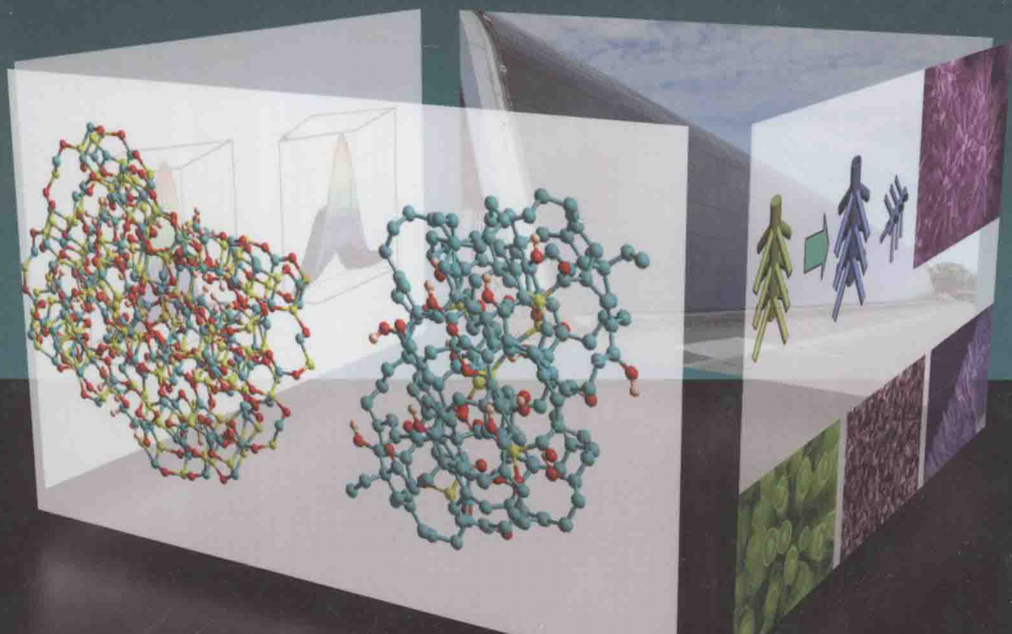
Handbook of
Nanostructured Thin Films and Coatings

Nanostructured Thin Films and Coatings

Mechanical Properties



Edited by

Sam Zhang

CRC Press
Taylor & Francis Group

Handbook of
Nanostructured Thin Films and Coatings

Nanostructured
Thin Films and Coatings

Mechanical Properties

Edited by
Sam Zhang

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

International Standard Book Number: 978-1-4200-9402-2 (Hardback)

Visit the Taylor & Francis Web site at
http://www.taylorandfrancis.com

and the CRC Press Web site at
http://www.crcpress.com

Nanostructured
Thin Films and Coatings

Preface

The twenty-first century is said to be the century of nanotechnologies. In a way, it is. The development of science and technology has come to a stage where "microscopic" is no longer enough to properly describe or depict a scientific phenomenon or a technological process. With the advance of nanoscience and nanotechnology, the world technological landscape changes not only affect the way scientists do research, technologists carry out development, and engineers manufacture products, but also the way ordinary people go about their daily life, through, for instance, nanomedicine, cell phones, controlled drug delivery, no-pain operations, solar cell–powered gadgets, etc. Thin films and coatings play a very important and indispensable role in all of these. This three-volume book set aims to capture the development in the films and coatings area in relation to nanoscience and nanotechnology so as to provide a timely handbook series for researchers to refer to and for newcomers to learn from, and thus contribute to the advancement of the technology.

The three-volume book set, *Handbook of Nanostructured Thin Films and Coatings*, has 25 chapters where 11 chapters in volume 1 concentrate on the mechanical properties (hardness, toughness, adhesion, etc.) of thin films and coatings, including processing, properties, and performance, as well as a detailed analysis of theories and size effect, etc., as listed here: Chapter 1, The Fundamentals of Hard and Superhard Nanocomposites and Heterostructures; Chapter 2, Determination of Hardness and Modulus of Thin Films; Chapter 3, Fracture Toughness and Interfacial Adhesion Strength of Thin Films: Indentation and Scratch Experiments and Analysis; Chapter 4, Toughness and Toughening of Hard Nanocomposite Coatings; Chapter 5, Processing and Mechanical Properties of Hybrid Sol-Gel- Derived Nanocomposite Coatings; Chapter 6, Using Nanomechanics to Optimize Coatings for Cutting Tools; Chapter 7, Electrolytic Deposition of Nanocomposite Coatings: Processing, Properties, and Applications; Chapter 8, Diamond Coatings: The Industrial Perspective; Chapter 9, Amorphous Carbon Coatings; Chapter 10, Transition Metal Nitride–Based Nanolayered Multilayer Coatings and Nanocomposite Coatings as Novel Superhard Materials; and Chapter 11, Plasma Polymer Films: From Nanoscale Synthesis to Macroscale Functionality.

