# Laser CVP of Ultrafine Ceramic Powders of Si and $Si_3N_4$

## A Study of the Flow Pattern of the Laser Flame

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## ABSTRACT

The flow patterns of flames in a Laser Chemical Vapor Precipitation Reactor (L-CVP) for the production of Si and $Si_3N_4$ submicron powders have been studied using interferometry and the shadow method. In the case for $Si_3N_4$ production, the reactant gases, $SiH_2Cl_2$ and $NH_3$ were mixed in the laser beam, thus preventing low temperature reactions. The methods used give detailed information about flows in and out of the flame. This information is important for controling the uniformity of the physical and chemical properties of the synthesized powder and to maintain long production times. Interferometry also provides information on the temperature distribution in the flame.

**Index Entries:** Si; $Si_3N_4$; $SiH_2Cl_2$; $NH_3$ flames, flow patterns of.

## INTRODUCTION

Recent interest in high temperature structural ceramics has led to the development of chemical vapor phase synthesis techniques for the for-

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mation of a variety of high quality oxidic and nonoxidic ceramic powders. Regarding the gas phase reaction process, we have described Chemical Vapor Precipitation (CVP) (*1*) of submicron $Si_3N_4$ powders using thermal (*1*) and laser (*2,3*) activation.

The primary characteristic of the laser-driven gas phase synthesis process is a well defined reaction zone that facilitates a considerable degree of control over composition, size, and size distribution of the product powders. In the laser-CVP of Si, SiC, and $Si_3N_4$, $SiH_4$ is invariably used as the silicon reactant (*4–8*), whereas in the traditional thermally-activated CVP of powders and thin films of $Si_3N_4$ chlorinated silanes, i.e., $SiH_2Cl_2$ and $SiCl_4$, are frequently employed (*1,9*). It has been shown that ultrafine spherical silicon powder can be produced using $SiH_2Cl_2$ as a reactant in L-CVP (*2,3*). In the production of $Si_3N_4$, $NH_3$ reacts with chlorinated silanes, such as $SiH_2Cl_2$ and $SiCl_4$, to form silicon diimides at ambient temperatures. To avoid this reaction, a laser reactor was equipped with a specially designed nozzle to inject the reactants separately into the laser beam.

Earlier experiments (*2,3*) have shown that the silicon nitride powders contain hard agglomerates and some imide contamination. Normally, the silicon nitride powders are collected at a high temperature to separate silicon nitride from the waste product, $NH_4Cl$, which dissociates above 610 K. However, the collection at ambient temperature also leads to powders that are agglomerated. Therefore, the agglomeration is probably caused by collisions of the particles in the flame. Although the particles leave the laser beam within a millisecond, the gases and particles take tens of milliseconds to be cooled down. To lower the agglomeration rate, the cooling down must be more rapid. By entering $NH_3$ in the flame above the laser beam, silicon powder is first formed and subsequently nitrided in the upper part of the flame. Using this method, silicon nitride will be formed at a lower temperature; hence, the cooling down is expected to occur faster because of mixing with surrounding nitrogen. This method of injection will also avoid imide formation.

When $NH_3$ is injected directly into the laser flame, the flow pattern shows disturbance, illustrated by the fact that the powder does not leave the reactor through the exhaust funnel, but spreads through the reactor. The collection of powder on the KCl windows causes a breakdown because of laser heating. Furthermore, spreading of the powder lowers the transmission of the $CO_2$ laser beam (*2,3*).

Various techniques, such as the shadow method, interferometry, and visual observation, are being used to study the gas flow pattern. The shadow method shows the contour of the gas flows and flow pattern of clouds of powder. With interferometry, the density distribution of the gases in place and time can be determined. With these techniques, the $NH_3$ flow into the flame and the emission of the powder and exhaust gas out of the reactor can be optimized; these methods also give an indication of the temperature distribution in the flame.

