Deterministic Silicon Pillar Assemblies and their Photonic Applications

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Cover picture: The left panel top image (SEM) shows tapered Si nanopillars array, fabricated by colloidal lithography and dry etching and the bottom image is corresponding second-harmonic generation intensity graph vs wavelength. In the middle panel, top image is ZnO nanowire grown hierarchically on Si micropyramid arrays by hydrothermal process and bottom image is its total reflectivity graph vs wavelength in comparison to planar Si. The right panel top image (SEM) is showing vertical Si nanopillars in an aperiodic arrangement fabricated by nanoimprint lithography and dry etching for color filter applications and bottom picture shows reflected and transmitted light by the nanopillar color filters.
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Abstract

It is of paramount importance to our society that the environment, life style, science and amusement flourish together in a balanced way. Some trends in this direction are the increased utilization of renewable energy, like solar photovoltaics; better health care products, for example advanced biosensors; high definition TV or high resolution cameras; and novel scientific tools for better understanding of scientific observations. Advancement of micro and nanotechnologies has directly and positively impacted our stance in these application domains; one example is that of vertical periodic or aperiodic nano or micro pillar assemblies which have attracted significant research and industrial interest in recent years. In particular, Si pillars are very attractive due to the versatility of silicon. There are many potential applications of Si nanopillar/nanowire assemblies ranging from light emission, solar cells, antireflection, sensing and nonlinear optical effects. Compared to bulk, Si pillars or their assemblies have several unique properties, such as high surface to volume ratios, light localization, efficient light guiding, better light absorption, selective band of light propagation etc.

The focus of the thesis is on the fabrication of Si pillar assemblies and hierarchical ZnO nanowires on Si micro structures in top-down and bottom-up approaches and their optical properties and different applications. Here, we have investigated periodic and aperiodic Si nano and micro structure assemblies and their properties, such as light propagation, localization, and selective guiding and light-matter interaction. These properties are exploited in a few important optoelectronic/photonic applications, such as optical biosensors, broad-band anti-reflection, radial-junction solar cells, second harmonic generation and color filters.

We achieved a low average reflectivity of ~ 2.5 % with the periodic Si micropyramid-ZnO NWs hierarchical arrays. Tenfold enhancement in Raman intensity is also observed in these structures compared to planar Si. These Si microstructure-ZnO NW hierarchical structures can enhance the performance and versatility of photovoltaic devices and optical sensors. A convenient top-down fabrication of radial junction nanopillar solar cell using spin-on doping and rapid thermal annealing process is presented. Broad band suppressed reflection, on average 5%, in 300- 850 nm wavelength range and an un-optimized cell efficiency of 6.2 % are achieved. Our method can lead to a simple and low cost process for high efficiency radial junction nanopillar solar cell fabrication.

Silicon dioxide (SiO2) coated silicon nanopillar (NP) arrays are demonstrated for surface sensitive optical biosensing. Bovine serum albumin (BSA)/anti-BSA model system is used for biosensing trials by photo-spectrometry in reflection mode. Best sensitivity in terms of limit of detection of 5.2 ng/ml is determined for our nanopillar biosensor. These results are promising for surface sensitive biosensors and the technology allows integration in the CMOS platform.

Si pillar arrays used for surface second harmonic generation (SHG) experiments are shown to have a strong dependence of the SHG intensity on the pillar geometry. The surface SHG can be suitable for nonlinear silicon photonics, surface/interface studies and optical sensing.

Aperiodic Si nanopillar assemblies in PDMS matrix are demonstrated for efficient color filtering in transmission mode. These assemblies are designed using the “molecular dynamics-collision between hard sphere” algorithm. The designed structure is modeled in a 3D finite difference time domain (FDTD) simulation tool for optimization of color filtering properties. Transverse localization effect of light in our nanopillar color filter structures is investigated theoretically and the results are very promising to achieve image sensors with high pixel densities (~1 µm) and low crosstalk. The developed color filter is applicable as a stand-alone filter for visible color in its present form and can be adapted for displays, imaging, smart windows and aesthetic applications.

Keywords: nanopillar, nanowires, nanophotonics, nanofabrication, silicon, photovoltaics, second-harmonic generation, top-down approach, colloidal lithography, color filter, biosensor
Deterministisk Silicon pelare församlingar och deras fotonik användningar

Sammanfattning

Det är av största vikt för vårt samhälle att miljö, livsstil, vetenskap och nöje blomstrar tillsammans på ett balanserat sätt. Några trender i denna riktning är den ökade användningen av förnybar energi, solceller, bättre sjukvårdsprodukter, till exempel avancerade biosensorer; HD TV eller högupplösta kameror; och nya vetenskapliga verktyg för bättre förståelse för vetenskapliga observationer. Framsteg inom mikro- och nanoteknik har direkt och positivt påverkat vår ställning inom dessa tillämpningsområden; ett exempel är vertikala periodiska och icke-periodiska nano- och mikropolärstrukturer som har lockat betydande intresse inom forskning och industri under de senaste åren. I synnerhet kiselpelare är mycket attraktiva på grund av mångsidigheten hos kisel. Det finns många potentiella tillämpningar av kisel-nanopolärstrukturer/-nanotrådstrukturer som sträcker sig från ljusemission, solceller, antireflex till avkänning och icke-linjära optiska effekter. Jämfört med bulkmaterial har kiselpelare och deras strukturer flera unika egenskaper, såsom hög ytta per volym, ljuslokalisering, effektiv ljusledning, bättre ljusabsorption, bandselectivitet för ljusutbredning etc.

Fokus i avhandlingen ligger på tillverkning av kiselpelarstrukturer och hierarkiska ZnO-nanotrådstrukturer på kiselmikrostrukturer med top-down och bottom-up-metoder och deras optiska egenskaper och olika applikationer. Här har vi undersökt periodiska och icke-periodiska kiselnano- och kiselmikrostrukturer och deras egenskaper, såsom ljusutbredning, lokaliseringsverkan, och selektiv styrning och ljusmateria-växelverkan. Dessa egenskaper utnyttjas i några viktiga optoelektroniska/fotoniska tillämpningar, såsom optiska biosensorer, breddbandigt antireflex, radiell-övergångs-solceller och frekvensdubbling och färgfilter.

Vi uppnådde en låg genomsnittlig reflektivitet av ~2,5% med periodiska kiselmikropyramid-ZnO-nanotrådstrukturer på kiselplatta. Tiofaldig ökning i Ramanintensitet observeras också i dessa strukturer jämfört med plant kisel. Dessa hierarkiska kiselstrukturer-ZnO-nanotrådstrukturer kan förbättra prestandan och mångsidigheten hos fotovoltaiska enheter och optiska sensorer. En praktisk top-down tillverkning av radiell-övergångs-nanopolär-solcell med hjälp av spin-on dopning och snabb termisk glödgning presenteras. Breddbandigt dämpad reflektion på i genomsnitt 5% i våglängdsområdet 300-850nm och en icke-optimerad cellverkningsgrad på 6,2% uppnås. Vår metod kan leda till en enkel och billig process för tillverkning av högeffektiva radiell-övergångs-nanopolär-solceller.


Si-polarupptäckningsfrån det experiment med frekvensdubbling i ytskiktet har visat sig ha ett starkt beroende av frekvensdubblingsintensiteten över pelargeometrin. Ytskiktssfrekvensdubbling kan vara lämpligt för icke-linjär kiselfonotik, yt- och gränssnittundersökningar och optisk avkänning. Icke-periodiska kiselpolärstrukturer i PDMS-matris demonstreras för effektiv färgfiltering i sändningsläge. Dessa enheter är utformade med hjälp av "molekylodynamik-kollision mellan hårda sfärer"-algoritmen. Den utformade strukturen modeleras i ett simuleringsverktyg för optimering av färgfilteringsegenskaper som använder 3D-finita tidsdifferensdomänen (FDTD). Den transversella lokaliseringen av ljus i våra nanopelar-färgfilterstrukturer undersöks teoretiskt och resultaten är mycket lovande för att uppnå bildsensorer med hög pixelätthet (~1pm) och låg överhörmning. Det utvecklade färgfiltratet är tillämpligt som ett fritående filter för synlig färg i sin nuvarande form och kan anpassas för visning, avbildningssmart fönster och konstnärliga tillämpningar.
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Retrospection of last few years of my research brings to my mind the names of all those who have guided, helped and encouraged me to accomplish my thesis. I am truly indebted to all of them beyond narratives and altitudes.

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Bikash Dev Choudhury

Stockholm, April 2016
List of papers

Papers included in this thesis and contribution


[Major part of writing, Si pillar fabrication, sample preparation for ZnO growth and major part of optical measurements]


[Major part of writing, processing, device fabrication and characterization, simulations and analysis]


[Major part of writing, fabrication of Si pillar arrays, fabrication of planar test samples for bio-functionalization experiments, electromagnetic simulations and part of analysis]


[Major part of writing, sample fabrication, participated in the measurements, major part of electromagnetic simulations and associated analysis]


[Proposed and adapted the existing (in the group) embedded semiconductor nanopillar concepts/technologies for color filter applications; Major part of writing, major part of fabrication, measurements, electromagnetic simulations and analysis]


[Si pillar array fabrication, part of electromagnetic simulations, part of analysis, minor part in writing]
Other relevant contributions not included in this thesis

Patent application:


Journal paper:


Conference contribution:


# Acronyms

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<th>Acronym</th>
<th>Description</th>
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<tr>
<td>EMT</td>
<td>effective medium theory</td>
</tr>
<tr>
<td>EMA</td>
<td>effective medium approximation</td>
</tr>
<tr>
<td>ARC</td>
<td>antireflection coating</td>
</tr>
<tr>
<td>CMOS</td>
<td>complementary metal-oxide semiconductor</td>
</tr>
<tr>
<td>DL</td>
<td>limit of detection, (biosensor context)</td>
</tr>
<tr>
<td>ICP</td>
<td>inductively coupled plasma</td>
</tr>
<tr>
<td>I-V</td>
<td>current-voltage</td>
</tr>
<tr>
<td>FDTD</td>
<td>finite difference time domain</td>
</tr>
<tr>
<td>FEM</td>
<td>finite element method</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>ICP-RIE</td>
<td>inductively coupled plasma reactive ion etching</td>
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<tr>
<td>IPF</td>
<td>initial packing fraction</td>
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<tr>
<td>LED</td>
<td>light emitting diode</td>
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<tr>
<td>NIR</td>
<td>near-infrared</td>
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<tr>
<td>NP</td>
<td>nanopillar</td>
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<tr>
<td>NW</td>
<td>nanowire</td>
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<td>PDMS</td>
<td>polydimethylsiloxane</td>
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<tr>
<td>PV</td>
<td>photovoltaic</td>
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<tr>
<td>RGB</td>
<td>red, green and blue, (color filter context)</td>
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<tr>
<td>RI</td>
<td>refractive index</td>
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<td>RIE</td>
<td>reactive ion etching</td>
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<tr>
<td>RTA</td>
<td>rapid thermal annealing</td>
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<tr>
<td>SOD</td>
<td>spin-on doping</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SHG</td>
<td>second –harmonic generation</td>
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<tr>
<td>UV</td>
<td>ultraviolet</td>
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<td>ZnO</td>
<td>zinc oxide</td>
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1 Introduction

Silicon is one of the most versatile semiconductor materials for electronics and photonic applications [1, 2]. In fact, there has been a strong emphasis on incorporating active optoelectronic functionalities in silicon technology. In the last few decades there has been lot of research on the utilization of low dimensional Si structures for photonic applications [3].

While migrating from bulk to nano-/sub-micron structures, several material properties also change. One obvious change is in its geometrical appearance in terms of mechanical transformations. Similarly, optical, electrical, transport and thermal properties of nanostructures deviate from bulk [4]. In addition, depending on the size of the structures quantum mechanical behavior can dominate their electronic properties. There has been extensive research to understand the fascinating properties of nano or micro structures and their utilization in a variety of applications ranging from electronics, photonics, renewable energy, security to health care, to meet societal needs [5]. In addition to human innovation, many nano or micro structure related phenomena (e.g. colors, hydrophobicity etc.) are found in nature and have inspired researchers to adapt such functional structures, so called biomimetic or bioinspired structures, in device applications.

If we look at nature, there is a widespread of structural colors mostly generated by light scattering, interference and diffraction by visible wavelength scale nanostructures [6-9]. In several cases, the arrangement of such structures is periodic, more like photonic crystals, and vary in refractive index either one, two or three dimensions. However, the structures can have long range periodicity or short range periodicity or a completely random arrangement, with each case giving rise to different observational optical effects for specific purposes.

There are several birds, butterflies, beetles, and marine animals that exploit periodic photonic nanostructures on their surfaces to change color with viewing angle (iridescence) [10]. On the other hand, the non-iridescent structural colors of the feathers of some birds (e.g. male plum-throated Cotinga) are generally produced by three-dimensional, quasi-ordered nanostructures [11]. On a different note, the dome shaped structures found in ‘moth eyes’, the reason for its dark eyes, is an example of antireflective structures in nature [12]. Such examples from nature, in a way, can act as guiding principles for many practical applications.

In a laboratory environment, nanostructure or micro structure assemblies are fabricated and utilized for many applications ranging from antireflection, sensing, color imaging etc. Broadly speaking, there are two ways to realize these kinds of structures: a top down approach, where one typically starts with a planar substrate and etch it down with particular
patterns to achieve assemblies of nano/microstructures [13-16]; and a bottom up approach, where one builds the nano/microstructure assemblies on a substrate by growth/deposition methods [17]. However, combinations of both approaches are also often used.

Vertical nanostructures, in particular periodic nanopillars arrays have generated lot of industrial and academic interest for their unique properties [18]. Vertical Si nano structures (nanopillar or nanowire) are used for generation of light, sensing applications, solar cells, photo detectors etc. [19-21]. Recently, efforts on aperiodic assemblies of nanostructures are also gaining momentum in fundamental and applied research in nanophotonics. The utility of aperiodic structures has been reported for solar photovoltaics and for antireflection, and useful phenomena such as light localization have been observed which is absent in periodic systems [22-26].

