= Silicon nitride =

Silicon nitride is a chemical compound of the elements silicon and nitrogen , with the formula Si
3N
4 . It is a white , high @-@ melting @-@ point solid that is relatively chemically inert , being attacked by dilute HF and hot H
2SO
4 . It is very hard (8 @.@ 5 on the mohs scale) . It is the most thermodynamically stable of the silicon nitrides . Hence , Si
3N
4 is the most commercially important of the silicon nitrides and is generally understood as what is being referred to where the term " silicon nitride " is used .

= = Production = =

The material is prepared by heating powdered silicon between 1300 ° C and 1400 ° C in an atmosphere of nitrogen :
3 Si + 2 N
2 ? Si
3N
4
The silicon sample weight increases progressively due to the chemical combination of silicon and nitrogen . Without an iron catalyst , the reaction is complete after several hours (~ 7) , when no further weight increase due to nitrogen absorption (per gram of silicon) is detected . In addition to Si
3N
4 , several other silicon nitride phases (with chemical formulas corresponding to varying degrees of nitridation / Si oxidation state) have been reported in the literature , for example , the gaseous disilicon mononitride (Si
2N) ; silicon mononitride (SiN) , and silicon sesquinitride (Si
2N
3) , each of which are stoichiometric phases . As with other refractories , the products obtained in these high @-@ temperature syntheses depends on the reaction conditions (e.g. time , temperature , and starting materials including the reactants and container materials) , as well as the mode of purification . However , the existence of the sesquinitride has since come into question .
It can also be prepared by diimide route :
SiCl
4 + 6 NH
3 ? Si (NH)
2 + 4 NH
4Cl (s) at 0 ° C
3 Si (NH)
2 ? Si
3N
4 + N
2 + 3 H
2 (g) at 1000 ° C
Carbothermal reduction of silicon dioxide in nitrogen atmosphere at 1400 ? 1450 ° C has also been examined :
3 SiO
2 + 6 C + 2 N
2 ? Si
3N

4 + 6 CO

The nitridation of silicon powder was developed in the 1950s , following the " rediscovery " of silicon nitride and was the first large @-@ scale method for powder production . However , use of low @-@ purity raw silicon caused contamination of silicon nitride by silicates and iron . The diimide decomposition results in amorphous silicon nitride , which needs further annealing under nitrogen at 1400 ? 1500 ° C to convert it to crystalline powder ; this is now the second @-@ most important route for commercial production . The carbothermal reduction was the earliest used method for silicon nitride production and is now considered as the most @-@ cost @-@ effective industrial route to high @-@ purity silicon nitride powder .

Electronic @-@ grade silicon nitride films are formed using chemical vapor deposition (CVD) , or one of its variants , such as plasma @-@ enhanced chemical vapor deposition (PECVD) :

3 SiH

4 (g) + 4 NH

3 (g) ? Si

3N

4 (s) + 12 H

2 (g)

3 SiCl

4 (g) + 4 NH

3 (g) ? Si

3N

4 (s) + 12 HCl (g)

3 SiCl

2H

2 (g) + 4 NH

3 (g) ? Si

3N

4 (s) + 6 HCl (g) + 6 H

2 (g)

For deposition of silicon nitride layers on semiconductor (usually silicon) substrates , two methods are used :

Low pressure chemical vapor deposition (LPCVD) technology , which works at rather high temperature and is done either in a vertical or in a horizontal tube furnace , or

Plasma @-@ enhanced chemical vapor deposition (PECVD) technology , which works at rather low temperature and vacuum conditions .

The lattice constants of silicon nitride and silicon are different . Therefore , tension or stress can occur , depending on the deposition process . Especially when using PECVD technology this tension can be reduced by adjusting deposition parameters .

Silicon nitride nanowires can also be produced by sol @-@ gel method using carbothermal reduction followed by nitridation of silica gel , which contains ultrafine carbon particles . The particles can be produced by decomposition of dextrose in the temperature range 1200 ? 1350 ° C. The possible synthesis reactions are :

SiO

2 (s) + C (s) ? SiO (g) + CO (g) and

3 SiO (g) + 2 N

2 (g) + 3 CO (g) ? Si

3N

4 (s) + 3 CO

2 (g) or

3 SiO (g) + 2 N

2 (g) + 3 C (s) ? Si

3N

4 (s) + 3 CO (g) .

= = Processing = =

Silicon nitride is difficult to produce as a bulk material ? it cannot be heated over 1850 ° C , which is well below its melting point , due to dissociation to silicon and nitrogen . Therefore , application of conventional hot press sintering techniques is problematic . Bonding of silicon nitride powders can be achieved at lower temperatures through adding additional materials (sintering aids or " binders ") which commonly induce a degree of liquid phase sintering . A cleaner alternative is to use spark plasma sintering where heating is conducted very rapidly (seconds) by passing pulses of electric current through the compacted powder . Dense silicon nitride compacts have been obtained by this techniques at temperatures 1500 ? 1700 ° C.

