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Reactions between silicon and nitrogen

Part 2 *Microstructure*

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The silicon nitride that forms as a result of reaction between solid silicon and nitrogen has several morphologies and occurs in the two phases, alpha and beta. Reasons are proposed that account for observations linking certain reaction conditions to particular microstructural features of the product. The reaction conditions considered were (1) temperature, (2) addition of other gases to the nitrogen, and (3) whether or not the gas is flowing over the reacting surface. Both the morphology and the phase composition of each microconstituent in the product were examined. The results were using high-purity single-crystal silicon slices and purified nitrogen at temperatures below the melting point of silicon.

1. Introduction

At temperatures between about 1250 and 1400° C gaseous nitrogen reacts with solid silicon to form silicon nitride (Si_3N_4). At higher temperatures, nitrogen encourages reaction with liquid silicon. The mechanisms that control the reaction and lead to one or the other of the two phases, alpha or beta, as well as the various morphologies of the product are complex and not fully understood. The reaction is worthy of detailed consideration because a structural ceramic for high-temperature applications is made from powder compacts of silicon, and the microstructure of this product depends on the conditions of its formation.

The system has indeed been studied extensively, and several reviews [1–3] summarize most of the available results. Investigations of reaction mechanisms have included a variety of types of observation, such as (1) kinetics, (2) morphology of the products, and (3) phase composition of the products. The influence of temperature, impurities in the gas, impurities in the solid, the size of solid particles, and gas flow rate have been documented. All of these variables, individually and in combination, have a marked effect on the microstructure of the product.

Most of the research has been done using powder compacts of silicon as the starting solid. Although this system has practical importance, the microstructure resulting from a reacting powder is complex and difficult to interpret. A few studies have focused on the reaction between high-purity single-crystal silicon and nitrogen [4–7], and, because of the well-defined nature of the starting solid, they have provided additional insight into the reaction process.

Part 1 [1] of this paper summarized much of the published literature that is relevant to reaction mechanisms, primarily with a view towards further defining the difference between the mechanism that leads to the alpha and that which produces the beta phase. The present paper (Part 2) summarizes selected published information that may help to identify the reasons for various morphologies and presents experimental results that are discussed in relationship to (1) the separate phases, and (2) the reasons for the various morphologies. Consideration is given only to reactions that occur below the melting point of silicon. At temperatures above the melting point, with silicon in the liquid state, the rate of reaction is increased, the formation of the beta phase is encouraged, and, in general, the microstructure is significantly altered.

2. Background

A number of reported experimental results have suggested that, at least under the conditions considered, definite relationships exist between specific processing parameters and the nature of the products formed. This section discusses selected results that will be used later in this paper. They are summarized in Table I.

Atkinson *et al.* [4] reported several observations including: (1) during the early stages of nitridation the rate is linear with time, and the rate constant is proportional to nitrogen pressure, (2) the final stages of nitridation are characterized by a gradual slowing of the rate, and this is attributed to a nitride layer that gradually covers the reacting surface, until finally the reaction stops, and (3) the final thickness of the layer is a function of the temperature and nitrogen pressure – high temperature and low pressure producing a thicker, coarser layer than low temperature and high pressure. Taken together these results indicate that adsorption of nitrogen on to the solid surface is a critical step, encouraged by low temperature and high pressure, and leading to nucleation and growth of Si_3N_4.

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TABLE I Selected factors that control nitridation (below the melting point of silicon)

Variable	Observation	Reason	Ref.
N_2 pressure	High-pressure produces fine grain	Absorption of N_2 important	[4]
	Low pressure produces thick product	Coarse grain does not form continuous layer	[4]
Type of surface for product	Alpha encourages alpha phase	Reaction occurs on surface	[8, 9]
Added gas to N_2 atmosphere	Alpha/beta ratio altered	Influences presence of atomic nitrogen	[1]
	Degree of reaction before stage III	Influences viscosity and thermal conductivity	[16, 17]

The importance of nucleation and growth occurring on a surface is supported by results of seeding experiments in which Si_3N_4 was incorporated in the original compacts [8, 9]. When α-Si_3N_4 was added, the formation of alpha product was encouraged, whereas addition of the beta modification promoted the formation of the beta phase. Clearly, the structure of the substrate influences the kind of phase formed.

In part 1 [1], the suggestion was advanced that one difference in the mechanisms of formation of the alpha and the beta phases is that production of the alpha phase involves complexing of silicon with molecular nitrogen whereas the beta phase results from complexing with active nitrogen, possibly atomic nitrogen. Here again, a surface may be important because atomic nitrogen may form on a surface by dissociative chemisorption.

The kinetics of nitridation can be summarized as shown in Fig. 1 (adapted from [10, 11]). The initial period of slow reaction is attributed to the removal of a protective silicon oxide layer. A rapid reaction follows, and finally the reaction is very slow, controlled by diffusion. Because the reaction is exothermic, the nitridation process could be self-accelerating if uncontrolled [12].

The reaction kinetics can be altered in a number of ways, most of which are summarized in Part 1 [1]. Atkinson *et al.* [4] showed that a relatively slow reaction during Stage II typically leads to more product before the start of Stage III, and the authors attributed this to the lack of continuum of a fine, uniform surface layer of product, with a resultant continued exposure of some of the silicon to the nitrogen atmosphere. In this case, a few nuclei grow to a large size and the product is coarser than it is if there is fast early reaction; therefore, a correlation can be made between the degree of reaction before Stage III and coarseness of product.

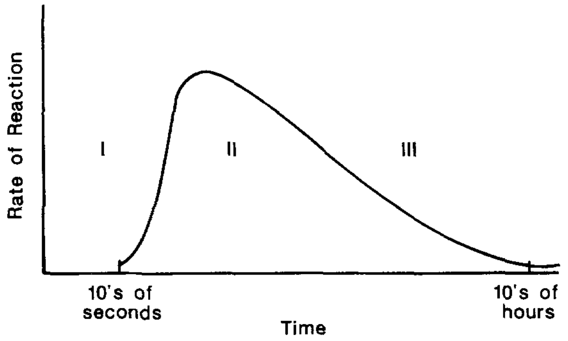

Figure 1 Variation of nitridation with time. The scales are arbitrary and depend on reaction conditions, such as temperature and specific surface area of silicon.

