96,577 (87)
fd 9-15-87
S-65,150
RL-9947

PATENTS-US--A7096577

DE89 011782

PROCESS FOR PRODUCING HIGH PURITY
SILICON NITRIDE BY THE DIRECT
REACTION BETWEEN ELEMENTAL SILICON
AND NITROGEN-HYDROGEN LIQUID
REACTANTS

096,577

PROCESS FOR PRODUCING HIGH PURITY SILICON NITRIDE
BY THE DIRECT REACTION BETWEEN
ELEMENTAL SILICON AND NITROGEN-HYDROGEN LIQUID REACTANTS

By: Eloise A. Pugar   Citizenship: USA
     6657 El Colegio, Apt. 27
     Isla Vista, California 93117

     Peter E. D. Morgan   Citizenship: USA
     1049 Camino Dos Rios
     Thousand Oaks, California 91360

DISCLAIMER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PROCESS FOR PRODUCING HIGH PURITY SILICON NITRIDE
BY THE DIRECT REACTION BETWEEN
ELEMENTAL SILICON AND NITROGEN-HYDROGEN LIQUID REACTANTS

BACKGROUND OF THE INVENTION

5   The invention described herein arose in the course

of, or under, Contract No. DE-AC03-85SF16018 between the

FG03-85ER45221

United States Department of Energy and Rockwell Internation-

al Corporation.

This invention relates to an improved process for

10   the production of high purity silicon nitride which includes

the manufacture of a novel liquid solution consisting essen-

tially of silicon, hydrogen, and nitrogen dissolved therein

which may be further employed as an intermediate in a varie-

ty of chemical synthetic preparations, including usage as a

15   precursor for the production of silicon nitride. More par-

ticularly, this invention relates to the production of high

purity silicon nitride by the reaction of elemental silicon

with a nitrogen-hydrogen reactant in its liquid state to

produce high purity intermediate materials consisting of

20   silicon, nitrogen, and hydrogen from which high purity

silicon nitride may be formed by heating the intermediate materials.

Silicon nitride is an important structural material having outstanding potential for use in high strength applications, such as cutting tools for aerospace alloys, ball bearings, etc. The material is currently contemplated for use at high temperatures in turbine blades and ceramic diesel engines. The dielectric properties of this material also enable silicon nitride to be an important component in semiconductor barriers.

It would be desirable to have an industrial process for manufacturing high purity silicon nitride using elemental silicon, which is inexpensively available in high purity and which could be reacted at ambient temperature in a continuous automated process with a nitrogen-hydrogen reactant in its liquid state to form a high purity intermediate product consisting of silicon, nitrogen, and hydrogen from which high purity silicon nitride could be formed directly upon heat treatment without additional purification steps.

The original investigation of low and high temperature direct reactions between elemental silicon and nitrogen compounds was conducted by E. Vigouroux, as quoted by J.W. Mellor in A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VI, New York: Wiley, 1961, p. 163. He discovered that ammonia reacts with silicon at

bright red heat, forming the nitride with liberation of

hydrogen. High temperature nitridation of silicon is also

detailed by Mangels U.S. Patent 4,235,857 and is otherwise

well known. However, ultra-high-purity silicon is extremely

5   difficult to nitride at high temperature due to formation of

protective nitride layers (exactly of the type used on

semiconductors for passivation). According to S.S. Lin in

an article entitled "Mass Spectrometric Studies on High

Temperature Reaction Between Hydrogen Chloride and Silica/

10 silicon" in the Journal Electrochem. Society, Vol. 123,

1976, pp. 512-514 and another article entitled "Comparative

Studies of Metal Additives on the Nitridation of Silicon" in

the Journal Am. Ceram. Soc., Vol. 60 (1-2), 1977, pp. 78-81;

halide, iron, or other cation catalysts are required in such

15 nitriding processes. D. Campos-Loriz et al, in an article

entitled "The Effects of Hydrogen on the Nitridation of

Silicon" in the Journal Mat. Sci., Vol. 14, 1979, pp. 1007-

1008, and H. Dervisbegovic et al in an article entitled "The

Role of Hydrogen in the Nitridation of Silicon Powder Com-

20 pacts" in the Journal Mat. Sci, Vol. 16, 1979, pp. 1945-55,

further explored the catalytic effects of hydrogen and water

vapor on nitridation of silicon with a view to overcome the

sluggishness and high expense of the process.

