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Reaction of Germanium Tetrachloride with Oxygen under MCVD Fiber Preform Fabrication Conditions

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Abstract—The GeO_2 yield in the reaction between $GeCl_4$ and oxygen has been determined as a function of the reaction time under typical MCVD fiber preform fabrication conditions. It is shown that the yield increases steadily over time and may attain 100%. In the case of the cooxidation of germanium and silicon tetrachlorides under the same conditions, there is an optimal reaction time corresponding to a maximum in GeO_2 yield. The temperature profile along the reaction zone has been optimized in terms of germania yield.

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INTRODUCTION

Chemical vapor deposition on the inside surface of a silica glass substrate tube (MCVD process) is among the most widely used vapor-phase processes for the fabrication of single-mode silica-based optical fiber preforms. Typically, the process utilizes high-temperature reactions of silicon tetrachloride and dopant halide (most frequently, $GeCl_4$) vapors with oxygen. A gas mixture is passed through a rotating silica glass tube, and an oxygen–hydrogen flame slowly traveling along the tube (usually, in the gas flow direction) initiates the reactions

$$SiCl_4 + O_2 \longrightarrow SiO_2 + 2Cl_2, \tag{1}$$

$$GeCl_4 + O_2 \rightleftharpoons GeO_2 + 2Cl_2. \tag{2}$$

The resulting oxide particles are deposited on the inside tube surface under the action of thermophoretic forces and are fused by the flame to form a transparent glass layer.

The effectiveness of the reactions in the gas flow can be characterized by the reaction time τ and conversion β. The latter is the ratio of the number of moles of a component in the reaction product to the initial number of moles of that component:

$$\beta = \frac{N_1 - N_2}{N_1}, \tag{3}$$

where N_1 and N_2 are the numbers of moles of the starting substance at the inlet and outlet of the reaction zone, respectively.

At typical MCVD temperatures, full $SiCl_4$ conversion to silica takes on the order of 0.01 s [1], whereas the $GeCl_4$ conversion is 0.31 at this reaction time [1] and takes 0.5 s to reach unity [2].

At the same time, when reactions (1) and (2) are run concurrently, as is typical in the MCVD process, the GeO_2 yield is ~0.5 even at reaction times close to 1 s [3], which seems to be associated with the small equilibrium constant of reaction (2) [1, 3]. The considerable volume of additional molecular chlorine resulting from reaction (1) must reduce the GeO_2 yield, especially because, in the MCVD process, the silicon tetrachloride concentration in the gas mixture, as a rule, notably exceeds the germanium tetrachloride concentration.

High-purity germanium tetrachloride is among the most expensive starting chemicals in the MCVD process. Clearly, a detailed understanding of the processes underlying the deposition of fiber preform material is of practical interest for the fabrication of both conventional germanium-doped silica glass fiber preforms and germania-glass-core preforms.

The purpose of this work was to study the effect of reaction time on the germania yield in the reaction of germanium tetrachloride with oxygen under typical MCVD fiber preform fabrication conditions.

EXPERIMENTAL AND RESULTS

Optimization of the reaction temperature. Our experiments were conducted in a standard MCVD apparatus for fiber preform fabrication, equipped with a system for forced cooling of the tube in the thermophoretic deposition zone [4].

First, we optimized the $GeCl_4$ conversion temperature. To this end, a gas mixture (table) was passed through the hot zone produced inside the tube by a torch (the maximum temperature of the outer tube surface was measured by an IR pyrometer with an accuracy of ±15°C).

In our experiments, germanium tetrachloride was oxidized at different temperatures of the outer tube surface in the reaction zone, both individually (Fig. 1, curve *1*) and in the presence of silicon tetrachloride (curve *2*) or carbon tetrachloride (curve *3*). The germanium tetrachloride concentration in the gas mixture at the tube outlet end was determined by IR spectroscopy.

In all of the experiments, the germanium tetrachloride conversion increased with increasing temperature in the reaction zone. The highest conversion was achieved when the temperature of the outer tube surface in the reaction zone was ~2000–2050°C. At this temperature, the $GeCl_4$ conversion in reaction (2) attained 80% (Fig. 1, curve *1*). If reactions (1) and (2) were run concurrently, the $GeCl_4$ conversion was 60% (curve *2*). The use of carbon tetrachloride instead of silicon tetrachloride reduced the $GeCl_4$ conversion to ~30% (the initial carbon tetrachloride concentration in the gas mixture was lower than the $SiCl_4$ concentration by more than a factor of 2).