Iron accelerates by helping to remove the oxide layer [11], and it dramatically affects the morphology of the product [4]. For example, at temperatures approaching the melting temperature of silicon, the presence of iron as an impurity lowers the melting point and encourages melting; this has been shown to lead to the rapid formation of the beta phase [1, 13]. (No accelerating effect is observed in the absence of melting, although the induction period is shortened [11].) The presence of hydrogen in the nitriding atmosphere also has been shown [1, 14, 15] to shorten Stage II, to increase the alpha : beta ratio and the fineness of the product [14], and to increase the degree of reaction before Stage III.

The results of many experiments [1, 14] have shown that there are important differences between reactions that occur in flowing nitrogen as compared with static nitrogen. It has been suggested, but not proven [1], that this is linked with the introduction or removal of gaseous impurities such as oxygen or water vapour.

Kim and Kim [16–18] have used relationships that result from the principle that, when two molecules of dissimilar mass collide, energy is transferred to the lighter molecule as a result of conservation of energy and momentum, to show that an added gas alters the viscosity, the thermal conductivity, and the thermal diffusivity of a nitrogen atmosphere. The added gas can also become somewhat segregated from the nitrogen. When gases lighter than nitrogen are added, the rate of thermal diffusion is increased, and the lighter gas diffuses up any thermal gradients which might be in the nitrogen atmosphere. When gases heavier than nitrogen are added, there is a decrease in the rate of thermal diffusion, and the added gas diffuses down any thermal gradients.

The formation of pores has been discussed elsewhere [1, 4]. They can form either (1) by direct evaporation of silicon, or (2) by formation of vacancies that then coalesce.

3. Comment on evidence used to understand mechanisms

Mechanisms of chemical reactions can almost never be directly observed, but they may be deduced from a variety of characteristics of a reaction. For example, although the degree of nitrogen adsorption on a solid surface is difficult to detect, Atkinson *et al.* [4] deduced its importance from the fact that it explained a wide variety of observations. Similarly, the reasons proposed here to explain many observations have not been checked directly. For example, although concentration of a particular gas or a temperature gradient near the solid silicon surface are difficult to detect, there is a good reason to believe that, under some conditions, these gradients do indeed exist [18]; they can be invoked to explain a wide variety of otherwise perplexing observations.

3.1. Possible reasons for the formation of various microstructures

Although the ideas discussed in the previous sections have been applied to specific aspects of the reaction, i.e. the fineness of the product, degree of reaction, etc., they have not, heretofore, been applied generally to all of the important reaction conditions to formulate fundamental reasons for the formation of the observed morphologies and/or the phase compositions of the product. For example, the roles of temperature, added gases and gas flow rate, have not been incorporated into general rules of microstructure formation. This section explores possible reasons for the formation of different kinds of microstructure under different experimental conditions, and, although the proposals are not complete, they are promising as attempts at finding some basic rationales. In most cases, the reasons have evolved by generalizing mechanisms already proposed and considering several phenomena discussed in the literature.

For the purpose of analysis, the microstructure may be separated into (1) early product, (2) inner product, and (3) outer product. After an initial surface layer of product forms, additional product must form either inside or outside of the original silicon surface. In each case, the reaction proceeds by either having a grain of Si_3N_4 grow, or by nucleating a new grain. If formation occurs on the silicon surface, nitrogen must first be adsorbed; if formation occurs on the Si_3N_4 surface, then both silicon and nitrogen must be transported to the reaction site. In order to form inner product, pores must first be created, to an extent which will accommodate a 22% expansion of solid (Si_3N_4 is more voluminous than silicon). Thus, there arises a kinetic competition between formation of pores and formation of product.

3.2.1. Early product

Atkinson *et al.* [4] described the formation sequence of initial product, which is illustrated in Fig. 2. Nucleation on the silicon surface is followed by growth along the surface. As will be shown, after the initial nucleation process product can form outside, inside, or along the surface of the silicon, depending on the reaction conditions.

3.2.2. Outer product

In order to form outer product, both silicon and nitrogen must be adsorbed at the reaction site, and adsorption of both gases is most likely at high pressure and low temperature. Fig. 2a illustrates two possibilities. For outer product, the partial pressure of silicon probably varies from place to place. If there is a gradient in either temperature or concentration such that adsorption on an Si_3N_4 nucleus becomes more likely with increased distance away from the silicon surface, then needles will grow as illustrated in Fig. 2b. This mechanism has similarities to the mechanism that produces dendritic growth in constitutionally supercooled fluids. If adsorption on a Si_3N_4 nucleus occurs preferentially on the sides of the growing grain, perhaps involving surface diffusion, then the product will tend to grow together and seal off the surface.

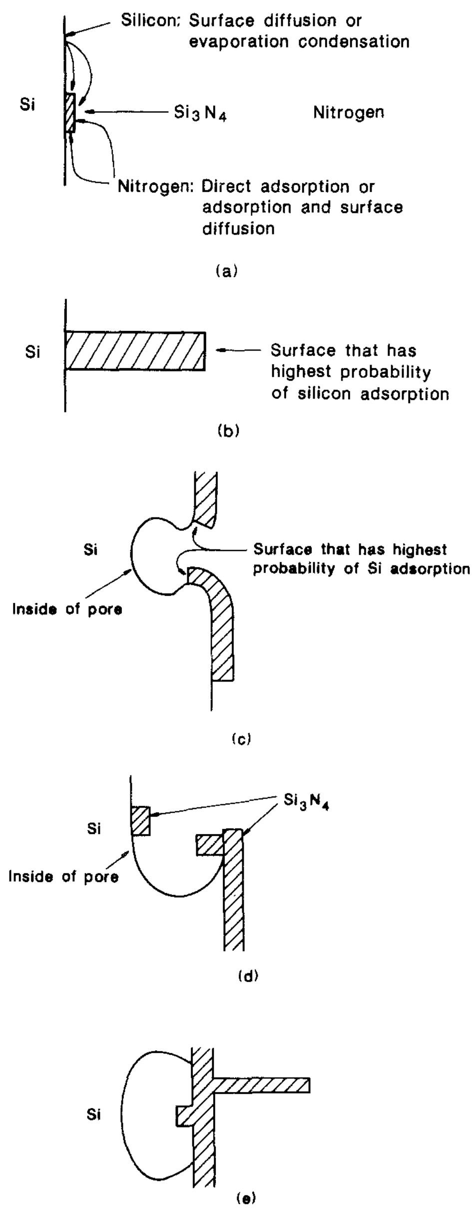

Figure 2 Schematic representation of the reaction during stages II and III. (a) Initial nucleation of product, subsequent growth is either along the surface or away from the surface. (b) The product will form needles that grow into the open volume if the reactants adsorb preferentially on the outer surface of the nuclei: this is encouraged when the temperature of the gas decreases with distance away from the surface of the silicon, or when the concentration of silicon vapour increases with distance away from the surface (only possible when a second gas is added). (c) The product will grow along the surface if the reactants adsorb preferentially on the sides of the nuclei. (d) After the formation of a pore a needle may grow inwards if the reactants adsorb preferentially on the end of the growing needle and new nuclei may form if nitrogen adsorbs on the inside surface of the pore. (e) Reaction product eventually forms a barrier between unreacted silicon and nitrogen.

