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Gagik Ayvazyan

Black Silicon

Formation, Properties, and Application

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ISSN 2691-1930 ISSN 2691-1949 (electronic)
Synthesis Lectures on Materials and Optics
ISBN 978-3-031-48686-9 ISBN 978-3-031-48687-6 (eBook)
https://doi.org/10.1007/978-3-031-48687-6

This book was supported by the Science Committee of the Republic of Armenia in the frames of the research Project No. 21AG-2B011.

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

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I dedicate this book to my six grandchildren—
Gagik, Anna, Hakob, Maria, David and Eric—
whom I love dearly

Preface

There's Plenty of Room at the Bottom

—Richard P. Feynman

Nobel-prizewinning in Physics (1965)

Nanostructured materials are typically defined as materials in which structural elements, such as clusters, crystallites, or molecules, have dimensions in the range of 1–100 nm. The concept of nanostructured materials was first articulated by American physicist and Nobel Prize laureate Richard Feynman in 1959. He stated, "The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom". Since then, the "nanomaterial revolution" has followed, confirming their superior electronic, thermal, magnetic, and optical features.

Nanostructured silicon is currently a pioneering research topic worldwide due to its enormous potential applications in modern electronic devices, such as sensitive photodetectors, solar cells, biochemical sensors, hydrogen generators, and display devices. The main structural modifications of this nanomaterial are porous silicon and black silicon. The first is crystalline silicon with nanopores, and the second is crystalline silicon with nanoneedles. Historically, porous silicon is considered a sort of "precursor" to black silicon.

Previously, several interesting and useful books about porous silicon have been published, which can be regarded as comprehensive reference encyclopedias on this material. However, there is currently no book dedicated to black silicon. This monograph attempts to fill this gap.

The monograph consists of four chapters.

Given that porous silicon serves as a precursor to black silicon and shares numerous structural, electronic, and optical properties, Chap. 1 is dedicated to exploring this material. The properties and practical aspects of forming and applying porous silicon are briefly outlined. This will make it possible to carry out correlations between two structural modifications of nanostructured silicon to clearly and reasonably show their advantages

and disadvantages. In addition, this introductory chapter offers essential information about the structure of crystalline silicon and its fundamental electro-physical, structural, optical, and mechanical properties.

Chapter 2 discusses the features of black silicon fabrication. Different formation methods are introduced, and their pros and cons are critically analyzed. The main attention is given to the reactive ion etching method used in our experiments.

Chapter 3 presents our theoretical and experimental research results on the properties of black silicon layers, such as structural, optical, photoelectric, and wetting properties. Readers will be especially interested in comparing the antireflection features of porous and black silicon.

Chapter 4 describes some of the practical applications of black silicon that we have developed and tested: gas sensors, external gettering of metallic impurities, and antireflection surfaces for single-junction and tandem solar cells. Some of them were held for the first time.

Finally, we present the concluding remarks of this book and perspectives for future research on this subject.

The monograph contains many references to the vast resources of recently published literature on porous and black Si layers. Most of the material presented in the monograph includes results obtained by the author. Dr. Ayvazyan has been dealing with porous silicon since 2000 and with black silicon for the last 7 years.

It is intended that this monograph is useful for the widest range of specialists—from M.S. and Ph.D. students in physics disciplines to researchers in the field of semiconductor physics and micro- and nanoelectronics. The book will also be interesting for practicing engineers or project managers working in industries and national laboratories, who intend to design various nanostructured silicon-based devices. The author encourages readers to contribute their valuable comments/suggestions so that the book can be improved further.

Yerevan, Armenia
September 2023

Dr. Gagik Ayvazyan

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About the Author

Dr., Assoc. Prof. Gagik Ayvazyan earned his Ph.D. in physics and technology of semiconductor materials and devices at St. Petersburg State University of Information Technologies, Mechanics and Optics in 1989. He is a Corresponding Member at the International Academy of Engineering (Moscow, RF).