It follows from the kinetic curves of reactions (1) and (2) [5] that the temperature range of reaction (1) is ~100°C wider than that of reaction (2). The temperature profile created by the traveling torch in the reaction zone (Fig. 2) is asymmetric along the tube axis, with a flat trailing edge and steep leading edge. Therefore, for a laminar gas-mixture flow and at moderate temperatures, the extent of reaction (2) in each section of a significant part of the reaction zone is a factor of 3–5 greater than that of reaction (1). For this reason, the excess chlorine concentration in the gas mixture in each section of the reaction zone must be substantially lower than might be expected. Replacing $SiCl_4$ with CCl_4, which reacts with oxygen at a considerably lower temperature in comparison with germanium tetrachloride, must raise the excess chlorine concentration in each section of the reaction zone compared to $SiCl_4$, which seems to be responsible for the lower germanium tetrachloride conversion.

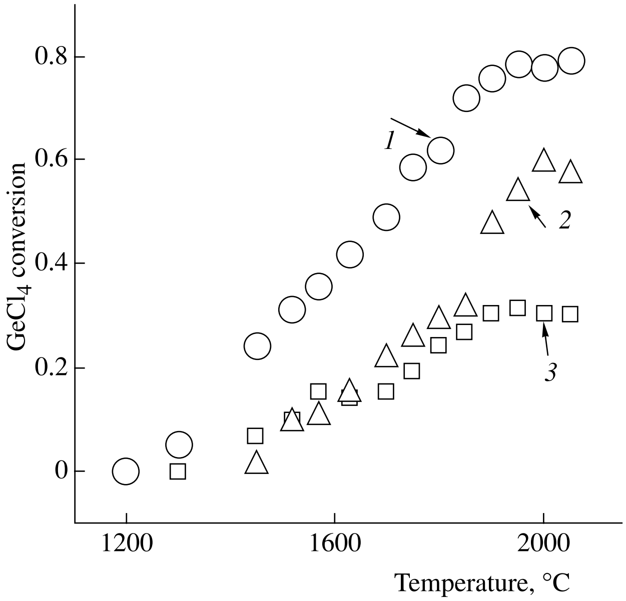

Fig. 1. Germanium tetrachloride conversion as a function of the outer-surface temperature in the reaction zone for different gas mixtures: (*1*–*3*) see the table.

Flow rates of gas-mixture components (normal conditions)

Curve no. in Fig. 1	Flow rate, cm^3/min			
	oxygen	$GeCl_4$	$SiCl_4$	CCl_4
1	1325	11.9	–	–
2	1325	11.9	39.7	–
3	1325	11.9	–	16.9

If the above reasoning is correct, increasing the reaction time for concurrent reactions (1) and (2) must reduce germanium tetrachloride conversion.

Effect of reaction time on $GeCl_4$ conversion. The average reaction time in a flowing gas mixture can be determined as

$$\tau = \frac{Sl}{W}, \qquad (4)$$

where S is the cross-sectional area of the channel, W is the volumetric flow rate of the gas mixture, and l is the effective length of the reaction zone (hot zone). However, since only the temperature of the outer tube surface in the reaction zone was measured in our experiments, the true size of the hot zone inside the tube was difficult to determine. In connection with this, as a reaction time criterion we used the flow speed along the tube, W/S.

To assess the efficiency of germanium tetrachloride conversion in reaction (2) as a function of reaction time, a layer of SiO_2 particles was deposited on the inside tube surface by translating the flame in the direction opposite to the flow of a mixture of oxygen and silicon tetrachloride ($SiCl_4$ flow rate, 100 cm^3/min) (Fig. 3a).

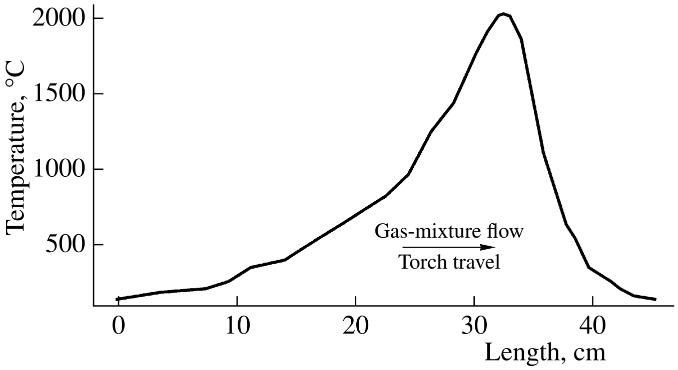

Fig. 2. Axial temperature profile produced by the traveling torch.

