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Inorganic Fibres and Microfabricated Parts by Laser Assisted Chemical Vapour Deposition (LCVD): Structures and Properties*

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Abstract: Laser assisted chemical vapour deposition (LCVD) is a new generic process for fabricating advanced inorganic fibres, as well as three-dimensional microsprings and solenoid, directly from the vapour phase. Using high reactor pressures (> 1 bar) and a unique rate control mechanism, chemically pure and structurally uniform boron, carbon, silicon, silicon nitride and carbide, and germanium fibres with small diameters (> 6 μm) and high growth rates (0.3–1.1 mm/s) were obtained. Among others, ultra strong (> 7.5 GPa) boron and stoichiometric silicon carbide fibres were obtained, as well as highly flexible carbon fibres representing a new form of carbon. This paper deals with structure–property relationships relative to market requirements. Growth rates and process economics are comparable to those by which commercial sapphire fibres are obtained from the melt. The process promises to afford new continuous single crystal fibres (including silicon and tantalum carbide) for structural composites uses at temperatures ranging from 1500 to 2200°C, new sensor fibres (including ZnSe) and fibres for consumable high temperature sensor systems. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

High pressure laser assisted chemical vapour deposition (HP-LCVD) is a new generic fibre process. It facilitates the formation of advanced inorganic fibres and microstructures directly from the vapour phase. The new process is capable of affording chemically pure, structurally uniform, small diameter fibres of almost any substrate that can be produced as a film or as a part by conventional CVD. Amorphous, polycrystalline and glassy (amorphous) fibres can be fabricated. This process[1–13] resembles growth of whiskers by solvent, or metal particle, catalyzed CVD[14] except that continuous fibres, as well as multi-filament yarns, are possible.

Growth of small diameter fibres directly from the vapour phase by laser assisted chemical vapour deposition (LCVD) is a process whereby the laser beam has a focal point adjusted to coincide with the tip of a growing fibre (Fig. 1). The growing fibre is not in contact with reactor walls or foreign materials. It is chemically pure and suitable for optical uses and demanding applications requiring high structural uniformity.

In 1972, only large (> 200 μm) diameter carbon fibres[15] with low growth rates (< 10 μm/s) were obtained. A CO_2 laser and low reaction pressures (< 1 bar) were used. In the mid-80s, smaller (< 20 μm) diameter carbon, boron and silicon fibres were obtained[16,17] with an Ar^+ laser, but the continued use of low reaction pressures (< 1 bar) continued to result in low growth rates. Fibre growth rates and diameters increased in the low pressure regime when the reaction chamber pressure was increased.[16]

More recently, a low pressure LCVD reactor,[17] equipped with a three-dimensional linear micropositioning system (Fig. 2) allowed the first *direct*

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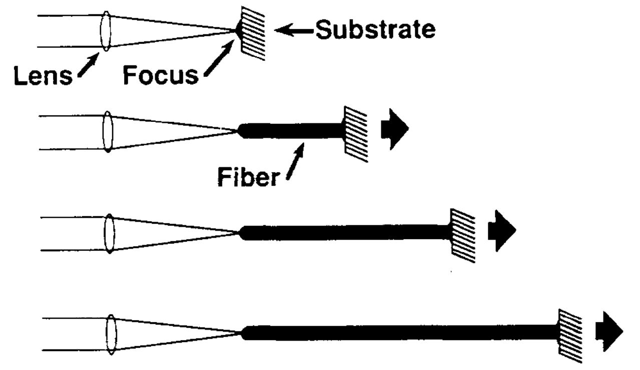

Fig. 1. Containerless growth of continuous fibres by LCVD (schematic).

