Chemical Vapour Precipitation of Silicon Nitride Powders in a Laser Reactor†

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Abstract

The Laser Chemical Vapour Precipitation (L-CVP) of Si₃N₄ powders from mixtures of halogenated silanes and NH₃ has been studied. The reactant gases were mixed at varying position in the laser beam, thus preventing low temperature reactions. The Si₃N₄ was collected and separated from the waste product, NH₄Cl, by electrostatic precipitation. A major problem in utilizing SiHCl₃ and SiCl₄ is their poor absorption of radiation from CO₂-lasers. SF₆ and SiF₄ have been explored for possible use as an inert sensitizer. Silicon can be prepared from SiH₂Cl₂ without the use of a sensitizer. The diameter of the Si₃N₄ particles is typically between 15 nm and 110 nm dependent on the process conditions.

1. Introduction

This paper concerns the preparation of fine ceramic powders, specifically silicon nitride, by chemical vapour precipitation. The eventual quality of a ceramic product is dependent upon the properties of the powder before it is compacted and sintered. The morphology of the powder is usually specified through its particle size distribution and the degree of agglomeration of the powder. Chemical Vapour Precipitation, CVP, is an attractive route to prepare powders of very fine particle size, less than 1 μm. The eventual particle size is dependent upon the nucleation rate and growth of the aerosol particles which, in turn, can be controlled mainly by the temperature profile in the reactor. However, when using conventional heating sources, not only is the lower limit of the particle size restricted, but also the degree of agglomeration increases with decreasing particle size due to a long residence time at conditions of temperature and high number density.

The alternative use of a laser beam as the source of heat has been investigated and reported by several laboratories. In this paper, we summarize our experience with this novel and promising technique. Exciting the gas mixture thermally by laser radiation increases the heating and cooling rates enormously, whilst the process temperature is not restricted by the reactor construction material. The excitation of the reactants can be made selectively by separate reactant injection and by matching the laser frequency with the absorption bands of one of the reactants. This introduces flexibility and an additional variable to control the reaction mechanism.

The success of the technique is also dependent upon the choice of reactants. Most previous research has concerned the production of silicon nitride, Si₃N₄, from a reaction of silane, SiH₄, and ammonia, NH₃. The silane is strongly absorbent of the light emitted by a CO₂-laser which has a wavelength of 10.6 μm. In this process it is difficult to obtain a stoichiometric product, an excess use of silicon has often been reported. We have based our investigations on the alternative use of chlorinated silanes, SiHCl₃ and SiCl₄, for this process which are potentially commercially more attractive and safer. They have, however, a much lower absorption coefficient of the CO₂-laser radiation. This problem can be overcome by the addition of a
third gas which acts as a sensitizer, for example SF₆ or SiF₄. Whereas SF₆ absorbs strongly the 10.6 µm radiation (10P20 line) of CO₂-lasers, SiF₄ absorbs only at 9.4 µm the 9P42 line of a CO₂-laser. The wavelength of a tuneable laser can be adjusted to optimize the absorption by particular reactants. Another interesting alternative is to excite the ammonia instead of the silicon containing precursor. The use of alternative precursors and of sensitizers does lead to more complex reaction products and can lead to contamination of the product if it is not collected at high temperatures.

It is clear that the process has great potential for numerous variations in reactants and in reactor design. In this paper, CO₂-laser light absorption by NH₃ at atmospheric pressure was used to form Si₃N₄ powder, starting with absorbing and non-absorbing chlorinated silanes.

2. Experimental Procedure

A schematic diagram of the apparatus is shown in Fig. 1 and a photograph in Fig. 2. The reactants are introduced through separate nozzles immediately below the laser beam. The sudden rise in temperature and subsequent cooling cause a chemical reaction and condensation of aerosol particles within a stable flame. A picture of a typical flame is shown in Fig. 3.

The reactor was constructed of stainless steel and the laser was introduced through two KCl windows which were flushed with N₂ (467 sccm). The reactor was operated at atmospheric pressure. A 200 W cw CO₂-laser, with a wavelength tuneable between 9.166 µm and 10.886 µm, was partially focused with a ZnSe lens, of focal length 30 cm, to a spot 1.5 mm in diameter and shone orthogonally to the stream of the reactants.
The gas inlet nozzle consisted of four jets which directed the ammonia onto a central jet of the chlorinated silane. The gases were mixed in or above the laser beam to avoid low temperature reactions since they react at low temperature to form solid silicon diimide, Si(NH)$_2$. The concentric inlets could be adjusted in both the horizontal and vertical directions. The plan view of the different configurations tested are shown in Fig 4. Normally configuration A was used.