E. Vigouroux was cited in Mellor, p. 163, as unsuc-

25 cessfully attempting to react silicon with liquid ammonia at

low temperatures. These findings made it apparent to

workers in the field that more reactive silicon derivatives, such as silicon chloride, silane, etc., would have to be employed to manufacture Si_3N_4 at temperatures below 100°C, the preferred temperature range for industrial processing.

5   Silicon nitride is, therefore, now industrially produced on the largest scale by the low temperature reaction of silicon tetrachloride with liquid ammonia as described in Iwai et al, U.S. Patent 4,196,178. The amorphous silicon diimide intermediate may be crystallized to alpha

10   silicon nitride upon heat treatment in a nitrogen atmosphere. However, the product formed tends to retain chloride on particle surfaces thereby not possessing the requisite purity needed for the above described desirable applications. Lengthy extractions with liquid ammonia or vacuum

15   treatments to remove the halide from the final product incur additional processing costs. Oxygen contamination can result during this purification procedure due to the air and moisture sensitivity of the diimide intermediate. Even in the gas phase reaction between silicon tetrachloride and

20   ammonia at temperatures over 700°C, chlorine and oxygen contamination cannot reasonably be eliminated as described by M. Rahaman et al in an article entitled "Surface Characterization of Silicon Nitride and Silicon Carbide Powders" in the Am. Ceram. Soc. Bull., Vol. 65 (8), 1986, pp. 1171-

25   76.

          The use of silicon halides as the source of

silicon for reaction with a nitrogen-containing material to form silicon nitride is well known, and such reactions have been described in a number of U.S. Patents, such as, for example, Mazdiyasni et al 3,959,446; Buljan et al 4,073,845;

5   Mazdiyasni et al 4,113,830; Sussmuth 4,122,220; Mehalchick et al 4,145,224; Kleiner et al 4,208,215; Inoue et al 4,368,180; Buljan et al 4,376,652; and Sato et al 4,399,115.

Formation of silicon nitride using a silane as the source of silicon for reaction with a nitrogen compound has

10   also been proposed. Prochazka et al in U. S. Patent 4,122,155 and Kasai et al in U.S. Patent Nos. 4,346,068; 4,387,079; and 4,612,297 teach the use of a silane as the source of silicon in such a reaction. Usage of silane (SiH_4), a highly reactive gas at temperatures above -112°C,

15   can be problematic due to its explosive nature, lengthy product deposition times, inadequate control of product stoichiometry and morphology, and the overall costly economics of the process. Reactions with halogen-substituted silanes, as cited in the latter two patents, can add impuri-

20   ty problems, requiring extra purification costs.

Synthesis of silicon nitride can be achieved at elevated temperatures (from 1000°C to 1700°C) by carbothermic nitriding of silicon dioxide. This method is described in U.S. Patents Mori et al 4,122,152; Komeya et al

25   4,428,916; and Hasimoto et al 4,590,053.

Processes for producing silicon nitride from

mono- and di- sulfides of silicon with ammonia have been
demonstrated at high temperature in Forsyth U.S. Patent
3,211,527 and Morgan et al U.S. Patent 4,552,740. These
synthetic routes are more attractive than the above men-

5 tioned high temperature methods because high reactivity and
varied morphologies can be produced by vapor transport and
VLS mechanisms. In addition, sulfur volatilizes more clean-
ly from the product.

It would be desirable to have a process wherein
10 elemental silicon, which is available as a high purity
starting material, could be reacted at a temperature, equiv-
alent at atmospheric pressure to below 200°C, and preferably
below 100°C, with a nitrogen-hydrogen reactant in its liquid
state to form a high purity intermediate product consisting
15 essentially of silicon, nitrogen, and hydrogen from which
high purity silicon nitride can be formed by a heat
treatment.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to
20 provide a process for forming high purity silicon nitride
from elemental silicon and a reactive nitrogen-hydrogen
compound that is in its liquid state at temperatures desir-
able for industrial purposes.

It is another object of this invention to provide
25 a process for forming high purity silicon nitride from an

initial reaction of elemental silicon and a reactive nitrogen-hydrogen liquid at a low temperature, i.e., below 200°C, and preferably below 100°C.