3.2.3. Inner product

As shown by Atkinson *et al.* [4], product may form along the surface until it encounters a cavity created by evaporation of silicon, at which point it starts to grow into the cavity as shown in Fig. 2c. This inner product will continue to form as long as silicon pores continue to form, and nitrogen can enter them. High temperature encourages evaporation of silicon, with consequent formation of the coarse product. Turbulence in the atmosphere may also foster both the removal of silicon and the entrance of nitrogen into the pores. Nucleation of product on a fresh silicon surface within the pore structure obeys the same rules as for the initial product. In this paper, the inner surface of the pore structure refers to a surface away from the original silicon surface as shown in Fig. 2d.

4. Experiments

Single-crystal wafers of semiconductor-grade silicon roughly 250 μm thick and several tens of millimetres in length and width were cut so that the large area surfaces were either (1 0 0), (1 1 1), or (1 1 0). Just before placing the specimens in the nitrogen atmosphere of the nitriding furnace, they were chemically polished in a solution of 12% CH_3COOH, 25% HF, and 63% HNO_3, thoroughly rinsed in deionized water, and dried with alcohol and ether.

The reaction chamber was made of two concentric tubes of recrystallized alumina, and nitrogen was sent through the passage between the outer wall of the inner tube and the inner wall of the outer tube in the hope of forestalling the diffusion of atmospheric gases through the tubing wall into the reaction chamber. Studies were made with both a static and flowing atmosphere surrounding the specimens. Nitrogen was passed over soda-lime to remove CO_2 (to < 10 p.p.m.), magnesium perchlorate and a molecular sieve to remove H_2O (to < 10 p.p.m.), and through heated copper wool to remove oxygen (to < 10 p.p.m.). For all the high-purity experiments, the partial pressure of oxygen was further reduced by surrounding the specimen boat with degreased zirconia filings.

The specimens were oriented as illustrated in Fig. 3. In most experiments three specimens, placed several millimetres apart, were nitrided at the same time, and they were lined up so that if the atmosphere was flowing they were parallel to the direction of flow. The centre specimen and the inside surfaces of the two outer specimens, which face other silicon slices, will be referred to as "shadow" surfaces, whereas the outer two surfaces will be labelled "exposed." The latter surfaces are exposed to a large volume of gas. If the gas at some distance away from the specimen surface is cooler than the specimen surface, there will be a temperature gradient away from the surface. Because the shadow surfaces are in close proximity to another solid surface, the gas in between is likely to be heated to a uniform temperature.

The reaction chamber was heated electrically. Resistance wire was wound around the outside of the alumina tubing in the region of the specimens. A thermocouple, placed next to the silicon boat, controlled two reaction temperatures, 1270 and 1350° C, both below the melting point of silicon (1410° C). In all cases, the nitriding process has entered Stage III by 24 h, and additional nitriding times produced no significant changes in the microstructure.

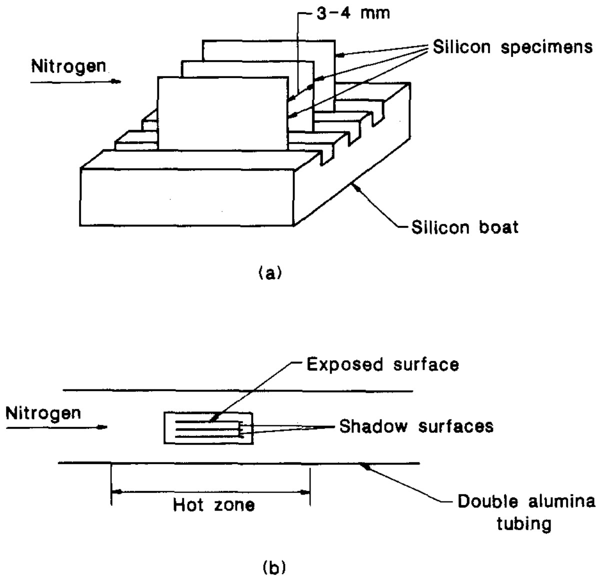

Figure 3 Specimen orientation in the hot zone of the furnace. (a) The centre specimen and the inside surface of the outer two specimens are in the "shadow" region; the outer surface of the outer two specimens are in the "exposed" regions. (b) View from the top of the specimens.

Specimens were weighed before and after nitridation. Each specimen was fractured in the direction perpendicular to the reaction surface, and examined in cross-section in a scanning electron microscope. X-ray diffraction patterns of the surfaces were used to determine approximately the amounts of alpha and beta phases and any preferred orientation. Because of the highly oriented nature of the products of single-crystal nitridation, only a qualitative assessment of the relative abundance of the two phases could be made by X-ray analysis.

5. Results and discussion

The experiments, designed to help formulate and test the ideas outlined in Section 3 above, are not exhaustive, but they furnish enough information to give significant insight. This section is divided into two parts. The first part deals with general observations that are applicable to all of the specimens observed, and the second illustrates particular results. A summary of the microstructural features observed under specific conditions are given in Table II, along with a possible rationale for the effects produced by each condition.

5.1. General results

The physical configuration of the nitriding specimens produced a result which was not anticipated. In almost every experiment, marked differences appeared between the microstructure of the product formed on the shadow regions (Fig. 3) and that formed on the exposed regions. The principal difference is that the shadow region contained much less outer product than the exposed regions, and outer product was

TABLE II Proposed reasons for microstructural features

Microstructural feature	Conditions leading to formation	Reasons for formation
Early formation of dense surface layer	Shadow region, static nitrogen, low temperature	Adsorption of Si on side of nucleus. No temperature gradient. High concentration of silicon near surface.
Outer needles	Exposed region, flowing nitrogen, added gas	Adsorption of silicon on outside surface. Temperature gradient. Concentration gradient.
Inner Product	High temperature, added gas	Removal of silicon as vapour to form pores faster than product layer can form. Adsorption of N_2 inside pores.

always needle-like. Needle-like product was almost never observed in the inner product.

