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Alumina particle reinforced TiO_2 composite films grown by direct liquid injection MOCVD

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ABSTRACT

The use of a liquid injection delivery system to form composite films containing nanoparticles was investigated. Al_2O_3–TiO_2 films were grown on silicon substrates by direct liquid injection MOCVD (DLI-MOCVD) at 400 °C. The α-Al_2O_3 nanoparticles (α-Al_2O_3NPs) dispersed in TiO_2 films resulted from co-deposition using colloidal α-Al_2O_3 solution and titanium tetraisopropoxide as titanium precursor. Scanning electron microscopy coupled with EDS as well as Raman spectroscopy confirmed the presence of α-Al_2O_3NPs aggregates embedded in the TiO_2 matrix. The liquid injection system coupled with CVD technique can be promising to form composite films containing preformed nanoparticles.

1. Introduction

Mechanical properties of materials are strongly dependent on their microstructure and they can be improved by adding a reinforcing phase to the matrix. It has been shown that the addition of a TiN, TiC or inorganic fullerene phase to ceramic matrix increases hardness, fracture toughness and thermal resistance [1–4].

Chemical and thermal stability, relatively good strength, thermal and electrical insulating characteristics have made aluminum oxide attractive for many engineering applications. Al_2O_3 nanopowders are usually added into ceramic-metallic materials to improve the toughness [5,6]. The quality of ceramic composite is controlled by the dispersion state of reinforcements in ceramic matrix. The colloidal dispersion of Al_2O_3 powders has been successfully applied in the field of structural ceramics [7,8]. For example, Laarz et al. [9] obtained homogeneous and agglomerate-free microstructures of Al_2O_3–TiC composites sintered by hot pressing technique. Colloidal solutions were prepared by adding dispersant and controlling pH.

Several deposition techniques have been used for elaborating composites containing alumina such as hot pressing sintering process [10], the liquid metallurgy [11] or the infiltration techniques [12]. Other works have investigated the synthesis of noble metal nanoparticles (NPs) on different substrates by atomic layer deposition [13–15], thermal evaporation [16,17] or magnetron sputtering [18,19]. Also, Parkin et al. [20] synthesized gold nanoparticle nanocomposite films by aerosol assisted chemical vapor deposition (CVD), using preformed nanoparticles. Recently, it has been reported the elaboration of nanostructured composite coatings, incorporating metal NPs by using liquid injection CVD from several precursors to obtain nanostructured composite coatings, incorporating metal NPs [21–23]. However, the use of a liquid injection using a preformed NPs colloidal suspension has not yet been reported for the insertion of NPs during the CVD growth of a matrix layer.

In this work, we explored the potential of a liquid injection delivery system on the feasibility of the dispersion of micro-scaled Al_2O_3 particles in a TiO_2 matrix. The main purpose was to develop an optimized process of the liquid injection system for Al_2O_3–TiO_2 composite films which yields dense and compact layers with homogeneous microstructure.

2. Experimental details

2.1. DLI-MOCVD deposition

Titanium tetraisopropoxide (TTIP, $Ti((OCH(CH_3)_2)_4$, Strem, 99.99%) was used as a precursor for TiO_2 thin film deposition by direct liquid injection MOCVD (DLI-MOCVD) and dissolved in anhydrous cyclohexane (C_6H_{12}, 99.99%, Sigma Aldrich) with a concentration of 1 M. Cyclohexane was chosen as solvent because it meets the requirements for the DLI-MOCVD process [24]. α-Al_2O_3 commercial nanopowder with an average particle size of 40 nm (PlasmaChem, 99.80%) was dispersed in isopropyl alcohol with a

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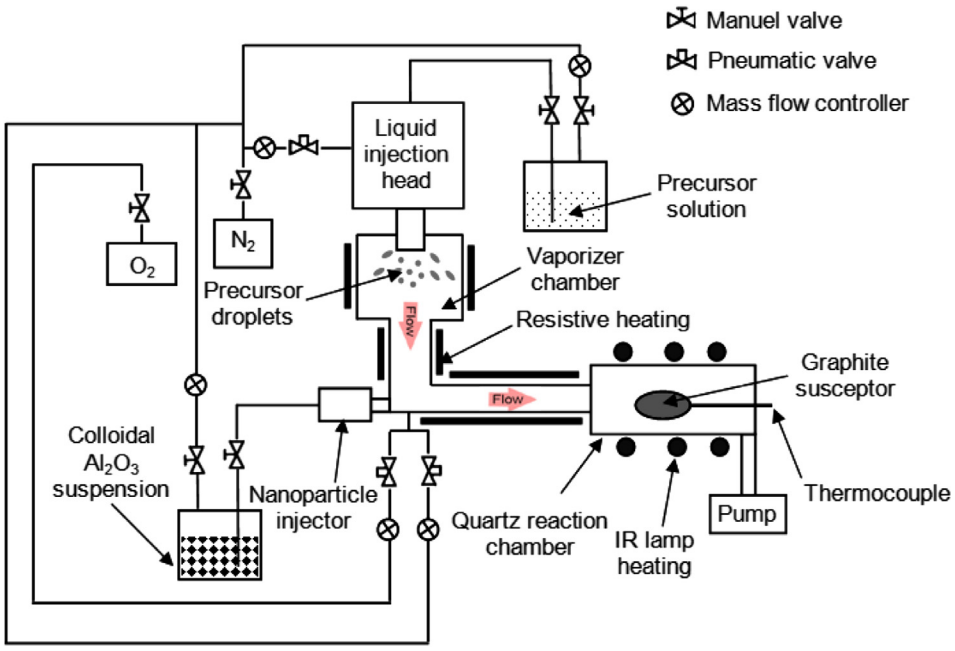

