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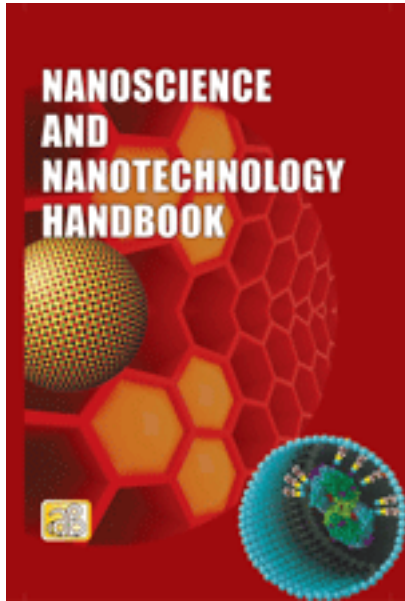
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Nanoscience and Nanotechnology Handbook



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Nanotechnology is the engineering of functional systems at the molecular scale. In its original sense, nanotechnology refers to the projected ability to construct items from the bottom up, using techniques and tools being developed today to make complete, high performance products. In this rising world of rapid technological developments, the role of state of art materials & composites is pivotal in frontier applications like aerospace, aviation, automobile, defense, electronics, chemical, biomedical, energy & nuclear sectors etc. with the advent of 21st century & initiation of Nanotechnology the atomic & molecular structures of materials is redefined. This shall result in new smart materials namely nanoparticles, powder, wires, rods, carbon nano tubes & so on. Nanotechnology is very diverse, ranging from novel extensions of conventional device physics, to completely new approaches based upon molecular self-assembly, to developing new materials with dimensions on the nanoscale, even to speculation on whether we can directly control matter on the atomic scale. Potential of nanotechnology to manipulate and program matter with atomic precision has invited the attention of scientists to explore innumerable applications of nanotechnology was an inspiration for the benefit of researchers, academicians and industries associated with this field. The global market for nanotechnology products is worth an estimated compound annual growth rate (CAGR) of 11.1% from 2010 to 2015. The largest segment of the market, made up of nanomaterials, is expected to increase at a 5 year CAGR of 14.7%.

This book basically deals with design of protein based nanomachines, metastabilities in nanocrystalline, nanoscale characterization of nanowires, thermopower measurements on nickel nanowires, a nanoporous  $\text{TiO}_2$  electrode, nanoscale in investigation of ultrathin, silicone oxide thermal decomposition, cylindrical nanodot arrays, nanocrystalline silicon films, dispersion of carbon nanotubes, electrical conductivity study of nanocomposite films, magnetic properties of nanospheres, generation spectroscopy of nanoparticle monolayer, Au nanoparticles on light emitting polymers, etc.

This handbook deals with the technology frontiers, its applications, the current & future challenges etc. This book will be an invaluable resource to all academicians, industrialists, scientists, upcoming entrepreneurs & technocrats.

## **Content:**

## PREFACE

### 1. DESIGN OF PROTEIN BASED NANOMACHINES

#### Introduction

Renowned Nanomachines of the Biological Cell Confirm Engineering Principles and Inspire Nanomachine Design

De Novo Design of Diverse Elastic-Contractile Protein Machines

Hydrophobic and Elastic Consilient Mechanisms: Definitions

Hydrophobic Consilient Mechanism and the Inverse Temperature Transition

The Elastic Consilient Mechanism and the Nature of Near Ideal Elasticity

Coupled Hydrophobic and Elastic Consilient Mechanisms

Principal Thermodynamic Quantities Controlling Diverse Energy Conversions in Model Proteins

The Change in Gibbs Free Energy for Solubility,  $\Delta G(\text{solubility}) = \Delta H - T\Delta S$

The Change in Gibbs Free Energy for a Phase Transition

The Change in Gibbs Free Energy for an Inverse Temperature Transition

Apolar-Polar Repulsive Gibbs Free Energy of Hydration,  $\Delta G_{\text{ap}}$

Calculations of the Entropic Elastic Force and Energy

Biological Protein-based Nanomachines Confirm the Hydrophobic and Elastic Consilient Mechanisms

The Three Classes of Energy Conversion Within the Cell

Complex III of the Electron Transport Chain Within the Inner Mitochondrial Membrane

ATP Synthase of the Inner Mitochondrial Membrane

The Myosin II Motor of Muscle Contraction

Confirmation of the Hydrophobic and Elastic Consilient Mechanisms

Designing Protein-based Nanomachines Using the Hydrophobic and Elastic Consilient Mechanisms

