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Carbonaceous alumina films deposited by MOCVD from aluminium acetylacetonate: a spectroscopic ellipsometry study

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Abstract. Spectroscopic ellipsometry was used to characterize carbonaceous, crystalline aluminium oxide films grown on Si(100) by low-pressure metal organic chemical vapour deposition, using aluminium acetylacetonate as the precursor. The presence of carbon in the films, attributed to the use of a metalorganic precursor for the deposition of films, was identified and analysed by secondary ion mass spectroscopy and X-ray photoelectron spectroscopy, for the elemental distribution and the chemical nature of the carbon in the films, respectively. Ellipsometry measurements over the photon energy range 1·5–5 eV were used to derive the pseudo-dielectric function of the aluminium oxide-containing films. Multi-layer modelling using linear regression techniques and the effective medium approximation were carried out to extract the structural details of the specimens. The excellent fit between the simulated and experimental optical data validates the empirical model for alumina-containing coatings grown by MOCVD.

Keywords. Aluminium oxide; optical properties; ellipsometry; MOCVD.

1. Introduction

Films of aluminium oxide are useful in a number of applications such as abrading and protective coatings (Haanappel *et al* 1993), electrical, optical and semiconductor devices (Pande *et al* 1983; Zhao and Suhr 1992; Ealet *et al* 1994). In the context of progressive miniaturization of CMOS devices, there is compelling need to consider alternatives to SiO_2 as the gate dielectric. Aluminium oxide has, therefore, been studied as a prospective gate oxide material for the next generation of MOSFET devices (Buchanan 1999; Ludeke *et al* 2000). Aluminium oxide films are also currently being investigated as a barrier layer in novel magnetic tunnel junction devices (Montaigne *et al* 2000; Gilbert *et al* 2001).

The metalorganic chemical vapour deposition (MOCVD) technique has been employed to prepare Al_2O_3 thin films using various chemical precursors in different ambient (Maruyama and Arai 1992; Kim *et al* 1993; Cilioberto *et al* 1995; Chryssou and Pitt 1997; Singh *et al* 2000), because MOCVD offers relatively low deposition temperatures and uniform deposition over large areas, both of which are significant process advantages. Moreover, the microstructure of materials can also be tailored by the use of an appropriate CVD precursor. However, the MOCVD process can lead to the incorporation of hetero-atomic species, such as carbon, into the film, as a direct result of the chemical composition of the precursors themselves. The presence of carbon may be expected to affect the dielectric and optical behaviour of such aluminium oxide films.

In present study, the deposition of aluminium oxide films was carried out in the inert ambient of argon by low pressure MOCVD at different growth temperatures, using aluminium acetylacetonate [denoted by $Al(acac)_3$], as the source material. This metalorganic complex has advantages over organometallics such as trimethyl aluminium (TMA) with respect to safety, availability, and cost. Spectroscopic analysis was used to examine the presence of carbon embedded in the films deposited, and to identify the chemical nature of the carbon present. To deduce the effect of carbon on the dielectric properties of this aluminium oxide-containing composite material, optical measurements were carried out using spectroscopic ellipsometry on the as-grown films.

2. Experimental

The deposition of thin films was carried out on Si(100) in a home made, low-pressure, horizontal, hot wall CVD reactor, using $Al(acac)_3$ as the precursor. The depositions

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were carried out at 600°C, 700°C, and 750°C, with ultra high purity (UHP) argon as the carrier gas. No reactive gas, such as oxygen, was used. The details of the deposition process are given in table 1. Prior to deposition, the substrates were cleaned in trichloroethylene (TCE) ultrasonically for 10 min, following which they were boiled in TCE for 10 min. The surface morphology of the deposited films was examined by optical and scanning electron microscopy. The depth profile of the elemental (chemical) composition of the films was obtained by secondary ion mass spectroscopy (SIMS), using the IMS4f CAMECA system. X-ray photoelectron spectroscopy (XPS) analysis was carried out using a VSW spectrometer with a resolution of 1 eV, employing the Al K_α source, with Ag $3d_{5/2}$ as the calibration standard. Prior to gathering the XPS spectra, all films were etched by an argon ion beam for 30 min, to remove the top layers of the film contaminated by exposure to air. A commercial spectroscopic ellipsometer (Sopra ESVG) was used to carry out the measurement of the real and imaginary parts of the pseudo-dielectric constants in the energy range of 1·5–5 eV, with a step size of 0·01 eV and a 75° incidence angle. To interpret these data, a simulation was carried out on the basis of a multi-layer model for the film–substrate structure, based on the compositional analysis of the films. Standard (n, k) values were used for the constituent layers of the model, and a multi-parameter non-linear regression technique was employed. The Bruggeman effective medium approximation was used to extract the dielectric constants of the composite layer.

