Laser excited synthesis of sub-micron powders

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ABSTRACT

The laser activated synthesis of silicon and silicon nitride powders has been studied using gaseous reactants. The use of non-IR-absorbing, chlorinated silanes requires the application of a sensitizer, which transfers the thermal energy to the reactants. The influence of the sensitizer sulphur hexafluoride on the laser activated reactions of dichloro silane and silicon tetrachloride in the presence of ammonia has been studied.

1. INTRODUCTION

Silicon nitride Si_3N_4 is a suitable material for construction purposes for applications under extreme conditions. Its use is limited by the fact, that sintering of an end product from powder requires the use of sinter additives. These additives affect the high temperature properties of the end product in a negative sense. Sintering without additives is possible when the powders meet high requirements: 1) have a small particle size, and 2) a narrow size distribution, 3) agglomerate only weakly, 4) have spherical particles, and 5) have high purity¹.

Gas phase synthesis methods are most suitable to prepare such ideal powders, because in general diluted reactants will result in fine, weakly agglomerated powders. Small particles and a narrow particle size distribution demand high initial nucleation rates, without substantial growth. Agglomerates can be avoided by reducing the resident time of the powders particles at high temperatures. A high purity can be achieved by the use of a cold wall reactor and the use of high purity reactants². Traditional heating methods (furnaces, high frequencies, plasmas) can give rise to less favorable temperature profiles and reaction zones, resulting in a distribution in nucleation and growth rates and therefore in particle

size. However, the conditions in a laser heated reaction are such, that uniform nucleation and growth rates can be achieved. The high gas flow rate and the narrow laser beam induce² temperature gradients in the range of 10^6 °C/s and reaction times in the range of 10^{-3} s. This strongly reduces the growth of larger particles and the formation of agglomerates. Furthermore, the process can be conducted in very clean conditions, since the walls of the reactor do not take part in the reaction.

A prerequisite for laser heating is the absorption of IR-radiation from the CO_2 -laser by the reactants. Therefore the strongly absorbing silane, SiH_4 , and ammonia, NH_3 , are commonly³ chosen as reactants for the laser activated synthesis of Si_3N_4 . SiCl_4 , which is employed in the traditional⁴, thermal synthesis of Si_3N_4 , is much cheaper, but does not absorb IR-radiation. This necessitates the use of a sensitizer, a compound which absorbs IR-radiation and transfers it to the reactants, without being dissociated itself. Sulphur hexafluoride, SF_6 , is such a sensitizer⁵.

Here we discuss the formation of silicon nitride out of silicon tetrachloride and ammonia by IR-radiation in the presence of a sensitizer. Also the reactions of dichloro silane, taking an intermediate position between silane and silicon tetrachloride with respect to IR-absorption, will be discussed.

2. EXPERIMENTAL ASPECTS

Silicon and silicon nitride powders have been prepared with Laser Chemical Vapor Precipitation (L-CVP) using dichloro silane, SiH_2Cl_2 (Air Products, 97% SiH_2Cl_2 , 3% other chloro silanes), silicon tetrachloride, SiCl_4 (Janssen Chimica, 99.8%), and ammonia, NH_3 (Air Products, 99.999%). Sulphur hexafluoride, SF_6 (Air Products, 99.97%) has

been used as sensitizer. The carrier gases nitrogen, N_2 , and hydrogen, H_2 , have been purified with, respectively, a copper (BASF, R 3-11) and a palladium (BASF, R 0-20) catalyst and finally by a zeolyte (Dow A4). Silicon tetrachloride is a liquid, having a boiling point $57^\circ C$. The vapor is transported with the carrier gases. The vapor pressure is controlled by adjusting the temperature in the evaporator (Tamson TLC 3).

The stainless steel reactor is schematically depicted in Figure 1. The KCl windows are flushed with N_2 in order to prevent precipitation of powders. IR-radiation of an industrial cw CO_2 laser (Electrox PB 2000) with wave length $10.6 \mu m$ is partially focussed with a ZnSe lens (focal length 30 cm) perpendicular to the gas stream. Instabilities in the process parameters, such as flow rates and laser intensity, occur because of a periodical pressure built up in the gas scrubbing system after the precipitator and because of the inevitable whirling of powder particles which scatter the laser beam. The reactants chosen can react at low temperature to form silicon diimide, $Si(NH)_2$. This reaction has to be avoided, because this would determine the particle size distribution, instead of the laser driven gas phase reaction to silicon nitride. This requires a special nozzle design. The nozzle in Figure 1 exists of a central tube for the chlorinated silanes, sensitizer and possibly a carrier gas. This tube is surrounded by four concentric inward bent tubes for ammonia. The gases are mixed at the place where they are irradiated. The formation of imides is thus largely prevented. The gases are shielded by a nitrogen stream, concentrating the gases to a narrow region and feeding them into the collecting funnel. The choice of reactants also implies the formation of ammonium chloride, NH_4Cl , as a side product. Separation between Si_3N_4 and NH_4Cl is achieved in an electrostatic precipitator, kept at $750^\circ C$, which is above the condensation point of NH_4Cl .

The powders have been characterised by IR-spectroscopy, X-ray spectroscopy and fluorescence, X-ray and electron diffraction. The particle sizes have been estimated from transmission electron microscopic pictures.

3. RESULTS AND DISCUSSION

Silicon and silicon nitride have been prepared at atmospheric pressures both by direct laser excitation of SiH_2Cl_2 and by indirect excitation of SiH_2Cl_2 and $SiCl_4$ in

the presence of SF_6 . The process conditions and powder characteristics are summarized in table 1.

