NITRIDES

1. Introduction

At elevated temperatures and pressures, nitrogen combines with most elements to form nitrogen compounds. In the presence of metals and semimetals, it forms nitrides where nitrogen has a nominal valence of -3. Atomic nitrogen, which reacts much more readily with the elements than does molecular nitrogen, forms nitrides with elements that do not react with molecular nitrogen even at very high pressures. The binary compounds of nitrogen are shown in Figure 1 (1). These compounds may be classified, according to their chemical and physical properties, into four groups: salt-like, metallic, nonmetallic or diamond-like, and volatile nitrides. The nitrides of the high melting transition metals, eg, TiN, ZrN, and TaN, are characterized by high melting points, hardness (qv), and resistance to corrosion and are referred to as refractory hard metals (see REFRACTORIES). The nonmetallic compounds, eg, BN, Si_3N_4, and AlN, are corrosion- and heat-resistant ceramic-like industrial materials having semiconductor properties (see ABRASIVES; SEMICONDUCTORS, SILICON-BASED SEMICONDUCTORS).

An alphabetical list of nitrides together with CAS Registry Numbers is given in Table 1.

2. Properties

2.1. Salt-Like Nitrides. The nitrides of the electropositive metals of Groups 1 (IA), 2 (IIA), and 3 (IIIB) form salt-like nitrides having predominantly heteropolar (ionic) bonding and are regarded as derivatives of ammonia. The composition of these nitrides is determined by the valency of the metal, eg, Li_3N, Ca_3N_2, and ScN. The thermodynamic stability of the salt-like nitrides increases with increasing group number. For example, the nitrides of the alkali metals are only marginally or not at all stable, whereas the rare-earth metals are effective nitrogen scavengers in metals and alloys (see LANTHANIDES). The salt-like nitrides generally are electrical insulators or ionic conductors, eg, Li_3N. The nitrides of the Group 3 (IIIB) metals are metallic conductors or at least semiconductors and thus represent a transition to the metallic nitrides. The salt-like nitrides are characterized by sensitivity to hydrolysis. These compounds react readily with water or moisture to give ammonia and the metal oxides or hydroxides.

Lithium nitride can be prepared by the reaction of lithium metal and nitrogen. Lithium nitride crystals are dark red and melt at 845°C. The electrical ionic conductivity of the bulk material is 6.6×10^{-4} S/cm at 25°C and 8.3×10^{-2} S/cm at 450°C. The ionic conductivity of single crystals of Li_3N is extremely anisotropic. The value parallel to the c-axis is 1×10^{-5} S/cm at 20°C; the value perpendicular to the c-axis is 1.2×10^{-3} S/cm.

2.2. Metallic Nitrides. Properties of metallic nitrides are listed in Table 2. The nitrides of the transition metals of Groups 6 and 7 (IVB–VIIB) generally are termed metallic nitrides because of metallic conductivity, luster, and general metallic behavior. These compounds, characterized by a wide range of homogeneity, high hardness, high melting points, and good corrosion resistance,

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are grouped with the carbides (qv), borides (see BORON OXIDES, BORIC ACIDS and BORATES), and silicides (see SILICON COMPOUNDS: ANTHROPOGENIC SILICAS and SILICATES) as refractory hard metals. They crystallize in highly symmetrical, metal-like lattices. The small nitrogen atoms occupy the interstitial voids within the metallic host lattice forming interstitial alloys similar to the generally isotypic carbides. Metallic nitrides can be alloyed with other nitrides and carbides of the transition metals to give solid solutions. Complete solid solubility has been demonstrated for a great number of combinations (2). Similarly, oxynitride and oxycarbide interstitial alloys form over wide O−N and C−N composition ranges (3). At high temperatures, all pseudobinary systems between cubic mononitrides and monocarbides of the 4 (IVB) and 5 (VB) metals show complete miscibility, with the exception of the pairs ZrN−VN, HfN−VN, ZrN−VC, HfN−VC, and HfC−VN. TaN has a cubic high temperature modification that is completely miscible with all other cubic monocarbides and mononitrides (4,5) (Table 3).

Although there are several hundred binary nitrides, only a relative few ternary bimetallic metal nitrides are known (6). A group of ternaries of the composition $M_xM'_yN_z$, where M is an alkali, alkaline-earth, or a rare-earth metal and M′ is a transition or post-transition metal, have been synthesized (6). Most of these compounds react readily with available oxygen, including H_2O. These compounds have simple stoichiometries, integral values of x,y, and exhibit conductivities ranging from insulating to metal-like.

Metallic nitrides are wetted and dissolved by many liquid metals and can be precipitated from metal baths. The stoichiometry is determined not by the valency of the metal, but by the number of interstitial voids per host atom. The metallic nitrides are stable against water and all nonoxidizing acids except hydrofluoric acid. The thermodynamic stability decreases with increasing group number from the nitrides of the 4 (IVB) metals. The nitrides of Mo and W can be prepared only by the action of nitrogen under high pressure or reaction with atomic nitrogen or dissociating ammonia. The same is true for the nitrides of the iron group metals (7,8). No nitrides of the platinum-group noble metals are known.

2.3. Nonmetallic (Diamond-Like) Nitrides. Some properties of nonmetallic nitrides are listed in Table 4. The nitrides of some elements of Groups 13 (IIIA) and 14 (IVA) eg, BN, Si_3N_4, AlN, GaN, and InN, are characterized by predominantly covalent bonding. These are stable chemically, have high degrees of hardness (eg, cubic BN) and high melting points, and are nonconductive or semiconductive. The structural elements of diamond-like nitrides are tetrahedral, M_4N, which are structurally related to diamond. Although the most common graphite-like form of BN does not contain these structural elements, boron nitride is considered a diamond-like nitride for two reasons: the existence of a diamond-like form at high pressures and the chemical and physical behavior of BN. Diamond-like nitrides have stoichiometric compositions having no homogeneity range and, as a rule, do not form solid solutions with each other. The preparation and properties of hexagonal BN are discussed elsewhere (see REFRACTORY BORON COMPOUNDS).

Silicon nitride can be heated in air up to 1450–1550°C. In nitrogen, inert gas, or reducing atmosphere, Si_3N_4 can be heated up to 1750°C. Above 1750°C, decomposition and sublimating evaporation become severe. When in the presence of carbon, however, Si_3N_4 stability depends on temperature and pressure. The equilibrium temperature for the reaction

$$Si_3N_4 \;+\; 3\,C \rightarrow \;3\;SiC \;+\; 2\,N_2 \tag{1}$$

at normal pressure is 1700°C. Under reduced pressure of 130 mPa (1 μm Hg), the decomposition temperature is <1100°C and at 3.0 MPa (435 psi), the decomposition temperature is >1900°C (9).

Aluminum nitride (AlN) can be synthesized by reacting alumina oxide in a reducing environment in the presence of nitrogen, as shown by the overall reaction,

$$Al_2O_3 \;+3\,C+N_2 \rightarrow \;2\;AIN \;+3\,CO \tag{2}$$

at temperatures above approximately $T = 1960$ K (1687°C) in a closed system at atmospheric pressure. Aluminum nitride can be synthesized at lower temperatures by removing CO with flowing N_2. In this manner, ρ_{co} (in atm) is kept below its equilibrium value which can be calculated for 0.1MPa (1 atm) total pressure ($CO + N_2$) from Ref. 10.

$$(\rho_{co})^3 + A\rho_{co} - A = 0 \tag{3}$$

Where,

$$A = \exp\left(\frac{\Delta G}{-R_g T}\right) \tag{4}$$

$$\Delta G(\mathrm{kJ/mol}) = 689.9 - 0.353\ T(K) \tag{5}$$

For electronic applications, the use of AlN is highly dependent on reaching a minimum thermal conductivity of $k = 150$ W/m^*k. The combination of high thermal conductivity, high electrical resistivity, good dielectric properties and a linear thermal expansion coefficient makes AlN an exciting ceramic material for electronic applications (11).

AlN's wurzite structure has significantly greater ionic bond character. This feature provides both benefits and limitations. The weaker atomic bonding allows for higher diffusion rates and hence better sinterability. However, from a mechanical perspective, AlN has only moderate hardness and modulus values. To achieve high sintered densities and the desired electrical and thermal characteristics, sintering additives selected from rare and alkaline earth compounds are necessary. Commonly used sintering additives are yttria, calcium oxide, yttrium fluoride and calcium fluoride.

Interest in carbon nitride solids was initially stimulated by theoretical studies of a hypothetical compound having a structure analogous to silicon nitride, β-C_3N_4 (12). This theoretical work suggested that β-C_3N_4 should be reasonably stable and have a hardness comparable to or greater than diamond. Since it was postulated in the mid-1980s, carbon nitride has seen most effort focused on its mechanical properties because of its predicted hardness, unusual Poisson's ratio, etc. Far less work has been carried out on the optical and electronic characteristics.

Theoretical Band Structure Calculations–Carbon Nitride. Band structure calculations have been carried out for the β-C_3N_4 modification by several different methods, which give broad agreement. Detailed calculations by Duan (13), shown in Figure 2, show a direct bandgap with a minimum value of 4.2 eV located at the Γ point (14). Other methods have indicated values between 3.2 and 6.75 eV (15). Density of states (DOS) calculations (13) show that near the conduction band edge the DOS is composed of all orbitals of both N and C, and at the top of the valence band the DOS mainly consists of N_2 p-orbitals. The bandgap of β-C_3N_4 is less than that of β-Si_3N_4 because there are no d-orbitals in the C valence shell, unlike Si.

The band structure of amorphous carbon nitride is critically dependent on the bonding nature of the material, by analogy with amorphous carbon. With carbon, the band structure varies from that of diamond with a bandgap of 5.3 eV while in graphite there is an overlap between the conduction and valence bands. Materials with a mixture of sp^3 and sp^2 bonds behave rather like a mixture of the two (16).

Carbon Nitride Conductivity. The conductivity of carbon nitride materials ranges from $<10^{-14}$ to 1 $(\Omega m)^{-1}$, largely dependent on the sp^3 content—high sp^3 content gives low conductivity. Despite the possibility of N being an n-type donor in carbon nitride, it is found that conductivity reduces with increasing N content, notwithstanding the concomitant increase in the sp^2 content. This is true for both hydrogenated and hydrogen-free films. For example, films deposited by magnetron sputtering have shown a decrease of five orders of magnitude in the conductivity from an N content of 0% up to ~35 at.% as shown in Figure 3 (18).

Figure 4 shows electron spin resonance data presented by a number of authors (14,19–21). It is clear that there is a general reduction in unpaired electron density as N content increases over a range of different deposition processes.

