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To cite this version:

A. Jones, D. Houlton, S. Rushworth, G. Critchlow. A New Route to the Deposition of Al2O3 by MOCVD. Journal de Physique IV Proceedings, 1995, 05 (C5), pp.C5-557-C5-560. 10.1051/jphyscol:1995566 . jpa-00253928

HAL Id: jpa-00253928
https://hal.science/jpa-00253928

Submitted on 4 Feb 2008

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JOURNAL DE PHYSIQUE IV
Colloque C5, supplément au Journal de Physique II, Volume 5, juin 1995

A New Route to the Deposition of Al_2O_3 by MOCVD

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Abstract. Thin films of aluminium oxide, Al_2O_3, have been deposited by atmospheric pressure MOCVD using trimethylaluminium (Me_3Al) and iso-propanol (Pr^iOH) as precursors. The films were deposited over the temperature range 400-600°C and had growth rates of up to 67 Å min^{-1}. Analysis by Auger electron spectroscopy showed that films deposited at 400°C were high purity with carbon contamination < 0.5 at %.

1.INTRODUCTION

Thin films of aluminium oxide, Al_2O_3, have a variety of important applications such as, optical and electro-optical coatings, oxidation and wear-resistant coatings, and in semiconductor device fabrication, e.g. as passivating layers, as a gate oxide and for photolithographic masking [1].

Chemical vapour deposition (CVD) is an attractive technique for the growth of Al_2O_3 films as it has the capability to produce uniform films of excellent quality, at relatively low temperatures, on substrates which may have a complicated geometrical shape.

The CVD of Al_2O_3 is most frequently carried out by the oxidation or hydrolysis of aluminium trihalides, such as $AlCl_3$ [2-4] at elevated substrate temperatures (typically > 950°C) resulting in exceptionally hard coatings which are useful in anti-corrosion and wear-resistant applications.

Where lower deposition temperatures are required, for instance in the production of certain semiconductor devices, metalorganic aluminium compounds, e.g. trimethylaluminium (Me_3Al), have been used as precursors to Al_2O_3, using either O_2 [5-7] or N_2O [8,9] as oxidants. However, although this approach allows the growth of Al_2O_3 films at low/moderate temperatures (*ca.* 400-700°C), the high reactivity of the pyrophoric Me_3Al compound can lead to a serious problem of premature reaction and to powder deposition upstream of the substrate. In addition, incomplete oxidation of the R_3Al species can lead to severe carbon contamination in the resulting Al_2O_3 films.

The use of aluminium isopropoxide $Al(OPr^i)_3$, either with or without added O_2, avoids the problem of prereaction and permits the deposition of Al_2O_3 at temperatures of 250-450°C [5,10]. However, $Al(OPr^i)_3$ is a polymeric solid (m.pt. 118°C) with a low vapour pressure of only 5 Torr at 134°C, necessitating the heating of source and reactor inlet lines to >100°C to prevent precursor condensation. In addition, $Al(OPr^i)_3$ is extremely hygroscopic and the hydroxide content and thermal history of the precursor have been shown [11] to have a significant effect on the deposition rate of the Al_2O_3 film.

It is therefore desirable to develop an alternative precursor system which may avoid the problems of prereaction, and those associated with the use of the low vapour pressure precursor $Al(OPr^i)_3$. In this paper we report a new approach to the deposition of Al_2O_3 by metal-organic CVD in which the 'active' $Al(OPr^i)_3$ precursor is formed *in situ* in the gas phase from vapour mixtures of the volatile

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphyscol:1995566

precursors Me_3Al and isopropanol (Pr^iOH). This has allowed the deposition of Al_2O_3 at low/moderate substrate temperatures without significant prereaction.

2. EXPERIMENTAL

2.1 General Techniques

Auger electron spectroscopy (AES) was carried out using a Varian Auger electron spectrometer. The atomic compositions quoted are from the bulk of the film and were obtained by combining AES with sequential Ar^+-ion bombardment until comparable compositions were obtained for consecutive data points. Film thicknesses were estimated from the time taken to sputter through the layer using Ar^+-ion bombardment.