3.1. Formation of silicon

If dichloro silane is irradiated in the absence of any other reactants, a yellow reaction flame develops, caused by laser excitation and dissociation of SiH_2Cl_2 , followed by nucleation of elementary silicon. The product is amorphous silicon, dark brown colored, virtually monodisperse, with an average particle size of 50 nm. It contains only a small amount of chlorine. The yield is nearly 100 %, (1.7 g/hour).

Sausa and Ron⁶ have studied the dissociation of SiH_2Cl_2 after irradiation with a tunable, pulsed CO_2 laser at reduced pressure. The only products in this case are particles containing polymerised silicon dichloride $(SiCl_2)_n$ and hydrogen. Our experiments show, that dichloro silane can absorb sufficient energy from an untuned, cw industrial CO_2 laser to dissociate completely under the formation of ultra fine silicon powders.

3.2. The formation of silicon nitride particles by direct laser excitation of SiH_2Cl_2 and the reaction with NH_3

If ammonia is mixed with dichloro silane, the reaction flame turns white-yellow, indicating a higher temperature than in the absence of ammonia. The characteristic absorption band in the IR-spectrum (950 cm^{-1}) shows, that amorphous silicon nitride has been formed. Small amounts of ammonium chloride and diimide are present. The tan colored silicon nitride powder has an average particle size of 30 nm. This is smaller than can be achieved⁷ in the thermally activated CVP, but comparable with the results of laser activation of the reaction between silane and ammonia⁸. The particles are moderately agglomerated. The reaction flame is stable and the reaction time is limited to one hour by the capacity of the precipitator. No whirling of the powders in the reactor occurs because of the good draft into the collecting funnel. The synthesis of silicon nitride powder by means of Chemical Vapor Precipitation in a continuous reactor using chlorinated silanes has not been reported before.

3.3. The formation of silicon nitride by indirect laser excitation of SiH_2Cl_2 and NH_3 using SF_6

A small flow of SF_6 (<0.4 l/hour) does not affect the color of the reaction flame. However, at a higher flow (1 l/hour) a blue fluorescence can be observed around the center of the flame. Such a blue fluorescence has been reported before^{9,10} and has been assigned to fluorescence of sulphur particles, arising from the dissociation of laser excited sulphur hexafluoride in the presence of hydrogen or hydrogen containing compounds. This explanation is corroborated by our observation of sulphur in the silicon nitride particles with X-ray fluorescence. The presence of SF_6 seems to have no influence on the particle size. The spread in the distribution is ascribed to instabilities in the process. Silicon nitride is amorphous and contains small amounts of imides and ammonium chlorides.

3.4. The formation of silicon nitride by indirect laser excitation of SiCl_4 and NH_3 using SF_6

Direct laser excitation of SiCl_4 is impossible, therefore the use of SiCl_4 in the silicon nitride synthesis always implies the use of a sensitizer. After mixing 2 l/h SiCl_4 , 7 l/h NH_3 , 0.5 l/h SF_6 and 2 l/h N_2 in the laser beam, a small yellow reaction flame exists. Powder is whirling in the reactor. This powder is a low temperature product, since it is also present if the laser is switched off. It consists of large, ~ 1 μm , diimide particles. Since silicon tetrachloride reacts faster with ammonia than dichloro silane does, the control of the gas stream needs to be improved, in order to avoid imide formation. Furthermore, the imide formation results in a strong reduction of the transmitted laser radiation.

The reaction flame gets smaller when the flow rate of reactants reduces. If the SF_6 flow is increased, the flame turns blue, if the SiCl_4 and NH_3 flows are increased, the thermal emission reduces. The tan colored powder consists of very fine Si_3N_4 particles, 15-25 nm, and is contaminated with the previously mentioned large diimide particles and with a small amount of ammonium chloride.

3.5. Stability of SF_6 in the presence of H_2 and SiCl_4

When only SiCl_4 and SF_6 with N_2 as a carrier gas are irradiated, a thin white flame exists. Although SiH_2Cl_2 under these circumstances dissociates into silicon, no powder formation has been observed in the case of SiCl_4 , neither with a He-Ne laser probe, nor in the precipitator. The height of the flame is strongly dependent on the amount of SF_6 . On reduction of the amount of SiCl_4 the flame turns blue. A blue flame has also been observed when hydrogen is added to the reaction mixture. This indicates the dissociation of SF_6 and hydrogen acts like a getter for fluorine from SF_6 instead of for chlorine from SiCl_4 as was intended. The experiments show that SF_6 dissociates irreversibly instead of transferring the absorbed energy. This can be understood if we consider the enthalpy of formation of the various products¹¹:

The reaction between hydrogen and SF_6 is thermodynamically more favorable than that between hydrogen and SiCl_4 . But to dissociate SiCl_4 the presence of hydrogen is a prerequisite. The solution of this dilemma lies in another, more stable sensitizer. In the literature¹² silicon tetrafluoride has been mentioned as a stable, non-reactive sensitizer.

4. CONCLUSIONS

The formation of silicon nitride from chlorinated silane with laser excitation in the presence of a sensitizer proves to be feasible. SF_6 is not sufficiently stable in the presence of H_2 and SiCl_4 . In all cases Si_3N_4 is amorphous and the particle sizes are in the range of 20-30 nm.

5. ACKNOWLEDGEMENT

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