Gagik Ayvazyan has more than 30 years of experience as a teacher and scientific researcher. In particular, from 1989 to 2001, he headed the Technology Department at Transistor Co. (Yerevan) and then the Advanced Technology Group at Barva Innovation Center (Talin, Armenia). Since 1992, he has been an Associate Professor at the National Polytechnic University of Armenia in Yerevan. He is also a Scientific Expert at the International Commercialization Reactor (Riga, Latvia).

Gagik Ayvazyan specializes in the field of defect engineering in microelectronics, silicon-based solar cells, and sensors. His early research included the formation features and new possibilities for using porous silicon layers. Currently, his research interests are focused on the structural, optical, and sensing properties of black silicon. e-mail: gagik.ayvazyan@polytechnic.am

Abbreviations

μc-Si	Microcrystalline silicon
AFM	Atomic force microscopy
ALD	Atomic layer deposition
AR	Average reflectance
ARS	Antireflection surface
b-Si	Black silicon
CA_{adv}	Advancing contact angle
c-Si	Crystalline silicon
CVD	Chemical vapor deposition
CZ	Czochralski
DRIE	Deep reactive ion etching
EDS	Energy-dispersive spectroscopy
EPD	Etch pits density
ETL	Electron transport layer
FDTD	Finite-difference time-domain
FZ	Float zone
HAL	Hole accumulation layer
HTL	Hole transport layer
IC	Integral circuit
ICP	Inductively coupled plasma
IR	Infrared
LC	Length correlation
LIE	Laser-induced etching
MACE	Metal-assisted chemical etching
mc-Si	Multicrystalline silicon
mono-Si	Monocrystalline silicon
MOS	Metal–oxide–semiconductor
NP	Nanoparticle
n–Si	Doped with electronic conductivity
OISF	Oxidation induced stacking fault

PECVD	Plasma-enhanced chemical vapor deposition
PERC	Passivated emitter rear cell
PIII	Plasma immersion ion implantation
poly-Si	Polycrystalline silicon
p-Si	Doped with hole conductivity
PSi	Porous silicon
PV	Photovoltaic
RF	Radiofrequency
RIE	Reactive ion etching
RMS	Root mean square
SEF	Surface enhancement factor
SEM	Scanning electron microscopy
SF	Stacking fault
TCO	Transparent conductive oxide
TMM	Transfer matrix method
UV	Ultraviolet
WAR	Weighted average reflection
XRD	X-ray diffraction

Notations

(hkl) Plane in the lattice, the crystal face;
{hkl} A family of planes or facets of a simple form of the crystal with the same symmetry;
[rst] The direction in the lattice, the edge of the crystal;
⟨rst⟩ A family of directions or edges of a simple form of a crystal with the same symmetry.

Crystalline and Porous Silicon

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Crystalline Si (c-Si) has many advantages over other semiconductor materials: low cost, nontoxicity, practically unlimited availability, and decades of experience in purification, growth and electronic device fabrication. Nanostructured Si possesses numerous unique merits, including outstanding electronic and optical properties, substantial surface-to-volume ratios, and easy surface modification. The first identified self-organized nanostructured Si was porous Si (PSi), which can be considered Si with a network of voids. Historically, PSi is thought to be a kind of "precursor" to black Si. Section 1.1 presents the basic concepts and properties of c-Si necessary to explain some of the features of nanostructured Si. The next sections focus on the main properties and practical aspects of the formation and applications of PSi. Comprehensive information about PSi can be found in monographs, book chapters, and review manuscripts [1–9].

1.1 Crystalline Silicon

1.1.1 Basic Concepts

Throughout human history, there have been epochs defined by the prominence of specific materials, such as the Bronze Age or Iron Age. With ample justification, the current era, the second half of the last century and, at least, the first quarter of this century can be regarded as the Silicon Age. It is unlikely that even the discovery of graphene with its amazing electro-physical properties will be able to narrow down the technological predominance of Si.