## EXPERIMENTAL PROCEDURE

### *Reactants*

The reactants for silicon and silicon nitride synthesis by Laser Chemical Vapor Precipitation were dichlorosilane (Air Products and Chemicals, Inc., Pacoima, CA, 97% $SiH_2Cl_2$, 3% other chlorosilanes), and $NH_3$ (Air Products, 99.999%) were utilized. The carrier gases, $N_2$ and $H_2$, were purified with copper (BASF Wyandotte Corp., Parsippany, NJ, R 3-11) and palladium (BASF, R 0-20) catalyst, respectively, and a zeolite (Dow Chemical Co., Midland, MI, A4).

### *Laser CVP*

The selection of the present reactants for the synthesis of $Si_3N_4$ implies the formation of silicon diimide, $Si(NH)_2$, at room temperature unless precautions are taken in the introduction of the reactant gases into the laser beam. This can be achieved by a special nozzle design. In addition ammonium chloride is a waste product, requiring adequate separation of $Si_3N_4$.

A schematic drawing of the stainless steel reactor is presented in Fig. 1. The two KCl windows were flushed with $N_2$. The reactor was operated at atmospheric pressure. An industrial untuned 150 W cw $CO_2$-laser (Electrox, PB 2000) radiating at 10.6 μm was partially focused with a ZnSe lens (focal length, 30 cm) in an orthogonal stream of reactants. A conic and straight exhaust funnel were explored to optimize the gas and powder emission from the laser flame.

The nozzle was built up of four separated concentric outlets for $NH_3$ pointed toward the middle and a centered outlet for the chlorinated silanes, sensitizer, and carrier gas. The outlets for $NH_3$ can be altered in horizontal, as well as in a vertical direction. The gases were mixed in or above the laser beam, thus avoiding low temperature reactions.

The reaction products were confined to a small well-defined reaction zone by a concentric $N_2$ gas stream. This gas stream was also used to feed the products into a horizontal electrostatic precipitator.

### *Interferometry and the Shadow Method*

To study the flow and temperature profiles, interferometry and shadow measurements have been made. Schematics of the interferometry and shadow measurement setups are shown in Fig. 2 top and bottom, respectively. A Mach-Zehnder interferometer was used, consisting of a HeNe laser beam (632.8 nm) expanded by two lenses. This expanded beam was split with a beam splitter and one beam was passed through the reactor and the other was guided around the reactor. Finally, the two were combined and directed to a photographic plate without the use of