This thesis investigates the fabrication aspects of periodic and aperiodic assemblies of silicon nano and micro pillars in a top down approach and hierarchical ZnO nanowires on Si micro structures combining top-down and bottom-up approaches. The optical properties of the fabricated nano/micro structures are studied experimentally. Electromagnetic simulations of the optical properties of the Si nano/microstructures are also performed both for validation of the experimental observations as well as for the design of the structures for specific optical properties. Selected applications that utilize the designed specific/unique optical properties of the structures are demonstrated. Primarily, optical properties such as light propagation, localization and wavelength selective guiding have been studied for periodic and aperiodic Si nano and micro structures assemblies. These optical properties are advantageously utilized to develop novel anti-reflection coatings, radial junction solar cell, surface sensitive biosensors and color filters; and to demonstrate surface second harmonic generation (SHG).

1.1 Si micro/nano structures for antireflection and photovoltaics

Surface reflection is one of the major problems in many practical applications like solar cells, eye wear etc. In solar cells, reflection at various interfaces leads to overall decrease in efficiency. So lot of academic and industrial research is carried out to overcome this problem. The antireflection strategy using a planar slab of index matching layer is well known. With modern day technologies different non-planar architectures are investigated for omni-directional broadband antireflection. One of the technological approaches in this direction is based on hybrid material systems, which in the broadest sense refers to inorganic-organic materials. In recent times much research interest has been on developing hybrid material systems for various optoelectronic devices. Hybrid material systems, e.g. crystalline ZnO/Si,
combine two or more different materials with different compositional and geometrical forms to enhance overall performances and add new useful properties. One such hybrid system with hierarchical design has found many applications in photovoltaics [27], UV detection [28] sensing [29] and as light source [30].

Si and ZnO Nanowires (NWs) hierarchical system where ZnO NWs are grown over structured Si has advantages such as large surface to volume ratio and tailored refractive index profiles. They can provide superior antireflection properties, higher light absorption [5], enhanced photoluminescence intensity [31] and multi-functionality [32]. Hierarchical ZnO NWs and micropyramid Si solar cell with reflectance of 3.2 % is reported [33]. Si-ZnO hybrid structures can be useful for many applications including antireflective coating (ARC) [33-35], solar water splitting and H₂ generation [36] and sensing [37].

Another important class of nanostructured materials is the nanopillar array. Nanopillar solar cells have several advantages, like antireflective property, broadband absorption, better carrier collection etc. compared to planar bulk solar cells [38-40]. These properties can improve the solar cell’s photon to current conversion efficiency in a cost effective manner. There are several reports where radial junction Si nanopillar or nanowires are used for solar photovoltaic power conversion [41,42]. On the other hand different doping methods are used for the p-n junction formation, including chemical vapor deposition (CVD), solid source dotation (SSD), monolayer doping (MLD) and also spin-on doping (SOD) [43-45]. Normally all these processes are carried out in conventional furnaces and need relatively high temperatures, more than 800 °C and long anneal times. These process conditions could introduce unwanted defects. On the other hand, rapid thermal annealing (RTA) process is a fast process which typically takes 60 s or less and is quite good for shallow doping which is desirable in radial PN junction formation without introduction of defects [46-48]. Combination of SOD and RTA is also reported for doping in nanopillar based devices [49,50].

In this thesis, a combination of dry and wet etch process is used to create different Si based micro and nanostructures, like nanopillars, micropillars, periodic and randomly arranged micro pyramids. A hydrothermal solution-based process is used to grow ZnO NWs on structured Si surfaces to obtain hierarchical ZnO/Si structures. Their optical properties are evaluated by total reflectivity and Raman measurements (paper I). We have also utilized the radial PN junction geometry with Si nanopillar solar cells using SOD and RTA processes. The anti-reflective properties as well as the performance of the fabricated solar cells are evaluated (paper II).
1.2 Si nanopillar arrays for Optical Biosensing

The large demand for highly selective and sensitive biosensors for detection down to single molecule levels has led to several new techniques for biosensing [51-53]. There are several reports on methods to increase sensitivity of optical biosensors using different interrogation approaches [54, 55], materials [56, 57] and technologies [58, 59]. Nanostructure based biosensors with their unique advantages like higher surface to volume ratios and light manipulation, have been widely studied to achieve higher sensitivities [60, 61]. In biosensors based on nanopillars arrays improved sensitivities and signal to noise ratios can be obtained due to the higher effective sensing area for a given volume compared to their bulk counter parts. Nanopillars with vertical orientation can be used for many sensing applications such as fluorescence imaging [62], field enhanced fluorescence analysis [63] and enhancing signal intensity in DNA microarrays [6]. Because of the mature Si micro- and nano-fabrication technologies and superior material quality, structured Si has been increasingly used in different biosensing applications [60, 63-65].

In this thesis, we demonstrate the use of Si nanopillar arrays coated with SiO₂ for biosensing. The utility of the Si nanopillar arrays together with the behavior of light in such structures is investigated both for surface and volume sensing (papers III and VI). Explicit biosensing responses were evaluated by immobilization of BSA protein and the recognition of its specific antibody (anti-BSA) (paper III; chapter 5).

1.3 Surface Second Harmonic (SHG) generation in Si nanopillar arrays

A comprehensive development of Si photonics is stalled mainly by inefficient light emission from silicon (Si) due to its indirect minimum-energy bandgap and its centrosymmetric crystalline structure hindering its use as an electro-optic modulator [3, 66]. Although many other optical functionalities of Si have been incorporated in a single platform with microelectronic devices, functions/devices such as switches, nonlinear optical devices, high speed and low power consumption are still not fully achieved [3,66]. Higher-order (> 2) nonlinearities of Si are used for different optical processes [66,67] but necessitate relatively high optical powers and are not very efficient. The problem in crystalline Si is that the second-order term of the nonlinear susceptibility tensor is forbidden in the dipole approximation due to its centro-symmetric crystal structure and the residual higher-multipole processes are too weak for practical applications [68]. However, if the inversion symmetry can be broken using inhomogeneous strain and/or by structuring (the crystal symmetry is
naturally broken at the surface) second order nonlinear susceptibility can be induced [69-71], thus making processes like second-harmonic generation (SHG) feasible. Surface SHG was originally reported by Bloembergen and Pershan [72] and subsequently experimentally demonstrated [73]. In case of surface SHG from Si, structural and optical field discontinuities can equally contribute [74]. This property has been used to exploit SHG for probing planar surface/interfaces [75,76]. It can perhaps apply for non-planar geometries as well [77-80]. Besides surface SHG, strained sub-100 nm Si nanowires have been demonstrated to enhance SHG [81].

In this thesis, we have investigated surface SHG from hexagonal Si pillar arrays fabricated by a top down approach, including the effects of geometry of the nanopillar and modal analysis. A pump–probe setup in reflection geometry was used for SHG measurements, with the pump wavelength at 1030 nm to generate green light at 515 nm (paper IV; chapter 6).

1.4 Aperiodic Si nanopillar assemblies for color filtering applications

Color is one of the main distinctive properties of vision for living beings. In human eyes colors are distinguished by responsiveness of rods and cones to visible light of different energy/wavelength to perceive different colors. Similarly, color filters enable selection of individual colors or wavelength bands from white light, hence are key components for color imaging and display. Color pigments and dyes are the most commonly used materials in color filters. Such filters rely on material selective absorption in the visible band [82,83]. There are other means of color generation, so called structural colors, based on the interaction of light with wavelength/sub-wavelength scale structures along with the material properties. A given material but with different structuring can, in principle, give different colors. This attractive solution for color filters might offer possible ways of cost reduction. But there are problems to be overcome before they become commercially attractive. For example, transmission color filters based on metallic hole arrays have been reported, but they suffer from low transmission [84]. Similarly, guided mode resonance based and photonic crystal based color filters exhibit a strong angular dependence [84-87]. Nanostructured Si has also been utilized for structural color generation but mostly in reflection mode [88].

Recently, a lot of work has been devoted to comprehend light transport as well localization effects in disordered media [89]. The results indicate several similarities between the electronic and optical wave phenomena in disordered systems for example, disorder induced localization (Andersson’s localization) [90]. Also, aperiodic structures generated in a deterministic route have attracted significant attention in optics and electronics for the
optimization possibilities in their design to obtain specific application relevant properties [91,92]. Thus, it is worth investigating the physical mechanisms in aperiodic photonic nanostructures that can enable better performance and/or unique properties (compared to conventional as well as periodic photonic nanostructures) in photonic applications.

In this thesis, we demonstrate “stand-alone” transmission RGB color filters based on deterministically aperiodic Si nanopillar assemblies embedded in a flexible host matrix. This includes technology development, design, electromagnetic simulations and optical characterization of the color filters. The photonic properties of the assembly (pillar arrangement, pillar geometry and size) including the wavelength dependent optical absorption is used for vivid color filtering in transmission mode. Aperiodic design of Si nanopillar assemblies are implemented to get angle independent color and also transverse light localization properties are examined (paper V; chapter 7).

1.5 Thesis outline
This thesis is structured in eight chapters. Chapter 1 gives an overview of the field including different application areas and briefly discusses the relevance of the thesis work. Chapter 2 describes the most essential background and theory pertinent to this thesis. In chapter 3, the experimental procedures including the fabrication methodology, measurement and characterization procedures are elaborated. Chapter 4 describes broad-band anti-reflection and photovoltaic applications of Si nano and microstructures including hierarchical ZnO NWs on structured Si. In chapter 5 biosensing applications of Si nanopillar are reported. Surface second harmonic generation (SHG) from Si sub-micron/nanopillars is described in chapter 6. In chapter 7 color filtering properties of aperiodic Si nanopillar assemblies is discussed. A summary of the thesis and an outlook discussing the future prospects and potential applications of the thesis work are given in chapter 8.
2 Background and Theory

2.1 Optical properties of Silicon

Since the thesis predominantly deals with Si-based micro-/nano-structures, we give a brief account of the general optical properties of crystalline silicon at room temperature [93]. Figure (2.1a) shows the optical absorption coefficient of silicon as a function of wavelength. Silicon being an indirect bandgap semiconductor, it has a long tail in absorption for above bandgap wavelengths. There is a sharp drop in absorption around 1100 nm, corresponding to the band edge of Si. From a photovoltaic perspective, crystalline Si is a suitable material for solar cells since it has very good absorption in terrestrial solar radiation band [94] (described in the sec. 2.2.3). However, the difficulty in crystalline Si solar cells is that for complete absorption of above band-gap solar radiation the active region is very thick (~ 500 µm). In this regard, nanostructured surfaces can offer a way for enhanced absorption with less material. Appropriate nanostructuring can, in principle, provide broad-band omni-directional antireflection as well as a radial pn junction configuration for the solar cell enabling efficient carrier collection. Besides the use of absorption in structured Si for solar cells, the absorption of Si in the visible wavelength region can be also be utilized for a completely different application context such as transmission color filters. In fact, as described in chapter 7 and paper V, absorption is essential for our color filter.

The refractive index (RI) for Si is shown in fig. 2.1b. Si has an appreciably high refractive index compared to many dielectric materials such as SiO₂, SiNₓ, and this property has made it a very good candidate for optical waveguides and other light confinement applications. The high refractive index of Si can be utilized to design miniature optical devices in the nano or
micron scale for controlling/molding the flow of light as well as for light trapping and localization.

The surface reflectivity is another important property that needs to be considered for device design and practical applications like solar cells, sensors etc. Since this thesis uses a top-down approach to structure Si, the reflectivity of the starting material - flat single crystalline Si substrate is often used as the reference to qualify changes in the reflectivity spectra due to structuring and/or surface coatings. Here we show the measured total reflectivity of (single-side) polished Si for normal incidence (figure (2.1c)). It is clear that reflectivity is significantly high, ~70% in UV to ~30% at 1000 nm; in the green-near IR the variation is not appreciable (40-30%). As discussed in the subsequent sections high surface reflection is a menace for high efficiency solar cells. As shown in this thesis, appropriate surface structures can be developed for broad-band suppression of reflectivity for light harvesting applications (Chapter 4; papers I, II) while for other applications such as biosensors the reflectivity spectra can be modified to obtain particular peaks in reflectivity that are sensitive to refractive-index changes (Chapter 5; papers III and VI).

2.2 Optical properties of Nanopillars

The interaction of light with structured materials (media) is dependent on the structure, which controls the optical field distribution and propagation of light. The structuring of materials basically changes the original geometry and invariably increases surface to volume ratios. Often structuring or structured materials could also refer to surface topography modification of a material(s). The refractive index of structured materials also no longer remains a simple function spatially and varies along different directions depending on the structuring. The detailed arrangement of the structure may also become important in determining the optical properties of structured materials; for example, some optical properties vary considerably between periodic and aperiodic arrangements of nanopillars. However, with reference to periodic nanopillar assemblies most of the optical properties are equally observable in an aperiodic system with some variations [95].

Here, we briefly describe the properties of structured materials wherein at least two of the geometric dimensions of the individual structures are in the sub-wavelength scale. In a simple classification, the photonic nanostructures can be divided in to three different categories, namely zero dimensional particle, one dimensional nanowires placed horizontally and vertical nanopillars (horizontal and vertical orientation is defined with respect to light incidence).
This categorization makes it easy to differentiate phenomena responsible for a particular observation in one structure to another depending on geometry. Referring to Fig. 2.2a,b, when illuminated from the –z direction, localized optical resonances can be excited in the particles and horizontally placed NWs. Here, we have implicitly assumed the refractive index of the substrate is much lower. In horizontal structures light can be confined in the direction of light propagation (z direction) and to some extent in the sideways directions (x and/or y directions). Whereas in vertical pillar arrays/assemblies light propagation (Fig. 2.2 c) is more dominant and their properties can be understood by understanding their wave guiding properties. Also in an assembly of pillars, be it periodic or aperiodic, the length scales, mainly period of arrays or nearest neighbor distance and filling fraction of material are important to evaluate the optical effects and also for modeling of these structures. Thus, it is not only the individual pillars but also their assembly that determines the optical properties [96]. In this thesis, we discuss the vertical nanopillars and their optical properties.

