oxidation and reduction cycling were also investigated in these alumina films. We have previously shown that oxygen vacancy concentrations in non-stoichiometric oxides can lead to significant changes in the stress values [6,9]. This effect is not expected to play a role in crystalline  $\text{Al}_2\text{O}_3$ , however, reduction produced variations in the amorphous structure of these coatings at sufficiently high temperature. In alumina, these preliminary experiments resulted into a systematic drop in tensile stresses while subjected to reducing atmosphere (inlet gas composition of 0.55%  $\text{CO}$ , 5.53%  $\text{CO}_2$ , 44.72%  $\text{H}_2$ , 49.2%  $\text{N}_2$ , at 100 Torr). Repeating the oxidation treatment completely reversed this stress, as seen in Fig. 4.

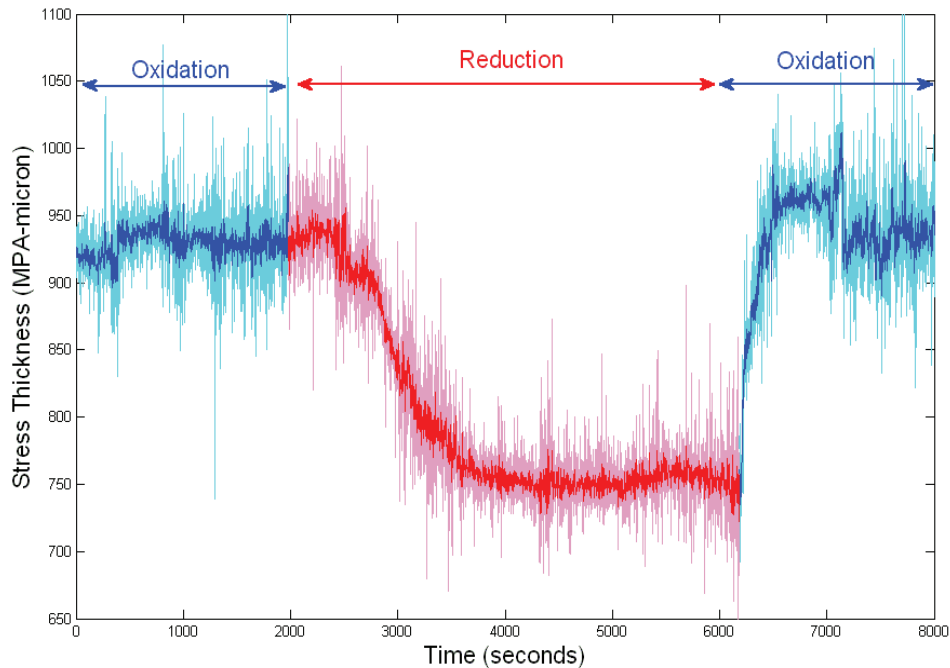


Figure 4 Compositional stress behavior of Alumina coating at 1223 K.

### Discussion and Conclusions

The residual stress in these films is dominated by the large, tensile stress produced by the growth process. While these values exceed the fracture stress for bulk materials, they are sustainable in thin film form. Growth stresses of this magnitude that have been observed in polycrystalline films are generally attributed to grain boundary formation. With these amorphous films, the mechanism responsible for such large stresses is not clear at this point. However, the tensile stress implies that there is some type of densification of the film material, either after or as material is added to the growth surface. Similar behavior has been observed in evaporated, amorphous Ge films, however, the cause of these stresses is not currently understood [10]. If growth stresses reported in Table II (298 K values) are primarily associated with structural rearrangements of the amorphous oxide, one might expect to see higher stresses at lower growth temperatures. However, the reverse effect was observed here, with an average stress increase of roughly 25% when the growth temperature was increased from 623 to 823 K. This increase may be associated with the higher growth rates that occur at higher temperature.

The additional stresses produced by subsequent heat treatments in air produced were more modest, even at temperatures up to 1123 K, where significant crystallization to gamma alumina occurs. Thus, while the crystallization indicates that short-range atomic rearrangement is occurring, the limited change in the stress indicates that longer range diffusion of at least one species, Al or O, is limited (i.e., because diffusion of both species would lead to stress relaxation).

The cause of the large compressive stresses observed under reducing conditions is also unclear at this point. This effect may be related to either oxygen removal, or hydration (due to the hydrogen in the reducing atmosphere). Since these stresses are reversible, they do not appear to be strongly affected by crystallization.

In general, the large residual tensile stresses observed here are detrimental because they promote the formation of tensile cracks. However, for possible applications on metal substrates, the large tensile stresses that occur during growth can potentially be used to offset large thermal compressive stresses that occur during cooling. Thus, in these systems the control of growth stresses can potentially be used to optimize the final residual stress state.

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