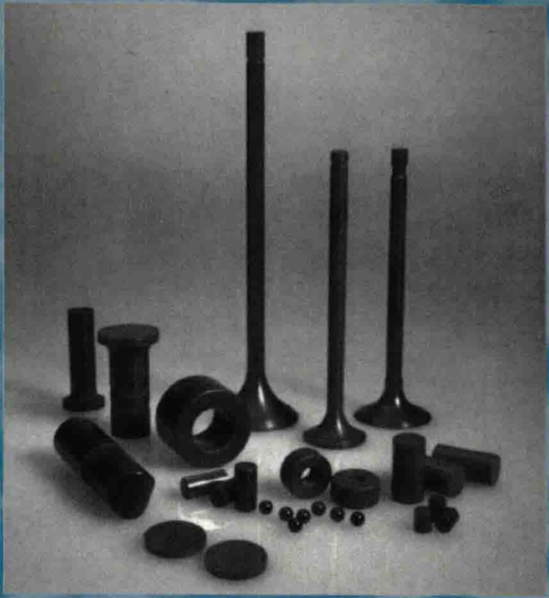
Formation of Silicon Nitride From the 19th to the 21st Century

A Comprehensive Summary and Guide to The World Literature

Second Edition - Revised and Updated



Raymond C. Sangster
Updated and revised by David J. Fisher

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The New In-Depth Reference for Fundamental Concepts and Phenomena
A Continually Expanding Encyclopedia for the New Millennium

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Aims and Scope

Materials are highly diverse, and yet many of the principles, phenomena and processes which are involved in preparing and forming alloys, ceramics, electronic materials, plastics, composites and porous solids are strikingly similar. The very rapid progress of the past two decades, which has transformed not only the silicon-based economy but also the global market, has understandably led to gaps in understanding among busy industrial and academic personnel alike. We are therefore very pleased to announce the publication of a new series of monographs, entitled *Materials Science Foundations*.

Each monograph is treating its chosen topic exhaustively, and seeks in particular to draw together the strands of current theory and industrial practice. The series has the reading level of a scientific review. Each monograph contains greater detail (theoretical, experimental, and - where applicable - industrial) than is usually to be found in an academic review. For example, in such reviews critically important equations are usually presented without further ado; even though their derivation may no longer be familiar or understandable to the reader. In the new series, all derivations which are necessary to a complete understanding of the topic are provided. Similar criteria are applied to the description of experimental details, and their relationship to the use of materials in the real world is carefully pointed out.

New monographs will be published annually and, with the passage of time, the collection will grow to become a library of lasting value: a basic reference source covering all of the fundamental concepts and phenomena which are the very foundation of materials science research and technology.

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The table of contents of each volume is available on TTP's Web Server at: http://www.ttp.net/1422-3597.html

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We are always searching for new authors and ideas for this series, and would be pleased to receive your proposal for a future title. To discuss further details, please contact Thomas Wohlbier, Editorial Director TTP, 105 Springdale Lane, Millersville, PA 17551, U.S.A., Fax: +1 872 4327, email: t.wohlbier@ttp.net.
We are looking forward to hearing from you.

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Formation of Silicon Nitride From the 19th to the 21st Century

A Comprehensive Summary and Guide to The World Literature

Second Edition
Revised and Updated

2005

I dedicate this publication to the thousands of authors and their supporters who have made this work possible, through many years of trials and triumphs, those still with us and the pioneers who are not. Think on them as you consult the lists of their works.

I dedicate this work to my wife, Kathie Bryant Sangster, for whom (all of our married life) this publication has been a driving force in our life together, and without whose firm participation and steadfast support it could never have come to fruition. My combining home and workplace I suspect has been a challenge for her that I can only now truly come to appreciate.

I dedicate this publication to Friedrich Schröder, Fred Fenter, and Thomas Wohlbier, without whose faith, understanding, and support it would never have seen the light of day.

