Rapid Prototyping Directly from the Vapor Phase

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Rapid prototyping is a concept whereby a "design" of a part in the form of a computer file can be used to generate the finished item in solid form. Processes of this kind share a common feature, a significant reduction in research iterations, and a significant reduction in lead time, often years, from research to commercialization. Rapid prototyping processes based on fast chemical reactions are commercially available but only with submillimeter resolution. In a recent paper, Lehmann and Stuke (*1*) showed that laser-assisted chemical vapor deposition (LCVD) is suitable for rapid prototyping of amazingly complex and free-standing microstructures (Fig. 1) with micrometer resolution.

This pioneering contribution marks an exciting turn in the evolution of LCVD. For decades, it served as a research tool for elucidating the kinetics of vapor phase reactions (*2*). Since 1992, it has evolved into a commercial process for making advanced inorganic fibers (*3–5*), and I have highlighted its utility as a rapid prototyping process for fabricating fibers directly from the vapor phase in a recent review article (*6*). The LCVD technique also became an experimental method for making microsprings (*7*, *8*) and microlattices (*9*).

Chemical vapor deposition (CVD) is a process whereby two gases enter a chamber and undergo reaction, which is sustained by a suitable energy source, usually heat. If the reaction proceeds by a vapor-liquid-solid phase transformation, the gas is deposited as a liquid that solidifies. If it proceeds by a vapor-solid transformation, a solid film or coating is formed directly. With a focused energy source (for example, a focused laser beam), a film will be deposited also, but only in the small area of the focus. Fibers with small (<20 μm) diameters are obtained by LCVD by pulling the substrate away from a stationary focus of a Nd-YAG (neodymium-yttrium-aluminum-garnet) or Ar^+ laser (Fig. 2A) under controlled conditions. LCVD is a containerless process; no material enters from a source other than the feed gases. As a result, LCVD fibers are ultrapure. In principle, any substrate that yields a film by conventional CVD can yield a free-standing fiber by LCVD.

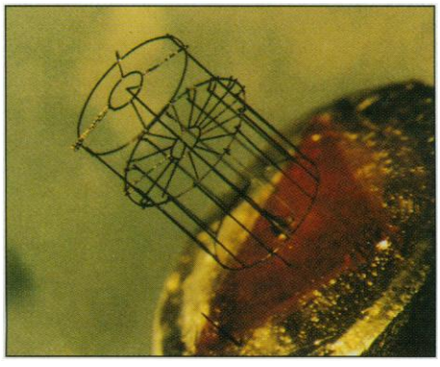

Fig. 1. Three-dimensional free-standing alumina microstructure fabricated directly from the vapor phase by LCVD. The fiber segments, each having a diameter of 20 μm, were continuously formed and joined in this two-laser LCVD process. [Reprinted from (*1*) with permission; copyright, Elsevier Science]

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The LCVD method is a continuous process, capable of yielding endless fibers. Most researchers (*1*, *2*, *7–9*) use low reaction-chamber pressures (<<1 bar), where the growth rates are low (<100 μm/s). Short fibers were grown from hundreds of substrates (*2*), including silicon, carbon, boron, oxides, nitrides, carbides, borides, and metals such as aluminum. Under these conditions, the growth of endless fibers, although possible, is not practical. Building on the contributions by Bäuerle (*2*), my co-workers and I (*3*, *4*, *6*) increased the growth rates for straight fibers by factors of 30 to 200 by designing an LCVD process that operates at high pressures (>1 bar). Using a single laser (Fig. 2A), we observed the highest growth rates (>1.1 mm/s) for small-diameter (<20 μm), amorphous boron fibers. They were ultrapure, structurally uniform, and therefore ultrastrong (tensile strength, >7 GPa). Other high-pressure LCVD fibers (*3*, *4*, *6*) include carbon, silicon, silicon nitride, silicon carbide, and germanium. Attainment of cost-effective fibers is possible. The observed growth rates (>0.5 mm/s) correspond to those (*10*) of commercial single-crystal sapphire fibers made by a melt process. One would therefore expect similar product economics for LCVD.