Volume 2 contains eight chapters focusing on functional properties, i.e., optical, electronic, and electrical properties, and the related devices and applications: Chapter 1, Large-Scale Fabrication of Functional Thin Films with Nanoarchitecture via Chemical Routes; Chapter 2, Fabrication and Characterization of SiC Nanostructured/Nanocomposite Films; Chapter 3, Low-Dimensional Nanocomposite Fabrication and its Applications; Chapter 4, Optical and Optoelectronic Properties of Silicon Nanocrystals Embedded in SiO_2 Matrix; Chapter 5, Electrical Properties of Silicon Nanocrystals Embedded in Amorphous SiO_2 Films; Chapter 6, Properties and Applications of Sol-Gel-Derived Nanostructured Thin Films: Optical Aspects; Chapter 7, Controllably Micro/Nanostructured Films and Devices; and Chapter 8, Thin Film Shape Memory Alloy for Microsystem Applications.

Volume 3 focuses on organic nanostructured thin-film devices and coatings for clean energy with six chapters discussing the processing and properties of organic thin films, devices, and coatings for clean energy applications: Chapter 1, Thin Film Solar Cells Based on the Use of Polycrystalline Thin Film Materials; Chapter 2, Anodized Titania Nanotube Array and its Application in Dye-Sensitized Solar Cells; Chapter 3, Progress and Challenges of Photovoltaic Applications of Silicon Nanocrystalline Materials; Chapter 4, Semiconductive Nanocomposite Films for Clean Environment; Chapter 5, Thin Coating Technologies and Applications in High-Temperature Solid Oxide Fuel Cells; and Chapter 6, Nanoscale Organic Molecular Thin Films for Information Memory Applications.

A striking feature of these books is that both novice and experts have been considered while they were written: the chapters are written in such a way that for newcomers in the relevant field, the handbooks would serve as an introduction and a stepping stone to enter the field with least confusion, while for the experts, the handbooks would provide up-to-date information through the figures, tables, and images that could assist their research. I sincerely hope this aim is achieved.

The chapter authors come from all over the globe: Belgium, China, the Czech Republic, Egypt, Germany, India, Korea, Singapore, Taiwan, the Netherlands, the United Kingdom, and the United States. Being top researchers at the forefront of their relevant research fields, naturally, all the contributors are very busy. As editor, I am very grateful that they all made special efforts to ensure timely response and progress of their respective chapters. I am extremely indebted to many people who accepted my request and acted as reviewers for all the chapters—as the nature of the writing is to cater to both novice and experts, the chapters are inevitably lengthy. To ensure the highest quality of the chapters, more than 50 reviewers (at least two per chapter) painstakingly went through all the chapters and came out with sincere and frank criticism and suggestions that helped make the chapters complete. Though I am not able to list all the names, I would like to take this opportunity to say a big thank you to all of them. Last but not least, I would like to convey my gratitude to many CRC Press staff, especially Allison Shatkin and Jennifer Ahringer at Taylor & Francis Group, for their invaluable assistance rendered to me throughout the entire endeavor that made the smooth publication of the handbook set a reality.

Sam Zhang
Singapore

Editor

Sam Zhang Shanyong, better known as Sam Zhang, received his BEng in materials in 1982 from Northeastern University (Shenyang, China), his MEng in materials in 1984 from the Central Iron and Steel Research Institute (Beijing, China), and his PhD in ceramics in 1991 from the University of Wisconsin-Madison (Madison, Wisconsin). Since 2006, he has been a full professor at the School of Mechanical and Aerospace Engineering, Nanyang Technological University (Singapore).