2015

It was a great privilege to be invited to update Dr Sangster's monumental reference work on this important material, and I hope that I have succeeded in keeping to the aim and spirit of the original. David J.Fisher

2005 PREFACE

This book summarizes and integrates what is recorded in the world literature from 1857 through mid-2004 as being known about the formation of silicon nitride – Si_3N_4 – and its close relatives. "Formation" is interpreted very broadly, from traces in meteorites to large-scale manufacturing. Some 4242 source documents are cited, plus Internet sources and Gmelin Handbook volumes. This book effectively completes the Gmelin Handbook Silicon Nitride series, but is free-standing, complete within itself, with its own style, organization and scope.

The literature search was based on scanning Chemical Abstracts indices, from vol 1 of 1907 into vol. 140 in April 2004. Internet-based journal and US patent searches continued into August 2004 and later (yielding two 2005 publication dates). Review of reference lists led to the earliest and many other important documents. The final, selective, search decisions were often based on direct study of the documents (not just abstracts), the standard policy up into 1997. The book also includes a few personal comments about my own unpublished observations.

I handled similar volumes while working within the Gmelin Institute 1980-85, before leaving to pursue some international consulting opportunities. In 1989 I resumed working for Gmelin, as a contract author dealing with silicon nitride, during evenings in the library of the University of Petroleum and Minerals in Saudi Arabia, where I was then a consultant. My initial focus was on its preparation. On my way home, my library work continued at the Gmelin Institute in Germany, and in Maryland, Missouri and Kansas in the USA. Thus writing this book can truly be called both a tricontinental and a 15-year project for me – with time off getting other things done, such as getting married in 1993, travel, acquiring seven grandchildren, and completion of two Gmelin Handbook volumes on the reaction chemistry of silicon nitride, published in 1995.

This book is based on manuscripts still in preparation when the Gmelin series was discontinued in 1998, and on study of an additional seven years of literature (an almost 50% addition). It continues the Gmelin tradition of analysis, interpretation and integration, not just compilation and tabulation. Key information from related Gmelin volumes has been incorporated. The scientific scope has been broadened to include summary descriptions of peripheral technical areas, the economic scope summaries of the applications of Si_3N_4 and its commercial markets.

I thank Ceradyne, Inc., for its assistance in preparing the two "Illustrative Applications" pages (212, 356), and the several other companies I contacted. I thank the many institutions and librarians whose libraries I have used, most especially my "home libraries" at the California Polytechnic State University at San Luis Obispo, Stanford University, and the University of California at Berkeley; and the library staff of the Gmelin Institute. I thank Dr. Friedrich Schröder, my Gmelin chief editor and valued friend, for offering me the opportunity to work on this project.

I must also stress the fact that my wife, Kathie Bryant Sangster, has aided me immeasurably by many direct contributions to this work. We worked side-by-side for many days in libraries. She has taught me most everything I know about computer word processing. And she was responsible for preparing most of the figures in this book, aided by her son, David L.Christensen, Jr.

Templeton, CA, USA, March, 2005 Raymond C. Sangster

2015 PREFACE

This revised edition of the book continues the coverage of the world literature from 2005 to late-2014 concerning the formation of silicon nitride, Si_3N_4, SiN_x and closely-related materials. As there is obviously little new to be said about the formation of silicon nitride itself, most means of synthesis having already been identified, the accent of the new material is largely on refinements of existing techniques and on the formation of new types of product; especially those of nanoscale-type. It is ironic that, just as Dr Sangster had to report the 1998 demise of the venerable Gmelin series in 2005, the present writer has to mention the 2010 demise of the equally venerable Chemical Abstracts series which was so integral to the preparation of Dr Sangster's original manuscript. Searching of the relevant scientific literature of the past decade was performed by using the last years of Chemical Abstracts plus the electronic data-banks which undoubtedly led to the disappearance of that information source. Revision of the format itself has largely been confined to cosmetic changes, and certainly no attempt was made to remove any of Dr Sangster's now dated comments or his delightfully idiosnycratic turns of phrase.