Design of an AFM-Based Stress-Strain Nanomachine for the Detection of a Single Molecular Event

Use of the 3 kHz Mechanical Resonances in the Design of an AFM-Based Nanomachine for Detection of Interactions at Fixed Length

An Additional Opportunity in the Deciphering of Engineering Principles for the Design of Protein-Based Nanomachines

### 2. METASTABILITIES IN NANOCRYSTALLINE

#### SILICON

Experimental Procedure

Results

Discussion

Conclusion

### 3. INTERACTION OF SULPHURIC ACID WITH

#### GRAPHENE

Sulphuric Acid in Gas and Solid Phases

Sulphuric Acid on Graphene

Conclusions

### 4. NANOSCALE CHARACTERIZATION OF

#### NANOWIRES

Experimental Methods

Nanowire Morphology, Periodicity and Diameter

Chemical Analysis of the CoPt/Pt Nanowires

Structural Analysis of the CoPt/Pt Nanowires

Discussion

Conclusions

## 5.THERMOPOWER MEASUREMENTS ON NICKEL NANOWIRES

Experimental Details

Results and Discussion

Structural Characterization of the NWs

Initial Characterization of the Measurement Device

## 6.MULTI-WALLED CARBON NANOTUBE EMITTERS EXPERIMENT

Fabrication of CNT Cathode

Experimental Structures

Current-Voltage Characteristics

Simulations

Simulated Structures

Predicted I-V Characteristics

Cathode Support Structure Geometry

Conclusion

## 7.VIBRATION OF A CARBON NANOTUBE

The Model for a CNT filled with a C-chain

Vibration of a CNT filled with a C-chain

Axisymmetric Radial Breathing Vibration ( $n = 0$ )

Coupled Vibration with  $n = 1$

Vibration of Higher-order Modes ( $n > 2$ )

