UNCONVENTIONAL STRUCTURED SEMICONDUCTORS AND THEIR APPLICATIONS IN OPTOELECTRONICS AND PHOTOVOLTAICS

BY

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DISSERTATION

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ABSTRACT

“Unconventional structured semiconductors” have novel structures that provide improved optical and electrical properties compared with the conventional crystalline semiconductors. Two kinds of semiconductors are discussed within this thesis: gallium nitride (GaN) and silicon (Si).

A novel Pt-assisted electroless etching technique is used to produce porous GaN (PGaN), which is of particular interest for optoelectronics due to its large direct bandgap (3.4 eV). PGaN is also promising for use as a substrate for epitaxial growth and for chemical and biosensing. Several possible applications for PGaN have been explored. PGaN is able to be functionalized for use as a surface enhanced Raman spectroscopy (SERS) substrate by solution-based electroless deposition and vacuum evaporation of Au and Ag. SERS enhancement factors of up to $10^8$ have been observed for Ag-coated porous GaN. Other efforts are focused on using the porous film as conductivity sensors. The improved optical properties observed in porous GaN make it a promising candidate to replace crystalline GaN in ultraviolet photodetector.

Si, an indirect bandgap semiconductors (1.1 eV), is currently used in >90% of the photovoltaic (PV) production. The main limitation of Si solar cell is the high cost of the wafer production. One attractive strategy to reduce the substrate cost is to use ultrathin Si films (1-5 μm thick) combined with effective light trapping methods. We have developed a new capillary-driven self-assembly process to generate three-dimensional (3D) Si structures in millimeter range from a 2D precursor. Based on these 3D Si structures, we have constructed spherical and cylindrical shaped Si
solar cells. These 3D constructs allow the microcells to harvest both the directly incident and diffuse components of sunlight, thereby improving the solar energy conversion efficiency. The output power of the 3D solar cell was observed to be about 2 times as compared to that of a conventional planar Si solar cell with the same thickness and equivalent mass. We also developed a mechanics model that successfully predicts the critical conditions for folding of thin foils with complicated shapes. Further interests are focused on using the micro-structured single crystalline Si sheets/ribbons as the basic structure for novel light trapping photovoltaic devices, including plasmonic solar cells and deployable solar cells.
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CHAPTER 1

INTRODUCTION

1.1 Properties and Applications of Crystalline GaN

Although silicon (Si) is the dominant semiconductor in the electronics industry in terms of usage and applications, there are a number of operating conditions for which Si is not ideal, such as high temperatures, high frequency, high power operation, and exposure to corrosive environments. In addition, because Si is an indirect bandgap material, it is difficult to fabricate optoelectronic devices such as LEDs and lasers based on Si. Gallium nitride (GaN)-based devices would overcome these limitations. GaN is a wide direct bandgap semiconductor ($E_g = 3.4$ eV at 300K), and has several material properties that are superior to Si, such as the high breakdown field (4.0 MV/cm), and a high value of CFOM (489, the figure of merit used to evaluate the suitability of a material for high power, high frequency, high temperature device applications). The key limitation of GaN is the lack of a reliable growth process. Currently, epitaxial growth on a different host substrate is the most widely used method to grow GaN films. The host substrates, however, are limited and not ideal, resulting in very high dislocation densities (up to $10^8$ cm$^{-2}$) in the resulting heteroepitaxial GaN films due to lattice mismatch and differences in thermal expansion between GaN and the substrate materials [1, 2]. Despite the high defects level, many successful devices based on this material have been realized. Recently, epitaxial growth of GaN layers on other substrates, such as single crystal diamond structure, AlN and Si substrates, have been reported [3-5].
In order to discuss the potential applications of porous GaN (PGaN), it is imperative to assess applications of crystalline GaN in sensor and device technology. A summary of the main device applications of crystalline GaN is described below.

### 1.1.1 Optoelectronic Applications

GaN is a suitable material for opto-electronic applications because of its wide, direct bandgap. Furthermore, GaN is able to be alloyed into ternary III-N (AlGaN or InGaN) compounds with either Al or In, allowing bandgap to be tuned over much of the UV and visible spectra range, 1.9 eV (200 nm) to 6.2 eV (650 nm). III-nitrides have become a dominant material in blue and green electronic lighting applications [6-8]. The first GaN-based LED was reported by Pankove, et al., in 1971 [9], but this device was not very efficient. Amano and Akasaki reported the first p-n junction GaN-based LED in 1989 [10]. In the early 1990’s, Nakamura, et al. [11-13] demonstrated high efficient blue-green-light-emitting-diodes created from AlGaN/InGaN. Based on these, blue and green LEDs based on GaN material were commercialized rapidly, and applied widely in portable electronics, displays, etc. Another application based on the luminescent properties of GaN is the GaN-based laser diodes [14].

In addition to light emitting devices, GaN-based ultraviolet photodetectors have also been developed, especially for some applications, where it is important for the detector to be unresponsive to visible light, so-called solar-blind. Historically, photomultiplier tubes were normally used for solar-blind devices, but the equipment is
bulky, and easily damaged. UV-enhanced Si photodetectors have also been developed, but still have several drawbacks [15]. GaN UV photodetectors have become promising in overcoming the limitations of Si-based detectors, and there are a few examples of commercialized devices [15]. Many different types of device architectures based on GaN have been developed for UV photodetection, including simple photoconductors, Schottky diodes, and metal-semiconductor-metal (MSM) devices. Photoconductors show excellent detectivity, but slow response times and slow photoconductivity decay, while Schottky diodes and MSM detectors show improved response time and dark current over photoconductors, but relatively low sensitivity [16-19]. Schottky and MSM detectors have quantum efficiencies of 30-40%, which is competitive with Si-based photodetectors [19, 20], and they exhibit improved solar-blindness and device stability.

1.1.2 Sensing Applications

In addition to the optoelectronic applications, the properties of GaN as a chemical sensor have attracted considerable interest. GaN is often used as a working electrode in an electrochemical cell. The interaction of the solution anions with the Lewis acidic surface Ga atoms creates detectable changes in the anion concentration and pH. GaN- and AlGaN-based devices have also been used to detect hydrogen at high temperatures (200°C – 400°C) [21-26]. These devices may not be used at low temperatures, because H₂ must dissociate and H atom must then diffuse through Pt for the sensor to function. This would not be an issue since most of the applications for
H$_2$ sensing are at high temperatures. There are two different device architectures used to achieve this effect: a Pt/GaN Schottky diode with one ohmic and one Schottky (Pt) contact on the surface of the epitaxial GaN film, and a transistor structure where two ohmic contacts on the surface serve as the source and drain, and a Pt Schottky contact acts as the gate [23-25]. The detection mechanism is that hydrogen gas adsorbs on the Pt surface, dissociates, and diffuses to Pt/GaN interface where it modifies the surface electronic structure and changes the current. These device architectures can be used for sensing other gases as well, such as alkanes, CO, and NO$_x$ species [23-25].

For studies regarding porous GaN, the creation of high surface area GaN would offer possibilities for the improved sensing capability over crystalline GaN. However, the processes to create the porous layers of GaN could also produce considerable changes in the GaN surface chemistry within the pores. Thus the sensing properties of PGaN may be completely different compared to the crystalline GaN.

1.1.3 Extreme Condition Applications

The intrinsic properties of GaN make it possible to create devices operating at high temperature, high power, and high frequency. For example, researchers have found that a GaN based Schottky diode has great durability operating in high radiation exposure conditions [27]. Recently, a variety of device architectures based on GaN material have been created for use in high temperature, high frequency, and high power applications, including Schottky diodes, p-i-n diodes, heterojunction field effect transistors (HFETs), metal-oxide-semiconductor field effect transistors
MOSFETs), and bipolar devices (BJTs) [28-31].

1.2 Potential Applications of Porous GaN

By making crystalline GaN porous, it is possible that new or improved material properties may be created and utilized in a variety of applications. For example, PGaN has a higher surface area than crystalline GaN, and since GaN has been used as a chemical sensor, PGaN may allow a huge increase in sensing capability.

There are a few reports describing enhanced luminescence of PGaN in the literature [32, 33]. The origin of this enhancement is based on the intrinsic properties of GaN films. Epitaxially grown GaN inherently has a large amount of strains and dislocations that are detrimental to the luminescence. Therefore, any material processing method able to eliminate these defects should have a positive effect on the overall luminescence of the material. During the formation of PGaN films, the pores are created and possibly propagate along the defects and remove them from the bulk material, resulting in the improved luminescence of the film. This is an important motivation for creation of PGaN by electroless etching.

Unlike other III-V porous semiconductors, there are no reports describing tunable emission from PGaN. It is commonly accepted that the origin of tunable luminescence for porous semiconductors is the quantum confinement. Two sources for quantum confinement are proposed in porous semiconductors. One is the small, nanometer-scale features produced on the surfaces, and the other is the extremely thin material of the pore walls, which effectively create quantum wells confined within the
porous structures. The requirement for these to occur is that the feature size must be on the order of the Bohr radius of the semiconductor material. For GaN, the Bohr radius is 11 nm [34], too small to be processed even for porous semiconductors. This is probably the reason that tunable emission from PGaN is not available.

The most practical method to grow GaN films is the epitaxial growth technique, such as metallo-organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), and hybrid vapor-phase epitaxy (HVPE). Only limited substrates can be used for GaN epitaxial growth, which is one of the reasons for high fabrication costs of GaN films. Although SiC has the best lattice match with GaN and a similar thermal expansion coefficient, sapphire is the most commonly used substrate, because it is difficult to prepare atomically smooth SiC films, and also GaN-based LEDs grown on sapphire have improved device properties over GaN-based LEDs grown on SiC. A significant amount of strains and dislocations has been found in GaN films grown on sapphire due to the large lattice mismatch (~14%) and big difference in thermal conductivity. However, researchers found that the large amount of defects negatively impacts the device performance. The better substrates for epitaxial growth are still under development.

Porous semiconductors are often proposed as one kind of substrates for epitaxial growth. PGaN is obviously the best choice for epitaxial growth of high quality GaN films because it is inherently lattice matched and has the same thermal expansion coefficient. The pores would also act as sinks for dislocations and strain during growth. There are some literatures describing the use of PGaN for epitaxial growth of
GaN films, and these GaN films have demonstrated improvement in the film quality over conventional substrates [35, 36]. The more concisely morphology control of PGaN will further improve the quality of GaN films.

An increased photoconductivity of PGaN created by electrochemical etching over crystalline GaN is first reported by Mynbaeva, et al. [37]. If the electrolessly etched PGaN has the similar effect, it is possible to construct simple photoconductive detectors based on PGaN. In addition, since Lewis bases are able to interact with the GaN surface [34, 38-42] to cause a change in the local electronic structure of the surface, it should be possible to use these devices for chemical sensing applications based on the change of the photocurrent affected by Lewis base absorption. These devices may have improved sensitivity over conventional GaN devices because of the large surface-to-volume ratio in the porous material.

Crystalline GaN has been reported as a gaseous chemical sensor for alkanes, NO2, CO, and H2 [22, 24-26]. PGaN is promising to improve the sensing capabilities of these devices by taking use of the large surface area of the porous structures. Functionalizing the PGaN surface with Pt makes it possible to create a sensitive, selective H2 sensor with improved properties over the current technology.

There are many other sensing applications based on the large area, nanostructured surface of PGaN. One is to use the PGaN as a template for surface enhanced Raman spectroscopy (SERS) substrate. In general, SERS substrate is an Au or Ag surface with nanostructured features. PGaN offers high surface area, nanoscale features, and a homogeneous morphology over the large surface area, which makes PGaN a good
candidate for SERS application with improved sensitivity and signal uniformity. The nanoscale multi-faced PGaN surface also offers an attractive morphology for a sizeable SERS effect. Additionally, it is possible to create a three dimensional (3D) SERS substrate based on the 3D porous layer.

1.3 Solar Energy and Solar Cells

1.3.1 Solar Energy as a Primary Source of Energy

Solar energy is considered as a major source of energy because it transmits enormous amount of energy, radiant light and heat, to the Earth’s surface every day. The spectrum of solar light at the Earth's surface is mostly spread across the visible and near-infrared ranges with a small part in the near-ultraviolet. The average flux of energy from the sun is 1395 W m\(^{-2}\) (per unit of a surface that is perpendicularly exposed to the flux itself) measured outside the atmosphere at a distance half-way between earth and the Sun [43]. Therefore, the Earth’s surface receives about 1.73 \times 10^{17} \text{ W} of incoming solar radiation [44]. Approximately 30% of this flux is reflected back to space; 47% is absorbed by the atmosphere, oceans and land masses; the remaining 23% is consumed through evaporation, convection, precipitation, and run-off, which characterize the hydrological cycle [43]. Only a small fraction (about 0.03%) is converted into chemical energy by green plants during photosynthesis, which produces nourishment for life itself, and the biomass from which fossil fuels are derived.

The total solar energy absorbed by Earth's atmosphere, oceans and land masses is
approximately $3.85 \times 10^{24}$ J per year, which is as much energy in one hour than the world used in one year [45], and about twice as much as will ever be obtained from all of the Earth's non-renewable resources of coal, oil, natural gas, and mined uranium combined. If the tiniest fraction of that radiation energy is able to be captured, there would be no need to emit any greenhouse gases from any power plant. Solar energy is of course harnessed in different levels around the world depending on a geographical location. The closer to the equator the more "potential" solar energy is available.

Solar energy can be converted into different forms of energy that are useful to humanity, and there are a variety of methods to do this. Solar technologies are normally characterized into either passive or active based on the way they capture, convert, and distribute sunlight. Passive solar techniques use selecting materials with favorable thermal properties to help the design of buildings collecting and transforming solar energy used for passive heating, daylighting and natural ventilation. Through a combination of a high-performance thermal envelope, efficient systems and devices, and full exploitation of the opportunities for passive solar energy, 50 to 75% of the energy needs of buildings as constructed under normal practice can be either eliminated or satisfied through passive solar means [46]. Active solar techniques use photovoltaic panels, pumps, and fans to convert sunlight into useful outputs, such as electricity and heat. They have been widely used in water heating, cooking, and electrical generation, etc. Active solar technologies increase the supply of energy and are considered supply side technologies, while passive solar technologies reduce the need for alternate resources and are generally considered
1.3.2 Solar Cell Devices and Materials

A solar cell is a device that converts the solar energy directly into electricity. The cells are connected in series and parallel to give the desired voltage and current. Solar cells have many small to large-scale applications, from the calculator powered by a single solar cell to off-grid homes powered by solar cell arrays. Historically they have been used in situations where electrical power from the grid is unavailable, such as in remote area power systems, Earth orbiting satellites, consumer systems, etc. Recently solar cells are particularly used in assemblies of solar modules connected to the electricity grid through an inverter.

Solar cells are classified into three generations [47] which indicate the order that each became important. The ‘first generation’ cells are based on silicon wafers. They consist of large-area, high quality and single p-n junction devices, which are capable of generating usable electrical energy from sunlight. First Generation technology is the dominant technology in the current commercial production of solar cells. These devices were initially designed to be high-quality and high-efficiency, which make it difficult to reduce the production cost. A recent study has shown that material costs, namely those of the silicon wafer, would account for over 70% of total manufacturing costs, and module efficiency above 16% is difficult to achieve in the single junction devices [48].

For at least the past 15 years, the advantage of using a thin-film of material was
noted. The solar cell industry has been making a transition to a “second generation” of thin-film solar cell technology. Thin-film technology offers many advantages, such as a major reduction in starting material costs required for cell design by eliminating the silicon wafer usage, and the increase in the size of the unit of manufacturing from that of a silicon wafer (~ 100 cm²) to that of a glass sheet (~1 m²) [47]. However, most of the assembly costs for depositing thin film solar cells are still significantly higher than that for bulk silicon technologies.

Various thin-film technologies have been developed based on the different light-absorbing materials. The first consideration concerning thinner silicon wafers for creating solar cells was made by Wolf and Loferski [49, 50]. With decreasing cell thickness, the open circuit voltage increases due to the reduced saturation current, while the photocurrent decreases due to the weak absorption in thin-film silicon. In their papers, they pointed out the importance of low surface recombination velocities and a good optical confinement to fulfill the advantages of thin-film silicon absorber. Different strategies of light trapping are developed to improve the light absorption efficiency, including back side structuring, front side structuring/passivation, diffuse back side reflector (Lambertian) [51], etc. Nowadays, there is a wide range of research activities that have demonstrated the efficiency potential of thin crystalline silicon with conversion efficiencies of up to 21% under ideal conditions [52].

Amorphous silicon is also widely accepted as a thin-film solar cell material because of its abundance, inherent high absorption coefficient, low materials requirement (1-2 μm thick), low process temperature, and capability for flexible,
large-area deposition. The inherent high disorder (dangling bonds of the order of $10^{19}$/cm$^3$) in the material allows all optical transitions, resulting in the high absorption of light, but acts as recombination centers that greatly reduce the carrier lifetime and pin the Fermi energy level [53]. The density of the defects can be reduced to $10^{16}$/cm$^3$ by incorporation of 10% hydrogen in the film during deposition. The resulting new material, $\alpha$-Si:H has a well-defined optical bandgap at 1.75 eV, and is suitable for doping and alloying with other materials for junction device fabrication. The main problem of this material is the light-induced degradation due to the light-induced creation of metastable defects, known as the Staebler-Wronski effect. Reducing the $\alpha$-Si:H layer thickness can help to solve this problem, but also results in lower light absorption so that the optical confinement techniques are required. A lot of research work on deposition techniques and device structure has been done to support the development of high efficient single-junction and multijunction devices. Other Si-based materials, such as micro/nanocrystalline and polycrystalline silicon films with lower optical absorption compared with the high optical absorption in $\alpha$-Si, have also been extensively studied for solar cell applications [54-57].

Another big category of thin-film absorber is chalcogenide-based material, such as cadmium sulphide (CdS), cadmium telluride (CdTe), and copper indium gallium diselenide (CIGS). These materials have some very desirable properties for high efficiency, low-cost thin-film photovoltaic applications. They are direct bandgap materials with an energy bandgap of around 1.5 eV, which is an ideal bandgap for solar cells. Their high absorption coefficient in visible range means that a layer
thickness of a few micrometers is sufficient to absorb most of the incident photons. High performance solar cells based on CIGS with conversion efficiency of 19.2% has been reported [58]. Even though the efficiency and stability of these devices are very promising, there are several factors that limit the large-scale production of such devices, such as the lack of reliable and precise deposition techniques, high cost of the rare metals, and the difficulty of forming an ohmic contact without degrading the device [53], etc.