Cardiff, UK, January 2015 David J.Fisher

* * * * * * *

NOTE!: Although every effort has been made to ensure that this handbook covers its given subject comprehensively, thoroughly, and authoritatively, its main aim is to cover the whole range of work on this material rather than attempting to assess the data and provide standard reference values. The writer cannot guarantee the accuracy of specific measurements found in the literature, and only rarely reports the statistical uncertainties in the data. He has also probably, and inevitably, created his own errors of both omission and commission. On the other hand, this project has given him a comprehensive understanding of the totality of its subject matter, reflected in this text, and he feels that this cannot fail to be communicated to the reader. That it, this work is much more than just the sum of its parts: the subject-matter has been integrated and interpreted; not just compiled.

Like all handbooks destined to become standard reference works, there is always the risk that the most recent research may render incorrect and obsolete, at least to some extent, many of the thermodynamic calculations in the latest edition. Also, it is possible that very basic questions connected with the relationships of the long-established crystalline forms, namely α- and ß-Si_3N_4, may be rendered either moot - or complicated even further - by the fact that ß-Si_3N_4 may really exist in two modifications; with only very slight energetic differences between the α- and two ß- silicon nitride species. Such very basic uncertainties suggest that a few words of caution are needed: use this handbook confidently to get a broad and basic understanding of what has been reported in print concerning the subjects covered. Do not use it blindly to design multi-million-dollar plants or projects without personally consulting the primary literature and adequately resolving any relevant uncertainties!

CONTENTS

* * * * * * *

Parts B-O each begin with their own tables of contents, which for each Chapter include section and subsection headings (listing all Si-N reactants and reaction promoters described in the text), plus all Figures and numbered (major) Tables. A Reference list concludes each Chapter.

* * * * * * *

The "Í" is used instead of "I" for the Part between H and J, to forestall misreading I as 1.

Initializations Frequently Used in This Book

CVD: **C**hemical **V**apor **D**eposition
APCVD: **A**tomospheric **P**ressure **C**hemical **V**apor **D**eposition
LPCVD: **L**ow **P**ressure **C**hemical **V**apor **D**eposition
PECVD: **P**lasma-**E**nhanced **C**hemical **V**apor **D**eposition
ECR: **E**lectron **C**yclotron **R**esonance, as in ECR-PECVD
ALD: **A**tomic **L**ayer **D**eposition
SSN **S**intered **S**ilicon **N**itride
RBSN: **R**eaction **B**onded **S**ilicon **N**itride
SRBSN: **S**intered **R**eaction **B**onded **S**ilicon **N**itride
SHS: **S**elf-propagating **H**igh-temperature **S**ynthesis
VLS: **V**apor-**L**iquid-**S**olid
VLSI: **V**ery **L**arge **S**cale **I**ntegration

@5nm: Si_3N_4 thin film technology potentially of critical importance in Si microelectronics. Note that my use of this label may at times be naive (the industry does have its proprietary knowledge), and non-use an oversight.

P = pressure, **T** = Temperature and other commonly used technical symbols and abbreviations are employed, usually in circumstances such that context or the adjacent text provide clues for those not familiar with the fields involved. *Ad hoc* subscripts are often appended, e.g., as in T_{proc} and T_{react} for the process (control) temperature and the actual exothermic reaction temperature.

ΔE_a = activation energy of a reaction or process

The format "[something]" is used extensively to mean "the amount of something".

When an official (NIST or Gmelin) conversion factor is available, non-SI quantities (e.g., sccm) are converted into accepted SI units (e.g., mL/min, with standard conditions of T and P implied).
Other non-SI units are used as found in the literature.