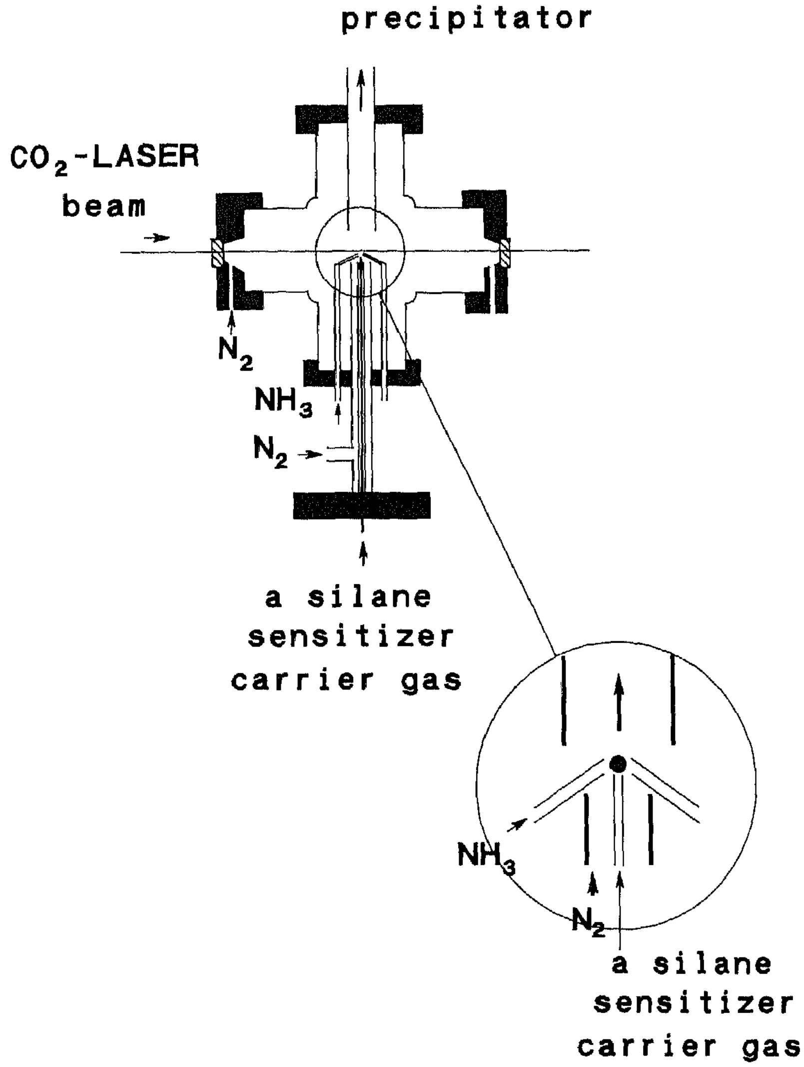


Fig. 1. Schematic of the reactor and the nozzle with the gases used.

lenses. By adjusting one of the mirrors, the difference in optical path length could be changed, and consequently, the size and direction of the fringes could be altered. For the shadow measurements, the reference beam was not used.

Both methods rely on the difference in refractive index. Since the density is strongly a function of the temperature, the influence of the variation in the composition of the gases can often be neglected compared to the influence of a difference in temperature (*12*). For ideal gases, the relation between the refractive index, $n$, and the temperature, $T$, is

$$(n-1)T = \text{constant} \tag{1}$$

The fringes seen with interferometry represent areas where the difference in optical length is a multiple of the wavelength