Westberg (*7*) and Boman *et al.* (*8*) demonstrated the direct fabrication of simple free-standing microstructures from the vapor phase (Fig. 2B). Using a single laser, low-reaction pressures, and a goniometer to facilitate the growth of helical fibers, they obtained microsprings with a fiber diameter of <10 μm and a coil diameter of <350 μm. Lehmann and Stuke (*1*) demonstrated the fabrication of complex free-standing lattice structures from the vapor phase by LCVD. Using a two-beam setup, they created a three-dimensional fiber growth process that permits the direct one-step fabrication of complex free-standing microstructures (Fig.

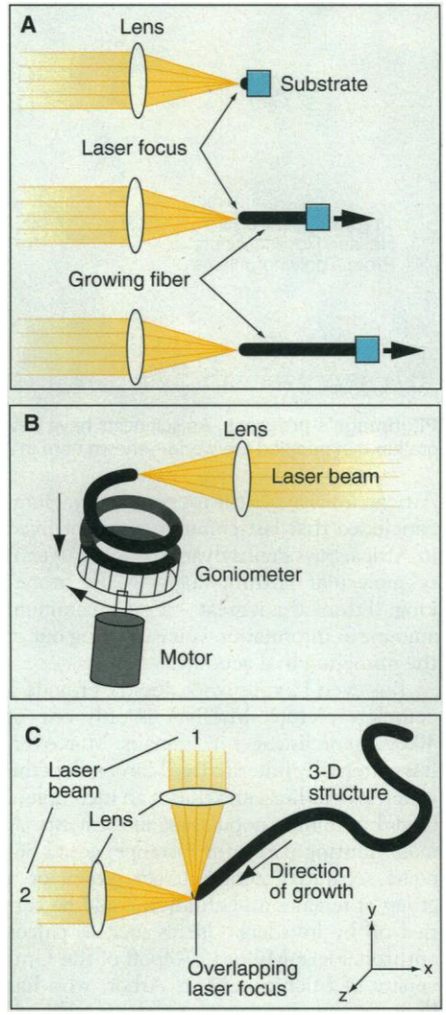

Fig. 2. (**A**) Linear and potentially continuous growth of an advanced inorganic fiber by high-pressure LCVD with a single laser. By this process, Wallenberger and Nordine (*3*) made a pure boron fiber with a tensile strength of >7 GPa and a fiber diameter of 12 μm with growth rates of up to 1.1 mm/s. (**B**) Helical growth of fiber by low-pressure LCVD with a single laser and an in-line microgoniometer. Boman *et al.* (*8*) used this process to make a pure boron microspring with a fiber diameter of 5 μm and a coil diameter of 350 μm with growth rates of up to 10 μm/s. (**C**) Formation of complex microstructures by low-pressure LCVD with a two-laser system adjusted so that the two lasers superimpose. The two-laser system was used by Lehmann and Stuke (*1*) to fabricate the complex microlattice shown in Fig. 1 directly from the vapor phase with linear growth rates of up to 80 μm/s.

2C) with linear growth rates of <80 μm/s. In the experimental process, the sample holder in the reaction chamber can be moved in any space direction (Fig. 2C). New material is always deposited on the fiber tip. Almost any three-dimensional structure consisting of fiber segments can be made, such as that shown in Fig. 1. The electrical properties of a structure can then be changed by metallization.

The commercial potential of endless LCVD fibers, for prototyping versus fabricating, is best illustrated with an example (6) from the aerospace composites community. New inorganic reinforcing fibers, such as hafnium boride or tantalum carbide, are needed to perform satisfactorily for longer periods of time at much higher in-use temperatures than possible with incumbent silicon carbide or sapphire fibers. However, a very costly and time-consuming development would be required to merely fabricate a small amount of a suitable test specimen by known processes. In contrast, LCVD promises to yield suitable prototype samples quickly and with minimum cost. Once a prototype fiber is identified, it can be commercially developed on the basis of cost and performance by way of LCVD or an existing commercial process.

