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Germania nanocrystals in Modified Chemical Vapour Deposition

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ABSTRACT

The Modified Chemical Vapour Deposition process for fabrication of silica-based optical fibres is used to generate nanoscale soot particles which are deposited on a substrate by thermophoresis and then sintered and collapsed into a preform from which optical fibre can be drawn. To increase the refractive index of the fibre core silica and germania soots are often generated together and co-deposited. The silica soot is invariably amorphous in character but for certain configurations of the preform lathe it has been found that germania soot particles may be crystalline. A systematic study has identified parameters controlling germania crystallinity in soot nanoparticles and transition from crystalline germania nanoparticles to glassy germania has been observed. The implications of possible retention of germania nanocrystals in preform and fibre are discussed with regard to fibre quality and optical performance.

1. Introduction

Addition of germania (GeO_2) is widely used to increase the refractive index of the core in silica-based optical fibres. Vapour Axial Deposition (VAD) and Modified Chemical Vapour Deposition (MCVD) are two processes commonly used for making optical fibre preforms with germanosilicate cores by simultaneously reacting halide compounds of Si and Ge to form oxide particles which are then deposited in layers to build up the refractive index profile (RIP) of the fibre core. The silica–germania ratio can be varied to create layers with different refractive indices [1].

In the MCVD process gaseous halides are reacted at high temperature with oxygen inside a high purity silica rotating substrate tube mounted in a glass lathe. The heat source is an oxy-hydrogen burner which traverses the outside of the substrate tube [2,3]. The solid oxide particles (soot) formed by the reaction are carried downstream from their point of generation by the gas flow. When they reach cooler regions away from the reaction zone the particles experience a radial thermophoretic force which causes them to be deposited on the inner surface of the substrate tube [4]. After deposition the layers of soot are sintered by increasing the burner temperature and finally the substrate tube is collapsed at even higher temperatures to form a solid preform rod which can be drawn into fibre.

Irregularities in the generation and deposition of the silica and germania soot particles lead to inhomogeneities in the RIP [5] and other defects which have a deleterious effect on the optical properties of the final fibre. In particular, crystallites in the fibre would be a gross defect since the transmitted light would be scattered by these, resulting in loss of optical intensity. There has been some limited early work by other authors on characterisation of oxide soot particles formed in MCVD [6]. Recent studies of silica soot particles (SiO_2) in MCVD have found them to be invariably amorphous [7]. Several studies of the VAD process [8–14] have reported that under certain conditions some of the GeO_2 soot particles formed are crystalline. Crystalline GeO_2 has never been reported in MCVD.

The objective of the present work is to characterise the morphology of germania soot generated by MCVD and to relate this to the mechanisms by which it is generated and deposited and to the details of the process and the MCVD equipment.

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2. Experimental procedure

Germanium oxide (GeO_2) soot particles were generated by reacting germanium tetrachloride ($GeCl_4$) with oxygen inside a silica glass tube (ID = 17mm, OD = 20 mm). The oxy-hydrogen burner was kept stationary for this and the hot-zone temperature was set at 1200 ± 50 °C. The temperature was monitored by a pyrometer focussed on the hottest part of the exterior of the substrate tube. Before soot generation was commenced the inner surface of the quartz tube was etched with sulphur hexafluoride (SF_6) to remove surface contamination and minor defects. Steady flows of a reactant mixture (O_2 and $GeCl_4$ at 50 cc/min), with additional O_2 at 600 cc/min, as a carrier gas were established through the substrate tube for about 7 minutes before starting the oxy-hydrogen burner. Since the burner was stationary soot samples were generated over as short a time as practicable to avoid deformation of the substrate tube, though long enough to produce a sufficient quantity of soot for analysis. Precursor flow-rates and temperatures were kept constant. The substrate was either kept stationary or rotated at 30 rpm.

Two different burner designs (A and B) were used. Burner A was larger and heavier in construction and had higher thermal mass than Burner B. The two designs are illustrated in Fig. 1 and their dimensions are compared in Table 1. Both types of burner were used to deposit germania soot inside a non-rotating substrate tube. Burner A was also used to deposit soot inside a rotating substrate tube which is the normal condition used in optical fibre preform fabrication. Soot generation rate was slower with Burner B and longer soot collection times were required. Soot was deposited for 4 minutes with Burner A and 12 minutes with Burner B.