Professor Zhang serves as editor in chief for *Nanoscience and Nanotechnology Letters* (United States) and as principal editor for the *Journal of Materials Research* (United States), among other editorial commitments for international journals. He has been involved in the fields of processing and characterization of thin films and coatings for the past 20 years, his interests ranging from hard coatings to biological coatings and from electronic thin films to energy films and coatings. He has authored/coauthored more than 200 peer-reviewed international journal articles, 14 book chapters, and guest-edited 9 journal volumes in *Surface and Coatings Technology* and *Thin Solid Films*. Including this handbook, he has authored and/or edited 6 books so far: *CRC Handbook of Nanocomposite Films and Coatings*: Vol. 1, *Nanocomposite Films and Coatings*: *Mechanical Properties*; Vol. 2, *Nanocomposite Films and Coatings*: *Functional Properties*; Vol. 3, *Organic Nanostructured Film Devices and Coatings for Clean Energy*, and *Materials Characterization Techniques* (Sam Zhang, Lin Li, Ashok Kumar, published by CRC Press/Taylor & Francis Group, 2008); *Nanocomposite Films and Coatings—Processing, Properties and Performance* (edited by Sam Zhang and Nasar Ali, Published by Imperial College Press, U.K., 2007), and *CRC Handbook of Biological and Biomedical Coatings* (scheduled for a 2010 publication by CRC Press/Taylor & Francis Group).

Professor Zhang is a fellow at the Institute of Materials, Minerals and Mining (U.K.), an honorary professor at the Institute of Solid State Physics, Chinese Academy of Sciences, and a guest professor at Zhejiang University and at Harbin Institute of Technology. He was featured in the first edition of *Who's Who in Engineering Singapore* (2007), and featured in the 26th and 27th editions of *Who's Who in the World* (2009 and 2010). Since 1998, he has been frequently invited to present plenary keynote lectures at international conferences including in Japan, the United States, France, Spain, Germany, China, Portugal, New Zealand, and Russia. He is also frequently invited by industries and universities to conduct short courses and workshops in Singapore, Malaysia, Portugal, the United States, and China.

Professor Zhang has been actively involved in organizing international conferences: 10 conferences as chairman, 12 conferences as member of the organizing committee, and 6 conferences as member of the scientific committee. The Thin Films conference series (The International Conference on Technological Advances of Thin Films & Surface Coatings), initiated and, since, chaired by Professor Zhang, has grown from 70 members in 2002 at the time of its inauguration to 800 in 2008. It has now become a biannual feature at Singapore.

Professor Zhang served as a consultant to a city government in China and to industrial organizations in China and Singapore. He also served in numerous research evaluation/advisory panels in Singapore, Israel, Estonia, China, Brunei, and Japan. Details of Professor Zhang's research and publications are easily accessible at his personal Web site: http://www.ntu.edu.sg/home/msyzhang.

Contributors

Alsayed Abdel Aal
Surface Protection and Corrosion Control Lab
Central Metallurgical Research and Development Institute
Cairo, Egypt

Ali S. Argon
Department of Mechanical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts

Harish C. Barshilia
Surface Engineering Division
National Aerospace Laboratories (CSIR)
Bangalore, India

B.D. Beake
Micro Materials Ltd.
Wrexham, United Kingdom

S.J. Bull
School of Chemical Engineering and Advanced Materials
University of Newcastle
Newcastle upon Tyne, United Kingdom

Vladimir Cech
Institute of Materials Chemistry
Brno University of Technology
Brno, Czech Republic

Lei Chen
Department of Mechanical Engineering
National University of Singapore
Singapore, Singapore

B. Deepthi
Surface Engineering Division
National Aerospace Laboratories (CSIR)
Bangalore, India

G.S. Fox-Rabinovich
Department of Mechanical Engineering
McMaster University
Hamilton, Ontario, Canada

S.R. Goodes
Micro Materials Ltd.
Wrexham, United Kingdom

Haiyan Jiang
Department of Materials Science and Engineering
National University of Singapore
Singapore, Singapore

Ming-Chi Kan
KINIK Company
Taipei Hsien, Taiwan

Alexander M. Korsunsky
University of Oxford
Oxford, United Kingdom

Amit Kumar
Department of Mechanical Engineering
National University of Singapore
Singapore, Singapore