The activation energy of the conductivity can indicate the position of the Fermi energy within the band or mobility gap. Again there is contradictory evidence here. With hydrogenated films, a decrease in activation energy from 0.27 to 0.18 eV has been found over the range of N content 0 to ~8% whereas with sputtered hydrogen-free films the activation energy rose from 0 to ~0.5 eV as N changed from ~0 to ~35 at.% showing a transition from metallic or degenerate to semiconductor behavior (18) as shown in Figure 5.

These results can be reconciled by considering the starting properties of the nitrogen-free material. Material with high sp^3 content has been found to be p-type (22–24) whereas material with high sp^2 content is *n*-type (18). Hydrogenated films typically have higher sp^3 content due to the termination of many bonds by H therefore increasing the N content which has the effect of increasing the sp^2 content will bring the Fermi energy closer to the conduction band edge. Whereas, in sp^2-rich films, increasing the N content increases the concentration trapping centers which have the effect of reducing the free electron concentration so decreasing the conductivity and moving the Fermi energy out of the conduction band.

Optical Absorption. There exits a major division between the optical absorption of hydrogenated and hydrogen-free films. Hydrogenated films have a higher optical gap. The gap has been shown to increase from <0.1 to ~ 1 eV as H content increased from 0 to ~ 17 at.% in amorphous CN_x films (25). PECVD films have shown optical gaps of approximately 2 eV with no systematic variation over the range of N contents from 0 to ~ 14 at.% (14,20). For nonhydrogenated films with a higher sp^2 content, the optical gap reduces from approximately 0.5 eV for 0% N down to approximately zero when N is incorporated (18,26,27). For filtered cathodic arc (FCA)-deposited films with higher sp^3 content, the optical gap may be as high as high as 3.8 eV (28). It seems likely that the nitrogen incorporation plays a minor role in the formation of the optical gap compared with the sp^2/sp^3 bonding ratio and gross effects of defect density, etc., compared to the effect of the bonding structure.

2.4. Volatile Nitrides. The nitrogen compounds of the nonmetallic elements generally are not very stable. These nitrides decompose at elevated temperatures. Some are explosive and decompose upon shock. They form distinct molecules similar to organic compounds, and at low temperatures are gaseous, liquid, or easily volatilized solids. Exceptions are $(SN)_x$, which is polymeric, chemically stable, and has semimetallic properties; and $(PNCl_2)_x$, which has attracted some scientific interest as inorganic rubber (see INORGANIC HIGH POLYMERS). None of the volatile nitrides has obtained any substantial industrial application except ammonia (hydrogen nitride) and nitrogen oxide (oxygen nitride). Gaseous nitrogen fluorides are explosive; Cl_3N, a dark-yellow liquid, evaporates somewhat on heating and explodes. I_3NNH_3 [15823-38-8] detonates at the slightest touch.

3. Preparation

3.1. Nitriding Metals or Metal Hydrides. Metals or metal hydrides may be nitrided using nitrogen or ammonia. Pure metal powders or pure metal hydride powders yield nitride products that are nearly as pure as the precursors.

The nitrides of Groups 4(IVB) and 5(VB) elements form at ca 1200°C. The nitrides of magnesium and aluminum form at 800°C. Aluminum nitride, obtained by heating aluminum powder in the presence of ammonia or nitrogen at 800–1000°C, is formed as a white to grayish blue powder. A grade of especially high purity results from the decomposition of $AlCl_3{-}NH_3$ vapor mixtures.

The nitrides of the alkali earth metals form at 300–400°C and lithium nitride can form at room temperature. Raising the temperature shortens the reaction time and promotes a complete reaction. Nitrides of metals that do not react or react slowly with molecular nitrogen at normal pressure may require pressures up to 100 MPa (14,500 psi) or more (7). Even these high pressures do not suffice for the preparation of thermodynamically unstable nitrides, eg, the nitrides of the iron group metals (Fe, Co, Ni), rhenium nitride, Re_2N, and the high nitrides of Mo and W (8). In these cases, nitriding in a stream of purified ammonia at 600–1000°C leads to the formation of the desired nitrides. Atomic nitrogen is an even more powerful nitriding agent and can be produced by ionizing molecular nitrogen by the action of electrical discharges (29). These transition-metal nitrides can also be formed at high temperatures in a self-propagating, high temperature combustion reaction of loosely packed metal exposed to a gas. A combustion front separates the products from reactants and the procedure can be made self-sustaining by gas recycle-restock and careful control of the combustion regime (30).

3.2. Metal Oxides. A process based on the reaction of metal oxides and nitrogen or ammonia in the presence of carbon is economical and has possibilities for large-scale production because less expensive metal oxides can be used in place of metal powders. However, the products, which contain oxygen and carbon, are not very pure. Removal of residual amounts of oxygen and carbon is difficult, especially in cases where carbon and oxygen atoms are taken into solution within the nitride lattice, which is usually the case for nitrides of the transition metals. Low reaction temperatures generally favor the formation of nitrides and high temperatures promote stable carbides, leading to carbon contamination.

3.3. Metal Compounds. Many nitrides, eg, BN, AlN, TiN, ZrN, HfN, CrN, Re_2N, Fe_2N, Fe_4N, and Cu_3N, may be prepared by the reaction of the corresponding metal halide and ammonia. An intermediate step in this method is the thermal decomposition of the ammonia–halide complex that forms. Nitrides also may be obtained by the reaction of ammonia and oxygen-containing compounds, eg, oxyhalides such as $VOCl_3$ and CrO_2Cl_2; ammonium-oxo complexes, eg, NH_4VO_3 and NH_4ReO_4; or oxides such as GeO_2, B_2O_3, and V_2O_3, and ferrous metal oxides. These nitrides, however, are not very pure and may contain residual oxygen and halogen. On nitriding pure carbides at 3–30 MPa (435–4350 psi) and 1100–1700°C, the carbides of the 4(IVB) and 5(VB) metals are transformed into carbonitrides and free carbon, with the exception of TaC, which is stable. The carbides of the 6(VIB) metals react to form $Cr_3(C,N)_2$ and Mo(C,N). Like TaC, WC is stable under these conditions (31).

3.4. Precipitation from the Gas Phase. The van Arkel gas decomposition process gives especially pure nitrides and nitride films, which under certain conditions may precipitate as single crystals. The nitrides include TiN, ZrN, HfN, VN, NbN, BN, and AlN. In this process, a gaseous reaction mixture consisting of a volatile metal halide, nitrogen, and hydrogen is conducted over a hot substrate, eg, tungsten wire. The metal halide decomposes and the resulting nitride deposits on the wire. The deposition temperature is from 1000 to 1500°C, and this procedure is limited by the thermal stability of the nitride.

3.5. Other Methods of Preparation. The nitrides, Si_3N_4, Ge_3N_4, Zn_3N_2, Cd_3N_2, and Ni_3N, also may be produced by thermal decomposition of the corresponding metal amide or imide. Rb_3N and Cs_3N are obtained by azide decomposition. AlN and Si_3N_4 can be produced by the carbothermal reduction of intercalation compounds, magadiite–and montmorillonite–polyacrylonitrile (32). Nitrides low in nitrogen also can be synthesized from nitrides having a higher nitrogen content by decomposition in a vacuum or by reduction with hydrogen. For example, UN can be produced from U_2N_3, Co_3N from Co_2N, and Ta_2N from TaN. Nitrides and complex nitrides of ferrous metals and of high melting transition metals present in steels and superalloys can be isolated by electrolysis (33).

Silicon nitride occurs in two forms, α-Si_3N_4 and β-Si_3N_4. Pure Si_3N_4 is white, but the colors of commercial materials may be tan, gray, or black because of residual silicon or impurities. Si_3N_4 may be prepared by nitriding silicon powder at 1200–1400°C or, for extremely fine-grained Si_3N_4, by the reaction of $SiCl_4$ or SiH_4 and N_2 or NH_3 (see also ADVANCED CERAMICS, ELECTRONIC CERAMICS).

The formation of nitrides from gaseous halides, ammonia, and nitrogen (atomic and molecular) in a plasma torch is possible (see PLASMA TECHNOLOGY). A specific type of plasma processing called cathodic arc plasma deposition (CAPD) has been used successfully to produce films of nitrides and carbonitrides (34). Material is evaporated by vacuum arcing. The source of the material is the cathode in the circuit and is ignited from this surface to create the arc. The voltages necessary range from 15 to 50 V and the arc spots generate the plasma supply. Plasma nitriding offers several advantages over other processes. It is nonpolluting and energy efficient, provides flexible deposition conditions without sacrifice of quality, minimizes distortion, and is easily applicable to compound film deposition.

Ion implantation (qv) directly inserts nitrogen into metal surfaces. A carefully polished and cleaned metal surface at room temperature in a vacuum ($\sim$0.133 mPa (1-µm Hg)) can be directly implanted with 80-keV nitrogen ions (29) (see METAL SURFACE TREATMENTS). In an alternative synthesis, argon ions (Ar^+) of 8 keV can be used to ionize gas-phase nitrogen to obtain the same results (35).

3.6. Nitride-Containing Layers. Besides case hardening, the hardening, ie, increase in nitrogen content, achieved by nitriding special alloy steels is technologically significant in the heat treatment of high quality parts, such as gears. Hardness (qv) properties are imparted by the resulting coatings of needle-shaped precipitates of the nitrides and carbonitrides of iron, aluminum, chromium, molybdenum, etc. The nitriding steels (nitroalloy steels) that are developed especially for this process contain ca 0.4% C, 1% Al, 1.5% Cr, 0.2% Mo, 1% Ni, and trace amounts of other elements. In gas nitriding, the parts made from such steels are annealed in ammonia at ca 500°C for up to 100 h, whereby 0.1–1-mm thick coatings form. The hardness of these coatings exceeds that of the precipitation-hardened parts by ca 30%.

In nitriding or carbonitriding of condensed materials, molten cyanides (qv) are used at ca 570°C; this method produces fairly thick coatings of nitrides or carbonitrides after ca 1 h. Another process involves the use of an atmosphere containing activated nitrogen atoms or ions that are formed by the action of an electrical glow discharge; the temperature is ca 560°C and the time required for completion of the ion nitriding is 10–12 h (29). The advantage of all of these methods is the lack of distortion during surface hardening, unlike quench hardening, which usually results in at least small changes in dimensions and, at worst, in distortions.

Wear-resistant layers can be deposited on the surface of nearly every kind of material (eg, steel, cast iron, and cemented carbides) by a chemical vapor deposition (CVD) process (36–38) (see THIN FILMS, FILM FORMATION TECHNIQUES). Passing a stream of a mixture of gases containing, for example, $TiCl_4$ vapor, H_2, and N_2, over the surface of heated metallic or nonmetallic bodies results in the deposition of a thin uniform film of TiN. Optimum temperature for this process is 900–1100°C. The film is extremely hard and wear resistant and improves the cutting performance of carbide tips for machining steel and long chipping materials. Carbonitride Ti(C,N) can be deposited analogous to TiN by feeding N_2, $TiCl_4$, H_2, and CH_4 into the gas stream. Whereas the color of TiN is pure golden yellow, the color of $Ti(C_xN_{1\text{-}x})$ can be varied from red golden (ca $Ti(C_{0.1}N_{0.9})$) to a deep purple (ca $Ti(C_{0.4}N_{0.6})$). These films can be polished to a good finish with consequent excellent luster.