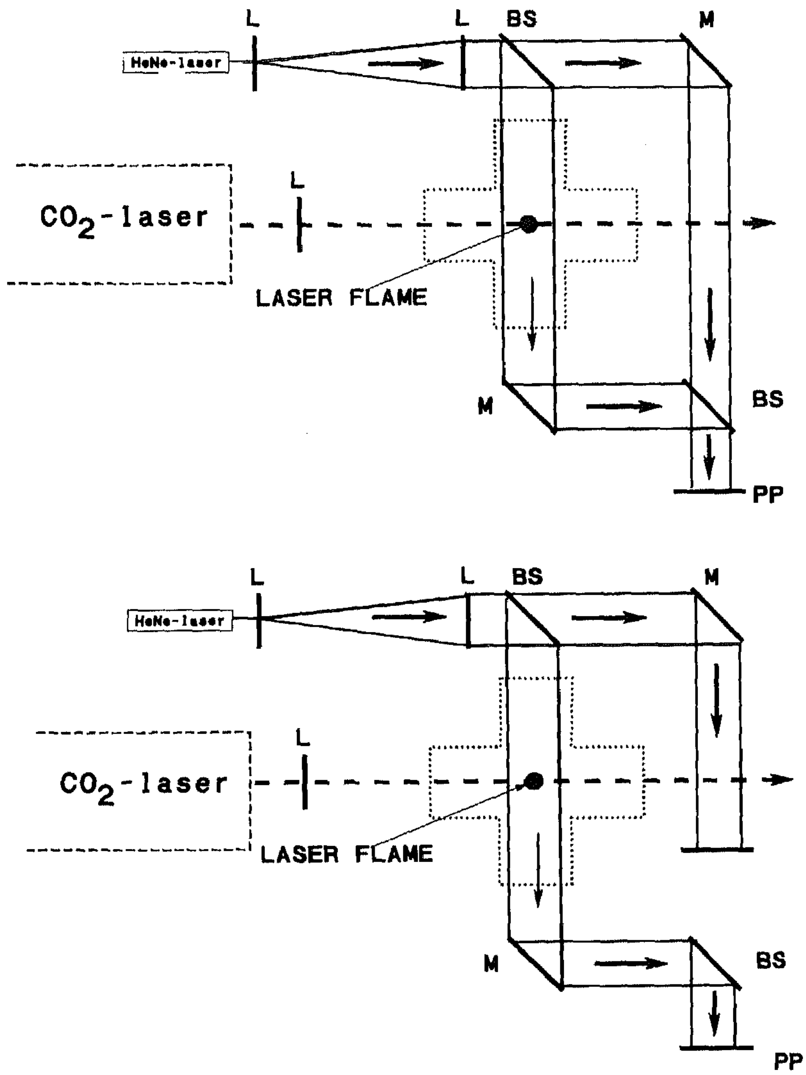


Fig. 2. Schematics of the setup for interferometry (top) and the shadow method (bottom): L = lens, BS = beam splitter, M = mirror, and PP = photographic plate.

$$\int_{flame} n_{flame} dx - \int_{ref.} n_{air} dx = p\lambda \tag{2}$$

If the wave fronts of the two separated beams are perfectly parallel, the photographic plate is uniformly illuminated or completely black, i.e., the fringe is infinite. In other cases, the fringes are finite and fringes will be seen at a distance q from one another. If there is a small disturbance, the fringes will be shifted by $\delta q$, and can be related to the refractive index as follows

$$\int_{flame} (n_{flame} - n_{nitrogen}) dx = (\delta q/q)\lambda \tag{3}$$

The variation in refractive index can be calculated and from which the relative temperature can also be calculated. To calculate the absolute temperature, the temperature dependence of the refractive index has to be known. By measuring a reference point, the constant can be calculated. The exact interpretation of complex flow patterns is often difficult with interferometry.

Using the shadow method, the dark lines represent areas where $d^2(n - l)/dx^2$ is maximal. This means that regions in the flame with strong variations are visible, so the contour lines of flows within the flame are shown. Line broadening of the shadow line gives an indication of the turbulence.

## RESULTS AND DISCUSSION

The flow pattern in the flame has been studied for a variety of process conditions using interferometry and the shadow method.

Figure 3a shows the shadowgraph of an unheated $SiH_2Cl_2$ stream, which hardly expands upon leaving the nozzle. If $SiH_2Cl_2$ is heated with the $CO_2$ laser radiation, the gas stream expands strongly, as is shown in Fig. 3b, and a long yellow flame was seen. When $N_2$ was injected, the flame flattened and small flames were observed in the center and between the centric and concentric outlets. This was corroborated by interferometry and the shadow method. Injection of reactive $NH_3$ resulted in the formation of additional, small flames associated with the $NH_3$ outlets. The overall flame became whitish and brighter. The shadowgraph revealed only slight broadening of the flow. However, the interferogram showed a larger shift of the fringes at the concentric part of the flame.

When the concentric outlets were increased in height in order to change the reaction mechanism, growth of a deposit was observed on the concentric outlets, as shown in Fig. 4. Although the outlets were outside the luminescent part of the flame, this shadowgraph shows that in reality the outlets were inside an outer, non-luminescent, part of the flame. The particle formation clearly occurs in a larger region than the luminescent area, as can be seen with shadowgraphs. The outlets had to be altered in a horizontal direction in order to avoid growth on the nozzle.

Using interferometry, flames with low $N_2$ flow as well as those with low $NH_3$ flow, had flow patterns that were only slightly perturbed, compared to the flame with only $SiH_2Cl_2$. Both flames were yellow but shorter than the $SiH_2Cl_2$ flame. Visual observation showed that the flame with a nitrogen injection showed a sharp decrease of luminescence and a narrowing of the luminescent area above the place where the $N_2$ was injected. The flame with $NH_3$ was separated into two parts, one with only $SiH_2Cl_2$ below the injection point of $NH_3$ and the upper part including $NH_3$. The upper part of the flame seemed to be even broader than the lower part. Both parts produced about the same luminescence. The reaction