Sandor Nemeth
Singapore Institute of Manufacturing Technology
Singapore, Singapore

K.S. Rajam
Surface Engineering Division
National Aerospace Laboratories (CSIR)
Bangalore, India

Sahendra Pal Sharma
Department of Materials Science and Engineering
National Cheng Kung University
Tainan, Taiwan

J.F. Smith
Micro Materials Ltd.
Wrexham, United Kingdom

James Chien-Min Sung
KINIK Company
Taipei Hsien, Taiwan

and

National Taiwan University
Taipei, Taiwan

and

National Taipei University of Technology
Taipei, Taiwan

Jyh-Ming Ting
Department of Materials Science and Engineering
National Cheng Kung University
Tainan, Taiwan

S.C. Veldhuis
Department of Mechanical Engineering
McMaster University
Hamilton, Ontario, Canada

Stan Veprek
Department of Chemistry
Technical University of Munich
Garching, Germany

Maritza Veprek-Heijman
Department of Chemistry
Technical University of Munich
Garching, Germany

Huili Wang
School of Mechanical and Aerospace Engineering
Nanyang Technological University
Singapore, Singapore

Wan-Yu Wu
Department of Materials Science and Engineering
National Cheng Kung University
Tainan, Taiwan

Kong Boon Yeap
Department of Mechanical Engineering
National University of Singapore
Singapore, Singapore

Kaiyang Zeng
Department of Mechanical Engineering
National University of Singapore
Singapore, Singapore

RuiFeng Zhang
Department of Chemistry
Technical University of Munich
Garching, Germany

Sam Zhang
School of Mechanical and Aerospace Engineering
Nanyang Technological University
Singapore, Singapore

Contents

1 The Fundamentals of Hard and Superhard Nanocomposites and Heterostructures

Stan Veprek, Maritza Veprek-Heijman, Ali S. Argon, and RuiFeng Zhang

CONTENTS

The original finding of Veprek and Reiprich that in nc-TiN/a-Si_3N_4 and related nanocomposites,* deposited under the optimum conditions that allow a complete phase segregation, and provided the impurity content is about 100 ppm or less, a maximum hardness of ≥50 to more than 100 GPa is achieved when the thickness of the interfacial SiN_x phase is about 1 monolayer (1 ML), has been recently confirmed both theoretically and experimentally. In this chapter, we summarize these results and discuss the thermodynamic and kinetic limitations of experiments on heterostructures and nanocomposites. In Section 1.1, we discuss generally what are strong, hard, and superhard materials, and

* Here "nc" means nanocrystalline, "a" x-ray amorphous and the stoichiometry "Si_3N_4" symbolizes that the Si 2p binding energy as measured by x-ray photoelectron spectroscopy (XPS) corresponds to that of stable, stoichiometric silicon nitride.

what fundamental properties determine their hardness. Section 1.2 is devoted to the discussion of different approaches to the design of superhard, nanostructured materials. In Section 1.3, we discuss in more detail the thermodynamic and kinetic conditions needed for the preparation of super- and ultrahard nanocomposites with high thermal stability and oxidation resistance. In Section 1.4, we discuss why one monolayer of the interfacial covalent silicon nitride separating hard transition metal nitride domains is the strongest configuration that provides the heterostructures and nanocomposites with the highest hardness. Section 1.5 explains in a simple manner why it is possible to achieve hardness in excess of 100 GPa, i.e., higher than that of diamond. The first principle *ab initio* density functional theory (DFT) calculations confirm and explain how the maximum cohesive and shear strength of the TiN–SiN_x–TiN sandwich is achieved with one monolayer (1ML) of SiN_x and why they are much higher than that of bulk SiN_x. These results combined with the Sachs average of the yield strength for randomly oriented polycrystalline material and the Tabor relation between hardness and tensile yield strength, accounting for the pressure enhancement of the flow stress, explain in a simple, rational way the experimentally achieved values of hardness in excess of 100 GPa. The extraordinary mechanical properties of the superhard nanocomposites can be understood in terms of the nearly flaw-free, strong state of these materials. Thus, there is no need to invoke any new mechanism of strengthening. Because these results are of a generic nature, ultrahardness of >100 GPa may be achievable in a variety of nanocomposites of different chemical compositions, such as nitrides, carbides, borides, etc. A brief discussion of the issue of reproducibility follows in Section 1.6 with suggestions on how to further improve the properties of these nanocomposites. Finally, we discuss several typical examples of large-scale industrial applications in Section 1.7 and finish with conclusions.