Conclusions

## 8.A NANOPOROUS TiO<sub>2</sub> ELECTRODE

Experimental Details

Preparation of the ILSE Films

Characterization of the ILSE Films

Electrode and DSSC Fabrication Containing the ILSE

Electrode Characterization

Results and Discussion

Conclusions

## 9.FREEZING BEHAVIOUR OF AN NANOMETER-SIZED Au DROPLET

Numerical Simulations

Results and Discussion

Conclusions

## 10.NANOSCALE IN INVESTIGATION OF ULTRATHIN SILICONE OXIDE THERMAL DECOMPOSITION

Experimental Details

Results and Discussion

High Temperature STM in situ Observation of the Thermal Decomposition Process

Individual Void Growth Kinetics at the Initial Decomposition Stage

Decomposition Rate Variation and Rate Limiting Steps

Morphology Effects on the Decomposition Process

Conclusions

## 11. CARBON NANOTUBE FIELD-EFFECT TRANSISTOR

Methodology

Results and Discussion

Conclusions

## 12. CYLINDRICAL NANODOT ARRAYS

System and Units

Theoretical Model

Vortex-core Magnetization

Total Energy Calculation

Results and Discussion

Conclusions

## 13. SUPERELASTICITY OF ENGINEERING CERAMICS BY NANOTUBES

Experimental Details

Results and Discussion

Conclusion

## 14. POROUS ANODIC ALUMINA

Experimental Details

Results

Initial Specimens and Anodizing

Film Morphology

Film Composition

Discussion

Conclusions

## 15. METAL NANOCLUSTERS IN GLASS

Experimental Procedure

Results and Discussion

Ion-Beam Mixed Ag in Silica

Ion-Exchanged Ag in Soda Lime Glass

Conclusion

## 16. LIGHT EMISSION FROM NANOCOMPOSITES

Experiments

Results and Discussion

Conclusion

## 17. NANOCRYSTALLINE SILICON FILMS

Experimental Details

Results

Optical Absorption Study

X-ray Diffraction Study

Infrared Absorption Study

Raman Study

Electron Microscopy

Discussion

Conclusion

## 18.CARBON NANOTUBES IN CHEMICAL VAPOUR DEPOSITION

### 19.NANOSCALE DEEP INDENTATION

Simulation Methodology

Results and Discussion

Conclusion

### 20.REDUCTION OF NANOWIRES

Experimental Details

Results and Discussions

Summary and Conclusion

### 21.DISPERSION OF CARBON NANOTUBES

Experimental Details

Purification and Dispersion of MWCNTs

Preparation of Nanocomposite Films

Carbon Nanotube Dispersion Study in Solution and in Nanocomposite Films

Electrical Conductivity Measurement

Results and Discussion

MWCNT Dispersion in Solution

Nanocomposite Preparation and Carbon Nanotube Distribution in Composite Films

Electrical Conductivity Study of Nanocomposite Films

Conclusion

### 22.CREATION OF CARBON ONIONS AND COILS

Experimental Details

Result and Discussion

Conclusions

### 23.MAGNETIC PROPERTIES OF NANOSPHERES

Experimental Details

Results and Discussion

Conclusion

### 24.LUMINESCENCE OF CRYSTALS NANORODS

Experimental Section

Results and Discussion

Conclusions

### 25.NANONECKLACE MORPHOLOGY

Experimental Details

Growth of Cu-Pt Nanoparticles

Growth of Cu-Pt Nanonecklace Nanowires

Conclusions

### 26.OPTICAL PROPERTIES OF NANODOT ARRAYS

Experimental Details

Results and Discussion

Conclusions

### 27.GENERATION SPECTROSCOPY OF NANOPARTICLE MONOLAYER

Experimental Section

Materials

Synthesis of AuNPs

Synthesis of Dense AuNPs Monolayer

Dodecanethiol SAM Formation

Characterization

SFG Set-up

Results and Discussion

Conclusions

28. CHEMICAL DOPING WITH CARBON NANOTUBES

Experimental Details

Results and Discussion

Summary

29. DIRECT-WRITE PROGRAMMING OF  
NANOSCALE DEMULTIPLEXER ARRAYS

30. POLY(N-ISOPROPYLACRYLAMIDE)

NANOPARTICLES

Introduction

Experimental Details

PNIPAM-coated Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@CdTe Nanoparticles and ZnPcS Loading

Biological Systems

PL and Fluorescence Measurements

ZnPcS Released from the Nanoparticles in PBS Solution

ZnPcS Released from the Nanoparticles in the CHO Cells

Results and Discussion

ZnPcS Embedded in the PNIPAM of Nanoparticles

Release of ZnPcS from the ZnPcS-loaded Nanoparticles in PBS Solution

Release of ZnPcS from the ZnPcS-loaded Nanoparticles in CHO Cells

Release of ZnPcS from the ZnPcS-loaded Nanoparticles in Zebra Fish

Movement of the Nanoparticles in Zebra Fish by the Magnetic Field Gradient

Phthalocyanines and PDT

Conclusion

31. COBALT FERRITE NANOPARTICLES

Experimental Details

Synthesis

Characterization Methods

Results and Discussion

Fundamental Characteristics, Crystallite size Versus Coercivity and Remanence

Mossbauer Spectra and Distribution of Cations

Heating Efficiency from Calorimetric Measurements and ac

Hysteresis Loops

Conclusions

32. Au NANOPARTICLES ON LIGHT-EMITTING POLYMERS

Experimental Section

Measurements

Device Fabrication and Characterization

Materials

Synthesis of PDOFT-bis-4-thiol

End-capping at AuNP onto PDOFT-bis-4-thiol (PDOFT-Au 10, PDOFT-Au15, PDOFT-Au 20 and PDOFT-



Au 30)

Results and Discussion

Synthesis and Characterization

Photophysical Properties

Electroluminescent Properties and Current Density-Voltage-Luminescence (J-V-L) Characteristics of the PLED Devices

Conclusions

### 33.CARBON NANOSTRUCTURE BASED NANOCOMPOSITES

Experimental Details

Results and Discussion

Conclusions

### 34.Au NANOPARTICLE CHAINS

Experimental Results and Discussion

Sample Preparation and Measuring System

General Considerations on Dielectrophoresis

Dielectrophoresis on Flat Substrates

Dielectrophoresis on V-groove-etched Substrates

Discussion of Results on Patterned Substrates, Electric Field Numerical Calculation