Recently, many research activities with organic and mixed organic-inorganic cells have emerged. One general strand is based on dye-sensitization of porous titania films [59], and the other strand is based on the organic light emitting diodes. Organic solar cells have the advantage of using chemically tailored materials with the desired properties and can be fabricated by inexpensive processes to reduce the production costs. However, the organic solar cells have relatively low conversion efficiencies compared with other types of devices and have a stability and durability problem common to conjugated polymers [60]. These problems need to be overcome to meet the demands of the outdoor power market in the future.

Thin-film solar cells are playing an increasing important role in the market, and as thin-film ‘second generation’ technology matures, cost again will become dominated by the constituent material. To progress further, conversion efficiency also must be increased substantially. New concepts of ‘third generation’ solar cells are developed to obtain high performance photovoltaic products while maintaining low cost. These include tandem cells, where efficiency can be greatly increased by
stacking more cells on top of one another, hot-carrier cells based on creating multiple electron-hole pairs per photon, concentrating solar cells, where solar energy is concentrated onto cells to increase the efficiency and output power of the device, and more recently, cells based on excitations between semiconductor energy bands apart from the normal valence and conduction bands [47].

1.4 Three Dimensional Energy Generation

The above discussion highlights two key questions affecting the commercialization of solar cells: (1) How can the conversion efficiency of solar cells be increased to a competitive level with other energy sources? (2) How can the cost of solar cells be reduced to a suitable level for both secondary and primary power generation? [61] These questions lead to some new approaches to tailor the materials more effectively compared with the conventional solar cells. There are a number of concepts for increasing the efficiency of solar cells above the single junction limit (~31% [62]), such as stacking multi-junction cells [63], and intermediate band cells [64]. However, these kinds of solar cells are developed mostly based on the types that receive sunlight with a flat absorbing surface, and they still need a large area to collect sunlight considering the low energy density of solar radiation.

Three-dimensional (3D) architecture is a new concept of energy generation device designs proposed to challenge the conventional two dimensional (2D) photovoltaic systems. The 3D architecture significantly increases the design space for high-performance photovoltaic devices in terms of materials, device structures, and
manufacturing technology. It has multiple promising benefits, including increased theoretical efficiency, new architectures that circumvent material/cost trade-offs, improved performance from non-ideal materials, and increased flexibility in material choices [65].

A variety of designs based on 3D architecture have been developed for high efficiency solar cells. One big group of these designs is based on nanostructured materials: nanocomposites, quantum wells, nanowires, nanoparticles and quantum dots. One of the first examples of using 3D nanostructured materials in solar cells is the dye-sensitized solar cell (DSC), developed by Grätzel and O’Regan [66]. The nanostructured titania film in DSCs, produced by sputtering [67] or electrodeposition [68], is combined with new absorbing molecules to help improve the performance of DSCs. More recent work has attempted to use inorganic nanocomposites [69, 70]. Another example is based on nano/micro-wires. CVD grown Si nanowire solar cells have been demonstrated as potentially low cost alternatives to conventional wafer-based Si photovoltaics [71-74], and simulation results showed that even a sparsely packed array (14%) is expected to absorb moderate (66%) amounts of above bandgap solar energy, yielding a simulated photovoltaic efficiency of 14.5% [75].

Recently, Zhonglin Wang and coworkers have created 3D dye-sensitized solar cells (DSSCs) that are much more efficient than traditional 2D devices. The new device combines optical fibers with ZnO nanowires and dye-sensitized solar cell materials to construct a novel hybrid, 3D structure [76]. The surface area, the most important factor affecting the performance of DSSCs, is increased not only by the
presence of the ZnO nanowires, but also by multiple reflections along the fibers. The conversion efficiency of this new 3D device is reported up to 3.3%, six times more efficient than planar ZnO solar cells with similar surface area [76]. Some further improvements have been developed by Liu [77, 78]. They fabricated a novel 3D solar cell with a spiral photo-electrode instead of the sandwich structure, normally used in the DSSCs. The spiral photo-electrode can increase the effective area to obtain scattered and reflected light, and receive the sunlight from all directions, therefore track the sun passively.

In addition to the nanostructured materials, other solar cell designs are based on 3D structures/shapes. Georgia Institute of Technology developed a 3D solar cell structure by depositing a cadmium telluride thin film on top of carbon nanotube towers, which act as both a scaffolding and electrical interconnect [79, 80]. Multiple light reflections between these towers greatly increase the absorption efficiency. Their theoretical model and computer simulation show that by optimization of parameters to maximize the number of photon interactions, a 3D solar cell can obtain up to a 300% increase in power production over traditional planar cells.

3D architectures have attracted increasing interest for energy generation applications due to their strong potential in 3D light utilization and improved conversion efficiency. 3D cells extend to space to increase the effective area exposed to the sunlight, therefore increase the power generation of the same bottom unit area and reduce the mounting area. The 3D solar cell concept is also a step forward towards large-scale solar energy applications. Future work will be focused on
optimizing the cell’s performance, and improving the stability and durability for practical applications.

1.5 Overview of Thesis

The initial work on developing unconventional structured semiconductors and devices in optoelectronic and photovoltaic applications is described in this document. “Unconventional” means that these semiconductors have novel structures that provide improved optical and electrical properties compared with the conventional crystalline semiconductors. This document includes two parts: porous GaN study (Chapter 2 and 3) and unconventional Si solar cells (Chapter 4 and 5).

Chapter 2 discusses the efforts to develop an electroless etching protocol to create PGaN and the application of PGaN as a template for surface enhanced Raman spectroscopy (SERS). The metal functionalization of PGaN explored in SERS study, which is an important step in many other applications of the material, has the additional benefit of developing metallization protocols that may be applied to future sensor applications.

Chapter 3 details photoconductivity (PC) studies of PGaN. The improved optical properties of PGaN make it a promising candidate to replace crystalline GaN for applications in ultraviolet photodetector and chemical sensing.

Chapter 4 describes the efforts to create three dimensional (3D) solar cells based on thin film single crystalline Si. The 3D solar cell is able to trap light in three dimensions to improve the light absorbing efficiency of the device. The method to
fabricate 3D Si solar cells provides a new way of self-assembly to fabricate 3D structures. A mechanics model is also developed to understand the physics.

The ongoing work and future work on unconventional light trapping solar cells involving plasmonic and deployable solar cells based on single crystalline Si ribbon arrays are discussed in Chapter 6.

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CHAPTER 2

POROUS GaN AS A TEMPLATE TO PRODUCE SURFACE ENHANCED RAMAN SCATTERING (SERS)-ACTIVE SURFACES


Electroless Ag deposition was done by T.L. Williamson, and A. Zukoski, and the associated SERS measurements and figures were captured by T.L. Williamson.

2.1 Abstract

In the work detailed in this chapter, we have sought to create a novel surface enhanced Raman scattering (SERS) active substrate based on the highly anisotropic large surface area of porous GaN (PGaN) template generated by electroless etching. *Fig. 2.1* shows plan-view and cross-sectional scanning electron micrographs (SEM) of PGaN. The porous area created is very uniform and may be created across entire GaN epiwafers. The depth of the porous layer can be controlled by varying the etch solution composition and the time of etching. If the etching time is long enough, the pores can propagate through the entire thickness of the GaN layer. In the studies reported here, the depth of the PGaN layer was kept between 2 and 3 μm. As is evident from *Fig. 2.1* the porous structures produced in GaN are characterized by high aspect ratio, approximately cylindrical pores which impart a large surface-to-volume ratio to the material. Given the optical transparency of GaN above 370 nm, the large, consistent nanostructured area that may be created and the depth of the porous layer, PGaN offers a compelling surface for functionalization into a SERS-active substrate.
The most heavily investigated SERS-active metals are Au and Ag. To create a
SERS active PGaN film, Au- and Ag-coated PGaN have been fabricated. Both metals
have been deposited by solution-based electroless deposition, as well as by vacuum
evaporation. The electroless Au deposition method was adapted from a protocol used
to coat Au on the interior pores surfaces of nanocapillary array membranes [1], and
the electroless Ag deposition was adopted from previous work on general electroless
plating of metals [2]. The experiments presented here focus on the relationship among
metallization processing strategies, metal morphology, and SERS spectral intensities,
so that we may understand the competence of metalized PGaN as a robust and widely
applicable SERS substrate.

2.2 Introduction

2.2.1 Creation of Porous GaN by Electroless Etching

In general, pure chemical etching of GaN is extremely difficult [3]. Very few
etchants may be used to pattern material, such as aqueous KOH [4] to etch N-polar
GaN, and the etching is limited to polarity determination and defect identification, as
defects are revealed by a number of etchants, including H₃PO₄ [5]. In recent years,
people are interested in the electrochemical etching process to produce porous
structures in GaN. In terms of etching types and mechanisms, both electrochemical
etching and electroless etching of semiconductors are electrochemical etching
processes. They are normally used to etch semiconductors through the injection of
holes into the semiconductor, which oxidizes the surface of the semiconductor that are
subsequently dissolved into the solution. In GaN, the surface oxides are created by the unsaturated bonding sites, different from the chemical etching. The main difference between electrochemical and electroless etching is the method of injection of holes.

Electrochemical etching is typically performed in a standard 2-electrode electrochemical cell and mediated by the electrochemical potential of the semiconductor/electrolyte cell. The semiconductor to be etched is electrically connected as one electrode and illuminated by above bandgap radiation to excite electrons to the induction band, which facilitates the injection of holes into the semiconductor by the electrolyte. The first report of electrochemical etching of GaN was made by Minsky et al. [6]. The authors proposed that photo-generated holes injected into the semiconductor promoted the oxidation of Ga, which enabled the etching. In comparison, electroless etching does not require electrical connection, but is driven by an oxidizing agent in the electrolyte, which injects holes, oxidizes the surface and promotes etching. Electroless etching is also often performed by illuminating the semiconductor with photon energies above the semiconductor bandgap. Although the overall etching process/mechanism of both processes is the same, electroless etching offers a number of advantages over electrochemical etching, such as simplifying the procedure, allowing the large-scale production of porous structures. The key drawbacks of electroless etching are that the etching speed is slower than that of electrochemical etching, and the oxidizing agent is depleted during etching, which must be replenished during etching, ultimately limiting the process [7, 8].
The ability to generate PGaN effectively makes it possible to study the properties and applications of porous wide bandgap semiconductors. However, the big limitation in producing and studying PGaN is the lack of high quality of substrates with low dislocation density and homogeneous properties, and the lack of reliable methods for generating specific porous structures. The only demonstration of ordered porous arrays in GaN was generated by dry etching through a porous alumina mask, reported in 2004 [9]. In addition, the etching mechanisms, reactivity of PGaN, and structural properties are still not well understood.

Our group has developed the metal-assisted electroless etching technique, which was motivated by protocols for rapid stain etching of Si in HF/HNO₃ solutions in the presence of a thin Al film [10, 11]. Our electroless etching scheme starts with deposition of ultrathin (~ 10 nm) Pt island films on the semiconductor, followed by etching in a CH₃OH:HF:H₂O₂ solution under UV illumination. Pt acts catalytically by assisting in the injection of holes into GaN [8], and provides the fastest, most efficient etching [10, 12] compared with other metals. The catalytic reduction of H₂O₂ at the Pt islands can be combined with UV illumination, \( hν > 3.41 \text{ eV} \), to inject holes into the valence band of GaN. This method has been effective for generating porous Si [10, 13-15], GaN [11, 16-18], and SiC [19].

### 2.2.2 Surface Enhanced Raman Spectroscopy (SERS)

SERS is a commonly used method for spectroscopic characterization of molecular adlayers that offers significant signal enhancement over normal Raman
scattering. In some instances signals strong enough to achieve single molecule
detection [20, 21] have been observed. Two mechanisms: the electromagnetic
mechanism and the chemical mechanism have been proposed to account for the large
enhancements of the SERS-effect. The electromagnetic enhancement mechanism of
SERS is the most pertinent to these studies. It involves an enhanced electric field
present at a noble metal surface that couples to, and enhances, the efficiency of the
Raman modes of nearby molecules. This field is caused by locally confined surface
plasmons in the metal, meaning that for a noble metal surface to be SERS active, it
must have nanoscale features to create the large local optical fields required. There are
several excellent reviews on the subject [22-25].

Since the initial discovery of the SERS effect on roughened silver electrode
surfaces [26, 27], researchers have explored numerous other substrates that exhibit the
SERS effect, including, but not limited to, roughened metal electrodes [28, 29], metal
films deposited over nanospheres [30, 31], metal island films [32, 33], nanoscale
metal features patterned by nanosphere lithography [34, 35], and metal colloids [20,
21, 36]. In addition to creating SERS-active substrates, researchers have also observed
the SERS effect by bring a nanostructured feature, normally in the form of an AFM,
STM, or apertureless NSOM tip of appropriate geometry, into very close proximity (<
5 nm) to probe molecules on a surface [37-39]. The efficacy of SERS substrates is
typically noted by their enhancement factor (EF), which is the increase in the Raman
signal in the SERS experiment over an unenhanced experiment. Values of the EF
range from $10^4$ to $10^{12}$ depending on the substrate in question, while a value of
$10^6$-$10^7$ is considered typical [1].

### 2.2.3 Electroless Deposition of Metals

The porous structures often need to be metalized in order to make electrical connections, to create an electronic device, or for catalysis or sensing. For the purpose of this work, it is ideal to prepare high surface area cluster deposits and smooth conformal coatings to fully evaluate the capability of PGaN as a SERS substrate. There are several possible approaches, including vacuum evaporation, sputtering, electrochemical, and electroless deposition methods [40, 41]. Evaporation or sputtering are suitable for metallization of planar surfaces, but they are ineffective when plating surfaces are rough or of high surface area, resulting in non-uniform metal coverage, largely confined to the outer surface. Electrochemical deposition is cheaper and easier to do at a large scale than vacuum methods, but it is affected by IR drops, mass transport, and the overall conductivity of the material to be plated. Electrochemical plating also shows limitations for high aspect ratio surfaces.

Electroless methods are able to overcome some of such limitations. Electroless deposition generally has two different processes: (1) direct electroless deposition, in which the metal ions in the solution is directly reduced by a reducing agent; (2) a displacement reaction, in which a more noble metal replace the less noble metal [42]. While most conducting films are metalized by direct electroless deposition, the deposition on semiconducting or insulating films is more like the displacement reaction and usually requires an activator metal.
Several groups have reported electroless depositions of Au on a variety of surfaces and by a variety of techniques [43-45]. The method used in this work of electrolessly depositing Au was adapted from the previous work by Martin and co-workers [46, 47]. The electroless deposition of Ag is also well-researched, and our methodology is based on a method described by Mallory [43].

2.3 Experimental

2.3.1 Fabrication of Porous GaN Film

GaN films used in this work were obtained from TDI, Inc (Silver Spring, MD). Two different films were used; an unintentionally doped film of 6.0 μm thickness with a free carrier concentration of n ~ 5.0×10^{16} cm^{-3} and a Si-doped film of 4.0 μm thickness with n ~ 5.0×10^{17} cm^{-3}. PGaN was created from cleaved pieces of GaN (ca. 4 mm×4 mm) by the Pt-assisted electroless etching protocol described in 2.2.1. The samples were pre-cleaned by sonication in acetone for 3 min, followed by sonication in isopropanol for 3 min. After rinsing in DI water, the samples were immersed in concentrated HNO_3 under UV illumination at 65 °C for a period of time, followed by rinsing once in distilled H_2O and three times in CH_3OH, then drying with N_2. In the experiments here, the samples were etched for 90 min to allow a sufficiently deep porous morphology to develop. This etching time is about 50% longer than times reported previously for the creation of similar morphology [16, 17]. The difference here is that these materials seem to etch more slowly than previously studied films, and the distance between the Hg-arc lamp and the samples being etched was increased.
Following etching, the samples were sonicated in methanol for 15 min in order to remove the ridge structures aerated upon etching, resulting in the uniform porous morphology evident in Fig. 2.1a. The morphology in Fig. 2.1a extends across the entire PGaN surface. SERS studies were conducted on metal-functionalized PGaN created from both GaN films mentioned above. The results were identical for both films, and distinctions between them will not be made.

2.3.2 Electroless Au Deposition

Prior to deposition, the freshly prepared PGaN samples were cleaned in HF for 10 min to remove surface oxides, and then soaked in methanol for 15 min. The Au deposition followed a three-step sensitization, activation and plating scheme. The sensitization step involved placing the samples in a solution of 22 mM SnCl₂ (dehydrate 99.995+%, Aldrich) and 70 mM trifluoroacetic acid (98% min, titration grade, Aldrich) in a 50:50 (v:v) deionized (DI) water:methanol solution of AgNO₃ (98+%%, ACS grade, Aldrich) in NH₄OH (certified ACS, Fisher Scientific) for 15 min. The activation required the preparation of a Ag(NH₃)₂⁺ complex, which was prepared by the dropwise addition of NH₄OH, causing the solution to change from clear to cloudy and brown, and then back to clear.

The plating step involved placing the samples in an 8 mM Au solution obtained by dilution of a commercially available Au plating solution (Oromerse Part B, Technic, Inc). The solution was adjusted to also contain 25 mM NaHCO₃ (ACS grade, Fisher), 130 mM Na₂SO₃ (Anhydrous, certified ACS, Fisher), and 580 mM formaldehyde
The formaldehyde acts as the reducing agent. The plating solution had an initial pH ~ 12, which was adjusted to 10 for these studies by dropwise addition of 0.5 M H$_2$SO$_4$ (Mallinckrodt) using an Accumet AB 15 pH meter (Fisher) to monitor the pH. Altering the pH of the plating solution was necessary to control the rate of deposition. It was empirically determined that pH 10 plating solutions offered the best mix of control/repeatability and speed. The samples were rinsed in DI water for 5 min. Upon completion of the plating procedure the samples were soaked in 25% HNO$_3$ overnight.