3. Ellipsometry of thin film structures

Ellipsometry is a sensitive technique wherein the polarization state of the light reflected from a surface is analysed in terms of the relative phase and amplitude of the parallel and perpendicular components of the electric field vector (Azzam and Bashara 1989). The changes in the polarization state are characteristic of the effective dielectric response of the materials. The measured ellipsometric parameters ψ and Δ are related to the Fresnel's coefficients by

$$\rho = (r_p/r_s) = \tan \psi \exp(i\Delta), \quad (1)$$

where ρ is the ratio of r_p and r_s, the complex Fresnel's coefficients for parallel and perpendicular components of the light, respectively. In (1), ψ and Δ correspond to the ratio of the modulus of the amplitudes of parallel and perpendicular components of the electrical fields and the phase difference between them. Using the Fresnel's relation, the real and imaginary parts of the complex dielectric response can be deduced, as a function of energy of the incident light, from the ellipsometric parameters.

In the case of a thin film dielectric material, the ellipsometric response may be understood by building a suitable multi-layer model of the specimen, including the various interfaces, and using this model to fit the experimental data. It is possible, through such a fitting procedure, to extract the depth-resolved information on the structure of the specimen, incorporating the multi-layer structure and, including the thickness of the dielectric layer(s) and the structure of the interfaces. In this work, the Levenberg–Murquard linear regression algorithm was used for this purpose.

Table 1. Conditions used during MOCVD of carbonaceous aluminum oxide films.

Substrate	Si(100)
Deposition temperature	450–900°C
Carrier gas	UHP Argon
Gas flow	20–35 sccm
Total reactor pressure	2–8 Torr
Deposition time	30–90 min
CVD precursor	Aluminum acetylacetonate [Al(*acac*)$_3$]

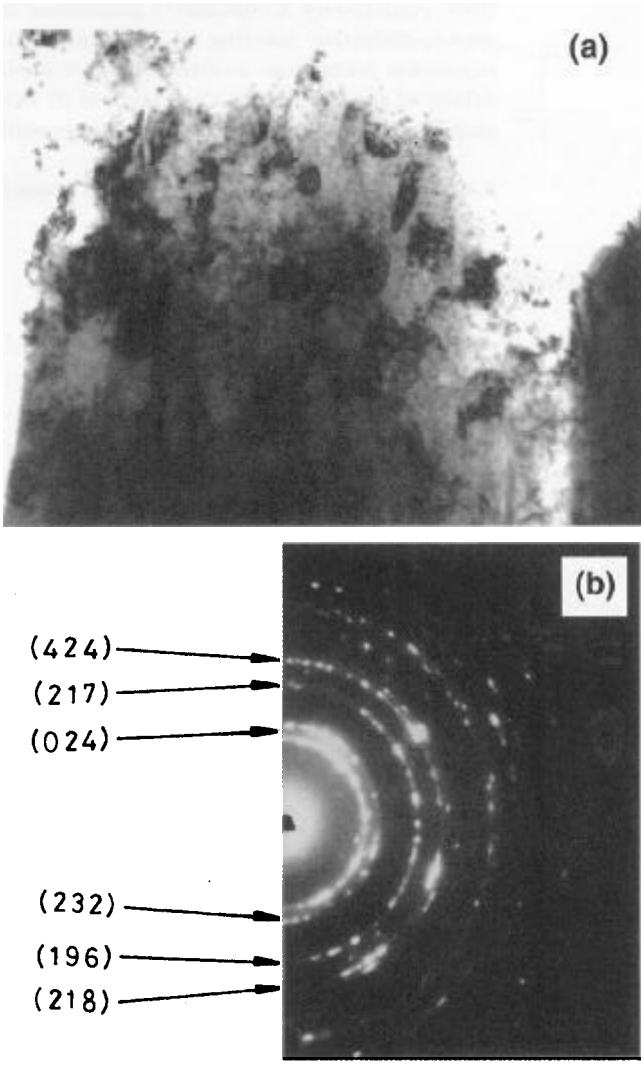

Figure 1. (**a**) Planar TEM image of film grown at 600°C on Si(100) and (**b**) the corresponding selected area electron diffraction pattern.