CONCLUSION

### 35.GOLD-SILICA NANOCOMPOSITES

### 36.NANOPINS BY CHEMICAL VAPOUR DEPOSITION

Experimental Section

Preparation

Characterization

Results and Discussion

Conclusions

### 37.OXIDATION RESISTANT METAL NANOPARTICLES

Experimental Details

Thermo-Gravimetric Studies

Particle Size Reduction

Synthesis and Coating of Metal Nanoparticles

Results and Discussion

Thermo-Gravimetric Analysis

Fluidized Bed Processing

Particle Size Reduction

Passivation of Metal Nanoparticles by in situ ALD

Conclusions

### 38.MOLECULAR CARBON-ONIONS

Experimental Details

Discussion of Results

Conclusion

### 39.ATOMIC SCALE MANIPULATION

Tip-Surface Interaction

Experimental Response

Discussion and Conclusion

### 40.SILICONE NANOWIRES

Experimental Session

Results and Discussion

Conclusion

#### 41. CARBON NANOFIBERS

Experimental Details

Results

Discussion and Conclusion

#### 42. SINGLE-CRYSTALLINE NANOWIRES

Experiments

Results and Discussion

Conclusion

#### 43. SILICONE OXIDE NANOSTRUCTURES

Experimental Details

Results and Discussion

Conclusion

#### 44. A SQUARE TITANIUM NANOMESH

Experimental Details

Results and Discussion

Conclusions

#### 45. NANO-POROUS ANODIC ALUMINIUM OXIDE MEMBRANES

Experimental Details

Results and Discussion

Conclusions

#### 46. CO NANOPARTICLES

Experimental Section

Materials

Synthesis and Assembly of Cobalt Nanoparticles

Characterization

Results and Discussion

Conclusions

#### 47. ZERO-BIAS CONDUCTANCE OF GOLD MOLECULAR

JUNCTION

Methodology

Results and Discussion

Conclusion

#### 48. ALL-INKJET-PRINTED ELECTRONICS OF METAL NANOPARTICLES

Fabrication and Experimental Details

Nanoparticle Solution Preparation

Semi-conducting Polymer Preparation

Organic Field Effect Transistor Fabrication Process and Characterization (Inkjet Printing of Nanoparticle Solution, Polymer Dielectric Layer and Semi-conducting Polymer)

Results and Discussion

Nanoparticle Sintering Characterization

OFET Characterization

Summary

#### 49. TRIODE TYPE CARBON NANOTUBE FIELD EMITTER

Experimental Details

Results and Discussion

Conclusions

## 50.PROTEIN AND POLYMER IMMOBILIZED NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

Methodology

Chemicals and Materials

Experimental Set-up

Analyses

Results and Discussion

Protein Estimation

Conjugation Studies

Magnetic Studies

Microscopy Studies

Cytotoxicity Studies

Leaching Studies

Hyperthermia Studies

Conclusion

## 51.3D STRUCTURES OF NANOWIRES

Methods

Nanowire Growth

TEM Characterization

Image Simulations

Result

Crystal Structure

Image Simulations

Discussion

Summary

## 52.SUPERIOR CONDUCTIVITY OF NANOPARTICLES

Experimental Details

Synthesis of Nanocomposites

Characterization

Results and Discussion

Conclusions

## 53.STRUCTURAL AND ELECTRONIC PROPERTIES OF ZnO

NANOTUBES

Computational Method

Results and Discussion

Conclusions

## 54.SYNTHESIS OF NANOCRYSTALLINE CERAMIC POWDERS

Experimental Procedure

Results and Discussion

Nanocrystalline CeO<sub>2</sub> Powders Through Glycine-Nitrate and Citrate-Nitrate Combustion

Auto-Ignition Synthesis of Monophasic BaTi<sub>4</sub>O<sub>9</sub> and Ba<sub>2</sub>Ti<sub>9</sub>O<sub>12</sub> Powders

Combustion Synthesis of TbO<sub>2</sub>, and MTbO<sub>3</sub> (M = Ba and Sr)

Conclusions

## 55.NANOCLUSTERS ON POLYMER SURFACES

Organization of Nanoparticles on the Polymer Matrices: Why?

Nanoclusters Organization on Polymers: How?

Electrostatic Organization

Covalent Organization

Vander-Waals Organization

Different Preparation Strategies

Nanocomposites Versus Surface Functionalisation

Selection of Polymers

Selection of Clusters

Metallic Nanoclusters

Semi-conducting Nanoclusters

Characterisation Techniques

Selected Applications

Catalytic Applications

Photovoltaic Applications

Biological Applications

Limitations of Cluster Organization on Polymers

Conclusion

**Sample Chapter:**

# Design of Protein Based Nanomachines

## Introduction

Renowned Nanomachines of the Biological Cell Confirm Engineering Principles and Inspire Nanomachine Design

## Definition of a Machine

A combination of rigid or resistant bodies having definite motions and capable of performing useful work. Proteins and protein based polymers constitute the resistant bodies of interest here. Proteins are polypeptides and protein based polymers are composed of repeating peptide sequences in which the repeating unit may be as small as a dipeptide or as large as hundreds of residues. The definite motions of protein arise from changing hydrophobic associations that result in deformations and relaxations of protein chain segments capable of performing mechanical work. The changing hydrophobic associations are also capable of performing a range of other forms of work most commonly chemical work.