### 2.3.3 Electroless Ag Deposition

The Ag plating procedure is similar to the Au plating procedure detailed above except for the plating solution, which was initially identical to the activation solution described above. Immediately prior to deposition, formaldehyde was added to the plating solution to act as a reducing agent. The concentration of formaldehyde in the final plating solution ranged from 0.3 mM to 15 mM, which allowed the deposition speed to be controlled. Plating was done at 4°C for varied amounts of time ranging from 10 s to 2 h, depending on the amount of formaldehyde in the plating solution. Upon completion of the Ag plating, the samples were soaked in DI water overnight.

### 2.3.4 Vacuum Vapor Deposition of Au and Ag

Au was deposited onto PGaN by thermal evaporation in a vacuum evaporation chamber (Varian, Model NRC 3117) at pressures below 5×10$^{-6}$ Torr. Au thickness
ranging from 10 nm to 100 nm were deposited and monitored by a Sloan Model 200
digital thickness monitor. Due to chamber constraints Ag deposition was carried out
by thermal evaporation in a different chamber (Denton Vacuum) at P < 5×10^{-6} Torr.
Ag thickness ranging from 10 nm to 100 nm were deposited and monitored by a
Denton Vacuum STM-100 thickness monitor.

2.3.5 SERS Measurements

Raman spectra were obtained using a SPEX 500M monochromator equipped with
a 600 groove/mm grating and a Photometrics 200 Series liquid N\textsubscript{2} cooled CCD
detector. Spectra were collected in a true backscattering geometry using a 3 mm×3
mm right angle prism in the center of the collection axis to steer the beam through the
collection lens onto the sample. Malachite green isothiocyanate (MGITC) (molecular
Probes) was used as the SERS probe (see Fig. 2.2). Self-assembled monolayer films
were deposited on the SERS substrates by immersing them in 0.5 mM MGITC in
ethanol (Aaper) for 2h. For PGaN samples coated with Au, a 752.5 nm beam was
generated from an SEO Tian VW Ti:Saphire laser that was pumped by a Coherent
Innova 300 Ar\textsuperscript{+} laser operating in multi-line mode. For PGaN samples coated with Ag,
the 514.5 nm line from the Coherent Innova 300 Ar\textsuperscript{+} laser was used. In both cases,
Super Notch-Plus notch filters from Kaiser Optical Systems were used to reject
Rayleigh scatter. All spectra presented have been normalized to the 1001.1 cm\textsuperscript{-1} mode
of benzoic acid as an intensity standard, to account for run-to-run experimental
variations.
2.3.6 SEM Characterization

Scanning electron microscopy (SEM) images were obtained on a Hitachi S4700 SEM. All SEM images were taken at 0° tilt angle, with 10 kV accelerating voltage and imaging at 10 mm separation. Cross-sectional SEM analysis was carried out with a cross-sectional analysis stud. For cross-sectional imaging, a thin strip of carbon tape was used to cover the back of the sample, to prevent drift and charging.

2.4 Results and Discussion

2.4.1 Au-coated Porous GaN

The conditions for the electroless deposition of Au on PGaN were varied until the surface with the highest SERS activity was found. A SERS spectrum of MGITC for Au deposited on PGaN with high SERS response is shown in Fig. 2.3a. This film was obtained by electroless deposition of Au at pH 10 for 55 min. Figs. 2.3b-c show plan view and cross-sectional SEM images of the film used to obtain the spectrum in Fig. 2.3a. As can be seen in the SEM images, the morphology of the deposited Au is dominated by spheroidal Au Structures that rest on the surface and are attached in the pores. The morphology of Au within the pores displays spheroidal particles of similar size from top to bottom, suggesting that solvent exchange and material diffusion are sufficient during the deposition steps to deliver Au deposition reagents to a significant depth (>1 μm) below the outer surface. Significant effort was made to alter the morphology of the deposited Au to create smoother, conformal films of Au, rather
than the colloid-like structures shown in Fig. 2.3, in an attempt to exploit the morphology of the PGaN to achieve a higher SERS response.

Several avenues to achieve the target smooth, conformal morphology were pursued. A first hypothesis focused on the speed of deposition as the cause of the clustering of the Au on the surface of the PGaN. To control the speed, the pH of the deposition solution was varied in 0.5 pH unit increments from pH 8 to pH 12. As noted above, lower deposition solution pH values lead to slower deposition. Figs. 2.4a-b show an example of a pH 8.75 deposition and Figs. 2.4c-d show an example of a pH 12 deposition. In another effort to slow the deposition the concentration of one of the reactants was poised at a stoichiometrically limiting level, in the hope that the resulting morphology would be smoother. The concentration of the Au plating solution and the formaldehyde in the deposition solution were reduced by up to a factor of 10, both independently together. Figs. 2.4e-f show an example of a deposition done with the Au solution reduced by a factor of 5. The same spheroidal morphology of colloid-like Au particles was achieved independent of the pH of the deposition solution or concentration of key reactants.

A second hypothesis attributed the clustering in the electroless deposition of Au to surface wetting phenomena. To address this hypothesis, the oxide content of the PGaN surface was altered by immersion in either HNO₃ or HF to increase, or remove, the oxide, respectively. The oxide-free surface produced by immersion in HF did lead to more reproducible Au morphologies, but neither approach produced a smooth conformal coating in the interior spaces of the pores. Figs. 2.5a-b show an example of
a deposition done after pre-cleaning in HF, and Figs. 2.5c-d show an example of a deposition done after pre-cleaning in HNO₃. In another attempt to control surface wetting, the ratio of H₂O to CH₃OH was varied in 20% increments in the three deposition solutions. However, solvent compositions with large methanol volume fraction led to irreproducible depositions. An example of a deposition done with 20% methanol by volume is shown in Fig. 2.5e. Additionally, a surfactant, dodecylbenzene sulfonic acid salt (DBSA), was added to the deposition solutions. At higher concentrations of surfactant deposition in the pores ceased, while the deposition on the surface continued. An example of a deposition done with DBSA added is shown in Fig. 2.5f. Neither surfactant addition, nor varying the solvent composition, yielded smooth Au films on PGaN.

In light of the difficulty in obtaining a smooth Au surface on the interior of the cylindrical nanopores of PGaN by electroless deposition, substrates were also coated with Au by vacuum evaporation, it is not possible to coat the walls of the pores to any significant depth due to the directional nature of deposition. Therefore, a substantial amount of potential SERS-active surface is unavailable. Au of varying thickness was evaporated onto PGaN, and the SERS response from different films was measured. Fig. 2.6 shows a SERS spectrum of MGITC on an optimum thickness 60 nm film of Au evaporated on a PGaN substrate. The inset contains a plan view SEM image of the surface. All of the spectra presented in this work have been normalized to the same scattering standard to enable quantitative comparison of SERS activity among various substrate preparations. Thus, the relative scale bars in Fig. 2.3a and Fig. 2.6 show that
the evaporated Au-coated PGaN substrate produced a larger SERS signal than the Au-coated substrate prepared by electroless deposition. The relative SERS-activity of these two Au-PGaN preparations suggests that the Au spheroids contained deep within the interior of the nanopores are relatively ineffective at producing detectable Raman scattering. This could be due to multiple scattering of radiation at the Raman wavelength or to intrinsically small enhancement factors (EFs).

2.4.2 Ag-coated Porous GaN

The conditions used for Ag electroless deposition were varied until an optimum SERS substrate was obtained. A SERS spectrum of MGITC on Ag-coated PGaN with optimal signal strength is shown in Fig. 2.7a. This substrate was obtained by plating for 10 min in a 15 mM formaldehyde solution. Figs 2.7b-c contain plan-view and cross-sectional SEM images, respectively, of the substrate used to obtain the spectrum in Fig. 2.7a. Similar to the case with the electrolessly deposited Au, the Ag was deposited as clusters, rather than as a smooth film. In contrast to the Au deposition, Ag deposition was not uniform throughout the pores, with Ag nanoparticles remaining primarily on the surface, with very little Ag depositing deep in the pores, viz. Fig. 2.7b. Because the solutions used to achieve electroless deposition of Au and Ag are very similar, it is unlikely that diffusion of reactants was the reason for the limited Ag deposition in the pores. Rather, the high reactivity of the Ag(NH$_3$)$_2^+$ complex is likely the culprit. A sufficiently reactive species would be prevented from diffusing deep into the pores, because it would react on an already-growing Ag cluster near the
mouth of the pore.

Significant efforts were made to fabricate smooth Ag films on PGaN by electroless deposition. Pursuant to the experience with Au electroless deposition on PGaN, all PGaN substrates were pre-cleaned in HF. Two parameters were modified to lower the speed of deposition. The pH of the deposition solution was varied from pH 8 to pH 11, but with minimal effect on the speed. The main factor in determining the speed of the deposition for Ag was the formaldehyde concentration of the plating solution, which, when varied from 0.3 to 15 mM, resulted in significant changes in the speed of deposition, but had little effect on the morphology of the Ag films. To create smoother Ag film on PGaN, 10 to 100 nm of Ag was deposited by vacuum evaporation. Fig. 2.8 shows a SERS spectrum of MGITC acquired from an optimally thick 75 nm evaporated Ag film on PGaN, along with a plan-view SEM image of the film. Comparing the normalized signal levels in Fig. 2.7a and Fig. 2.8, it shows that, despite the morphology and being confined to the surface openings of the nanopores, the electrolessly deposited Ag film produced a higher SERS response.

2.4.3 Processing Dependence

To determine the processing conditions leading to the optimum response for each of the different types of SERS substrate evaluated in this study, a series of samples were created in each case with varying metal thickness and under varying solution conditions. Fig. 2.9 shows a series of spectra for vacuum evaporated Ag on PGaN, and Fig. 2.10 shows the relevant SEM images of these samples. The strongest signal
was obtained with 75 nm thick Ag on PGaN (the solid line in Fig. 2.9), although good signals were obtained a fairly broad range of Ag film thickness. Similar results and spectral series were obtained for electrolessly deposited Au and Ag and evaporated Au. The variation in SERS response as a function of film thickness can reasonably be ascribed to tuning of the surface plasmon response of the metal film to match the optimal combination of excitation and scattering wavelengths, as recently shown by Van Duyne and coworkers. The film with the most favorable surface plasmon frequency in a given series of film thicknesses, *e.g.* the 75 nm in Fig. 2.9, shows the strongest SERS enhancement.

### 2.4.4 Comparison to Other SERS-Active Substrates

To determine the SERS enhancement factor of the metal-coated PGaN, SERS spectra were compared to the normalized spectra of MGITC chemisorbed to thermally evaporated, flat Au or Ag films on planar crystalline GaN measured under identical sampling conditions. Fig. 2.11 shows a SERS spectrum of MGITC on vacuum evaporated silver and a reference spectrum of MGITC on a 100 nm thick Ag film on GaN. The enhancement factor was determined by computing the ratio:

\[
EF = \frac{I_{\text{SERS}} N_{\text{ref}}}{I_{\text{ref}} N_{\text{SERS}}}
\]

Where \( N_{\text{ref(SERS)}} \) is the number of molecules sampled in the flat surface (SERS) experiment, and \( I_{\text{ref(SERS)}} \) is the Raman signal in the flat surface (SERS) experiment. Pemberton and coworkers showed that smooth Au and Ag films have inherent enhancement factors of 64 (Au, 720 nm) and 5300 (Ag, 514.5 nm), respectively, for
thiophenol. Assuming that the enhancement effect is similar for MGITC, the enhancement factors are calculated to be $1 \times 10^8$ and $5 \times 10^7$ for the solution-deposited and evaporated Ag films, respectively. Similarly for Au, the enhancement factors are $2 \times 10^4$ and $2 \times 10^5$ for the solution deposited and vacuum evaporated films.

The EF values for the Ag-coated SERS substrates created in this study are somewhat larger than the typical value of $10^6$-$10^7$ that is common for many SERS substrates. The original motivation in pursuing SERS spectroscopy on PGaN template metal films was to take advantage of the extremely anisotropic, high surface-to-volume ratio morphology of the PGaN to produce structures with very large SERS signal strengths. Even though it was not possible to create metal-decorated surfaces deep within the nanopores by electroless deposition methods, the SEM micrographs shown in Figs. 2.3b-c, and Figs. 2.7b-c clearly shown an enhanced surface area relative to metals deposited on planar surfaces. Thus, it is reasonable to assign some fraction of the additional enhancement to enhanced surface area. In addition, it is clear that morphologies exhibited by the PGaN-supported metals show significant structuring on the nanoscale, so some fraction of the large EF may be assigned to the unique morphology of the PGaN-templated structures. While the EFs for the Ag-coated PGaN were larger than typical values, the EFs for the Au-coated PGaN were comparable to those obtained for other substrates. In order to attain a strong SERS response, the surface plasmon resonance and the geometry of the deposited metal need to be optimized. Examination of the related SEM micrographs for the Au- and Ag-coated PGaN (Figs. 2.3b-c, and Figs. 2.7b-c), shows no
significant difference between the size and shape of the metal nanoparticles obtained on the Au and Ag substrates. Therefore, the electronic enhancement due to geometry is likely similar for both metals. This suggests that the size of the Au clusters on the Au-coated PGaN is not well-matched to production of a surface plasmon resonance at 752.2 nm.

Besides the robust signal levels in comparison to other SERS substrates, metal functionalized PGaN offers other advantages, as well. The creation of PGaN is well understood and reproducible. Also, the deposition techniques employed to functionalized the surface are well understood and simple, particularly vacuum evaporation. Commonly-prepared SERS substrates may contain a few hot spots, which are responsible for the larger enhancements observed, while the majority of the surface is inactive. While the presence of hot spots on metal-decorated PGaN substrates could not be discounted or confirmed, in these experiments the signal strength did not vary or decrease across the sample on the length scale of the laser focal area, *i.e.* ca. 50 μm. Thus, metal deposition by thermal evaporation or electroless deposition from solution on to high porosity PGaN produces very uniform, large-area SERS active surfaces with sizeable SERS enhancement factors.

### 2.5 Conclusions

We have described a novel SERS substrate based on the metal functionalization of PGaN. Both electroless deposition and vacuum evaporation of Au and Ag were employed to create SERS-active surfaces. The SERS enhancement factors measured
on these substrates ranged from $2 \times 10^4$ for electrolessly deposited Au to $1 \times 10^8$ for electrolessly deposited Ag. These EFs are comparable to conventional SERS substrates, and the ease of fabrication and uniformity make a compelling case for the use of metal-coated PGaN as a SERS-active substrate.

2.6 Acknowledgements

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2.7 References


2.8 Figures

**Figure 2.1** (a) Plan-view image of porous GaN produced by the metal-assisted electroless etching technique. (b) Cross-sectional image of PGaN. These images were obtained from films prepared from a 6 μm thick GaN film with a carrier concentration \( n \sim 5 \times 10^{16} \text{ cm}^{-3} \).

**Figure 2.2** Structure of malachite green isothiocyanate (MGITC).
Figure 2.3: Top: (a) SERS spectrum of MGITC on Au electrolessly deposited on PGaN. The Au was deposited for 55 min from a pH 10 deposition solution. The scale bar quantitates the signal axis in units of A/D counts mW\(^{-1}\)s\(^{-1}\). Bottom: Plan-view (b) and cross-sectional (c) SEM images of the Au coated PGaN film used to obtain the SERS spectrum in (a).
Figure 2.4  
Top: (a) plan-view and (b) cross-sectional SEM images of Au electroless deposition on PGaN done at pH 8.75 for 180 min.  
Middle: (c) plan-view and (d) cross-sectional SEM images of Au electroless deposition on PGaN done at pH 12 for 15 min.  
Bottom: (e) plan-view and (f) cross-sectional SEM images of Au electroless deposition on PGaN done at pH 11.5 for 4 hours. The concentration of Au was reduced by a factor of 5 relative to the standard deposition procedure.
Figure 2.5: *Top:* (a) plan-view and (b) cross-sectional SEM images of Au electroless deposition on PGaN done at pH10 for 60 min. The samples were pre-cleaned in HF for 15 min prior to deposition. *Middle:* (c) plan-view and (d) cross-sectional SEM images of Au electroless deposition on PGaN done at pH 10 for 60 min. *Bottom:* (e) plan-view SEM image of Au electroless deposition on PGaN done at pH 10 for 60 min with the Au deposition solution containing 20% methanol by volume. (f) plan-view SEM images of Au electroless deposition on PGaN done at pH 10 for 30 min with the Au deposition solution the DBSA surfactant.
Figure 2.6 SERS spectrum of MGITC on a 60 nm (mass thickness) thermally evaporated Au film on PGaN. The scale bar quantitates the signal axis in units of A/D counts mW^{-1}s^{-1}. (Inset) Plan-view SEM image of the film used to obtain the spectrum.
Figure 2.7 *Top:* (a) SERS spectrum of MGITC on Ag electrolessly deposited on PGaN. The Ag was deposited for 10 min in a Ag plating solution containing 15 mM formaldehyde. The scale bar quantitates the signal axis in units of A/D counts mW⁻¹s⁻¹. *Bottom:* Plan-view (b) and cross-sectional (c) SEM image of the Ag coated PGaN film used to obtain the SERS spectrum in (a).
Figure 2.8 SERS spectrum of MGITC on a 75 nm (mass thickness) thermally evaporated Ag film on PGaN. The scale bar quantitates the signal axis in units of A/D counts mW^{-1}s^{-1}. (Inset) Plan-view SEM image of the film used to obtain the spectrum.
Figure 2.9 SERS spectra of MGITC on Ag thermally evaporated on PGaN to different mass thicknesses. The scale bar quantitates the signal axis in units of A/D counts mW⁻¹s⁻¹.
Figure 2.10 (a), (b), (c), and (d) plan-view SEM images of vacuum evaporated silver on PGaN of 55, 65, 75, and 85 nm thickness, respectively. (e) and (f) cross-sectional SEM images of 65 nm and 75 nm thick vacuum evaporated Ag on PGaN.
Figure 2.11 Raman spectra of MGITC on 100 nm thick planar Ag on GaN (line) and MGITC on 75 nm thick vacuum evaporated Ag on PGaN (dots) (SERS). Please note that the spectrum for MGITC on planar Ag has been multiplied by a factor of 1000.
CHAPTER 3

ENHANCED ULTRAVIOLET PHOTOCONDUCTIVITY IN POROUS GaN
AND ITS APPLICATIONS

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3.1 Abstract

GaN is an intrinsically interesting material for solar-blind ultraviolet (UV) photodetector applications due to its wide direct bandgap [1]. In addition, its superior radiation hardness characteristics and high temperature resistance make it suitable for working under extreme conditions [2]. UV/solar-blind photodetectors based on crystalline GaN (CGaN) with acceptable performance specifications have been commercialized [3], although the effect of impurities and defects on the electrical and optical properties are still not well have attracted significant interest due to their promising features, e.g. large surface area. Unfortunately, some limitations on the utilization of this material arise when grown by epitaxial techniques, such as persistent photoconductivity (PPC), and optical quenching (OQ).