One disadvantage of CVD is the necessary high temperature for adherent and pore-free coatings. Deposition of TiN by a sputtering process obviates the use of high temperatures and results in substrate temperatures below 200°C; but consequently deposition rates generally are low (<1 mm/h). Ion plating is a process in which the following occur simultaneously: evaporation of titanium atoms, reaction with very dilute nitrogen gas in the gas phase, and deposition of these highly active atomic clusters onto a solid metallic surface. Thus higher deposition rates occur without a substrate temperature increase when ion plating is used (39). Cemented carbides also can be treated by this process, eg, TiC–Mo_2C(Mo)–Ni or WC–TiC–TaC–Co. If the latter is high in TiC, it can be nitrided at 1150–1350°C in an autoclave. After ca 20 h at 4–8 MPa N_2, a 10-mm thick film that is high in Ti(C,N) is produced (40).

4. Manufacture and Processing

4.1. Nitride Coatings. Carbide tips coated with titanium nitride or titanium carbonitride usually are manufactured by a CVD process using $TiCl_4$, H_2, and N_2 in a hot-wall reactor. Most of the large carbide producers, eg, Metallwerk Plansee (Austria), Sandvik AB (Sweden), Carboloy, Division of Seco-Tools Company (Sweden), and Firth Sterling (U.S.), and Milacron (U.S.), manufacture nitride-coated carbide tips. The portion of tips that are coated is as high as 50–70%. Most are nitride coated. Firth Sterling manufactures HfN-coated tips as well as TiN- and Ti(C,N)-coated tips (40).

To obtain an adherent, uniform nitride coating, the lapped tips are positioned on grids made of heat-resistant wire inside the hot-wall reactor. The reactor is thoroughly flushed with nitrogen and hydrogen, the temperature is brought to ca 950–1100°C by moving the preheated furnace over the reactor, and $TiCl_4$ vapor is fed to the gas stream. The pressure within the furnace is usually kept below atmospheric, but it can be maintained at ambient pressure with equally good results. After completion of the coating cycle, the reactor is cooled by removing the furnace. The tips are removed after cooling and may be conditioned by sand blasting or tumbling to round the cutting edges.

Union Carbide (now GE Advanced Ceramics) developed a process similar to CVD to produce pyrolytic boron nitride-shaped bodies. The process employs graphite mandrels in a high temperature, low pressure reaction chamber. Vapors deposit on the mandrel to produce a thick, high purity, anisotropic, impervious BN layer. In many cases, the desired product is simply slipped off the cooled graphite mandrel. Increasingly, the desired product is not the free-standing pyrolytic BN object but a BN coating on a shaped graphite body. Graphite shapes having adherent BN coatings are used routinely for r-f susceptors, resistance heaters, heat shields, and nozzles (see ABLATIVE MATERIALS; REFRACTORY COATINGS).

4.2. Silicon Nitride. Silicon nitride is manufactured either as a powder as a precursor for the production of hot-pressed parts or as self-bonded, reaction-sintered, silicon nitride parts. α-Silicon nitride, used in the manufacture of Si_3N_4 intended for hot pressing, can be obtained by nitriding Si powder in an atmosphere of H_2, N_2, and NH_3. Reaction conditions, eg, temperature, time, and atmosphere, have to be controlled closely. Special additions, such as Fe_2O_3 to the precursor material, act as catalysts for the formation of predominately α-Si_3N_4. Silicon nitride is ball-milled to a very fine powder and is purified by acid leaching. Silicon nitride can be hot pressed to full density by adding 1–5% MgO.

Self-bonded reaction-sintered Si_3N_4 is manufactured according to the flow sheet in Figure 6. Silicon powder, ball-milled to $<63\ \mu m$, eventually is purified by acid leaching to remove abraded iron particles, and is conditioned by adding an organic agent as a plasticizer or deflocculant. The mixture can be cold pressed, isostatically pressed, or extruded. Slip casting or pressure slip casting has been applied successfully to obtain complex preforms.

The organic bonder or the deflocculant is removed by heating the preforms and prenitriding them at 1000–1250°C. The prenitriding treatment imparts a strength level to the preforms that is sufficient to allow them to be handled, machined, milled, or drilled to the required tolerances using conventional tools. During the final nitriding stage at 1300–1500°C, all the silicon particles are converted to Si_3N_4. No shrinkage takes place either during the presintering process or during the final sintering stage.

4.3. Aluminum Nitride. The emergence of aluminum nitride (AlN) technology spawned several powder-specific synthesis methods. Carbothermal reduction and direct metal nitridation were the two manufacturing methods that received the most attention. These methods have been carried out in operational units such as moving bed furnaces, pusher bed furnaces, and aerosol flow reactors. There are fundamental differences in several critical categories and these distinctions seemed to be more dependent on the manufacturing method rather than the manufacturer.

Carbothermal Reduction. Carobothermally produced powders were fine, uniformed equiaxed particles with low metallic impurities and higher carbon and oxygen levels. The parts produced from these powders were more easily sintered, had better color uniformity, but started with a lower green density. Excess carbon is often used during the carbothermic reduction and has been removed using an oxidation step at modest temperatures, <1273 K (1000°C) (41). This step may partially oxidize the surface of AlN particles sufficiently to form contiguous AlON layer, which is highly resistant to hydrolytic attack (42). Thus, reactivity with moisture is greatly reduced for carbothermally synthesized powders.

One disadvantage to carbothermal reduction may be the necessity of the additional oxidation step. During carbothermal synthesis, carbon monoxide is created as a by-product from the reaction between aluminum oxide and carbon. The unreacted carbon in the product is removed by the aforementioned controlled oxidation process, but results in the further release of more oxides of carbon (43).

Direct Metal Nitridation–Aerosol Flow Reactor. Direct metal nitridation has been used to manufacture AlN in such equipment as aerosol flow reactors, moving bed and pusher bed furnaces. The general aerosol process begins with gaseous precursors and forms the condensed phase by homogenous nucleation. Pure aluminum nitride (AlN) powders were produced in an aerosol flow reactor by direct nitridation of aluminum vapor in excess ammonia and flowing argon from 1400 to 1873 K (43). As the reactor temperature was increased from 1673 to 1873 K, the grain diameter increased from 46 to 64 nm. The effect of temperature on grain size suggests that grain growth takes place through sintering, and some pore coalescence while the crystallite size remained invariant.

At 1873 K and $Q_{\mathrm{Ar}} = 2690$ cm^3/min the AlN collection rate improved from 0.22 g/h to 2.34 g/h as $Q_{\mathrm{NH_3}}$ increased from 375 to 860 cm^3/min. Increasing the ammonia flow rate corresponds to a higher equivalence ratio, thus leading to a higher conversion of Al to AlN. In comparison to commercially manufactured AlN, the Pratsinis AlN had a specific surface area in the range of 26–40 m^2/g, where as the Dow powder was 3.2 m^2/g. The crystallite size of the Dow AlN was 50 nm, which is larger than the Pratsinis AlN. Pure AlN as determined by XRD was obtained in the ammonia flow rate range of 375–860 cm^3/min. The crystallite size decreased from 34 to 28 nm as the corresponding BET specific surface area increased from 26 to 32 m^2/g, and the corresponding grain size decreased from 71 to 64 nm (43).

Direct Metal Nitridation–Moving Bed Reactor. Pusher and moving bed furnaces have been used for the continuous production of ceramic powders. Synthesis of nonoxide ceramic powders occurs at high temperatures (ie, above 1773 K (1500°C)). Moving bed characteristics as a reactor include: Continuous operation; plug flow of solids having a uniform residence time; and gas-solid contacting whereby the gas is supplied as a reactant or as a purge to remove by-products such carbon monoxide.

These characteristics affect the product quality, the process scale-ability, and the reactor performance. Moving bed furnaces are typically operated using counter-current flow (41).

Executing direct nitridation using a moving bed reactor required close attention to three key areas. Feed characteristics, reactor temperature profile and gas dynamics were inspected for the successful operation of a moving bed reactor. The patent describes a synthesis process with a potential capacity of approximately 5000 kg/yr. The AlN product created by this method contained properties that were comparable to that of AlN powders produced commercially by carbothermal nitridation. The surface area (SA) ranged between 2.4–2.8 m^2/g and the oxygen content was observed between 0.7–1.2 percent (44).

Another study placed emphasis on the importance of process uniformity in which each particle of the reactant participates completely in the reaction and all particles participate equally. Their results include a preferred length to diameter ratio in the range of 8–15. Their process uses uncalcined feed pellets of carbon and alumina, which are held together by a binder and fed to the top of the reactor. Calcination is the first step of their process. AlN particles with a SA ranged between 2–5 m^2/g and the oxygen content was observed to be $<0.5\%$ O (45).

Effect of Manufacturing Oxygen Contamination. There are three primary forms of oxygen present in AlN powders. The first is absorbed water that contains atomic oxygen, which can be easily eliminated by modest heating of the powders to approximately 373K (100°C). Oxygen could also be present on the powder surface. It is important to note that this oxide coating may have profound effects of the powder handling, processing and ceramic quality. Lastly, oxygen can also dissolve into the AlN matrix via oxygen-nitrogen substitution in the wurzite structure. This leads directly to Al vacancies in the AlN matrix (41).

Phonon conduction is the primary heat transfer pathway with AlN. Heat transfer is easily disrupted by factors such as grain boundaries and lattice defects. Aluminum vacancies (produced by the presence of oxygen contamination) act as defect sites, which inhibit phonon conduction. Understanding the role of oxygen contamination on the inhibition of thermal conductivity was instrumental to the development of appropriate sintering additives that allow AlN to achieve high thermal conductivity.

Effect of Other Impurities. In addition to oxygen, carbon and other trace impurities such as Si and Fe can inhibit the AlN powder quality. Carbon can be present in several forms in the AlN powder. Free carbon can be generated as a result of incomplete reaction or contamination from the furnace internals. AlN is completely miscible with $Al_2(OC)$, thus there is a possibility for carbon-nitrogen exchange within the wurzite lattice. Organic residue may also, contain small amounts of amorphous carbon. The inclusion of carbon in the AlN lattice promotes coarsening, which is a negative effect on the sinterability (41).