A *de novo* design approach using elastic contractile model proteins gives rise to engineering principles. The approach to the elucidation of engineering principles required for the design of protein based nanomachines as reviewed in the following section began with a relatively simple repeating pentapeptide sequence from an extra cellular matrix protein. Then without recourse to an already known protein based machine *de novo* design involving stepwise introduction of compositional changes in elastic contractile model proteins resulted in the demonstration of diverse energy converting capacities. The approach of designing and characterizing elastic contractile model proteins allowed recognition of engineering principles that have now been used as demonstrated in the following section to describe the function of key intracellular protein machines. By this means engineering principles for design of protein based nanomachines have been developed and substantiated.

Nanomachines of living cell confirm engineering principles

*Driving forces for cellular machines differ from those of man made macroscopic machines.* The protein machines within the cell are of nanometer dimensions and require an aqueous milieu in which to function. These protein nanomachines are remarkable structures capable of operating at high efficiencies. In some cases they bear astonishing structural analogy to machines of the macroscopic world even though composed of very different rigid or resistant materials that operate by means of very different forces. The forces that dominate in protein based machines are not so familiar to the mechanical engineer. The forces of hydrophobic association/dissociation and those concerned with the extent of irreversible deformation of single protein chain segments replace gravitation and surface frictional loss of the macroscopic world. The interior of the living cell therefore provides the ultimate site for confirming model protein derived engineering principles for the design of protein based nanomachines.

*The difficulty of determining engineering principles from cellular protein machines.* The compositional complexity of the evolutionarily optimized protein nanomachine of the cell makes difficult a direct attack on elucidating the engineering principles. Rather a *de novo* design approach in which the energies and forces can be dissected by careful control of composition and selection of experimental method provides the opportunity one variable at a time to characterize the energies and forces involved in function. Elastic contractile model proteins capable of a phase transition unique to aqueous systems exhibit the properties essential for revealing the sought after engineering principles.

*Engineering principles from designed elastic contractile model proteins confirmed by crystal structure in two key functional states of three vital cellular protein machines.* Once a set of engineering principles is derived using elastic contractile model proteins these principles can be tested by detailed consideration of cellular

protein machines for which crystal structural detail is available in critical functional states. In the present case the principles are remarkably demonstrated in Complex III of the electron transport chain of mitochondria that produces the proton gradient in the adenosine triphosphate (ATP) synthase of the inner mitochondrial membrane that uses the proton concentration gradient to produce nearly 90% of the ATP for an organism and in the myosin II motor of muscle contraction that uses ATP to produce motion essential to function of the organism.

Nanomachine designs inspired by intracellular protein constructs and properties

An elastic extracellular protein provided the starting point that led to the design of energy converting elastic contractile model proteins. On the other hand the elastic intracellular protein titin composed of a linear array of repeating small globular units functions within the muscle cell as a series of shock absorbing elements that irreversibly absorb energy of deformation. When a single globular element is combined with subtending elastic contractile model protein the potential exists for the detection of single molecular events. As seen by single chain force extension studies using the atomic force microscope (AFM) a single chain of titin globular elements gives a sawtooth profile. Each sawtooth represents a single unfolding globular protein element irreversibly absorbing a unique packet of deformation energy. On the other hand the elastic contractile model proteins give a simple monotonic curve in the AFM single chain force extension curve. By the design of a single globular sensing element subtended by elastic contractile sequences a single chain force extension curve is obtained with a single sawtooth. As a single interaction with the globular element can change the characteristic sawtooth for that globular element it becomes a sensing element for detection of that interaction.

*De Novo* Design of Diverse Elastic Contractile Protein Machines

The potential for more effective design of new protein based nanomachines arises from the previous *de novo* design of elastic contractile model proteins capable of performing the set of energy conversions familiar in living organisms. The set of energy conversions involves the intensive variables of mechanical force pressure chemical potential temperature electrochemical potential and electromagnetic radiation covering the frequency range from the ultraviolet to the acoustic. The interconversions of energy involving the 6 intensive variables result in 15 possible pair wise energy conversions. When chemo chemical transduction (the conversion of one chemical energy into another) electro electrical transduction (the use of the reduction of one redox group to change the reduction potential of another redox group) and energy conversions between different frequencies of the electromagnetic radiation spectra are included the number of 15 expands to 18 classes of pair wise energy conversions.