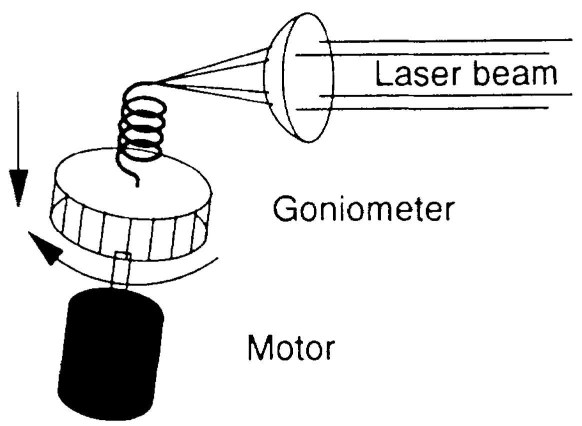

Fig. 2. Containerless growth of three-dimensional microsprings (schematic).

fabrication of free-standing boron and silicon microstructures at linear growth rates of 3.5 μm/s, e.g. a 360 μm wide and 1 mm high helical microspring with a fibre diameter of < 10 μm.

Using the same rotatable goniometer stage, a three-dimensional microsolenoid[17] was made, consisting of a single crystal silicon rod with a helical tungsten coil deposited on its surface by a laser direct write method. It was 2.5 mm long, and 140 μm in diameter. The use of low pressures resulted in small (1.2 μm/s) deposition rates.

Still relying on low pressure LCVD, thus low deposition rates, the first *indirect fabrication* afforded free-standing, three-dimensional aluminium structures.[18a] A grid of aluminium lines was deposited on to the surface of a pre-formed polycarbonate substrate. The latter was dissolved, leaving behind a shaped aluminium grid (3x3x7 mm) of 10 μm diameter fibres. The first *direct fabrication* of similar free-standing, three-dimensional cage-like microstructures, still using low pressure LCVD, thus yielding low deposition rates, was accomplished with a dual laser system.[18b] The use of laser assisted CVD as a new rapid prototyping tool has been discussed elsewhere.[11–13]

Table 1. Growth of HP-LCVD fibres (status)

HP-LCVD fibres	Reactant gasses	Diameter, μm		Rate, μm/s	
		Low	Avg.	Avg.	High
Boron	B_2H_6/H_2	6	19	625	1100
Carbon	CH_4	10	63	125	331
Germanium	GeH	59	70	18	35
Silicon	SiH_4	15	45	460	500
SiC	SiH_4/C_2H_4	13	120	75	125
Si_3N_4	SiH_4/NH_3	21	45	338	740

Table 2. Morphology of fibres obtained by high pressure LCVD (current status)

Structure	Fibres
Single crystals	Silicon fibres and germanium fibres
Polycrystalline	Silicon fibres and silicon carbide fibres
Amorphous/glassy	Silicon, boron, carbon, silicon carbide and nitride

2 GROWTH OF HP-LCVD FIBRES

A major advance in the field of laser assisted chemical vapour deposition was demonstrated in 1992,[3] potentially affording the same fibres and microstructures but at much higher deposition rates. The use of a small wavelength Nd–YAG laser and high reaction chamber pressures (1–10 bar) made it possible to fabricate small (>6 μm) diameter fibres which were chemically pure and structurally uniform (Table 1) at high (0.3–1.1 mm/s) growth rates. To date, boron, carbon, silicon, silicon nitride, silicon carbide and germanium fibres[1–13] were obtained by the new high pressure process.

The laser beam (schematically shown in Fig. 1) was focused on to a point inside a reactor, where localized heating promotes vapour deposition in the direction of the laser. Specifically, the beam from a one-watt, TEM_{00} mode, continuous wave Nd–YAG laser (emission wavelength 1.064 μm) was passed through a polarizer, a Linconix laser power stabilizer, a variable neutral density filter, a beam expander, and then focused with a 10 cm focal length lens into the fibre growth reactor.[1,2]

The system provided actual cw power up to 270 mW. Laser power ranged from 0 to 200 mW, with a stability of one mW, as measured outside the reactor. Most specimens were 14 mm. A semi-continuous process produced two-meter-long fibres[3] and a continuous process is possible. Growth of the fibre at a location where the laser beam was converging to its focal point provides self-regulating growth.[1–12] The new growth mechanism and the phase transformations will be discussed separately.[12]