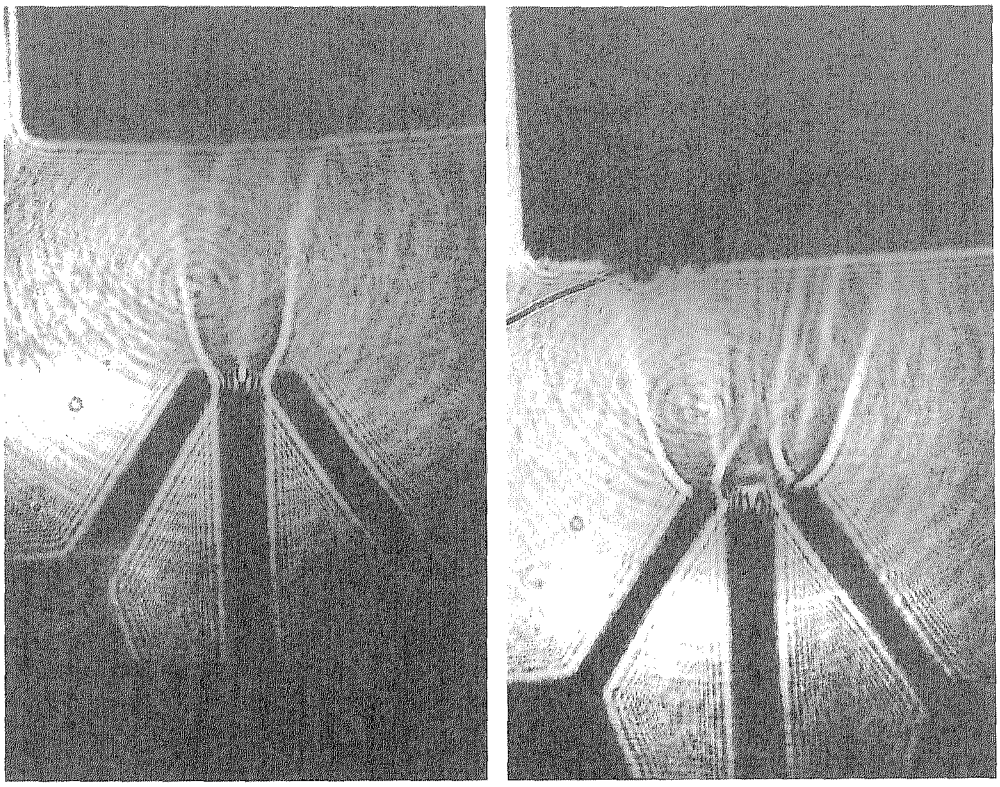

Fig. 3. Shadowgraphs of laser flames (a) with only dichlorosilane and (b) with ammonia and dichlorosilane.

$$6\,Si + 8\,NH_3 \longrightarrow 2\,Si_3N_4 + 12\,H_2\,(\Delta H(298K) = -607\ kJ/mol\ Si_3N_4)$$

is clearly exothermic.

Fig. 5 shows interferograms of different flames with a large conic exhaust funnel. With only $SiH_2Cl_2$ used as a reactant (Fig. 5a), the shift of the fringes was fairly constant over the whole flame and did not change noticeably in time, which indicates that the turbulence in the flame must be small. The injection of up to 7.5 L/h $N_2$ into the laser beam causes the occurrence of turbulence as indicated by a less constant and time dependent shift of the fringes (Fig. 5b). The injection of more than 4.5 l/h $NH_3$ into the laser beam creates a totally disturbed flow (Fig. 5c), and the flame could not be observed any more with the employed methods, because a mist of powder occurred in the reactor. The interferogram in Fig. 5c also illustrates this turbulence by the vagueness of the fringes.