G. Ayvazyan, *Black Silicon*, Synthesis Lectures on Materials and Optics,
https://doi.org/10.1007/978-3-031-48687-6_1

Si is the second chemical element after oxygen. It is interesting to note that despite the chemical inertness of pure Si under normal conditions, pure Si is not common on Earth, although it is approximately a quarter of the planet's mass (~28% by weight of the Earth's crust). In nature, it is mostly distributed in the form of silica or Si dioxide SiO_2, which makes up approximately 12% of the Earth's crust by weight and appears in various forms, such as river sand and quartz. Additionally, SiO_2 serves as a fundamental component in hundreds of different natural silicates and aluminosilicates.

Si is a chemical element located at number 14 in the periodic table of elements. The Si atom has 14 electrons, and in the ground state, its electronic configuration is described by $1s^2 2s^2 2p^6 3s^2 3p^2$, i.e., in this state, Si is divalent. However, the energies of the electrons in the s- and p-states are close, so the Si atom easily passes to an excited state with the M-shell configuration $3s^1 3p^3$. In this excited state, the Si atom has four unpaired valence electrons, i.e., tetravalent. In a Si crystal, each atom forms four covalent bonds with other atoms. s- and p-orbitals themselves do not take part in forming bonds; instead, their linear combinations, the so-called sp^3-hybrid orbitals, take part in this process. Figure 1.1 shows the spatial distribution of the valence electrons in the Si atom for four of its sp^3-orbitals and a three-dimensional representation of the cubic unit Si cell.

The Si crystal structure comprises stacked cubes, with each atom surrounded by four others, forming covalent bonds. These bonds are established through the sharing of two valence electrons, one from each atom, creating localized connections along which electrons move back and forth with opposing spins. This form of bonding is exceptionally strong, highly localized, and directional, as valence electrons become concentrated around their nearest neighbors. Under typical operating temperatures, atoms maintain relatively fixed positions relative to each other on average. Nevertheless, they continually vibrate around their equilibrium positions.

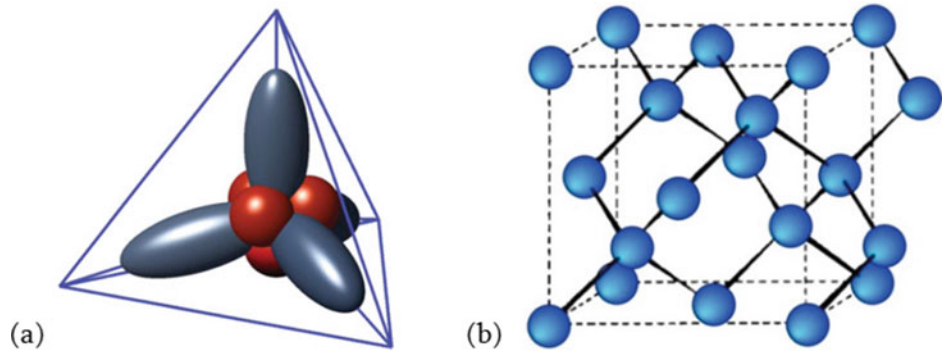

Fig. 1.1 Hybrid sp^3-orbitals of the Si atom (**a**) and three-dimensional representation of the cubic unit Si cell (**b**)

Crystalline Si (c-Si) is the crystalline form of Si. The semiconducting properties of c-Si appear in all its types—monocrystalline (mono-Si), multicrystalline (mc-Si), microcrystalline (μc-Si), and polycrystalline (poly-Si) [10–12].