![Fig. 4 Nozzle configurations](image)

When NH$_3$ was the excited gas, configuration C gave the best results because in this case the highest temperature was recorded. An arrangement which exchanged the reactant flows, with the NH$_3$ gas coming through the middle and the SiH$_2$Cl$_2$ gas from the outside inlets, produced poor results. In that case, only with low reactant flows was a stable flame observed and the powders produced were also very poor since they contained a relatively large amount of imide. The reaction products were confined to a small, well-defined reaction zone by a concentric N$_2$ gas flow. The gas and particle stream was fed into a horizontal electrostatic precipitator (ESP) which separated the Si$_3$N$_4$ powder from the NH$_4$Cl. The potential of the central wire electrode was about +20 kV, whilst the external cylindrical counter electrode was earthed. This cylindrical counter electrode was placed outside the pyrex collection tube in order to prevent electrode corrosion by the product gas stream. The temperature of the ESP furnace was maintained at 570 K during operation to achieve optimum collection. The powder collected was subsequently heated to 770 K, under vacuum, for fifteen hours in order to remove the remaining traces of NH$_4$Cl. This temperature is low enough to avoid a reaction of imides, if present, to nitrides. In order to measure the flame temperature, a 2-color pyrometer in combination with a spectrometer was used, as shown in Fig. 5. The setup consisted of a pair of mirrors to scan the flame. One lens was used to focus the flame onto the aperture stop, and behind this stop another lens was used to focus the light, split by a beam splitter, onto two hotodiode detectors. Bandpass filters were used to define the wavelength of the light received on the detectors. The light beam was chopped in order to be able to use lock-in amplifiers for phase sensitive detection of the small emission signals. The radiation emitted from an ideal black body at temperature $T$ is given by the Planck function,

$$I_{B\lambda} = \frac{2c^2h}{\lambda^4} \frac{1}{e^{\frac{kT}{\lambda}} - 1}$$  \hspace{1cm} (1)

The temperatures were calculated$^{10}$ from the intensity ratio of two different wavelengths $I_{\lambda}$, corrected for the extinction of the particles:

$$R = \frac{I_1}{I_2} = \frac{\lambda_2 I_{B\lambda_2}}{\lambda_1 I_{B\lambda_1}}$$  \hspace{1cm} (2)
Some of the light is fed to a spectrometer, equipped with a photomultiplier and a Si/PbS-photodiode detector. The lock-in amplifiers were also used to amplify the signals from the detectors. The spectra were recorded in a small computer.

The powders were analyzed using IR-spectroscopy, and characterized by X-ray diffraction (XRD), and electron diffraction in a transmission electron microscope (TEM). The amount of nitrogen in the powders was determined by decomposing the samples in LiOH at 950 K and measuring the amount of NH₃ released⁷. The particle sizes and the state of agglomeration were measured from transmission electron micrographs. In Fig 6 are shown examples of spherical particles of 100 nm, the required product, whereas Fig. 7 shows an example of a heavily agglomerated product. The critical factors in this technology are so to control the reaction, condensation and agglomeration rates that particles of the required size are eventually produced.

3. Experimental Results

3.1 Absorption of CO₂-laser radiation

All reactants and sensitizers show luminescence if CO₂-laser radiation is being absorbed. The excited molecules have been shown to be in an thermal equilibrium state at pressures above 10 m Bar⁸). To determine the wavelength dependence of the laser heating, the intensity of the luminescence from reactants and sensitizers in the reactor was measured in the conditions used during synthesis. The luminescence is shown to be mostly thermal. Using SiH₂Cl₂, a yellow flame was observed if radiation of one of the 10P or 10R lines around the 10.4 μm region of the CO₂-laser was focussed onto the reactant flow. This luminescence varied little with the wavelength radiated by the laser. The 9P and 9R lines of the CO₂-laser were not absorbed. Using either SiHCl₃ or SiCl₄ no luminescence was observed using any line. NH₃ showed emission if the reactant was excited by radiation of several lines of the CO₂-laser. When using the 9R30 line especially strong emission was observed in the reaction zone. Less prominent emission was observed using the 9R16, 10P32 and 10P34 lines of the CO₂-laser. SF₆ is a well-known⁹,¹⁰) sensitizer used in IR-laser chemistry and is known to absorb the 10P20 line of CO₂-lasers strongly. SiF₄ is also used as sensitizer if SF₆ is not inert in the prevalent condition¹¹).
When SiF₄ was injected into the reactor strong emission was observed using the lines around 9P42 of the CO₂-laser.