The similarities of the Si and Al atoms, allow Si to substitute at Al sites within the AlN lattice and disrupt thermal conductivity. The equation below displays that Al vacancies are generated when silicon enters the lattice.

$$\mathrm{SiO_2} \rightarrow \mathrm{Si_{Al}} + 2\,\mathrm{O_N} + \mathrm{V_{Al}} \tag{6}$$

This substitution effect is most significant when Y_2O_3 was used as the primary sintering additive (46). In addition to Si, Fe was also shown to decrease the thermal conductivity in AlN (47). There has been slight concern over the concentration of trace radioactive elements found in AlN powders. Stray α-particle emissions from Th and U have lead to soft errors in electronic devices.

4.4. Gallium Nitride. Significant advances in the sophistication of growth techniques, source purity improvements, and controlled introduction and activation of selected dopants: all fueled the rapid commercialization of GaN-based light emitting diodes (LEDs). However, manufacture of GaN for high power, high frequency power-transistors for rf transmission applications covering the 1–50 GHz band has been difficult. GaN boule growing is extremely difficult due to the disassociation of GaN beginning at 900°C and a melting point above 2200°C. The absence of commercially viable “bulk” GaN wafers have made GaN research efforts focus on methods that use substrates that support thermal runaway in RF power devices, create significant lattice mismatches, and place GaN films under compressive stresses.

The manufacturability and cost benefits are uncertain, although the performance benefits of GaN are well documented. The SIGANTIC technology developed by Nitronex utilizes heteroepitaxial growth of GaN on silicon. This innovative technology addresses both cost and manufacturability issues in order to propel GaN’s acceptance of microelectronics and optoelectronic applications.

Material Issues. GaN boule growing is extremely difficult due to the disassociation of GaN beginning at 900°C and a melting point above 2200°C.

The absence of commercially viable "bulk" GaN wafers have made GaN research efforts focus on methods that use substrates that create significant lattice mismatches.

Although both sapphire and silicon carbide are readily available in 50-mm diameters, substrates with much larger diameters are needed to enable high-volume commercialization of GaN, especially for microelectronic applications. Prior to the 1990s, research was done using ordinary silicon; consequently the successes using sapphire substrates completely outweighed those of silicon. This led to the abandonment of silicon as a viable substrate.

Due to the lattice mismatches of GaN and sapphire, either amorphous aluminum nitride (AlN) or GaN buffer layers approximately, 25-nm thick are used to promote growth of GaN device layers. The negative differences in the thermal expansion coefficient of GaN and sapphire place the GaN layer under a compressive stress. This stress is capable of fracturing the film in which the microelectronic devices are held. This is in contrast with GaN growth using SiC. When using SiC, a monocrystalline AlN buffer layer of approximately 100nm thick are employed and only result in approximately 1% of lattice mismatches.

For the growth of crack-free, device-quality GaN-on-silicon, both the large lattice mismatches and gross positive TEC differences must be overcome. Many research groups have attempted with limited success to do so by using various buffer layers between GaN and silicon, including GaAs, AlAs, ZnO, LGO, SiO_2, Si_3N_4, sputtered AlN, LT-GaN, LT-AlN, and deposited and converted SiC films.

The SIGANTIC epitaxial growth platform developed exclusively by Nitronex Corporation (Raleigh, N.C., U.S.) for depositing GaN on large-area silicon wafers resolves these thermal expansion and lattice mismatch problems. Though the composition of the transition layer scheme is proprietary, the layer components were chosen after carefully examining and comparing their thermal expansions versus GaN and silicon as a function of temperature. Precise temperature, composition and film thickness control must be obtained to eliminate radial stress gradients.

4.5. Carbon Nitride. Experimentally, a variety of preparation techniques have been used in efforts to synthesize β-C_3N_4 these methods include atmospheric-pressure chemical processes, including pyrolysis and explosive shock; ion-beam deposition, including cathode arc; laser techniques; chemical vapor deposition processes, including direct-current (dc) arc, hot-filament chemical vapor deposition (HFCVD) and plasma-enhanced chemical vapor deposition (PECVD).

Hot Filament Chemical Vapor Deposition. This technique is a modified version of that used for diamond growth, but here CH_4 was mixed with either N_2 or NH_3/H_2. In both cases the CH_4 concentration was very low; for the first instance, approximately 1% (48), and for the second instance, a 98% H_2 dilution was used with a NH_3 to CH_4 ratio of one (49,50). The filament temperature was 2100°C and the substrate temperature varied from 800 to 900°C. The gas pressure was varied between 1 and 15 torr.

The modification consisted of the use of an r-f or d-c bias between the substrate and filament, or a grid near the filament. The bias was sufficiently higher to generate plasma around the substrate zone and only an amorphous carbon-rich deposit was formed without this discharge (51). Both nickel (seeded with 1 mm diamond paste) and silicon substrates have been used successfully. Initially it was reported that a crystalline deposit, with no amorphous phase, could be prepared; in a more recent paper it was reported that the N/C ratios for d-c- and r-f-assisted films were 0.36 and 0.16 (50), respectively. These values were very different from the N/C ratios from 1.3 to 2.5 originally reported (52).

Diffraction measurements were interpreted as showing the existence of a deposit of a mixture of α- and β-C_3N_4 plus two new phases which are probably monoclinic and tetragonal CN_x ($x = 0.5-1$). As is commonly found, not all of the predicted diffraction phenomena were observed, several of the intensities of the peaks did not agree with the calculated data, and a few unidentified peaks were observed (53). The crystals grown on silicon and nickel substrates had lattice constants of ~10 and 1, respectively, which are larger than the theoretical values. Raman spectroscopy showed that no graphitic phase was present, but possibly more importantly none of the expected Raman peaks from C_3N_4 were observed.

It was argued that hydrogen plays a similar role in carbon nitride formation as it does in diamond growth and that plentiful amounts of both atomic hydrogen and atomic nitrogen are required to create C_3N_4 (54). The results mentioned above, if the deposits are of high-density carbon nitride, indicate that there may be two regimes that can be used to grow crystalline C_3N_4: one with high hydrogen dilution and the other with high nitrogen dilution.

Plasma Enhanced Chemical Vapor Deposition. A considerable amount of work has been carried out on the preparation of CN deposits by means of microwave or r-f plasmas. The microwave work has been motivated by the success of this technique in the preparation of diamond films. It has been shown that hydrogenated amorphous carbon nitride films, α-C(N):H, deposited by r-f PECVD of methane-nitrogen mixtures can be as hard as diamond line carbon films (55). r-f and d-c work has demonstrated that the incorporation of small amounts of nitrogen causes a considerable reduction of the internal stress, with little change in the film's hardness. This result, together with the accompanying improvement in the adhesion of the films, has made a variety of applications possible: antireflecting coatings in ir sensors, protective coatings for computer hard discs, etc. (56).

5. Economic Aspects

Small amounts of TiN, HfN, and other metallic nitrides are produced on a pilot-plant scale. Titanium nitride is sold for $40–100/kg, depending on purity and grain size. Prices for HfN are ca $400/kg.

Annual production of powdered BN is ca 180–200 metric tons per year and its cost is $50–250/kg, depending on purity and density. The price of cubic boron nitride is similar to that of synthetic diamond bort. Hot-pressed, dense BN parts are 3–10 times more expensive than reaction-sintered parts.

Annual production of aluminum nitride is 50–100 t and it is sold for ca $40/kg. Extra high purity, ie, high heat conductive aluminum nitride, is sold for $50–70/kg.

Annual production of silicon nitride is ca 100–200 t. Utility-grade silicon nitride costs \$4–5/kg in 100- to 500-kg quantities. The reaction-sintered parts are sold for \$120 to \$300/kg, depending on complexity of shape. Hot-pressed, fully dense Si_3N_4 parts are priced 5–10 times higher than reaction-sintered parts.

The approximate costs for the year 2005 of selected nitride powders are given based on quantities of 2–220-kg, particle size and product purity. The cost of high density powdered BN is \$226–371/kg and off-white, low density BN cost is \$205–337/kg.

Aluminum nitride powder, white to gray hexagonal crystals costs \$140–225/kg, while regular AlN powder can be purchased for approximately \$130–221/kg.

Technical-grade silicon nitride powder can be sold for \$23–38/kg, while high density silicon nitride powder costs \$116–221/kg.

6. Analytical Methods

Procedures for the quantitative analysis of nitrogen in nitrides are similar to those used for carbides (qv). The same is true for chemical assay methods, although the stability of many nitrides to acids creates difficulties, especially in the Kjeldahl determination of nitrogen content. Consequently, modifications of the Dumas combustion method have been developed (57,58). The Dumas method entails heating the nitride sample in a CO_2 stream in the presence of an oxidant. The nitrogen in the sample is given off and detected, usually by a gas chromatograph. Cu_2O, CuO, and V_2O_5 are commonly used as oxidants (59). Generally good results are obtained for most transition-metal nitrides, but a small amount of the nitrogen typically is not evolved and must be accounted for by hot extraction. Some of the commercially important nitrides cannot be analyzed by this modified method. AlN requires a V_2O_5 oxidant to obtain good results; BN and Si_3N_4 do not react with any of these oxidants. Boron nitride and silicon nitride can be analyzed by a method that makes use of the reaction of nitrides with molten alkalies (60). Nearly all of the nitrides, including the very stable ones, can be dissolved in polytetrafluoroethylene (PTFE) bombs using a mixture of hydrofluoric acid and perchloric acid at 190°C under pressure (61). The resulting solution contains all of the nitrogen in the form of NH_4^+ ions, unlike the Dumas method. Reproducible nitrogen values also are obtained by direct gas determination according to modified high temperature extraction processes (62).

Numerous spectroscopic methods for the qualitative and quantitative analysis of nitrides are available. Methods include x-ray diffraction, which is commonly used for identification of nitrides and the determination of crystalline structure. X-ray diffraction has also been used to characterize residual stress distributions in coated steels (see NONDESTRUCTIVE EVALUATION) (63). Electron microscopies and electron diffraction are commonly used to characterize high strength nitrides and alloys. Auger electron and Rutherford back-scattering spectroscopy are useful for determining the spatial distribution of atoms in nitride films (64). Auger electron spectroscopy is a useful method to analyze interfacial regions and in-depth profiling when combined with ion sputtering (65). X-ray photoelectron spectroscopy (xps) characterizes the nature of nitride chemical bonding by the determination of oxidation states of metals and defect structures (66). High resolution solid-state nmr has been utilized to describe nonstoichiometric nitrides and oxynitrides (67).

7. Health and Safety Factors

As a chemical group, toxicity of nitrides generally stems from the possible reactions with water to form toxic fumes (especially ammonia) rather than from the nitride. There are, of course, exceptions. The salt-like nitrides decompose when in contact with water or moisture to form ammonia, which can irritate the respiratory organs and mucous membranes. The metallic nitrides are very stable chemically, but fine powder or dust of the nitrides of the transition metals can be pyrophoric, especially the nitrides of the actinide metals, UN, ThN, PuN, and those having high surface area, eg, Mo_2N and W_2N. These can ignite in air and during communitive operations. Moreover, nitrides of the actinide metals are carcinogenic.