Mono-Si consists of Si in which the crystal lattice of the entire solid is continuous, unbroken on its edges, and free of any grain boundaries. Mono-Si can be made either highly pure or doped to change its semiconducting properties. Mono-Si can be manufactured mainly using Czochralski (CZ), float zone (FZ), micro pulling down, Bridgman-Stockbarger technology, and laser-heated pedestal growth processes. It is a more expensive type of Si because of the careful and slow manufacturing process as well as the control of impurities needed. It is estimated that 95% of all c-Si is produced by the CZ method, and the rest is mainly produced by the FZ method [11].

Mc-Si is composed of small crystals known as crystallites, with sizes ranging up to hundreds of microns. However, the material quality of mc-Si is lower than that of mono-Si primarily due to the presence of grain boundaries. These grain boundaries give rise to highly localized regions of recombination, introducing additional defect energy levels within the band gap. Consequently, this reduces the overall minority carrier lifetime in mc-Si. Furthermore, the scattering of phonons and charge carriers at grain boundaries results in decreased thermal and electrical conduction in mc-Si compared to mono-Si. Notably, the techniques required to produce mc-Si are simpler and more cost-effective than those needed for monocrystalline materials. Mc-Si is grown using various methods, including ingot casting, heat extraction, electromagnetic casting, edge-defined film-fed growth, and ribbon growth on the surface, among others.

μc-Si is a form of c-Si that has crystallites of sizes in the range of ~20–200 Å. μc-Si has a low bandgap and can be efficiently used as the bottom cell in tandem solar cells. The dark conductivities of undoped μc-Si at room temperature are $\sim 10^{-10}\ \Omega^{-1}\ \text{cm}^{-1}$ and $10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$ for samples deposited at approximately 110 and 260 °C, respectively. The activation energy for μc-Si is in the range of 0.52–0.87 eV. Deposition techniques for μc-Si include but are not limited to plasma-enhanced chemical vapor deposition (PECVD), the RF-glow discharge method (for hydrogenated μc-Si), magnetron and electron cyclotron resonance plasma, photoexcited chemical vapor deposition (CVD) in SiH_4 diluted with Ar and H_2, and sputtering in Ar and H_2 plasma.

Poly-Si is often confused with mc-Si and is sometimes referred to as mc-Si. Poly-Si, however, is a high-purity, polycrystalline form of Si consisting of small crystals called crystallites, with sizes typically ranging between 0.01 and 1 μm. Poly-Si is produced from metallurgical grade Si by a chemical purification process. The common manufacturing techniques that have been studied exhaustively are the following: seed layer approach, direct growth of fine c-Si layers at higher temperatures, and liquid crystallization process.

1.1.2 Electro-physical Properties

The electro-physical properties of c-Si are significantly influenced by the presence of micro impurities. By introducing small quantities of other elements, the intrinsic semiconductor can be transformed into either an impurity with hole conductivity (p-Si) or electronic conductivity (n-Si), depending on the type of impurity added. Single crystals of p-Si are produced by adding group III elements, such as boron, aluminum, gallium, and indium. n-Si is produced by adding group V elements such as phosphorus, arsenic, or antimony. This controlled addition of impurities, known as doping, is a fundamental process in semiconductor manufacturing and plays a critical role in tailoring the electrical properties of Si for various applications.

The main electro-physical properties of c-Si are summarized in Table 1.1. These properties with sufficient accuracy remain unchanged for the semiconductor and do not depend on the size and shape of the crystal if its size can be considered macroscopic [13]. For Si nanostructures, however, due to quantum-size restrictions, both optical and electro-physical properties depend on particle size.

C-Si is an anisotropic material whose properties depend on its relative orientation to the crystal lattice as well as an orthotropic material, i.e., a crystal with at least two orthogonal planes of symmetry. Different growth planes and orientations have different arrangements of the atoms or lattice as viewed from a particular angle. Orientation is defined by the Miller index, with (100) or (111) faces being the most common for Si wafers.