Vertical nanopillar assemblies are very important because of their higher surface to volume ratios and their ability to guide light from visible to infrared spectral range. In vertically oriented Si nanopillar arrays light can couple into a nanopillar from the top with few waveguide modes supported. In fact in subwavelength diameter wires (100 nm or less) coupling of light is possible to the allowed HE_{11} mode [97]. In subwavelength nanopillars, diameter dependent coupling of input plane wave at a select wavelength band of light is prominent and can lead to a dip in the reflection spectrum. In this case, with an absorbing material like Si different color in the reflected light can be produced. In finite length of pillars, only selective wavelengths may be possible to couple due to Fabry–Perot resonances in the vertical direction of pillar [98]. Another important observation of Si pillar arrays is the enhancement of light absorption. This is analyzed as coupling of the array mode to the nanostructure [99]. As explained in [99] the nanopillars can be well absorbing only for

Figure 2.2. Three of the most generic photonic nanostructures; periodic arrangement is shown for simplicity. (a) Zero dimensional nanoparticles. (b) One dimensional nanopillars or wires lying horizontally. (c) One dimensional nanopillars or wires standing vertically.
incident light that efficiently couples to selected modes which also have strong Fabry-Perot resonance between the top and bottom interfaces of the pillars, and are well guided within the silicon pillar.

In this thesis work, we have mostly studied the optical properties of Si nanopillars, related to enhanced absorption, guiding, optical field distribution in the pillars and some geometry related enhancement for different applications.

2.3 Antireflection property and solar cells

While reflection of light gives fascinating effects in nature and artificial structures it is a serious problem in applications like eyewear, solar cells and photo-detectors. For example, unwanted reflection in eyewear can be dangerous particularly while driving. Regarding solar cells, an illustration (Fig. 2.3) is given below to underline how solar cell performance is retarded by reflection or rather how it can be improved by its reduction. Figure 2.3 shows the breakup of different loses in crystalline silicon solar cell illuminated by a 100 mW normalized solar power (radiation). It include loses due to material properties, defects, cell architectures-carrier collection inefficiency, incomplete absorption, resistance and reflection. The reflections lose accounts for the percentage of useful photons lost by reflection at the top surface of the cell. Polished crystalline Si on an average has 33% of reflection, which implies that there is plenty of scope to increase efficiency of the cell by reducing surface reflection.

![Figure 2.3 Loses in crystalline silicon solar cell (rough estimation)](image-url)
In the following we will elaborate different anti-reflection schemes, their evolution, merits and demerits.

The basic theory of suppressing reflection can be understood in the form of refractive index matching slab on the substrate (fig. 2.4a) [100]. For a slab of thickness $m\lambda/4$, where $m$ is an odd number, it follows from Fresnel’s law the reflection ($r$) at normal incidence is

$$r = \left[ \frac{n_{\text{air}}n_s - n^2}{n_{\text{air}}n_s + n^2} \right]^2$$

(2.1)

$$r = 0 \text{ , when } n = \sqrt{n_{\text{air}}n_s}$$

(2.2)

Where $n_s$ is refractive of the substrate, $n_{\text{air}}$ is RI of air, and $n$ is the RI of the slab.

The problem with this type of structure is that it can reduce reflection perfectly at a specific wavelength and only for normal angle of incidence. To make the antireflection effect broadband and omnidirectional, a gradient RI anti-reflection (AR) coating is desirable. Broadband antireflection can be obtained by a graded index layer. In a holistic way, it can be a single graded index layer; the refractive index variation is such that it matches that of air and the substrate at the top and bottom interfaces, respectively. Because of this gradual refractive index increment, out of phase reflected beams can interfere destructively for broad band
illumination, so reducing the overall reflection [101,102]. But it is quite difficult to realize for practical applications.

With the advent of surface structuring techniques, like wet chemical or plasma etching, gradient index can be created on the surface. In a good approximation, for light wavelengths much longer than the period and structure dimensions such structured surfaces (schematically illustrated in Fig. 2.4 c,d) behave like a gradient-index coating with (a depth wise) increasing or decreasing effective RI \( n_{\text{eff}} \) in light propagation direction. The optical properties of this structure can be analyzed by the effective medium theory (EMT) [103]. With EMT it is possible to calculate the reflectivity of structured surfaces of various one-dimensional (1D) antireflection coatings and substrate materials. Structured or rough surfaces can be treated as a multiple layers of homogeneous refractive index film with the effective refractive index varying from substrate and air (fig. 2.5). The effective RI \( n_{\text{eff}} \) of the whole structure can be calculated from the packing fractions \( f \) of the individual structured or rough surfaces; this approach was originally developed by ellipsometric measurement techniques [104].

\[
\text{EMA or EMT methods are well suited for planar graded index or one dimensional arrays of structured surface. But for two or three dimensional wavelength and subwavelength scale structures (arrays) rays optics based methods are insufficient. For such two dimensional arrays of structures, e.g. moth eyes or inverted pyramid or nanopillar/wire arrays more rigorous}
\]

\[
\text{Figure 2.5 : Effective medium approximation (recreated after [106])}
\]

In Bruggeman’s effective medium approximation (EMA) [105] model for homogeneous mixtures of two constituent layers of refractive indices \( n_1 \) and \( n_2 \), we have the relation for effective index, \( n \) for whole structure as

\[
f_1 \frac{(n_2^2 - n^2)}{(n_1^2 + 2n^2)} + f_2 \frac{(n_1^2 - n^2)}{(n_2^2 + 2n^2)} = 0
\]  \hspace{1cm} (2.3)

For multiple numbers of layers, EMA gives (‘i’ is a positive integer):

\[
\sum_{i=1}^{n} f_i \frac{(n_i^2 - n^2)}{(n_i^2 + 2n^2)} = 0.
\]  \hspace{1cm} (2.4)

EMA or EMT methods are well suited for planar graded index or one dimensional arrays of structured surface. But for two or three dimensional wavelength and subwavelength scale structures (arrays) rays optics based methods are insufficient. For such two dimensional arrays of structures, e.g. moth eyes or inverted pyramid or nanopillar/wire arrays more rigorous
methods based on wave optics are needed to fully understand the actual effects. In many cases simple analytical solutions are not possible and numerical methods like finite difference time domain (FDTD) or finite element method (FEM) are required. In this thesis, we used the FDTD method to solve two dimensional arrays of micro and nanostructures for different applications.

In this thesis, we have implemented three dimensional antireflecting hierarchical structures consisting of Si microstructures decorated with ZnO NWs for suppressing reflection. We will discuss more on this in chapter 4.

2.4 Radial junction (pillar) solar cell

In a planar pn junction Si solar cell, contribution to output current is less probable from photo-generated carriers generated deep inside the material as they can recombine before reaching the junction. So, the carrier generation volume should be within a diffusion length of the (collecting) junction. In general, this also requires that the material be highly crystalline and free of non-radiative defects/traps. In radial junction solar cells, carriers generated deeper down in the pillar, especially, for longer wavelength photons, can reach the radial junction quickly before recombination and thereby contributing to current even for a semiconductor with a minority-carrier diffusion lengths shorter than its optical absorption depth [106]. In the radial junction geometry, the pillar can be optically long enough for absorption and at the same time the generated charge-carriers can easily reach the junction or electrode along the shorter radial distances. Also, in a radial junction pillar solar cell light can scatter or reflect from the pillar surface multiple times increasing the optical path length within the cell. Thus the pillar (arrays) geometry can contribute for much better absorption compared to the planar cell and can lead to cost effective efficiency enhancement.

2.5 Solar spectrum

It is needless to say that the solar energy is the principal source of renewable energy. The solar radiation touching the earth is more than sufficient to fulfill our energy requirements if utilized effectively. The solar radiation extends from ultraviolet to far infrared, but as shown in the Fig.2.6 the major portion of the photon flux is between 300 nm to 1800 nm [94].
The above AM1.5 spectrum (fig. 2.6) is for terrestrial solar cell applications and it has collective power density of 1000 W/m² or 100 mW/cm². For crystalline Si solar cell the effective region of the solar spectrum is from 350 to 1100 nm. The excess energy due to absorption of photons with energy much higher than the silicon band gap is dissipated in the form of phonons (carrier relaxation). Secondly, high energy photons are absorbed near the surface and the generated carriers are more prone to non-radiatively recombine at the surface (defects) and reduce photo current response at shorter wavelengths. Photons with less than the band gap of silicon are not absorbed in the cell [107].

Another important aspect of solar energy utilization is the cost-benefit ratio. Higher cost/efficiency ratio is one of the major concerns for useful utilization of otherwise hugely abundant solar energy source. One possibility of cost reduction is to increase the efficiency with less use of materials. Less use of processed materials also has a positive implication for the environment. In this regard, nanostructured and thin film solar cells have been extensively studied for efficiency enhancement and as low cost alternatives for bulk solar cells [106].

### 2.6 Nanopillars and Optical biosensing

In a generic sense, in an optical biosensor, when an input, such as a biomolecule comes in the range of interaction of the sensor it causes a change in the characteristics of the sensor, for example in its reflection or transmission spectrum or output power. The sensitivity of the sensor to a particular species depends on the magnitude of the change in the output signals it returns in a repeatable manner. Fig. 2.7a shows a generic biosensor.
In dielectric nano pillar arrays, selective reflection can be taken to advantage for biosensing. Depending on its lateral dimensions, nanopillars can guide light with a large optical power outside, which can facilitate interaction with the surrounding environment. Thus, control over the optical field distribution is an important aspect that determines the performance of the nanopillar biosensor [108,109]. Another important aspect is the higher surface to volume ratio as this can lead to a sensitive miniaturized biosensor.

In a reflectivity based biosensor, the working principle is based on effective wavelength shifts in the interference fringes in the reflected light spectrum caused by the change of refractive index due to biomolecule attachment. Hence, such sensors are in general called refractive index sensors. In a nanopillar biosensor, binding of biomolecules on the pillar surface induces changes in the effective refractive index of the nanopillar medium. In the presence of biomolecules, wavelength shifts in the interference fringes in the reflection spectrum are observed (fig. 2.7 b). Normally, the wavelength shifts are proportional to the amount of the biomolecule present [110,111].

![Figure 2.7 (a) Schematic of generic biosensor (b) Nanopillar biosensor](image)

In a refractive index sensor, the sensitivity is influenced by the portion of the optical power that interacts with the sample. For resonant refractive index sensors, such as Fabry-Perot sensors, effective refractive index variations due to biomolecules (and their different concentrations) $\Delta n_s$ leads to a spectral shift $\Delta \lambda$ which can be expressed as,

$$\Delta \lambda = \eta \Delta n_s \frac{\lambda}{n_{\text{eff}}}$$

(2.5)

Where $\eta$ is the portion of light intensity that interacts with the sample and $n_{\text{eff}}$ is the effective refractive index experienced by the resonant modes present in the system [112,113].

Since the biosensor system consists of a optical readout section the spectral shift (i.e., the sensitivity) alone does not determine its sensitivity but also the readout accuracy. So it is
important to define the sensor resolution as the smallest possible spectral shift it can detect with selectivity and precision. Hence, the spectral resolution of the readout and its noise parameters are important [114]. The lowest amount of biomolecules a sensor can detect accurately is called the limit of detection (DL) and is related to the sensitivity (S) and resolution (R) of the sensor as:

\[
DL = \frac{R}{S}
\]  

(2.6)

In most of the refractive index biosensors, the concentration of biomolecules and the observed spectral shift is not always linear and can saturate at high biomolecule concentrations. The estimation of DL is discussed further in paper III.

2.7 Second harmonic generation and Si nanopillars

In nonlinear optics, light induced non-linear changes in the optical properties of materials are studied. To observe nonlinear phenomenon sufficiently intense light, usually using high power laser light, is required to modify the optical properties of a material system. The induced polarization \( P \) is described by the following equation [115]:

\[
P = \varepsilon_0 \left[ \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \chi^{(4)}E^4 \cdots \right] \equiv P^{(1)} + P^{(2)} + P^{(3)} + P^{(4)} \cdots
\]  

(2.7)

Where \( E \) is the electric field of light, \( \varepsilon_0 \) is the permittivity of free space. \( \chi^{(2)} \) and \( \chi^{(3)} \) are the second-order and third-order nonlinear optical susceptibilities and so on.

As the nonlinear response of materials depends on the crystallographic orientation and direction of the electric field (\( E \)), it can more conveniently be described by a tensor relationship.

The second-order nonlinear polarization for SHG in tensor form can be written as follows:

\[
P_{(2)} = \varepsilon_0 \sum_{j,k=x,y,z} \chi_{ijk}^{(2)} E_j E_k
\]  

(2.8)

Where \( \chi_{ijk}^{(2)} \) is the 2nd order nonlinear susceptibility and subscripts represents three orthogonal directions. To represent nonlinear polarization in all possible directions, \( \chi_{ijk}^{(2)} \) can be written as a tensor with 27 components, but effectively only 18 and hence in a more simplified version the tensor is written with respect to the nonlinear optical coefficient tensor, \( \sigma_{ij} \) as [116],
In centrosymmetric crystalline materials like Si, all of these 18 components cancel each other due to inversion symmetry and second harmonic generation of light is completely forbidden in this category of bulk materials [117,118].

There are reports on second harmonic generation at a (100) Si surface which is independent of crystal orientation; the only requirement is the electric field component normal to the surface of the material [118-121]. Initial research predicted SHG in centrosymmetric semiconductors to originate from one or two atomic layers at the surface, where the surface normal electric field is discontinuous allowing quadrupole-type surface oscillations of valence electrons. This leads to some finite contributions to $\chi_{ijk}$.

A simplified sketch is shown in Fig. 2.8 for possible SHG in both centrosymmetric and non-centrosymmetric crystals. As seen in Fig.2.8(a), in non-centrosymmetric materials both bulk and surface contributions are possible for SHG generation; whereas in centrosymmetric crystals only surface contribution is possible since the crystal symmetry is broken at the surface.