The initial elastic contractile model protein

The starting protein based polymer was found as a repeating pentapeptide sequence in the mammalian elastic protein elastin. The repeating pentapeptide sequence is glycine valine glycine valine proline or Gly Val Gly Val Pro or simply GVGVP which in bovine elastin is found to repeat as many as 11 times in a single unbroken sequence. High molecular weight protein based polymers of this repeating sequence (GVGVP)<sub>n</sub> were found to be soluble in water at temperatures below 25°C and phase separate on raising the temperature above 25°C to form a more ordered viscoelastic and filamentous state. When cross linked for example by irradiation the resulting elastic sheets swell on lowering the temperature and contract on raising the temperature above 25°C and do so when loaded with a weight. *Thus the cross linked polymer is capable of thermo mechanical transduction.*

Changing hydrophobicity to change temperature range for contraction

Changing the polymer composition by addition of a CH<sub>2</sub> group per pentamer achieved by replacing a Val residue by an isoleucine (Ile I) residue makes the polymer more hydrophobic and the contraction begins at 10°C. When deleting two CH<sub>2</sub> groups by replacing a Val residue by an alanine (Ala A) residue the contraction begins on raising the temperature above 45°C. *Accordingly the temperature at which*

*contraction occurs becomes lower as a polymer becomes more hydrophobic and higher as a polymer becomes less hydrophobic.*

Introduction of functional groups with different states of hydrophobicity

Now it becomes possible to change the temperature of the phase separation by substitution of an aliphatic amino acid residue by an amino acid residue with a functional side chain. For example the charged carboxylate of glutamic acid (Glu E) or of aspartic acid (Asp D) or the charged amino function of lysine (Lys K) are less hydrophobic and more polar than the uncharged (more hydrophobic) state of the side chain. Accordingly changing the pH to form the uncharged side chain lowers the temperature of the transition. When at an intermediate temperature therefore neutralizing the charged side chain lowers the temperature of the transition and drives contraction. *Thus the suitably substituted cross linked polymer becomes capable of efficient chemo mechanical transduction.* Similarly a redox function can be bound to the protein based polymer. Since the oxidized state can be more polar and the reduced state can be more hydrophobic *designed polymers capable of electro mechanical transduction result.*

Phenomenological control of diverse energy conversions

Thus *de novo* designs of diverse energy conversions utilizing elastic contractile model proteins are achieved phenomenologically by exercising design control of the temperature at which hydrophobic association occurs. These protein based motors were not simply derivative of then known biological machines. Subsequent extensive analysis of these phenomenological designs gave rise to new understandings of the factors that control hydrophobic association/dissociation and the nature of entropic elasticity. These new understandings referred to as the hydrophobic and elastic consilient mechanisms become the engineering principles for the design of diverse protein based nanomachines.

Relevance to biology s protein based machines

*Coherence of phenomena between designed elastic contractile model protein machines and biology s protein machines.* When considering coherence of phenomena between the behaviours of elastic contractile model proteins designed for energy conversion and the natural energy converting proteins of the cell the hydrophobically associated state is identified with the contracted (rigor) state of a muscle protein or the taut tense T state of a globular protein such as hemoglobin. Formation of this contracted or T state occurs with loss of hydration. As concerns muscle contraction clinically there are recognized acid rigor (association of protein caused by acids) calcium rigor (contraction caused by excess calcium ion) heat rigor (heating that drives hydrophobic association) and rigor mortis (contraction on loss of ATP e.g. dephosphorylation). These muscle phenomena have demonstrable correlation with the elastic contractile model proteins designed for energy conversion.

Another well characterized protein is hemoglobin with its T (taut) state and R (relaxed) state. Increased temperature favours the T state binding polar oxygen favours the R state that forms with the uptake of water and ionpairing decreases charge to favour the T state. Thus there exists a clear coherence of phenomena.

*Remarkable positive cooperativity of designed elastic contractile model proteins when compared to biology s renowned protein machines.* These elastic contractile model proteins of translational symmetry are designed as chemo mechanical transductional model proteins that exhibit positive cooperativities with Hill coefficients as large as 8. This is a greater positive cooperativity than seen by Monod and others when concerned with symmetries of associating globular proteins. This was not expected from the prevailing view of cooperativity. As stated by Monod One may set aside the simple problem of fibrous proteins. Being used as scaffolding shrouds or halyards they fulfill these requirements by adopting relatively simple types of translational symmetries.