Mynbaeva and coworkers first reported photoconductivity (PC) in porous GaN (PGaN) generated by electrochemical anodization [4]. If the sensitivity could be enhanced, PGaN could replace CGaN in UV detectors. Moreover, since PGaN has a higher surface/volume ratio than CGaN, it could also function as a gas or solution sensor based on changes in photoconductivity during exposure to analytes [5, 6]. This
chapter describes studies focused on the novel optical properties that porous GaN has over crystalline GaN, and evaluated its application in UV detectors. We found sizeable, etch-dependent enhancement of PC in PGaN generated by metal-assisted electroless etching, a contact-free patternable approach to creating porous semiconductors [7-9].

3.2 Introduction

3.2.1 Ultraviolet Photodetectors

In UV photodetectors, photons are absorbed within the bulk material by interaction with electrons, creating electron-hole pairs which are separated by an electrical field. These detectors make use of the internal photoelectric effect where the energy of photons is larger than the bandgap in order to raise the electrons into the conduction band of the semiconductor material. In the case of photovoltaic detectors, the electron-hole pairs are separated by the internal electrical field of the junction, Schottky barrier, or metal-insulator-semiconductor (MIS) capacitors, which leads to an external photocurrent proportional to the intensity of the incident radiation [1].

There are different types of semiconductor photodetectors [10]: photoconductors, Schottky barrier photodiodes, metal-semiconductor-metal (MSM) photodiodes, metal-insulator-semiconductor (MIS) structures, p-n and p-i-n photodiodes, and field-effect and bipolar phototransistors. The schematic structures of these devices are shown in Fig. 3.1 [3]. Basically, the photodetector is a slab of homogeneous semiconductor with the actual “electrical” area $A_e$ which is coupled to a beam of
radiation by its optical area $A_o$. Usually, $A_o$ and $A_e$ are close, but the use of optical concentrators can increase the $A_o/A_e$ ratio.

The current responsivity of the photodetectors is determined by the quantum efficiency $\eta$, which describes how well the detector is coupled to the radiation to be detected, and by the photoelectric gain $g$, which describes how well the generated electron-hole pairs are used to generate the current response of a photodetector. The quantum efficiency $\eta$ is usually defined as the number of generated electron-hole pairs per incident photon, and the photoelectric gain $g$ is the number of carriers passing electrical contacts per generated pair. Both values are assumed as constant over the whole device. The spectral current responsivity is equal to [1]

$$R_i = \frac{\lambda \eta}{hc} q g,$$

(3.1)

where $\lambda$ is the wavelength, $h$ is Planck’s constant, $c$ is the light velocity, $q$ is the electron charge, and $g$ is the photoelectric current gain.

The photoconductive detector (photoconductor) is a radiation-sensitive resistor. **Fig. 3.2** [1] shows the operation of a photodetector. A photon with energy larger than the semiconductor bandgap energy is absorbed to produce an electron-hole pair, resulting in the change of the electrical conductivity of the semiconductor. Electrodes are attached to the sample in order to measure the change in conductivity. The applied voltage across the sample is preferred to be constant for high resistance photodetectors, and the signal is detected as a change in current in the bias circuit. However, for low resistance material, a constant current circuit is usually used, and the signal is detected as a change in voltage across the sample as shown in **Fig. 3.2**.
3.2.2 Space Charge Model

Based on the idea of a conductance modulation, Garrido et al. [11] proposed a model to explain the behavior of GaN photoconductive detectors. Fig. 3.3 shows the charge density and the band diagram associated with a negatively charged semiconductor surface in the dark (broken line), and under illumination (full line) [11]. This band diagram is the same for a metal-semiconductor diode with a high density of surface bound states for electrons. These surface states, lying inside the bandgap and close to $E_F$, produce $E_F$ pinning effect. The surface charge density is related to the surface band-bending, $\Delta V$, and the space charge region (SCR) width is given by the surface charge density and the doping level by

$$w_{\text{dark}} = \left( \frac{2\varepsilon}{qN_d} \Delta \Psi_0 \right)^{1/2} \approx \left( \frac{2\varepsilon}{qN_d} \Delta V \right)^{1/2}.$$  \hspace{1cm} (3.2)

Here, we assume the band-bending, $\Delta V$, equal to the potential barrier, $\Delta \Psi_0$. When the sample is illuminated by radiation, the photogenerated carriers are swept by the SCR, producing a variation in both $Q_{ss}$ and the SCR width. A photovoltage $V_{ph}$ is developed across the sample. In this way the conductive volume inside the photoconductor, rather than the carrier density in ‘fixed’ volume, is actually increased because of the reduction of the SCR width. Many studies [12, 13] have shown that this spatial modulation effect surpasses any carrier density increase effect.

3.2.3 Persistent Photoconductivity

Persistent photoconductivity (PPC) is a light induced change in the free carrier
concentration which persists after the illumination is removed. This effect has been found in many compound semiconductors and can be due to a variety of reasons. It is commonly accepted that the PPC is related to the existence of defect states or traps, which are bistable between a shallow and a deep energy state. One such defect is the DX center, which forms when shallow donors undergo a large lattice relaxation and convert into deep donors [14]. Under illumination, these deep donors are able to be converted back into metastable shallow donor states. The barrier, developed due to the difference in lattice relaxation between the two states, prevents recapture of the electrons into the stable deep donor state, thus giving rise to PPC [15]. There are also many other physical models proposed to explain the origin for PPC for different semiconductors. The most common mathematical description for the time evolution of PPC uses the stretched exponential, called KWW decay function [16, 17].

3.3 Experimental

3.3.1 Preparation of Porous GaN

The GaN films investigated in this study were obtained from TDI, inc. (Silver Spring, MD). Three different films were used. (A) an unintentional doped film of 17.4 \textmu m thickness with n \sim 9.0\times10^{16} \text{ cm}^{-3}, (B) a Si-doped film of 11.3 \textmu m thickness with n \sim 5.0\times10^{17} \text{ cm}^{-3}, (C) a Si-doped film of 8 \textmu m thickness with n \sim 1.0\times10^{18} \text{ cm}^{-3}. For PC measurements, samples were cut into 10 mm × 5 mm pieces and selectively etched by Pt-assisted electroless etching [7-9], described in Chapter 2, in the center to generate a 5 mm × 5 mm PGaN layer flanked by two CGaN regions. By using a
physical mask, two 2 mm × 5 mm coplanar Ti/Al/Mo/Au (15 nm/60 nm/35 nm/50 nm) composites [18] were deposited onto the CGaN areas on each end by electron-beam evaporation. Rapid thermal annealing of the samples was then performed at 850 °C in an N₂ ambient. The ohmic character of the contacts was confirmed by I-V measurement, cf. Fig. 3.4.

3.3.2 Photoconductivity Measurements

A He-Cd laser (λ = 325 nm) was used as for photoexcitation, and a biopotentiostat provided a bias of 1.5 V for dc conductivity measurements. To avoid white light PC [19], samples were kept in the dark at ~ 300 K for more than 24 h before each measurement.

3.4 Results and Discussion

The morphology of the PGaN films was characterized by plan-view and cross-sectional scanning electron micrographs (SEM). As seen in Fig. 3.5, the porous area is very uniform, with pore diameters in the range 50-100 nm. The depth of the porous layer is controllable by varying the etch time. At the longest etch time (2h), the average depth of pores are ~ 5 μm, 2 μm, and 1 μm for samples A, B, and C, respectively. The gain area is, therefore, composed of a bottom CGaN layer and a top PGaN layer, cf. Fig. 3.4 (inset). I-V measurements indicate that the (dark) conductivity of PGaN is reduced relative to the CGaN from which it is produced, consistent with the porous morphology and the higher defect density in the remaining...
The composite nature of the samples is reflected in the n-type conductivity, \( \sigma = n e \mu_{\text{eff}} \), where an effective electron mobility, \( \mu_{\text{eff}} \), is used, because the measured mobility is an average over bulk and porous layers. Note also that with above-bandgap excitation most of the photogenerated carriers are created within the near-surface region, which is precisely the porous region of the structure, cf. Fig. 3.4 (inset).

The PC photoconductivity, \( R = \Delta I/P_{\text{opt}} \), was characterized for both PGaN and CGaN by measuring the change in current, \( \Delta I \), as a function of optical power, \( P_{\text{opt}} \). Fig. 3.6 shows for illumination of 2 mW (\( \Phi_{\text{ph}} = 1.4 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1} \)) at 325 nm. For undoped sample A, \( R \) decreases by \( \sim 50\% \) in samples etched for 1h or 2h, while for Si-doped samples B and C, \( R \) increases for etched samples. The increase is especially notable in sample C, being \( \sim 15 \) times larger for the porous sample compared to the corresponding CGaN.

According to the space charge model of photoresponsivity described above, illumination of GaN above the bandgap produces photoionized electrons, which sweep through the space charge region (SCRs) around pinned surfaces, interfaces, grain boundaries and threading dislocations, thus becoming spatially separated from localized capture centers. This process induces a change in potential barrier heights, \( \Phi_{\text{b}} \), and a shrinking of the SCRs, thus modulating the conduction area, \( S \). In this model, changes in conductivity result both from photogenerated carriers, \( \Delta n \), and from light-induced changes in the effective conduction area, \( \Delta S \), according to

\[
R = \frac{\Delta I}{P_{\text{opt}}} = \frac{qV_b \mu_c}{LP_{\text{opt}}} (S\Delta n + n\Delta S), \tag{3.3}
\]
where $q$ is the electron charge, $\mu_e$ is the electron mobility, $L$ is the distance between contacts, $S$ is the effective cross-sectional area for current conduction and $n$ is the free carrier concentration. In these experiments $V_B$, $L$, and $P_{opt}$ were controlled to be constant, whereas $\mu_e$ was altered by etching. Although electroless etching has no influence on native defects in bulk CGaN, it introduces additional defects in the porous region, which modulate the effective conduction area. In addition, photogenerated holes may interact with surface traps, resulting in changes in $\Phi_b$ and a significant conductance change. Samples B and C would naturally have large intrinsic SCRs, so photopumping would lead to significant changes in $R$, even though $\mu_{eff}$ is smaller than in CGaN.

As in CGaN [17, 19, 22, 23], PGaN also shows persistent photoconductivity (PPC), which is detrimental to photodetector performance [24]. As shown in Fig. 3.6, the PC persists after irradiation ceases; however, the response is different for PGaN and CGaN. Fitting the decays to a stretched exponential function [22]

$$I = I_d + I_o \exp[-(t / \tau)^\alpha]$$  \hspace{1cm} (3.4)

yields values for $\tau$, the PPC decay constant, and $\alpha$, which confirm that the decay in PGaN is faster than in CGaN, as summarized in Table 3.1. From Table 3.1, the time constant, $\tau$, decreases with increasing etch time, especially for heavily doped sample C. This can also be understood from the space charge model [11], where the PPC temporal evolution is dominated by the rate of change of the surface charge, $Q_{SS}$. This is related to the thermoionic current across the barrier, $J_{th}$, and the tunnel current, $J_{tunnel}$, according to
where the currents are related non-linearly to the photovoltage, \( V_{ph} \), by

\[
V_{ph}(t) = \psi_0 - \frac{Q^2(t)}{2qN_d e}
\]  

(3.6)

Porous structures are subject to larger modulation of the space charge region, compared to CGaN. Thus, because the PPC temporal evolution is dominated by the rate of change of \( Q_{SS} \), which, in turn, is related non-linearly to \( V_{ph} \), increasing the rate of change of \( Q_{SS} \) produces a larger \( V_{ph} \), consistent with a faster relaxation of the PPC in the porous structure. The dominant effect apparent from Table 3.1 is the dramatic reduction in \( \tau \) upon etching for the \( n \sim 10^{18} \text{ cm}^{-3} \) sample. Since the width of the SCR scales approximately with \( n^{1/2} \), reduction of the physical width of the columnar nanostructures upon etching would be expected to have the most pronounced effect on sample C, as is observed. Sample A and B are characterized by relatively low carrier concentration and, thus, exhibit a much smaller change in PPC between CGaN and PGaN. Although the PPC effect has previously been associated with the density of surface traps, and PGaN shows a much large surface area than CGaN [18], the dramatic reduction in PPC in sample C clearly points to the importance of the SCR width in modulating the surface charge density in nanostructured features in PGaN.

In samples B and C, the photocurrent exhibits optical quenching (OQ), when the laser irradiance is varied, \( \text{viz. Fig. 3.7.} \) In PGaN when the photon flux is relatively low \((1.4 \times 10^{16} \text{ cm}^2 \text{ s}^{-1})\), there is no quenching even over long illumination times, \( \text{viz. trace a.} \) Under medium optical power \((1.0 \times 10^{17} \text{ cm}^2 \text{ s}^{-1} < \Phi_{ph} < 2.0 \times 10^{17} \text{ cm}^2 \text{ s}^{-1})\), the photocurrent exhibits a sharp rise at the start followed by a slow decay, with a steady state.
state current somewhat higher than the dark current. When the illumination is switched off, a slow recovery to the unquenched value occurs. Further increasing $\Phi_{ph}$ to $2.6 \times 10^{17}$ cm$^2$ s$^{-1}$, produces a steady state quenched current less than the dark value, i.e. a negative PC. Similar behavior is also found in CGaN, traces b and c.

A recently developed theoretical model [25] assigns PC to the competition between the capture of conduction band electrons by deep electron traps and recombination with trapped holes. When the probability of recombination is greater than that of capture, OQ, as well as NPC, can be observed. As the photon flux increases, the photocurrent increases, but then becomes saturated as the increased photon flux generates more metastable states and increases the recombination rate. Thus, the carrier distributions quickly reach a quasi-steady state, and after illumination is removed, the trapped electrons tunnel out through the potential barrier with characteristic kinetics. The observed dependence of OQ on $\Phi_{ph}$ also confirms that the metastable trap states are photoinduced. Analogous results have been obtained with sub-bandgap excitation from simulations using this model [25].

3.5 Conclusions

In summary, we have observed a photoresponse in PGaN produced by Pt-assisted electroless etching of Si-doped CGaN 15× larger than that in the original CGaN. Porous structures provide enhanced populations of surface defects, which trap holes to form SCRs, which can be effectively modulated by above-bandgap illumination, resulting in improved photoresponse relative to CGaN. The improved photoresponse
results principally from changes in carrier density, $\Delta n$, because the overall conductive area is smaller in the porous region of the sample, so that the same absolute change in SCR area would result in a larger fractional change in the porous material. Furthermore, like CGaN, PGaN exhibits PPC and OQ, although the PPC decays more rapidly, and the OQ is weaker, than CGaN under comparable conditions. Furthermore, the PPC decay enhancement is most dramatic in the most heavily doped sample, which is precisely the sample exhibiting the largest photoresponse enhancement. These improved properties, *i.e.* enhanced photoresponse, faster PPC decay and less OQ, of PGaN relative to CGaN make PGaN a promising candidate for application in UV photodetection and chemical sensing.

### 3.6 Acknowledgements

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### 3.7 References

22. Qiu CH and Pankove JI (1997) Deep levels and persistent photoconductivity in


### 3.8 Tables and Figures

<table>
<thead>
<tr>
<th>Sample</th>
<th>unetched</th>
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<tr>
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<td>31.2 s</td>
<td>12.0 s</td>
</tr>
</tbody>
</table>

\(^a\) All fits produced a stretch parameter of \(\alpha = 0.4 \pm 0.1\).

**Table 3.1** PPC decay time of n-type GaN epilayers\(^a\)
Figure 3.1 Schematic structures of different semiconductor photodetectors. Reprinted with permission from Monroy E, et al., *Semicond Sci Technol* 2003 vol. 18, p. R33-R51. Copyright © 2003, IOP Publishing Ltd.

Figure 3.3 (a) Band diagram and charge density associated with a negatively charged semiconductor surface in the dark (— — —) and under illumination (——). (b) Experimental setup showing the air–semiconductor (upper) and the bulk–substrate (lower) SCRs. Reprinted with permission from Garrido JA, Monroy E, Izpura I, and Munoz E, *Semicond Sci Technol* 1998 vol. 13, p. 563-568. Copyright © 1998, IOP Publishing Ltd.
Figure 3.4 Current-voltage characteristics in the dark for one of the CGaN/PGaN devices used in these studies (n ~ 5 \times 10^{17} \text{ cm}^{-3}) as a function of etch time. (Inset) Geometry of the samples used for both dark and photoconductivity measurements.
Figure 3.5 (a) Plan-view image of PGaN generated by metal-assisted electroless etching method. (b) Cross-sectional image of PGaN. These images were obtained from sample B.
Figure 3.6 Buildup, steady state and decay transients of the photoresponse for sample A (top), sample B (middle) and sample C (bottom); (a) crystalline (unetched) GaN, (b) PGaN after 1 h etching, and (c) PGaN after 2 h etching. Illumination is turned on near ~ 800-1000 s and turned off near ~ 1800-2000 s. in all traces. (Inset) Detailed PC decay transient used to obtain decay times summarized in Table 1. The open symbols are the experimental data and the full line is the fit.
Figure 3.7 Photocurrent transients in sample C for both PGaN and CGaN. The illumination fluxes for PGaN are: (a) $1.4 \times 10^{16}$ cm$^{-2}$ s$^{-1}$, (b) $1.0 \times 10^{17}$ cm$^{-2}$ s$^{-1}$, (c) $2.0 \times 10^{17}$ cm$^{-2}$ s$^{-1}$, and $2.6 \times 10^{17}$ cm$^{-2}$ s$^{-1}$. The fluxes for CGaN are: (a) $1.4 \times 10^{16}$ cm$^{-2}$ s$^{-1}$, (b) $6.0 \times 10^{16}$ cm$^{-2}$ s$^{-1}$, and (c) $2.0 \times 10^{17}$ cm$^{-2}$ s$^{-1}$. 
CHAPTER 4

TWO- AND THREE- DIMENSIONAL FOLDING OF SINGLE CRYSTALLINE SILICON FOR PHOTOVOLTAIC POWER APPLICATIONS


The mechanics derivation and Figures 4.11, 4.12, and 4.15 were prepared by H. Li, and the direct ink writing was done by B.Y. Ahn, and E.B. Duoss.