A thesis of this paper is that the temperature of the gas and its temperature profile with distance from the reacting surface are important in determining the structure of the product. We suggest that in the shadow region between the silicon slices the gas has a relatively uniform temperature whereas, above the exposed surfaces, the gas has a temperature gradient, the gas being cooler the further it is from the heated sample. The cooler the gas, the greater the likelihood of adsorption on a solid, which would therefore take place preferentially at a location as far as possible from the hot sample, namely at the tip of a growing needle. Flowing nitrogen will encourage a temperature gradient by introducing cool nitrogen. Added gases in the nitrogen may also alter the gradient by altering the thermal conductivity of the atmosphere.

Inner product, which grows in the pores, never contains needles that grow outwards from the inner surfaces of the pore. Only rarely does a needle appear to grow inwards from the outside surface of a pore as shown in Fig. 2d. This is thought to be because there is little or no temperature gradient within the pore structure. Needles that grow inwards could result from a concentration gradient of silicon vapour that increases towards the unreacted silicon on the inner surface.

Another general result is that specimens displaying only inner product do not gain weight during nitridation (specimens become measurably lighter), in contrast with some of the specimens containing outer product. Thus, specimens without outer product lose at least enough (almost always more) silicon (by evaporation) to compensate for the weight of any Si_3N_4 formed. Because the density of Si_3N_4 is $3.18\,g\,cm^{-3}$ and the density of Si is $2.33\,g\,cm^{-3}$, inner product must be at least 27% porous (this is the lower limit associated with no weight loss). If this is the case under all reaction conditions, the nitridation of powder compacts containing large grains of silicon that produce large amounts of inner product, will always be porous and may never produce high-strength material.

5.2. Examples of product formation

This section illustrates some of the results obtained from nitridation experiments and discusses the morphology and composition of the products in the light of concepts discussed above. In order to reduce the number of micrographs in this section, only some of the morphologies will be described.

5.2.1. Sandwich specimens

In an attempt to investigate the influence of a nearby surface on the microstructure, two silicon slices were placed lying down on the silicon boat, one on top of the other. Both (1 1 1) and (1 0 0) specimens were nitrided. Fig. 4 shows a nitride coating after 65 h at 1350° C. The thin product layers formed along the inner surfaces of the sandwich have no fibrous outer product and very little porosity. X-ray analysis indicated the presence of very little beta phase, and a highly oriented alpha phase formed with (2 0 0) parallel to (1 1 1). These observations can be rationalized by taking into account the suggestion, made in Part 1 [1], that the alpha phase forms when silicon complexes with molecular nitrogen, the beta form complexes with active (atomic) nitrogen. It has been observed that, in the presence of oxygen [1], active nitrogen is extremely rare, thus precluding the formation of the beta phase. The absence of beta phase in the sandwich configuration could result because the sandwich traps any oxygen which was adsorbed on the silicon surface after chemical polishing. The sandwich configuration would also be expected to hinder the escape of silicon vapour, thereby hindering the subsequent formation of porosity.

The lack of a needle-like outer product in the presence of both nitrogen and, probably, a relatively high partial pressure of silicon, must be explained. The temperature of the gas above the surface and between the slices was probably uniform near 1350° C (i.e. no temperature gradient). This lack of outer product is explained as resulting from preferential adsorption of silicon on the sides of nuclei (perhaps caused by

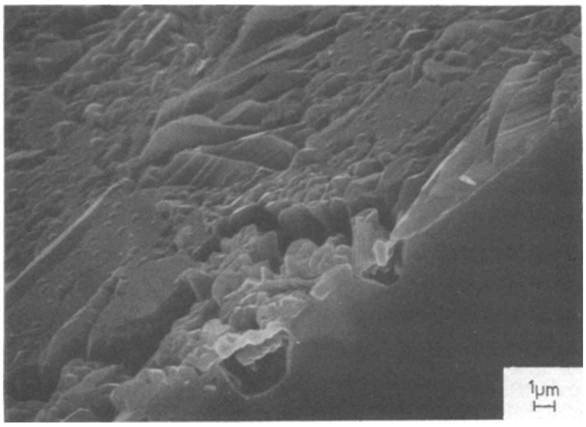

Figure 4 (1 0 0) contact surface, 1350° C, 65 h, static nitrogen. Top left is the surface and the lower right is the cross-section.

TABLE III Description of pores and inner products

	Static nitrogen		Flowing nitrogen	
	1350° C	1270° C	1350° C	1270° C
Pores	Max. size > 10 μm	1–2 μm	> 10 μm	1–2 μm
(1 1 1)	Flat bottom; base has no reaction product.	Flat bottom; reaction product within the around pores.		
(1 0 0)	Pyramidal; no reaction product on inner sides of pores.	Clean pores at reaction front appear pyramidal; most pores contain or are surrounded by reaction product and have irregular shape.		
Product	Weight loss		Possible weight gain	
(1 1 1)	Thick coarse-textured dense nitrides with large pores, in all 8 to 10 μm deep.	Thinner, finer textured nitrides, 3 to 4 μm deep.	Thick surface layer of dense nitrides, with large underlying pores, in all 6 to 12 μm deep.	More open, fine texture nitrides, 3 to 4 μm deep.
(1 0 0)	Thin dense nitrides 1 to 2 μm, deep, with large pores extending to 12 μm deep.	Thick fine-textured porous nitrides, 6 to 8 μm deep.	Thick surface layer of dense nitrides, with large underlying pores, in all 6 to 12 μm deep.	Thick fine textured porous nitrides 8 to 12 μm deep.

surface diffusion [4]) leading to fast growth of Si_3N_4 along the surface.

If argon is mixed with the nitrogen (1 : 1 by volume) some aspects of the above results are altered. The product covers only about 50% of the surface, indicating an insufficiency of nitrogen. There was no porosity or pitting of the surface, thus indicating that evaporation of silicon was slight; this could have been because its equilibrium vapour pressure had already been established rapidly and maintained throughout the experiment in the volume between the slices. In the presence of argon, the beta phase was formed almost exclusively, which may be due to active nitrogen, formed in the presence of argon [20]. Relatively large amounts of argon apparently overrule the influence of trace amounts of oxygen.