The diamond-like nitrides, especially as dust, can irritate the lungs or cause scratching of the eyes owing to mechanical means. BN is particularly troublesome because of a lack of solubility in many compounds. Nitrides of the 11(IB) and 12(IIB) metals and especially the volatile nitrides have to be handled with extreme care because of their instability and high degree of toxicity. Hazards associated with the nitrides of the Group 11(IB) and 12(IIB) metals are determined by reactivity with other substances. For example, the addition of concentrated HNO_3 to copper(I) nitride creates a violent explosion. Mild heating of Hg_3N_2 evolves highly toxic mercury vapors and an eventual explosion (65).

8. Uses

8.1. High Strength and Hardness.

Most applications of metallic nitrides stem from their hardness. For example, aluminum nitride can be used to form structural parts that exhibit high degrees of hardness (see ADVANCED CERAMICS, STRUCTURAL CERAMICS). AlN can be prepared in the same way as ceramics (qv), ie, by powder metallurgy from nitride powders or by sintering mixtures of Al_2O_3 and C in the presence of nitrogen. These parts are stable to oxidizing and carbon-containing furnace gases up to 800°C. Above 800°C, they are stable only under a protective gas or in a vacuum. Because of good chemical and thermal stability, sintered parts made of AlN have been proposed for use in nozzles, thermocouple-protecting tubes, crucibles, and boats, eg, in the manufacture of semiconductors (69).

More recently, a liquid-phase metal sintering process was successfully applied to nitrides and carbonitrides, which normally have poor wetting properties. The oxygen content of the prematerial is kept below 0.05% and suitable bonding alloys based on Ni–Mo and Ni–Mo–C are introduced (70,71). This binder composition is especially effective in wetting the nitride or carbonitride particles during sintering and in removing the adhering oxide layers. Cemented titanium carbonitrides having a nickel–molybdenum binder compare well with cemented carbides of this ISO-P series corresponding to C-5 to C-8 grades of the U.S. industry code for cemented carbides (see CARBIDES, CEMENTED). TiN is scarcely soluble in solid iron and is much less so than TiC, hence TiN has favorable frictional qualities and little tendency toward local welding and seizing during cutting operations. Sealing rings of cemented carbonitride have proved satisfactory in difficult chemical environments.

Quaternary carbonitride alloys based on (Ti,Mo)(C,N) tend to separate into two isotypic phases: one (eg, Ti(C,N)) is rich in nitrogen and poor in molybdenum, and the other (eg, (Ti,Mo)C) contains nearly all of the molybdenum but little nitrogen. This spinodal decomposition reaction has been applied to the production of cemented carbonitride alloys, ie, spinodal alloys, that show superior cutting performance and very little wear, especially when used to machine cast iron and chilled cast iron (72). More recent work has been carried out with regard to TaN(HfN)−TaC(HfN) alloys and alloys containing the cubic TaN (73,74). Hot-pressed cemented hard metals based on $TaN-ZrB_2$ are far more suitable for the machining of high melting metals and superalloys than are cemented carbides (75).

The nitride coating of cemented carbide tips, ie, throwaway tips, has increased greatly. Layers of TiN, Ti(C,N), and HfN that are 3–6 mm thick are applied using CVD (35-37). HfN-containing layers also are produced. In a U.S. process, HfN coatings are manufactured by treating Hf sponge with elemental chlorine, thus introducing $HfCl_4$ *in situ* (57). An important European development features multilayers on carbide tips. The carbide surface first is coated with TiC, then with Ti(C,N), and finally by TiN layers; thus the excellent flank wear of TiC coatings is combined with the excellent crater wear of TiN coatings (76). The golden-colored TiN layers are used in the jewelry industry, mainly as the coating of scratch-free watch cases. In Japan, Ti(C,N,O) layers with up to 1.60% O_2 are used instead of carbide, nitride, or carbonitride layers (77).

Within the system Mo−C−N, a molybdenum–carbonitride-phase Mo(C,N) having the WC-type structure can be prepared (30). This phase is completely miscible with WC. Solid solutions (Mo,W)(C,N) between Mo(C,N) and WC behave similarly to WC when sintered with a cobalt or nickel binder and give cemented carbonitrides with properties that are similar to those that are based on WC−Co. In these cemented carbonitrides, a substantial part of tungsten can be replaced with molybdenum, with two parts of tungsten equivalent to one part of molybdenum. In situations of tungsten shortage, such as occurred in the mid-1970s, this replacement is expected to gain technical and economical significance (78).

Transition-metal nitrides improve hardness properties. Nitrogen-alloyed chromium steels, as compared to nitrogen-free austenitic steels, are characterized by increased strength without loss of toughness (79). The corrosion resistance does not decrease if the chromium content is increased to compensate for the amount of chromium that is bound by nitrogen. The industrial preparation of these steels takes place in pressure-melt equipment at ca 2.0 MPa (290 psi) nitrogen, whereby as much as 1.8% N may go into solution. As an alloying constituent, nitrogen can be applied not only by melting under pressure but by employing ferrochromium. This is obtained by treating 50–70% ferrochromium with nitrogen at 950–1150°C in calcium cyanamide pusher furnaces. From 3.5 to 4.5% N is taken up. Research on the ternary system of Group 4 (IVB), 5 (VB), and 6 (VIB) metals as bases for future nitride applications has been reported (70,71). Cubic NbN and Nb(C,N) are superconductors having high transition temperatures (NbN, 17.3 K; Nb(C,N), 17.8 K). Pseudobinary systems containing nitrides have topped these values (NbN–TiC and NbN–NbC, ~18.0 K). There have not been technical applications because of the extreme brittleness of these compounds.

8.2. Nuclear Applications. Use of the nitrides of uranium-235 and thorium as fuels and breeders in high temperature reactors has been proposed (see NUCLEAR REACTORS, WASTE MANAGEMENT, INTRODUCTION). However, the compounds most frequently used for this purpose are the oxides and carbides. Nitrides could be useful in high temperature breeder reactors because of their stability when in contact with molybdenum as a cladding material. Only those mononitrides that are prepared by powder metallurgy, eg, by hot pressing into sintered parts, and those that are high melting, chemically stable, and metallic, as well as the solid solutions of such nitrides and monocarbides, possibly in the form of dispersions in stainless steels, may be suitable for use as nuclear fuel materials (80). The properties of interest for use in reactors have been studied in detail (see Table 2). The higher nitrides of uranium, ie, β-U_2N_3 and α-UN_{2-x}, and of thorium, ie, Th_3N_4, which might be formed during the reaction of the metals with ammonia or pressurized nitrogen, can be decomposed easily by treating the compounds in vacuum at high temperatures.

The rare-earth nitrides do not have any technical applications. These are high melting compounds but are hydrolyzed easily by moisture and are not stable under normal atmospheric conditions.

8.3. Solid Electrolytes. Of the salt-like nitrides, only Li_3N has attracted technical interest. Lithium nitride has an uncommonly high ionic conductivity in the solid state and hence is considered a suitable electrolyte for lithium–sulfur batteries, conferring a favorable capacity as compared to conventional batteries (qv). Lithium nitride is used as a solvent catalyst in the production of cubic BN.

8.4. Refractories. ED: Name used in headHexagonal boron nitride is a soft white powder and resembles graphite in crystal structure, in texture, and in many other properties, except that it is an electrical insulator. It is used in the refractories industry as a mold-facing and release agent. Structural parts made of BN are manufactured by hot pressing. Characteristics include low density, easy workability, good heat resistance, and especially good thermal conductivity and stability to thermal shock, excellent corrosion resistance, and the ability to provide electrical insulation. Boron nitride-based structural parts are used as wall liners in plasma-arc devices, such as gas heaters, arc-jet thrusters, and high temperature magnetohydrodynamic devices (81) (see MAGNETOHYDRODYNAMICS). BN also is used as a crucible material for reactive metal melts because of its nonwetting properties. Boron nitride composites, eg, BN–Si_3N_4 and BN–SiC, are stable to molten zinc and to covering salts, such as borax. As an additive, BN adjusts the electrical conductivity of sintered TiB–TiC boats that are used in vacuum evaporation of aluminum. Boron nitride also is used as a solid dopantsemiconductors source for semiconductors and would be a good material for use in electronic devices operating at high temperature.

Sintered parts of Si_3N_4 may be manufactured from Si_3N_4 powder or from silicon powder by means of cold pressing or slip casting with subsequent sintering in the presence of nitrogen. Silicon preforms that have been sintered under nitrogen at 1200°C have sufficient strength to be machined using conventional carbide tools to close dimensional tolerances. Thus even complicated forms (holes, grooves, threads, etc) can be prepared. During final sintering at 1200–1400°C, no change in dimensions occurs but hardness is increased to a level where only grinding with diamond wheels is effective. Parts with good strength may be obtained, however residual porosities are 15–30%. Such parts are characterized by low thermal expansion, good thermal shock resistance, resistance to creep, and high electrical resistivity. They exhibit good resistance to corrosion by acids but are less resistant to hydrofluoric acid and alkali–hydroxide solutions. They are also stable toward reactive gases and nonferrous metals (82,83).

Sintered parts of Si_3N_4 can be made into tubes, crucibles, boats, nozzles, etc. The tubes can be used for protecting thermocouples or for measuring the temperature in nonferrous melts or gas temperatures in the steel industry (see TEMPERATURE MEASUREMENT). Other parts are suitable as linings of cooling and purification towers for SO_2 roasting gas, cyclone dust separators, spray nozzles, and combustion nozzles, or they may serve as parts in pumps for melting of light metals and linings for Wankel engines. An extensive research effort is being made to develop reaction-sintered or hot-pressed silicon nitride turbine blades as a high temperature material for use in automotive engines (84).

Silicon nitride is one of the few nonmetallic nitrides that is able to form alloys with other refractory compounds. Numerous solid solutions of β-Si_3N_4 and Al_2O_3 have gained technical interest. Many companies have begun to mass produce reaction-sintered and hot-pressed Si_3N_4 parts.

8.5. Abrasives. The graphitic form of BN can be converted into a high pressure diamond-like form by applying pressures of 5–9 GPa (50–90 kbar) and temperatures of 1500–2000°C in the presence of catalysts, such as alkali metals, alkaline-earth metals, antimony, tin, and lead (qv). Lithium nitride seems to be the best catalyst. Pure cubic BN is colorless, but the technical product always contains either excess boron and is brown or black, or excess lithium nitride and is yellow. The cubic boron nitride is stable in air at atmospheric pressure to 2000°C. Cubic boron nitride approaches the hardness of diamond and has been introduced successfully as an abrasive for steel, especially high alloy steel and superalloys (see ABRASIVES). Cubic BN is not used for grinding cemented carbides. The commercial use of cubic BN grit for grinding wheels has grown steadily over the years. The material competes with diamond bort (85) especially for grinding operations involving high alloy steels.