Different chimneys are used to observe the stabilization of the flame, as shown in Fig. 6. When a small tube is used to guide the gas and the powder from the flame into the exhaust funnel, only little improvement was observed. The shadowgraph shows that the powder circulates back from the conical funnel into the reactor. When a tube with an increased

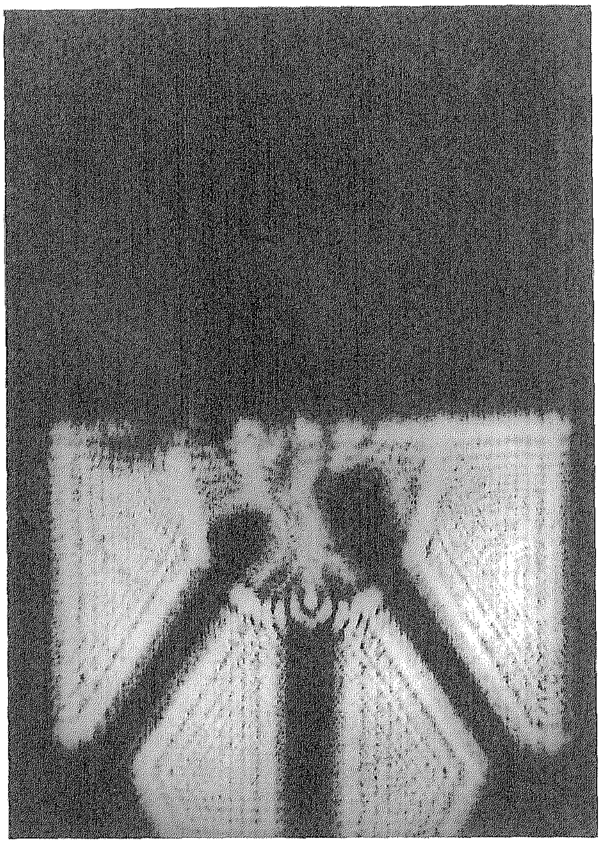

Fig. 4. Shadowgraph of the flame and nozzle with growths on the outlets for ammonia.

length was used, thus forming a straight tube to the precipitator, the disturbance was minimal, as shown in Figs. 3 and 7.

These experiments demonstrate that using interferometry and the shadow method, information can be obtained on the flame and particle formation. This information is necessary in order to improve the performance of the reactor. An example of these improvements is the replacement of the exhaust funnel.

Preliminary results of $Si_3N_4$ powder synthesis show that when using the modified exhaust funnel and injecting $NH_3$ above the laser beam, considerably smaller agglomerates of $Si_3N_4$ particles are formed than in the preceding experiments.

## CONCLUSION

The employed methods, i.e., interferometry and the shadow method, provide detailed information on the flow pattern of the laser-activated flame, which cannot be determined with visual observation.