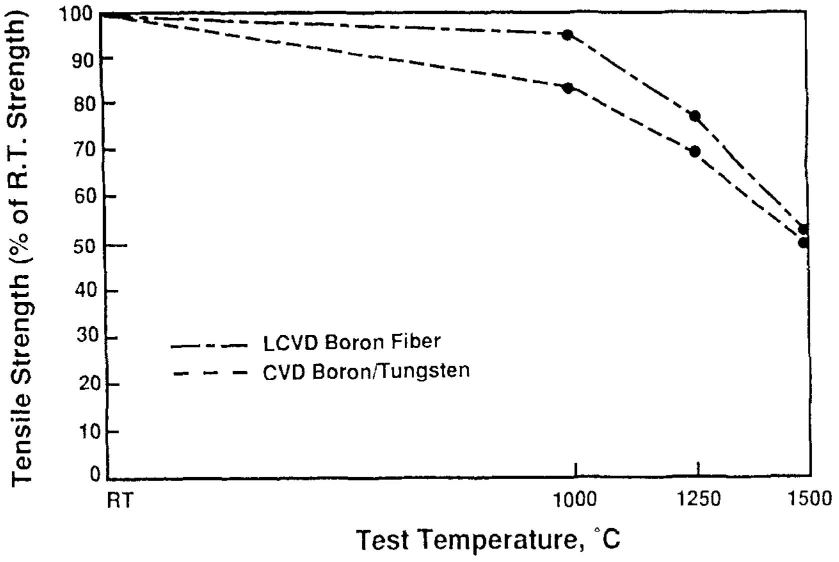

Fig. 3. Percent strength retention of CVD boron/tungsten and LCVD boron fibres

In summary, a range of new fibres[1–12] was grown directly from the vapour phase by the HP-LCVD process. These fibres had both small diameters (< 20 μm) and high growth rates (0.3–1.1 mm/s). The growth rates and the resulting process economics are comparable to those noted for the growth of single crystal sapphire fibres by the edge defined film fed (EFG) growth[19] process.

3 FIBRE STRUCTURES

3.1 Overview

Depending on the process conditions used, HP-LCVD fibres were obtained with a range of structures (Table 2). Boron,[3] carbon,[4,5] silicon,[6] silicon nitride[8] and silicon carbide fibres were obtained as amorphous materials. Other silicon carbide[1] and silicon[6] fibres were found to be polycrystalline. Germanium[9] and silicon[6] fibres were also obtained as single crystals.

The relationships between these structures and the most important fibre properties, such as chemical purity, structural uniformity, microstructure, tensile strength, tensile modulus and mechanical toughness, will be analysed in the following discussion.

3.2 Amorphous glassy fibres

In general, amorphous HP-LCVD fibres are formed by vapour–solid transformation. The following examples show the powerful effect of specific process conditions on the formation of amorphous structures and on selected performance characteristics.

The first example pertains to a comparison of HP-LCVD and CVD boron fibres.[3] The HP-LCVD fibres did not have a tungsten or carbon core. Their overall diameters ranged from 9 to 25 μm and their tensile strengths from 5.2 to 7.6 GPa. These fibres showed higher strength retention at elevated temperatures (Fig. 3) than commercial CVD boron fibres having a tungsten core, overall diameters ranging from 100 to 140 μm and tensile strengths ranging from 3.5 to 4.0 GPa.

Since both processes are containerless, the difference in strength appears to depend not only on the difference in fibre diameters but also on the difference in microstructures. The boron/tungsten fibres are nanocrystalline, a structure prone to limit the strength of a fibre at ambient and, even more so, at elevated temperatures. Since the pure boron fibres were amorphous, the result documents the powerful effect of the HP-LCVD process in affording, in general, highly amorphous fibre structures.

The second example pertains to a comparison of selected HP-LCVD carbon fibres[4,5] which had tensile strengths ranging from 0.2 to 3.0 GPa (Table 3). Depending upon growth conditions and feed gas chemistry,[5] these fibres were either flexible (elastic), brittle (thickened, i.e. having a sheath–core structure) or graphitic (strong).