Room temperature measurements of the SH signal from Si, as expected shows a quadratic dependence on incident intensity, and is spectrally centered at the SH wavelength. Also the

\[
\begin{bmatrix}
    P_x^{(2)} \\
    P_y^{(2)} \\
    P_z^{(2)}
\end{bmatrix} =
\begin{bmatrix}
    d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\
    d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\
    d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36}
\end{bmatrix}
\begin{bmatrix}
    E_x^2 \\
    E_y^2 \\
    E_z^2 \\
    2E_xE_y \\
    2E_yE_z \\
    2E_xE_z
\end{bmatrix}
\] (2.9)

Figure 2.8 Bulk and surface second harmonic generation in (a) non-centrosymmetric (b) Centrosymmetric crystals (redrawn from ref. 115)
second harmonic intensity is strongly dependent on crystal orientation. It was also observed that longer wavelength of input light requires higher average power densities than at shorter wavelengths [120,122].

For a Si (100) oriented surface there can be some non-vanishing components of the nonlinear optical coefficient tensor $d_{ij}$ as shown below [120-122].

\[
\chi^{(2)}_{(100)} = \begin{pmatrix}
0 & 0 & 0 & 0 & d_{15} & 0 \\
0 & 0 & 0 & d_{15} & 0 & 0 \\
d_{31} & d_{31} & d_{33} & 0 & 0 & 0
\end{pmatrix} \quad (2.10)
\]

So the second harmonic contribution from the silicon surface contains a dipole contribution given by,

\[
P^{s,dp}(2\omega) = \chi^{s,dp}_{ijk} E_j(\omega) E_k(\omega) \quad (2.11)
\]

Also a quadrupole contribution is possible because of the discontinuity of the normal component of electric field given by,

\[
P^{s,qp}(2\omega) = \chi^{s,qp}_{ijzz} E_j(\omega) \nabla_z E_z(\omega). \quad (2.12)
\]

So it is evident that there are both dipole and quadruple contributions to surface SHG.

In recent experiments, the surface SHG in nanopillar geometry was demonstrated [78]. There are also reports on SHG from Si surfaces or from Si photonic crystal structures [79,80]. To enhance surface SHG it is desirable to have higher surface to volume ratio and high optical excitation field at the surface. In this context, the pillar geometry is definitely a promising case for investigation.

### 2.8 Photonic nano structures and color filters

#### 2.8.1 Human eye and color vision

It is important to know how our eyes respond and perceive color, while designing imaging or display devices and color filters. In human eyes the photoreceptors - rods and cones - convert information in an optical image into chemical and electrical signals. At low luminance levels ( <1 cd/m²), rods are active for vision, while cones at higher luminance levels (>100 cd/m²). Individual rod receptors have peak spectral responsivity at approximately 510 nm, whereas the three types of cones have responsivities in different parts of the visual spectrum and named as L, M, and S cones.
L refers to long-wavelength, M to middle-wavelength, and S to short wavelength sensitive cones. As shown in Fig. 2.9a the spectral responsivities of the three types of cones overlap unlike typical color filters in physical imaging or displays that have much lesser overlap. This is one of the reasons that color reproduction, as seen by our eyes is often difficult to implement in practical imaging and display systems. The relative distribution of three cone types in the retina is very interesting (Fig. 2.9b). The S cones are much less present throughout the retina compared to the L and M cones and there are twice as many L cones as M cones. The relative proportion of the L:M:S cones is approximately 12:6:1. This is quite important information to understand the formation of images by our eyes and the possible replication in artificial eyes mimicking this imaging system [123].

2.8.2 Colors in nature

Two distinctive categories of structural colors found in nature are the iridescent and non-iridescent colors. These two categories are abundant, if we take the example of the colors of several birds’ feathers generated by structures in the feathers. Detailed analysis of these structures reveals that iridescent color are mostly generated by 1D, 2D or 3D periodic nano or microstructures; whereas non-iridescent colors are generated by 1D, 2D or 3D aperiodic nano or microstructures which range from short range correlated structures to random structures.

One of the examples of iridescent color is the ‘gorget’ (throat feathers) of many hummingbird species [10]. This is due to diffraction of incident light caused by the periodic microscopic structure present in the feathers which diffracts white light to different colors and
as in the case of diffraction color changes with the viewing angles, leading to glowing iridescent display.

On the other hand, in birds like ‘Eastern Bluebird’ (Fig. 2.10a) or ‘Male purple-throated Cotinga’ (Fig. 2.10b) the colors are non-iridescent; i.e. color does not change with viewing angles. These non-iridescent structural colors of the feathers are generally produced by 3D quasiperiodic nanostructures in combination of b-keratin and air in the medullary cells of the feather barbs [124]. For example, channel type nanostructures in Eastern Bluebird (Fig. 2.10c) and sphere nanostructures morphology in the vivid turquoise-blue plumage of the Plum-throated Cotinga (Cotinga maynana) (Fig. 2.10d). The color shows no appreciable change with viewing angle under ambient lighting condition [11].

This is a very interesting observation to consider in the design of our aperiodic nanopillar color filters since it can lead to non-iridescent color from the filter and is of prime importance for image sensors and displays.

Figure 2.10 Example of non-iridescent bird feathers (a) Male Eastern Bluebird (Sialia sialis, Turdidae). (b) Male Plum-throated Cotinga (Cotinga maynana, Cotingidae). (c) Channeltype b-keratin and air nanostructure from back contour feather barbs of S. sialis. (d) Sphere-type b-keratin and air nanostructure from back contour feather barbs of C. maynana. Scale bars (c–d) 500 nm. [Reproduced with permission from ref.124 (Royal Society of Chemistry)]
2.8.3 Quantitative description of color:
Quantitative description of color was developed by the Commission Internationale del’Éclairage (CIE) in 1931 with specification of color stimuli for understanding additive color mixing [125]. It actually defines three primary attributes of color perception, namely:

(i) **Hue** of a given color is how much it appears to be similar to one of the perceived colors: red, yellow, green and blue, or to combination of two of these; (ii) **Brightness** is the intensity of a particular color and can be in the range of black (no brightness) to white (full brightness); (iii) **Saturation** refers to the intensity and pureness of a given hue. A 100% saturation means there is no addition of gray to the hue and it is pure, whereas a hue with 0% saturation appears gray.

![Figure 2.11. a. CIE color-matching functions; b. chromaticity coordinates map](image)

In the 1931 CIE (x, y) scheme the chromaticity coordinates are calculated from the spectral power distribution of the light source or color filters and the CIE color-matching functions x-bar, y-bar and z-bar (Fig.2.11a). In the first step it converts the spectral power distribution (SPD) of light from a source or object into tri-stimulus values X, Y and Z as,

\[
X = \int p\overline{x} \, d\lambda ; \quad Y = \int p\overline{y} \, d\lambda ; \quad Z = \int p\overline{z} \, d\lambda
\]  

(2.13)

where \( p \) is spectral power distribution of the light source or color filter. From the tri-stimulus values the chromaticity coordinates x, y can be obtained as follows:

\[
x = \frac{X}{X + Y + Z}
\]  

(2.14a)

\[
y = \frac{Y}{X + Y + Z}
\]  

(2.14b)
The quantitative description is given by the brightness value $Y$, and the chromaticity coordinates $x$, $y$ represent the color with respect to hue and saturation on the 2D CIE chromaticity diagram. The illustration in Fig. 2.11 (b) shows the representation of color perception (of the spectrum in Fig. 2.11 (a)) in terms of CIE coordinates $x$ and $y$ and it provides a basis for examining color. It can be used to define an image sensor or display device in terms of the human color perception range. The outline shows the full range of perceivable colors. The triangle represents the range covered by red, green, and blue colors accessible to a given process which is referred to as the color gamut [125].

### 2.8.4 Nanophotonic color filter

Color filter is a device which separates different bands of colors from a broadband illumination when transmitted through it or reflected from it (Fig. 2.12a). Color filters are largely used in CMOS image sensors or display devices. In Fig. 2.12 b & c schematic sketches of our nano color filters (NCF) are shown in the color display and image sensor contexts.

![Figure 2.12 a. Generic color filter. Nano color filters (NCF) in (b) display and (c) CMOS image sensor contexts.](image)

In commercial applications, dye or pigment based absorbing color filters are being used. But there are demands to replace these due to resolution issues, shorter life time etc. In recent times structural color filters have attracted extensive interest from both academia and industry due to its advantages such as high resistance and stability with respect to degradation and performance, high compactness, tune-ability, low loss and other functionalities. But there are issues to be solved before they can be commercially viable. For example, as mentioned in chapter 1 metallic hole array, guided mode resonance and photonic crystal based filters suffer from different limitations.
In our filter type, we used selective wavelength band absorption in silicon nanopillar aperiodic arrays (Fig.2.13). It shows the propagation of broadband light at different wavelengths through the nanopillar filter with particular pillar diameters and inter-pillar separations. 465 nm wavelength light is completely absorbed at the top of the pillar itself. 525 nm wavelength light passes through the pillar arrays without much absorption and give rise to considerable light in transmission; whereas 665 nm light is coupled to the pillar when propagating and absorbed significantly. So in our filter color generation is due to both structural and absorption effects (chapter 7, paper V).

Interestingly, because of its aperiodic design it can provide transverse light localization, an effect that can lead to compact high resolution filters.

2.8.5 Transverse localization effect in aperiodic nanopillar assemblies

In an optical system if the refractive index is perturbed in the direction transverse to light propagation but invariant in propagation direction, the incident light wave front can travel through the system with a maximum broadening not more than transverse localization length [126]. Thereafter, light propagates without further broadening and this behavior is similar to light propagation through a random fiber.

Schrödinger-type paraxial equation for monochromatic light can be used to represent this type of propagation [127] as shown below:

\[
\frac{i}{\hbar} \frac{\partial \Psi}{\partial z} = \left[ -\frac{1}{2\kappa} \left( \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} \right) - \frac{k}{n_0} \Delta n(x, y, z) \right] \Psi = \hat{H} \Psi
\]  

(2.15)

where \(z\) is the propagation direction, \(x\) and \(y\) are the transverse directions of propagation, \(\Psi\) is the slowly varying envelope of the field \(E(r, t) = Re [\Psi(x, y, z) \exp( i(kz - \omega t))]\) of frequency
ω and wavenumber k = \omega n_0/c, n_0 is the bulk refractive index and Δn is the change in the refractive index light experiences in the system [126,127].

As discussed in chapter 7 and paper V, with our nano color filter we met the requirement of propagation direction invariant index change by the inherent filter design. The cylindrical Si nanopillars are embedded in PDMS with their axis oriented parallel to the direction of propagation of light, whereas the correlated disorder pattern with respect to xy plane ensures that the refractive index change Δn(x, y) is z invariant within the filter slab.

2.9 Numerical methods

When the dimensions of individual entities of the optical system are of the order of light wavelength, ray optics can’t give accurate analysis of the system but wave optics based methods must be utilized. Although there are many methods, it is difficult to choose a versatile numerical method capable of solving all problems related to nanostructures for photonics. But one has to choose the method according to its suitability to the problem under consideration.

Nanophotonics comprises of a variety of problems, their characteristic solutions and physical observations. Their physical properties are associated with one or several observables or phenomena, which are ways to understand the underlying physics and design new systems. For example, the electric field distribution in a photonic cavity, the scattering cross sections of a nanoparticle or wave propagation in nano waveguide are some observables which need to be modelled properly to understand their consequences or design. For analysis of the physical behavior of complex nanophotonics systems analytical solutions may not be possible, so numerical methods must be considered. The system needs discretization, a physical problem is modeled with respect to a set of appropriate analytical functions defined on a finite or infinite domain. A set of equations, linear or nonlinear, is setup to describe the system and solution of the approximated problem is computed. As in ref [128], the physical observations in a nanophotonics system can be divided into four broad categories: those involving light propagation, light localization, light scattering, or multiscale problems.

In a system involving light propagation the guided modes are studied through their resonance frequency, field distribution and propagation. The coupling efficiency between different entities of a system, e.g., periodic or aperiodic vertical nanopillars is important in many applications such as nanopillar solar cells and sensors. In this thesis, (NP application chapters 4, 5, 6, 7) we have modeled nanopillar based antireflection coatings, biosensors,
SHG and color filters considering different above mentioned optical properties and observations.

Some nanophotonics systems show two or three-dimensional confinement of light below the diffraction limit, possibly with resonant effects or with light localization. In such cases insight into the optical field (vectorial) and intensity distributions is important, for example to understand and design efficient systems like low-threshold lasers [129] or sensors with a high signal-to-noise ratio [130] or transverse Anderson localization of light [126]. Two dimensional (transverse) light localization is discussed with respect to nanopillar color filter technology (chapter 7; paper V) in this thesis.

Scattering of light by nanostructures is measured in terms of scattering, absorption and extinction cross sections [131]. Interaction of light in nanophotonics systems with low dimensional arrays of nanostructures with various geometries, the nanostructures are modeled as scatterer with observables such as reflection, transmission and absorption of light.

In nanophotonic systems involving nonlinear phenomena mere solution of Maxwell’s equations is not enough to obtain all the information. The examples of such system include magneto-optical systems [132] or nonlinear optical effects such as second harmonic generation (SHG) or third harmonic generation (THG) in plasmonic nanostructures [133]. Also systems involving gain media or active optical components need to be complemented by other modeling approaches. Surface second harmonic generation is discussed in chapter 6 and paper IV.

In a differential method like finite difference time domain (FDTD) approach, Maxwell’s equations are directly discretized in time and space using finite differences, the method which is used in this thesis. On the other hand, the finite element (FE) method consists of expanding the electromagnetic fields as local functions in elements. In integral methods Maxwell’s equations are transformed to an integral form through the use of the Green’s functions and discretization is reduced to the nanostructured objects; examples are volume integral equation (VIE) methods and surface integral equation (SIE) methods.