5.2.2. Nitridation with purest nitrogen

The textures of the product and pores formed under various experimental conditions incorporating pure nitrogen and specimens aligned as shown in Fig. 3, are summarized in Table III, which is a modification of a table published in [6]. Table III is compiled from a large number of micrographs, some of which have been published previously [6, 7]. The table refers primarily to inner product, although it is not always possible to determine exactly the boundary between inner and outer product. As discussed above, the presence of a nearby surface can influence the morphology of product and pores, particularily the outer product. Previous publications [6, 7] have not included detailed analysis of the outer product and an evaluation of "shadow" compared to "exposed" areas is included for the first time.

Pore size and shape are related to temperature of the reaction and the crystallographic orientation of the silicon slice. Larger pores form at higher temperature. The innermost pores that do not contain large amounts of product may have a well-defined orientation. When the orientation of the reacting silicon was (1 1 1), the pores were formed parallel to the surface, with flat bottoms. When the orientation was (1 0 0), the pores were triangular in cross-section, with one face parallel to the original surface and the others parallel to (1 1 1).

5.2.2.1. (1 1 1). (a) Static nitrogen, 1350° C. At 1350° C, the reaction with static nitrogen produces a dense surface product with underlying porosity that contains only a small amount of product on its inside surface. This experiment was performed before the importance of shadow and exposed regions was documented.

(b) Static nitrogen, 1270° C. Fig. 5 shows a (1 1 1) specimen reacted at 1270° C. The product is thinner, has a finer texture, and a pore size and depth that is smaller than that formed at a higher temperature. At 1270° C, silicon evaporates less rapidly and nitrogen adsorbs in greater quantity than at higher temperatures. Fig. 5 shows the microstructure formed in an exposed region, where there is a temperature gradient in the atmosphere. This gradient produces favourable conditions above the surface and, therefore, an abundance of needle-like outer product results. In a shadow region, Fig. 6, where there is no temperature gradient, there is no outer product although the inner product is similar to that formed on exposed surfaces, Fig. 5.

(c) Flowing nitrogen, 1350° C. At 1350° C, a dense layer of product forms, with a thickness varying

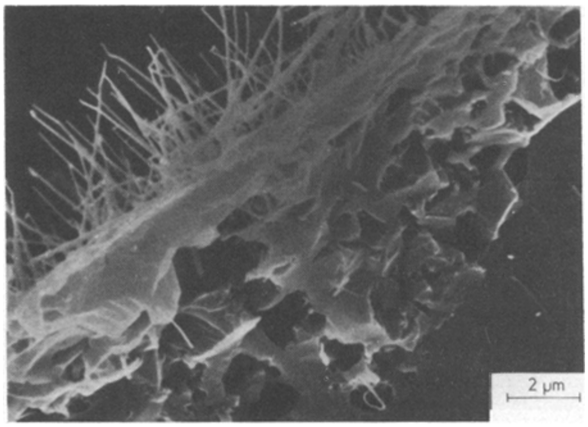

Figure 5 (1 1 1) exposed surface, 1270° C, 65 h, static nitrogen. Cross-section.

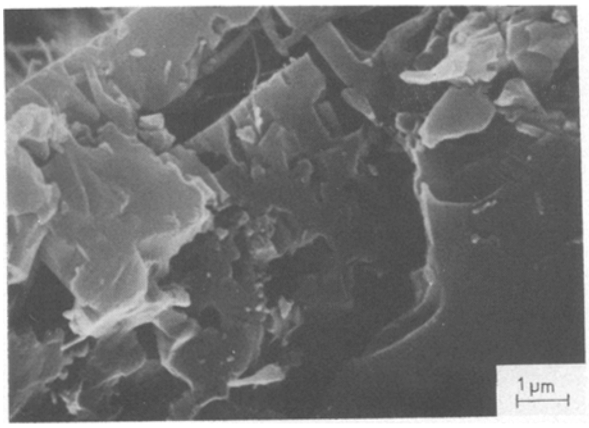

Figure 6 (1 1 1) shadow surface, 1270° C, 65 h, static nitrogen. Cross-section.

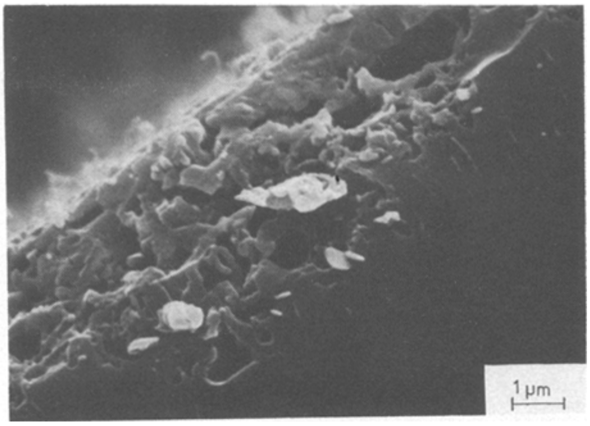

Figure 8 (1 1 1) 1270° C, 65 h, flowing nitrogen. Cross-section.

between 8 and 15 μm, Fig. 7. Product penetrates the first generation pores, which are flat bottomed and up to 10 μm across, but often the innermost pores do not contain product on their inner surface. The micrograph shown in Fig. 7 is of an exposed surface, where the atmospheric temperature gradient would be expected to lead to silicon adsorption to produce the observed needle-like outer product. A micrograph of a shadow region of the same specimen (Fig. 4 of [6]), published before the importance of the shadow region was realized, shows, as is expected according to our present thesis, no outer product. Flowing and static conditions appear to differ little in their effect on the structure of inner product; in both cases, X-ray analysis revealed both alpha and beta phase with (0 0 1) parallel to (1 1 1).

(d) Flowing nitrogen, 1270° C. At 1270° C, and in flowing nitrogen, the (1 1 1) slice has fine pores filled with product, Fig. 8. The main difference between this microstructure and that formed under static conditions is the relative lack of outer product and a dense surface layer. The former may be explained by assuming that the flow of the gas has reduced the temperature at the silicon surface below that necessary for reaction, and/or the flow has reduced the partial pressure of silicon as compared to static conditions.

5.2.2.2. (1 0 0). (a) Static nitrogen, 1350° C. The product formed at 1350° C shows a great difference between exposed and shadow regions. A micrograph of a shadow region has been published elsewhere (Fig. 6 of [6]). It shows only small amounts of inner and outer product; there is some triangular porosity with no product on the inner surface of the pore. In the shadow region, the temperature of the atmosphere is uniform leading to preferential growth along the surface. An exposed surface contains both outer and inner product. The product on the inside surface of the first generation pores is very similar to that obtained on the sandwich specimens of Fig. 4. It has sealed the surface and has only a little underlying porosity. The exposed surface allows silicon to evaporate into the region of lower temperature where it preferentially adsorbs on to the outer solid surfaces to form needle-like product.