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Part A. In the Beginning

The Basic Facts

The elements Si, N, O, C and H have strong chemical affinities for each other. In the proper circumstances, Si-N bonding will occur in almost any Si-N-(O/C/H) and many related reaction systems. But Si-O and Si-C are formidable competitors for Si-N. The most favored Si-N compound is the stoichiometric Si_3N_4. It comes in three common varieties: the amorphous a-Si_3N_4 and the crystalline α-Si_3N_4 and β-Si_3N_4. How they interrelate and how you find them and (overwhelmingly) how you make them, and how they sometimes just happen to form, is the subject of this book, with due attention paid to closely related matters.

Chapter A-1. From the Cosmic to the Mundane

A general interest scientific article entitled "Stardust Memories" begins with paraphrase from William Blake: "*To see a World in a Grain of Sand, And a Heaven in a ...* Meteorite ...." For the last decade or so "cosmochemists" have been extracting from meteorites some extraordinary crystalline dust grains, some of which have distinctive isotopic compositions which indicate that they cannot be of solar origin and that they often *must* have been made by *stars that died before ours was born.* Diamond is the most common stardust species, but others found include SiC, graphite, Al_2O_3, trace amounts of carbides of Ti, Zr and Mo ... and silicon nitride, Si_3N_4 [SZP01].

The earliest known report concerning a synthetic silicon nitride dates from 1857 [DEV09]. There was immediate speculation that, during the earth's formation, Si reacted with N_2 to form Si_3N_4, and that hot Si_3N_4 reacted with water to form NH_3, leading to introduction of nitrogen into organic compounds, enabling terrestrial life [RIL10]. The some 55 papers and patents on Si nitride appearing through 1949 dealt mostly with fixation of atmospheric nitrogen.

The "modern" era of study of silicon nitride began with 6 publications in 1952, 34 by 1956, 101 by 1961, or ~10 per year. *Yearly* rates since 1961 are, for Chemical Abstracts and US Patents, (na = not available; data are incomplete for 2004):

Year:	62-6	67-71	72-6	77-81	82-6	87-91	92-96	'97	'98	'99	2000	'01	'02	'03
CA:	37	111	293	570	1330	2200	2770	3740	3480	4080	4460	4970	4960	4260
USP:	-	na	na	32	65	109	141	175	211	309	369	442	394	369

Some 70,000 abstracts have been indexed by CA under the heading "silicon nitride", and some 4,280 abstracts of US patents issued 1976-2003. "One need only consult *Chemical Abstracts* to realize the vastness of the literature .... More single volumes of the Gmelin handbook have been devoted to Si_3N_4 than to any other single compound" [OHA02]. – When the first Gmelin Si-N volume appeared in 1987, C.A.S. had published some 11,800 abstracts related to Si_3N_4. Another 11,000 appeared by 1991, the year of the first Gmelin Si_3N_4 volume. Some 43,600 more abstracts were published 1992-2003, nearly twice as many as in the previous 85 years ....
This was the state of affairs as summarized by Dr Sangster. The present writer would be derelict in his duty if he did not update the relevant figures, see page 141. Dr Sangster's original statement still applies ... in spades: "There is thus a very mundane question that faces anyone interested in silicon nitride: How can I possibly master and keep up with this flood of knowledge?" ... Read on.

You hold in your hands a powerful answer to this question.
This book is a key to what was has been learned over the past 150 years about how silicon nitride comes to be: in nature, the laboratory or the factory, in many reaction systems; plus how it is used in ceramics, electronic films, optical coatings and many other ways, along with an introduction to closely related substances. It can aid the researcher in designing new projects, the supervisor in briefing new employees, the salesman in working with new customers., the patent attorney in assessing patents, and the professor in designing graduate course assignments.
Often, the fundamental formation chemistry behind current papers and patents has long since been worked out and is summarized here. The sources of this knowledge are cited, so that you can trace your way selectively back into the literature to discover more fully what has been learned in areas of specific interest. The literature coverage is broader than that of either Chemical Abstracts or the Gmelin Handbook, and extends into mid-2004. You begin to be on your own only for knowledge published after late 2003, for which on-line data bases can provide ready access. And the Gmelin Handbook (which ceased publishing in 1998) covers the literature on *all* other aspects of the subject of silicon nitride up to literature cut-off dates ranging from 1987 to1996, with 1992 for the most relevant volumes.