It is a further object of the invention to provide a process for forming high purity silicon nitride from an intermediate reaction product consisting essentially of silicon, nitrogen, and hydrogen which, in turn, is produced at a temperature below 200°C, and preferably below 100°C, from a reaction between high purity elemental particulate silicon and a high purity nitrogen-hydrogen reactant in its liquid state.

It is yet a further object of this invention to provide a process for making, at a temperature below 100°C, an intermediate product consisting essentially of silicon, nitrogen, and hydrogen.

These and other objects of the invention will be apparent from the following description and accompanying flow sheet.

BRIEF DESCRIPTION OF THE DRAWINGS

The sole figure is a flow sheet illustrating the process of the invention.

DETAILED DESCRIPTION OF THE INVENTION

High purity silicon nitride is produced, in accordance with the invention, by the initial formation of a high

purity intermediate formed by reacting high purity elemental particulate silicon with a high purity nitrogen-hydrogen reactant in its liquid state at a temperature, equivalent at atmospheric pressure, to below 200°C, and preferably below

5   100°C as showed in the reaction equation below:

$$Si + [N_nH_{(n+m)}]_l \longrightarrow (Si,N,H) \text{ intermediate}$$

wherein: n = 1-4; and m = 2 when the nitrogen-hydrogen reactant is straight chain and 0 when the nitrogen-hydrogen reactant is cyclic.

10   The high purity reactive nitrogen-hydrogen liquified compound, which will hereinafter be referred to as the $[N_nH_{(n+m)}]_l$ reactant, consists essentially of liquid ammonia (NH_3) when n = 1 or a hydrazine (N_nH_{n+m}) when n is 2 or more. The preferable hydrazine compound is N_2H_4. However,

15   the use of higher molecular weight hydrazines as the reactive nitrogen-hydrogen liquid, such as, for example, triazane (N_3H_5), tetrazine (N_4H_6), and isotetrazine (N_4H_6), as well as cyclic hydrazines such as cyclotriazane (N_3H_3), are also within the scope of the invention.

20   The purity of the high purity $[N_nH_{(n+m)}]_l$ reactant should be at least 99.9 wt.%, preferably 99.995 wt.%, to obtain the desired high purity intermediate. Liquid ammonia is easily obtainable in such purity, for example, by condensing it from the corresponding gas, while liquid anhy-

25   drous hydrazine (N_2H_4) at such a purity level is commercially available (in Mil Spec. grade) as a component of rocket fuel.

The other reactant comprises a elemental silicon
in particulate form. The product of the reaction of elemen-
tal silicon with liquid ammonia is a solid imide which
cannot easily be purified. Surprisingly, hwoever, the reac-

5 tion with liquid hydazine produces a clear liquid suggesting
immediately that chemical methods of purification are possi-
ble in this instance. Therefore, the need for high purity
silicon starting material may be avoidable when a liquid
hydrazine is used and the use of lower purity silicon, e.g.,

10 95 wt.% or higher, may even be economically preferable. The
well known methods of purification for liquids: distilla-
tion, solvent extraction, crytallization, etc. could be
applied in such a case.

Thus, the silicon purity requirements differ de-

15 pending upon whether n = 1 or greater than 1 for the
$[N_nH_{(n+m)}]_l$ reactant. When n = 2-4 (see Example II below),
usage of high purity silicon is not required and a silicon
of purity of 95 wt.% or higher may be used for this reac-
tion.   However, since product formed when n = 1 (see

20 Example I below) is not easily purified, the use of high
purity silicon is necessitated when liquid ammonia is used
as the other reactant. By high purity silicon is meant a
silicon having a purity of 99.9 wt.% or better, preferably
99.999 wt.% pure.