8.6. Coatings and Lubrication. Union Carbide has developed proprietary water-based and aerosol boron nitride coatings for use in plastics, metals, ceramics (qv), glass (qv), and composite material production. Typical applications include use as a release agent, high temperature lubricant, and protective coating for casting, forging, molding, heat treating, welding, brazing, and laser cutting. The coatings are inert to 800°C in oxidizing environments and 2000–3000°C in inert environments or vacuum.

8.7. Catalysis. The development of high surface area porous Mo_2N and W_2N has spurred interest in nitrides for catalytic applications (86–92). High surface area powders are produced by slow (0.6 K/min) heating of the respective oxides in rapidly flowing ammonia or nitrogen–hydrogen mixtures. Surface areas as high as 220 m^2/g have been produced. The freshly prepared nitrides are pyrophoric, oxidizing vigorously if exposed directly to air, and must be passivated by slow, controlled oxidation. It is possible to manipulate the solid-phase chemistry, replacing nitrogen in the metal lattice to form high surface area molybdenum carbides, borides, and metal. High specific surface area Mo_2N has been studied as a catalyst for NH_3 synthesis, ethane hydrolysis, quinoline hydrodenitrogenation, CO hydrogenation, and hydrodesulfurization.

8.8. Electronic and Optoelectronic Applications. Aluminum nitride, characterized by covalent bonding, is a semiconductor having a relatively wide band gap. Owing to the high thermal conductivity and resistivity and reasonably constant dielectric constant of aluminum nitride, commercial applications exist as substrates for semiconductor chips and in manufacturing sintered polycrystalline ceramic heat sinks (93). Primarily because AlN has the highest known surface acoustic wave velocity, usage as an excellent surface acoustic wave device, even under adverse conditions, could be developed. The only problem is the difficulty in obtaining good single crystals (93). Optoelectronically, AlN emits in the uv range (200 nm). However, AlN is hydrolyzed slowly by water vapor and moisture. A p–n junction diode utilizing cubic BN with a part of the emission spectrum in the uv range has been created (93).

The mononitrides of Group 13(IIIA) metals Ga and In also have desirable electronic and optoelectronic properties (see also Table 4). GaN has potential usage as blue light-emitting diodes, in color displays, and in solid-state lasers. The same holds for InN, except the emission wavelength is around 600 nm (red). These compounds can be prepared by the solid-state reactions of Ga_2O_3 or In_2O_3 and ammonia. The utilization of the luminescence properties of GaN and InN is, however, limited by the thermal decomposition of these compounds, which occurs above 600°C (see LASERS; LIGHT EMITTING DIODES).

8.9. Field Emission—Carbon Nitride. The most extensive investigations of carbon nitride for optoelectronic use have focused on its field emission properties for use in plasma panel displays. It has been found that field emission occurs in CN_x films at a very low threshold voltage of $\sim$2.5 V μm^{-1} in films made by ECR-PECVD (51). As shown in Figure 7, a figure which is achieved partly by field enhancement due to roughness effects in the film.

It is not clear, however, what are the affects of nitrogen. There is evidence that the field emission characteristics are dominated by the conductivity of the films; the more sp^2 content in films, the higher the conductivity and the higher the field emission. This has been demonstrated for FCA-deposited and sputtered films. As usual, this explanation is contradicted by other results which suggest emission comes from sp^3 clusters which have a lower work function than their surrounding sp^2-rich boundaries (94).

8.10. GaN High Electron Mobility Transistors (HEMT). Future modulation schemes and air interfaces demand very high linearity power amplifiers, which in turn depend on power transistors with very high compression points, excellent thermal stability and increasingly higher frequency response. These requirements are beginning to place severe constraints on LDMOS technology. GaN HEMTs can alleviate many of them due to its inherently higher transconductance (which helps linearity), good thermal management and higher cutoff frequencies (Nitronex corp).

GaN's material properties position it as a prime candidate for high power microwave applications. GaN maintains a 3.4 eV room temperature energy gap. This gap width enables GaN to support internal electric fields about five times greater than that of Si or GaAs. The ability to support a higher electric field, results in GaN maintaining a higher breakdown voltage, which is an idea characteristic of power devices. High electron speeds are a necessity in minimizing internal device relays. Table 5 details the comparison of the material properties between some of the common semiconductor materials.

In addition, high electron speeds are necessary to minimize internal device delays. Figure 8 shows how the electron drift velocity is related to the electric field.

At low fields, the velocity increases linearly with the electric field, with the electron mobility serving as the proportionality constant. As the electric field increases, the electron velocity overshoots and then saturates to a steady value. The low field mobility is limited by the presence of doping impurities and lattice vibrations, which scatter the electrons while traveling in the device channel. However, this limitation can be partially removed by physically separating the scattering impurities from the channel by growing a modulation-doped heterostructure, as illustrated in Figure 9.

In this configuration, silicon-doped aluminum gallium nitride (AlGaN) is grown on top of GaN. AlGaN has an even higher energy gap than GaN. The silicon impurities in the AlGaN donate electrons to the crystal, which then tend to accumulate in the regions of lowest potential–a quantum well–just beneath the AlGaN/GaN interface. This forms a "sheet" of electrons, which constitutes a two-dimensional electron gas (2DEG). Here, the electrons experience higher mobility because they are physically separated from the ionized silicon donor atoms residing in the AlGaN.

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1 (IA)	2 (IIA)	3 (IIIB)	4 (IVB)	5 (VB)	6 (VIB)	7 (VIIB)	8 (VIIIB)	9 (VIIIB)	10 (VIIIB)	11 (IB)	12 (IIB)	13 (IIIA)	14 (IVA)	15 (VA)	16 (VIA)	17 (VIIA)	18 (VIIIA)
H_3N																	He
Li_3N	Be_3N_2											BN	$(CN)_2$ CN_2	N_2	O_2N ON_2 ON	F_3N	Ne
Na_3N	Mg_3N_2											AlN	Si_3N_4	PN	SN	Cl_3N	Ar
K_3N	Ca_3N_2	ScN	Ti_2N $TiN_{0.9}$ TiN	V_2N VN	Cr_2N CrN	Mn_4N Mn_2N Mn_3N_2	Fe_4N Fe_2N	Co_3N Co_2N	Ni_3N	Cu_3N	Zn_3N_2	GaN	Ge_3N_4	AsN	SeN	Br_3N	Kr
Rb_3N	Sr_3N_2 Sr_2N	YN	ZrN	Nb_4N_3 Nb_2N NbN $NbN_{0.95}$	Mo_2N MoN	$TcN_{0.75}$	Ru	Rh	Pd	Ag_3N	Cd_3N_2	InN	Sn_3N_2 Sn_3N_4	SbN	TeN	I_3N	Xe
Cs_3N	Ba_3N_2	LaN	Hf_3N_2 HfN	Ta_3N_5 Ta_2N TaN $TaN_{0.8}$ $TaN_{0.1}$	W_2N WN	Re_2N	Os	Ir	Pt	Au_3N	Hg_3N_2	TlN	Pb_3N_4 Pb_3N_2	BiN	Po?	At?	Rn
Fr?	Ra?	Ac?	Rf?	Ha?	106?												
				CeN	PrN	NdN	Pm?	SmN	EuN	GdN	TbN	DyN	HoN	ErN	TmN	YbN	LuN
				Th_3N_4 ThN	PaN_2	U_2N_3 UN	NpN	PuN	AmN	CmN	BkN	Cf?	Es?	Fm?	Md?	No?	Lr?

Fig. 1. Binary compounds of nitrogen. See Table 1.

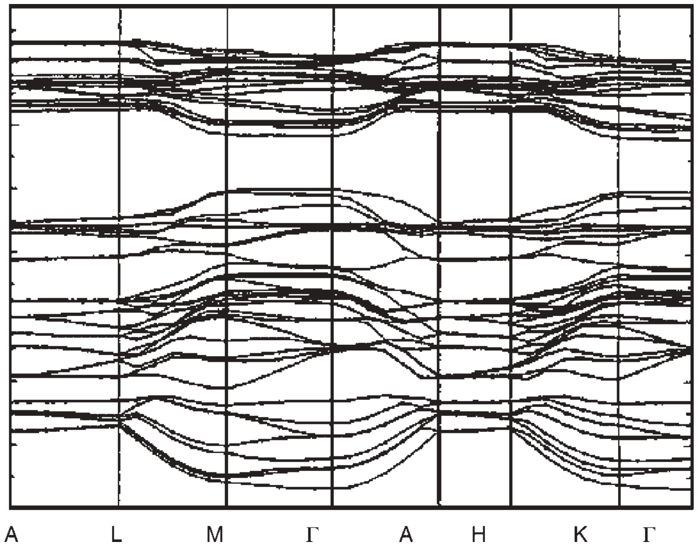

Fig. 2. Calculated band structure for β-C_3N_4.

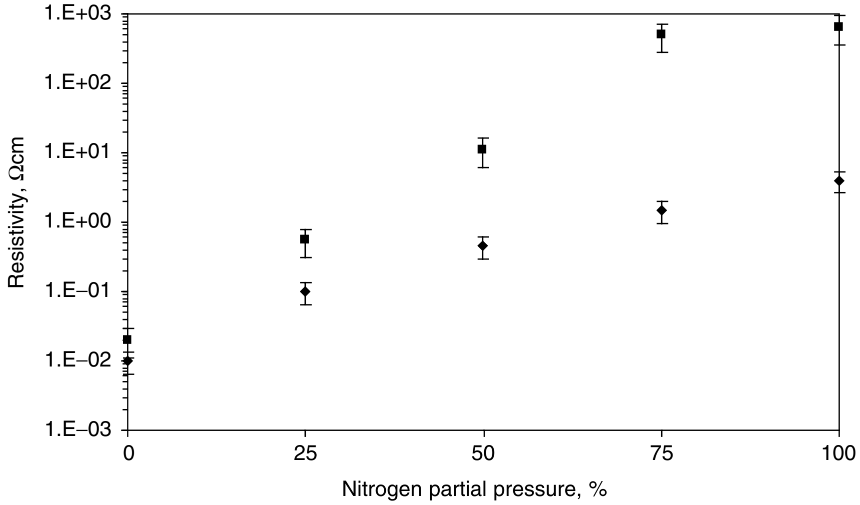

Fig. 3. Resistivity as a function of nitrogen partial pressure for films deposited by opposed target magnetron sputtering (18). Pressures: 1 Pa (■); 0.1 Pa (◆).