3. 2 Silicon particle formation

SiH₂Cl₂ was used in the L-CVP of silicon powders. A yellow, thermal flame developed in the reactor due to laser excitation with the 10P20 laser line and decomposition of SiH₂Cl₂ followed by nucleation of elemental silicon. Dark brown powders of amorphous and crystalline silicon were produced, which were fairly monodisperse. The mean particle diameter of the amorphous powders was 30 nm and that of the crystalline powders was 100 nm. The product contained small amounts of chlorine impurities as observed with EDX. A few minutes after starting the deposition experiments, the reaction flame stabilized and long production times could be maintained. The spectra recorded revealed only a smooth curve, indicating black body radiation. The calculated temperature was about 1770 K. The capacity of the electrostatic collector limited the experiments to one hour. As shown above, dichlorosilane is clearly capable of absorbing sufficient power from an untuned CW industrial laser to dissociate completely, and to produce ultrafine silicon powders at atmospheric pressures.

Utilizing SiHCl₃ or SiCl₄ as reactant with either SF₆ or SiF₄ did not result in particle formation. In both cases a blue flame was observed. Spectroscopy showed a broad band around 450 nm in the SF₆ experiment and three narrow bands around 440 nm in the SiF₄ experiment which can be attributed respectively to S₂ and SiF radicals.

3. 3 The influence of the process conditions on the Si₃N₄ formation from excited SiH₂Cl₂

Using 50 sccm of SiH₂Cl₂ and 110 sccm of NH₃ the height of injection of the NH₃ into the reaction zone was changed. By injecting the NH₃ below the laser beam the maximum temperature, between 2400 and 2600 K, was measured at the area where the NH₃ flow entered the central SiH₂Cl₂ flow. It seems likely that laser light absorption by the Si(NH)₂ particles formed caused this high temperature. Strongly agglomerated particles were formed during synthesis at low NH₃ injection height. The particle size distribution is also relatively wide. The diameter calculated from BET surface measurements is similar to the primary particle size as observed with the electron microscope. The particles were shown to be amorphous by X-ray and electron diffraction in the TEM. IR-spectroscopy revealed the silicon nitride particles to contain a considerable amount of imide impurities. The amount of nitrogen (around 33%) was close to the stoichiometric value for Si₃N₄ (40%).

When NH₃ was injected into the laser beam the temperature was maximal in the area between the central and the concentric outlets. This is illustrated in Fig. 8. Whereas the measured temperature in this area was similar to the previous experiment, the synthesized particles were larger and less agglomerated than those obtained in the previous experiment. Several of the particles contained a small amount of crystalline silicon as indicated by X-ray diffraction and electron diffraction. Several of the particles appeared to contain crystalline silicon cores. IR-spectroscopy revealed only a small number of N-H bonds. The nitrogen content of the particles was lower than in the previous experiments. Thus the powders were shown to consist mainly of silicon nitride with a minor contamination of imides and silicon. In addition to spherical particles a large number of fibers were observed as is shown in Fig. 9. The fibers were distorted and conically shaped with a spherical tip and were also amorphous.

When NH₃ was injected above the laser beam the region with the highest temperatures comprised the injection area of NH₃ in the upper part of the flame. The temperature was much
lower than in the previous experiments; between 1600 and 1700 K. In these experiments larger spherical and egg shaped particles were formed. The agglomeration grade was relatively low and the particle size distribution was narrow. The equivalent diameter calculated from BET measurements was smaller than the diameter observed with TEM. The particles may be porous which is probably caused by the nitridation. The majority of the particles had large crystalline silicon cores as detected by XRD and electron diffraction on the TEM but their exterior was amorphous. IR measurements revealed the relative number of Si-N bonds to be very high. Using EDX, no chlorine could be detected in these powders and the amount of nitrogen was quite low (18%). This indicated that only the outside of the particles had been converted to amorphous silicon nitride.