X-ray analysis reveals that the product formed after 12 h is almost totally composed of alpha phase with (0 0 2) orientation parallel to the (1 0 0) silicon substrate. At 12 h, the surface is completely covered with product as was shown in Fig. 3 of [7]. By 48 h, the product contains a highly oriented beta phase with the (0 0 2) orientation parallel to the (1 0 0) substrate and, although the pores have not grown any larger, features that may be the beta phase (spikes about 2 μm long) have appeared in the microstructure; this feature is shown in Fig. 4b, [7], but the micrograph label is misleading as the reaction time was 48 h. The diffusion constants reported in Part 1 suggest that the slow growth of beta phase by diffusion of nitrogen through the Si_3N_4 structure would lead to 1 to 2 μm spikes after

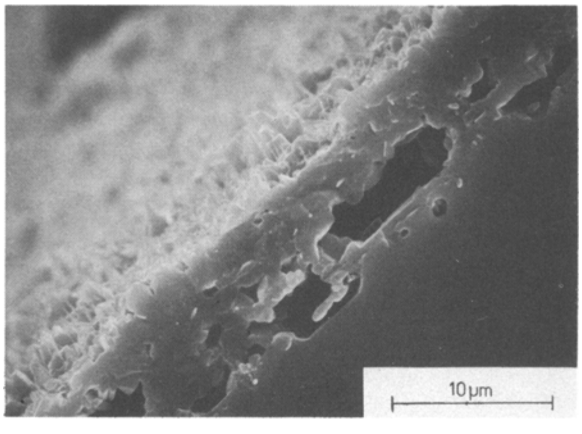

Figure 7 (1 1 1) exposed surface, 1350° C, 65 h, flowing nitrogen. Upper left is the surface and lower right is the cross section.

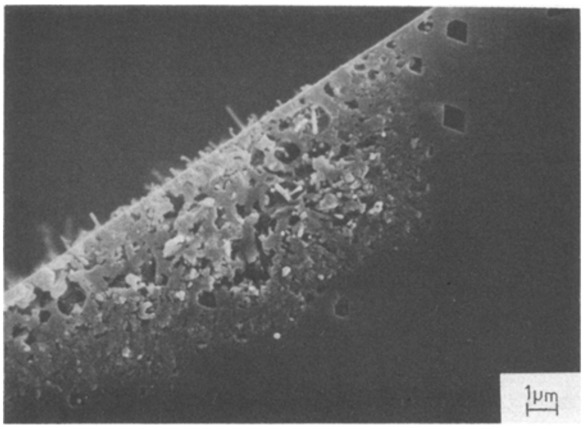

Figure 9 (1 0 0) 1270° C, 48 h, static nitrogen. Cross-section.

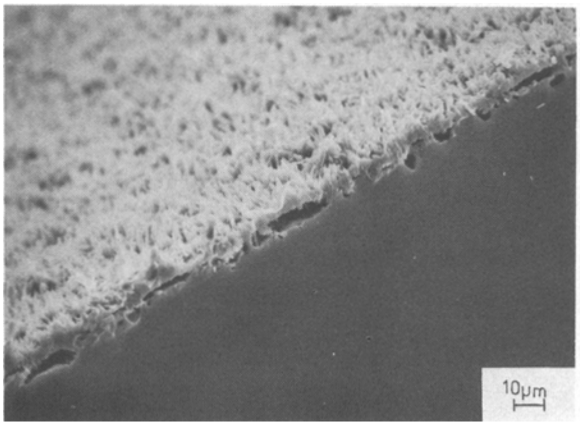

Figure 10 (1 0 0) 1350° C, 48 h, flowing nitrogen. Upper left is the surface and lower right is the cross-section.

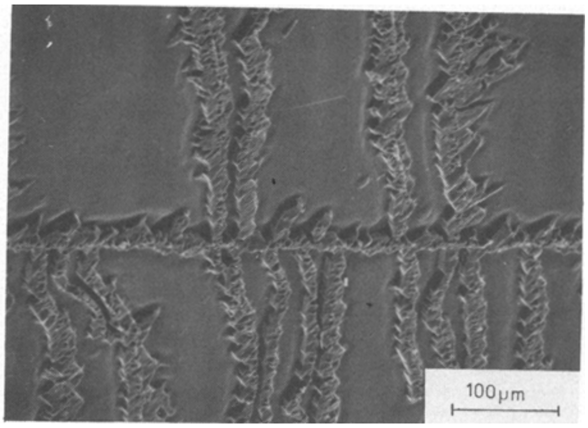

Figure 12 (1 1 1) exposed surface, 1350° C, 65 h, static argon/nitrogen 50/50. Looking down on the surface.

48 h of reaction. This supports the idea [1, 19] that, although the process is slow, growth of the beta phase by diffusion of nitrogen through the beta nitride structure becomes a viable mechanism if no faster growth mechanisms are available.

(b) Static nitrogen, 1270°. At 1270° C, and in a static atmosphere, a fine product, with no outer product, is formed, Fig. 9. This micrograph is from an early experiment, before the difference in shadow and exposed positions of the silicon slices had yet been noted; lack of outer product suggests that it was in a shadow region. Diamond-shaped innermost pores in this sample are often isolated within the silicon crystal; this suggests the possibility of pore formation by vacancy coalescence, as opposed to direct evaporation.

(c) Flowing nitrogen, 1350° C. Under flowing nitrogen conditions at 1350° C, both inner and outer product were formed as shown in Fig. 10. As discussed in a previous paper [6], product that formed on the inside surface of the pores of this specimen had the morphology indicative of the presence of a nearby surface (sandwich specimen), i.e. a thin layer along the silicon surface as in Fig. 4.

5.2.2.3. (1 1 0). Only a few (1 1 0) silicon specimens were nitrided and, unfortunately, almost all of them were reacted in the shadow region. Under these conditions, product rapidly formed along the surface and was composed largely of the alpha phase, Fig. 11. Little porosity and no outer product formed. Further experiments with (1 1 0) samples are necessary.

5.2.3. Gases added to nitrogen

One thesis of this paper is that gases added to nitrogen play important roles because: (1) they affect the thermal diffusion of the gas; (2) they set up a concentration gradient of reacting species near a hot surface; and/or (3) they influence the formation of active nitrogen. The first two effects influence the morphology of the products, and the third influences the kind of phase formed.