= = Crystal structure and properties = =

There exist three crystallographic structures of silicon nitride (Si
3N
4) , designated as ? , ? and ? phases . The ? and ? phases are the most common forms of Si
3N
4 , and can be produced under normal pressure condition . The ? phase can only be synthesized under high pressures and temperatures and has a hardness of 35 GPa .
The ?- and ? @-@ Si
3N
4 have trigonal (Pearson symbol hP28 , space group P31c , No. 159) and hexagonal (hP14 , P63 , No. 173) structures , respectively , which are built up by corner @-@ sharing SiN
4 tetrahedra . They can be regarded as consisting of layers of silicon and nitrogen atoms in the sequence ABAB ... or ABCDABCD ... in ? @-@ Si
3N
4 and ? @-@ Si
3N
4 , respectively . The AB layer is the same in the ? and ? phases , and the CD layer in the ? phase is related to AB by a c @-@ glide plane . The Si
3N
4 tetrahedra in ? @-@ Si
3N
4 are interconnected in such a way that tunnels are formed , running parallel with the c axis of the unit cell . Due to the c @-@ glide plane that relates AB to CD , the ? structure contains cavities instead of tunnels . The cubic ? @-@ Si
3N
4 is often designated as c modification in the literature , in analogy with the cubic modification of boron nitride (c @-@ BN) . It has a spinel @-@ type structure in which two silicon atoms each coordinate six nitrogen atoms octahedrally , and one silicon atom coordinates four nitrogen atoms tetrahedrally .
The longer stacking sequence results in the ? @-@ phase having higher hardness than the ? @-@ phase . However , the ? @-@ phase is chemically unstable compared with the ? @-@ phase . At high temperatures when a liquid phase is present , the ? @-@ phase always transforms into the ? @-@ phase . Therefore , ? @-@ Si
3N
4 is the major form used in Si
3N
4 ceramics .

= = Applications = =

In general , the main issue with applications of silicon nitride has not been technical performance , but cost . As the cost has come down , the number of production applications is accelerating .

= = = Automobile industry = = =

One of the major applications of sintered silicon nitride is in automobile industry as a material for engine parts . Those include , in diesel engines , glowplugs for faster start @-@ up ; precombustion chambers (swirl chambers) for lower emissions , faster start @-@ up and lower noise ; turbocharger for reduced engine lag and emissions . In spark @-@ ignition engines , silicon nitride is used for rocker arm pads for lower wear , turbocharger for lower inertia and less engine lag , and in exhaust gas control valves for increased acceleration . As examples of production levels , there is an estimated more than 300 @,@ 000 sintered silicon nitride turbochargers made annually .

= = = Bearings = = =

Silicon nitride bearings are both full ceramic bearings and ceramic hybrid bearings with balls in ceramics and races in steel . Silicon nitride ceramics have good shock resistance compared to other ceramics . Therefore , ball bearings made of silicon nitride ceramic are used in performance bearings . A representative example is use of silicon nitride bearings in the main engines of the NASA 's Space Shuttle .

Since silicon nitride ball bearings are harder than metal , this reduces contact with the bearing track . This results in 80 % less friction , 3 to 10 times longer lifetime , 80 % higher speed , 60 % less weight , the ability to operate with lubrication starvation , higher corrosion resistance and higher operation temperature , as compared to traditional metal bearings . Silicon nitride balls weigh 79 % less than tungsten carbide balls . Silicon nitride ball bearings can be found in high end automotive bearings , industrial bearings , wind turbines , motorsports , bicycles , rollerblades and skateboards . Silicon nitride bearings are especially useful in applications where corrosion , electric or magnetic fields prohibit the use of metals . For example , in tidal flow meters , where seawater attack is a problem , or in electric field seekers .

Si3N4 was first demonstrated as a superior bearing in 1972 but did not reach production until nearly 1990 because of challenges associated with reducing the cost . Since 1990 , the cost has been reduced substantially as production volume has increased . Although Si
3N
4 bearings are still 2 ? 5 times more expensive than the best steel bearings , their superior performance and life are justifying rapid adoption . Around 15 ? 20 million Si
3N
4 bearing balls were produced in the U.S. in 1996 for machine tools and many other applications . Growth is estimated at 40 % per year , but could be even higher if ceramic bearings are selected for consumer applications such as in @-@ line skates and computer disk drives .

= = = High @-@ temperature material = = =

Silicon nitride has long been used in high @-@ temperature applications . In particular , it was identified as one of the few monolithic ceramic materials capable of surviving the severe thermal shock and thermal gradients generated in hydrogen / oxygen rocket engines . To demonstrate this capability in a complex configuration , NASA scientists used advanced rapid prototyping technology to fabricate a one @-@ inch @-@ diameter , single @-@ piece combustion chamber / nozzle (thruster) component . The thruster was hot @-@ fire tested with hydrogen / oxygen propellant and survived five cycles including a 5 @-@ minute cycle to a 1320 ° C material temperature .