4.1 Abstract

Fabrication of three-dimensional (3D) electronic structures in the μm-to-mm range is extremely challenging due to the inherently two-dimensional (2D) nature of most conventional wafer-based fabrication methods. Self-assembly, and the related method of self-folding of planar patterned membranes, provide a promising means to solve this problem. In this chapter, we investigate self-assembly processes driven by wetting interactions to shape the contour of a functional, non-planar photovoltaic device. This strategy is demonstrated for specifically designed mm-scale silicon objects, which are self-assembled into spherical, and other 3D shapes and integrated into fully functional light-trapping photovoltaic (PV) devices.

A mechanics model based on the theory of thin plates is developed to identify the critical conditions for self-folding of different 2D geometrical shapes. We exploit the mechanical bendability of thin, single-crystalline Si foils of a few μm in thickness,
coupled with capillary-driven, self-assembly to create folded 3D photovoltaic devices. These flexible constructs readily lend themselves to adopting non-planar shapes, such as triangular prisms, cylinders, and spheres, with less defects than would result from the deformation of thicker Si wafers [1, 2]. The resulting 3D functional architectures inherently serve as a light trapping element allowing for a substantial improvement in efficiency relative to its planar analogues.

4.2 Introduction

4.2.1 Photovoltaic Effect and Principle of Solar Cell Operation

The photovoltaic (PV) effect is a basic physical process through which a PV cell converts solar radiation directly into electricity. It is also called “Becquerel Effect” because it was first observed by Becquerel [3]. PV effect is generally defined as the appearance of a forward electric voltage between two electrodes attached to a solid or liquid system under illumination of sunlight. Practically all PV devices incorporate a p-n junction in a semiconductor across which the photovoltage is developed [4].

A p-n junction exists in a semiconductor material in the region where the impurity content changes from an acceptor p-type to a donor n-type, formed by diffusion of impurity atoms into the surface of a crystal, or other methods [5]. Fig. 4.1 shows the energy levels in the junction region at equilibrium. The valence band (VB) is almost filled with electrons, while the conduction band (CB) is almost empty at room temperature lying above the valence band. The Fermi energy is in the center of the gap for the intrinsic material; within the gap but below the center for p-type material;
within the center but above the center for n-type material. When two types of materials are joined together, the Fermi energy must be the same throughout the material at equilibrium. In order to satisfy this requirement, a charge double depletion layer \( W \) and associated electric field are created at the junction. When photons are absorbed by semiconductors, the energy of the photon can be transferred to an electron in an atom of the semiconductor. With this energy, the electron is able to escape from VB to CB, leaving a hole to form in VB. In particular, excess carriers generated within the depletion region \( W \) are separated by the junction field, electrons being collected in the n region and holes in the p region, as shown in Fig. 4.2. The \( I-V \) characteristics shows that the photogenerated current is proportional to the generation rate \( g_{op} \).

Depending on the intended application, the photodiode of Fig. 4.2a can be operated in different quarters of its \( I-V \) characteristics [6]. In the fourth quadrant, junction voltage is positive and the current is negative, thus power is extracted from the junction device to the external circuit, as a battery. These devices are called solar cells. The solar conversion efficiency \( \eta \) is given by:

\[
\eta = \frac{V_{OC} I_{SC} FF}{P}
\]

(4.1)

Where \( V_{OC} \) is the open circuit voltage, \( I_{SC} \) is the short circuit current, \( FF \) is the fill-factor (defined to be the ratio of the maximum output power generated by the device divided by \( V_{OC} I_{SC} \)), and \( P \) is the power of the incident light.

Because the efficiency depends on \( V_{OC} I_{SC} \), there is an optimum energy bandgap for producing maximum efficiency devices [7]. For terrestrial power generation (AM
1.5) the optimum energy bandgap is found to be 1.5 eV. In practice semiconductors
with energy bandgaps in the range in 1.0 – 1.7 eV are used [8], including
monocrystalline and multicrystalline Si ($E_g = 1.12$ eV), copper indium diselenide
(CuInSe$_2$, $E_g = 1.05$ eV), and amorphous Si ($E_g = 1.7$ eV). A cross-sectional schematic
of a typical solar cell is shown in Fig. 4.3 [4]. The semiconductor material needs to be
able to absorb large amount of the solar radiation. Even for weakly absorbing
materials like silicon, the light is absorbed in a region near the surface. So the typical
solar cell structure has a vertical p-n junction which separates the emitter and base
layer, and is very close to the surface in order to utilize a maximum amount of
available optical energy. The relatively high resistance of the thin emitter layer
requires a well designed contact grid on the top surface.

4.2.2 Conventional Si Solar Cells

The first Si solar cell was developed at Bell Laboratories in 1954 by Chapin et al.
[9] with an efficiency of 6%. It was rapidly realized that this technology could be
deployed for a wide range of applications including supplying power for consumer
products, in developing countries, and in remote locations.

Si has an indirect energy bandgap of around 1.1 eV at room temperature,
resulting in a low optical absorption coefficient, $\alpha \approx 100$ cm$^{-1}$. This means that the
silicon needs to be several hundred microns thick to absorb most of the incident light.
The electron-hole pairs generated by the illumination need diffuse up to that distance
to reach the electric field in the depletion region before they recombine. A
cross-sectional view of the conventional silicon solar cell structure is shown in Fig. 4.4 [7]. The base material is boron p-type monocrystalline Si, which is sawn from a boule of Si grown by Czochralski method. The p-n junction is formed by diffusing phosphorus impurities into the wafer. Silver contact fingers are screen-printed on the n-type Si surface to make electrical contacts and allow light to be transmitted to the junction region [10]. Aluminum paste is used as the back contact and annealed to introduce a p⁺ doped region at the back of the cell, to lower the back contact resistance and to supply a back surface field that reflects minority carriers back towards the junction [11]. The cell surface is textured to minimize unwanted reflection and to scatter internal light away from escape orientations to enhance the effective optical path length. An antireflection (AR) coating is deposited over the top surface to complete the device. To reduce the shading losses, Green and co-workers have developed solar cells in which the contacts are buried in the wafer either using photolithography or laser scribing [12]. A more advanced design is that of the PERL (passivated emitter rear locally diffused) solar cell [13].

Although crystalline silicon devices and modules have dominated production and sales, there is increased competition from devices based on the use of a variety of different types of materials, such as amorphous Si [14], multicrystalline Si [15], microcrystalline Si [16], Si ribbon [17], thin film Si [18], etc.

4.2.3 Light Trapping

Silicon, in crystalline and amorphous forms, is currently used in greater than 90%
of the PV production and is likely to increase its dominant position in the foreseeable future [19, 20]. Even so, its widespread adoption is limited by fabrication costs (e.g., wafer production accounts for nearly 40% of the cost of a module [21]). One attractive strategy to reduce such costs entails the use of ultrathin silicon films as the basic material for solar cells [22-24]. Thin film solar cells typically have lower efficiencies due to limited absorption thickness (e.g., for a single-crystalline Si film, a thickness of about 125 μm is needed to absorb ~90% of the transmitted light incident on it [25]). In order to achieve efficient optical absorption, thin-film solar cells need effective strategies to prevent reflective losses as well as light trapping mechanisms to enhance the effective optical path length of a cell. This requirement is especially important for silicon due to its high reflectivity, in which greater than 35% of incident photons are reflected from the surface and thereby lost [26], as well as its relatively low absorption cross-section, as an indirect band gap semiconductor [27, 28].

Numerous ideas involving modification of both the front and back surfaces of a Si-based device have been pursued, including the use of textured surface structures [29], anti-reflection (AR) coatings [30] and light-trapping (LT) schemes [31, 32]. Recently, more complex designs have been explored to improve light trapping efficiency through the use of various 3D architectures [33-37], including V-folded thin film organic solar cells [35, 36], 3D thin film cadmium telluride (CdTe) solar cells deposited over the top of carbon nanotube tower arrays [33, 37], spherical devices albeit from solid Si spheres [34] and cylindrical-shaped solar cells (Solyndra Inc) made of a thin film of copper indium gallium selenium (CIGS) deposited on a glass
tube. These designs are able to increase the optical path length through multiple internal and external reflections to enhance light absorption within an optically thin semiconductor absorber. Additionally, unlike conventional flat solar cells, such 3D optical structures can absorb light efficiently from a wide range of incident directions.

4.2.4 Self-Assembly to Fabricate 3D Structures

The creation of electronic devices with 3D form factors is challenging due in part to the inherently planar nature of wafer-based fabrication methods. The most practical methods currently employ planar microfabrication techniques, followed by other processes that transform planar objects into the desired 3D structures [38, 39]. Whereas microelectronics rely on stacking and interconnecting individual layers [40], folding and self-assembly routes are attracting increasing attention as an alternative approach to 3D microfabrication [41]. To date, folded 3D structures have been obtained through the use of magnetic forces [42], residual stresses [43], and electrical activation [44]. Capillary forces may also be harnessed to guide the assembly of 3D, sub-millimeter scale objects [45-47]. However the relationship between residual stresses (such as those found in epitaxial thin films) and these interfacial driving forces that guide material deformation during self-assembly are not fully understood.

In the molecular and nanoscale regimes, self-assembly is often used to fabricate regular 3D structures. Self-assembly of larger components with sizes in the μm-to-mm range (meso-scale) is less familiar to chemists, but may become technologically more important in the future. The rules for self-assembly in these
ranges are similar, but not identical. Meso-scale self-assembly (MESA) has several advantages over molecular self-assembly [48]: (1) Fabrication of μm-to-mm components is often simpler than molecular synthesis and it is easier to observe the process and products of self-assembly; (2) When using components larger than molecules, a wide range of interactions (van der Waals, ionic, steric, entropic, magnetic, gravitational, electrostatic, capillary, hydrodynamic, and others) can be used to cause self-assembly, and be adjusted over wide ranges of strength, range, and selectivity. The MESA system, thus, is more flexible in the design than molecular system; (3) Components with sizes in μm-to-mm range can be incorporated into structures with optical or electrical functionality, while molecules cannot. Self-assembly of μm-to-mm components fabricated using planar techniques also offers a possible route to a true 3D microstructures.

4.3 Experimental

4.3.1 Fabrication of Thin Si Foils

The starting material is a SOI wafer (Ultrasil) with a p-type device layer (thickness between 100 nm and 3 μm) and a buried oxide layer (thickness between 400 nm and 4 μm). Fig. 4.5a schematically shows the basic steps to fabricate a free-standing thin single-crystalline silicon film, which serves as the generic planar precursor to a specifically folded object. In the first step (top panel in Fig. 4.5a), spin casting, exposing (365 nm light, through a Karl Suss MJB3 Mask Aligner) and developing a layer of photoresist (AZ5214, Clariant; developer, AZ351, Clariant)
formed a pattern that defines the geometric shape of the intended free-standing Si foil. Reactive-ion etching (PlasmaTherm 790 series) using SF₆ (40 s.c.c.m., 30 mTorr, 100W, etch rate 200 nm/min) removed the exposed parts of the top silicon. These resist structures carry a square array of holes (~2.5 μm diameter, and ~40 μm pitch) that facilitate undercutting of the foil from a Si-on-insulator (SOI) wafer. After removing the resist with acetone, concentrated HF (Fisher, 49% concentration) was deposited over the patterned surface to remove the buried oxide (BOX) layer and undercut the platelet. Immersing the etched sample into a water tank released the top thin Si film from the underlying Si handle wafer. The thickness of the top Si on the SOI wafer defines the foil thickness. Though fragile, this foil can be manipulated, as shown in Fig. 4.5b for a prototypical square Si film (6mm × 6mm, 1.25 μm thick) held by tweezers. The thin silicon foil can be reversibly bent to a relatively small radius of curvature, if the maximum stress in the foil does not exceed the tensile strength of silicon. For a free-standing 2 μm thick Si foil, this maximum stress will reach the material’s tensile strength at a bending corresponds to a bending radius of curvature of ~ 40 μm [49].

4.3.2 Folding of Thin Si Foils with Different Shapes

During the folding experiment, a Si foil with a specific geometric shape, thickness and size is placed on a hydrophobic Teflon surface. A droplet of water is placed at the center of the foil. For reasons discussed in detail below, the volume of the water droplet needs to be large enough so that the water-Si-air triple junction line
reaches and pins near the corners of the foil. As water evaporates, the capillary forces at the receding water-silicon-air triple junction pulls the corners of the Si sheet up, causing it to wrap around the water droplet with a specific form directed by mechanics considerations. This phenomenon is illustrated by the time-lapse images of folding of a triangular- and two square-shaped foils shown in Fig. 4.6. For both the triangular and square Si foils (1.25 μm thick), the initial folding is symmetric, with all corners bending towards the center of the sheet. Such behavior is similar to that observed for PDMS sheet [46]. As the water evaporates further, the triangular sheet eventually folds into a hollow tetrahedral pyramid (Fig. 4.6a). By contrast, because the symmetric folding eventually becomes unstable for square sheets, they adopt one of two possible modes of cylindrical deformation as shown in Figs. 4.6b-c. Both of these folded states possess high symmetry, as discussed below. Finally, when the water droplet fully evaporates, the folded Si foils reopen to adopt their natural, flat shapes unless other methods are used to retain the folded shape, as desired for the construction of 3D photovoltaic devices.

For generating a variety of shapes, some problems of the folding still exist and need to be resolved in applied mathematics [50, 51]. The important one is mapping the surface of a 3D shape onto a flat sheet. Figure 4.7a shows how to design a planar pattern intended to generate a spherical shell. First, we create a polytope with six slices approximating a sphere. By selecting one polygon as the center, we unfolded the sphere into a flat flower-shape sheet consisted of a tree of faces using a modified version of a software package UNFOLD POLYTOPE FOR MATHEMATICA
This flower shape is then patterned and released to form a flat silicon sheet. The image sequence provided in Fig. 4.7b shows the precise folding of the Si foil into the expected (nearly) spherical shape. Further evaporation leads to collapse/overlapping of the spherical shell due to the negative internal pressure. For thicker Si membrane, which has higher stiffness, the thin membrane will reopen as water evaporated completely. To prevent this from occurring, we used a solid core to hold the folded structure. A silica bead was first soaked into the piranha solution for 5 min and then immersed into the Polyvinyl Alcohol (PVA) solution, which served as the glue, to form a thin polymer shell. Then we put the PVA coated silica bead on the center of Si membrane and deposited a droplet of water onto the membrane. When the membrane was folded reaching a closed shape, the spherical structure was stabilized, as shown in Fig. 4.7c.

### 4.3.3 Fabrication of 3D Si Solar Cells

The technique we used to fabricate 3D Si solar cells embraces many compromises that serve to simplify the fabrication requirements, albeit at the expense of ultimate device performance. The fabrication process began with a SOI wafer (p-type, Boron doped device layer, 2-3 μm thick, 10-20 Ω cm, 4 μm thick BOX, Ultrasil) that was coated with a layer of SiO$_2$ (400 nm) formed by plasma-enhanced chemical vapor deposition (PECVD) at 250°C. Photolithography defined the lateral dimensions of the planar solar cells (flower or square shapes), followed by etching the SiO$_2$ not protected by the photoresist and the underlying Si by buffered oxide etchant.
(BOE, 6:1 Transene) and reactive-ion etching (SF6 plasma, 40 s.c.c.m., 30 mTorr, 100W), respectively. After opening a window for doping, immersing the wafer in piranha solution (H2SO4/H2O2 v/v ratio is 3:1) cleaned the exposed silicon surface. The device top was then coated with a liquid source of Boron spin-on glass (SOG) dopant (Poly Boron, doping concentration: 5x10^{20} B/cm^3, Filmtronics Corporation) at a spinning velocity of 3000 rpm for 30 sec. This was followed by a prebake at 250°C for 15 min in air to remove the solvent. The samples were next annealed in a tube furnace with N2 atmosphere set at 600°C for 30 min and 1000°C for 60 min. The SOG was then striped by immersing in HF solution (1min), piranha solution (5min) and HF solution (1min). After deglazing, a 600 nm of PECVD SiO2 was again deposited on the surface of wafer. This oxide was patterned to serve as a mask for phosphorus doping. Following the same patterning and etching steps as above, a liquid source of phosphorus spin-on glass (SOG) dopant (P8545, Filmtronics Corporation) was coated on the device surface at a spinning velocity of 3000 rpm for 30 sec. This was followed by a prebake at 250°C for 15 min in air and annealing in a tube furnace with N2 atmosphere set at 1000°C for 30 min. The SOG was then striped using the same deglazing steps. Thus, the transverse junction n^-(emitter)-i(base)-p^+(collector) structure was formed in the top device layer. The spacing between n^+ and p^+ regions in the surface layer is set at 50 µm; this spacing provides a high internal electrical field to efficiently separate photogenerated electron-hole pairs.

The doped wafer was then cleaned and coated with metal electrodes that were defined by photolithography and lift-off. An electron-beam (Temescal, FC 1800)
evaporate ion source was used to deposit the metal Cr (3 nm) and Au (50 nm) metal layer. The device surface was patterned with a square holes array (≈2.5 μm diameter, ≈40 μm pitch) and the exposed Cr/Au and Si were removed with commercial etchants (Transene) and a SF₆ plasma, respectively. After releasing the top Si layers in HF, the patterned planar sheets were placed onto a Teflon substrate with the top surface (face with the metal contact pads) facing downwards. To retain the desired 3D shape (spherical or cylindrical shape) after the water drop has fully evaporated, we placed a size-matched bead coated with an adhesive poly(vinyl alcohol), PVA, layer at the center of the flower pattern to “freeze” the 3D structure in place, once it has reached its desired folded state. For spherical Si solar cells, a direct-write metallization process [52] is used to make electrical Ag-wire contacts to the bottom and top side contact pads (see 4.3.5).