3. 4 Excitation of NH₃ for the synthesis of Si₃N₄

Exciting NH₃ with the 9R30 line resulted in a flame consisting of three regions, as shown in Fig. 10. Where the CO₂ laser beam crossed the NH₃ injection, spectral measurements showed a discrete spectrum agreeing with that of the NH₂-radical spectrum. Directly above the central inlet, where SiH₂Cl₂ entered the system, no emission was observed. In the boundary layer between these regions a strong emission was observed. Measurements showed a continuous spectrum, due to black body radiation from the particles formed. Comparing this spectrum with the Planck formula (1), corrected for scattering (2), a temperature of around 2220 K was calculated. The powder characteristics are shown in Table 1. In another experiment a flow of only 20 sccm SiHCl₃ was used as the silicon source whilst the other experimental conditions were unchanged. In this experiment the yellow emission from the area close to the NH₂ emission was much stronger. Spectral analysis of this emission, lying between 350 and 850, showed a continuous spectrum with a black body temperature of 1770 K. The powder collected was also white. IR-measurements showed a much less prominent Si-NH absorption shoulder at 1200 cm⁻¹ on the Si-N
Table 1 Process conditions and powder characteristics of the formation of Si$_3$N$_4$

| Reactant  | SiH$_2$Cl$_2$ | SiH$_2$Cl$_2$ | SiHCl$_3$ | SiHCl$_3$ | SiCl$_4$ | SiCl$_4$ | SiCl$_4$ | SiCl$_4$ |
|-----------|--------------|--------------|-----------|-----------|---------|---------|---------|---------|
| Laser line| 10P20        | 9R30         | 10P20     | 9P42      | 9R30    | 10P20   | 9P42    | 9R30    |
| Excited gas| SiH$_2$Cl$_2$ | NH$_3$       | SF$_6$    | SiF$_4$   | NH$_3$  | SF$_6$  | SiF$_4$ | NH$_3$  |
| Reaction temperature (K) | 2520 | 2220 | 2070 | 1770 | 40 | 40 | 30 | 15 |
| d TEM (nm) | 20 | 26 | 30 | 40 | 40 | 30 | 15 | 15 |
| d SF$_3$ (nm) | 100 | 142 | 148 | 129 | 99 |
| d BET (nm) | 19 | 14 | 20 | 14 |
| Fibers | many | none | none | none | none | none | none | none |
| Color powder | light | brown | almost white | white | white | white | white | white |
| IR absorption NH-band (1200 cm$^{-1}$) | very weak | very weak | strong | weak | very weak | strong | very weak | strong |

band at 1100 cm$^{-1}$. The powder was amorphous to electron diffraction in the TEM. The particle size was around 40 nm, larger than the particles made from SiH$_2$Cl$_2$. Using SiCl$_4$ a weak flame was observed. The relative amount of imide in the product was very high. Transmission electron micrographs showed a mixture of larger ($d = 200$ nm) and small particles ($d = 15$ nm). The larger particles showed great resemblance to particles formed in a low temperature reaction between SiCl$_4$ and NH$_3$[12]. Thus little Si$_3$N$_4$ has been formed from excited NH$_3$ and SiCl$_4$.

3.5 Exciting a sensitiser for the synthesis of Si$_3$N$_4$

If reactants do not absorb laser radiation sufficiently other strong CO$_2$-laser absorbing gases can be used to act as an energy transfer media. For an untuned CO$_2$-laser SF$_6$ is often used as an sensitizer because of its strong absorption around 10.6 $\mu$m and its relatively inert character. At low SF$_6$ flow rates (below 10 sccm) a thermal flame color (yellow white) was always observed. However, at a high SF$_6$ flux (30 sccm) a blue fluorescence could be seen beyond the reaction flame core. Similar fluorescence has been observed$^9,10$ and ascribed to fluorescence of sulphur particles$^{13,14}$ formed during decomposition of the laser excited SF$_6$. This decomposition occurs in the presence of hydrogen, or hydrogen containing compounds. This latter observation is corroborated by the presence of minor amounts of sulphur in the product. When less than 10 sccm SF$_6$ was used with 20 sccm SiHCl$_3$ or SiCl$_4$ and 80 sccm of NH$_3$, all the powders contained a considerable amount of sulphur. The particles formed were amorphous and contained a considerable amount of imides as well as Si-N bonds. The slight activity of SF$_6$ prevents the synthesis of Si$_3$N$_4$ with low contamination.