Transmission electron microscopy (TEM) and electron diffraction (ED) were performed on a Jeol JEMI00CX instrument.

2.2 Al_2O_3 Film Deposition

The Al_2O_3 films were deposited at atmospheric pressure in a cold wall horizontal quartz reactor (Electro Gas Systems Ltd) using radiant substrate heating. The substrates used were 316 grade stainless steel and these were degreased with acetone and dried before use.

The Me_3Al and Pr^iOH sources were operated at or near room temperature (17.5 - 22.7°C) using conventional MOCVD 'bubblers' and N_2 carrier gas. The source vapours were mixed in a 'T-piece' at the reactor inlet and this was heated at 80°C to prevent condensation of $Al(OPr^i)_3$ formed *in situ*. The specific growth conditions used for each Al_2O_3 film are summarized in Table 1.

Table 1. Growth conditions used to deposit Al_2O_3 films

Run No.	1	2	3	4	5	6	7	8	9
Me_3Al Flow Rate (μmol min^{-1})	14.8	28.0	27.1	35.2	29.0	24.4	23.9	27.1	28.4
Pr^iOH Flow Rate (μmol min^{-1})	77.8	148.0	144.4	358.5	305.5	264.5	389.2	433.1	449.7
O:Al ratio	5.2:1	5.3:1	5.3:1	10.2:1	10.5:1	10.8:1	16.3:1	16:1	15.8:1
Substrate temp. (°C)	400	500	600	400	500	600	400	500	600

3. RESULTS AND DISCUSSION

Al_2O_3 films were successfully deposited, without significant prereaction, using Me_3Al and Pr^iOH at substrate temperatures of between 400-600°C. The Al_2O_3 deposition rate was found to be in the region of 67Å min^{-1} at 400°C (VI/III ratio ~ 16:1) which is close to the deposition rate of 70Å min^{-1} reported [10] for Al_2O_3 deposition at 420°C from $Al(OPr^i)_3$.

The films showed strong interference colour fringes, characteristic of a high refractive index material, and showed good adherence to the substrate (scotch tape test), although they were rather soft and could be easily scratched.

The atomic composition of the films was determined by AES and the data are summarized in Table 2.

The AES data confirm the Al_2O_3 composition of the layers and show, that at substrate temperatures of between 400-500°C, carbon is either not detected or is present close to the estimated detection limit of 0.5 atom%. At substrate temperatures of 600°C, however, trace carbon is a residual impurity in the films especially at low O/Al ratios (film no.3).

Analysis by TEM of Al_2O_3 films grown at 400°C (No.1) and 500°C (No.2) at an O:Al ratio of 5:1 showed them to be mainly amorphous, typical of films grown at low temperature by MOCVD [1], but with some microcrystallites present, see figure 1. The dimensions of the microcrystallites decrease from approx. 0.1μm to 0.05μm with increasing deposition temperature. Electron diffraction confirms the structure of the films as being both crystalline and amorphous, see figure 2.

Table 2. AES analysis of Al_2O_3 films grown on stainless steel using Me_3Al and Pr^iOH

Sample (from run no.)	**Substrate Temperature (°)**	**Composition (atom %)** Al	O	C	**Al:O ratio**
1	400	40.0	60.0	0.0	0.66
2	500	38.4	61.6	0.0	0.62
3	600	40.4	55.2	4.4	0.73
4	400	40.1	59.1	0.8	0.68
5	500	46.3	53.0	0.7	0.87
6	600	39.7	59.0	1.3	0.67
7	400	39.0	61.0	0.0	0.64
8	500	43.6	55.6	0.7	0.78
9	600	43.1	55.4	1.5	0.77