4.3.4 Direct Ink Writing

Through a multi-step approach, highly concentrated silver nanoparticle inks (≥70 wt% solids) were prepared using an aqueous system that contains AgNO₃ as the silver precursor, poly(acrylic acid) (PAA) as the capping agent, and diethanolamine (DEA) as the reducing agent [52]. Ethylene glycol was added as a humectant, which allows the ink to be patterned in air without clogging. Finally these silver nanoparticle inks were printed on a pre-cleaned glass slide and in contact with the bottom metal contact (Cr/Au) of the spherical cell. Another silver microwire (≈20 μm) was printed directly onto the top metal contact of the spherical cell (Fig. 4.8b). The printed silver electrodes on Si were made
non-rectifying by subjecting them to 3 hrs of annealing at 200°C, 20 min of soaking in water, and 3 hrs of annealing at 250°C. The ohmic characteristic of this contact is demonstrated by the data given in Fig. 4.8c.

4.3.5 Electrical Measurements

Light and dark $I-V$ measurements of solar cells were carried out at room temperature using a d.c. source meter (model 2400, Keithley) operated by LabVIEW5, and a full-spectrum solar simulator (model 91192, 4×4 inch source diameter, ± 4° collimation, Oriel) equipped with AM 0 and AM 1.5 direct filters. The input power of light from the solar simulator was measured with a power meter (model 70260, Newport) and a broadband detector (model 70268, Newport) at the surface where the sample was placed.

4.4 Results and Discussions

Using capillary interactions to spontaneously fold planar/2D shapes has recently been explored by researchers as a means to self-assemble various 3D structures. Folding of planar polyhedral building blocks of metallic films into 3D structures driven by a droplet of solder was achieved by Gracias et al [53]. Folding of PDMS thin foil into 3D shapes driven by evaporating water droplets was studied Py et al [46]. In an effort to fabricate 3D photovoltaic devices, we developed a process of fabricating patterned Si thin film, and using an evaporating water droplet to fold the planar film into 3D structures [54].
The results of folding of a triangular and a square shaped Si films have been shown in Fig. 4.6. We also found that this method can be applied to a variety of thin film materials, such as PDMS films and plastic food wrap. The PDMS was spun on a Si wafer at spinning velocities of 1000 and 2000 rpm for 1 min. The cured PDMS thin films, which are used in the experiments shown in Fig. 4.9a and Fig. 4.9b, are measured to be 57 and 27 μm, respectively. The plastic food wrap (Fig. 4.9c-d) is a standard commercial grade linear low-density polyethylene with a thickness of about 14 μm. The thin films were cut into millimeter-sized squares and triangles for the experiments shown. For all cases, when a droplet of water is placed on the thin film, folding begins first with the corners bending over towards the center of the sheet. For sheets larger than a critical size (to be determined by the analysis in the following sections of this paper), as water evaporates (i.e., as the droplet shrinks), folding of the triangular sheets maintains a symmetric shape and finally forms tetrahedral pyramids, an endpoint observed for both the PDMS (shown in Fig. 4.9a) and plastic (shown in Fig. 4.9c) films. For the square sheets, however, the symmetric folding process becomes unstable beyond a certain stage, and instead bifurcates into asymmetric folding modes: for the plastic thin film, the edges fold up to each other forming a quasi-cylindrical shape as shown in Fig. 4.9d; and for the low-modulus PDMS thin films, which ultimately is twisted by the capillary force, a more irregular quasi-cylindrical shape is formed, as shown in Fig. 4.9b.

The competing components that comprise the mechanism are believed to be the surface tension $\gamma$, which promotes folding, and the bending of the thin sheet
(characterized by a bending stiffness, $B$), which resists folding. Based on this argument, Py et al. [55] defined an elasto-capillary length, as [55]

$$L_{EC} = (B/\gamma)^{1/2},$$

and measured the critical dimensions for folding, $L_{crit}$, of triangular and square foils as a function of $L_{EC}$. Their results show that the critical dimension for folding $L_{crit}$ follows a linear relationship with the elasto-capillary length $L_{EC}$. However, the coefficient of linearity (or slope) varies with the shape of the thin foil. The coefficient is 7.0 for square, and 11.9 for triangular shaped PDMS films [46].

Two issues raised by these experimental observations are: i) whether indeed the competition between surface tension and thin film bending is the dominant mechanism determining the folding process; and ii) whether there exists a parameter, dimensional or nondimensional, that governs the thin film folding process regardless of the sheet geometry. The answers to such questions will not only help explain the observations in square and triangular shaped foils, but may also provide insights beyond the specific shapes used in this experimental study and lead to a general descriptive form of the controlling parameter.

### 4.4.1 Mechanics Model

We start the modeling by considering the specific geometries – square and triangular shapes – investigated in the experiments by Py et al [46]. We further hypothesize that the competition between surface tension and thin film bending is the dominant mechanism controlling the folding process. This hypothesis will be
validated through comparison of model predictions to the experimental results.

For both triangular and square sheets, folding starts by bending of the corners symmetrically, a necessary condition to achieve the final wrapping. However, it is noted that regions within the dashed lines shown in Fig. 4.10a will not bend due to symmetric constraint. Therefore the folding is achieved by bending the corners of a thin sheet with varying width – tapered width in the case of square and triangular sheets. We can thus model each corner (the region beyond the dashed line) as a beam with fixed end and a tapered width. The configuration can be generalized to a tapered beam with an arbitrary base angle $\theta$ ($0 < \theta < \pi/2$) as shown in Fig. 4.10b. The loading on the beam is due to the capillary force at the fluid-solid junction line, $x = L_p$, as shown in Fig. 4.10b. Given that the vertical projection of the surface tension is $\gamma$, the magnitude of the pulling force is proportional to the beam width at the contact line, i.e., $F = \gamma d_p$, where $d_p$ is the width of the beam at $L_p$. This well-defined boundary value problem can be solved using any mechanics tools.

An examination of the boundary value problem reveals that, in order to induce deflection of the beam, the fluid-solid contact line can neither be at the tip of the beam ($x = L$) where $d = 0$, thus $F$ is zero, nor at the base of the beam ($x = 0$) since no deflection can be induced regardless of the force level at $x = 0$. This consideration argues for a contact line location, $x = L_p$, with which maximum deflection is induced. The value of $L_p$ is determined later (see below).

To develop a unified model for beams with different base angles $\theta$, we seek the equivalence between tapered beam and a simple, unique geometry – a beam with
uniform width. Consider a tapered beam of length L subjected to a force P at x = Lp, and a uniform width beam subjected to the same force P at the same position x = Lp, as shown in Fig. 4.10b. We consider these two configurations to be equivalent if the deflections of the tapered beam, \( \delta_{\text{taper}} \), and that of uniform width beam, \( \delta_{\text{uni}} \), at position x = Lp are equal, i.e., \( \delta_{\text{uni}} = \delta_{\text{taper}} \). Such assumption yields an effective bending stiffness of a tapered beam, \( B_{\text{eff}} \) as derived in the following.

For the tapered beam, using the small deformation beam theory [2] (the justification for using small deformation theory is discussed later), the governing equation for the deflection of the tapered beam is:

\[
B_x \frac{d^2w}{dx^2} = P(L_p - x), \quad (4.3)
\]

where \( w \) is the deflection, \( B_x \) is the local bending stiffness given by \( B_x = E' t_0 h^3 \left( \frac{1-x}{L} \right) \), \( E' = E/(1-\nu^2) \) is the plane strain Young’s modulus, \( t_0 \) the width at the base of the beam, \( h \) the beam thickness. It is noted that the bending stiffness, \( B_x \) in Eq. (4.3), is evaluated using the true width of the tapered beam, \( t_0 \left( 1 - \frac{x}{L} \right) \), thus its unit has an additional length dimension compared to the bending stiffness per unit thickness \( B \) used in Eq. (4.2). Integrating Eq. (4.3) twice and substitute \( x = L_p \) yields

\[
\delta_{\text{taper}} = w\big|_{x=L_p} = \frac{PL_p}{B_0} \left[ \frac{3}{2} \left( \frac{L_p}{L} \right)^2 - \frac{L_p}{L} \left( 1 - \frac{L_p}{L} \right) \ln \left( 1 - \frac{L_p}{L} \right) \right]. \quad (4.4)
\]

where \( B_0 = E' t_0 h^3 \left[ \frac{1}{12} \right] \). For an effective uniform beam,

\[
\delta_{\text{uni}} = \frac{PL_p}{3B_{\text{eff}}} \quad (4.5)
\]

Imposing the equivalence condition using the solution in Eqs. (4.4) and (4.5), two important parameters emerge. One is an effective bending stiffness, given as
\[ \frac{1}{B_{\text{eff}}} = \frac{1}{B_0} f(\xi) \]  \hspace{1cm} (4.6)

where the normalized location of the fluid-solid junction \( \xi = \frac{L_\nu}{L} \), and a nondimensional function of the location of the fluid-solid junction line

\[ f(\xi) = 3 \xi^{-1} \left[ \frac{3}{2} \xi^2 - \xi - (1 - \xi)^2 \ln(1 - \xi) \right]. \]

The second is an effective nondimensional parameter that characterizes the competition between an effective capillary force and the effective bending resistance, defined as:

\[ \alpha_{\text{eff}} = \frac{\gamma_{\text{eff}} L_\nu^3}{B_{\text{eff}}}, \]  \hspace{1cm} (4.7)

where the effective surface tension \( \gamma_{\text{eff}} = \gamma_0 \left( 1 - \frac{L_\nu}{L} \right) = \gamma_0 (1 - \xi) \). This effective surface tension takes into account the change of the beam width as the fluid-solid contact line is at different locations. Since this parameter is expected to control the folding of the beam, we call \( \alpha_{\text{eff}} \) the effective folding parameter.

It is noted that, for a tapered beam, the width at the base \( t_0 \), the base angle \( \theta \) and the length of the beam satisfies the relation

\[ t_0 = 2L \cot \theta \]  \hspace{1cm} (4.8)

From Eqs. (4.6-4.8), we arrive at a simple expression for the effective folding parameter,

\[ \alpha_{\text{eff}} = \frac{12 \gamma_0 L^3}{E h^3} \cdot \tan \theta \cdot F(\xi) \]  \hspace{1cm} (4.9)

where the nondimensional function \( F(\xi) = \frac{3}{2} (1 - \xi) \left[ \frac{3}{2} \xi^2 - \xi - (1 - \xi)^2 \ln(1 - \xi) \right] \).

The function \( F(\xi) \) determines the magnitude of the effective folding parameter when the fluid-solid contact line is at different locations. Fig. 4.11 shows the value of
\( F(\xi) \) as a function of location \( \xi \). As anticipated, \( F(\xi) \) (thus \( \alpha_{\text{eff}} \)) is zero at both
\( \xi = 0 \) \( (L_p = 0, \text{ i.e., at the base of the beam}) \) and \( \xi = 1 \) \( (L_p = L, \text{ i.e., at tip of the beam}) \).
Therefore there is no driving force for beam folding when the contact line is at these extreme locations. Further, \( F(\xi) \) reaches a maximum value \( F_{\text{max}} = 0.068 \) at \( \xi = 0.77 \),
giving rise to maximum driving force for folding. One can argue that, if folding does not occur when the contact line is at \( \xi = 0.77 \), it will not occur when the contact line is anywhere else along the beam. Therefore we substitute the function \( F(\xi) \) in Eq. (4.9) by its maximum value \( F_{\text{max}} = 0.068 \), which represents a necessary condition for folding, giving rise to the following expression of the effective folding parameter,

\[
\alpha_{\text{eff}} = 0.816 \frac{\gamma_\alpha L^2}{E h^3} \tan \theta = A \frac{\gamma_\alpha L^2}{E h^3} \tan \theta \quad (4.10)
\]

where \( A \) is a dimensionless constant representing the magnitude of the capillary interaction when the pulling force due to surface tension is the strongest. It is noted that this effective folding parameter is proportional to the square of the ratio of feature length and the elasto-capillary length in Eq. (4.2), \( \alpha_{\text{eff}} \propto \left( \frac{L}{L_{\text{EC}}} \right)^2 \). Notably however, \( \alpha_{\text{eff}} \) as defined here takes into account the feature geometry (in this case, for all sheets with tapered width, the base angle \( \theta \)).

Examination of Eq. (4.10) reveals that the effective folding parameter is a product of two components: an intrinsic parameter and a shape factor, both of which are dimensionless. The intrinsic parameter takes the form:

\[
\alpha_{\text{int}} = A \frac{\gamma_\alpha L^2}{E h^3} . \quad (4.11)
\]

For tapered beams the shape factor is a function of the base angle \( \theta \) only, as:

\[
S(\theta) = \tan \theta . \quad (4.12)
\]
We can now establish a criterion for spontaneous folding as follows:

\[
\text{if } \begin{cases} 
\alpha_{\text{eff}} < \alpha_{\text{crit}} & \text{no folding occurs} \\
\alpha_{\text{eff}} \geq \alpha_{\text{crit}} & \text{folding occurs}
\end{cases}
\] (4.13)

where \( \alpha_{\text{crit}} \) is the critical value of the effective folding parameter that is material- and geometry-dependent, and should be determined by experiments.

4.4.2 Experimental Validation of the Mechanics Model

If the spontaneous folding criterion based on this simple theory, Eq. (4.13), is correct, one needs to do a single experiment to determine the critical value of the folding parameter. Using that value, one should be able to predict the folding behavior specimens of different geometries. To check the validity of this simple model, we first look at the experimental data of Py et al [46] on PDMS by plotting \( \theta \) vs \( S(\theta) \). The results show that the two slopes for square and triangular foils indeed collapse onto one (See Fig. 4.12).

To determine \( \alpha_{\text{crit}} \) experimentally for Si thin sheets, we chose to measure the critical folding parameter using a specimen geometry that is independent of the shape – the uniform beam – as shown in Fig. 4.13. The value measured is thus the intrinsic critical folding parameter for single-crystalline Si (100) sheets. For the 1.25 \( \mu \text{m} \) thick Si foil, we obtain the critical folding parameter for Si thin foils:

\[
\alpha_{\text{int}} = 2.59 .
\] (4.14)

Therefore the critical effective folding parameter of the tapered beams is readily written as

\[
\alpha_{\text{eff}}(\theta) = 2.59 \tan \theta .
\] (4.15)
This means that, for tapered Si sheet with any base angle $\theta$, spontaneous folding will occur when the effective folding parameter reach the value given by Eq. (4.15), i.e., Eq. (4.15) gives a master curve governing spontaneous folding of any tapered sheets. This master curve is plotted as the solid line in Fig. 4.14.

Experiments were carried out to validate the model predictions. In order to measure the critical dimension for spontaneous folding easily, we designed a star shaped specimen shown as the inset in Fig. 4.14. Two different film thicknesses, 1.25 $\mu$m and 2 $\mu$m, were used. Specimens with five different angles $\theta$ are investigated. The experimental results are plotted and compared with master curve in Fig. 4.14. It is clear that the model predictions agree extremely well with the experimental data. The slight deviation at $\theta = 45^\circ$ is an artifact from geometric limitations. It is recalled that $\theta = 45^\circ$ is similar to the square sheet. However, as shown in Fig. 4.6, square sheets tend to undergo asymmetric folding, thus rendering a longer effective beam length and a lower critical value of the folding parameter.

### 4.4.3 Critical Folding Criteria of Flower-Shaped Beam

The above model can also be used to predict the spontaneous folding of planar patterns with curved edges. Assume a sphere of radius $R$ is cut along its longitudes. Between each two neighboring longitudes is there an undevelopable face, e.g. surface $ABC$ on sphere. But if we use straight lines to horizontally connect points on one longitude to the points on the neighboring longitude, a developable face, or one petal, is generated. Use this method to unfold a sphere into $n$ petals, which will be used in
the folding process.

Assume the sphere with radius $R$ will be unfolded to $n$ petals, i.e., sliced uniformly by $n$ longitudes. The unfold starts from a horizontal plane with the height $z_0$ from the bottom of the sphere, as shown in Fig. 4.15. On each horizontal plane with height $z$, the corresponding latitude intersects with $n$ longitudes to form an $n$ equilateral polygon. Radius of the inscribed circle of polygon is,

$$r = R \sqrt{1 - \left(1 - \frac{z}{R}\right)^2 \cos \left(\frac{\pi}{n}\right)}.$$  (4.16)

The nondimensional length of the petal after unfolding will be an incomplete elliptic integral of the second kind,

$$\frac{x}{R} = \frac{1}{R} \int_{z_0}^{z} \sqrt{1 + \left(\frac{dr}{dz}\right)^2} \, dz = \int_{1-\sin(z/R)}^{1-\sin(\pi/n)} \sqrt{\frac{1 - (\sin(n/\pi))^2 \frac{z^2}{x^2}}{1 - \frac{z^2}{x^2}}} \, dz,$$ (4.17)

where $z \in [z_0, 2R]$. The nondimensional width of the petal will be

$$\frac{t}{R} = 2 \sqrt{1 - \left(1 - \frac{z}{R}\right)^2 \sin \left(\frac{\pi}{n}\right)}.$$ (4.18)

The width at the base of the petal can be easily obtained by replacing $t$ by $t_0$ and $z$ by $z_0$ in Eq. (4.18) respectively. A typical petal shape is also shown in Fig. 4.15.