Table 3. Mechanical properties of HP-LCVD carbon fibres

Carbon fibre type	Strength (GPa)	Elongation (%)	Modulus (GPa)
Commercial IM	~3.5	~1.5	~250.0
HP-LCVD (Range)	0.2–3.0	>1.5	28–180
Flexible fibres	0.2–0.4	TBD	<30
Brittle fibres	TBD	TBD	TBD
Graphitic fibres	>0.5	TBD	180

Table 4. Growth of LCVD silicon nitride fibres

LCVD fibre	Ratio SiH_4:NH_3	Pressure (bar)	Fibre composition	Structure morphology	Diameter (μm)	Growth rate (μm/s)
Si–N	2.3	1.3	silicon rich	amorphous	36	496
Si–N	3.8	1.3	near stoichiometric	amorphous	30	403
Si_3N_4	4.0	1.3	stoichiometric	amorphous	30	400

Flexible carbon fibres could be readily bent to radii of curvatures of ~1 mm or less, with a force much less than that required for equal diameter HP-LCVD boron fibres having a modulus of 275–400 GPa[3] or equal diameter intermediate modulus (IM) carbon fibres having a modulus of 250 GPa.[3] Thus the HP-LCVD process can provide considerable control over the nature of the resulting amorphous structures.

The third example (Table 4) pertains to a comparison of amorphous HP-LCVD fibres having binary silicon–nitrogen, including silicon nitride, compositions.[8] Some of the fibres were silicon-rich Si–N compositions, others near stoichiometric Si–N compositions, and some were representative of stoichiometric silicon nitride. This example confirms that the HP-LCVD process offers wide latitude in the design of fibres with amorphous or glassy structures. These design options facilitate the production of amorphous fibres from equilibrium and non-equilibrium melt compositions and of amorphous fibres having stoichiometric, as well as non-stoichiometric, binary compositions.

In summary, the new process is capable of affording a wide variety of amorphous forms, including uniform and ultra strong boron fibres, flexible carbon fibres, and binary glass fibres, e.g. Si–N or Si–C, with stoichiometric and non-stoichiometric compositions.

3.3 Single crystal fibres

Polycrystalline HP-LCVD fibres develop internal and surface defects (imperfections) when they consolidate from the rapidly solidifying melt. They are weaker and offer lower light transmission, thus lower value-in-use, than single crystal or glassy fibres. Overall, single crystal fibres are of primary interest. They fully utilize their structural uniformity (freedom from defects) that is inherent in the containerless HP-LCVD process.

Single crystals were thus far obtained with silicon and with germanium fibres. Work with other substrates is in progress. The silicon fibres were grown from silane near the focal point of the cw Nd–YAG laser beam[6] and were obtained as single crystals, polycrystalline fibres and fibres exhibiting glassy fracture. Fibre growth rates ranged from < 1 to 500 μm/s and fibre tip temperatures from 525 to 1412°C.

Table 5. Growth of HP-LCVD silicon fibres

Tip temperature	Fibre morphology
> 1400°C	Single crystals
600–1400°C	Polycrystalline
< 600°C	Amorphous glass

Table 5 illustrates an important principle. The single crystal silicon fibres were formed at high laser intensities and fibre tip temperatures by vapour–liquid–solid (VLS) transformation.[6,7] The polycrystalline silicon fibres were formed at intermediate temperatures, most likely also by VLS transformation, and silicon fibres yielding glassy fracture were obtained at low fibre tip temperatures by vapour–solid (VS) transformation.

3.4 Phase transformations

Solvent catalyzed CVD was believed to be the only process proceeding by VLS.[14] Molten metal droplets dissolve the reaction product of a CVD process and catalyze the growth of filamentary single crystals, e.g. ultra strong silicon carbide whiskers for structural uses[20] and silicon, gallium arsenide and other whiskers[13,14] for semi-conductor uses. The liquid (L) is a supersaturated solution, the whisker a single crystal.

Laser assisted CVD, as seen in Table 5, has now also been found to be capable of forming fibres by vapour–liquid–solid transformation. In this variant of the VLS process, it is the laser focus, not a molten metal droplet, that catalyzes fibre growth. The liquid (L) is a melt. Although solvent catalyzed CVD yields short discontinuous whiskers and laser assisted CVD yields long and potentially continuous fibres, both afford the most uniform (and strongest) fibres available to date as discussed in the next section.