The FDTD method is one of the most popular methods in nanophotonics because it can deal with many different types of problems. In this method, both time and space are discretized, i.e. all spatial and temporal derivatives in Maxwell’s curl equations are replaced by finite difference quotients. The equations are solved for \( \mathbf{E} \) and \( \mathbf{H} \) fields with certain boundary conditions. Below we describe details about the method.

The propagation of electromagnetic wave (e.g. light wave) in vacuum can be described in terms of sinusoidal plane waves with the electric and magnetic field directions are orthogonal.
to one another and the direction of propagation, where the \( E \) and \( H \) fields are in phase, traveling at the speed light \( c \) as shown in Figure 2.14.

![Figure 2.14 Propagation of electromagnetic wave](image)

The interaction and behavior of electric and magnetic fields in free space is given by four sets of Maxwell’s equations, viz,

\[
\begin{align*}
\nabla \cdot \mathbf{D} &= \rho \\
\nabla \cdot \mathbf{B} &= 0 \\
\n\nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\
\n\nabla \times \mathbf{H} &= \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}
\end{align*}
\]

(2.16a) (2.16b) (2.16c) (2.16d)

Where \( \mathbf{E} \) is electric field, also called the electric flux density (V/m); \( \mathbf{H} \) is magnetic field strength (A/m); \( \mathbf{D} \) is electric displacement field (coulomb/m\(^2\)); \( \mathbf{B} \) is magnetic field.

In linear materials, the \( \mathbf{D} \) and \( \mathbf{B} \) fields are related to \( \mathbf{E} \) and \( \mathbf{H} \) by

\[
\begin{align*}
\mathbf{D} &= \varepsilon \mathbf{E} \\
\mathbf{B} &= \mu_0 \mathbf{H}
\end{align*}
\]

(2.17a) (2.17b)

Where, \( \varepsilon \) is the electrical permittivity of the material and \( \mu_0 \) is the magnetic permeability of free space.

With the above substitution we obtain Maxwell’s curl equations,

\[
\begin{align*}
\frac{\partial \mathbf{E}}{\partial t} &= \frac{1}{\varepsilon} \nabla \times \mathbf{H} - \frac{1}{\varepsilon} \mathbf{J} \\
\frac{\partial \mathbf{H}}{\partial t} &= \frac{1}{\mu_0} \nabla \times \mathbf{E}
\end{align*}
\]

(2.18a) (2.18b)
In FDTD methods the above Maxwell’s curl equations are solved temporally. It is common practice in FDTD method to use Yee’s algorithm to solve these equations [16, 17]. The simulated structure is discretized in two interconnected grids constituted in Yee–cells (Fig.2.15). At each lattice point or node the new value of a field vector component is calculated based on its previous value and by the components of the other field vector at adjacent points using a leap-frog scheme. At each position, E and H components at the centers of the grid lines and surfaces are surrounded by four other H or E components. This provides a good picture of 3D space being filled by interlinked collections of Faraday’s and Ampere’s law contours. The scheme is shown in Fig. 2.15.

![Yee–Cells in FDTD method](image)

For accurate modeling the computation time step $\Delta t$ should be such that there is no appreciable field changes between two nodes or in other words distance between two nodes should be much less than the wavelength of light. This situation sometimes leads to very high memory requirements and computation times. For periodic systems, the basic unit cell can be simulated using the Bloch or periodic boundary condition. Solutions are expressed as the product of a plane wave envelope function and a periodic function as below [134].

\[
E_{n+1} = E^n + \frac{\Delta t}{\epsilon} \left( \nabla \times H_{n+1/2} - \sigma E^n \right) \tag{2.19a}
\]

\[
H^{n+1/2} = H^{n-1/2} - \frac{\Delta t}{\mu} \left( \nabla \times E^n \right) \tag{2.19b}
\]

It is worth mentioning that aperiodic or random systems can be quite cumbersome since one has to solve whole structure and periodic or Bloch boundary conditions cannot be used.

In this thesis, we have used a commercial FDTD tool Lumerical FDTD from Lumerical Inc. [135]. It has many key features to model and simulate nanophotonics systems efficiently.
For example, interfaces are a problem for Maxwell’s equations on a discrete mesh, where fields can be discontinuous at interfaces and the positions of the interface cannot be resolved to better than spatial discretization step. Lumerical offers a solution for this in terms of a graded mesh (reduce mesh size near interfaces), conformal mesh technology or combination of both. Conformal mesh technology uses an integral solution to Maxwell’s equations near interfaces and it can handle arbitrary dispersive media.

During simulation, solutions of Maxwell’s equations in time domain are obtained, viz. \( E(t) \) and \( H(t) \). Then to get the field as a function of wavelength, \( E(\lambda) \), or equivalently frequency, \( E(\omega) \) the steady state, continuous wave (CW) field \( E(\omega) \) or \( H(\omega) \) is calculated from \( E(t) \) or \( H(t) \) by Fourier transform during the simulation as per the equation below. And this way one can obtain a broad band result.

\[
E(\omega) = \int_0^T e^{i\omega t} E(t) dt \quad (2.20)
\]

Advantages of FDTD method include very few inherent approximations, so better accuracy; it is a very general technique that can deal with many types of problems; particularly in nanophotonics, arbitrarily complex geometries can be implemented and broadband results can be obtained from one single simulation.

More application specific uses of the simulation tool are mentioned in subsequent chapters.
3 Experimental Methods

3.1 Fabrication methodology

Several process methods, such as colloidal, photo- and nanoimprint lithography, wet-chemical etching, solution chemistry for the growth of ZnO NWs, dielectric layer plasma deposition, dry etching and PDMS film preparation including moulding and embedding nanostructures have been used in this thesis. Here, accounts of some selected processes are given.

Fabrication of Si nano/micropillars (structures) arrays is schematically illustrated in Fig. 3.1. The basic processing can be divided into two broad steps, namely, pattern generation on Si substrate by a lithography technique, which in this thesis is done by either colloidal lithography or nanoimprint lithography depending on the specific requirements, followed by etching of Si to get the nano/micropillars (structures) by wet or dry etching.

![Figure 3.1 Top-down Si nano or micro structure fabrication process flow](image)

In the following sections we will describe different fabrication methods used in this thesis.

3.1.1 Colloidal lithography

Here we briefly describe the colloidal lithography (CL) mask patterning process. Broadly speaking CL is achieved by a self-assembly process of particles from a liquid suspension and in a sense is a deterministic assembly process. The two step CL process used in this thesis
includes monolayer spin casting of colloidal silica particles and subsequent size reduction by plasma reactive ion etching (RIE) process (Fig. 3.2).

The colloidal solution of nano or micro particles is spin coated on a clean Si wafer. As we use aqueous solution of SiO$_2$ particle for our processes, as a first step before spin casting the particles we increase the hydrophilicity of the substrate by oxygen plasma treatment. With appropriate spin recipes on a commercial photoresist spin coater, hexagonal close packed monolayer of SiO$_2$ particles arrays are formed on the substrate. Then SiO$_2$ particles are size reduced in a RIE chamber with Ar/CHF$_3$ chemistry. These silica particles act as etch masks for the subsequent pillar etching process [136].

![Figure 3.2](image)

(a) Particles dispersed on a substrate forming a hexagonal close-packed arrangement. (b) Hexagonally arranged particles after size reduction retain the original periodicity.

In this thesis, we have used colloidal lithography for fabricating hexagonal arrays of nano and micropillars for antireflection, radial junction solar cells, SHG experiments and biosensor applications.

### 3.1.2 Nanoimprint lithography

Although colloidal lithography is a simple process for generating required etch masks, defect free large area/wafer scale patterning is still difficult to achieve. Nanoimprint process is an useful alternative with the possibility of nanoscale pattern generation over large areas in a time efficient manner. We use this process for our NP color filter processing.

The principle of nanoimprinting is shown in fig. 3.3. A hard mold of required nano or micro scale pattern is pressed, at a controlled temperature and pressure, into a photoresist layer coated on the substrate. The photoresist is cured under an elevated temperature or by UV light exposure depending on type of resist used. The imprint of the mold is thus created on the surface of the photoresist and any eventual residual resist layer is removed by O$_2$ plasma-etching [137].
3.1.3 Dry etching of Si

Dry etching techniques have revolutionized the microelectronics and photonics industries due to its versatility in creating different structures. Plasma based etching process is one of the most common in this category. In semiconductor technology, plasma based processes are used in numerous applications like ashing, sputtering, physico-chemical etching, sputter deposition, chemical vapor deposition etc. In semiconductor processing use of plasma for reactive ion etching (RIE) is a major breakthrough. Important plasma types used in RIE are glow discharge plasmas (GDP), capacitive coupled plasmas (CCP) and inductively coupled plasmas (ICP). A simple schematic sketch of an ICP-RIE reactor is shown in Fig. 3.4. Here, the plasma is generated by a RF source where the plasma tends to circulate in the plane parallel to the bottom electrode of the ICP chamber. Inductive coupling is carried out through large 4 to 5 turn coils encircling the plasma chamber. It enables change of ion density and directionality of plasma without significantly disturbing the incident energy of the ions. This leads to higher etch rates and at the same time controlling the etch profile. The forward power can independently control the ion energies. Thus, unlike standard RIE, the ICP-RIE configuration with two RF power sources can to a large extent control the ion density and ion energy,
independently. Bosch process is one of the ICP-RIE etching processes very popular in Si industry. It can give very high etch rates and anisotropic etching profiles [138].

3.1.4 Pseudo Bosch process
For nanopillar fabrication the etching process needs good control on sidewall roughness, less undercut and slower etch rates. The commonly used ‘Bosch’ process however leads to sidewall scalloping and undercuts and is a rather rapid process, not suitable for nanoscale structures. Simultaneous introduction of passivation and etching gases can mitigate the issues of side wall scalloping or roughness and the high etch rates. The gas chemistry used is similar to the Bosch process i.e. SF$_6$/C$_4$F$_8$ and the process itself is called Pseudo-Bosch process. Since more ions are needed to remove the continuously deposited fluorocarbon polymer layer by the passivation gas, the etch rate is significantly less compared to Bosch process, only of the order of 100 nm per minute. Here SF$_6$ is introduced and ionized to provide fluorine ions and radicals to etch silicon with SiF$_4$ as etch product. C$_4$F$_8$ is introduced and ionized to make a polymer chain of CF$_2$ which is deposited on the substrate. This polymer film prevents chemical etching of the silicon. But the milling by the accelerated SF$_x$ and F$_y$ ions in the DC bias electric field can remove the passivation film on the horizontal surfaces faster than the polymer can redeposit. This leads to sidewalls being coated by the polymer but the exposed surfaces can be etched. With slower etch rates and smoother sidewalls, Pseudo-Bosch processes are ideal for nanoscale structure fabrication [138].
In the Pseudo-Bosch process the etch rates, selectivity, nanostructure sidewall profile, and roughness are controlled by a few main parameters which include ICP power, forward power, temperature, chamber pressure and gas flow rates. None the less, the optimized process parameters are reactor specific but have general trends. Keeping other parameters fixed, changing the ratio of the etch gas SF₆ to passivation gas C₄F₈, the sidewall profile can be controlled. Increasing the C₄F₈ flow while keeping the SF₆ flow constant at the optimum flow for near vertical etch profiles, tapered etch profiles can be achieved. This is because with more C₄F₈ there is more deposition of the passivation layer on the vertical wall with time; the top part of the structure gets etched more than the lower part. On the other hand the increase in the SF₆ flow keeping the C₄F₈ flow constant from the optimum flow for near vertical etch profile leads to an undercut or bottom tapered profile. Fig. 3.5 shows the different geometries of nano/micro structures fabricated with the Pseudo Bosch ICP-RIE recipes in our process chamber.

The ICP power controls the plasma density for a given gas flow rate and chamber pressure. With increase in ICP power the amount of ions increase, so both vertical and horizontal etch rates increase. At the same time, the milling (purely physical) rate also increases which reduces mask selectivity as well as the effect of passivation by bombarding the sidewalls (due to the angular ion distribution). So an increase in the ICP power makes the
etching more isotropic. The etch rate can’t be increased indefinitely; there exists an optimum for the ICP power for a given flow rate to get the highest possible etch rate.

An increase in forward power creates a larger electric field between the plasma and the bottom electrode where the substrate is placed. This leads to an increase in the ion energy and physical etching/milling rate increases. This increases mostly the vertical etch rate, but due to ion angular distribution, side wall etching also occurs to some extent. But overall higher forward power leads to more vertical structures. On the other hand due to bombardment of more energetic ion the mask material also get eroded so mask selectivity is sacrificed to some extent.

In our Pseudo Bosch process, a ratio of 1:3 for SF6 to C4F8 is used with chamber pressure of 10 mTorr and the flow of 30 and 90 sccm of SF6 and C4F8, respectively, leads to vertical Si pillar profiles. ICP power is around 600 W combined with a 15 W forward power.

3.2 Optical measurement and material characterization methods
Different measurement and material/device characterization tools such as scanning electron microscopy, secondary ion mass spectroscopy, and spectrophotometry including ellipsometry, micro-Raman spectroscopy and non-linear optical spectroscopy have been used in this thesis. Here, a brief account of some of these techniques is given.

As our structures are in the 100nm to a few micron dimensions, the physical inspection of the structures requires resolution in the nanometer scale. Here, we have used scanning electron microscope (SEM) for physical inspection of the structures. The tool can be used to examine the fabricated samples in top, cross sectional or titled views [139]. The height, diameter, period and slant (side-wall) angle measurements are determined from the captured SEM images and such analysis is used in this thesis extensively.

For measurement of the doping profiles in the RTA processed spin-on doped Si pn junctions, secondary ion mass spectrometry (SIMS) measurements with CAMECA, dynamic SIMS instrument IMS4F was used. The carrier profile is investigated with respect to depth from the surface [140]. For the electrical characterization of radial junction solar cells we have used an in-house solar Current-Voltage characterization set-up. It includes a Solar AM 1.5 simulator (under 1 sun illumination conditions) and an ‘Agilent’ semiconductor device parameter analyzer [141].