4. Results and discussion

As deposited, the films are smooth and shiny, and have a blackish tint, suggesting that carbon (from the precursor) might be incorporated in the films. Inspection with an optical microscope (400 ×) of the films grown at different temperatures shows that the films are free of pinholes. This is confirmed by SEM analysis. The films are poorly crystalline, as indicated by the very weak XRD patterns obtained. That the films consist of alumina crystallites embedded in an amorphous matrix is revealed by the planar TEM micrograph and selected area electron diffraction pattern shown in figure 1. The crystallites are of the polymorph κ-Al_2O_3, with an average size of ~ 50 nm. The amorphous matrix in which the crystallization takes place is illustrated clearly here.

SIMS depth profiles of the specimens reveal that the films are chemically homogeneous throughout their thickness (except near top of the surface, due to exposure to air). A typical depth profile of the specimen grown at 600°C is shown in figure 2. It is clear from this depth profile that carbon is present to a uniform degree throughout the thickness of the film. The presence of carbon in films deposited under these conditions is to be expected, as no oxidizing gas was employed. It may, therefore, be inferred that the amorphous matrix seen in figure 1 is made of carbon. It is also evident that the film–substrate interface is sharp and well defined.

The chemical nature of the carbon present in the alumina film would affect its dielectric behaviour—in particular, the dielectric response may be expected to depend on whether carbon is bound to aluminium forming a carbide (or an oxycarbide), or whether it is chemically unbound, "free" carbon. The core level XPS spectra of Al(2*p*) and C(1*s*) gathered on the film deposited at 600°C are shown in figure 3. The C(1*s*) spectrum reveals that the binding energy of carbon is of the order of 284·5 eV, which is assigned to graphitic carbon (Singh *et al* 2002). Furthermore, the symmetrical nature of the C(1*s*) spectrum shows that the carbon present in the films grown at various temperatures ranging from 500–800°C is graphitic in each case. The binding energy of the core-level Al(2*p*) is of the order of 74·5 eV, indicating that aluminium is in the Al^{3+} chemical state, corresponding to crystalline Al_2O_3 (Briggs and Seah 1989). Thus, films deposited by low pressure MOCVD on Si(100) from

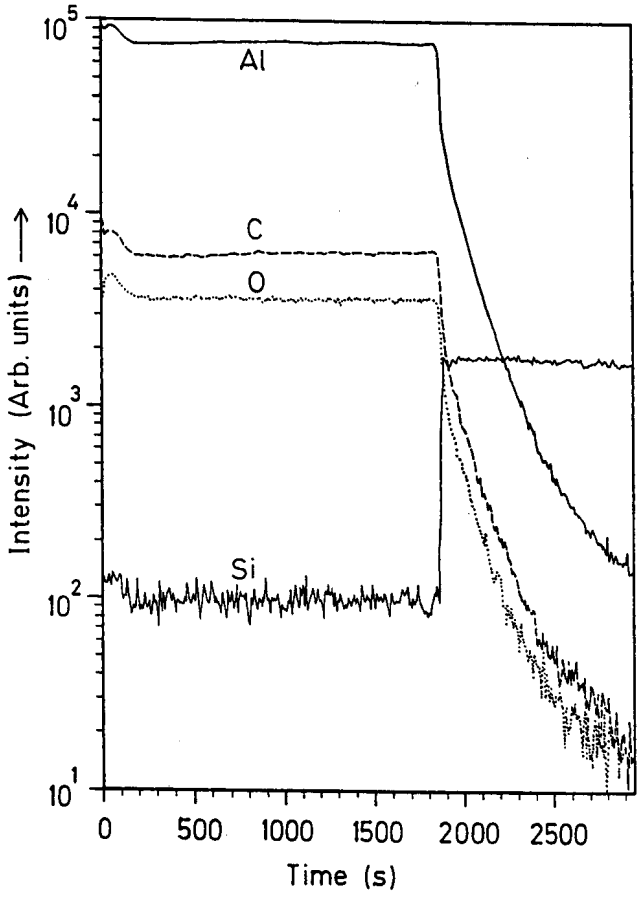

Figure 2. SIMS depth profile of film grown at 600°C on Si(100).