1.1.3 Optical Properties

Si is used as an optical window primarily in the 3–5 μm wavelength range and as a substrate for the production of optical filters [14]. In physics experiments, large blocks of Si with polished surfaces serve as neutron targets. CZ and FZ Si are produced to optimize transmission in the operation wavelength region. The selection of these grades depends on factors such as the wavelength range, thickness of the element, and particular application at hand.

Table 1.2 presents the index values n of c-Si for selected wavelengths λ. Figure 1.2 shows the typical reflectance spectrum of the polished mono-Si surface at normal incidence in the 200–1200 nm range.

1.1.4 Structural Properties

Single c-Si is a well-defined material of very high quality. Nevertheless, it may still contain various structural defects, which are formed either during c-Si crystal growth or during the processing of the Si wafer.

Table 1.1 Basic electro-physical properties of c-Si

Property	Value	Unit
Crystal properties		
Structure	Cubic	
Atomic mass (molar weight)	28.0855	a.amu. (g/mol)
Isotopes	28 (92.23%), 29 (4.67%), 30 (3.10%)	
Electronic shell	$1s^2 2s^2 2p^6 3s^2 3p^2$	
Conventional ion	Si^{4+}, Si^{4-}	
Radius of the atom	132	pm (=0.01 Å)
Covalent radius	111	pm
Radius of the ion	42 for +4 and 271 to –4	pm
Distance between neighboring atoms	0.235	nm
Lattice spacing at 300 K	0.54311	nm
Density at 300 K	2.3290	g/cm^3
Number of atoms in 1 cm^3	4.995×10^{22}	
Density of atoms on the surface with the crystallographic plane (hkl)	(100) 6.78, (110) 9.59, (111) 7.83	$1014/cm^2$
Critical pressure	1450	atm
Critical temperature	5193	K
Thermal properties		
Melting point	1687	K
Boiling point	2628	K
Specific heat	0.7	J/(g K)
Thermal conductivity at 300 K	156	W/(m K)
Thermal diffusivity	0.8	cm^2/s
Linear coefficient of thermal expansion	2.92×10^{-6}	K^{-1}
Debye temperature	640	K
Temperature dependence of the band gap width	-2.3×10^{-4}	eV/K
Heat: melting atomization	39.6/383.3/452	kJ/mol
Electrical properties		
Breakdown voltage	$\approx 3 \times 10^5$	V/cm
Refraction index	3.42	
Electron mobility	≈1400	$cm^2/(V\ s)$

(continued)

Table 1.1 (continued)

Property	Value	Unit
Hole mobility (300 K)	≈370	$cm^2/(V\ s)$
Diffusion coefficient of electrons	≈36	cm^2/s
Diffusion coefficient of holes	≈12	cm^2/s
Thermal velocity of the electron	2.3×10^5	m/s
Thermal velocity of holes	1.65×10^5	m/s
Energy of optical phonon	0.063	eV
Work function	4.15	eV
The band structure (at 300 K)		
Relative dielectric constant	11.9	
Effective density of states (conductive)	2.8×10^{19}	cm^{-3}
Effective density of states (valence)	1.04×10^{19}	cm^{-3}
Affinity for electron	133.6	kJ/mol
Band gap	1.12	eV
Minimal width of the forbidden line zone	3.4	eV
Concentration of intrinsic charge carriers	1×10^{10}	cm^{-3}
Intrinsic resistivity	3.2×10^5	Ohm cm
Auger recombination coefficient of electrons	1.1×10^{-30}	cm^6/s
Coefficient of holes Auger recombination	3×10^{-31}	cm^6/s
Width of the indirect gap at 0 K	1.17	eV

Table 1.2 Refractive index of c-Si for selected wavelengths

λ (μm)	n	λ (μm)	n
1.40	3.4900	5.00	3.4256
1.50	3.4841	5.50	3.4246
2.00	3.4561	6.00	3.4238
2.50	3.4431	6.50	3.4232
3.00	3.4360	7.00	3.4227
4.00	3.4289	8.00	3.4220
4.50	3.4270	9.00	3.4216