3.2.1 UV-visible Spectrophotometer measurements
The reflectivity and transmission measurements are extensively used in this thesis for optical characterization of all the devices and fabricated structures, be it antireflective structures,
SHG, biosensors or color filters. Here we have used PerkinElmer high performance Lambda 950 UV-Visible spectrometer. It includes Labsphere 150 mm integrating sphere for total reflectivity and transmission measurements. It is important to have the integrating sphere for such measurements of structured materials/surfaces due to possible scattering. A simple schematic of the tool is shown in Fig.3.6. Detailed description can be found in ref [142]. With the integrating sphere it is possible to measure the total reflection, i.e. both specular and diffused part together. There is also a possibility to exclude the specular part to get only the diffused part and then by subtracting the diffused part from the total reflectivity one can get the specular part.

Referring to Fig.3.6 the optics of the focusing part can focus the beam at the transmission port or at reflection port or at the center of the integrating sphere. It uses two radiation sources, a deuterium lamp and a halogen lamp, to cover measurement range from ultraviolet to infrared regions. The integrating sphere has two detectors viz., a photo multiplier tube (PMT) detector for wavelength up to 900 nm and a lead sulfide (PbS) detector for the range 860-2500 nm. For reflection measurements, the sample is placed at the reflection port and for transmission measurements it is mounted at the transmission port. The incident light is depolarized by a polarizer-depolarizer assembly. For polarization resolved measurements there is an option for mounting a film polarizer kit (range is from 300 nm to 800 nm) and polarization angle can be rotated from 0 to 180 degree with the help of a stepper motor control with 1 degree precision. For measurement with different angles of incidence (in particular for color filter transmission) we used a simple stack inclination technique, wherein one side of the sample is put on a higher stack and the angle is measured from a simple tangent rule.
4 Antireflection and photovoltaic applications

4.1 Silicon micro-structure and ZnO nano-wire hierarchical assortments

As presented in chapters I and II, the suppression of reflection is a very important factor in the solar cells for efficiency enhancement. A large body of academic and industrial research has been conducted on novel methods and materials to achieve broad-band omnidirectional antireflection. In chapter II, we noted that refractive index engineering is very important for broadband and omni-directional antireflection. Three dimensional structures such as hierarchical Si and ZnO nano/microstructures can be very useful for this purpose.

In this chapter, we describe our experimental investigations on the fabrication of different hierarchical Si-ZnO structures and their performance as antireflective layers. Here, by hierarchical structures we mean dimensional hierarchy – e.g. as in nano on micro. Since different materials (ZnO and Si) are used, it also implies different refractive indices, electronic band-gaps and optical properties. We have fabricated hierarchical ZnO NWs on periodic Si micropyramid or pillar arrays and on random Si micropyramid or pillar assemblies. These different types of hierarchical structures and ZnO NWs on planar Si are compared with respect to their antireflective properties. Fabrication is carried out using a colloidal lithography technique for patterning and both dry etching (ICP-RIE) and wet chemical etching processes are used to fabricate micro pillar and pyramid (hexagonal) arrays. ZnO NWs are subsequently grown on the etched Si structures by a hydrothermal process. Optical properties of the as-fabricated structures are evaluated by total reflectance measurements and Raman spectroscopy. The results are detailed in paper I.

4.1.1 Fabrication processes

A few of the fabricated (representative) structures - Si nanopillar and micropyramid arrays and hierarchical ZnO NW/Si structures - are shown in Fig 4.1. Wet chemical etching of Si by KOH is used for modifying the nanopillar arrays to produce micropyramid arrays [143]. The solution based ZnO NW growth process has advantages like low process temperatures, simple equipment, high growth rate and low-cost, over other processes [144]. In the colloidal lithography process silica particles of 2 and 3 µm diameters are used to create the micro pillar and micro pyramid hexagonal arrays of two different periods. ZnO NWs were grown for different durations to see the effect of geometry, density and length of the ZnO NWs on antireflection behavior.
4.1.2 Measurement

Applicability of the fabricated Si/ZnO NWs structures as antireflection coatings and for enhancement of Raman intensity is evaluated by total reflectivity and Raman measurements (Fig. 4.2).

Fig 4.1 SEM images of the fabricated Si and ZnO NW/Si structures (a) Si micropillar array (b) Si micropillar with 30 minute ZnO nanowire growth (c) Si micropillar arrays with 45 minute ZnO nanowire growth (d) high resolution SEM image of the sample shown in (c), (e) Si micropyramid arrays and (f) Si micropyramid arrays with 30 minute ZnO nanowire growth. [From paper I]

Figure 4.2(a) Measured total reflectivity spectra of various fabricated structures. (b) Measured Raman spectra of different Si and ZnO NWs/Si structures. In (a) and (b) the respective spectra for planar silicon are shown for comparison. [From paper I].
From the total reflectivity results (Fig. 4.2 a) it is evident that Si micro-pyramid/ZnO NWs hierarchical structures gives best possible antireflection down to only 2.5 % of reflection over 300 to 1110 nm wavelength range. Although this structure needs more processing steps it can improve efficiency in photovoltaic devices.

Raman measurements (Fig. 4.2 b) show that structured Si samples with ZnO NWs give two times more intensity than those without ZnO NWs. This increase is probably due to the excitation light trapping and/or the anti-reflective behavior of such structures. This enhancement of Raman intensity by this structure can lead to sensitive optical biosensors.

4.1.3 Conclusion

Here we have demonstrated the fabrication of hierarchical ZnO NWs/micro-structured Si assemblies and evaluated their optical properties. We have measured and compared the total reflectivity of different hierarchical structures for their antireflection performance. The lowest average reflectivity of ~ 2.5 % is achieved with the periodic Si micropyramid-ZnO NWs hierarchical arrays. The Raman measurements indicated 10 fold enhancement in intensity in these structures compared to planar Si. These ZnO NWs/Si hierarchical structures can enhance the performance and versatility of photovoltaic devices and optical sensors.

4.2 RTA processed radial junction Si nanopillar solar cell

Rapid thermal annealing in combination with spin-on doping is implemented in the top down fabrication of Si radial pn junction solar cells. The antireflective and photovoltaic properties of the fabricated radial junction solar cells are evaluated. The spin-on doping (SOD) method is relatively simple and results in pn junction formation radially in the pillar sections and also at regions without pillars. Thus, carriers generated by light absorbed below the pillars can also be collected. In addition such a continuous surface may be beneficial for lower contact resistance compared to axial junction solar cells. Full vectorial electromagnetic (EM) simulations are performed to determine optimal Si pillar array parameters for improved light harvesting by lowering surface reflection and increasing light absorption in the solar cell. The radial junction is formed by appropriate SOD with RTA processes and also the back contact with Al is treated by RTA for Al in-diffusion to Si to make a good ohmic back contact. The top contact is made by a transparent conductive indium tin oxide (ITO) deposited by magnetron sputtering.

SIMS was used to determine the doping profile generated by SOD and RTA for three different temperatures. As the n-type SOD we used Filmtronics- P500 diffusant. For
comparison, we fabricated planar pn junction solar cells made by SOD and RTA and using a commercial planar pn Si wafer. It is important to note that no specific surface passivation or contact optimization was performed for the solar cells. The fabricated planar junction solar cells and the SOD radial junction cells are characterized by current voltage measurements in dark and under 1 sun AM 1.5 illumination. The antireflection property of the structured cells (radial junction cells) is verified by spectrally resolved total reflectivity measurements. Detailed description is given in paper II.

4.2.1 Nanopillar Si solar cell

The architectures of the Si nanopillar solar cell is shown in Fig 4.3 a. We start with a p-type Si wafer, then etch the substrate to form nanopillars by our previously described fabrication procedures. In the next step, the junction is formed by diffusion of the spin-on dopant using RTA process. Then the back p-type and top n-type contacts are made by depositing Al and ITO, respectively (fig 4.3.b). The detail procedure is mentioned in paper II.

We optimise the structuring of the cell with the help of commercial Lumerical FDTD tool. Average absorption in 3000 nm height Si nanopillars and upto 1500 nm in the Si substrate is considered (indicated by dashed lines M1, M2 in the inset of Fig. 4.3 c). The absorption weighted with respect to solar AM1.5 irradiance in 300 nm to 1100 nm wavelength range is calculated for different combinations of pillar average diameters and period while taking in to account the shape of the pillars.

![Figure 4.3](image-url)
4.2.2 Characterization

Dopant profiles with respect to different diffusion (RTA) temperatures evaluated by SIMS measurements are shown on fig 4.4.a. RTA at 1050 °C gives the most appropriate result for the radial junction solar cell processing, considering the pillar diameters.

![Graph showing dopant concentration and total reflectivity spectra](image)

Figure 4.4 (a) Dopant concentration determined by SIMS and (b) measured total reflectivity spectra for the different samples [From paper II].

To quantify the suppressed reflection, here we performed total reflectivity measurements with a UV-Visible spectrometer fitted with an integrating sphere. As shown in Fig. 4.4, for the complete Si NP cell we obtain a nearly flat reflection spectrum with an average 5% reflectivity for the wavelength range from 300 to 850 nm. A slightly higher reflection (between 7-10%) in 300-400nm wavelength range is obtained for the cell without ITO coating. Detailed explanations of the observations are given in paper II.

The current voltage (I-V) measurements are shown in Fig. 4.5 for three different configurations of the Si solar cells (area: 1 cm²). The cells were illuminated by a solar simulator (AM1.5, 1 sun). Here, as shown in previous sections due to the nanopillar architecture we have much reduced surface reflection. Comparing Figures 4.5 (a) and (b) it can be seen that the short circuit current (I	extsubscript{sc}) has increased from 16 mA to 28 mA, clearly indicating the effect of the antireflection in the NP solar cell. On the other hand the open circuit voltage (V	extsubscript{oc}) decreases from 0.55 to 0.5 V and the overall cell efficiency increases to 6.2%. The increased photocurrent in the NP solar cell can be due to the ~ 25 % reduction in surface reflection or may be due to better carrier collection with the radial junction geometry. However, it adversely affects V	extsubscript{oc}. Reduction in V	extsubscript{oc} is attributed to surface defects [145,146] possibly introduced by SOD and dry etch processes. The SOD and RTA processes also
require optimization. Compared to standard planar cells (I-V curve, fig 4.5 (c)), spin-on doped planar cells also show a clear reduction in $V_{oc}$ and efficiency. Clearly, NP fabrication, pn junction formation by SOD and surface passivation has to be optimized in the NP solar cells to improve performance [145,146].

![Fig.4.5. IV measurements for (a) Planar RTA doped Si solar cell (b) radial junction NP Si solar cell and (c) standard planar pn junction Si solar cell [From paper II].](image)

### 4.2.3 Conclusion

In conclusion, here we have experimentally demonstrated radial junction Si solar cell and compared it with planar cells. Efficiency improvement is obtained with the radial junction cell, although much process optimization is necessary for it to reach performance levels of commercial crystalline Si cells. There are possibilities of improvement by surface passivation and electrical contact optimization as well as better control on the doping profile. From an optical point of view it clearly shows broadband suppression of reflection, down to an average of 5%. However, from the present results it is difficult to conclude on relative contributions to the photocurrent from carriers generated in the pillars and those in the material beneath. The nanopillar radial junction Si solar cell returns a 6.2% efficiency. We anticipate further improvements in efficiency by better front and rear electrical contacts, addressing defect related issues and optimizing the NP etching and radial doping processes.
5 Nanopillar optical biosensing

As introduced in Chapter I biosensors are very much in demand for detection of tiny amounts of biomolecules in a selective way. The nanopillar geometry can be useful for this purpose as it has high surface to volume ratio and very good surface sensitivity. In this chapter, we discuss bio-recognition applications of silicon pillars with a SiO$_2$ overlayer. Surface to volume ratio and optical field distributions in Si nanopillars are studied for better sensitivity. Here, we use two sets of Si pillar arrays with SiO$_2$ over-coating. The Si pillars are realized by colloidal lithography and dry etching. Colloidal SiO$_2$ particles having 500 and 1000 nm initial diameters, after appropriate size reduction by RIE were used as etch masks. Spectral shift is measured in the reflection spectra due to effective refractive index change by biomolecule attachment. Biosensing response of the pillar arrays is evaluated by BSA and anti BSA model system. Details of the experimental procedure and biomolecule recognition measurement results are given in paper III. We also investigated Si nanopillar arrays for visible/NIR range optical sensing, the motivation being the availability of low-cost high sensitivity Si detectors and light sources. Similarly, from a manufacturing perspective nanoimprint lithography was employed for patterning. Here, dielectric layers such as SiO$_2$ and SiN$_x$ were used to coat the nanopillar surfaces. As far as refractive-index sensing is concerned, such dielectric coatings mimic biomolecule layers. The investigations include determination of the overall RI change of the medium between the pillar arrays (volume sensor) and localized RI changes induced by surface coatings (surface sensor) (paper VI).

5.1 Si nanopillar array biosensors

Two sets of hexagonal pillar arrays are fabricated by colloidal lithography and dry etching. The period, diameter and height of the pillar arrays of set ‘A’ are 1000nm, 450 nm and 3000 nm respectively; and set ‘B’ has 500 nm, 200nm and 1600nm, respectively (fig.5.1(a) & (b)). The intension of the two sets is to determine the effect of optical field distribution and geometry of the pillars on sensing performance. FDTD Simulations of the spectral reflectivity of the NP arrays were carried out to theoretically evaluate the NP sensors’ responses. As shown in fig 5.1 (c) and (d), light is tightly confined inside the pillar in sample A, whereas in sample B a significant part of the optical field is outside the pillar. Hence in the latter case, the optical field will be effected by changes in the local environment adjacent to the pillars. We simulated their reflection spectra and the spectral shift due to a 20 nm SiO$_2$ extra over layer. It shows that shift in sample B is significantly larger than sample A and correlates with the optical field distribution in these two samples (paper III).
5.2 Biosensor Response

Fourier transform visible and IR (FT-VIS-IR) spectrometry is used for the spectrally resolved reflectivity measurements, which is used to detect/determine the spectral shifts with changes in the effective refractive index when the nanopillar surfaces are covered by biomolecules or due to a specific dielectric layer. BSA proteins are immobilized on the nanopillar surface following the procedure described in paper III. Spectral shifts due to anti-BSA incubation with concentrations of 0.1, 0.5, 1, 2.5, 5, 7, 10 and 20 µg/ml on the BSA immobilized on the pillar surfaces are measured for both samples (fig. 5.3). The Reflection spectra differ significantly in the two samples due to different pillar geometries (fig.5.2). The sensor response data, that is the spectral shift of the reflection peak at 1030 nm (Sample ‘A’) and 1040 nm (Sample ‘B’) with respect to anti-BSA concentration are shown in fig 5.3.