Single crystal fibres made by laser heated pedestal growth (LHPG) and edge defined film fed growth (EDF) are melt derived by solid–liquid–solid transformation. LHPG is a containerless process, EDF is not. Phase transformations and process mechanisms of these processes (LCVD, LHPG and EDF) have been discussed elsewhere.[10]

Table 6. Incumbent structural inorganic whiskers and fibres

Short whiskers and continuous fibres	Maximum fibre length	Fibre structure	Strength (GPa)	Modulus (GPa)	Lit. Ref.
VLS silicon carbide whiskers	< 28 mm	single crystal	> 7.5	578	20
Silicon carbide/carbon fibres	continuous	polycrystalline	3.5	400	21
Nicalon silicon carbide fibres	continuous	nanocrystalline	3.0	190	22
Sapphire whiskers	< 1 mm	single crystal	10.5	415	23
Saphikon sapphire fibres	continuous	single crystal	4.0	415	24
LHPG sapphire fibres	continuous	single crystal	5.7	415	25
Slurry spun alumina Fibre FP	continuous	polycrystalline	1.4	380	26
Sol–gel aluminate fibres	continuous	nanocrystalline	1.7	152	27
Melt spun aluminate fibres	continuous	amor., glassy	4.0	125	28
CVD boron/tungsten fibres	continuous	nanocrystalline	4.0	400	29
HP-LCVD boron fibres	continuous	amor., glassy	7.5	350	1–3

3.5 Summary

Single crystal HP-LCVD fibres of any given substrate will be formed at high fibre tip temperatures by VLS. They will therefore posses higher growth rates, structural uniformity (strength) and moduli (see next section) than amorphous glassy fibres.

4 MECHANICAL PROPERTIES

4.1 Overview

Modulus (stiffness) reflects the structural order of a material. It does not depend on internal or surface uniformity. Strength reflects internal and surface uniformity of a material rather than structural order (stiffness). High mechanical (as opposed to fracture) toughness depends either on high fibre strength or on high break elongations.

4.2 Tensile modulus

The highest modulus of a given substrate is obtained with a single crystal structure, e.g. VLS-SiC whiskers or sapphire whiskers and sapphire fibres, respectively. The modulus of polycrystalline silicon carbide/carbon sheath/core fibres or Fibre FP closely approaches that of single crystal silicon carbide whiskers or that of the two single crystal sapphire fibres shown in Table 6.

Fibre modulus (or stiffness) as reflected in Table 6 decreases (1) with increasing compositional complexity, e.g. oxycarbides vs carbides, or aluminates vs pure alumina, and (2) with decreasing crystallinity, e.g. from polycrystalline to nanocrystalline structures, and from the latter to glassy structures, respectively. As expected (Table 6), the nanocrystalline boron/tungsten fibres were stiffer than the amorphous HP-LCVD boron fibres which exhibited glassy fracture.

4.3 Tensile strength

Like modulus, the highest strength of a given substrate is also obtained with a single crystal structure, e.g. SiC or sapphire whiskers. Continuous single crystal SiC fibres are not known. Continuous single crystal sapphire (Saphikon) fibres are known. Their strength is lower than that of sapphire whiskers (Table 6). They are made by edge defined film growth (EDF), a process that is not containerless, and have internal strength-limiting voids. Sapphire fibres made by laser heated pedestal growth (LHPG), a containerless but slow process, are therefore stronger than Saphikon fibres.

The strength of polycrystalline oxide fibres (e.g. Fibre FP or Nextel 312) or polycrystalline carbide fibres (SCS and Nicalon) is much lower (Table 6) than that of single crystal fibres of the same substrate. (1) They were not made by a containerless process, and (2) their structure is weakened by grain boundaries and surface defects.

The strength of melt spun aluminate glass fibres with > 50% alumina is nearly as high as that of the two continuous sapphire fibres (Table 6), and much higher than that of the nanocrystalline Nextel 312 fibre having about the same composition, because of their higher internal and surface uniformity.