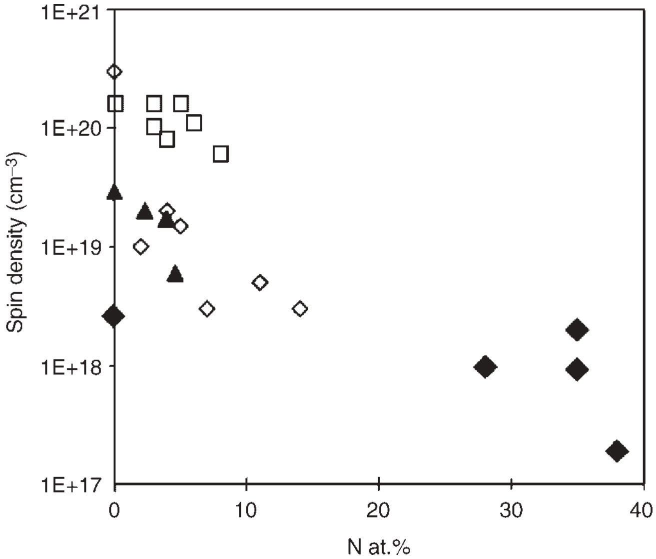

Fig. 4. Electron spin density as a function of nitrogen content for carbon nitride films. Ref. 20 (◇); Ref. 14 (□); Ref. 21 (▲); Ref. 19 (■).

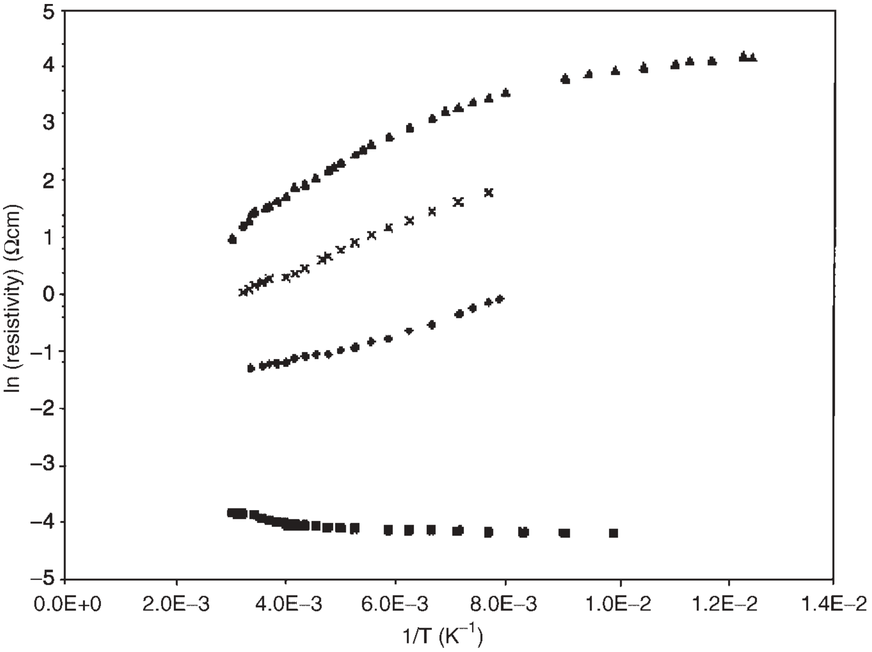

Fig. 5. Resistivity vs. $1/T$ for various carbon nitride films deposited by magnetron sputtering with different nitrogen partial pressures: 0% (■); 25% (◆); 50% (x); 100% (▲).

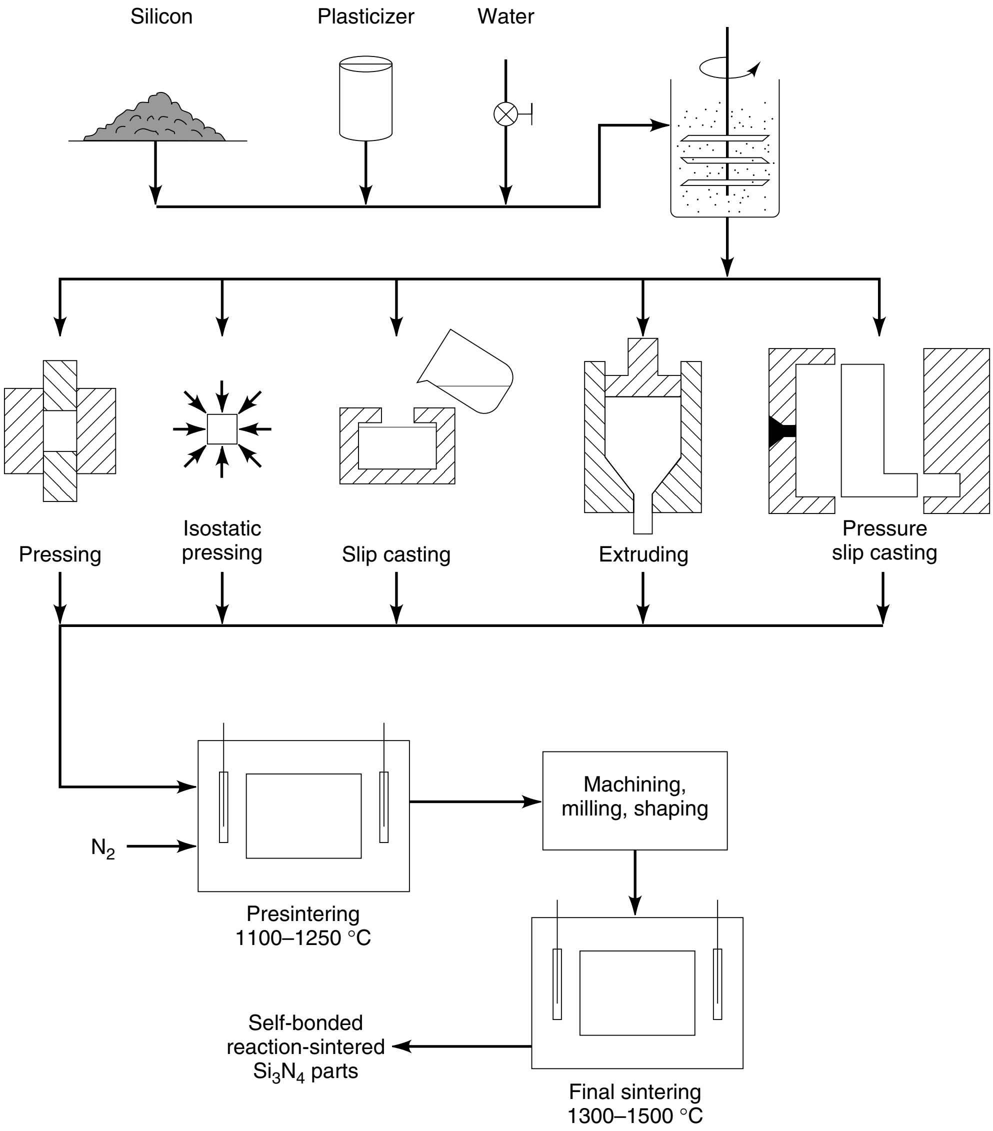

Fig. 6. Flow sheet for the manufacture of self-bonded, reaction-sintered silicon nitride. Courtesy of Annawerk, Ceranox (Roedental, Germany).

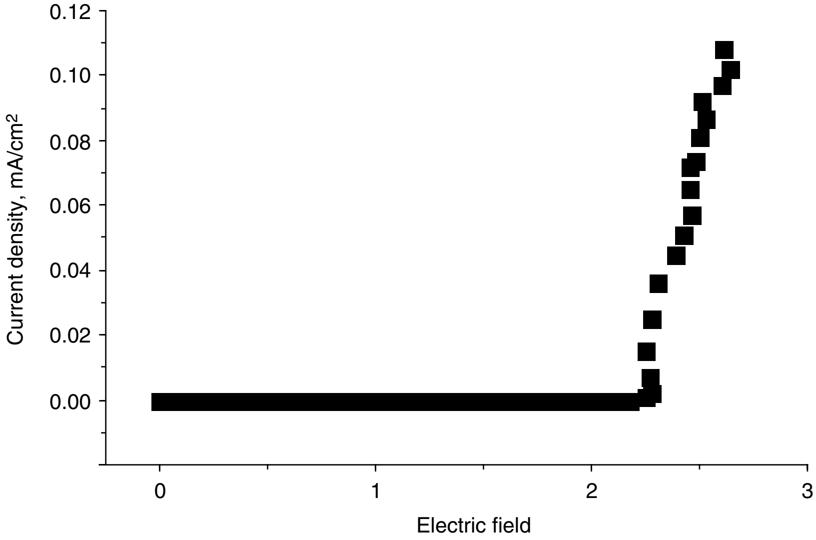

Fig. 7. Field emission characteristics of carbon nitride thin film (51).

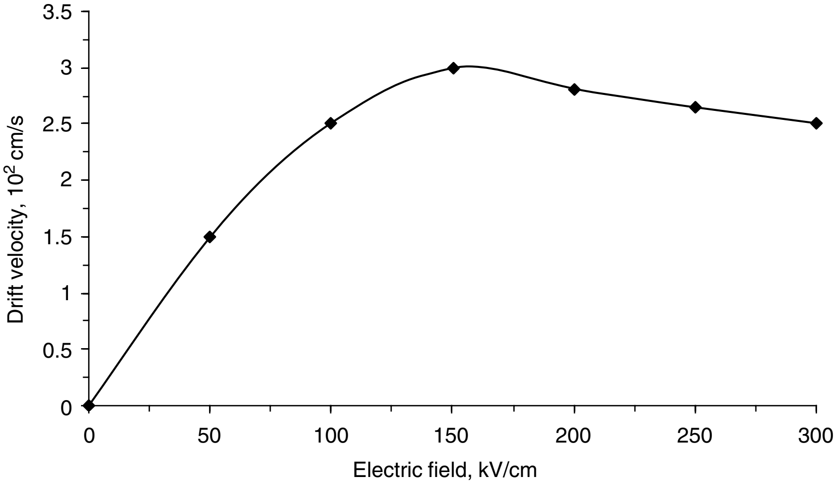

Fig. 8. Relation of the drift velocity to the electric field.

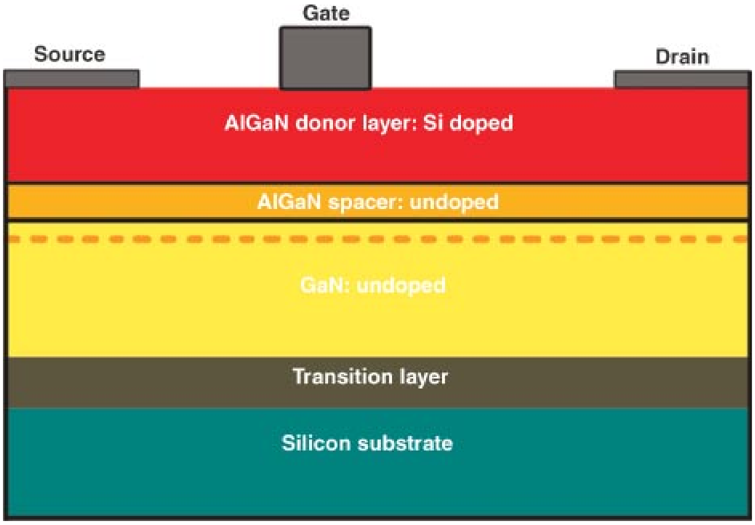

Fig. 9. Schematic of a modulation-doped growth heterostructure.