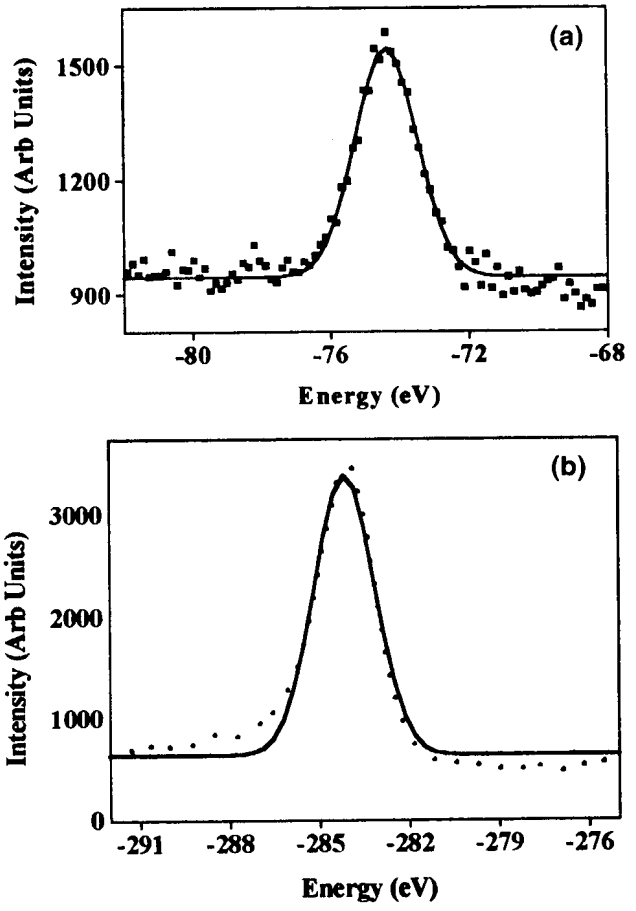

Figure 3. Core level XPS spectra of (**a**) Al(2*p*) and (**b**) C(1*s*) of film grown at 600°C on Si(100). Solid squares represent experimental data and solid line represents the Gaussian fit.

$Al(acac)_3$ under argon (inert) atmosphere at temperatures in the range 500–800°C comprise alumina grains embedded in a graphitic matrix, though the relative proportion of the two components in the film are not determined, and probably varies with the deposition temperature.

The ellipsometric parameters psi (ψ) and delta (Δ) measured in the energy range of 1·5–5 eV on all samples are shown in figures 4a and b, respectively. The complex pseudo-dielectric functions ε_1 and ε_2 were extracted from the measured ellipsometric parameters. The spectra of the specimens (figure 5) grown at different substrate temperatures are different. These data reveal that the pseudo-dielectric constants of the MOCVD-grown films are substantially different from those of the pure bulk aluminium oxide (Sopra 1997).

The ellipsometric data may be interpreted on the basis of a simulation using the multi-layer model shown schematically in figure 6. This model assumes that the bulk of the film is composed of crystalline alumina, graphitic carbon, and (optical) voids, the relative proportion of which may be expected to depend on the conditions of film deposition. Because thin films invariably have densities smaller than in the bulk, due to enhanced presence of quenched-in defects, we have added a void fraction of the films to the analysis. The film–substrate interface (interface I) is sharp, as revealed by the SIMS analysis, while the film–air interface (interface II) is of an unquantified roughness.

For the ellipsometric modelling of the dielectric spectra, dielectric spectra of high quality pyrolitic graphite were measured in the same ellipsometer. These data were then used in the structural modelling of the specimens. Stan-