1.1 INTRODUCTION: WHAT IS A "STRONG" AND "SUPERHARD" MATERIAL?

The ultimate properties of materials that find particular use with ultrahard nanocomoposites have been described by a variety of terms such as *strong*, *stiff*, *tough*, *ductile*, and the like, often with considerable ambiguity. We define these terms for our use as follows. By *high stiffness*, we refer to a high resistance to elastic deformation with complete reversibility when stress is removed, i.e., as in solids with high Young's moduli, shear moduli, or bulk moduli. By *high strength*, we refer to a material property terminating a certain useful range such as with elastic behavior at a substantial *yield strength* initiating plastic flow. Alternatively, when a desirable material's behavior is terminated by fracture, without or after considerable plastic flow at a high stress, we refer to the behavior as high *fracture strength*. Parenthetically, we use the term *stress* as an externally applied "driving force" and *strength* as a material property. When fracture is abrupt, with a sharp drop in stress, we refer to the behavior as *brittle fracture*, in distinction to a fracture behavior that requires considerable plastic work to accomplish it, and particularly for the cases where the final separation is not abrupt but requires a smooth and stable drop in stress for complete separation, we term the response a *ductile fracture process*. Such high energy absorbing fracture behavior is referred to as *tough*. Along these lines, we recognize that in common practice some materials such as many fcc metals, e.g., Cu and Al, and many bcc metals such as Fe and Mo, above a certain transition temperature are *ductile*, while these bcc metals below their transition temperatures and nearly all elemental solids and covalent compounds are *brittle* at all but the highest temperatures.

Fracture in most applications involves the propagation of a crack of either a pre-existing type or one initiated by some preparatory plastic deformation [1–4]. Such a crack propagation, often as an instability, occurs when the "driving force" consisting of a combination of the applied tensile stress, σ, and the crack length a, referred to as the (mode I) stress intensity factor $K_I = \sigma\,(\pi a)^{1/2}$, reaches a critical value of $K_{Ic} = (EG_{Ic}/\pi a)^{1/2}$ where E is the Young's modulus and G_{Ic} is the specific work of fracture also referred to as the critical energy release rate [2,3,5]. In brittle covalent substances and most nanocomposites that exhibit brittle behavior, G_{Ic} is often as low as only twice the surface free energy, but can be tailored to be considerably higher.

The indentation hardness is the resistance of a material against plastic indentation. It is determined in an experiment in which a very stiff and hard indenter (for hard and superhard materials a diamond pyramid of a given shape) is pressed into the surface of a material with a given load L, and the remnant contact area of the plastically deformed site A_C is measured by means of a microscope defining the indentation hardness to be $H = L/A_C$ [6,7]. Modern, automatic load-depth-sensing instruments have automated this process to allow determination of the "plastic" (or so called "corrected") indentation depth directly from the unloading curve from which the contact area and, consequently, the hardness is determined [8]. The tensile strength of brittle thin films can be estimated by the automated load-depth indentation measurements using the Hertzian theory in order to calculate the radial tensile stress at the periphery of the contact between the indenter and the material [9–11], which, while convenient, is incorrect since the radius of the fracture circle is nearly always significantly larger than the radius of the contact area [12,13]. Super- and ultrahard materials are those with indentation hardnesses of ≥40 and ≥80 GPa, respectively [14]. For comparison, natural diamonds have a hardness between 70 and 90 GPa, whereas an industrial diamond may have a higher hardness due to solid solution strengthening where a few 100 ppm of nitrogen atoms substitute for the carbon atoms on lattice sites. While elastic properties and plastic resistance are usually crystallographically anisotropic, for the majority of applications isotropic behavior is preferred.