The issues are the same with regard to microsprings (coiled fibers) and highly complex microstructures (Fig. 1). First of all, no other suitable technology is currently available that facilitates the fabrication of strong microsprings. If a specific need arises (7, 8), LCVD will be the preferred choice. In addition, several methods, including lithography techniques and the formation of microscopic molds, are available for the fabrication of three-dimensional microstructures, but they are derived from planar processes. Thus, structural variations in the direction perpendicular to the direction must be achieved in multiple, time-consuming steps (1, 9). Also, these methods require the production of photomasks before processing. Finally, rapid prototyping processes based on fast chemical reactions are industrially available but only with submillimeter resolution (1). In contrast, LCVD facilitates rapid prototyping with micrometer resolution.

Laser-assisted chemical vapor deposition is on the threshold of commercial exploitation. Fibers fabricated by LCVD are already commercially accessible (5), and commercial uses can be envisioned for simple and complex LCVD microstructures. Some of these structures are still seeking a powerful market pull; others satisfy a need that already exists in the market. The use of the LCVD as a rapid prototyping process should therefore be of interest to a wide range of scientists and technologists, in particular specialists who may eventually become the users of the technology, both in terms of research and commerce.

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Liposomes Revisited

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Liposomes—self-assembling colloidal particles in which a lipid bilayer encapsulates a fraction of the surrounding aqueous medium—have now successfully negotiated the crucial passage from basic research to clinical practice. This transition has relied on technical breakthroughs in the control of liposome stability and reactivity, producing a virtual renaissance in the field.

Thirty years ago Alec Bangham discovered that phospholipids in water form closed vesicles; the physicochemical properties of these liposomes were then characterized, including their ability to serve as a model for cell membranes (1). Initially liposomes were heralded as optimal drug carrier systems, but further research proved disappointing and led to a period of skepticism among some scientists in the field of drug delivery (2). The medical utility of what are now called conventional liposomes (CLs) is limited by their rapid uptake by phagocytic cells of the immune system, predominantly in liver and spleen [although this has fortuitously led to some clinically important applications in antiparasitic treatment of phagocytes and in vaccine formulations (4, 5)]. This uptake is due to the characteristic nonspecific reactivity of CLs, which results in their largely uncontrollable properties upon administration in vivo.

Interest in liposomes as drug carriers was rejuvenated by the introduction of new ideas from membrane biophysics, and this multidisciplinary approach has enhanced prospects for their use in medicine (2–5). Liposomes can now be designed rationally, resulting in nonreactive (sterically stabilized) liposomes (SLs), as well as polymorphic (catonic, fusogenic) liposomes. The SLs can also be designed to exhibit specific reactivity (targeting), while polymorphic liposomes can exhibit high reactivity to nucleic acids and cell membranes. Because of their reduced recognition and uptake by the immune system, these newly sophisticated liposomes have been referred to as "stealth" liposomes (6), and are proving useful in cancer chemotherapy. The polymorphic liposomes provide a promising approach to gene therapy because they greatly improve transfection by exogenous DNA. In parallel with these developments, more efficient loading and retention of drugs within liposomes (7) (based on active "accumulation" through ionic gradients) has contributed to the ultimate utility of this new generation of liposomes (Fig. 1A).

Sterically stabilized liposomes were created when it was realized that neither mechanical nor electrostatic stabilization could provide liposomes with enough stability in a biological environment such as the systemic circulation. Thus, in SLs (3), the lipid bilayer contains glycolipids or, more recently, lipids conjugated with ethylene glycol, which provide a steric barrier outside the membrane (8). SLs remain in the blood for up to 100 times longer than conventional liposomes and can thus increase the pharmacological efficacy of encapsulated agents (2, 3, 8). Furthermore, SLs revived the feasibility of ligand-dependent targeting to specific cells (9), because they are much less subject to nonspecific uptake than are CLs. SLs bearing attached antibodies or other ligands are accumulated much more readily in targeted cells than are CLs (9). This approach is presently limited to the vasculature and to internalizing receptors (4, 6).

The enhanced biological stability of SLs is a result of the inhibition of interactions with plasma proteins (such as opsonins and lipoproteins) and cell surface receptors by

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