In the popular hemoglobin example the Hill coefficient found for the oxygen binding curve is 3.2 which indicates a degree of positive cooperativity much less than that obtained with the most efficient design of

elastic contractile model proteins. Thus protein structure with translational symmetry is designed to exhibit positive cooperativity that is central to efficient function (e.g. energy conversion) of nanomachines and exceeds the positive cooperativity considered so remarkable in protein machines of biology.

*Direct demonstrations of relevance of the hydrophobic and elastic consilient mechanisms to biology's protein machines.* Even though these demonstrations of energy conversion by *de novo* designed elastic contractile model proteins proceeded visually and convincingly with the above noted coherence of phenomena suggestions that biology's protein based machines functioned similarly were not well received by specialists in their particular protein machine. These new understandings nonetheless have now been demonstrated to be significant in three key classes of biological energy conversion the formation of the proton gradient in the mitochondrion the use of the proton gradient to produce ATP by ATP synthase and the use of ATP to produce motion essential to life. Thus the important new engineering principles did not arise from examination of the more complex site localized and evolutionarily optimized energy converting machines of biology. Instead the new engineering principles arose from the design preparation characterization and data analysis of relatively simple model proteins. In doing so the model proteins could be designed to perform the energy conversions of biology by simple changes made in an elastic repeating sequence derived from the mammalian elastic fiber a fiber not recognized as an energy converting machine of biology.

Hydrophobic and Elastic Consilient Mechanisms Definitions

*Definition of consilience.* Consilience reflects the presence of a pervasive basic law of nature that underlies otherwise seemingly disparate phenomena. In this case the phenomena involve a diverse set of energy conversions with an underlying common mechanism a common groundwork of explanation in the words of E.O. Wilson. Accordingly the common groundwork of explanation for diverse energy conversions as discovered using designed elastic contractile model proteins is called a consilient mechanism.

*The hydrophobic and elastic consilient mechanisms.* Two inter linked consilient mechanisms have been identified in studies on the *de novo* designed elastic contractile model protein machines and also observed in the energy conversion of biology's protein machines. These are the hydrophobic and elastic consilient mechanisms. They derive their consilience from a general applicability in the former case to all amphiphilic polymers in water and in the latter case to all polymers of whatever composition containing chain segments with a backbone mobility that can become damped on deformation whether by extension compression or repulsion.

## Metastabilities in Nanocrystalline Silicon

Porous silicon (PS) is a form of nanocrystalline silicon and has attracted quite a lot of attention because of the possibility of its wide range of applications in optoelectronic devices gas sensors vapour sensors and chemical sensors. PS consists of nanometer size crystallites of silicon and shows photoluminescence (PL) in the visible in room temperature. The as prepared PS surfaces are naturally terminated with a covalently bonded monolayer of hydrogen but this monolayer does not give protection against chemical absorption and exposure to light. Further it has been found that after short light exposures the dark current (DC) is higher than the annealed state dark current. This higher dark current called persistent photocurrent (PPC) persists for several hours even at room temperature. It has been reported that the LS decreases PL and increases electron spin resonance (ESR). Some of these changes are partly reversible with annealing. Some authors have found that PL does not change when the light soaking is done with the sample in vacuum or in nitrogen atmosphere. On the other hand Matsumoto have reported that for long exposures the dangling bond density (ESR) increases and PL decreases for their sample. Therefore there is a need to study these phenomena more closely.

In this paper it has been reported for the first time that the dangling bond density in the nanocrystalline



silicon decreases after light exposures of short durations. This is accompanied by an increase in DC photocurrent (PC) and PL. Rapid cooling from high temperatures to room temperature also gives an increase in DC PC and PL and a decrease in ESR signal. Such an increase in DC after fast cooling has been observed by various authors in doped hydrogenated amorphous silicon (a Si H) also. However no decrease in ESR has been reported for a Si H. Further for long exposures the changes observed are in the opposite direction to the short exposures and are similar to the well known Staebler Wronski effect in a Si H. Authors suggest that the metastable changes caused by the thermal quenching and light exposures might be related to the structural changes in PS.