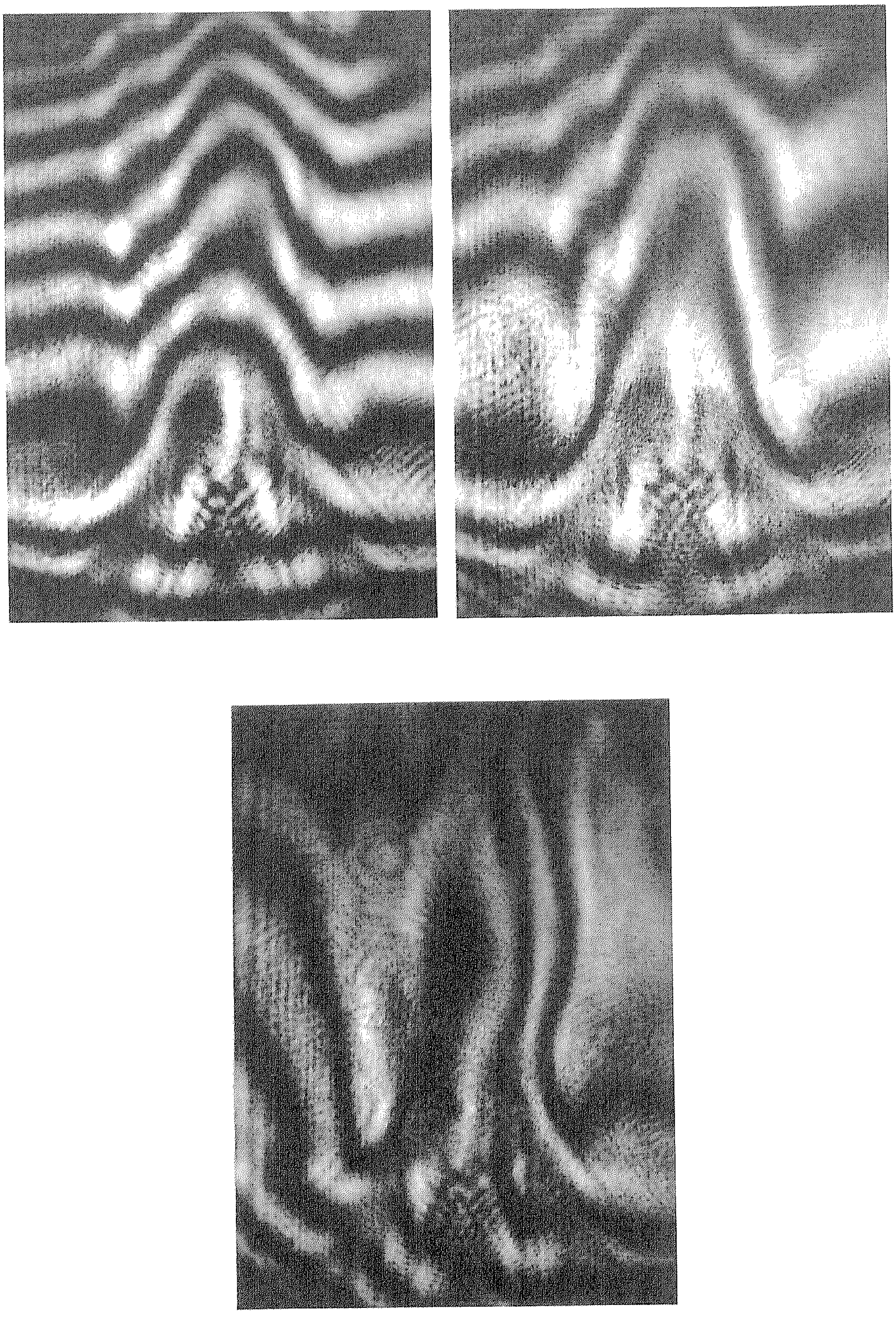

Fig. 5. Interferograms of flames without a chimney to stabilize the flame with reactants: (a) dichlorosilane, (b) dichlorosilane and nitrogen, and (c) dichlorosilane and ammonia.