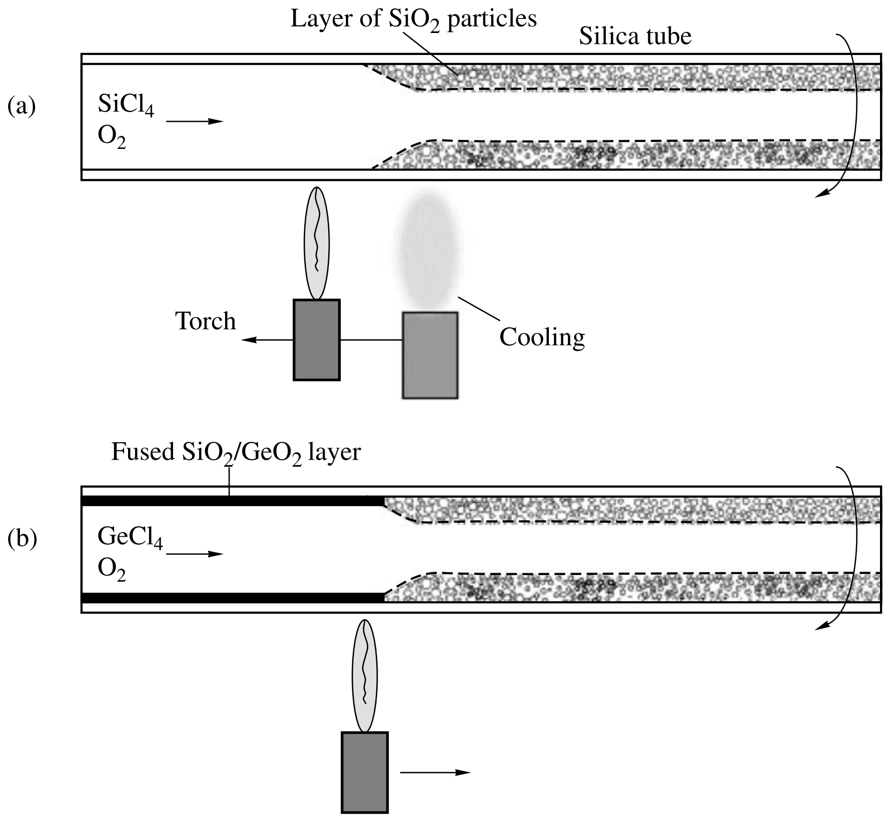

Fig. 3. Schematic illustrating the preparation of germanosilicate glass layers via successive oxide deposition from the vapor phase: (a) the flame is translated in the direction opposite to the flow of a mixture of oxygen and silicon tetrachloride; (b) the flame is translated along the flow of a mixture of oxygen and germanium tetrachloride.

The zone behind the flame, where particles were deposited, was cooled in order to create conditions similar to those produced by the flame traveling in the flow direction. After deposition, the layer of SiO_2 particles was fused in a mixture of oxygen and germanium tetrachloride at ~2050°C by translating the flame in the flow direction to give a transparent glass layer (Fig. 3b). In our experiments, the flow speed of this mixture was varied by changing the inner tube diameter and oxygen flow rate, with no changes in $GeCl_4$ flow rate. In this manner, in each experiment we deposited and fused several germanosilicate glass layers under identical conditions.

After collapsing the tube into a rod, we measured the difference in refractive index (Δn) between silica glass and the deposited material using a Photon Kinetics 2600 preform analyzer. The conversion efficiency was inferred from the variation of Δn with preform fabrication conditions.

Figure 4 plots Δn against the inverse of the flow speed relative to the reaction zone for silica glass fused into a transparent layer in a flow of germanium tetrachloride (30 cm^3/min) and oxygen. These data indicate that the GeO_2 yield ($GeCl_4$ conversion) increases with decreasing flow speed.

The arrow in Fig. 4 marks the data point obtained at the same flow speed as curve *1* in Fig. 1. Since this point corresponds to 80% germanium tetrachloride conversion, further reduction in flow speed under such deposition conditions makes it possible to achieve a near 100% GeO_2 yield.

In codepositing oxides by reactions (1) and (2), we used gas mixtures with a constant $O_2 : SiCl_4 : GeCl_4$ volume ratio of 250 : 10 : 3. The flow speed was varied by changing the inner tube diameter or volumetric flow rate in such a manner that the mixture composition remained unchanged since the germania yield in oxide codeposition depends on the oxygen concentration in the gas mixture [3]. The temperature of the outer tube surface in the heating zone was maintained at 2050°C. After deposition, the tube was collapsed into a rod, as above, and conversion was inferred from the refractive index of the deposited germanosilicate glass.