25 The particle size range of the elemental silicon
reactant is preferably about 100 mesh (Tyler) or smaller,

i.e., below about 150 microns. Although larger particle

sizes of silicon can be used to react with the $[N_n H_{(n+m)}]_l$

reactant, it will be appreciated that for a thorough and

efficient reaction, it is important that the surface area of

5   silicon in contact with the reactive nitrogen-hydrogen

liquid be large. Larger silicon particles, even lumps

(i.e., 2.5 cm. diameter) with reduced surface area will

react more slowly. Use of such large particles could be

desirable in a continuous flow of reactants in an industrial

10   process application of this invention. The lower limit of

the silicon particle size will be governed by the availabil-

ity of smaller particles as well as safety limitations from

the standpoint of the extent of the pyrophoric properties of

the fine particles. A range of particle size of from about

15   0.01 microns (colloidal) up to about 100 mesh (Tyler),

preferably from about .01 to 150 microns, will provide

particles which will react quickly and thoroughly with the

$[N_n H_{(n+m)}]_l$ reactant without incurring undue safety risks.

          If larger particle sizes of silicon are used,

20   e.g., larger than 100 mesh (Tyler), such particles may be

ground prior to the reaction, or in situ during the reaction

as will be discussed below, under conditions which will not

compromise the desired purity. For example, larger silicon

particles may be ground using large lumps of silicon as a

25   milling agent.

          Since it is recognized that silicon is technically

a metalloid and not a metal, the term "elemental" is used
herein with respect to the silicon reactant to define that
the element silicon, i.e., reduced silicon and not a silicon
compound, is what is being referred to as the high purity

5   reactant.

In accordance with the invention, the $[N_nH_{(n+m)}]_l$
reactant and the particulate elemental silicon reactant are
reacted together at a low temperature, comprising a tempera-
ture below the boiling point of the $[N_nH_{(n+m)}]_l$ reactant at

10   the pressure employed, and preferably from about 15°C to
about 100°C below the equivalent boiling point at the press-
ure employed. For example, when the reactive nitrogen-
hydrogen liquid is ammonia, the reaction temperature, at
atmospheric pressure, will be below -33°C. When hydrazine is

15   used as the liquid reactant, the reaction temperature, at
atmospheric pressure, will be below 113°C and preferably
below about 98°C.

The term "low temperature", as used herein, is
intended to define a temperature, equivalent at atmospheric

20   pressure, of under 200°C, preferably under 100°C, to distin-
guish this process from prior art processes wherein tempera-
tures of over 1000°C are used in the initial reaction be-
tween the silicon-containing reactant and the nitrogen-
containing reactant.

25   The preferred reaction temperature range, when am-
monia is reacted, is a temperature range, equivalent at

atmospheric pressure, from about -33°C to about -78°C. The preferred reaction temperature range, when hydrazine (N_2H_4) is reacted, is a temperature range, equivalent at atmospheric pressure, from about 0°C to about 75°C, most preferably

5   about 15°C to 50°C.

It should be noted that the above discussion with regard to reaction temperature ranges has been phrased in language indicating temperatures equivalent to the recited temperatures at atmospheric pressure because it is recog-

10   nized that the reaction may very well be carried out at other than atmospheric pressure. For example, when liquid ammonia is used as the $[N_nH_{(n+m)}]_1$ reactant, it may be more advantageous to react the liquid ammonia with the particulate silicon at a temperature higher than -33°C by raising

15   the pressure, e.g., reacting at room temperature under 12 atmospheres of pressure. Thus it will be recognized that the reaction temperature ranges discussed are not absolutes, but are relative to the pressure employed.

The reaction time of the reactants (or residence

20   time for a continuous reaction) will vary depending upon the reactants, the temperature/pressure at which the reaction is carried out, and other reaction conditions as will be discussed below. The reaction time, for a batch reaction containing specified quantities of reactants (e.g., 50 ml.

25   $[N_nH_{(n+m)}]_1$ and 5 grams silicon of 1 micron particle size), may vary from less than one hour to as many as 100 hours,

preferably from about 30 minutes to about 50 hours. Longer
reaction time periods, are possible, given greater particle
sizes of silicon and surface buidup of the SiO_2 layer.

For example, the batch reaction of hydrazine with
particulate elemental silicon at 25°C (atmospheric pressure)
may be carried to completion in several hours while the
batch reaction of liquid ammonia with particulate elemental
silicon at -78°C (atmospheric pressure) may be carried out
in 48 hours.