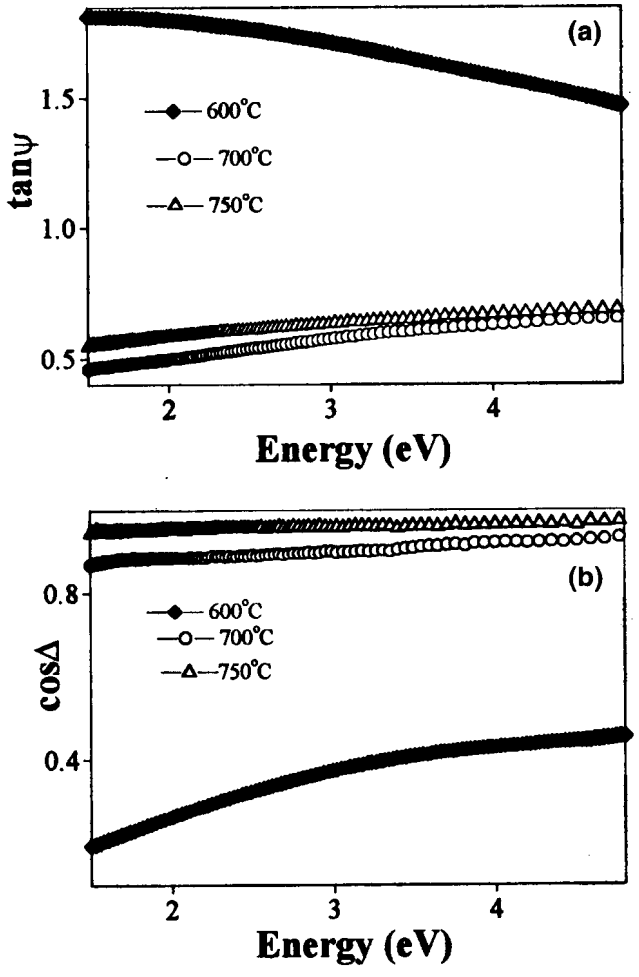

Figure 4. (**a**) Tan ψ and (**b**) cos Δ vs photon energy (eV) as measured by spectroscopic ellipsometry on specimens grown at different temperatures.

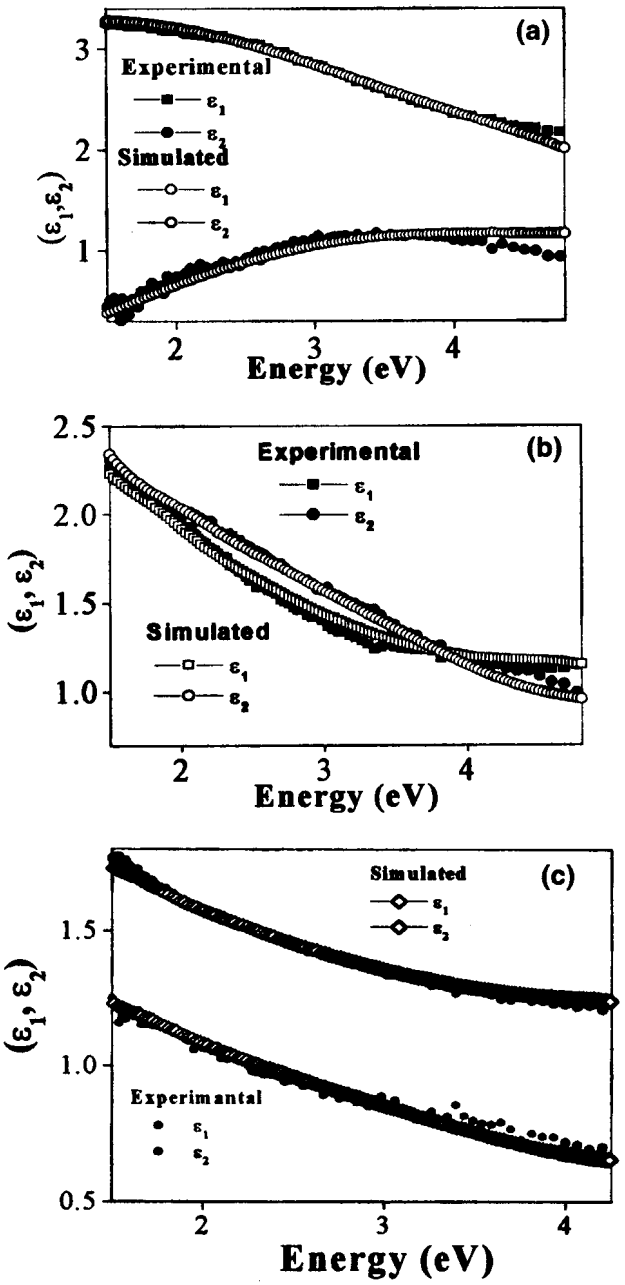

Figure 5. ε_1 and ε_2 vs energy for films grown at (**a**) 600°C, (**b**) 700°C and (**c**) 750°C.

Table 2. The parameters extracted from simulation of the ellipsometric data.