Elastic moduli that determine the resistance of material against elastic, i.e., reversible, deformation are related to the curvature of the interatomic binding potential or internal energy, U_C, of the crystal at the equilibrium position (i.e., at zero strain and stress). For Young's modulus, E_Y, and bulk modulus, B, relations (1.1a) and (1.1b), respectively, hold

$$E = \left(\frac{\partial^2 U_C}{\partial \varepsilon^2} \right)_{\varepsilon=0} \tag{1.1a}$$

$$B = \left(\frac{\partial^2 U_C}{\partial \varepsilon_d^2} \right)_{\varepsilon_d=0} \tag{1.1b}$$

where

$\varepsilon = da/a_0$ is the tensile uniaxial strain

$\varepsilon_d = dV/V_0$ is the dilatation

Thus, elastic moduli are defined for infinitesimal strain around the equilibrium position. While these moduli can be used to describe the ideal decohesion instability, they do not describe the fracture strength, which is governed by imperfections and occurs at a final strain typically of the order of 1%–2% for semi-brittle metals and less than about 0.1% for brittle ceramics and glasses, but they, nevertheless, provide a ranking. For an ideal material that is free of flaws, the ideal fracture strain is ca. 10%–20% (see [10,11,15] and references therein). At such a high strain, the electronic structure of the solid may significantly change, resulting often in phase transitions preceding fracture (see [16] and references therein) and, possibly, softening. Therefore, in order to predict the strength of a material, one cannot rely directly on the values of elastic moduli (or elastic constants) obtained, e.g., from high-pressure x-ray diffraction (XRD) measurements or from *ab-initio* theoretical calculations for infinitesimal strain.* One has to consider the relation between the applied stress and the

* There are two types of *ab initio* density functional theory (DFT) calculations of elastic moduli: (1) calculation of the dependence of total energy on volume and fitting that curve by an appropriate equation of state; (2) calculation of the dependence of stress vs. strain and taking the slope at small strains. The former method yields the bulk modulus, the latter one yields both Young's and shear moduli depending on which form of loading, i.e., tensile or shear, is applied. More complex calculations allow one to obtain the elastic constants.

resulting strain for final values of strain up to >10% (see Figure 4 in [10]). Tensile stress vs. strain curves, in the absence of flaws, give the ideal de-cohesion curve, which is relevant to brittle fracture, whereas shear stress vs. strain curves are relevant for plastic deformation that occurs under a constant volume.

Many crystalline materials show a certain correlation between hardness and shear modulus, *G*, however, often with a large scatter of the data [17]. Such a correlation is present when plastic deformation occurs by crystal plasticity involving generation and motion of dislocations, where the line energy of a dislocation is proportional to the shear modulus, *G*, and where also most processes resisting dislocation motion involve elastic interactions proportional to *G* [1,2]. In other instances, e.g., even in the plastic deformation of amorphous metals, polymers, and glasses, the plastic resistance is largely governed by elastic interactions and the plastic resistance remains proportional to the shear modulus [18]. Nevertheless, in the connection between plastic resistance and the level of indentation hardness, other factors, such as material microstructure with its constitution such as grain and phase boundaries, etc. enter, which can often significantly alter the form of the connection between the intrinsic mechanism and the ultimate level of hardness. Therefore, caution is required in concluding the level of high hardness from a high value of elastic moduli. For example, osmium has a very high modulus of about ≤444.8 GPa [19] comparable to that of diamond of ≥442 GPa [20], but low hardness of about 4 GPa [21],* even though it also has a high shear modulus of 222 GPa. Rhenium diboride, like other 5d metals, has a high elastic modulus and has been suggested to be superhard [21]. However, the hardness of 48 GPa reported by Chung et al. in that paper has been obtained at a load that is too low where the system responded in a mixed elastic-plastic regime. A correct, load-invariant hardness of this material is less than 30 GPa [22] in agreement with our theoretical *ab initio* DFT calculations of the ideal shear strength, which is smaller than that of c-BN [23]. Another example is osmium diboride that, because of its high value of elastic moduli, has also been suggested to be superhard (see e.g., [24]). However, experimental as well as theoretical works of others have shown that its hardness reaches only about 20 GPa [25] because its ideal shear strength in the (001)[010] slip system amounts to about 9.1 GPa, only slightly higher than that of pure iron of 7.2 GPa [26].