On the other hand: No work like this can ever be completely thorough, unbiased and accurate. If it were not selective, it would be useless to you. And selection inevitably involves some errors. You *must* do supplementary reviews of the earlier literature in areas of major importance to you.

Lastly, no matter how well you think you know the literature, browsing through the chapters here that are outside your own special areas of interest may well uncover information that you had no idea existed, providing new insights for your own work For instance, the reports on the high pressure γ-Si_3N_4 (Ch. B-4) reflect no awareness of reports in 1959 and 1983 of possible cubic-Si_3N_4 formation in Fe-Si-N systems (Ch. O-2), or of the 1983/89 theoretical work on N-ion implantation of Si wafers that demanded the existence of a high-density form of Si_3N_4 (Ch. D-4). uncovering just one new fact significant for you could far more than pay for the cost of this book.
Happy browsing!

And you might keep in mind that when Professor Henry Taube was awarded the Nobel Prize in Chemistry in 1983, he publicly credited as the source of the inspiration for the line of research that led to the Prize, the information he gathered while browsing through the Gmelin Handbook while designing a new course in advanced inorganic chemistry (which in turn inspired this writer).

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[RIL10] Riley, F.L. (J. Amer. Ceram. Soc. **83** [2000] 245/65).
[SOR21] Sorrell, C.C. (J. Austral. Ceram. Soc. **18** No. 2 [1982] 22/34).
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Chapter A-2. Book Purpose and Design, Writing Conventions

This book aims to be a concise and systematic summary of all knowledge ever reported in the world-wide technical literature on the formation of silicon nitride and a guide for its easy retrieval. *Formation* includes preparation and manufacture and unplanned or minor occurrence in various material systems. The book is organized primarily around the chemical reaction systems involved. It is neither a conventional literature review nor a compendium of standard reference data nor a belatedly published Gmelin Handbook "Supplement" volume. *It is a synthesis of and a guide to the totality of what has been said in print to be known about the formation of Silicon Nitride.*

The literature search supporting it is substantially complete through year 2003 and quite thorough into mid-2004. This book cites some 4130 sources. The data reported and documents cited are deemed to be of specific value for its purpose. Documents that do not significantly *enlarge* the scientific and engineering knowledge of Si_3N_4 are usually disregarded. The literature covered ranges from cosmology and basic theory to patents and new product announcements. Review papers cited tend to be the most recent and comprehensive or the oldest and most basic.

Both the name "silicon nitride" and the formula Si_3N_4 have long been loosely used in the literature to describe a vast range of materials. There is also a strong tendency to cite Si:N ratios close to 3:4 as evidence of the presence of stoichiometric Si_3N_4, ignoring the(possible or known) presence of major amounts of H, O, and/or C, in particular. Perpetual care is needed in ascertaining the compositions of the materials being discussed in a given work before drawing any conclusions about its relevancy to the compound Si_3N_4. Here, primary coverage is limited to phases or bulk materials within flexible limits of around ±10at% or wt% deviation from the ideal Si_3N_4 composition, whether due to nonstoichiometry, solid solution formation, surface contamination, or impurity phases. Use of some such limits is a practical necessity. This general range seems appropriate for allowing focus on the compound Si_3N_4 while acknowledging the inevitability of imperfections and impurities and solid solution formation. Exceptions are specifically made for pioneering studies giving products ascribed improper formulas in circumstances where it was not then really possible to know what was proper, or works closely related to and giving insight regarding significant Si_3N_4 preparation methods.

