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Scaleable stagnation-flow reactors for uniform materials deposition: Application to combustion synthesis of diamond

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We describe two inherently scaleable geometries for chemical-vapor-deposition and heat-transfer processes that are based on stagnation flows. The "coflow" and "trumpet-bell" designs result in radially uniform fluxes to surfaces and they optimize the use of reagents. Using a trumpet-bell burner, we have grown uniform films of diamond from a substrate-stabilized flat flame of $C_2H_2/H_2/O_2$.

We describe two concepts to achieve the high deposition and heat-flux uniformity characteristic of ideal stagnation flows while minimizing the consumption of reagents. We apply this technology to the chemical vapor deposition (CVD) of diamond in a premixed, substrate-stabilized flat flame. The CVD growth of diamond from flames was first demonstrated by Hirose in 1988 using a C_2H_2/O_2 torch.¹ Unfortunately, a torch results in a non-uniform deposit, making scaleup difficult. Murayama and co-workers^{2,3} demonstrated an important improvement by using a highly strained premixed flat flame that was stabilized in the stagnation flow above a flat deposition surface. Other groups have also investigated the use of flat flames for diamond synthesis.⁴⁻⁷ The present contribution enhances the stagnation-flow configuration with flow-control systems that optimize reagent use.

The inherent radial uniformity of a stagnation-flow geometry provides an important means for achieving uniform species and heat fluxes to large surface areas. For an ideal, finite-separation stagnation flow,⁸ there must be a uniform and radially infinite flow of fluid at a fixed distance above a uniform-temperature surface (see Fig. 1). This infinite geometry guarantees uniform heat and mass fluxes to the surface. In practice, however, any implementation of a stagnation flow must consider reagent-use efficiency and degradation of the ideal flow characteristics by edge effects. The streamlines of Fig. 1 show that the outer portions of the flow (streamlines in bold) do not intersect the finite-radius flame front (dashed, horizontal line) and therefore do not contribute to diamond growth at the surface. This effect is independent of the scale of the flame or substrate.⁹ While this wastes reagents, the outer, nonreacting flow is still crucial in maintaining the ideal flow of the streamlines that do intersect the flame front and do burn.

In Fig. 2, we illustrate two scaleable designs that can approach the ideal properties of a stagnation-flow geometry but in a finite-scale implementation—the "coflow" geometry and the "trumpet bell." In the former concept, there is an inner region of reagent gases whose streamlines intercept the flame front. Surrounding this flow is a coflow that forces the inner flow to follow the streamlines of an ideal stagnation flow. The streamlines of the coflow do not intercept the finite-radius flame front. The coflow prevents the intrusion of tank (e.g., atmospheric) gases into the

flame. If operated under ambient conditions, the coflow can be a combustible gas, resulting in a diffusion flame at the edges of the primary flame front.

As an alternative to the coflow design, consider the trumpet-bell geometry of Fig. 2(b). Here, a radially uniform fluid flow enters into an axisymmetric form resembling a trumpet bell. To first approximation, the shape of the trumpet bell is simply the ideal stagnation-flow streamline that originates at the same radius as the inlet edge. More exactly, the trumpet-bell shape should take into account the boundary layer that develops upon the no-slip wall of the bell. Importantly, the bell serves the same function as the outer flow in the coflow design—ensuring that the fluid flow behaves as an ideal stagnation flow. If the flame location is chosen to intersect the trumpet bell, then all of the inlet gas burns. The trumpet-bell design has compelling advantages: the ideal properties of a stagnation flow are approached on a finite scale, the use of inlet gases is optimized, the area for uniform deposition of materials or transfer of heat is maximized, and contamination by background gases and other edge effects are avoided. Both the coflow and trumpet-bell designs are inherently scaleable concepts for the uniform deposition of materials and heat.