With the petal shape, substituting local stiffness $B_t = E' \frac{2t(x)h^3}{12}$ into Eq. (4.3) and integrating twice leads to the deflection at $x = L_p$,

$$\delta_{\text{upper}} = \frac{P}{B_0} \int_{t_0}^{L_p} \left(\int_0^{t_p - \eta} \frac{t(\eta)}{t(t)} \, d\eta \right) \, dx.$$ (4.19)

Performing the same calculation as in Eqs. (4.5-4.7) yields the effective folding parameter,
\[
\alpha_{\text{eff}} = \frac{3\gamma_0 t}{B_0 t_0} \int_{t_0}^{t} \left( \frac{L_p - \eta}{t(\eta)/t_0} \right) d\eta \cdot \frac{\gamma_0 E^2}{E^2 h^2} \cdot 36 \cdot \left( \frac{t_0}{L} \right) \cdot \left[ \frac{1}{L} \int_{t_0}^{t} \left( \frac{L_p - \eta}{t(\eta)/t_0} \right) d\eta \right] dx
\]

(4.20)

where \( B_0 = E t_0 h^3 / 12 (1 - v^2) \), \( E' \) is the plane strain Young’s modulus, \( \gamma_0 \) the surface tension, \( h \) the thickness of the thin sheet, \( t_0 \) the width at the base of the petal, \( t \) the width at location \( x \), \( L \) the petal length, \( L_p \) the location of the capillary force. Like derivation before in tapered beam, this effective folding parameter has a maximum value (i.e., the critical effective folding parameter) for each combination of \( n \) and \( t_0/L \), which becomes a necessary condition for the petal to fold. The difference here is that it has to be done numerically, and the shape factor \( S(n, t_0/L) \) is lumped in the maximum value and cannot be separated as in Eq. (4.12). After the maximum value is reached, the effective folding parameter would be

\[
\alpha_{\text{eff}} = \frac{\gamma_0 E^2}{E^2 h^2} \cdot A' \cdot S(n, t_0/L),
\]

(4.21)

where \( A' \) is a dimensionless constant representing the magnitude of the capillary interaction when the pulling force due to surface tension is the strongest. \( S(n, t_0/L) \) is the shape factor considering petal number \( n \) and the ratio of the width at the base of the petal \( t_0 \) to the petal length \( L \).

Fig. 4.16 shows the results of the critical folding parameter for the flower-patterned sheets with 4, 6, and 8 petals. The solid lines are the predictions of the model. The symbols are the experimental measurements. They again agree with each other very well except for the ratio 0.15. The reason might be that the petal is long and the capillary force along the petal side plays an important role, which then renders a smaller \( \alpha_{\text{eff}} \) than the theoretical prediction.
4.4.4 Spherical Si Solar Cell Devices

Using the mechanics model to predict design dimensions, we created 3D photovoltaic devices from thin, single-crystalline Si foils. Fig. 4.17a schematically illustrates the steps for fabricating a 3D Si solar cell, which via assembly adopts the form of a thin spherical shell. The process begins with defining of a flower pattern with lateral dimensions beyond the critical folding condition defined by the mechanical modeling. In this demonstration, we used a leaflet fabricated using a SOI wafer (2 μm thick, p-type device top, 10-20 Ω cm). The flower-shaped planar device layer is released from the Si substrate and folded into a spherical shaped device with an embedded spherical glass bead. Figs. 4.17b-c shows a complete wired spherical device on a glass substrate and a close-up view of the top Ag-wire contact, respectively.

To ascertain the quality of the deformed 3D Si devices, current-voltage measurements of individual solar cells are made at room temperature in the dark and with a solar simulator set at 100 mW/cm² and Air Mass (AM) 1.5 direct filter. Fig. 4.17d shows I-V characteristics recorded for a typical spherical Si solar cell with and without a back-side reflector. The solar cell area, defined as the projected surface area of a sphere, is about 0.05 cm². Without the reflector, this spherical cell shows a short-circuit current density, $J_{sc}$, of 3.31 mA/cm², an open-circuit voltage, $V_{oc}$, of 351 mV, and a fill factor (FF) of 0.47 for an overall conversion efficiency of 0.56%.

This device, though functional, is one of relatively low performance from the perspective of Si-based devices. The relatively poor performance is a result of the
fabrication processes, which are not optimized. Among these, the performance is most affected by the elimination of the high temperature process needed to provide a back-surface doping field. Given its absence, the high surface area to volume ratio strongly accelerates losses due to recombination. The high recombination is evidenced by the low $V_{oc}$ of the folded 3D device and the high diode ideality factor [57] of 2 from the diode $J-V$ curve fitting. Fig. 4.18 shows the fitting results of a typical 2 μm thick Si solar cell fabricated in this demonstration. The series resistance is ~500 ohms, which is fairly high and greatly reduces the short circuit current, and the shunt resistance is ~3×10^5 ohms, which is fairly low for a Si solar cell. It seems possible that the polymer shell provides the photoconductive shunt. To enhance the short circuit current density ($J_{sc}$), an antireflective coating would also be needed to minimize the surface reflection loss. In addition, the metal contacts used for this foil are not optimal choices for photovoltaic devices. As might be expected, process modification unrelated to the folding steps can enhance performance; this improvement is illustrated by the data in Fig. 4.19, which shows $J-V$ characteristics from an on-wafer Si solar device with the same doping profile, but having a layer of SiO$_2$ (100 nm) deposited on the surface and thicker metal contacts (Cr/Au, 10/100 nm). The measured efficiency in this case reaches 2%, which is comparable to other transverse and vertical junction thin film Si solar cells with comparable dimensions [58-60].

An interesting property of the spherical device is illustrated by the data presented in the top $J-V$ curve of Fig. 4.17d, which shows the effects of a diffuse white reflector
(Al) on the electrical performance of the cell. We find that the values of $J_{sc}$, $V_{oc}$ and FF increase to 3.60 mA/cm², 401 mV and 0.49, respectively. The addition of a diffuse reflector leads to a 41.1% increase in the conversion efficiency, which is consistent with the prediction of Minemoto’s theory [34].

Spherical PV devices constructed from thin solar cells are attractive, because they embed an intrinsic light-trapping form factor [61-63]. Their spherical light-receiving surface also intrinsically serves as a passive tracking optic, accepting light from all directions. Nevertheless, the elegance of this 3D architecture is offset by the complexity of the fabrication processes needed to construct it. The “flower-like” form required for guided self-assembly does not “tile” the planar wafer, thus its Si content is not effectively used.

4.4.5 Cylindrical Si Solar Cell Devices

To overcome the above limitations, we examined 3D light trapping architectures that simplify the fabrication/assembly processes, can be efficiently tiled on planar surfaces, and are compatible with non-SOI sources [24, 64-67]. Specifically, we explored a simpler 3D structure composed of a cylindrical solar cell. Fig. 4.20a schematically illustrates the flat square solar cell design, including dimensions and doping profiles. The planar precursor used consists of Boron-doped ($L_{p+} = 0.5$ mm), phosphorus-doped ($L_{n+} = 5.4$ mm) and un-doped ($L_p = 0.1$ mm) regions. Two metal contacts (Cr/Au, 3/50 nm thick, 100 μm wide) are formed onto the n⁺ and p⁺ regions, respectively. This structure is fabricated on a SOI wafer with a 3 μm thick, $p$-type
(10-30 Ω cm) device top. As noted above, both sourcing and thickness of the device can be easily varied by substituting a bulk Si (111) wafer with a suitably modified process flow [24]. **Fig. 4.20b** shows a cylindrical solar cell made by folding a flat Si device, with the dimensions (**Fig. 4.20a**) lying beyond the critical lengths as deduced from the mechanics model (see 4.4.1), around a PVA-coated cylindrical rod (diameter = 2 mm) through the evaporation of water. The rod in turn was fabricated from a liquid, photocurable polymer (NOA73, Norland) by replica molding.

Representative $J-V$ measurements from a square Si solar cell sheet and the cylindrical device folded from the same sheet under AM 1.5 illumination are shown in **Fig. 4.20d**. The cell area in this case is defined as the projection area of the cylindrical device (12 mm$^2$). The flat cell has an open circuit voltage of 507 mV, a short circuit current of 1.51 mA/cm$^2$, a FF of 0.65, and the overall conversion efficiency of 0.52%. The cylindrical cell has an open circuit voltage of 467 mV, a short circuit current of 7.26 mA/cm$^2$, a FF of 0.42, and most notable, the overall conversion efficiency increases to 1.49%. As compared to the planar configuration, the $J_{sc}$ and efficiency are found to increase by 381%, and 187%, respectively. The 8% decrease in $V_{oc}$ is attributable to the large $A_{pn}/A_L$ ratio ($A_{pn}$ is the p-n junction area, $A_L$ is the light irradiation area). In our case, $A_{pn}$ can be regarded as the surface area of n$^+$ region (5.4mm × 6mm), and $A_L$ is the projection area of the cylinder (2mm × 6mm). Therefore, the $A_{pn}$ is 2.7 times larger than $A_L$ (for the flat Si solar cell, $A_{pn}/A_L$ ratio is 0.9, 5.4×6 mm$^2$/6×6 mm$^2$). The larger value $A_{pn}/A_L$ increases the saturation current density $J_0$, which is the dominant parameter leading to the reduction of $V_{oc}$ [34]. This
inherent decrease in $V_{oc}$ can be remediated by adding a diffuse white reflector. **Fig. 4.20c** schematically shows the cross-sectional view of a cylindrical Si solar cell integrated with a semi-concentration reflector system. The reflector has $\sim 3 \times$ light concentration ratio, defined here as the ratio of the aperture area of the reflector (6mm $\times$ 6mm) to the projection area of the cylinder, resulting in a reduced $A_{pn}/A_L$ ratio of 0.9. As shown in the top $I-V$ curve in **Fig. 4.20d**, the $V_{oc}$ of the cylindrical cell with reflector increased to 494 mV, a value close to that of the flat cell. The design of the reflector shown is one that is able to improve $J_{sc}$ by collecting reflected light coming from near the edge of the cylinder. In contrast to the flat solar cells, the incident angles ($\theta$) of lights are not always normal to the substrate ($\theta = 0^\circ$), varying significantly at different positions on the surface of a cylindrical shaped solar cell (from $0^\circ$ at the center to $90^\circ$ at the edge, as shown in **Fig. 4.20c**). The cylindrical shaped reflector mitigates reflective losses of this type and substantially improves the performance of the cell. The $I-V$ results shown in **Fig. 4.20d** in fact demonstrate a maximum output power with the reflector that is $\sim 2.1$ times larger than that without it. This enhancement, though, is still somewhat smaller than the expectation based on the geometrical concentration factor and suggests further improvements can be made. Even so, we obtain a higher total output power from the cylindrical cell (0.363 mW) than that from a flat sheet with the same thickness (0.182 mW) and an equivalent mass. This observation strongly validates the light trapping competency of this 3D structure and implicitly the assembly-based process used to fabricate it.
4.5 Conclusions

This work describes a strategy for fabricating 3D single crystalline Si structures through a combination of photolithography and self-folding driven by capillary interactions, and suggests a new route to 3D light trapping architecture for use in photovoltaic applications. We have constructed spherical and cylindrical shaped Si solar cells and evaluated their improved electrical performances and competencies for light trapping and mitigation of reflective losses. We believe 3D structures of this type can be combined easily with other light trapping/guiding principles [68] to generate device form factors that are low-cost, simple, yet capable of high efficiency performance.

This work also identifies the conditions under which folding of the patterned thin foil occurs, and provides a mechanics model that fully predicts the critical conditions for folding for thin foils with complicated shapes. The main hypothesis of the model is that the dominant mechanism governing the spontaneous folding of thin sheets upon water droplet evaporation is the competition between bending and pulling force by surface tension. Based on this assumption, the model is able to explain a wide variety of experimental observations, including tapered sheets of any base angle and flower-patterned sheets of different number of petals, with a single nondimensional parameter – the effective folding parameter. The excellent agreements between the model predictions and the experiments provide strong evidence that this assumption is indeed true.

Although focused mostly on specific geometries, the model is general in nature.
In principle, the approach can be applied to any planar geometry to determine whether spontaneous folding occurs. Further, we realize the effective folding parameter obtained for any patterned planar sheets can always be decomposed into two parts, an intrinsic parameter and a shape factor, and will take the form,

$$
\alpha_{\text{eff}} = \alpha_{\text{int}} \left( \frac{\gamma}{E' \cdot h^3} \right) \times S(\text{geometry})
$$

(4.22)

where $L$ is the characteristic dimension, $h$ the thickness, $\gamma$ the surface tension, and $E'$ the plain strain Young’s modulus of the thin sheet. Such realization leads to the interesting conclusion that, although there is limited room to change the shape factor $S$ since it is largely determined by the intended geometry of the 3D structure, one can profoundly manipulate the folding behavior by changing the material properties (e.g., modulus and magnitude of surface tension) and the characteristic dimensions of the sheet. This single parameter can thus provide guidance for self-assembly of complex 3D structures using thin sheets. An obvious corollary is that the above model is applicable to any materials, as long as they are in thin sheet form.

In our analysis, we made the small deformation assumption when calculating the deflection curve, so that analytical expressions of $B_{\text{eff}}$ and the nondimensional parameter $\alpha'_{\text{eff}}$ can be derived. The real deformation during the folding, however, clearly involves finite rotation of the foils. Precise description of such folding process requires large deformation theories. Furthermore, the real situation during self assembly of 3D structures is much more complicated than what is modeled here. The forces acting on the thin foil as the liquid droplet evaporates, for example, are not just the capillary force along the liquid contact line, but also include capillary interactions
along the edges, and include the pressure differential on the two sides of the foil due to droplet free surface curvature. Such effects are analyzed by us and will not be presented in the current paper. Nevertheless, the results presented here demonstrate that, if one is interested in whether folding occurs or not, the current simple analysis using small deformation theory seems to be sufficient. The elaborative treatment of the more realistic problem, although important to understanding the process of folding, does not play a critical role in determining the critical condition for spontaneous folding.

One additional detail in the current analysis is that, since the shape factor for tapered thin foils takes for form of $\tan \theta$ as in Eq. (4.12), the result will not be valid at $\theta = 90^\circ$ where the value approaches infinity. The underlying reason for this limitation is that we used the base angle $\theta$ as the geometric parameter for tapered foils which allows us to evaluate the ratio of $L$ and $t_0$. This in fact is not an issue for folding of the flower patterned thin foils. We expect that for geometric shapes, this problem will not be present as long as the characteristic length and width of the thin foils are independent parameters.

4.6 Acknowledgements

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4.7 References

103:113110.


4.8 Figures

Figure 4.1 Energy levels for electrons and the electro-static potential in the charge depletion region of a p-n junction.
Figure 4.2 Optical generation of carriers in a p-n junction: (a) absorption of light by the device; (b) I-V characteristics of an illuminated junction.

![Typical solar cell diagram](image)

Figure 4.4 Schematic cross-sectional view of a conventional silicon solar cell with screen printed contacts. Reprinted with permission from Miles RW, Hynes KM, and Forbes HI, Photovoltaic solar cells: An overview of state-of-the-art cell development and environmental issues. *Prog Cryst Growth Charact Mater* 2005 vol. 51, p. 1-42. Copyright © 2005 Elsevier Science B.V. All rights reserved.
Figure 4.5 Fabrication of a free-standing thin Si film from an SOI wafer. (a) Schematic illustration of the fabrication; (b) Optical image of a square silicon membrane (6mm × 6mm) with thickness of 1.25 µm suspended from a tweezers.
Figure 4.6 Spontaneously folding of (a) triangular and (b, c) square silicon sheets (1.25 μm thick) with a water droplet.
Figure 4.7 (a) Scheme illustrating the folding of the flower shape into a sphere; (b) Wrapping of a water droplet with a flower shaped Si sheet with thickness of 1.25 μm; (c) SEM micrograph of a spherical shaped Si structure incorporating an inner glass bead.
Figure 4.8 (a) TEM micrograph of silver nanoparticles designed for direct ink writing (DIW) of silver electrodes on silicon solar cells (Inset: Optical image of the concentrated silver ink); (b) Schematic illustration of printing silver wires as the bottom and top electrodes for a spherical solar cell; (c) Current-Voltage behavior of the silver electrodes printed on the Cr/Au (3nm/50nm) pads of a test Si wafer after thermal treatment.
Figure 4.9 (a) Spontaneous wrapping of the thin films with a water droplet on top in a time lapse sequence, including PDMS thin films of (a) 6 mm triangle; (b) 6 mm square; and food plastic wrap thin films of (c) 7 mm triangle; (d) 7 mm square.
Figure 4.10 (a) Modeling of each corner as a tapered beam. (b) Equivalence of a tapered beam to a uniform beam
Figure 4.11 Function $F(\xi)$ reaches maximum, 0.068, at $\xi = 0.77$.

Figure 4.12 Modified critical folding length vs elasto-capillary length (data obtained from Py et al [14]).
Figure 4.13 \( \alpha_{\text{int}} \) measured from the uniform beam. (a) design of the uniform beams; (b) corresponding side view. \( L, t, h \) are the beam length, width and thickness, respectively.

Figure 4.14 Comparison of experimental data to the theoretical prediction (\( \alpha \) infinite at \( \theta = 90^\circ \) because of the singularity of the equivalence from the tapered beam with \( \theta \to 90^\circ \) to the uniform beam). Critical \( \alpha_{\text{eff}} \) for folding vs shape (\( \theta \)). Insert shows the shape design: \( L \) is the measured beam length and \( \theta \) is chosen to be 45°, 50°, 60°, 70°, 75°. Solid line: prediction curve from the model; red circles: measured \( \alpha_{\text{eff}} \) for folding of 1.25 \( \mu \)m thick Si sheets; blue triangles: measured \( \alpha_{\text{eff}} \) for folding of 2 \( \mu \)m thick Si sheets.
Figure 4.15 Unfolding of a sphere with radius $R$, petal number $n = 6$. 
Figure 4.16 Comparison of experimental data to the theoretical prediction for flower-patterned sheets with $n$ petals
Figure 4.17 Spherical solar cells self-assembled from flower shaped flat Si leaflets with thicknesses of 2 μm: (a) Schematic illustration of steps for fabricating a spherical shaped Si solar cell; (b) Optical image of a complete device consisting of the folded spherical Si shell, inner glass bead, and printed silver electrodes; (c) Magnified view of the silver wire connected to the top contact of the spherical device; (d) Current density ($J$) - voltage ($V$) characteristics of a spherical solar cell under AM1.5 simulated sunlight irradiation, with and without a white diffuse reflector.
Figure 4.18 Diode $J-V$ curve fitting of a typical Si solar cell. (a) Current density-voltage behavior in the dark (black line) and under AM1.5 illumination (red line). Blue line is the algebraic fit of light curve. (b) Semilog plot of the same data used to extract the diode ideality factor of 2.0 for both dark and light curve.
Figure 4.19 Current density-voltage behavior of a 3 μm thick SOI solar cell tested on wafer. The whole top surface is coated with an antireflection coating (SiO₂, 100 nm).
Figure 4.20 Doping layout and electrical performance of a cylindrical Si solar cell with a thickness of 3 μm: (a) Dimensions and doping profiles of the flat square device; (b) Optical image of a cylindrical device mounted on a cylindrical lens; (c) Schematic images of a cylindrical silicon solar cell with a reflector system (cross-sectional structure); (d) $J-V$ curves under AM1.5 illumination from a flat cell and a cylindrical cell self-assembled from the same flat sheet.
CHAPTER 5
FUTURE DIRECTIONS BASED ON ULTRATHIN SILICON SOLAR MICROCELLS

This chapter briefly describes a few unconventional solar cell designs based on the ultrathin silicon micro-ribbons. Applications of these thin film silicon solar microcells focus on the novel light trapping schemes that are able to improve the performance of the devices. Results up to date are shown, and future directions are discussed. These projects are collaborated with Lanfang Li, and Jimin Yao. The silicon micro solar cells were prepared by X.Y. Guo, and L.F. Li, while the plasmonic crystals were fabricated by J.M. Yao.