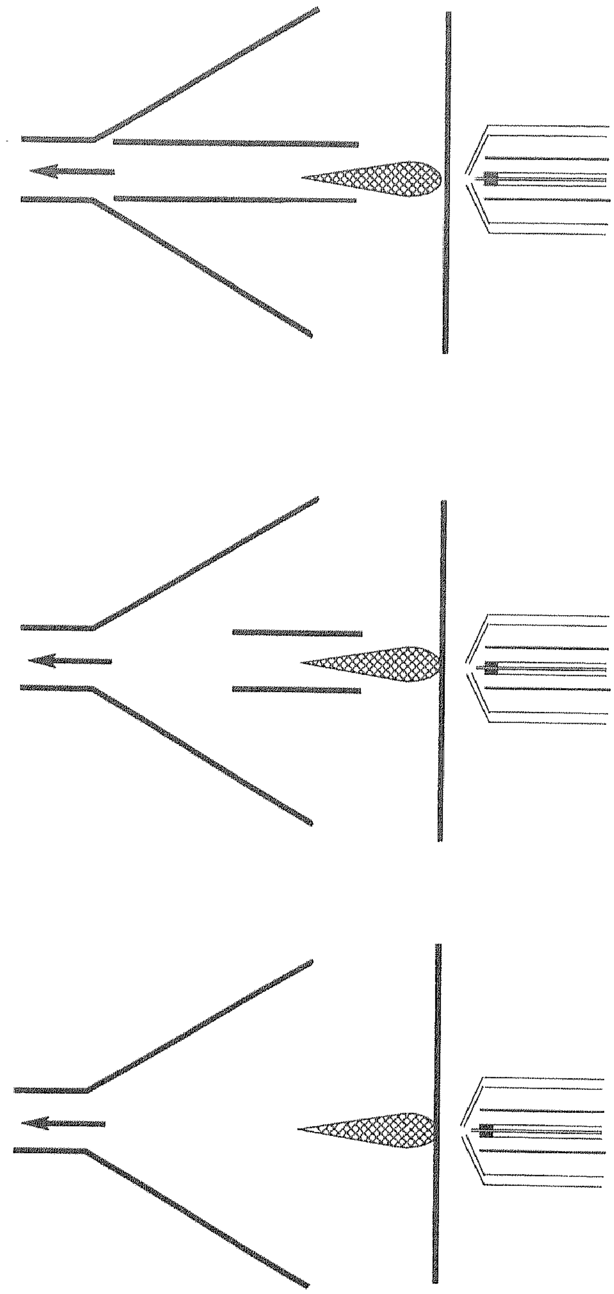

Fig. 6. Schematics of the nozzle and exhaust funnels with different tubes used as a chimney to stabilize the flame. From left to right, the flame is increasingly stable.

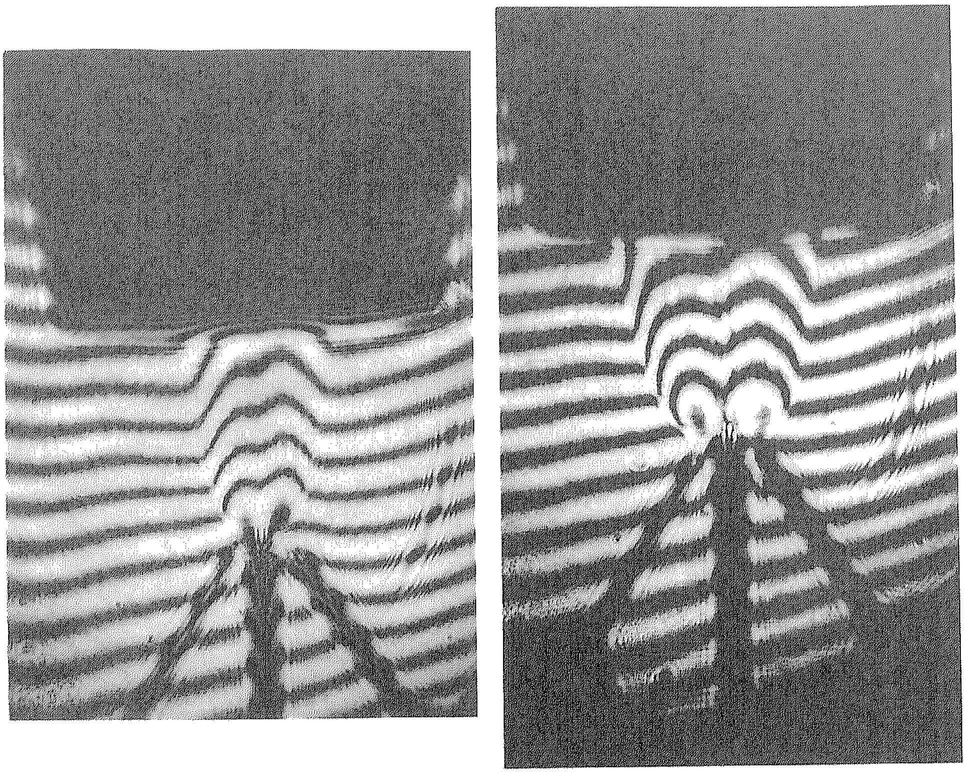

Fig. 7. Interferograms of flame stabilized by a modified exhaust funnel with the reactants: (a) only dichlorosilane and (b) dichlorosilane and ammonia.

With this information, the position of the reactant inlets can be optimized, the flame stabilized, and the flow of the powder out of the reactor improved. In addition the degree of powder agglomeration can be reduced. These aspects of the flow pattern are essential for the control of the uniformity of the physical and chemical characteristics of the powders and for achieving long production times.

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