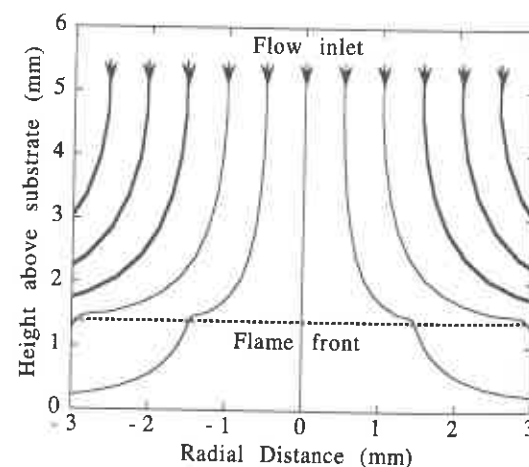


FIG. 1. The streamlines of an ideal stagnation flow. The horizontal, dashed line represents the location of a finite-radius, substrate-stabilized flame, such as that used in diamond synthesis. The kinks in the streamlines at the flame front arise from the large density gradient. While the innermost streamlines intersect the flame front and burn, the outer streamlines (bold lines) do not burn.

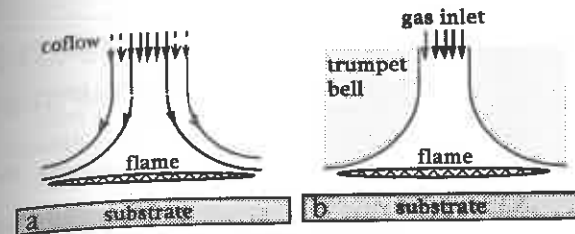


FIG. 2. Schematic illustration of (a) coflow design and (b) trumpet-bell design for efficient, uniform, and scaleable CVD and heat-transfer processes.

In this letter, we demonstrate the ability of the trumpet-bell design to produce uniform films of diamond from substrate-stabilized flames of $C_2H_2/H_2/O_2$.

We have numerically simulated the synthesis of diamond in a stagnation-flow flame, including detailed kinetic descriptions of both the gas-phase combustion¹⁰ and the diamond (or graphite) growth.¹¹ Details have been reported previously.¹² Our calculations have shown that stagnation-flow streamlines for a given flame position are independent of the pressure, choice of feed gas, and stoichiometry of the feed even for a chemically reacting flow. However, the streamlines and thus the required trumpet-bell shape do depend strongly on the inlet-to-substrate distance and flame location. For the conditions described below, we predict a substrate-stabilized flat flame with a flame front located about 1.5 mm above the substrate, a peak flame temperature of nearly 3500 K, and mole fractions at the surface of 0.047 and 1.7×10^{-4} (without inclusion of surface chemistry) for H and CH_3 , respectively. The streamlines for this calculation are shown in Fig. 1.

A trumpet-bell burner was constructed with a shape that approximates the streamline at 1 mm radius in Fig. 1. A uniform flow at the inlet of the temperature-controlled bell was achieved by placing an array of 25- μ m-diam holes at the 2-mm-diam entrance to the bell. The inlet-to-

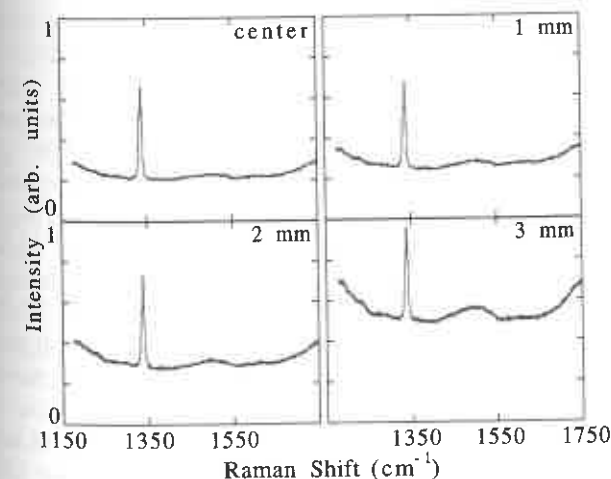


FIG. 3. Raman spectra of a diamond film produced during 30 min of growth using a trumpet-bell burner. Spectra are given as a function of radius from the center of the film. All spectra have the same intensity scale and were obtained using the 496.5-nm laser line of an argon-ion laser.