In 2010 silicon nitride was used as the main material in the thrusters of the JAXA space probe Akatsuki .

= = = Medical = = =

Silicon nitride has many orthopedic applications . The material is also an alternative to PEEK (polyether ether ketone) and titanium , which are used for spinal fusion devices . It is silicon nitride ? s hydrophilic , microtextured surface that contributes to the materials strength , durability and reliability compared to PEEK and titanium .

= = = Metal working and cutting tools = = =

The first major application of Si
3N
4 was abrasive and cutting tools . Bulk , monolithic silicon nitride is used as a material for cutting tools , due to its hardness , thermal stability , and resistance to wear . It is especially recommended for high speed machining of cast iron . Hot hardness , fracture toughness and thermal shock resistance mean that sintered silicon nitride can cut cast iron , hard steel and nickel based alloys with surface speeds up to 25 times quicker than those obtained with conventional materials such as tungsten carbide . The use of Si
3N
4 cutting tools has had a dramatic effect on manufacturing output . For example , face milling of gray cast iron with silicon nitride inserts doubled the cutting speed , increased tool life from one part to six parts per edge , and reduced the average cost of inserts by 50 % , as compared to traditional tungsten carbide tools .

= = = Electronics = = =

Silicon nitride is often used as an insulator and chemical barrier in manufacturing integrated circuits , to electrically isolate different structures or as an etch mask in bulk micromachining . As a passivation layer for microchips , it is superior to silicon dioxide , as it is a significantly better diffusion barrier against water molecules and sodium ions , two major sources of corrosion and instability in microelectronics . It is also used as a dielectric between polysilicon layers in capacitors in analog chips .

Silicon nitride deposited by LPCVD contains up to 8 % hydrogen . It also experiences strong tensile stress , which may crack films thicker than 200 nm . However , it has higher resistivity and dielectric strength than most insulators commonly available in microfabrication (1016 ? · cm and 10 MV / cm , respectively) .

Not only silicon nitride , but also various ternary compounds of silicon , nitrogen and hydrogen (SiNxHy) are used insulating layers . They are plasma deposited using the following reactions :

2 SiH
4 (g) + N
2 (g) ? 2 SiNH (s) + 3 H
2 (g)

SiH
4 (g) + NH
3 (g) ? SiNH (s) + 3 H
2 (g)

These SiNH films have much less tensile stress , but worse electrical properties (resistivity 106 to 1015 ? · cm , and dielectric strength 1 to 5 MV / cm) .

Silicon nitride is also used in xerographic process as one of the layer of the photo drum . Silicon nitride is also used as an ignition source for domestic gas appliances . Because of its good elastic properties , silicon nitride , along with silicon and silicon oxide , is the most popular material for cantilevers ? the sensing elements of atomic force microscopes .

= = History = =

The first reported preparation was in 1857 by Henri Etienne Sainte @-@ Claire Deville and Friedrich Wöhler . In their method , silicon was heated in a crucible placed inside another crucible packed with carbon to reduce permeation of oxygen to the inner crucible . They reported a product they termed silicon nitride but without specifying its chemical composition . Paul Schuetzenberger first reported a product with the composition of the tetranitride , Si
3N
4 , in 1879 that was obtained by heating silicon with brasque (a paste made by mixing charcoal , coal , or coke with clay which is then used to line crucibles) in a blast furnace . In 1910 , Ludwig Weiss and Theodor Engelhardt heated silicon under pure nitrogen to produce Si
3N
4 . E. Friederich and L. Sittig made Si3N4 in 1925 via carbothermal reduction under nitrogen , that is , by heating silica , carbon , and nitrogen at 1250 ? 1300 ° C.

Silicon nitride remained merely a chemical curiosity for decades before it was used in commercial applications . From 1948 to 1952 , the Carborundum Company , Niagara Falls , New York , applied for several patents on the manufacture and application of silicon nitride . By 1958 Haynes (Union Carbide) silicon nitride was in commercial production for thermocouple tubes , rocket nozzles , and boats and crucibles for melting metals . British work on silicon nitride , started in 1953 , was aimed at high @-@ temperature parts of gas turbines and resulted in the development of reaction @-@ bonded silicon nitride and hot @-@ pressed silicon nitride . In 1971 , the Advanced Research Project Agency of the US Department of Defense placed a US $ 17 million contract with Ford and Westinghouse for two ceramic gas turbines .

Even though the properties of silicon nitride were well known , its natural occurrence was discovered only in the 1990s , as tiny inclusions (about 2 µm × 0 @.@ 5 µm in size) in meteorites . The mineral was named nierite after a pioneer of mass spectrometry , Alfred O. C. Nier . This mineral might have been detected earlier , again exclusively in meteorites , by Soviet geologists .