Fig. 5.1 Left, SEM images of Si pillar arrays: (a) 500 nm period and (b) 1000 nm period. Right, Electrical field intensity in (c) Sample A and (d) sample B [From paper III].
The limit of detection (DL) for anti-BSA recognition is estimated by sigmoidal fitting of the spectral shift curves. DL for anti-BSA recognition is found to be 50.8 ng/ml and 5.2 ng/ml for samples ‘A’ and ‘B’, respectively. Considering the simplicity in fabrication and interrogation method in our sensors, it is interesting to note that the results are comparable to previously reported sensing experiments using ring resonators and photonic crystals [147,148].

5.3 Optical RI Sensing by Silicon Nanopillar Arrays

We studied optical sensing properties of Si nanopillar array structures with a hexagonal period of ~530 nm, a height of ~1500 nm and a diameter (top-bottom) of ~280-350 nm for sensing applications in the visible/NIR spectrum compatible with Si photodetector responsivity. Although the highest sensitivities in the Si NP arrays are pre-dominantly reported for the IR region, here a sensing option in the visible/NIR region is assessed as a more practical method; related to the light source and detector type. Similarly, from a manufacturing perspective nanoimprint lithography (NIL) (chapter 3) was investigated for pattern generation. Using silica particles as etch masks, discussed previously, works well for NP fabrication. However, the spherical shape of the mask particle and possibly its density result in in-situ mask erosion by ion bombardment during dry etching. While this mask-erosion is advantageous to produce tapered and conical pillar arrays for anti-reflection purposes, high reflectivity and well defined
reflectivity peaks are desirable for sensing. The imprinted pattern in the NIL resist was transferred to a SiO₂ (etch mask) layer provided on the Si wafer. The SiO₂ layer was deposited by plasma enhanced chemical vapor deposition (PECVD). Subsequently, the Si pillars were etched using a pseudo-bosch process, described in chapter 3. The reflectivity spectra of fabricated Si nanopillars show well defined reflection peaks with appreciable intensities, which are useful characteristics for sensing (paper III). In a sequence of experiments, SiO₂ layers of different thicknesses were deposited on the Si NP arrays by PECVD. Similar experiments were conducted using SiNx (n≈2) which has a higher refractive index than SiO₂ (n≈1.5). The refractive indices of the dielectric layers deposited on planar were independently measured by ellipsometry. For the fabricated Si nanopillar arrays, electromagnetic (EM) modeling and simulations and optical characterization of the reflection spectrum have been performed in order to investigate its (refractive-index) sensing characteristics. The wavelength shifts of characteristic reflection peaks are correlated to RI changes of either the medium between the pillar structures or to local RI changes due to a (thin) RI material layer coverage on the pillar structures. For the change of the RI of the medium between the pillars, the theoretical/simulated refractive index sensitivity is determined.

Simulations of the NP structure for volume and surface sensing in the wavelength range 500 to 850 nm are shown in Fig. 5.4. Well defined peaks in reflection with as high as 10-20% reflectivity are obtained. As expected, with the coating of a dielectric layer the reflectivity peaks systematically red-shift with layer thickness and as expected the peak magnitudes also decrease. As a volume sensor, the highest sensitivity of 384 nm/RIU was found for the reflectivity peak at 805 nm. The simulation data shows a sensitivity of ~0.8 and ~1.5 nm/ nm (at 735 nm) of added layer of SiO₂ and Si₃N₄, respectively. Higher values are obtained at 805 nm: ~1.1 nm and ~1.8 nm/nm for SiO₂ and Si₃N₄, respectively.

Specular as well as total reflectivity measurements were performed, and did not show significant differences in the spectra. Fig. 5.5 shows the specular reflectivity data for the fabricated NP samples. The measurements show the similar trends predicted by simulations. However, the overall measured reflectivity is lower and the position of peaks in the longer wavelength range (as well as peak widths) deviate most likely due to fabrication induced irregularities and the shapes could also differ from that assumed in the simulations. The optical characterization data shows a sensitivity of ~0.6 and ~1 nm/nm of added layer of (around 740 nm) SiO₂ or Si₃N₄, respectively.
Fig. 5.4 Simulated total reflectance spectra for Si NP arrays: (a) reflection peaks shift related to the RI change of the medium between the pillar arrays (volume sensing) and (b) an example of the peak shift due to a change in effective RI of a 10 nm layer (SiO2 or Si3N4) on the pillar structures. (c) and (d) show the linearly fitted curves obtained from data in (a) and (b), respectively. [From paper VI]

Fig. 5.5 Optical characterization of the peak shift in reflectance spectrum for Si NP array sample showing in (a) the total and specular reflectance spectra, in (b) reflectance spectra showing the peak shifts due to an over layer of either SiO2 or Si3N4 and in (c) and (d) the linearly fitted peak shift data as a function of the estimated thickness of the SiO2 and Si3N4 over layer, respectively. [From paper VI].
5.4 Conclusion

Refractive index sensors based on Si nanopillar arrays are developed and proof of principle experiments are performed using surface dielectric coatings and in a bio-sensing context using the BSA-anti-BSA model system. The vertical interrogation method, as used here, is simpler compared to in-plane coupling as in waveguides etc. which, however, are advantageous for on-chip integration. Spectrally resolved reflectivity measurements of the vertical NP arrays are used to determine the reflectivity peak shifts induced by refractive index changes in the structure by the presence of biomolecules etc. In the BSA-anti BSA biosensing experiments, achieved sensitivity was as high as 5.2 ng/ml. The optical field distribution in the pillars and its surroundings plays a very important role in the performance of these sensors. Highest surface sensitivity is obtained at wavelengths for which Si is not absorbing and for which the guided light in the nanopillars has an appreciable evanescent field probing the surroundings. As a trade-off between best possible sensitivity and practical implementation, NP arrays were also investigated to have higher reflectivity and well defined reflectance peaks in the wavelength range easily accessible with Si photodetectors. The refractive index sensing experimentally tested using dielectric coatings on the NPs shows a sensitivity of ~0.6 and ~1 nm/ nm of added layer (at ~740 nm) SiO₂ or Si₃N₄, respectively. For a reflectivity peak at 805 nm, simulations indicate a sensitivity of 384 nm/RIU (volume sensing) and shifts of ~1.1 nm and ~1.8 nm/nm of added layer for SiO₂ and Si₃N₄, respectively.
6 Surface second harmonic generation with vertical Silicon pillar

In this work, we have explored surface SHG from hexagonal Si pillar arrays. As detailed earlier in chapter II, Si is a centro-symmetric crystal and bulk second order non-linearity is forbidden. Hence, predominantly only surface-related contributions to second order non-linear processes, for example SHG, are present. Methods to enhance light matter interaction at the surface can be investigated to improve surface SHG from Si. Si pillar arrays with different array and pillar geometries are investigated to understand the role of high surface areas and the excitation optical field at the surface regions on SHG. SHG is experimentally observed in the fabricated Si pillar arrays and a strong dependence of the generated SHG on the pillar geometry is evidenced. To understand the experimental observations, we simulated the distribution of the electric field (pump) to show the suitability of a particular structure for enhanced SHG. The enhancement of the SHG intensity is in direct correlation with the optical excitation field with the requirement of higher surface normal component of the E-field. The details of the experimental procedures, observations and findings are presented in paper IV.

6.1 Experimental methods

Here, we fabricated three distinct pillars sample sets namely ‘A’, ‘B’ and ‘C’ as shown on Fig.6.1 using our generic nanopillar fabrication process described in chapter 3. All samples are cleaned by RCA process to remove surface contamination created during the etching process. The SHG measurements were performed at room temperature in reflection geometry with a femtosecond laser pump source operating at 1030 nm wavelength; the pulse duration is 350 fs; repetition rate, 500 KHz; and average power 1.3W. The measured laser spot diameter of 20 µm corresponds to an energy density of 0.65 J/cm². This energy density is well below the damage threshold of Si and previously reported value for SHG with pump wavelength longer than 1000 nm. Thus, laser ablation related effects are not influencing the measurements.

Fig 6.1 (a) SEM images of three different Si pillar array samples; (b) Observed SGH from the three samples shown in (a) [From paper IV].
As can be seen in fig.6.1 (b) the measured SHGs have peaks at 515 nm for all three samples. The observation shows that sample ‘B’ has the highest SHG, more than an order magnitude higher than the others. We further investigated the physical origins behind the experimental observations by detailed analysis with full vectorial analysis of the optical field (pump) distribution using FDTD method.

6.2 FDTD Simulations

To understand observed SHG in the three samples we performed FDTD simulation using commercial Lumerical FDTD tool. We calculate the optical field distribution for the pump wavelength (at 1030 nm) in three modeled pillar array structures.

The results above show that the surface normal E-field intensity is strongly dependent on the pillar dimensions and shape. The integrated surface $\left| \text{Ex} \right|^2$ is proportional to the SHG intensity, for the total available pillar surface area determined by considering hexagonal arrays of pillars in a circular laser spot of diameter 20 µm. The calculated ratio of integrated surface $\left| \text{Ex} \right|^2$ for the three samples A, B and C is found to be 2:12:1. It clearly supports, qualitatively, the observed higher SHG in sample B.

6.3 Conclusion

Here, we have demonstrated and analyzed enhanced surface SHG from Si pillar arrays. A strong dependence of SHG intensity on pillar geometry is experimentally evidenced and is theoretically verified by FDTD simulations in terms of surface normal E-field component. The surface SHG in Si structures together with potential methods for enhancement can be useful for nonlinear silicon photonics, surface/interface characterization and high resolution biosensing.
7 Nanopillar color filter

Color filters are one of the most important components of CMOS image sensor and display devices. It influences the performance of these devices in many ways, from spatial and spectral resolution, cross-talk, color rendering, viewing angle to durability. So novel nanophotonics designs for color filters are in high demand and we can see an extensive research thrust in this direction. In commercial applications, dye or pigment based absorbing color filters have been used. But their replacement by other technologies is deemed necessary due to resolution issues, shorter life time etc. [149,150]. Structural color filters have potential advantages such as high durability, stability, compactness, tuneability, low loss and other functionalities.

Here, we have presented a novel design for nanophotonics color filters using deterministic aperiodic Si nanopillar (NP) assemblies. It is basically a transmission color filter with high color purity and contrast. The device is essentially Si nanopillars in 2D assemblies supported in a PDMS matrix. The NPs are arranged in a correlated disordered manner in 2D assemblies and have specific optical properties associated with their arrangements. Hence, in this context the assemblies are deterministic. The minimum distance between NPs and their diameter are adjusted such that the filter only transmits light of selective wavelength band which corresponds to particular color. For a particular nearest neighbour distance, increase in NP diameter can generate different colors from violet to red on transmission from a white light source. The effective refractive index of the NP arrays changes in a correlated (perturbed) manner in transverse X and Y directions.

The patterns for NP assemblies are generated using a “molecular dynamics-collision between hard sphere” algorithm [151]. The NP assembly is modeled electromagnetically by a 3D finite difference time domain (FDTD) simulation tool for optimization. Nanoimprint lithography is used to get large area patterns. The NP filters are fabricated in a clean room environment for standard semiconductor processing and the whole process chain involved in their fabrication is compatible with standard CMOS processing.

The filter is applicable as a standalone filter for visible color in its present form and in modified versions for display and imaging applications. Other application areas could include aesthetic applications, for example in smart windows. For integrating the filters for display and image sensing applications, the color filters for red, green and blue (RGB) or for other suitable colors such as violet, blue, cyan, green, yellow, orange and red should be arranged in particular mosaic forms.
7.1 Design and fabrication of the nanopillar color filter

For deterministic pattern generation for the aperiodic NP assemblies we have used a physical phenomenon based design routine. Molecular dynamics of collision between hard spheres is utilized in 2-D and implemented in accordance with Lubachevsky-Stillinger algorithm [151]. The details are given in paper V in this thesis. Briefly, a certain number of spherical particles are allowed to collide/evolve inside an imaginary box with hard boundaries (no leakage). After a certain time interval, according to parameters of the particles or physical conditions of collision the particles arrange themselves in a pattern which is some degree of deviation from a hexagonal close packed array. Our control parameter to create aperiodic patterns with different degrees of correlation is the initial packing fraction (IPF) of particles per unit area while implementing the algorithm. In our procedure a 75% IPF gives hexagonal arrays, while decreasing the IPF from 75% gives increased deviation from the hexagonal arrangement but in a correlated manner and leads to aperiodic assemblies. For our NP color filters, we used 70% IPF to generate the aperiodic pattern as shown schematically in Fig.7.1 (a).

![Image](image1.png)

Figure 7.1. (a) Aperiodic pattern of the NP color filter. (b) Fabrication steps of the Si NP color filter. (c) Schematic sketch of a flexible stand-alone NP color filter where Si NPs are embedded in PDMS [From paper V].

The generated aperiodic pattern’s coordinates are used for mask design in nanoimprint lithography for fabrication of NP color filters. The fabrication process steps are
depicted in Fig.7.1 (b) and a schematic sketch of a standalone NP color filter with Si NPs embedded in PDMS is shown in Fig.7.1(c). The fabrication processes start with a crystalline Si wafer and we use top down approach of nanopillar fabrication as described in chapter 3. The fabrication processes include nanoimprint lithography of photoresist on SiO₂ coated Si wafer followed by dry etching (Fig.7.2 (a,b,c)). The bottom (base) part of the nanopillars is undercut following an isotropic ICP-RIE etching recipe for ease of subsequent peel-off process (Fig.7.2(d)). Then NPs are embedded in PDMS by pouring PDMS solution and curing it at 80⁰C and Si NPs are peeled off from Si substrate applying mechanical force on the cured (harden) PDMS. Figures 7.2 (a), (b) and (c) show tilted views of aperiodic assemblies of NPs of three different diameters in descending order for red, green and blue NP filters, respectively.