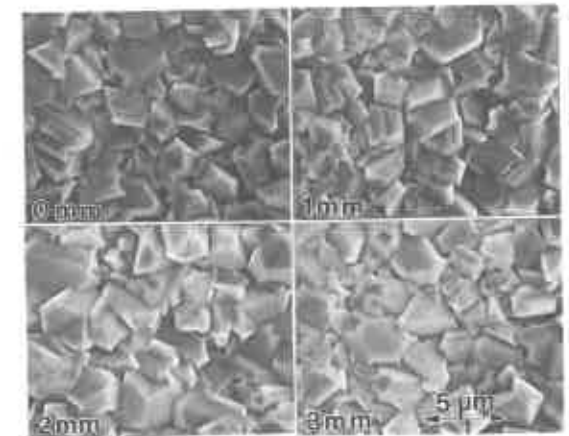


FIG. 4. SEM images of the diamond film of Fig. 3. All images are the same magnification and are given as a function of radius from the center of the film.

substrate separation was 5.5 mm. Diamond films were grown at atmospheric pressure on scratched molybdenum substrates 9.5 mm in diameter; the temperature was measured using a thermocouple positioned in a well 1 mm from the flame-exposed surface. The total flow of premixed feed gas was 8.8 slpm with $C_2H_2/H_2=0.97$ and $H_2/O_2=0.57$. The resulting substrate-stabilized flat flame was about 5–6 mm in diameter.

In Fig. 3 we show Raman spectra of a film deposited for 30 min using the trumpet-bell burner. The peak at 1338 cm^{-1} from the first-order phonon scattering of diamond¹³ establishes the synthesis of diamond. There is no indication of sp^2 -bonded carbon in the Raman spectra, as judged by the absence of phonon-scattering structure between 1550 and 1580 cm^{-1} .¹⁴ The intensity of the diamond phonon is relatively constant between $r=0$ and 3 mm, but the background luminescence is greater at $r=3$ mm. The film morphology is radially uniform between $r=0$ and 3 mm, as shown in the scanning electron microscopy (SEM) images of Fig. 4. The diamond film was continuous and had well-formed facets even to the edges of the 9.5-mm-diam substrate, well beyond the flame itself. Thus, reactive species (primarily H and CH_3) formed in the flame result in diamond growth well removed from the flame front, albeit at a slower growth rate.

In conclusion, we propose two inherently scaleable designs for CVD and heat-transfer processes that result in radially uniform fluxes to surfaces. Both the coflow and trumpet-bell geometries maintain the uniform surface fluxes of ideal stagnation flows while optimizing reagent usage and minimizing finite-dimension effects. We have demonstrated the trumpet-bell concept by growing uniform films of diamond from a substrate-stabilized flat flame fed by $C_2H_2/H_2/O_2$.

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- ¹³The diamond film remained firmly attached to the substrate during cooling, resulting in compressive stress from the differential thermal contraction of the substrate and the film. Thus the diamond phonon is upshifted from the natural-diamond value of 1332 cm^{-1} . In addition, the phonon has a pronounced shoulder at about 1334 cm^{-1} , suggesting a substantial stress gradient through the film. Different substrate preparation resulted in delaminated films with the diamond phonon at 1332 cm^{-1} and a phonon linewidth (FWHM) $< 3.7\text{ cm}^{-1}$, indicating very high quality diamond.
- ¹⁴The broad peak centered around 1490 cm^{-1} is luminescence, as established using 514.5-nm excitation.

Cross-sectional scanning tunneling microscopy of electrodeposited metal oxide superlattices

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We have used scanning tunneling microscopy to characterize cleaved cross sections of Pb-Tl-O superlattices. The metal oxide ceramic superlattices were electrodeposited from a single solution, with layer thicknesses as small as 1.5 nm. The lattice parameter of the fcc fluorite-type oxides is approximately 0.536 nm. Modulation wavelengths were determined using Fourier analysis of the STM images and found to be in good agreement with Faraday calculations and x-ray diffraction measurements. The STM is especially well suited for the measurement of modulation wavelengths that are too large to measure by x-ray diffraction, but too small to measure by scanning electron microscopy.