Table 1. **Alphabetical List of Nitrides**

Compound	CAS Registry number	Formula
aluminum nitride	[24304-00-5]	AlN
americium nitride	[12296-96-1]	AnN
ammonia	[7664-41-7]	NH_3
antimony nitride	[12333-57-2]	SbN
arsenic nitride	[26754-98-3]	AsN
barium nitride	[12047-79-9]	Ba_3N_2
berkelium nitride	[56509-31-0]	BkN
berylium nitride	[1304-54-7]	Be_3N_2
bismuth nitride	[12232-97-2]	BiN
boron nitride	[10043-11-5]	BN
bromine nitride	[15162-90-0]	Br_3N
cadmium nitride	[12380-95-9]	Cd_3N_2
californium nitride	[70420-43-8]	CfN
calcium nitride	[12013-82-0]	Ca_3N_2
carbon nitride	[12069-92-0]	CN_2
cerium nitride	[25764-08-3]	CeN
chlorine nitride	[10025-85-1]	Cl_3N
chromium nitride	[24094-93-7]	CrN
chromium nitride (2:1)	[12053-27-9]	Cr_2N
cobalt nitride (2:1)	[12259-10-8]	Co_2N
cobalt nitride (3:1)	[12432-98-3]	Co_3N
copper nitride	[1308-80-1]	Cu_3N
curium nitride	[56509-28-5]	CmN
cyanogen	[2074-87-5]	$(CN)_2$
dinitrogen tetraoxide	[10544-72-6]	N_2O_4
dysprosium nitride	[12019-88-4]	DyN
erbium nitride	[12020-21-2]	ErN
europium nitride	[12020-58-5]	EuN
fluorine nitride	[13967-06-1]	F_3N
gadolinium nitride	[25764-15-2]	GdN
gallium nitride	[25617-97-4]	GaN
germanium nitride	[12065-36-0]	Ge_3N_4
gold nitride	[13783-74-9]	Au_3N
hafnium nitride (1:1)	[25817-87-2]	HfN
hafnium nitride (3:2)	[12508-69-9]	Hf_3N_2
holmium nitride	[12029-81-1]	HoN
indium nitride	[25617-98-5]	InN
iodine nitride	[21297-03-1]	I_3N
iron nitride (2:1)	[12023-20-0]	Fe_2N
iron nitride (4:1)	[12023-64-2]	Fe_4N
lanthanum nitride	[25764-10-7]	LaN
lead nitride (3:2)	[58572-21-7]	Pb_3N_2
lead nitride (3:4)	[75790-62-4]	Pb_3N_4
lithium nitride	[26134-62-4]	Li_3N
lutetium nitride	[12125-25-6]	LuN
magnesium nitride	[12057-71-5]	Mg_3N_2
manganese nitride (2:1)	[12163-53-0]	Mn_2N
manganese nitride (3:2)	[12033-03-3]	Mn_3N_2
manganese nitride (4:1)	[12033-07-7]	Mn_4N
mercury nitride	[12136-15-1]	Hg_3N_2
molybdenum nitride	[12033-19-1]	MoN
molybdenum nitride (2:1)	[12033-31-7]	Mo_2N
neodymium nitride	[25764-11-8]	NdN
neptunium nitride	[12058-90-1]	NpN

Table 1. (*Continued*)

Compound	CAS Registry number	Formula
nickel nitride	[12033-45-3]	Ni_3N
niobium nitride	[11092-17-4]	NbN
niobium nitride (2:1)	[12033-63-5]	Nb_2N
niobium nitride (4:3)	[12163-98-3]	Nb_4N_3
nitrogen	[7727-37-9]	N_2
nitrous oxide	[10024-97-2]	N_2O
phosphorus nitride	[17739-47-8]	PN
plutonium nitride	[12033-54-4]	PuN
potassium nitride	[29285-24-3]	K_3N
praseodymium nitride	[25764-09-4]	PrN
protactinium nitride	[75733-54-9]	PaN_2
rhenium nitride	[12033-55-5]	Re_2N
rubidium nitride	[12136-85-5]	Rb_3N
samarium nitride	[25764-14-1]	SmN
scandium nitride	[25764-12-9]	ScN
selenium nitride	[12033-59-9]	SeN
silver nitride	[20737-02-4]	Ag_3N
α-silicon nitride	[12033-89-5]	Si_3N_4
sodium nitride	[12136-83-3]	Na_3N
strontium nitride	[12033-82-8]	Sr_3N_2
sulfur nitride	[28950-34-7]	SN
tantalum nitride	[12033-62-4]	TaN
tantalum nitride (2:1)	[12033-63-5]	Ta_2N
tantalum nitride (3:5)	[12033-94-2]	Ta_3N_5
tellerium nitride	[59641-84-8]	TeN
terbium nitride	[12033-64-6]	TbN
thallium nitride	[12033-67-9]	TlN
thorium nitride	[12033-65-7]	ThN
thorium nitride (3:4)	[12033-90-8]	Th_3N_4
thulium nitride	[12033-68-0]	TmN
tin nitride (3:2)	[75790-61-3]	Sn_3N_2
tin nitride (3:4)	[75790-62-4]	Sn_3N_4
titanium nitride (1:1)	[25583-20-4]	TiN
titanium nitride (2:1)	[12169-08-3]	Ti_2N
tungsten nitride	[12058-38-7]	WN
tungsten nitride (2:1)	[12033-72-6]	W_2N
uranium nitride	[25658-43-9]	UN
vanadium nitride	[24646-85-3]	VN
vanadium nitride (2:1)	[12209-81-3]	V_2N
ytterbium nitride	[24600-77-9]	YbN
yttrium nitride	[25764-13-0]	YN
zinc nitride	[1313-49-1]	Zn_3N_2
zirconium nitride	[25658-42-8]	ZrN

Table 2. **Properties of Metallic Nitrides**[a]

Nitride	Color	Lattice parameter,[b, c] nm	Density, g/cm^3	Hardness[d]	Mp, °C	Heat conductivity, W/(m·K)	Coefficient of thermal expansion, $K^{-1} \times 10^{-6}$	Electrical resistivity, μΩ·cm	Transition temperature, K
TiN	golden yellow	0.4246	5.43	2000	2950	29.1	9.35	25	4.8
ZrN	pale yellow	0.4577	7.3	1520	2980	10.9	7.24	21	9
HfN	greenish yellow	0.4518	14.0	1640	3330	11.1	6.9	33	
VN	brown	0.4139	6.10	1500	2350	11.3	8.1	85	7.5
NbN	dark gray	0.4388	8.47	1400	2630 dec	3.8	10.1	78	15.2
ϵ-TaN	dark gray	[e]	14.3	1100	2950 dec	9.54		128	1.8
δ-TaN	yellowish gray	0.4336	15.6	3200	2950 dec				17.8
CrN	gray	0.4150	6.14	1090	1080 dec[f]	11.7		640	not superconductive
Mo_2N	gray	0.416[g]	9.46	1700	790 dec[h]		6.7		5.0
W_2N	gray	0.412[a]	17.7		dec				
ThN	gray	0.5159	11.9	600	2820			20	
UN	dark gray	0.4890	14.4	580[i]	2800	15.5	8.0	176	
PuN	dark gray	0.4907	14.4		2550				

[a] Ref. 1.

[b] Structures are fcc of the NaCl type, unless otherwise noted.

[c] Lattice parameters are room temperature values.

[d] Value is microhardness unless otherwise noted.

[e] Structure is hexagonal B 35. Lattice parameters are *a:* 0.5191 nm; *c:* 0.2906.

[f] At 0.1 MPa (14.5 psi).

[g] Structures are fcc.

[h] At 0.7 MPa (101.5 psi).

[i] Value is Knoop hardness.

Table 3. **Solubilities in the Nitride–Nitride and Nitride–Carbide Systems**[a]

					TaN	
Compound	ZrN	HfN	VN	NbN	Cubic	Hexagonal
			Nitride–nitride system			
TiN	●	●	●	●	●	◐
ZrN		●	○	●	●	◐
HfN			○	●	●	◐
VN				●	●	◐
NbN					●	◐
TaN (cubic)						◐
			Nitride–carbide system			
TiC	●	●	●	●	●	◐
ZrC	●	●	○	●	●	◐
HfC	●	●	○	●	●	◐
VC	○	○	●	●	●	◐
NbC	●	●	●	●	●	◐
TaC	●	●	●	●	●	◐

[a] Completely miscible (●), partially miscible in the cubic phase (◐), and not at all or very slightly miscible (○).

Table 4. **Properties of Nonmetallic (Diamond-Like) Nitrides**

Nitride	Structure	Lattice parameter,[a] nm	Density, g/cm^3	Micro-hardness	Maximum stability temperature, °C	Heat conductivity, W/(m·K)	Coefficient of thermal expansion, $\beta \times 10^{-6}$
BN	hexagonal		2.3	[b]	3000	15	7.51
	a	0.2504					
	c	0.6661					
	fcc, Zn blende	0.3615	3.4	[c]			
AlN	hexagonal wurtzite		3.05	1230	2200	30	4.03
	a	0.311					
	c	0.4975					
GaN	hexagonal wurtzite		5.0		600[d]		
	a	0.319					
	c	0.518					
Si_3N_4	hexagonal		3.2	3340	1900	17	2.75
	a	0.7748					
	c	0.5618					
	hexagonal						
	a	0.7608					
	c	0.2911					

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[a] Values are at room temperature.

[b] Like graphite.

[c] Approcahing diamond.

[d] *In vacuo.*

Table 5. **Material Properties of Common Semiconductors**

Attribute	Sl	GaAs	SlC	GaN
energy gap, ev	1.11	1.43	3.2	3.4
breakdown E-field, V/cm	6.0×10^{5}	6.5×10^{5}	3.5×10^{6}	3.5×10^{6}
saturation velocity, cm/s	1.0×10^{7}	2.0×10^{7}	2.0×10^{7}	2.5×10^{7}
electron mobility, cm^2/Vs	1350	6000	800	1600[a]
thermal conductivity, W/cmK	1.5	0.46	3.5	1.7
heterostructures	SlGe/Sl	AlGaAs/GaAs InGaP/GaAs AlGaAs/InGaAs	none	AlGaN/GaN InGaN/GaN

[a] Typical two-dimensional electron gas mobility for AlGaN/GaN heterostructures.