5.2.3.1. Argon. At 1350° C in a static 1 : 1 Ar : N_2 atmosphere, ribbons of product are produced, Fig. 12. The reaction has stopped, and it appears that nitrogen was not adsorbed in significant quantities on to the surface, as is expected at a high temperature. The paucity of pores indicates that there was no substantial evaporation of silicon to produce them, even though this was an exposed surface. For such a surface, a temperature gradient must be present in the adjacent atmosphere and, as argon is heavier than nitrogen, the thermal conductivity of this atmosphere would have been reduced, and the gradient increased from that which would exist with pure nitrogen. Argon is also heavier than silicon and this would tend to cause silicon to diffuse up the temperature gradient,

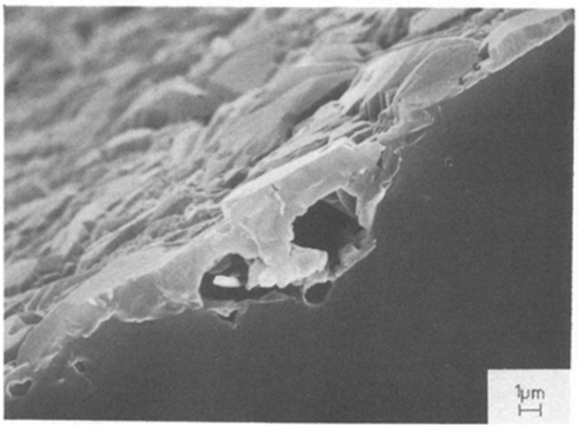

Figure 11 (1 1 0) shadow region, 1350° C, 48 h, static nitrogen. Upper left is the surface and lower right is the cross-section.

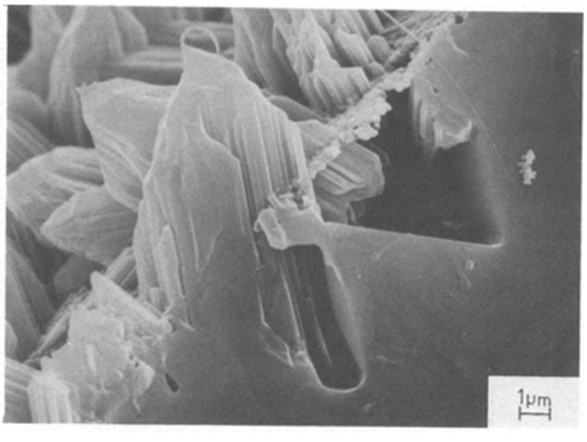

Figure 13 (1 0 0) exposed surface, 1270° C, 65 h, static argon/nitrogen 50/50. Cross-section.

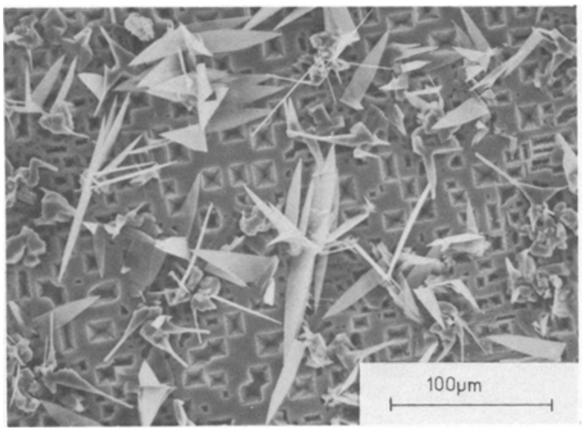

Figure 14 (1 0 0) shadow surface, 1270° C, 65 h, static argon/nitrogen 50/50. Looking down on the surface.

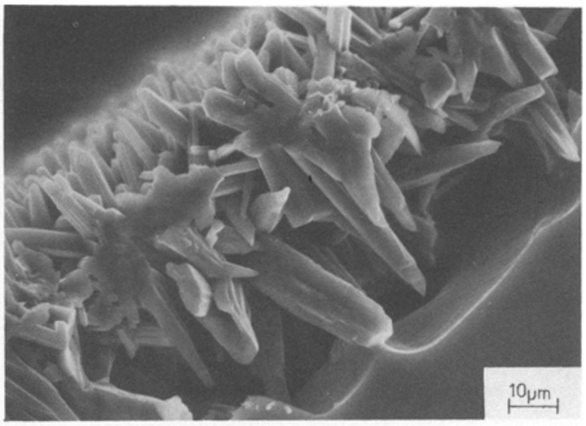

Figure 15 (1 0 0) exposed surface, 1350° C, 65 h, flowing helium/nitrogen 1/15. Cross-section.

which keeps silicon vapour nearer the solid surface, thereby both hindering silicon evaporation and encouraging lateral growth. X-ray analysis shows that the product is both alpha and beta, with the alpha oriented with (0 0 4) and (0 0 2), and the beta with (2 0 0), parallel to the (1 1 1) silicon surface. There is much more beta phase than is typical of early product in pure nitrogen; this can be attributed to the ability of argon to encourage the formation of active nitrogen [20].

In the presence of argon and at 1270° C, the product from an exposed area shows a dense inner and outer product, Fig. 13. At this temperature, nitrogen and silicon are both adsorbed in greater quantities than at the higher temperature. A temperature gradient encourages formation of outer product. The abundance of porosity implies that, in the presence of argon, silicon evaporates more easily at lower temperature than at high temperature. This is unexpected and contrary to observations made with pure nitrogen. The behaviour is perhaps due to a steep temperature gradient at the higher temperature which, in the presence of argon, provides a barrier to the escape of silicon, i.e. lighter silicon diffuses up the temperature gradient and towards the surface. This trap keeps silicon from evaporating. At a lower temperature, the temperature gradient is less steep resulting in less of a trap, i.e. less thermal segregation in the presence of argon. In the shadow region the density of the product is lower, and outer blades are common, Fig. 14. In this region the temperature gradient is reduced. Product does not appear to grow along the surface on silicon (1 0 0).

With flowing nitrogen, the product density was greater than under static conditions, consistent with more nitrogen being available for adsorption becuase it was continually being replenished. At 1350° C, beta phase with the (0 0 2) parallel to the (1 0 0) formed almost exclusively.

The above results are very similar to those for nitridation of the (1 1 0) silicon, except that the pores in the shadow region are long and thin, forming trenches.