The HP-LCVD boron fibres (Tables 2 and 6) are stronger than the B/C fibres. They are glassy and have higher structural uniformity. In summary, glass fibres are strong, single crystal fibres are ultra strong. The strength of polycrystalline fibres is variable, depending only on the level of internal and surface defects. Any new premium fibre should therefore be a single crystal or an amorphous glass fibre.

4.4 Mechanical toughness

Mechanical toughness (or work-to-break) measures the damage resistance of a material before an initial fracture occurs, as opposed to fracture toughness

Table 7. Proposed fibres for ultra high temperature composites and sensors

Cont. single crystal fibres vs comm./exper. fibres	*T*m (°C)	Max. (use °C)	Diam. (mm)	Strength (GPa)	Modulus (GPa)	Process speed (mm/s)
S. C. LCVD HfO_2 (Est.)	2845	2375*	>5	10.0	550	0.3–1.1
S. C. LCVD ZrO_2 (Est.)	2765	2350*	>5	10.0	294	0.3–1.1
S. C. Sapphire (Comm.)	2040	1734*	≥125	≤4.0	415	0.58[19]
S. C. LCVD HfB_2 (Est.)	3250	2762*	>5	10.0	1000	0.3–1.1
S. C. LCVD B (Est.)	2300	1955*	>5	10.0	>400	>1.1
Amorph. LCVD B (Actual)	2300	1955*	>5	≤7.6	350	0.8–1.1
S. C. LCVD TaC (Est.)	3880	3298*	>5	10.0	510	0.3–1.1
S. C. LCVD TiC (Est.)	3140	2675*	>5	10.0	448	0.3–1.1
S. C. LCVD SiC (Est.)	2827	2302**	>5	10.0	578	0.3–1.1
Poly-C. SiC/C(Comm.)	2827	1400***	≥100	≤4.0	400	N.A.

Maximum use temperature limited by creep (0.85 × T_m)*, volatization** or degradation***.

which measures the residual damage resistance after an initial crack has occurred.

Mechanical toughness corresponds to the area under the stress–strain curve. It is very high for single crystal whiskers and fibres because of their high structural uniformity and strength, except for those known to have internal voids. It is high for glassy fibres because of their high break elongations, but low for some, but not all, nanocrystalline and all polycrystalline fibres because of the inherent strength-limiting defects.

4.5 Summary

Strength and stiffness of single crystal HP-LCVD fibres are expected to approach those of single crystal whiskers of the same substrate. The mechanical toughness (damage resistance) of glassy HP-LCVD boron fibres was comparable to that of commercial single crystal EDF sapphire fibres. That of single crystal HP-LCVD boron fibres, when available, and that of other single crystal HP-LCVD fibres is expected to be comparable to that of single crystal silicon carbide and sapphire whiskers, respectively.

5 GOALS AND OUTLOOK

5.1 Product requirements

The need for new single crystal fibres was recently summarized[30,31] and the HP-LCVD process, as shown in Table 7, is suitable and available for their fabrication. The moduli, melt temperatures and maximum use temperatures for these compositions were assembled from the literature.[30,31] The projected fibre strength and process speeds were discussed in the previous section of this paper. The most important factors affecting the projected maximum use temperatures are creep, volatilization and/or degradation. They may occur at lower or higher temperatures than projected, and only experimental fibre data will help resolve the issues.

Single crystal sapphire or YAG fibres are either commercially available or are being developed. There is no sufficiently strong economic driving force for developing a new process for these fibres. The HP-LCVD process is, however, expected to yield other continuous single crystal fibres having an equally high, if not higher, value-in-use in advanced composites and/or sensor markets.

5.2 Structural and sensor fibres

New HP-LCVD fibres, such as single crystal B, HfB, TaC, TiC, SiC, or HfO_2 (Table 7), will exceed the long standing requirement for inorganic composites that they must withstand long range and repeated exposure to maximum use temperatures exceeding 1500°C,[30] while at the same time possessing (1) small diameters, (2) the strength of silicon carbide or sapphire whiskers, (3) moduli ranging from 400 to 1000 GPa, and (4) Saphikon-like process speeds and economics. These fibres will possess higher densities than the incumbent reinforcing fibres, and density is known to affect the part weight.