An example par excellence of how, based on the high values of calculated zero-pressure elastic moduli, an incorrect prediction of the strength may result is the story of C_3N_4 (see e.g., [14] and references therein). More than 20 years ago, Liu and Cohen calculated a high value of bulk modulus of this hypothetical compound that had not been synthesized at that time, comparable to that of diamond, and concluded that it had to be as hard as diamond and harder than cubic boron nitride, c-BN [27]. Many researchers tried to prepare this compound but never achieved the predicted high hardness. There are two main reasons for this lack of success: a fundamental difficulty to prepare such a material and the fact that the strength of a material cannot be predicted on the basis of the high values of elastic moduli alone. As explained above, these values are defined at equilibrium, i.e., at zero pressure and strain, whereas plastic deformation at an atomistic level occurs at a finite, relatively large strain of 0.2–0.4.

The difficulty in preparing this material is related to the high (endothermic) value of the enthalpy of formation of carbon–nitrogen compounds, such as paracyanogen (a solid, graphite-like CN compound) and even more of C_3N_4 [28]. Thin films of stoichiometric, amorphous C_3N_4 have been prepared for the first time by plasma-induced chemical vapor deposition (P CVD). The deposition process has to include a high flux of atomic nitrogen (in order to provide the high reaction enthalpy needed for the formation of the endothermic compound) as well as energetic ion bombardment (in order to promote graphitic C-sp^2 into the tetrahedral C-sp^3 hybridization) and a high temperature of 800°C in order to remove paracyanogen by sublimation from the growing film (see [28] for

* Note that although the shear modulus, *G*, is relevant for crystal plasticity and Young's modulus to brittle fraction [1,2], the knowledge of the bulk or Young's modulus allows an estimation of *G* from the well-known relationships that involve only the value of Poisson's ratio (see e.g., [3]).

further details). The measured hardness of ≤30 GPa [28] was high, but far from being comparable with that of diamond, and it was lower than that of c-BN.

A deeper insight into the mechanical behavior of cubic single crystals of C_3N_4 is provided by the recent *ab-initio* DFT calculations of the stress–strain dependence for diamond, c-BN, and C_3N_4 by Zhang et al. [29]. Figure 1.1a shows the shear stress–strain relation $\sigma - \varepsilon$, for pseudo-cubic pc-C_3N_4, diamond, and c-BN calculated by Zhang et al. for the easiest shear mode on a (111) lattice plane in the <11$\bar{2}$> direction. For small strain, the slope $(d\sigma/d\varepsilon)_{\varepsilon=0}$ is similar for C_3N_4 and c-BN and somewhat higher for diamond, yielding a similar value of zero-pressure elastic moduli of C_3N_4 and c-BN. However, for finite strains $\varepsilon > 0$, differences are seen, and for shear strains larger than about 0.15, pc-C_3N_4 has the smallest stiffness, $(d\sigma/d\sigma)_{\varepsilon \geq 0.14}$. Furthermore, the fracture stress and strain are significantly lower for pc-C_3N_4 than for diamond and c-BN. Figure 1.1b displays the change of the crystal energy, ΔE, as a function of the shear strain which, upon increasing strain, shows a continuous increase up to the elastic limit where a sudden decrease due to the onset of plastic deformation occurs. For diamond and c-BN, ΔE approaches zero because, when the plastic event occurs, the elastic energy almost vanishes and the contribution of the plastic energy is small. However, ΔE is negative for pc-C_3N_4. This is due to a change of electronic configuration under large elastic strains associated with the non-binding electron pairs on nitrogen and concomitant transformation to a soft, graphitic-like polymorph (see [29] for further details).

The above mentioned prediction of Cohen and Liu was based on the presumption stated by Cohen: "Since B_0 is related to the strength of a bond, it is ultimately related to hardness." (see [30] p. 47. left column). Based on a semi-empirical theory, Cohen derived a formula:

$$B_0 = \frac{\langle N_C \rangle}{4}(1971 - 220 \cdot \lambda) \cdot d^{-3.5} \tag{1.2}$$

where

$\langle N_C \rangle$ is the average coordination number
λ describes the "ionicity" of the bond (i.e., polarity; $\lambda = 0$ for non-polar bonds)
d is the bond length in Ångströms to give the value of the zero pressure bulk modulus in GPa

The number 1971 in parentheses multiplied by $d^{-3.5}$ describes essentially the electron density of a non-polar covalent bond between the neighbor atoms, and the second term 220·λ describes the weakening by the polarity of the bond between two atoms with different electronegativities.