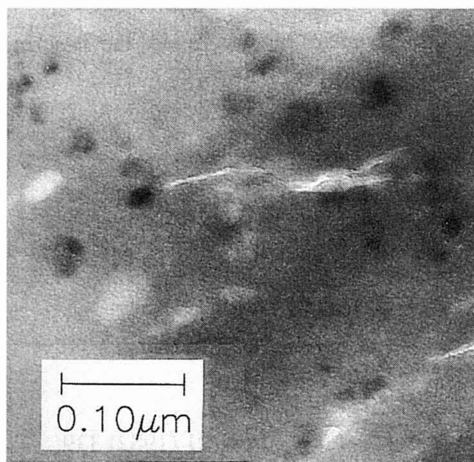


Fig. 1. TEM data for an Al_2O_3 film grown at 400°C using Me_3Al and Pr^iOH

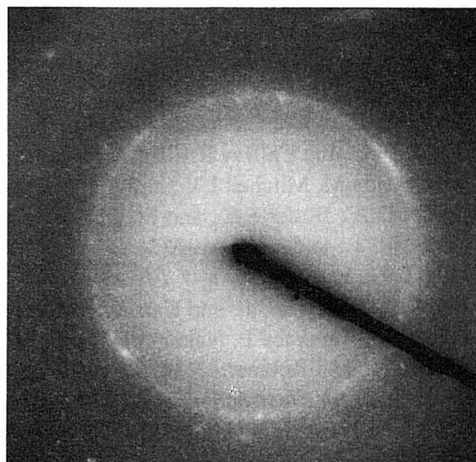


Fig.2. ED data for an Al_2O_3 film grown at 400°C using Me_3Al and Pr^iOH

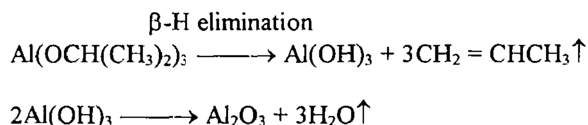
The mechanism of Al_2O_3 deposition from Me_3Al/Pr^iOH mixtures has not been established, however the very low levels of carbon contamination in films grown at 400-500°C indicates that an effective mechanism exists for the removal of carbon-containing alkyl radicals (e.g Me•) away from the growth zone. It is well established [12] that Me_3Al readily reacts with alcohols ROH to eliminate methane and form aluminium alkoxides $Al(OR)_3$. It is therefore probable that $Al(OPr^i)_3$ is formed as a gas phase intermediate from vapour mixtures of Me_3Al and excess Pr^iOH, scheme 1.

Scheme 1

$$Al(CH_3)_3 + 3(CH_3)_2CHOH \longrightarrow Al(OCH(CH_3)_2)_3 + 3CH_4 \uparrow$$

The deposition of Al_2O_3 from the gas-phase $Al(OPr^i)_3$ intermediate may then proceed by the mechanism proposed by Morssinkohof et al [13] in which the carbon containing fragments are removed by the ß-hydride elimination of propylene, see scheme 2, to produce $Al(OH)_3$ which subsequently decomposes on the hot substrate surface to deposit Al_2O_3, essentially free from carbon.

Scheme 2



The absence of carbon in Al_2O_3 films deposited at 400-500°C at VI/III ratios as low as 5:1 (i.e. films no. 1 and 2) indicates that the elimination reaction shown in scheme 1 is highly efficient. The increased levels of carbon contamination (1-4 at %) detected by AES in films grown at 600°C may be due to the decomposition of the iso-propyl radical via α-methyl elimination to produce surface (Me) species which subsequently decompose to deposit carbon [14].

4. CONCLUSIONS

Al_2O_3 films have been deposited, without significant prereaction, by atmospheric pressure MOCVD using Me_3Al in combination with Pr^iOH. The films were deposited over the temperature range 400-600°C and had growth rates of up to 67Å min^{-1}. Analysis by AES showed that films deposited between 400 and 500°C were high purity (C < 0.5 at %), although trace carbon (1-4 at %) was evident in films deposited at 600°C. A growth mechanism involving the *in situ* formation of $Al(OPr^i)_3$ in the gas phase prior to Al_2O_3 deposition has been proposed.

Acknowledgements

This work has been partially supported by the U.K. Department of Trade & Industry under the Teaching Company Scheme. David Houlton is a Teaching Company Associate (University of Keele).

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