Topics intimately related to Si_3N_4 formation, such as thermodynamic and diffusion properties, that were previously covered in Gmelin Handbook volumes are also covered here, with cross-reference to the Handbook for data not currently relevant. Some tangential fields, such as Si_3N_4 solid solution formation and preparation of densified Si_3N_4 ceramics, are covered here in a summary fashion, with citation of relevant Gmelin Handbook volumes and recent major papers, review articles and books. Others, such as the amorphous SiN_x and SiN_xH_y thin films outside the ca. ±10% tolerance range, are handled primarily by reference to Gmelin Handbook volumes.

The master table of Contents allows ready location of reactant systems based on the Si-precursors involved and major N-precursors. Contents tables at the beginning of the Parts provide much more detail. The Index at the end of the volume allows systematic location of many minor reactants plus reaction systems and types of end product. The flag "**@5nm**" is used in the text and Contents (and is indexed) to draw attention to those reaction systems relevant to formation of the ~≤ 5nm thick Si_3N_4 films that appear to be of critical importance in allowing semiconductor microelectronic device technology to reach its ultimate atomic-scale limits.

The most basic organizational principle used is that of presenting the simplest and/or most fundamental reactions or topical areas first, with complex or derived topics following. Cross-references are used to link different portions of this volume. Some overlap of coverage is employed to allow individual topical sections to be substantially complete and self-contained.

The literature considered was derived primarily from *Chemical Abstracts* and the US Patent Office, and secondarily from references cited in the more significant papers. Up into 1997 a determined effort was made to review every interesting document and to rely on abstracts or secondary sources alone only when necessary. Recently much more reliance has been placed on CA and secondary sources. Whenever information is taken only from any secondary source, the original source is always cited, followed by "from." the secondary source. A CA reference may be appended after a semicolon and without the "from", when doing so is believed useful. Two or more documents are cited together under one reference number only when they are functionally duplicates, e.g., an original paper and its English translation. "See also" documents are generally those that can help an interested user develop a fuller picture of the status of a specific technical area than that given by the primary references alone. "Cf." citations tend to merely strengthen that picture, and often will not provide any new insights. On occasion I will record undocumented personal insights stimulated by this writing project or from past experience.

Little is said in the text about *who* did what or when: the reference lists must usually be consulted for such purposes. Historical aspects are covered briefly in introductions or by parenthetical citing of years in the text. I have sought to acknowledge the initial authors and papers reporting significant new developments. Assessing the chemical/ceramic data reported here is often complicated by the fact that many papers have been written by authors who are not specialists in the materials sciences, or who have suffered from translation errors, or are not writing in their native languages, or are writing for patent purposes. "Creative reading" may be needed to uncover very significant information.

Often little is said regarding the nature of the underlying raw empirical observations and instrumental methods. In reporting Si_3N_4 syntheses, the use of normal procedures and precautions is usually just assumed, e.g., etching Si wafers to remove surface oxide films, or of protective atmospheres, or readily available high vacuum systems. Such essential background factors are reported here only in exceptional circumstances. Other methodology is reported only in novel and exceptional circumstances. In other words, when normal, well-established methods are used to obtain a particular type of data, only the data are reported. Here, what was done and how, are mentioned only as deemed necessary for evaluation or understanding of what was learned.

No systematic attempt has been made to judge the relative validity of the reported results, except to omit obviously unsound data and marginal papers, e.g., those involving grossly impure samples or early instrumentation inadequacies. Borderline cases may be introduced by such phrases as "It is said that ...". Contradictory results are often reported just as they are found in the literature. Speculative interpretations or explanations of empirical observations are normally omitted, only solidly based models and theories described. Reporting contradictory observations, uncluttered by the guesses in the literature, may stimulate a reader of this volume to develop a powerful theory. Or may stimulate experiments that can resolve the apparent contradictions. One goal of this work is to stimulate new research, by simply presenting – *what has been said to be known.*