## Experimental Procedure

PS layers were prepared by the standard method of electrochemical anodization of boron doped (100) crystalline silicon wafers having resistivity between 0.6 to 1.0  $\Omega\text{-cm}$ . The electrolyte was HF (49%) mixed with equal volume of ethanol. A current density 20 mA/cm<sup>2</sup> was used and a two hours anodization yielded about 70  $\mu\text{m}$  thick PS. Free standing PS were also made by passing 1A current for a few minutes after 2 h of anodization to lift off the PS from the silicon wafer. These gave flakes of size = 2 x 5 mm. After anodization PS was rinsed thoroughly in ethanol to remove HF and dried in air. Freestanding PS samples were mounted on Corning 7059 glass substrate by putting silver paint at the two ends of the sample which also served as electrodes for current measurements. Electrical measurements done on the free standing PS gave results similar to the PS samples attached to the silicon substrate. For the PL and ESR measurements PS removed from the Si wafer in the form of flakes was sealed in 10<sup>-1</sup> torr helium atmosphere in a quartz tube. The samples were annealed at 150°C for 1 h in vacuum 10<sup>-6</sup> torr for removing the effect of previous light exposures if any and slowly cooled (rate 0.5 K/min) to room temperature (state A). ESR was measured using a X band (Varian E 3) spectrometer at microwave power of 5 mW. For PL the sample was excited by a 15 mW He Ne laser (632 nm) and the emitted light was analyzed using a grating spectrometer and a CCD detector. A bias of 40 V was applied for the DC and PC measurements. The samples showed a symmetric sub ohmic I V behaviour upto this voltaged. For thermal quenching experiments the samples were heated in vacuum (10<sup>-6</sup>torr) at 150°C for one hour. Then the heater was switched off and chilled water was circulated without breaking the vacuum through the copper block upon which the sample had been mounted using silver paint. Using this set up we could obtain cooling rates upto 400 K/min.

Light soaking was done in vacuum using heat filtered white light from a 250W tungsten halogen lamp kept at a distance of about 15 Cm. X ray diffraction and atomic force microscopy (AFM) show that our PS consists of crystallites of sizes 2.5 nm and bigger. Our Raman measurements show the presence of a Si H (broad peak  $\sim 480\text{cm}^{-1}$ ) along with a nanocrystalline peak ( $\sim 512\text{cm}^{-1}$ ) whose position and width depend upon the size distribution of crystallites and the stress present in the porous silicon.

## Results

Figure 1 shows the ESR signal of our PS in the annealed state (state A). This ESR signal is asymmetric and is similar to that reported by others. This can be fitted to three signals one isotropic signal with  $g = 2.0055 \pm 0.0006$  (width  $\sim 6.4\text{G} \pm 0.5\text{G}$ ) corresponding to the dangling bonds in a Si and two anisotropic signals having  $g = 2.0081 \pm 0.0006$  (width  $\sim 1.5\text{G} \pm 0.5\text{G}$ ) and  $g = 2.0028 \pm 0.0006$  (width  $\sim 1.8\text{G} \pm 0.5\text{G}$ ). The last two have been attributed to the dangling bonds in PS by some authors.

Fig. 2 shows the variation in current upon light exposures of durations varying between 30s and 4500s. After switching off the light the dark current reaches a value (B1 B8) which is higher than the annealed state (state A) dark current. For short exposures (upto 2700s) the excess DC increases with the duration of exposure (B1 B6 Fig. 2) but start decreasing for long exposures ( $> 3600\text{ s}$  B7 B8 Fig. 2). For very long exposures ( $> 6\text{h}$  not shown) the final state DC value is lower than the state A. This is similar to the Staebler

Wronski effect in a Si H. The excess dark current persists for several hours even at room temperature. Fig. 3 shows the effect of exposing the sample to infrared light ( 3600 s) exposures with a maximum at about 2700s exposure time. For the 900s exposure PL increases by about a factor of 2 and ESR decreases by 70% compared to the initial state A. Also it is seen that for very long exposures ESR increases with a decrease in DC PC and PL. Interestingly ESR shows a minimum at about the same exposure duration (2700s) at which DC PC and PL show a maximum.

Let us now look at the thermal quenching results. Fast cooling from 150°C to room temperature (400 K/min) brings PS to another metastable state (C) which has higher DC PC and PL than the annealed state A. This is also accompanied by a decrease in the ESR signal. The state A can be recovered by annealing at 150°C (1h) and slow cooling but not by IR exposure. Table 1 shows the values of DC PC PL and ESR signal before (state A) and after rapid thermal quenching (state C).

It might be mentioned that the position and shape of the PL and ESR signals do not change significantly after various treatments. It is noted that the increase in DC PC and PL is always accompanied by a decrease in ESR and vice versa. Hence there is an anti correlation between DC PC PL and ESR on one hand and ESR on the other.

## Discussion

The decrease in the ESR signal accompanies an increase in PC and PL for short exposures (

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