The reaction time may be accelerated, in accor-
dance with a preferred embodiment of the invention, by
conducting a grinding or milling action during the reaction.
This is thought to accelerate the reaction by constantly
exposing fresh unreacted silicon surfaces and contacting
them with the $[N_nH_{(n+m)}]_l$ reactant. For example, a reaction
between 100 mesh (Tyler) silicon particles and liquid am-
monia at -78°C at atmospheric pressure may be shortened from
48 hours or more down to 1 hour or less by milling the
silicon particles during the reaction with the liquid ammon-
ia reactant.

Such milling or grinding of the elemental silicon
serves to remove any coatings on the surface of the elemen-
tal silicon (i.e., SiO_2) which, but for such removal, might
interfere with the reaction between the silicon and the
$[N_nH_{(n+m)}]_l$ reactant. Such coatings may also be optionally
removed prior to the reaction by chemical treatment of the

particulate silicon with stripping reagents such as hydro-
fluoric acid or ammonium bifluoride and/or heat treatment to
at least 1300°C in a reducing atmosphere such as an argon/
hydrogen atmosphere to promote the reaction time considerab-
5   ly, e.g., to less than 0.5 hours.

It should be noted that when such grinding or
milling is carried out as a part of the reaction, the use of
larger size elemental silicon particles, i.e., particles
larger than 100 mesh (Tyler) can be used which will be
10   ground down in situ during the progress of the reaction. It
should be further noted that the reaction may be carried out
on a continuous basis with product removed as it is pro-
duced, or on a periodic basis, and the use of large size
elemental silicon particles which are ground in situ during
15   the course of the reaction may be of particular value when
the process is run on a continuous basis and liquid, con-
taining the intermediate product formed by the reaction, is
continuously removed from the reaction zone, leaving the
large particles of elemental silicon to be further ground
20   and reacted with fresh $[N_nH_{(n+m)}]_l$ reactant, continuously
fed into the reaction zone.

When the reaction is carried out on a batch basis,
the $[N_nH_{(n+m)}]_l$ reactant may be used in stoichiometric ex-
cess which then permits recovery of the reaction product by
25   solvent evaporation of the remaining $[N_nH_{(n+m)}]_l$ reactant.
When a continuous process is used, liquid may be

continuously removed from the reaction zone containing both the intermediate product and the $[N_nH_{(n+m)}]_l$ reactant which may then be separated from the intermediate product and recycled back to the reaction zone if desired.

The intermediate solution, formed by this reaction, comprises a solution or dispersion consisting of silicon, nitrogen, and hydrogen, with less than about 5-10 ppm impurities. This intermediate product may be employed in applications which require one or more elements in liquid form, e.g., such as for polymer processing to fibers. The intermediate product formed in accordance with the invention could also be used as a reagent in a wide range of chemistry to synthesize complex molecules containing silicon, nitrogen, and hydrogen, and possibly other elements. in turn, this intermediate can also be used to produce silicon ceramics (e.g., silicon nitride or silicon carbide) by appropriate reaction paths. For example, the intermediate could be heated to 800°C in an argon atmosphere to produce silicon nitride with ammonia and hydrogen gas.

As stated above, recovery of the intermediate reaction product can be carried out by solvent evaporation of the remaining $[N_nH_{(n+m)}]_l$ reactant. When the $[N_nH_{(n+m)}]_l$ reactant is hydrazine, the product is a clear stable solution which deposits a white residue upon evaporation. Infrared analysis of the solution shows a peak splitting of the N-N stretch (normally centered at approximately 1098

cm^{-1}) to two peaks of equal intensity at 1050 and 1120 cm^{-1} which may arise from Si-N association in solution and does not indicate the presence of any elements other than silicon, nitrogen, and hydrogen in amounts over 0.05 wt.% indicating that the solution is of high purity.

After evaporation of the solvent, high purity crystalline alpha silicon nitride (Si_3N_4), i.e., an alpha silicon nitride product having a purity of at least 99.9 wt.%, preferably 99.995 wt.%, can be formed from the amorphous intermediate powder residue by heating the residue up to a temperature range of about 1200-1700°C in a non-reactive atmosphere, such as argon, and then maintaining the residue at this temperature for at least about 15 minutes up to about 2 hours. Longer time periods may be employed but are thought to be unnecessary to achieve complete conversion of the residue to alpha Si_3N_4 having a particle size range of about 0.01 to 0.5 microns. It should be noted that the detection of the final product as alpha silicon nitride is another indication of the cationic purity of the material because it is known that lower purity amorphous silicon nitride generally forms beta silicon nitride as well as the alpha form upon high temperature heat treatment. On the other hand, if beta silicon nitride is a desired product, this can be achieved by adding agents known to promote the formation of the beta form.