Fig. 1. Schematic layout of the direct liquid injection MOCVD system.

concentration of 10^{-3} M and pH of 8–9 [25]. Then the colloidal suspension was ultra-sonicated during 15 min.

The Si(100) substrates were ultrasonically cleaned in octane and in acetone. Then they were rinsed in ethanol and dried under N_2 gas flow. They were laid on a silicon carbide coated graphite susceptor supported by a quartz holder in the reaction chamber.

Al_2O_3–TiO_2 composite films were grown on Si(100) substrates by DLI-MOCVD process (Fig. 1) by using a MC-050 Annealsys CVD set-up which is equipped with a liquid injection head (Kemstream) which allows introducing a precursor aerosol, a NPs injector of the precursor, thermal vaporizer chamber and a quartz reaction chamber which is surrounded by halogen infrared lamps for heating monitored by a K-type thermocouple and proportional-integral-derivative (PID) controller. The liquid injection head is used for the introduction of a precursor aerosol while the NPs injector allows the injection of solution droplets. The liquid injection head is composed of liquid injector, mixture chamber and mixture injector (Fig. 2). The liquid injector pulses the precursor liquid into the mixing chamber where the liquid and the N_2 gas were blended. Finally, the mixture injector introduces in a pulsed regime a precursor aerosol.

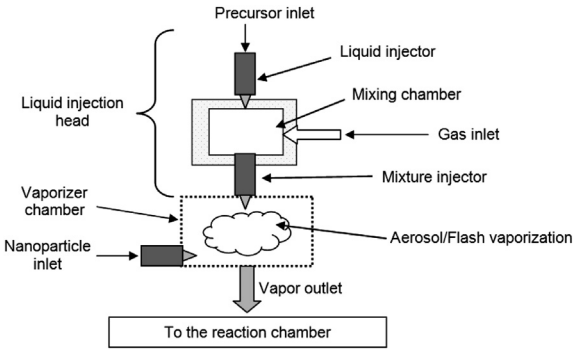

Fig. 2. Schematic layout of liquid injection head.

Table 1
Parameters used for Al_2O_3–TiO_2 composite film deposition by DLI-MOCVD.

Working pressure	10 mbar
Substrate temperature	400 °C
TTIP flow rate	0.1 g/min
Al_2O_3NPs solution opening time	3 ms
Al_2O_3NPs solution frequency	2 Hz
N_2 carrier gas flow	500 sccm

The precursor and α-Al_2O_3NPs solutions were kept in vessels at room temperature and pressurized under 3.5 and 1 bar of N_2 atmosphere, respectively. The precursor and Al_2O_3 were simultaneously introduced in the vaporizer chamber. After flash evaporation of both solutions in the vaporizer heated at 150 °C, the resulting vapor was transported into the reaction chamber by a N_2 and O_2 gas flow. N_2 was used as carrier gas whereas O_2 was used as a reactant. The deposition time is 20 min at the deposition

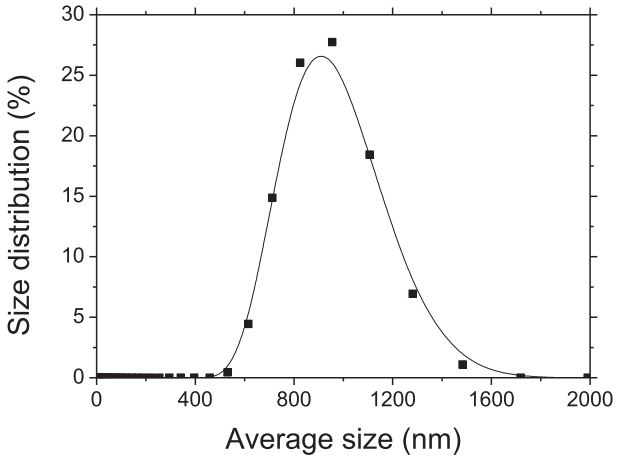

Fig. 3. Volume size distribution of Al_2O_3 suspension ultrasonicated during 15 min.