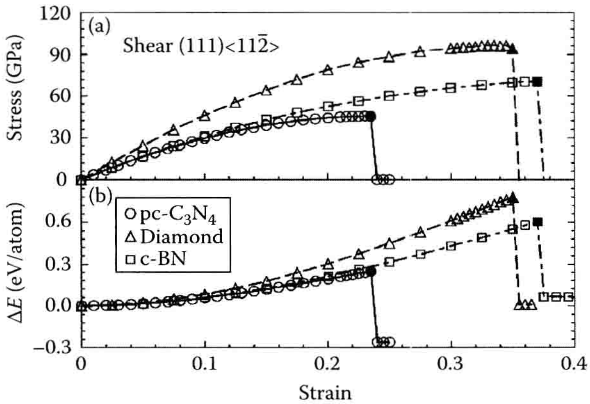


FIGURE 1.1 Calculated shear stress–strain relation for shear within the (111) lattice plain in <11$\bar{2}$> direction for pc-C_3N_4, diamond, and c-BN. (From Zhang, Y. et al., *Phys. Rev. B*, 73, 064109-1, 2006. With permission.)

More recently, several groups have used a similar idea to derive semi-empirical formulae directly applied to hardness [31–33]. In order to illustrate this approach, we discuss it briefly as described in the recent paper of Li et al. [33]: "The bond hardness represents electron-holding energy of a covalent bond per unit volume …" (see [33] p. 235504–2, left column).* Then the hardness is given by formula (1.3), where X_{ab} is the "electron-holding energy" and N_v is the "bond density." The constants $p = 423.8\,\mathrm{GPa} \cdot \text{Å}$ and $q = -3.4\,\mathrm{GPa}$ are determined so that the hardness obtained from formula (1.3) "… agree well with the experimental Knoop hardness H_k (in unit of GPa) of typical covalent crystals diamond and silicon …" (ibid, p. 235504–2 bottom of left column).

$$H = p \cdot N_v \cdot X_{ab} + q \tag{1.3}$$

Obviously, formula (1.3) is physically equivalent to Cohen's formula (1.2) for bulk modulus, and the "theoretical hardnesses" derived in the quoted papers by the fitting of hardnesses of known materials in order to obtain the needed coefficients [31–33] are based on the same assumption that the electronic structure at equilibrium determines the strength of solids under a large strain, i.e., there is no significant change of the electronic structure at large strains. From the examples discussed above, it should be clear that these theories are physically unsound.

1.2 EXTRINSICALLY SUPERHARD NANO-SIZED AND NANO-STRUCTURED MATERIALS

So far we have discussed the so called "intrinsically" hard and superhard materials, which attain their high strength and hardness because of their high ideal shear (and de-cohesion) strength, which has been obtained on the basis of first principle calculations. The maximum achievable shear and de-cohesion strengths of ideal single crystals free of flaws, such as dislocations, grain boundaries, microcracks and the like, σ_{ideal}, can be estimated on the basis of a simple atomic model using Equation 1.4a for plastic deformation when applying shear stress parallel to the crystal lattice planes and by using Equation 1.4b for de-cohesion upon uniaxial tensile strain [1–3]:

$$\sigma_{\mathrm{ideal}} \cong 0.1 \cdot G \tag{1.4a}$$

$$\sigma_{\mathrm{ideal}} \cong \sqrt{\frac{2 \cdot \chi_S \cdot E_Y}{\pi \cdot a_0}} \tag{1.4b}$$

Here, χ_S is the surface energy; the meaning of the other symbols has been given above. Because the correctly measured, load-invariant indentation hardness corresponds to the ratio of applied load to the remnant contact area under no load for conditions of fully developed plasticity, formulae 1.4a and 1.4b are of little use. The plastic resistance of materials can be significantly influenced by their microstructure and its scale. Therefore, in this section, we shall discuss "extrinsically" hard and superhard materials that attain their mechanical properties due to proper control and design of their microstructure. The first examples are heterostructures consisting of periodically alternating layers of two materials with different elastic moduli and a repetition period of several nm. The emphasis of this chapter will be, however, on polycrystalline nano-sized materials in which the control of the crystallite size is achieved by an appropriate preparation technique (see e.g., [34,35]).

* Let us point out that the term "bond hardness," as used by Li et al. does not have any well-defined meaning.