The following examples will serve to better

illustrate the process of the invention.

Example I

     Ammonia gas was liquified over a six hour period in a polyethylene bottle using dry ice at about -78°C to

5   produce 50 milliliters of liquid ammonia which was then contacted with 5 grams of particulate silicon having a particle size of 1 micron or less and a purity of 99.9 wt.%. The reactants were milled in the reaction vessel for three hours at a temperature of -78°C for 48 hours. The intermed-

10   iate was recovered by evaporation of the remaining NH_3 as a brown colored residue.

     This residue was found to be amorphous by X-ray diffraction with some unreacted silicon, hence the brown color. Infrared spectroscopy of the residue showed peaks

15   distinct from a silicon IR reference pattern. Sharp absorp-tions were found at 1180 cm^{-1}, 1210 cm^{-1}, and 3000 cm^{-1} associated with the presence of NH and NH_2 groups and a heightened shoulder between 960-1050 cm^{-1} due to the broad Si-N stretch. Scanning electron microscopy (SEM) inspection

20   of the residue revealed non-crystalline matter interdis-persed among silicon particles.

     The residue was heated to a temperature of 1300°C in argon for two hours. Possible oxygen contamination was avoided with a double enclosed crucible arrangement with

25   silicon nitride powder surrounding the walls of the inner

crucible. The resulting product yielded an x-ray pattern indicative of alpha silicon nitride at 1400°C and unreacted silicon. The formation only of alpha silicon nitride at 1400°C, as well as SEM EDS analysis in which only silicon was found (nitrogen cannot be detected), confirms the high purity of the reaction product.

Example II

To 50 milliliters of liquid hydrazine was added 0.05 grams of particulate silicon having an average particle size of about or less than 10 micron and a purity of greater than 99.9 wt.% and the mixture was reacted in a reaction vessel under an inert Argon atmosphere for 3 hours at a temperature of 25°C. The resulting reaction product was a clear solution containing silicon as confirmed by inductively coupled plasma atomic absorption.

Vacuum solvent evaporation of the hydrazine left a polymeric residue which exhibited an IR absorption band at 950 cm^{-1} due to the Si-N stretch, a broad N-N stretch between 1100-1220 cm^{-1}, and the wags and anti-symmetrical stretches due to NH, NH$_2$ groups in the 1250-1600 cm^{-1} and broad stretch 2800-3500 cm^{-1} regions respectively. The product generated a broad band Raman peak centered at 800 cm^{-1} which flattens with air exposure. Heating the residue in air caused disappearance of the Si-N, NH, and NH$_2$, groups with replacement by SiO at 1150 cm^{-1}. The Si/N$_2$H$_4$ intermediate complex also absorbs in the ultraviolet at 240, 288,

and a broad shoulder at 278 nm. The near ultraviolet tran-

sition at 288 nm may indicate some double bonded nitrogens,

i.e., -N=N- due to an electronic transition from the pi

orbital state to an antibonding pi orbital state. The

5   electronic transition from the ground state to an anitbond-

ing sigma orbital state normally seen at 220 nm in silanyl-

hydrazine complexes is red-shifted to 240 nm. Back donation

from nitrogen to silicon may be inhibited due to the multi-

ple nitrogen-nitrogen linkage. Thermal gravimetric analysis

10   in argon of the residue showed a 79 wt.% loss. This corres-

ponds to approximately six N_2H_4 molecules to every silicon

atom. X-ray diffraction analysis of the intermediate pro-

duct showed it to be amorphous. SEM inspection indicated

that the intermediate product residue after evaporation is a

15   fine colloidal powder.

The residue was subsequently heated at a tempera-

ture of 1400°C for three hours in an argon atmosphere under

a nitrogen buffer as described in Example I. Finely divided

white crystals were recovered which X-ray diffraction indi-

20   cated to be alpha Si_3N_4.