Nanometer-scale materials are of great interest because they offer the possibility of engineering a normally intrinsic property, such as the band gap, by simply changing the dimensions of the material. Most of the work in this area has been on semiconductor-based superlattices. Our work has focused on the electrodeposition of superlattices based on conducting metal oxides in the Pb-Tl-O system.¹ These degenerate *n*-type semiconductor materials have an optical band gap between 1.4 and 1.8 eV, with a sharp plasma resonance in the 1000–1500 nm range of the near-infrared region.^{2,3} The nonstoichiometric oxides have metallic conductivity and semiconductorlike optical properties. Little is known about quantum confinement effects in materials of this type.

Electrodeposition offers several possible advantages over vapor-phase methods such as molecular beam epitaxy and chemical vapor deposition. The low processing temperatures (room temperature in our work) minimize interdiffusion, layer thicknesses can be designed by selecting the appropriate current and dwell time, composition can be controlled, films can be deposited onto complex shapes, and the technique is not capital intensive. Electrochemically grown superlattices have not been sufficiently characterized relative to their vapor phase counterparts to determine whether these advantages of the electrochemical method can actually be realized.

We have previously used the scanning tunneling microscope (STM) to compare the electronic topography of superlattices produced under current and potential control.⁴ In the present work we use the STM to measure modulation wavelengths (i.e., bilayer thicknesses) in Pb-Tl-O superlattices, and compare the results to wavelengths calculated from Faraday's law and measured by x-ray diffraction. Our interest is in developing the STM as a technique for measuring modulation wavelengths that are too large to measure by x-ray diffraction ($> 20\text{ nm}$ for our samples), but too small to measure by scanning electron microscopy. The ceramic oxide superlattices were scanned directly in air, with a Digital Nanoscope II instrument. Nanometer resolution was obtained by keeping the tunneling current constant and allowing the height to vary, while scanning a cross section of the Pb-Tl-O superlattice.

Mechanically formed Pt/Ir probe tips were used and checked for atomic resolution on highly ordered pyrolytic graphite before each experiment. Samples were held in place with conducting silver paint by mounting them on edge to a vertical stainless-steel substrate. All images were obtained at a positive voltage bias of 200 mV, tunneling current of 0.5 nA, and scan rate of 4.38 Hz.

We obtained superlattices in the Pb-Tl-O system from a single solution, by depositing thin epitaxial layers of two different compositions.¹ Prelayers of the mixed oxide can be deposited which undergo a bcc to fcc transition at a Pb content greater than 40 at. %.⁵ The films were deposited onto a [210] oriented fcc prelayer from a 5 M NaOH solution containing 5 mM TlNO_3 and 100 mM $\text{Pb}(\text{NO}_3)_2$. Deposition current densities of 5 and 0.05 mA/cm² were used to form superlattices for this study. At 5 mA/cm², thallium ions in the solution were mass transport limited giving a Pb-rich layer of composition $\text{Pb}_{0.74}\text{Tl}_{0.26}\text{O}_{1.9}$, with Pb and Tl content determined by energy-dispersive spectrometry (EDS).³ At deposition current densities of 0.05 mA/cm² the resulting layer composition was $\text{Pb}_{0.46}\text{Tl}_{0.54}\text{O}_{1.7}$. The deposition time at each current density was controlled to give equal layer thicknesses ranging from 1.5 to 25 nm.

Figure 1 shows a STM line plot of a cleaved Pb-Tl-O superlattice with modulation wavelengths (Λ 's) of 3 [1(a)] and 50 [1(b)] nm. Resistivity measurements have shown that the thallium-rich films are less conductive than the lead-rich films.³ The compositionally different layers will therefore have varying electronic properties which appear as apparent height differences in the STM. By depositing alternating compositions with unequal layer thicknesses, it was shown that the Tl-rich layer appears at a higher apparent height than those layers with lower resistivity and higher Pb content. Images of both halves of a cleaved sample give the same profile, suggesting that the variation in height is due to electrical properties. Other researchers have also attributed height differences for their cleaved superlattices to differences in electronic properties.^{6–8}

A peak corresponding to Λ of the superlattice is obtained by taking the Fourier transform over many layers of the sample. Figure 2 shows an average power spectrum