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A study on film formation mechanisms and precursor/solvent compatibility in PP-MOCVD of Al_2O_3 films using aluminum tri-sec-butoxide with hexane and toluene

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ABSTRACT

Pulsed pressure metal-organic chemical vapor deposition (PP-MOCVD) has been used to deposit aluminum oxide films using aluminum tri-sec-butoxide (ASB) as a precursor and hexane and toluene as solvents at 475 °C. Comparisons between solvent compatibility with ASB have been made. In addition to the solvents, different precursor/solvent solution concentrations (0.125 mol% and 0.5 mol%) and a shield have been used to investigate film formation mechanisms. This was done by studying the influence of these parameters on film properties (morphology and deposition rate). A droplet vaporization numerical model has been used to support explanations given for the dependence of properties on the process parameters. The results suggest that film formation might take place by four mechanisms including vapor phase deposition, Leidenfrost aerosol formation, homogeneous particle formation and liquid droplet impingement. The results also suggest that hexane has a better compatibility with ASB and is a better solvent than toluene.

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1. Introduction

Alumina in the form of powder or coating is a material that has wide applications in optoelectronic and microelectronic components due to its high band gap (9 eV), as a wear resistant agent and protection against corrosion and temperature oxidation [1]. Alumina films have been produced by various techniques including sol-gel synthesis [2,3], atomic layer deposition (ALD) [4], electron beam deposition (*E*-beam) [5], sputtering [6], pulsed laser deposition (PLD) [7], ultrasonic spray pyrolysis [8–11], spray deposition [12] and chemical vapor deposition (CVD) [13]. CVD has the ability to yield high deposition rates, excellent film uniformity over large surface areas and conformal coating of objects with complex shapes [14–17], making it a preferred route for thin film deposition.

Pulsed pressure MOCVD (PP-MOCVD) is a cost-effective variant of CVD. PP-MOCVD is a unique variant of direct liquid injection CVD where precursors are dissolved in a suitable solvent and fed into a continuously evacuated reaction chamber via an ultrasonic atomizer without the assistance of any carrier gas [18]. The exposure of liquid droplets to a vacuum causes flash vaporization [19,20] resulting in a near-instantaneous pressure spike followed by a pump down for each pulse. The rapid change in the chamber pressure results in an expansion mass transport regime [21,22]. The injection has to be done instantaneously for the droplets to be exposed to the minimum chamber pressure [17], otherwise particles would agglomerate thereby forming aerosols. Deposition through the formation of aerosols has a deleterious effect on the conformal coating desired for objects with complex shapes. According to Lee et al. [17], aerosol formation yields a line of sight coating of the substrate and can be avoided through the use of a shield (aerosol receptor). The shield prevents aerosols from contributing to film formation and resultant morphology and also reduces the presence of aerosols by providing secondary vaporization of the particles.

In PP-MOCVD, the deposition mechanism is determined by the precursor/solvent compatibility, concentration and the reaction chamber base pressure [17,23]. The precursor/solvent compatibility can be indicated by the difference in their vaporization rates estimated by comparing their enthalpies of vaporization (ΔH) and specific heat capacities (C_p) [23]. Droplet vaporization models by Boichot and Krumdieck [23] using titanium isopropoxide (TTIP) in hexane and toluene have suggested that a low $\Delta H/C_p$ and a low ΔH of the components results in a better droplet vaporization. A significant difference in the vaporization rate of the precursor and solvent could cause one of the components to vaporize leaving the other to freeze and form aerosols during deposition. High liquid-vapor conversion can be achieved if a precursor/solvent pair is selected such that both vaporize at the same rate [24].

Previous work on PP-MOCVD of alumina films using various precursors with hexane and toluene has shown aluminum tri-sec-butoxide (ASB) to be compatible with both solvents [25]. This study seeks to

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make further comparisons between the compatibility of the solvents with ASB. In addition, film formation mechanisms and the factors controlling them are studied. The experimental variables include the choice of solvents (hexane and toluene), precursor concentration and the presence/absence of a shield. The surface morphology, film composition and the deposition rate under different deposition conditions are analyzed. A numerical model describing droplet behavior of TTIP particles in hexane/toluene, developed by Boichot and Krumdieck [23] is also included with ASB substituted for TTIP to corroborate the experimental observations.

2. Materials and methods

A research-scale vertical reactor was used to deposit alumina films on 1 cm^2 silicon (100) substrates. The substrates were cleaned using a piranha solution (3:1 H_2SO_4:H_2O_2) followed by dilute HF dip to remove the native oxide layer. As-received ASB (Sigma-Aldrich, >97% pure, CAS Number 2269-22-9) was mixed with dry hexane and toluene to form solutions of 0.125 mol% and 0.5 mol% concentrations. The precursor/solvent solution was prepared in a glove box filled with dry N_2 gas (purity > 99.99%, obtained from BOC Ltd.) to avoid exposure to air and moisture. The solution was maintained in a pressurized bottle (75–85 kPa) under constant stirring to ensure homogeneous distribution of the precursor molecules in the solution. Fig. 1 shows a schematic diagram depicting the setup of the substrates and the shield (in some deposition runs) in the reaction chamber during deposition.