New HP-LCVD sensor fibres could be designed to satisfy unexplored needs in ultra high temperature industrial and aerospace systems, where the design specifications exceed the thermal stability of commercial sapphire and YAG fibres. New single crystal HfO_2, HfB_2 and TaC fibres might be suitable for these applications, including their potential use as consumable sensors to monitor rocket exhaust temperatures. Other HP-LCVD sensor fibres including Si, Ge and ZnSe (Fig. 4) promise to offer high value in premium automotive and medical sensor systems. Single crystal HP-LCVD germanium[9] and silicon[6] fibres have already been demonstrated.

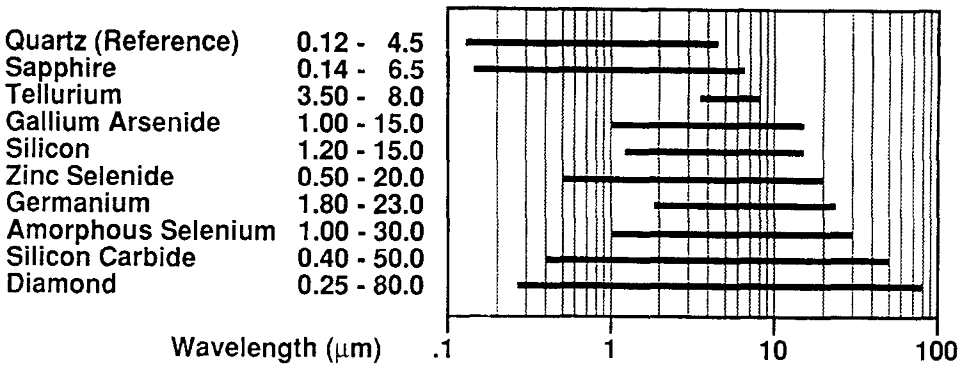

Fig. 4. Transmission windows of important electro-optic materials (schematic).

5.3 Part design

The fibres shown in Table 7 have higher moduli and higher densities, and would therefore afford reinforced composite parts which are proportionately stiffer and heavier than that, for example, of a saphhire fibre reinforced part having the same fibre volume fraction, part volume and part shape. But the latter, of course, might not meet the maximum use temperature required by the given design specifications.

In the design of a specific part, a leading edge, that must withstand ultra high in-use temperatures, it will therefore be important to meet the temperature requirements first, and then to determine whether the part stiffness can be rebalanced by the customary consideration of specific properties to best satisfy the other in use requirements also.

Assuming that fibres such as those shown in Table 7 are to be used as reinforcements with the oxides as the matrices, an additional condition was suggested[31] that the stiffness (per unit weight) of the reinforcements be at least twice that of the matrices. This condition[31] is not reflected here. It does acknowledge the effect of density but would *a priori* exclude potentially useful high temperature fibres from consideration, i.e. before any specific part is identified for a design program and before sufficient experimental data are available to select a suitable fibre–matrix pair for such an effort.

6 SUMMARY AND CONCLUSIONS

High pressure LCVD yields inorganic fibres with small diameters and high growth rates for premium structural and sensor applications. The economics of fibre growth is comparable to that by which commercial single crystal sapphire fibres are produced. In principle, any substrate that can be deposited by conventional CVD as a film is obtainable as a pure, structurally uniform and ultra strong fibre by HP-LCVD. So far, most experimental HP-LCVD fibres were 14 mm long, some over 200 mm.

A continuous single and multifilament process will be required to fully explore the commercial potential of the new technology. Fibres of interest for advanced composites applications include small diameter, single crystal B, HfB_2, TaC, TiC, SiC and HfO_2 fibres for use at maximum temperatures up to 3700°C. Some of these or other fibres may also be of interest for industrial sensor systems designed to perform at >1800°C, and for consumable sensors to monitor rocket exhaust temperatures. Single crystal (or glassy) fibres of interest for medical sensor systems include Si, Ge and ZnSe fibres.

Microgrids, microsprings, microsolenoids and other electronic devices were grown directly from the vapour phase by slow LP-LCVD processes. Such structures might attain commercial significance if made by the fast HP-LCVD process.

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