Example III

To further characterize the intermediate compound

formed by the reaction between elemental silicon and the

$[N_nH_{(n+m)}]_1$ reactant, the local silicon environment was

25   analyzed by ^{29}silicon NMR to determine the type of bonding

present in the intermediate product in a hydrazine solution.
Peaks were found at -73.1 ppm and -82.06 ppm, characteristic
of silicon-nitrogen bonding. No other peaks of any signifi-
cant magnitude were noted indicating that silicon-nitrogen-

5   hydrogen bonding predominates in the intermediate compound.
In particular, no silicon-hydrogen bonding was detected by
using INEPT Cross Polarization Techniques such as described
by David T. Pegg and M. Robin Bendall in "Polarization
Transfer Between Two Scalar-Coupled Systems of Arbitrary

10   Numbers of Nuclei of Arbitrary Spins", Journal of Magnetic
Resonance, Vol. 55 (1983), pp. 51-63.

The sample was also analyzed by proton NMR.
The proton chemical shift was as typically well known in
silyl-amines. This shows that hydrogen is bonded through

15   nitrogen to silicon, i.e., not simply a nitrogen-hydrogen
bond as in the hydrazine solvent. This confirms the reac-
tion between the elemental silicon and the $[N_n H_{(n+m)}]_1$ reac-
tant. Furthermore, since the ^{29}silicon NMR analyses in-
dicated no direct silicon-hydrogen bonding, the intermediate

20   compound must comprise a compound having silicon-nitrogen-
hydrogen bonding.

While a specific embodiment of the process for
forming high purity Si_3N_4 and its precursors has been illus-
trated and described in accordance with this invention,

25   modifications and changes of the apparatus and process,
including parameters and materials, etc. will become

apparent to those skilled in the art, and it is intended to cover in the appended claims all such modifications and changes which come within the scope of the invention.

Missing Page(s)
from
Original Document

PROCESS FOR PRODUCING HIGH PURITY SILICON NITRIDE
BY THE DIRECT REACTION BETWEEN
ELEMENTAL SILICON AND NITROGEN-HYDROGEN LIQUID REACTANTS

ABSTRACT OF THE DISCLOSURE

5   A process is disclosed for producing, at a low temperature, a high purity reaction product consisting essentially of silicon, nitrogen, and hydrogen which can then be heated to produce a high purity alpha silicon nitride. The process comprises: reacting together a particulate elemental high

10   purity silicon with a high purity nitrogen-hydrogen reactant in its liquid state (such as ammonia or hydrazine) having the formula: $N_n H_{(n+m)}$ wherein: n = 1-4 and m = 2 when the nitrogen-hydrogen reactant is straight chain, and 0 when the nitrogen-hydrogen reactant is cyclic. High purity silicon

15   nitride can be formed from this intermediate product by heating the intermediate product at a temperature of from about 1200-1700°C for a period from about 15 minutes up to about 2 hours to form a high purity alpha silicon nitride product. *The discovery of the existence of a soluble Si-N-H intermediate enables chemical pathways to be explored previously unavailable in conventional solid-state approaches to silicon-nitrogen ceramics*

E.P. 8/24/87.

RM 8/24/87

```
┌─────────────────────────────────────┐
│                                     │
│       CONTACTING HIGH PURITY        │
│    PARTICULATE ELEMENTAL SILICON    │
│    WITH A HIGH PURITY NITROGEN-     │
│      HYDROGEN LIQUID REACTANT       │
│                                     │
└─────────────────────────────────────┘
                   │
┌─────────────────────────────────────┐
│                                     │
│    REACTING THE MIXTURE TOGETHER    │
│    AT A TEMPERATURE OF LESS THAN    │
│    200°C FOR A PERIOD OF FROM 30    │
│       MINUTES UP TO 100 HOURS       │
│                                     │
└─────────────────────────────────────┘
                   │
┌─────────────────────────────────────┐
│                                     │
│      RECOVERING AN INTERMEDIATE     │
│           REACTION PRODUCT          │
│                                     │
└─────────────────────────────────────┘
                   │
┌─────────────────────────────────────┐
│                                     │
│       HEATING THE INTERMEDIATE      │
│       TO A TEMPERATURE OF FROM      │
│      1200 TO 1700°C FOR FROM 15     │
│     MINUTES TO 2 HOURS TO FORM      │
│     HIGH PURITY SILICON NITRIDE     │
│                                     │
└─────────────────────────────────────┘
```