Growth temperature	600°C	700°C	750°C
Interface (II)	Rough interface ~ 51 nm % Roughness ~ 69	Rough interface ~ 44 nm % Roughness ~ 46	Rough interface ~ 55 nm % Roughness ~ 55
Bulk	Thickness: 5·3 nm Al_2O_3 ~ 86% Carbon ~ 14% Voids ~ 0%	Thickness: 520 nm Al_2O_3 ~ 44% Carbon ~ 30% Voids ~ 26%	Thickness: 833 nm Al_2O_3 ~ 11% Carbon ~ 41% Voids ~ 48%
Interface (I)	Thickness: 0 nm	Thickness: 0 nm	Thickness: 0 nm
Substrate	Al_2O_3*	Si	Si

*As the film is highly absorbing, radiation does not reach the silicon surface.

dard (n, k) data for bulk Si and α-Al_2O_3 were used for the modelling of the ellipsometric data, as no experimental data on κ-Al_2O_3 are available, and as it has been shown theoretically that the optical properties of κ-Al_2O_3 are similar to those of α-Al_2O_3 (Holm *et al* 1999). As mentioned earlier, the Bruggeman effective medium approximation was used for the film that may be considered an "aluminium oxide–carbon composite". The details of the fits are given in table 2. The complex pseudo-dielectric functions ε_1 and ε_2 measured in the energy range of 1·5–5 eV on the various samples, and the respective simulated ε_1 and ε_2 (based on the above model), are shown in figure 5.

While thin films of pure alumina are transparent over the range of photon energies employed, the carbonaceous films obtained in this study absorb radiation in this range to a great degree. For example, the films grown at 600°C are very thick (~ 2 μm) and absorb nearly all the incident light. As such, the silicon substrate does not contribute to the ellipsometric (optical) signal in the range of photon energies employed in this work. The simulation data reveal that, with increasing growth temperature, the concentration of aluminium oxide decreases, whereas the carbon concentration and void fraction are enhanced. It is noteworthy that, in the film deposited at 750°C, the void fraction rises to as much as 48%, while the fraction of alumina reduces to 11%. This is consistent with the reduction in the dielectric constant to ~ 1·5, whereas the reported values are in the range 6–9 for thin films of alumina, depending on the growth process and parameters, including the nature of the substrate. Given the confirmed presence of graphitic carbon in the films, and the evidence from SIMS analysis that carbon is distributed uniformly over the thickness of the films, we infer that the MOCVD-grown films form a "carbon–alumina composite" whose dielectric behaviour is significantly different from that of crystalline, bulk alumina. As seen from table 2, the fitting reveals that the surface roughness is noticeably greater in the film deposited at 600°C than it is in the film grown at 750°C. This may be interpreted in terms of the increased mobility of the growth species on the substrate surface, rendering the surface smoother at higher growth temperatures.

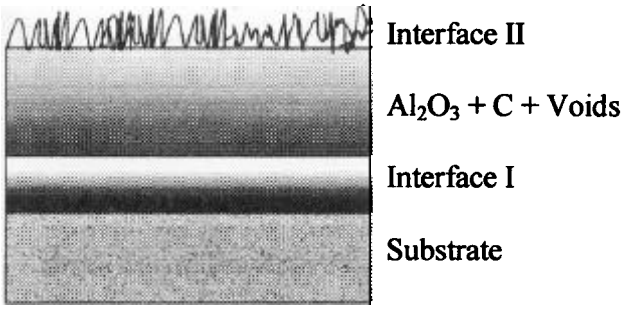

Figure 6. Three-layer model used for the simulation and analysis of ellipsometric data, including interfacial roughness.

5. Conclusions

The MOCVD process can be used to obtain films containing crystalline alumina—a refractory oxide—at relatively low growth temperatures, because of the Al–O bonds present in the molecular structure of a β-diketonate complex such as Al(*acac*)$_3$. If no reactive gas is employed, the resulting films consist of crystallites of alumina embedded in a carbon-rich matrix, as confirmed by compositional analysis. Spectroscopic ellipsometry reveals the significant influence carbon has on the dielectric behaviour of such a composite material over the optical range. The excellent fit that is obtained by including a large void fraction in the films, and the measured low dielectric constants of the films, suggest that the MOCVD process may be engineered to tailor the optical behaviour of thin alumina (-containing) films.

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