5.1 Plasmonic Ultrathin Silicon Solar Cells

5.1.1 Introduction

5.1.1.1 Plasmonics

Plasmonics is a growing field of research dealing with the generation, propagation, and detection of plasmonic waves, which are coherent oscillations of conduction electrons on a metal surface excited by an electromagnetic field that excites a metal/dielectric interface [1]. The electromagnetic excitations waves are confined to the surface because of their interaction with the conduction electrons on it, and propagate tens to hundreds of microns along the interface; they are called surface Plasmon polaritons (SPP) [2, 3]. As a result of the interaction between radiation and matter, the electromagnetic field amplitudes decrease exponentially perpendicular to
the interface, resulting in a subwavelength optical confinement [4-6]. In general, surface plasmons are non-radiative because there is a momentum mismatch at the same frequency of an incoming electromagnetic wave excitation, which means that there is no direct transformation between light and SPP [1]. Several techniques have been developed to match or couple the incoming electromagnetic momentum with that of the SPP. Prism coupling [7, 8] is one method to enhance the momentum of the incoming photons, while other methods are based on metallic gratings [9-11].

There are two types of surface plasmon resonances (SPRs): propagating surface plasmon polaritons (SPPs) and localized SPRs (LSPRs). LSPRs are non-propagating plasmonic excitations that can be resonantly excited on metal nanoparticles (NPs) and around nanoholes or nanowells in thin metal films. Gold (Au) and silver (Ag) metal nanostructures are frequently studied because they can exhibit strong LSPRs in the visible wavelength range [12]. The spectral position and magnitude of the LSPR depend on the shape, size, and composition of the nanostructure, as well as on the local dielectric environment [13-15]. These optical properties have been exploited for label-free optical sensing where adsorbate-induced refractive index changes near or on plasmonic nanostructures are used to detect binding events [16-20]. In recent decades interest has intensified since the discovery that Raman scattering can be increased by orders of magnitude through the use of metal nanostructures [21-23].

The surface plasmons have attracted much attention due to their wide range of potential applications in various areas of science, such as optics, biosensing, photonics, material science, and very recently in nanoelectronics and nanophotonics [24-26].
However, compared to photonics, plasmonics is still under development with many new concepts waiting to be demonstrated, and many proposed SPP devices waiting to be fabricated [1].

5.1.1.2 Plasmon Enhanced Solar Cells

Efficient thin-film solar cells have been shown great potential as an alternative to conventional wafer-based photovoltaics because of their low costs [27]. In typical thin film cells the thickness of the absorbing layer is governed by a tradeoff: the absorbing layer must be optically thick to absorb a significant fraction of the incident photons but must also be of sufficient quality to enable the diffusion length of minority carrier larger than the material thickness [28]. Therefore, one critical challenge in designing a thin-film solar cell is to design an efficient light-trapping scheme. Conventional wafer-based solar cells use wavelength-scale surface textures on the front or back of the cells to enhance light absorption. These surface textures, however, are usually several micrometers in dimension, and thus not feasible for ultrathin solar cells with thicknesses smaller than the dimension of surface roughness.

Plasmonic nanostructures have been proposed as a method for enhancing absorption in thin-film photovoltaic absorber layer [29-33], which is potential useful for thin-film solar cells. Excitation of the surface Plasmon resonances in the arrays of Au and Ag nanoparticles with diameters in the range of 50-350 nm deposited on a Si layer have been successfully used to improve the performance of the silicon thin-film solar cells [34]. Derkacs et al. reported an 8% overall increase in conversion
efficiency by using Au nanoparticles on thin-film amorphous silicon solar cells [35]. Pillai et al. deposited silver nanoparticles on 1.25 \( \mu \text{m} \) thick silicon-on-insulator solar cells, and achieve a photocurrent increase of up to a factor of 16 at long wavelengths and an integrated overall photocurrent increase of 33\% [36].

Following these initial studies, many research works have been performed to investigate the enhancement mechanisms, and to investigate the optimum particle parameters (shape, size, particle material, and dielectric environment) to determine some fundamental design principles for optimum particle plasmon enhanced light trapping [37, 38]. There are two main basic mechanisms proposed to explain photocurrent enhancement by metal particles: strong light scattering into the high-index substrate, and enhanced near-field coupling to trap light within the substrate. The contribution of each mechanism depends mostly on the particle size, the semiconductor absorption, and the electrical design of the solar cell [39].

Besides the random self-assembled nanoparticles, other plasmonic nanostructures have also been reported for light trapping in solar cells, such as periodic nanodisk/nanodots [40, 41], nanohole arrays [42], and nanoslit arrays [31, 43], etc. However, since all these metallic structures are placed on the front surface of the thin-film solar cells, there are strong front scattering and metallic absorption losses. Recently, some groups have designed plasmonic back structures incorporated in thin-film amorphous silicon to improve absorption of solar cells using metallic gratings consisting of periodic nanoridges [44, 45], or nanoholes [28]. The SPP-assisted back structures show noticeable enhancement in the cell absorption at
near Infrared radiation (NIR) wavelengths where silicon is normally transparent, while eliminate the decrease in efficiency at wavelengths shorter than 550 nm, which is normally seen in designs incorporating metal nanoparticles on top [28]. This photon energy up-conversion allows for more efficient use of the incident solar spectrum.

Our group has developed a new type of 3D plasmonic crystal that consists of multilayered, regular arrays of subwavelength metal nanostructures [10, 11]. This plasmonic crystal will be placed at the back surface of Si solar cells, so that the plasmonic structure will not affect the incident light on the top surface. The goal of this research is to study the electrical performance of these plasmonic Si solar cell devices, to understand the plasmonic enhancement mechanisms, and to provide design principles for optimum light trapping.

5.1.2 Experimental

5.1.2.1 Fabrication of Single Crystalline Si Micro-Solar Cells

Following the strategy of previous work done by Yoon [46], we can fabricate Si micro solar cells as illustrated in Fig. 5.1. The starting material is the p-type, boron doped single crystalline silicon (111) wafer with a resistivity of 10-20 ohm-cm. Photolithography is used to define a silicon ribbon pattern in the resist layer coated on the silicon wafer. The long axes of the ribbon should be along the preferential {110} etching plane for anisotropic, undercut etching with KOH. The exposed silicon is then etched by Bosch process to achieve deep vertical trenches into silicon, and followed by a refining step (one minute etching in an alkaline solution of KOH, IPA, and DI
water at 80°C) to smooth the side walls.

After etching, rectifying p-n junctions and top contacts are formed by selective-area thermal diffusion of boron (p⁺) and phosphorus (n⁻) through patterned diffusion barriers of SiO₂ layer (900 nm). The solid doping sources used here are boron nitride (p⁺, BN-1250 from Saint-Gobain ceramics) and P₂O₅ in a glass matrix (n⁻, PH-1000). A silicon nitride layer with thickness of 600 nm and an Au/Cr film of 5nm/800nm are then deposited over this doped structure as well as the side walls of the microbars to serve as the etch mask. An alkaline based preferential etchant (PSE 200 from Transene company, selectively etch silicon along {110} over {111} at 200:1 ratio) is used to release the micro silicon ribbons from the source wafer everywhere except at the anchor points. The exposed bottom surfaces of the micro ribbons are then doped with a solid doping source to form a back-surface field (BSF). The complete fully functional silicon micro solar cells are 45 um wide, 1.5 mm long and 26 um in between. The thickness of solar cells can be varied by changing the Bosch process time. In this work, the thickness of the micro solar cells is 19 um. The 3 um thick micro solar cells also shown in this chapter are fabricated from SOI wafers following the processes described in Chapter 4. After removing the surface oxide and nitride, the micro solar cells can be picked up by an elastomeric stamp and transfer printed onto the secondary substrate.

5.1.2.2 Fabrication of Plasmonic Back Nanostructures for Si Solar Cells

The fabrication of SPR crystal structure is the same as described in the literatures
Square arrays of cylindrical nanowells/nanoposts are molded into the surface of UV-curable spin on glass (SOG) by a soft nanoimprint technique [47] followed by sputter deposition of a continuous gold layer. The thickness of gold is chosen to be 35 nm (semitransparent) and 150 nm (no transmission). The diameter, depth, and periodicity of the cylindrical wells/posts are well-controlled by the master. One typical combination of the diameter, depth, and periodicity is 440, 200, and 740 nm, respectively. There are two types of plasmonic back nanostructures used in this work: nanohole, and nanopost arrays that are coated with gold, as shown in Fig. 5.2.

Two methods have been tried to transfer Si micro solar cells onto the plasmonic structures: transfer printing and capillary filling techniques. During transfer printing, a thin layer of SOG is spin coated onto the surface of the nanostructures to serve as the adhesive layer, and then cured after printing cells onto it. As a result, the thin SOG layer is also the spacing layer separating the plasmonic nanostructures and the devices to prevent potential shorting. The cross-sectional SEM images of this structure, shown in Fig. 5.3, indicate that the distance between the nanostructured Au and Si is around 200 nm. The problem with this method is that the yield is relatively low, sometimes below 50%. To improve the printing yield and make devices closer to the plasmonic structure, we tried another method. After placing the elastomeric stamp inked with silicon micro solar cells, Norland optical adhesive (NOA) is then filled into the space between the ribbons by capillary filling technique [48]. Curing the top and bottom surfaces of the device under UV light and then removing the stamp can transfer close to 100% of the silicon micro cells onto the plasmonic crystal substrate.
5.1.3 Results and Discussion

The preliminary results of the plasmonics solar cells are shown in Figs. 5.4-5.6.

**Fig. 5.4** shows the current-voltage characteristics of 19 μm thick Si solar cells with different back structures. The plasmonic nanostructures give increases in $V_{oc}$, $J_{sc}$, and thus the total conversion efficiency of the device compared with the solar cells without plasmonic structure. The highest enhancement comes from pattern P1600 (diameter = 960 nm, periodicity = 1.6 μm, relief depth = 200 nm), which shows a 24% increase in the output power with the total efficiency of 6.92%. This increase can be attributed to the enhancement in the absorption of Si layer at below bandgap wavelength through the plasmonic light coupling structure. It is interesting to notice that even for such a thick Si layer, the enhancement effect is obvious.

We expect a higher enhancement factor in the ultrathin plasmonic Si solar cell with a few micrometers in thickness. However, currently fabrication of such Si solar cells (with thickness < 3 μm) following the processes described above (**Fig. 5.1**) is not reliable, and under development. We fabricated such ultrathin solar cells from SOI wafers (p-type, Boron doped device layer, 3 μm thick, 10-20 ohm cm, 4-μm-thick BOX, Ultrasil) with the processes described in Chapter 4. **Figs. 5.5-5.6** show the current-voltage characteristics of 3 μm thick Si solar cells with different back structures, and the relief depth of the plasmonic nanostructures are 200 nm and 400 nm, respectively. The enhancement effect of the plasmonic back structures is more obvious for these 3μm thick solar cells compared with the 19 μm thick solar cells,
while the structure with relief depth of 200 nm shows an average larger increase in the efficiency than with the relief depth of 400 nm. Although the inherently huge variation between individual SOI cells makes it difficult to quantitatively compare data from cells with different back structures, it still provides promising results for the idea of incorporating plasmonic structure in the solar cell devices to couple light into Si absorbing layer to enhance the absorption.

5.1.4 Summary and Future Work

Our preliminary results have shown that the plasmonic back nanostructures provide feasible and effective SPP enhancement. A future research plan is to understand the enhancement mechanism of the whole system based on the experimental observations and theoretical simulation, and optimize the optical and electrical designs to achieve high efficient thin-film plasmonic solar cells. The reliable fabrication technique of ultrathin Si solar cells is under development, the plasmonic nanostructures coated with thick gold layer (150 nm) will be evaluated, and the doping profiles can also be modified to be beneficial for light absorption. Theoretical simulations are being performed through the 3D finite-difference-time-domain (FDTD) calculations using commercial software Lumerical (Lumerical Inc).

5.2 Deployable Solar Cells

In today’s small satellites environment, low cost and high performance are the important factors determining project success. The microsatellites and nanosatellites
for space application typically have a mass of a few hundred kilograms or less, a volume of less than a cubic meter, and electrical power levels ranging from a few watts up to several kilowatts [49]. These features identify a need for a simple, low-mass, and low packing volume solar array system for the small satellites. The traditional, rigid, body-mounted solar cells can meet some of the lower power requirements, but they are not suitable for power levels above about 100W because of their large stowage volume and mass. Deployable solar arrays incorporating thin-film flexible structures have been identified as one of the approaches to meet the solar array requirements of these small satellites. Several inflatable structures have been developed, such as ITSAT (Inflatable Torus Solar Array Technology) designs [49], and PowerSphere multifunctional ultraviolet-rigidizable inflatable structures [50, 51].

The development of inflatable structures requires a number of innovations in several technology areas: materials, structures, ultra-low-mass inflation systems, thin-film technology and associated thin-film applications and fabrications [51]. Thin-film photovoltaics is one of the new technologies utilized in the inflatable solar arrays. Several types of thin-film solar cells were considered including thin crystalline silicon, gallium arsenide (GaAs) on germanium (Ge), copper indium diselenide (CIS), and amorphous silicon (α-Si). Thin crystalline silicon and GaAs/Ge cells have good performance and reliable fabrication technologies, but they are brittle, which limit their applications in deployable structures. CIS and α-Si have the potential of being individually flexible, but their fabrication technology is less developed and requiring larger sizes [49].
The ability to transfer print microcells onto a secondary flexible substrate [52, 53] makes it possible to fabricate deployable solar cells based on the single-crystalline silicon. Our group and collaborators have developed complementary approaches that create fully functional ultrathin silicon bars, membranes, and ribbons from a bulk wafer [54-56] by using procedures originally developed for thin Si electronic devices [57, 58]. These Si microcells can be transferred onto the surface of a mechanical flexible, deployable structure to form a lightweight deployable solar cell array with high efficiency. There are a variety of possible designs, such as cylindrical and spherical structures. Fluorescent dyes or other scattering materials can also be incorporated within the structure to further improve the performance of solar cell devices due to their light trapping properties.

5.3 References


5.4 Figures

Figure 5.1 (a) Schematic illustration of steps for fabrication ultrathin μ-cells from a bulk wafer, printing them onto a target substrate and forming electrical interconnections to complete a module. (b) Optical image of a completed module. (c) SEM image of an array of μ-cells on a source wafer ready for printing. Reprinted with permission from Yoon JS, et al., *Nature Mater* 2008 vol. 7, p. 907-915. Copyright © 2008, Nature Publishing Group.
Figure 5.2 Schematic illustrations of the plasmonic back structure solar cells. Nanoholes/posts arrays are coated with Au (35 nm thick). The Si bars are 45 μm wide, 1.5 mm long and 26 μm in between.

Figure 5.3 Cross-sectional SEM image of the Si micro solar cell with plasmonic crystal on the back. The spacing layer is spin-on-glass (SOG) with thickness of about 200 nm.
Figure 5.4 $J$-$V$ characteristics of Si solar cells (19 μm thick) with a back background, a plain gold mirror back surface, and plasmonic back nanopost structures with different periodicity. The relief depth of the nanopost arrays is 200 nm. The thickness of gold on the nanopost structures and plain substrate are the same, 35 nm.

Figure 5.5 $J$-$V$ characteristics of Si solar cells (3 μm thick) with a back background, a plain gold mirror back surface, and nonplasmonic back nanohole structures with different periodicity. The relief depth of the nanohole arrays is 200 nm. The thickness of gold on the nanohole structures and plain substrate are the same, 35 nm.
Figure 5.6 $J$-$V$ characteristics of Si solar cells (3 μm thick) with a back background, a plain gold mirror back surface, and nonplasmonic back nanohole structures with different periodicity. The relief depth of the nanohole arrays is 400 nm. The thickness of gold on the nanohole structures and plain substrate are the same, 35 nm.
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Xiaoying Guo was born in Zhongxiang, Hubei province, P.R. China on February 8th, 1982. In the fall of 1998, she began her undergraduate study in Materials Science and Engineering at the University of Science and Technology of China. During her junior year, she began research in the laboratory of Professor Xiaoguang Li and worked with Dr. Guang Li on the superconductors and colossal magnetoresistance (CMR) materials. She received her Bachelor of Science degree in Materials Physics in 2003 with “Extraordinary Student Scholarship”. In the fall of 2003, Xiaoying entered the doctoral program of the Electronic Materials Division within the Department of Materials Science and Engineering at University of Illinois at Urbana-Champaign. She joined the research group of Professor Bohn and began research on the porous semiconductors and devices. In the April of 2006, she joined the research group of Professor Nuzzo and continued with her studies on the advanced electronic devices and unconventional light-trapping Si solar cells. After receiving her Ph.D. in Materials Science and Engineering in the spring of 2010, she will be joining the Dow Chemical Company as a Senior Engineer.