Figure 5 plots Δn against flow speed for glass deposited at a constant gas mixture composition. As seen, the germanium tetrachloride conversion first rises with increasing flow speed (decreasing reaction time), as would be expected from the data in Fig. 1. At the same time, the germanium tetrachloride conversion as a function of flow speed has a maximum (Fig. 5). At lower flow speeds, the germania yield is limited by the equi-

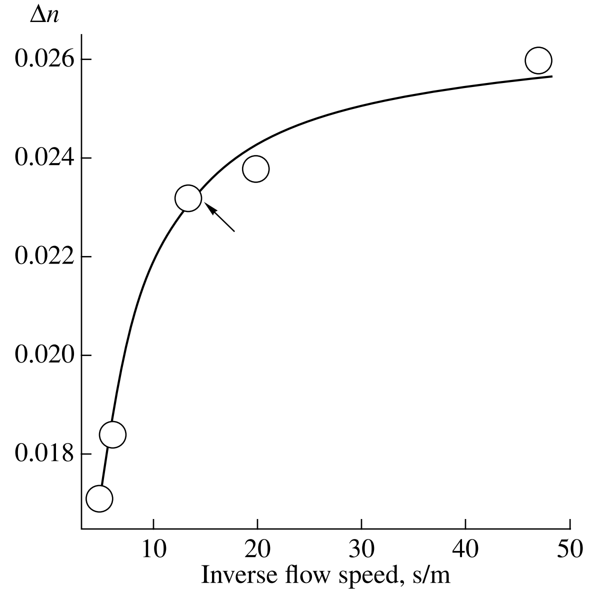

Fig. 4. Plot of Δn vs. inverse flow speed for silica glass fused in a flow of oxygen and germanium tetrachloride.

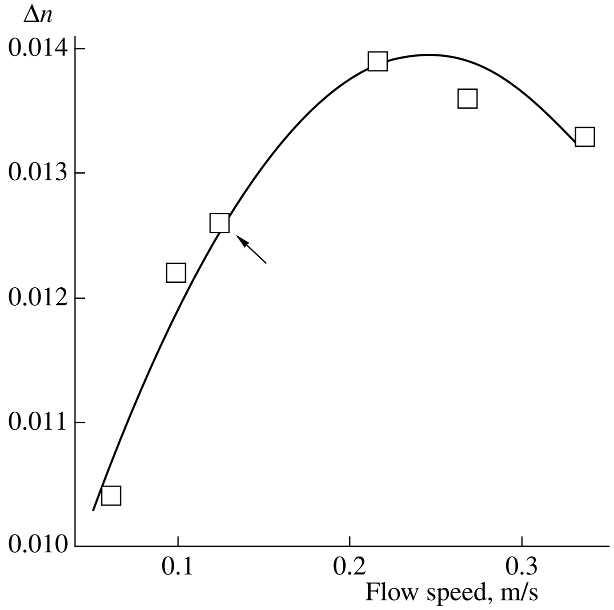

Fig. 5. Plot of Δn vs. flow speed for glass deposited by reactions (1) and (2) at a constant gas mixture composition.

librium of the reaction between germanium tetrachloride and oxygen in the presence of excess molecular chlorine, resulting from the concurrent oxidation of silicon tetrachloride. At higher flow speeds, the kinetic limitations of reaction (2) prevail.

The arrow in Fig. 5 marks the data point obtained at the same flow speed as curve *2* in Fig. 1. Since this point corresponds to 60% germanium tetrachloride conversion, the maximum conversion under these conditions can be estimated at ~70%.

CONCLUSIONS

The germania yield in the reaction between germanium tetrachloride and oxygen was determined as a function of the flow speed of the gas mixture under typical MCVD silica fiber preform fabrication conditions. The germania yield in the reaction between germanium tetrachloride and oxygen was shown to significantly depend on the reaction time. The GeO_2 yield increases with reaction time and may attain 100%, which means that the germanium tetrachloride conversion under such conditions is limited only kinetically.

In the case of the cooxidation of germanium and silicon tetrachlorides in the CVD process, there is an optimal reaction time corresponding to a maximum in GeO_2 yield. Under such conditions, the germanium tetrachloride conversion is limited both by the equilibrium of the reaction between $GeCl_4$ and oxygen in the presence of excess chlorine and by the kinetics of this reaction.

Our results on silica–germania codeposition indicate that the optimal temperature profile along the reaction zone is the one which ensures the maximum germanium tetrachloride conversion and the minimum silicon tetrachloride conversion over most of the reaction zone. $SiCl_4$ conversion must be completed at the downstream end of the heating zone, where the temperature is higher compared to the rest of the zone. The parameters of the temperature profile along the reaction zone depend on the inner diameter of the silica glass tube and the flow rate of the gas mixture.

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