Once soot deposition was complete the substrate tube was removed from the MCVD glass lathe. The substrate tube with the germania soot on it was then circumferentially scored in five places at ~50 mm intervals and carefully snapped into six sections, so as not to damage the deposited layer. The first section corresponded to the mid-point of the burner. Samples of the unfused soot adhering to the substrate wall were scraped off each of the six 50 mm sections. Each soot sample was then dispersed separately in ethanol for about 10 minutes in an ultrasonic bath.

Several droplets of each soot-in-ethanol mixture were placed on a transmission electron microscope (TEM) mesh grid and allowed to dry. The samples were characterised topologically, compositionally and by electron diffraction using a Phillips CM12 TEM at 120 kV, a JEOL 3000F High Resolution Transmission Electron Microscope (HRTEM) at 300 kV and a JEOL JSM6000F Field Emission Gun Scanning Electron Microscope (FEGSEM). For bulk crystallinity analysis dry soot samples were scattered on a silica glass slide and examined by X-ray diffraction (Shimadzu S6000).

3. Results

3.1. Crystallinity of germania soot particles

X-ray diffraction shows clearly that the germania soot produced by Burner A, with or without rotation, is crystalline. The XRD patterns for soot produced by this burner are shown in Fig. 2(a), where the background XRD of the silica glass slide without germania soot is also shown separately. Subtraction of this background from the XRD of the glass slide with the soot on it strongly suggests that the germania soot particles are almost entirely crystalline. The crystal peaks appear to be slightly more pronounced in the rotating substrate case. In contrast, the XRD of germania soot produced by Burner B shown in Fig. 2(b) indicates that it is only partially crystalline and that the bulk of the soot made with this burner is amorphous. By integrating the crystalline and amorphous signals the crystalline fraction in this case was estimated as 3% by volume. The peak around diffraction angle $2\theta = 32°$ corresponds to aluminium. This arises from the aluminium support on which the glass slide was placed. The other peaks in the diffraction pattern match those reported for pure crystalline GeO_2 with an hexagonal structure. Since the amount of soot obtained using Burner B was quite limited the sample size available for the XRD measurements was much smaller than for Burner A, so the background from the glass slide constituted a much larger fraction of the total.

Electron diffraction in both TEM and HRTEM of Burner A soot also revealed the presence of crystalline GeO_2 particles. The calculated atomic spacings were consistent with tabulated crystallography data for GeO_2 with hexagonal crystalline structure ($a = 4.98502$ Å, $c = 5.648$ Å). This is confirmed by XRD for both rotating and non-rotating substrates. Theoretical average crystallite sizes were estimated by applying the Full-Width Half-Maxi-

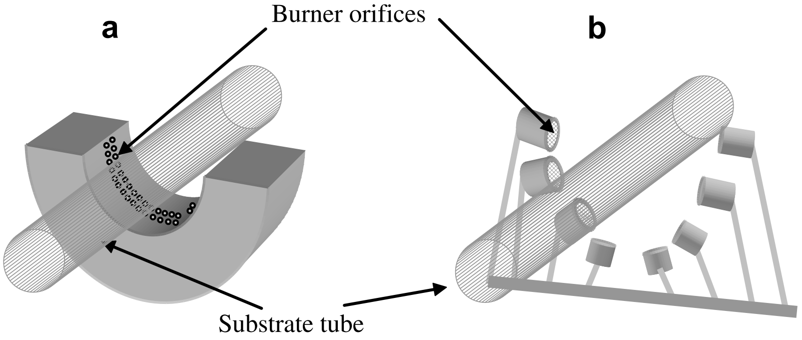

Fig. 1. Schematic diagrams of burner types used to generate GeO_2 soot. (a) Burner A, large thermal mass, wide hot-zone. (b) Burner B, low thermal mass, narrow hot-zone.

Table 1
Burner characteristics

Parameter	Burner A (wide, heavy)	Burner B (narrow, light)
Flame width	~5 cm	~3 cm
Burner width	~10 cm	~4 cm
Burner volume	~1400 cm^3	~80 cm^3
Flame orifice	Two parallel rows of pin holes on inner semi-circular face of a single large burner	Mesh grids (~10 mm diameter) in 8 separate small burners arranged in a semi-circle