7.2 Transmission characteristics of the color filters

The transmission spectrum gives quantitative information on color generated by the filter. Fig.7.3a shows the transmission spectra of color filters for the three primary colors, red, green and blue with NP diameters of 100, 140 and 200 nm, respectively. In all the filters the nearest neighbor distance is 430 nm. The transmission spectras are measured through a Perkin Elmer spectrophotometer fitted with an integrating sphere. A polarizer-depolarizer kit is used to completely nullify any inadvertant polarization of the incident light.
The transmission spectra of the RGB filters have some general trends along with independent characteristics. As seen from Fig 7.3(a), all three color spectrums have a peak and have two major dips on either side. These two transmission dips define the transmission pass band of a filter. The first dip position is solely dependent on the diameter of the NP constituting the filter; whereas the second dip position depends both on diameter and nearest neighbour distances. On average, the peak transmission intensity is 65% and rejection is around 10% for all the dips. The full width at half maximum varies from 150 nm to 180 nm for blue to red colors. It is also evident from Fig.7.3b that the reflection has not significantly effected the overall transmission but absorption has played a crucial role on the transmission spectrum of the filter. Table 1 lists the parameters of several of the fabricated NP color filters (for different colors); corresponding information on their (measured) transmission spectra are also included.

**Table 7.1: Geometric and transmission spectra parameters of the fabricated aperiodic NP color filters**

<table>
<thead>
<tr>
<th>Color</th>
<th>NP Diameter (D) nm</th>
<th>Nearest neighbor distance of NPs</th>
<th>NP length (nm)</th>
<th>Transmission peak position (wavelength, nm)</th>
<th>Transmission first dip position (wavelength, nm)</th>
<th>Transmission second dip position (wavelength, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Violet</td>
<td>70</td>
<td>430 nm for all colors</td>
<td>1300 nm for all colors</td>
<td>400</td>
<td>340</td>
<td>535</td>
</tr>
<tr>
<td>Blue</td>
<td>100</td>
<td></td>
<td></td>
<td>430</td>
<td>375</td>
<td>570</td>
</tr>
<tr>
<td>Cyan</td>
<td>120</td>
<td></td>
<td></td>
<td>500</td>
<td>415</td>
<td>610</td>
</tr>
<tr>
<td>Green</td>
<td>140</td>
<td></td>
<td></td>
<td>535</td>
<td>450</td>
<td>645</td>
</tr>
<tr>
<td>Yellow</td>
<td>150</td>
<td></td>
<td></td>
<td>575</td>
<td>470</td>
<td>670</td>
</tr>
<tr>
<td>Orange</td>
<td>170</td>
<td></td>
<td></td>
<td>620</td>
<td>490</td>
<td>675</td>
</tr>
<tr>
<td>Red</td>
<td>200</td>
<td></td>
<td></td>
<td>700</td>
<td>510</td>
<td>760</td>
</tr>
</tbody>
</table>
Fig. 7.4a below shows a photograph displaying the colors transmitted by different NP filters when illuminated with white light from a simple light emitting diode (LED) torchlight. Figure 5 (b) depicts the CIE 1991 color space showing the color coordinates and gamut of our RGB filters.

7.3 Transmission spectral characteristics: Angle, polarization and spatial tuning

One of the major issues for color filter has been the angular dependence of the transmission spectral response and intensity. We have used four different angles other than normal incidence, viz, $20^\circ$, $30^\circ$ and $40^\circ$ off-normal and the measured transmission spectra for the green filter is shown on Fig. 7.5(a). We observe that in the transmission spectra the positions of the first and second dips as well as the peak position are unchanged. The only change we notice is in the transmission intensity which reduces with incidence angle.

It is interesting to check if the filter characteristics can be modified by the spatial separation between the NPs. The PDMS matrix holding the NPs can be expanded uniformly by infusion of certain organic solvents. Such an uniform expansion would change the interpillar separations retaining the original relative arrangement. The spatial expansion is carried out by immersing the filter block in toluene solution for 15 minutes and immediately measuring the transmission spectra, since absorbed toluene can rapidly evaporate from the matrix. In the transmission spectrum (Fig. 7.5 (b)), we observe a clear increase in the full width at half maximum (FWHM) upon expansion; the second dip red-shifts by about 50 nm due to expansion, whereas the position of the first dip remains unchanged.
Due to polarization dependency of conventional color filters, image sensors and display devices use frontend and backplane polarizers to mitigate unwanted effects. However, using polarizers leads to loses decreasing the signal levels and picture sharpness. So it is beneficial to use color filters with polarization orientation insensitivity. Transmission spectra of the color filters (here shown for the green filter) for different incident beam polarizations are shown in Fig. 7.5c. Measurement shows no perceptible difference in the filter’s transmission spectrum for different polarizations: 0°, 45° and 90°.

7.4 Transverse light localization in aperiodic NP assemblies

In an optical system where refractive index is z (propagation direction) invariant but x-y variant, the transverse localization of light can be observed and is strongly dependent on the degree of disorder in x-y plane. To theoretically verify our system for transverse localization phenomenon we simulated three nanopillar arrangements: (i) the hexagonal system, which is perfectly ordered, (ii) with 30% deviation from hexagonal system and (iii) with 70% deviation from the hexagonal one. The deterministic deviations from the hexagonal system result in correlated disordered or aperiodic systems and are realized here by changing the initial packing fraction in the Lubachevsky-Stillinger algorithm. Initial packing fraction of 0.75 that is the minimum possible value for square shaped object gives the hexagonal arrangement. Whereas initial packing fraction of 0.7 and 0.3 give 30% and 70% deviations from the ordered hexagonal system, respectively. The arrangements are such that there are 100 nanopillars per unit area for all three patterns, only the relative inter-pillar positions are adjusted to make it completely ordered or with some percentage of disorder.
Here we have used Lumerical FDTD simulation tool to investigate behavior of light in such correlated disordered NP structures generated deterministically from an ordered system. We used a two micron square plane wave source with normal incidence and monitored the transmitted E-field intensity at the bottom of the filter block (i.e. consisting of the Si NPs in PDMS). The pillars assembly or the filter block extends almost twice the light source area in the transverse directions. Figure 7.6 shows the electric field intensity $|E|^2$ at the bottom of each of three different structures. The peak wavelength of transmission was at 512 nm.

As seen from Fig. 7.6, for the simulated intensity profiles in hexagonal arrangement of nanopillars the intensity profile is diffractive or propagation is ballistic which is showing the hexagonal symmetry of the intensity pattern. When a 30% (weak) disorder is introduced, hexagonal symmetry is lost, the propagation become diffusive and the intensity profile is rather distributed randomly amongst the nanopillar sites. When the disorder is increased to 70%, the output intensity profile becomes narrower. The maximum intensity is accumulated in the center of the filter structure and light is in the weak localization regime and there is no diffraction broadening. These observations are consistent with the reported experimental observation in ref. 152. The traverse localization of light through our color filter, when used in near field could be very attractive for image sensor or display applications to reduce cross-talk as well as to increase pixel densities (~ 1µm). The source wave-front which is quite large in size not only remains un-diffracted but also converges while propagating through the color filter (paper V).
7.5 Conclusion

Deterministic aperiodic Si nanopillar assemblies in PDMS matrix are demonstrated for efficient color filtering in transmission which is designed using the ‘‘molecular dynamics-collision between hard sphere’’ algorithm. The design is electromagnetically modeled in a 3D finite difference time domain (FDTD) simulation tool for optimization of the color filter properties. The nanophotonic aperiodic design makes the performance of the color filters angle and polarization independent. We have theoretically shown that transverse localization is possible with the aperiodic nano color filters. Implementation of this function in the color filters can lead to high resolution image sensors with reduced cross talk. The color filter fabrication is compatible with standard CMOS processing. The color filters are demonstrated as standalone filters for visible colors and with appropriate technological modifications can be integrated in display and imaging devices.
8 Summary and Outlook

Micro and nano scale structures are extensively present in nature from inception and have evolved over time in many ways to serve a variety of useful purposes in various life forms. The advent of modern micro and nanotechnologies has augmented their use in the development of new concepts on materials and devices for societal benefits. Micro and nanostructured materials have demonstrated impact in several application areas bringing new or added functionalities and advantages to several applications, like renewable energy generation, highly sensitive diagnostic devices, better imaging and display devices and advanced scientific tools, to name a few. Nano or microstructured devices in the form of individual or assemblies of vertical semiconductor pillars/nanowires have attracted significant research and industrial interest in recent years. Because of their unique optical and electrical properties, depending on constituent material, dimension and architecture they are worth investigation for novel application possibilities. In this thesis, fabrication of Si pillar assemblies and hierarchical ZnO nanowires on Si micro structures in top-down and bottom-up approaches are investigated. Their optical properties and different applications possibilities are evaluated. Four different application fields have been emphasized and explored: (i) Silicon-ZnO hierarchical structure for antireflection and Si nanopillar arrays for radial junction solar cells; 2. Si nanopillar arrays for biosensing; 3. Silicon pillars for surface SHG and 4. Aperiodic Si nanopillar assemblies for color filters.

We have fabricated different hierarchical Si-ZnO structure by inexpensive colloidal lithography (self-assembly) technique for ordered hexagonal pattern generation, inductively coupled plasma (ICP) dry etching for Si pillar etching and solution chemistry to grow ZnO NWs. The lowest average reflectivity of ~ 2.5 % is achieved with the periodic Si micropyramid-ZnO NWs hierarchical arrays. The Raman measurements indicated 10 fold enhancement in intensity in these structures compared to planar Si. These Si microstructure-ZnO NW hierarchical structures can enhance the performance and versatility of photovoltaic devices and optical sensors. We have proposed and demonstrated radial pn junction Si pillar solar cell. The near surface region of the Si pillars is doped n-type by a spin-on-doping method using rapid thermal annealing. The fabricated cells clearly show reduced average reflection of 5% in 300-900 nm wavelength range. An un-optimized cell efficiency of 6.2% is achieved with our radial junction nanopillar Si cell. There are possibilities of improving efficiency by surface passivation and electrical contacts optimization. The technology could be relevant in the development of thin film Si solar cells.
Higher surface to volume ratio of Si nanopillars and controllable optical field distribution/intensity at the Si nanopillar surface region is used for biosensing and surface second harmonic generation experiments. Conformal SiO$_2$ coated Si nanopillar is utilized for BSA and anti-BSA immobilization/biomolecule recognition testing. Best sensitivity of 5.2 ng/ml is achieved with our nanopillar sensor. The realized sensitivity is promising and comparable to other types of optical biosensors. It has advantages such as mass fabrication possibility and a relatively easier optical interrogation method. We have demonstrated and analyzed enhanced surface SHG from Si nanopillar arrays. Strong geometry dependent SHG intensity is observed from the Si pillars. The enhanced SHG light can be useful for nonlinear silicon photonics, surface/interface characterization and high resolution biosensing.

Aperiodic Si nanopillar assemblies in PDMS matrix is demonstrated for efficient color filtering in transmission. Color filter assemblies is design using “molecular dynamics-collision between hard sphere” algorithm. The design is modeled in a 3D finite difference time domain (FDTD) simulation tool for optimization. The NP filters are fabricated in clean room environment for standard semiconductor processing. Vivid transmitted colors are realized with our aperiodic nanopillar color filters (NCF) with well-defined transmission filter spectra and adjustable FWHM. Due to our nanophotonic aperiodic design we observed that the transmission spectrum is not influenced much by varying incidence angles and polarization orientations. We have theoretically shown that transverse localization is possible with our aperiodic nano filter. This can lead to very high resolution image sensors with reduced cross talk. The overall observed and simulated characteristics of the filters can be useful as standalone filters for visible colors or can be integrated for use as color filters for display and imaging and also for aesthetic applications.

The low reflection with Silicon-ZnO hierarchical structures will be very interesting for making heterojunction solar cell where shorter wavelength part (ultraviolet) of solar radiation can be harvested by ZnO wires whereas visible and near IR part of solar radiation can be harvested by Si cell. For useful utilization of nanopillar architecture for solar photovoltaic application, it is very important to control the doping profile of radial junction. In this regard further investigation on rapid thermal diffusion process with spin on dopant will be interesting. Another important possible direction of research is surface passivation with wet chemical or deposition of passivating layer. Although we have achieved significant broadband reduction in reflection, there is scope of further study in omnidirectional reduction of reflection with optimized device geometry. Also use of non-periodic assemblies of pillars can
be another important focus for enhanced absorption and reduced reflection in thinner solar cell material.

For nanopillar biosensors there is scope of enhancing sensing performance by optimizing pillars and their arrays parameters for increase wettability and surface sensitivity of optical modes. Extension of its use for bio analyzing test other than anti-BSA recognition will be of importance, however this may require intense efforts on surface chemistry and bio-chemistry. In the case of silicon nanopillars for surface second harmonic generation further scope for investigation is anticipated in terms of pillar shape, diameter and period for enhancement of surface normal E-field components for SHG.

Concerning the aperiodic assemblies of silicon nanopillar for color filter application, it is a pioneering work. There is plenty of scope of further research on this. The nanopillar assemblies and individual pillar geometry can be further optimized with more detailed analysis to increase color saturation and color gamut of the filtered colors. One direction is to try different kind of aperiodic designs other than used in this thesis; semiconductor materials other than silicon can be another important direction of investigation. Further theoretical study on transverse localization will be very intriguing and experimental demonstration of light localization phenomena in such structures will be of paramount interest both for fundamental physics and for device applications. Integration of our color filter technology on CMOS image sensor and LCD display device platform is next immediate extension of this work.
Bibliography:


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