Pre-deposition, the cold walled glass chamber was cleaned and maintained at a low pressure of 40–50 Pa. The deposition temperature was kept constant at 475 °C by resistive heating of a Kanthal coiled wire, measured using a type-K thermocouple. The temperature was controlled by adjusting the power supplied to the Kanthal wire. During each cycle of 6 s, 100 μl of the solution was injected into the chamber. The ultrasonic nozzle operating at a frequency of 120 kHz yielded droplets of 18 μm diameter. The injection of the droplets produced a sharp pressure pulse in the reaction chamber and is followed by a pump down to the base pressure (100–110 Pa) between each cycle. The details of experimental parameters varied during deposition are given in Table 1. In some deposition runs a shield was placed at a distance of 15 mm from the top of the susceptor to understand the growth mechanism. On the table, WS means the shield was present during deposition while NS means the opposite.

Table 1
Parameters used during film deposition.

Solvent	Concentration (mol%)	Shield	Pulses
Toluene	0.125	WS	1050
		NS	500
	0.5	WS	500
		NS	500
Hexane	0.125	WS	1000
		NS	475
	0.5	WS	500
		NS	500

No post-deposition annealing of the samples was done. The surface morphology and chemical composition were analyzed using a JEOL JSM 7000F field emission, high resolution scanning electron microscope (SEM) fitted with Gatan cathodoluminescence detector and JEOL energy dispersive X-ray analysis system (EDX). The average film thickness was determined from cross-sectional SEM images. The accelerating voltage was maintained at 5 keV. All samples were pre-coated with gold for 120 s at 25 mA to prevent any charging effects. FTIR spectra were obtained from Bruker Tensor II ATR-FTIR spectrophotometer using absorbance measurement accessory. EDX and FTIR were performed at multiple locations on the sample, and the values were averaged. The surface roughness was measured using a NanoScope IIIa scanning probe microscope with a scan rate of 0.5 Hz.

3. Numerical modeling of droplet behavior

The numerical model describing the droplet behavior considers only the change in droplet diameter/mass and chamber pressure variations after the droplet is introduced into the chamber. The simulation of the model has been carried out using the Matlab software. Key input parameters in the model include the solvent (hexane or toluene) and solution concentration (0 mol%, 0.125 mol%, and 0.50 mol%). The concentration of the precursors is quite low to affect the chemical properties of the

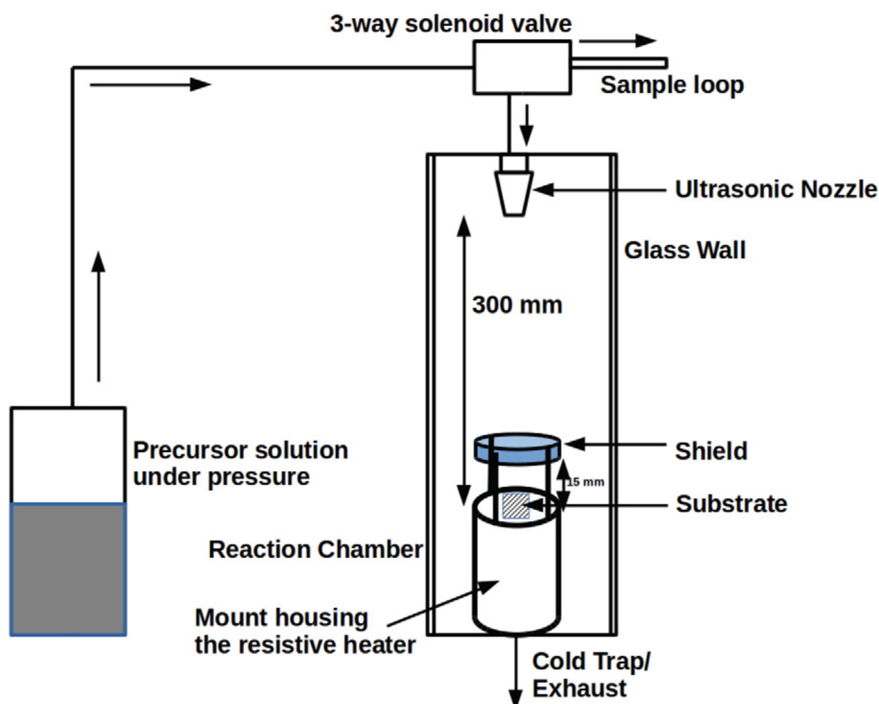

Fig. 1. Schematics of the pulse pressure MOCVD (PP-MOCVD) used in this study.

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