5.2.3.2. N_2/He and N_2/H_2. Helium and hydrogen have almost identical influences on the thermal conductivity and, therefore, on thermal separation of the two gases [18]. They are both lighter than nitrogen and will therefore increase the thermal conductivity of the gas mixture. Results from helium in the atmosphere are shown in Fig. 15, and results from hydrogen in the atmosphere are shown in Fig. 16. Both micrographs show inner and outer product, both with thickness of several tens of micrometres, which is much thicker than any other result reported here. In the presence of a temperature gradient, a light gas like helium or hydrogen causes heavier silicon to diffuse down the temperature gradient and away from the surface, thereby encouraging evaporation.

In the presence of helium, which has been shown to encourage the formation of atomic hydrogen [21, 22], the beta phase was produced almost exclusively, an observation consistent with the idea that the beta phase is derived from active nitrogen [1]. On the other hand, in the presence of hydrogen, the alpha/beta ratio is increased substantially; this may be attributed to the ability of hydrogen to discourage the formation of active nitrogen (see [1] for discussion). In spite of the fact that atomic nitrogen is more reactive than molecular nitrogen, the product layer thicknesses appear to be similar. The supply of silicon to the reaction site, therefore, may be rate controlling.

5.2.4. Iron in the reacting system

The possibility that atomic nitrogen influences the type of reaction product was tested in the following

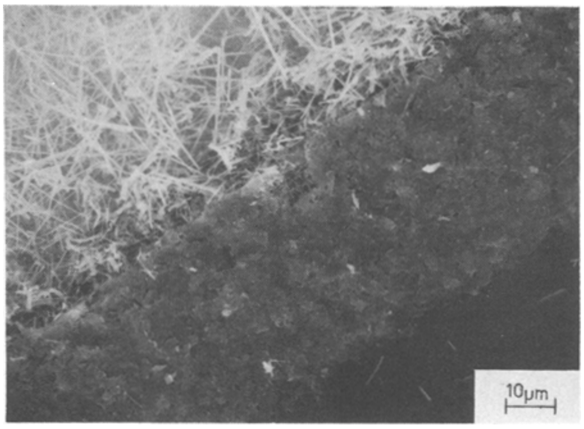

Figure 16 (1 1 1) exposed surface, 1350° C, 65 h, flowing hydrogen/nitrogen 1/9. Cross-section.

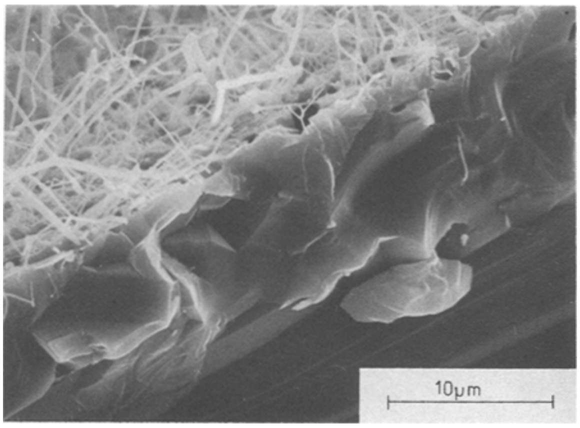

Figure 17 (1 0 0) exposed surface, 1350° C, 48 h, flowing nitrogen. Iron filings are located upstream but are not in contact with the specimen.

way. Hot iron is known to catalyse the formation of active nitrogen, especially if water is present [1]. Iron filings were placed in the reaction chamber, "upstream" from the silicon specimens. By removing the gettering system for water in the purification train for nitrogen, the concentration of water was increased to a few thousand p.p.m. The iron was kept out of contact with the silicon so that it would not encourage melting, a phenomenon that is known to influence the reaction [1]. At 1350° C, Fig. 17, the beta phase formed almost exclusively, and the shadow effect was particularly strong. Iron, therefore, must have an influence on the reaction through its influence on the nitrogen atmosphere. At 1270° C, the results were similar to those for pure dry nitrogen, and the effect of iron seems to have been small. Perhaps there is insufficient energy to produce active nitrogen. These results indicate that iron, in the presence of water, can influence the product without causing melting, and it further suggests that atomic nitrogen is an important factor.

5.3. General discussion

Neither the importance of a temperature gradient nor a concentration gradient of silicon vapour in the atmosphere around the nitriding surface have been considered in the past. Without taking gradients into account, it is impossible to rationalize the observed results. For example, if we consider just the effect of a given temperature or a given concentration of reactants, then shadow regions should have relatively high partial pressures of silicon that would result in outer product, and lower temperatures would always encourage adsorption and therefore encourage outer product. Neither of these results is observed. The formation of a needle-like outer product can be explained only by assuming that the crystal grows outward into an environment that is "supersaturated" with respect to adsorption of reactants on the surface where reaction takes place (i.e. the tip of the needle). Neither the actual temperature itself, nor the concentration alone, produces a consistent explanation.

6. Conclusion

This paper has suggested some possible reasons for the formation of some of the common microconstituents that form when solid silicon reacts with gaseous nitrogen. Experimental results at temperatures below the melting temperature of silicon are examined in the light of these reasons. Important points are:

1. A critical step in the formation of Si_3N_4 is the adsorption of nitrogen as suggested by Atkinson *et al.* [4]. High partial pressure and low temperature encourage this process.
2. Adsorbed silicon, either because of surface diffusion, or because of evaporation/re-condensation on to the reaction site, is important; for the latter case the conditions that encourage adsorption are low temperatures and high partial pressures of silicon.
3. The reaction takes place on a surface.
4. The morphology of the product depends upon the surface of the nuclei on which adsorption of the reactants is most likely. Usually silicon is in shortest supply. If it is an outer surface then needles will grow, otherwise a surface product will grow.
5. Outer-surface adsorption of silicon is more likely when a temperature gradient (decreasing with distance away from the surface) or concentration gradient (silicon increasing with distance away from the surface) is established. These conditions produce increased supersaturation (with respect to equilibrium adsorption on a surface) with increased distance away from the surface.
6. The most fundamental difference between the mechanisms that lead to the formation of the alpha and the beta phases is that the former results from reaction of silicon with molecular nitrogen, and the latter forms when silicon reaction with active nitrogen that may be atomic nitrogen.
7. The rate-controlling step during Stage II, at temperatures below the melting point of silicon, is the rate of supply of silicon to the reaction site. As a result, even though active (or possibly atomic) nitrogen is more reactive than molecular nitrogen, its presence does not influence the rate of reaction.
8. Inner product is at least 27% porous.

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