In these cases SiF$_4$ is preferred as a sensitizer. For this sensitizer a tuneable laser set at around 9.7 $\mu$m can be used. The powders produced with a small amount of SiF$_4$ (10 sccm) contained fewer Si-NH bonds compared to the SF$_6$ experiments. Using SiHCl$_3$ as the silicon source the product contained mostly Si$_3$N$_4$ according to IR-spectroscopy. All the powders were amorphous to electron diffraction. The particle sizes of the product from SiHCl$_3$ were around 40 nm compared to 15 nm of the particles formed from SiCl$_4$.

4. Thermodynamic Calculations on the Chemical Vapor Deposition of Si$_3$N$_4$ and Si from Chlorinated Silanes

Thermodynamic calculations are a useful tool in understanding a specific CVP system and thus to optimize the process conditions. A thermodynamic analysis should be completed before the kinetic effects are considered. Furthermore, kinetic models often include a thermodynamic term. In the case of the homogeneous nucleation of ceramic powders, for example, the supersuration, which is the driving force for the process, must be known.

The main limitations to the validity of these thermodynamic calculations result from the in-
accuracy or lack of the thermodynamic data and, of course, from the assumption that equilibrium is achieved. Concerning the thermodynamic data, a small change in the heat of formation of a major species can change the deposition efficiency considerably. It has been pointed out by several workers, especially Walsh\textsuperscript{15} and Ho\textsuperscript{16}, that some literature study is needed before attempting calculations, since standard tables such as JANAF\textsuperscript{17} and CATCH\textsuperscript{18} might not contain the latest results. We used the JANAF values of the heat of formation, except for the chlorosilanes, for which the values of Farber\textsuperscript{19} were used, and for the silicon subchlorides, for which 158.9 kJ/mol (SiCl) and -326.4 kJ/mol (SiCl\textsubscript{3}) were used. This set of values was tested on the experimental results of Woodruff\textsuperscript{20}.

The result of this work is presented in form of a CVP phase diagram, which depicts which solid phases would deposit as a function of experimental variables such as temperature and input gases. These diagrams show the phase boundaries and also the deposition efficiency of the Si\textsubscript{3}N\textsubscript{4} and Si phases. Kingon\textsuperscript{21} made some CVD-diagrams of the Si-H-Cl-N system, but only up to 1800 K, and using old JANAF values. In this work, temperatures up to 2600 K were used, in accordance with our experimental results. The calculations were carried out using the SOLGASMIX-PV program and also a control program which searches for phase transitions within 0.2% accuracy. One CVP-diagram takes several hours on a Compaq 386/25, making tens of thousands equilibrium calculations.

In Fig. 11 CVP-phase diagrams for 4 silane/NH\textsubscript{3} systems are depicted. The pressure is 1

![CVP phase diagrams](image_url)

Fig. 11 CVP phase diagrams
Bar. Si/(Si+N) = 0.1 means, for example, an input of 1 mol (chlorinated) silane and 9 mol NH₃. From the diagrams it is clear that the higher the chlorine content of the silane, the smaller the deposition efficiencies but also the smaller the regions of co-deposited Si and Si₃N₄. This is confirmed by the higher nitrogen content of the powders produced with SiHCl₃, compared with SiH₂Cl₂. An important result is that, in the SiHCl₃ and the SiCl₄ systems, there is a large region at higher temperatures where there are no condensed phases. This is confirmed by the experimental failure to make silicon from SiHCl₃ and SiCl₄.

5. Conclusions

It has been shown that Si₃N₄ powder can be formed from SiH₂Cl₂ by exciting NH₃ using the strongly absorbing 9R30 CO₂-laser line at 9.4 μm or by using a sensitizer such as SF₆ or SiF₄. SiF₄ is shown to be more inert in the conditions used and produces less contamination. A stoichiometric product, without fibers, is formed from SiH₂Cl₂ compared to using the 10P20 line at 10.4 μm. SiH₂Cl₂ can also be excited directly without another absorbing media. The injection height of NH₃ in the laser is, in this case, a major process variable. It is very difficult to use SiCl₄ as the silicon source to produce Si₃N₄ powder with CO₂-laser synthesis, because of the unfavorable energetic properties of this substance. The use of phase diagrams is a powerful tool in interpreting the process and is, in any case, a necessary precursor to Kinetic calculations.

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